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THE SYNTHESIS AND CHARACTERIZATION OF PHENYLENE-LINKED AB-TYPE POLYURETHANES

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Lorenzo Eric Sepulveda

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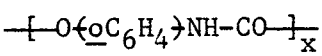
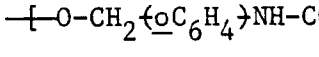
The author wishes to dedicate this work to the memory of his late grandfathers, Jose Lorenzo Sepulveda and John H. Elrod, both of whom were excellent fighters in the business world.

ABSTRACT

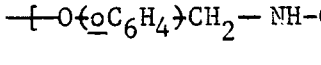
Polyurethanes are usually prepared by the reaction of diisocyanates with diols, and in terms of functional group incorporation, can be designated as AABB-type polymers. Much less investigated are the AB-type polyurethanes, which are necessarily prepared directly upon generation of the active isocyanate. The following eight AB-type polyurethanes are the subject of this study:

 polymer-ortho-00

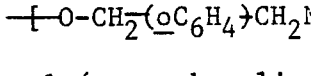
poly(oxycarbonylimino-1,2-phenylene)

 polymer-ortho-10

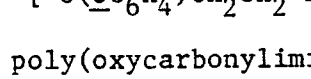
poly(oxycarbonylimino-1,2-phenylene methylene)

 polymer-ortho-01

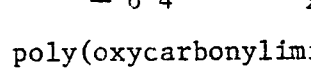
poly(oxycarbonylimino methylene-1,2-phenylene)

 polymer-ortho-11

poly(oxycarbonylimino methylene-1,2-phenylene methylene)

 polymer-ortho-02

poly(oxycarbonylimino-1,2-ethanediyl-1,2-phenylene)

 polymer-para-00

poly(oxycarbonylimino-1,4-phenylene)

$-[-O-(p-C_6H_4)-CH_2CH_2-NH-CO-]_x-$ polymer-para-02

poly(oxycarbonylimino-1,2-ethanediyl-1,4-phenylene)

$-[-O-(CH_2)_5-NH-CO-]_x-$ poly(pentamethylene urethane)

poly(oxycarbonylimino-1,5-pentanediyl)

The emphasis of the study was placed on the first seven polymers, which are phenylene-linked. The preparation of the first five ortho-disubstituted polymers was attempted via the Curtius reaction and the ring-opening reaction of cyclic carbamates. Polymer-ortho-00 could not be prepared by either method in homopolymeric form. Polymer-ortho-10 and polymer-ortho-01 could be prepared by both methods, though the cyclic carbamates were the predominant products in the Curtius reaction. Polymer-ortho-11 and polymer-ortho-02 were prepared only by the Curtius reaction. The two para-disubstituted polymers and the aliphatic polymer were also prepared by the Curtius reaction. These polymers were characterized by midrange and near infrared spectroscopy, X-ray diffraction, viscometry, isopiestic osmometry, DSC, TGA, and nonoxidative thermolysis.

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LIST OF ABBREVIATIONS

aq	aqueous
cm	centimeter
conc	concentrated
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
g	gram
GPC	gel permeation chromatography
hr	hour
IR	infrared
l	liter
m	moderate infrared absorption
min	minute
ml	milliliter
MW	molecular weight
N	normal
NIR	near infrared
nm	nanometer
NMR	nuclear magnetic resonance
PU	polyurethane
PZN	polymerization
s	strong infrared absorption
sh	shoulder on stronger infrared absorption
T_d	decomposition temperature

T_g	glass transition temperature
T_m	melting point
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMA	thermomechanical analysis
TMS	tetramethylsilane
VPO	vapor pressure osmometry
vs	very strong infrared absorption
w	weak infrared absorption

LIST OF SYMBOLS

cm^{-1}	reciprocal centimeters (wave numbers)
Δ	delta, heat applied
δ	delta units in NMR spectroscopy
θ	diffraction angle in degrees of arc
λ	wavelength of X-rays
μ	micron
Σ	summation
σ	standard deviation
$\int$	integral

VOLUME I

CHAPTER I

INTRODUCTION

A. CLASSICAL POLYURETHANES

The chemistry of classical polyurethanes (PU's) is broadly the reaction of diisocyanates with diols:

$$HO\text{-}R\text{-}OH + OCN\text{-}R'\text{-}NCO \longrightarrow \left(\text{-}O\text{-}R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R'\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\right)_x$$

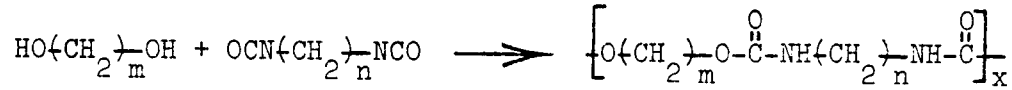
These will be termed AABB-type PU's, because two different kinds of difunctional molecules are employed.

The manufacture of most commercial PU's uses one diisocyanate compound, but two different diol compounds, such that the isocyanate and hydroxyl groups are stoichiometrically equivalent. One diol component is generally a short-chain glycol, such as ethylene glycol, 1,2-propylene glycol, or 1,4-butanediol. The other diol component, termed a macrodiol, is actually a polyether, polyester, or polybutadiene prepolymer which is terminated by hydroxyl groups. The most common macrodiols are polyethylene glycol and polyethylene adipate.

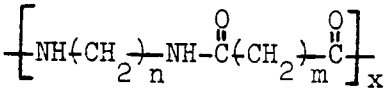
The manufacturing process may be stepwise or one-shot. In the stepwise process, the diisocyanate is first reacted with the macrodiol to form an isocyanate-terminated prepolymer. After much of the heat is dissipated, this prepolymer is

reacted with the short-chain glycol (also called "chain extender") to form the final PU product. In the one-shot process, the diisocyanate, short-chain glycol, and macrodiol are mixed together simultaneously. In either case, great care must be taken to assure stoichiometric equivalence of the isocyanate and hydroxyl groups. These commercial processes usually do not employ any solvent. Most commercial PU elastomers are linear polymers as discussed above. These are soluble and thermoplastic. Many commercial PU products, such as foams, coatings, etc., are crosslinked. In these cases either the isocyanate compound, the hydroxyl compound(s), or both are polyfunctional. These products consist of three-dimensional networks or gels, and the problem of assuring stoichiometric equivalence is not nearly as critical as in the linear products.

PU's that do not utilize a macrodiol component are mainly of academic interest at present, though such PU's have been commercially exploited in Germany for their fiber-forming properties. In these fiber-forming PU's, both the diisocyanate and diol components are aliphatic, consisting of polymethylene chains:

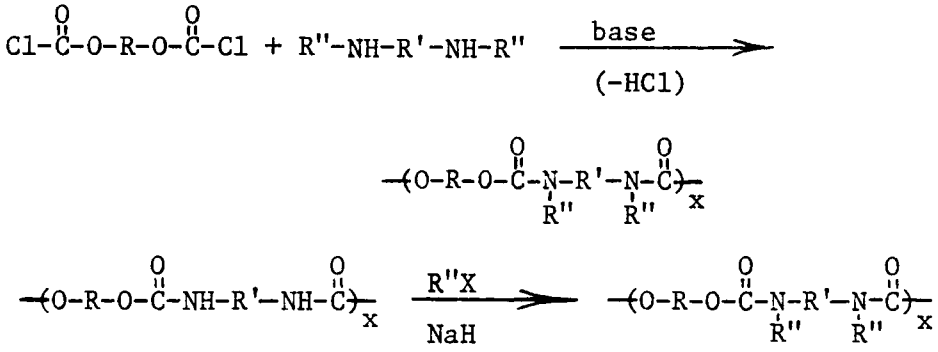


Commercially, these PU's have largely been displaced by the corresponding nylons



which are very similar in physical and mechanical properties. Although simple PU's made from a single small diisocyanate and a single small diol are not commercially important at present, they are nevertheless important to polymer science because the structure-property relationships found in the simple systems can help in understanding the more complex systems. Thus much effort has been spent in studying those AABB-type PU's that do not contain a macroglycol component. Although no AABB-type PU's were experimentally studied in this work, the extensive literature of the simple thermoplastic AABB-type PU's are highly relevant to the subject studied.

Some AABB-type polymers containing urethane units cannot be made from diisocyanates and diols. These are the poly(N,N-disubstituted carbamates), made either by the polycondensation of bischloroformates with diamines, or by the N-alkylation of the N-monosubstituted polymers:



Among both the simple AABB-type PU's and the commercial PU's, the most thoroughly investigated polymers contain in-chain benzene rings, usually as part of the diisocyanate component. The reason for this attention is two-fold: (1) the aromatic diisocyanates are in general less volatile than the aliphatic diisocyanates, thus presenting a lesser toxicity problem; and (2) aryl linkages generally impart improved mechanical, hydrolytic, and thermal stabilities. In contrast to the commercial manufacturing process, laboratory preparations of the simple PU's are usually done in an organic solvent which dissolves the diisocyanate, the diol, and the product.

The main purpose of the above discussion is to delineate the areas relevant to the present work. Among the AABB-type PU's, we are thus concerned with those simple PU's which are monosubstituted, because these most closely resemble the AB-type PU's which are the subject of this study.

B. CHARACTERIZATION OF POLYURETHANES

The most practical and useful methods of characterization of PU's can be roughly divided into five analytical areas: (1) spectral methods, (2) molecular weight methods, (3) thermal methods, (4) mechanical property methods, and (5) X-ray methods.

The most informative spectral methods for analysis of both linear and crosslinked polymers is midrange infrared spectroscopy, also called "ordinary" or NaCl-region IR. The large number of published assignments and correlations of PU absorptions, and the problems associated with those, require a separate chapter for complete discussion (see Chapter II). Infrared radiation in the "near infrared" range is also useful in analysis of both linear and crosslinked polymers. Near infrared spectroscopy (NIR), though little utilized to date in polymer analyses, is potentially a very powerful technique in systems of interest here. Therefore, a separate chapter is also devoted to NIR (see Chapter III). Nuclear magnetic resonance (NMR), principally proton NMR, has been utilized in several studies of PU's (1, 2, 3, 4, 5, 6, 7). The limited solubility and high resulting viscosities of most linear PU's, and the insolubility of crosslinked PU's, make NMR of limited utility in studies of PU structures.

The molecular weight (MW) methods can be subdivided into absolute and relative methods. The most common absolute MW methods are vapor pressure osmometry, membrane osmometry, and end group titration. Few workers have used the absolute methods for determining the MW's of PU's, and the methods reported invariably determine the number-average MW. Vapor pressure osmometry (8) is more common than membrane osmometry

(9), for two reasons: (1) the lack of membranes which are impermeable to the low MW fractions (cutoff about 10,000), and (2) the uncertainty in number-average MW due to disregarding the fraction below the cutoff. For the few low-MW PU's which have well-defined end-groups, end-group titration may be applicable (10). The relative methods determine a property which is a monotonic function of MW (for which the explicit functional relationship is often unknown), and include viscometry and gel permeation chromatography (GPC). The relative methods have been more routinely used than the absolute methods for determination of MW's of PU's, viscometry (11, 12, 13, 14, 15, 16, 17) being more routinely applied than GPC (8), due to experimental convenience and instrumental simplicity. The thermal methods of analysis include differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetric analysis (TGA). TGA has been used mainly to determine PU thermal stability or onset of degradation (18, 19, 20, 21) while DSC (22, 23, 24, 25, 26) and DTA (18, 27, 28, 29) have been used to examine subtle nondegradative changes in polymer structure with temperature.

The mechanical properties of PU's are extremely important in determining their applications, and are more widely reported than all the other characterizations combined. The most important mechanical properties are hardness, tensile strength, and various dynamic moduli. Since the present work

is mainly concerned with chemical structures and transformations, mechanical properties will not be further discussed.

X-ray methods are classifiable as either wide-angle X-ray diffraction (WAXD) or small-angle X-ray diffraction (SAXD), of which the former is the more commonly used. X-ray diffraction is a highly specialized technique for PU characterization. It is useful only for ordered systems, which have crystalline or paracrystalline domains. X-ray diffraction has been widely used to analyze those soft PU's which are useful as elastomers, and which contain a large weight percentage of a macrodiol (30, 31, 32). However, in these materials the urethane component per se receives very little attention, except insofar as it gives rise to domain separation from the non-urethane component. The paracrystallinity of the urethane component may be high, but the crystallinity is almost nil. Those X-ray studies concerned with the crystallinity of the urethane linkages in PU's are very few (24, 26, 33, 34, 35, 36), probably because unit cell determinations are presently possible only for a new very simple aliphatic polyurethanes (37, p. III-36).

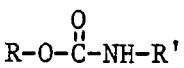
Of the characterization methods discussed above, infrared spectroscopy (midrange and NIR), viscometry, and thermal methods will be the most utilized in the reported studies, with information from several of the other methods being utilized in an auxiliary or complementary manner.

C. DEGRADATION OF POLYURETHANES

Much work has been done on the various modes of degradation of PU's, including thermal, hydrolytic, oxidative, photochemical, mass spectrometric, thermooxidative, photooxidative, and chemical degradations. Mechanical and sonic degradation of PU's has not attracted much attention. Probably the largest incentive for this degradation work is the well-known fire-hazard of polyurethane foams, especially those used as exposed interior building materials.

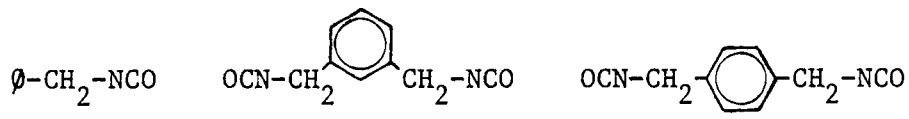
The fire-hazard of commercial PU's is due to two phenomena: (1) the facility by which the macrodiol component gives rise to volatile degradation products (combustible material), and (2) the actual ignition process which remains almost a complete mystery, though which must somehow involve the urethane linkage.

Most of the reported PU degradation work is concerned not with the breakup of the macrodiol component, but rather with the reactions of the urethane linkage. The nature of the oxygen and nitrogen substituents is known to be all-important, that is the nature of R and R' in the moiety



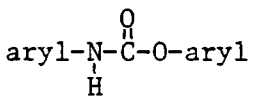
where R and R' designate alkyl, benzyl, or aryl linkages in a polymer chain. Most of the reported work clearly distinguishes

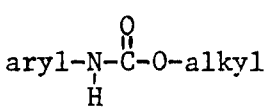
between the effects of alkyl and aryl substituents. A few studies make further distinctions between the effects of alkyl and benzyl substituents. As far as nomenclature is concerned, it is a common and acceptable practice to group benzyl substituents among the general alkyl substituents. However, one of the salient principles stressed by an elementary organic course is that benzyl and allyl groups show a reactivity greatly different from that of saturated alkyl groups, when such groups are bonded to almost any heteroatom. This consideration is important, because much research has been done on PU's and model carbamates made fron benzyl-type isocyanates, such as benzyl isocyanate (I-1), m-xylylene diisocyanate (I-2), and p-xylylene diisocyanate (I-3):

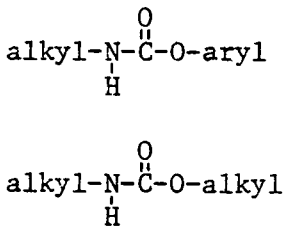


I-1 I-2 I-3

Considerably less work has been done with benzyl-type groups in the diol component. With these substituent considerations in mind, the following review of the various degradation modes will try to distinguish among the following structures:







Whenever a study treats a benzyl substituent, we will consider it along with the alkyl substituents in the same grouping.

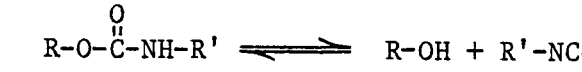
1. Thermal Degradation

Thermal degradations (pyrolyses or thermolyses) account for most of the degradation literature of PU's. Thermal degradations will be reviewed first on the basis of the possible products formed, and secondly on the basis of the N- and O-substituents of the starting material. In both reviews, it should be emphasized that the thermal transformation of the linkages in a model compound may be greatly different from the transformation of linkages in a polymer, because the various intermediates in the degradation of a model compound are much more likely to be volatile than the corresponding intermediates in the polymer. For a model compound, the intermediate could be quickly removed from the reaction zone, while in the polymer it is more likely to be trapped and forced to undergo further reactions.

The present study places much greater emphasis on the structures of the nonvolatile residues of thermal degradation than on the volatile products. Of primary importance here is

the preservation of useful polymeric properties on heating.

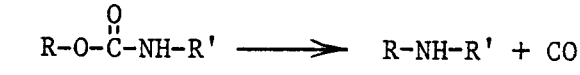
a. Products of thermal degradation. The older literature discussed three main routes of degradation of the urethane linkage. These were the reversible dissociation into isocyanate and hydroxyl moieties (38, 39),



pyrolysis to primary amines, olefins, and carbon dioxide (if a β-hydrogen is present in the hydroxyl moiety) (38, 40, 41),



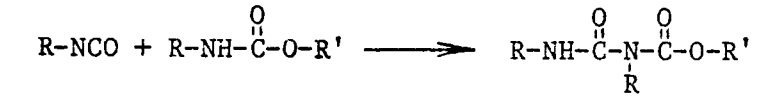
and pyrolysis to secondary amines and carbon dioxide (38, 42),



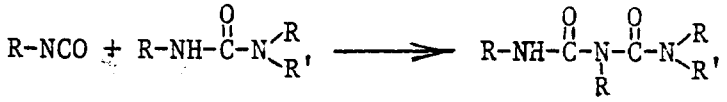
From the nonvolatile products of these initial reactions (especially if R or R' were part of a polymer chain), a host of subsequent reactions could ensue. A primary or secondary amine could react with an isocyanate to form a urea (41, 43, 44, 45).



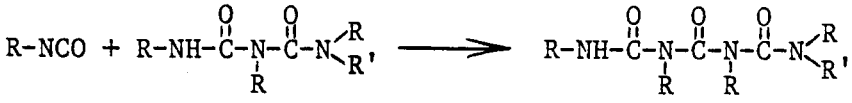
An isocyanate could react with a urethane linkage to form an allophanate (44, p. 71; 46; 47; 48; 49, 50, 51),



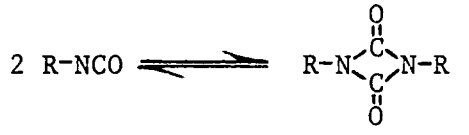
or with a urea linkage to form a biuret (14; 44, p. 69; 50; 51; 52),



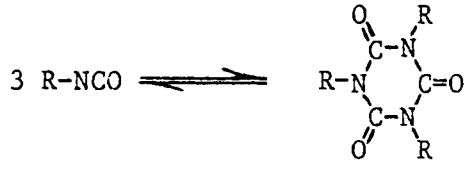
Some workers even postulated the further reaction of isocyanates with biurets or allophanates to form such compounds as triurets, etc. (44, p. 72).



Other possible reactions considered early were the dimerization and trimerization of isocyanates to form uretidinediones and isocyanurates respectively,

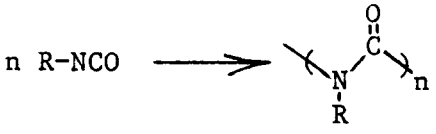


(50, 53, 54, 55, 56, 57, 58)



(41, 47, 57, 58, 59, 60, 61, 62, 63)

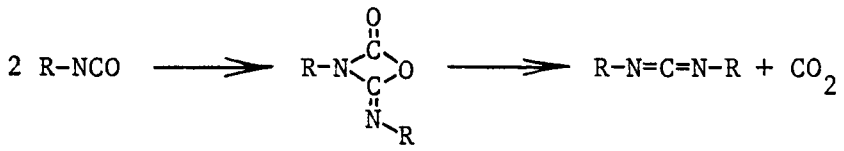
The formation of linear polyisocyanates as a PU degradation product was seriously considered by Beachell and Ngoc Son (46).



Many other workers have studied the scope of the reaction which forms such linear polymers (55, 57, 58, 64, 65, 66), but they have found the reaction to be much too easily reversible to be considered as a thermal degradation product

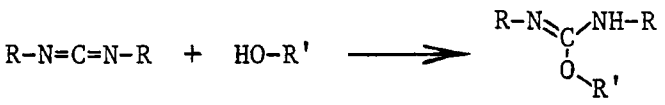
of any PU or model carbamate.

A very important reaction of two isocyanate groups, also early studied, is the condensation to form the carbodiimide linkage, with elimination of CO_2:



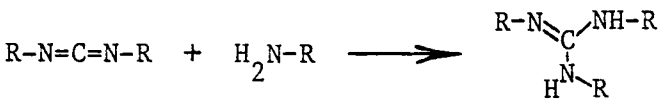
(41, 44, 46, 50, 56, 67, 68, 69, 70, 71, 72, 73).

This reaction has several further ramifications. One is the reaction with any available hydroxyl group to form an isourea,



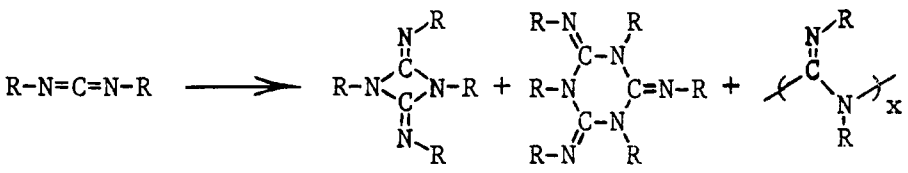
(38, p. 6; 41; 46; 62; 67; 71; 72).

Another is the reaction with an amino group to form a guanidine,



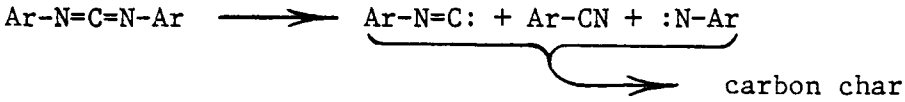
(38, p. 6; 41; 62; 68; 71; 72).

A third is the analogue of isocyanate polymerization, namely the formation of cyclic dimers or trimers, or linear polymers:



(10, p. 56; 38, p. 6; 74, p. 151; 75; 76).

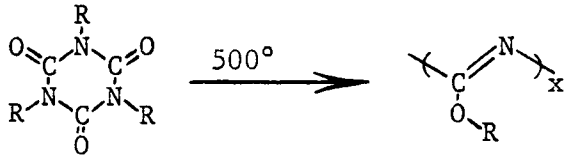
More exotic thermal degradation products have been proposed in scattered instances. Melamines might arise via guanidines, as suggested by Tilley et al. (41, p. 59). Carbodiimides might further degrade to biaryls or carbon char:



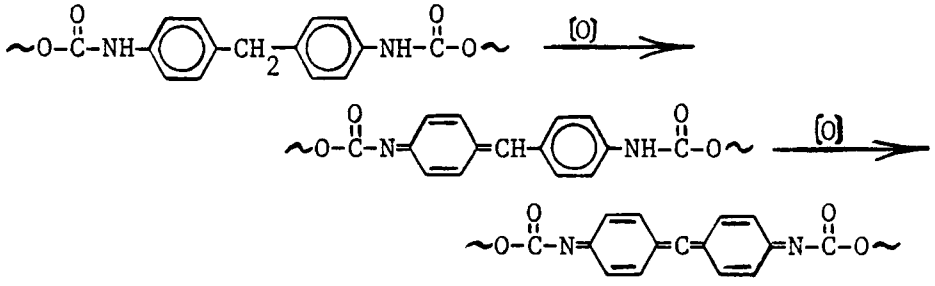


(77, p. 538).

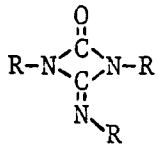
Isocyanurates at very high temperatures might degrade further to polycyanates (78).



Monoquinone-imides and diquinone-imides have been proposed by Schollenberger and Stewart (79), but it seems that these might require an external oxidizing agent:

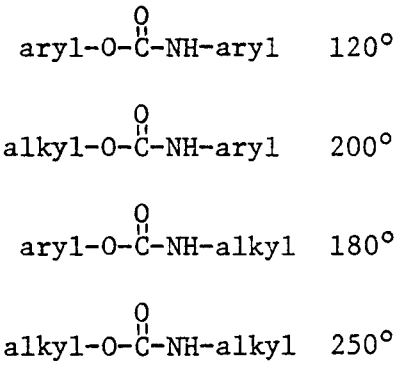


A species proposed by only one research group is the uretonimine, which allegedly forms at 230° (76, 80).



b. Substituent effects on the mechanism of thermolysis. Thermal degradations (or thermolyses) account for most of the degradation literature of PU's. The most significant of these studies are those that compare the effects of different substituents using the same experimental technique.

Probably the articles that treat the widest variety of N and O substituents are those of Frisch (81, p. 11) and Bruins (82, p. 12). The four general categories listed previously were covered, and the approximate onsets of degradation were listed as follows (81, p. 11):



These splitting temperatures were found for model compounds, and are presumed to apply to the corresponding polymers.

The type of degradation considered here is strictly the "splitting" of the carbamate into isocyanate and alcohol moieties.



Although the precise onset of degradation is open to question, in this and most other degradation works, the relative

stability order with respect to splitting is very clear. Alkyl substitution favors stability over aryl substitution.

At first glance this stability order may appear surprising, in view of a commonly held opinion that to maximize thermal stability in a given polymer type, one must maximize the aromatic ring content of the polymer backbone. Such an opinion may be a gross overgeneralization, though it is undeniable that many high temperature resistant polymers have a high content of in-chain aromatic rings (83, p. 32). Nevertheless, splitting is only one kind of degradative reaction, and it is reversible. In comparing systems according to thermal stability, it is very important to specify the type of degradation that is meant, and in some cases even to specify the operation or experiment by which it is defined. If we consider a degradative reaction where a carbon-heteroatom bond is broken (from a substituent moiety R$\{$-O-CO-NH-$\}$R'), then the aryl substituents are expected to confer more stability than alkyl substituents.

Unfortunately the above studies (81, 82) are the only ones in which the entire range of possible N- and O-substitutions are covered, for a specific degradative reaction (splitting). For the splitting reaction, the benzyl substituent would presumably have a similar effect as alkyl. All other studies have a much more limited coverage of substituent effects, and few of the other studies are directly comparable

with one another, due to differences of either experimental technique or type of compound studied (model compound or polymer). In order to attempt some organization, the studies will be ordered according to the N-substituent, since the N-substituent exerts a greater influence on the course and rate of thermolysis. The order of coverage will be N-aryl, N-benzyl, and N-alkyl urethane compounds. Within each broad topic both model compounds and polymers will be discussed, as well as variations in O-substituents.

The N-aryl-O-alkyl substitution pattern accounts for most of the degradation work on PU's and model carbamates, because this pattern is closely related to the high-tonnage commercial polymers based on TDI and MDI. Matuszak (38) used the evolution of CO_2 to measure the extent of degradation of model biscarbamates and of PU's. He assumed that the CO_2 arose entirely by the mechanism that results in the formation of secondary amines:

$$R\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}R' \longrightarrow R\text{-}NH\text{-}R' + CO_2 \quad (38).$$

He assumed that in his systems the production of carbodiimide, with concomitant formation of CO_2, played a negligible role:

$$R\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}R' \rightleftharpoons R'\text{-}NCO + ROH$$

$$2\ R'\text{-}NCO \longrightarrow R'\text{-}N{=}C{=}N\text{-}R' + CO_2$$

Some other workers would consider these mechanistic assumptions rather drastic. As in most other studies where the evolution of CO_2 is used as the experimental measure of degradation, the degradation was done in such a way that the volatile materials escaped as quickly as they were formed. If the volatile products were subjected to continued heating, the product analyses might be completely different. For this reason, degradation of model compounds might not be applicable to the corresponding polymer degradations, because the initial products of polymer degradation are probably not volatile.

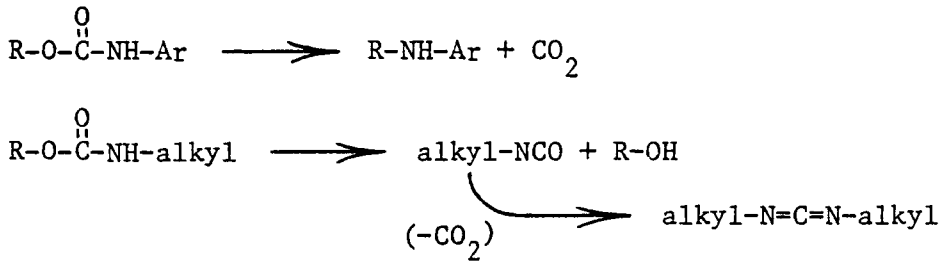
Matuszak considered a wide variety of model compounds and polymers. The model compounds were biscarbamates prepared from ethylene glycol and toluenediisocyanate, xylylenediisocyanate, and 4,4'-dicyclohexylmethane diisocyanate. Matuszak thus considered the general structures with the same O-alkyl substituent but different N-substituents. The relative rates of degradation of model compounds and polymers are shown in the following table (38) (Table I). In this study the stability order of the N-substituents was clearly found to be: N-phenyl <N-benzyl <N-alkyl.

TABLE I

RELATIVE RATES OF DEGRADATION

Substituents of Heteroatoms	Model Compounds		Polymers
	212°	250°	300°
N-aryl-O-alkyl	3	10	35
N-benzyl-O-alkyl	2	1.5	5
N-alkyl-O-alkyl	1	1	1

Tarakanov et al. (84) examined the degradation routes at 190° and 250° of two PU's made with ethylene glycol and either 2,4-tolylene diisocyanate or hexamethylene diisocyanate. The N-aryl PU gave secondary amine and CO_2, while the N-alkyl PU gave carbodiimide and CO_2:



These routes were supported by following the molecular weight changes of the residues, by obtaining elemental analyses of the residues, and by analyzing the volatile products. For the temperature range of 190° to 250°, this study demonstrates a fundamental difference in degradative pathways, depending on whether the N-substituent is aryl of alkyl. If the decrease in residue MW were taken as a measure of degradation, then the N-alkyl PU would clearly be the more stable. If the evolution of ethylene glycol, ethylene oxide, or acetaldehyde were taken as the measure of degradation, then the N-alkyl PU would clearly be the less stable. The "relative stability order" would thus depend strongly on the selected operational definition of degradation, because the mechanisms of degradation are not the same for these very different systems.

The variation of the O-substituent (keeping the same N-aryl group) in both model compounds and polymers was studied and reviewed by Tilley et al. (23, 41), for the change from O-n-alkyl to O-benzyl. The pair of N-phenyl models, with ethyl and benzyl O-substitution, was postulated to dissociate initially to isocyanate and alcohol, though they gave different ultimate products. This pair of model compounds had been previously studied by Dyer and Wright (42). At 245-250° and 1 atmosphere, the half-life of the O-ethyl model compound is about 5 times that of the O-benzyl model compound. For the O-ethyl carbamate, the residual phenyl isocyanate largely trimerizes. The same isocyanate from the O-benzyl carbamate gives mainly diphenyl carbodiimide, a difference which has not been satisfactorily explained.

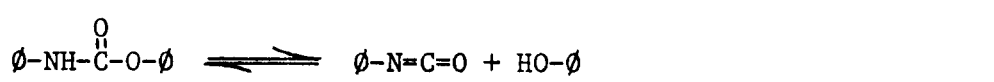
In the studies of Tilley et al. (23, 41), and that of Dyer and Newborn (67), an analogous pair of model biscarbamates based on MDI was also studied, with n-butyl and benzyl O-substituents. At 300° the O-n-butyl model had twice the half-life of the O-benzyl model. Both carbamates evolved CO_2 on thermal degradation. Carbodiimide was formed in these cases, which probably reacted further to form polymerized carbodiimide, pseudourea, or guanidine. For both pairs of model carbamates, the O-benzyl model was clearly less stable than the O-n-alkyl model.

Backus and coworkers (29) studied a wider variety of O-substituents in PU's. Three simple PU's were made by reacting MDI with hydroquinone, p-xylylenediol, and propylene glycol, and their degradation was studied by TGA under nitrogen at a heating rate of 15°/min. The data reported for the PU based on propylene glycol is less complete, but it appears to undergo a sharp weight loss at 250°. The polymers based on hydroquinone and p-xylylenediol are directly comparable however, their first sharp weight losses occurring at 320-390° and 275-340° respectively. At 800° the weights remaining were respectively 20% and 14%. Using these TGA criteria, the O-aryl polymer is clearly more stable than the O-benzyl polymer, which in turn appears more stable than the O-alkyl polymer, so increasing stability correlates with increasing aryl-content. Unfortunately the residue was not analyzed, so we do not know whether isocyanurate or carbodiimide products were formed. The order of TGA stability found above may not be the measure of PU stability, but rather of residue stability. If aromatic carbodiimides are formed by MDI, then the pseudourea adduct may be formed from the hydroxyl component. The propylene glycol molecule might not give such an adduct due to excessive volatilization.

The above studies on urethane-linkage degradation appear to be the only comparable studies which discuss the effect of

changing an N- or O-substituent among aryl, benzyl, or alkyl moieties, and which allow definite and explicit conclusions to be reached concerning the relative stabilities. Fortunately all these comparative studies treat N-aryl cases, which allows their discussion in the same section. The rest of the studies of N-aryl systems treat only a single type of substitution.

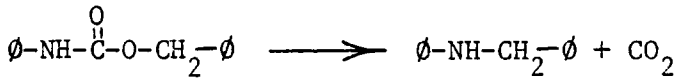
The N-aryl-O-aryl model carbamates have received a considerable amount of attention in the degradation literature, but it appears that only one study of such a PU has been made, probably because so few of these polymers are known. The use of phenol adducts as blocked or "masked" isocyanates accounts for most of the degradation literature of the model carbamates. The most important study is undoubtedly that of Lateef, Reeder, and Rand (39), who treated the thermal lability of the prototype N-phenyl-O-phenyl carbamate (phenyl carbanilate). This compound dissociates easily into its hydroxyl and isocyanate components:



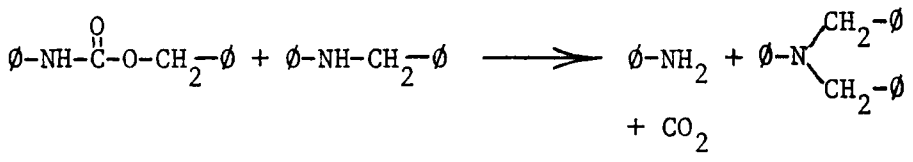
Lateef et al. measured the equilibrium concentrations in glyme solution by infrared absorption methods, finding that phenyl carbanilate dissociated to the extent of 23% at 90.4° and 63% at 150°. These values emphasize the extreme lability of this compound with respect to reversible splitting. Similar studies of this model have been done, notably those of Thompson et al. (85), Jerussi and Orlando (86), and Reilly (87). The study by

Backus et al. (29) on the polymer made with MDI and hydroquinone has already been mentioned. This polymer showed a surprising stability. A weight loss of 62% appeared in the interval 320-390°, while a residue of 20% remained at 800°. This would make it one of the most stable of all the PU's -- a huge contrast with the model compound. Unfortunately the composition of the residue was not elucidated, so we can only speculate on the further reactions of the isocyanate moiety.

For the substitution pattern N-aryl-O-benzyl (unknown in commercial polymers) much less has been done. The studies of Dyer and Newborn (67), Dyer and Wright (42), Tilley et al. (41), and Backus et al. (29) have been mentioned above as comparative studies. The thermal decomposition of the model compound benzyl carbanilate was first treated by Mukaiyama and Iwanimi (88), but since it was done in amine solvents, it is best considered later as a chemical degradation. In the Dyer and Wright (42) degradation study the volatile products of benzyl carbanilate were allowed to escape from the heating zone and trapped as quickly as they were formed. At 250° the following mole percentages of the various products were found: 93% CO_2, 34% ϕNH_2, 25% $\phi CH_2NH\phi$, 21% $(\phi CH_2)_2N\text{-}\phi$, and 1.5% $(\phi NH)_2C{=}O$. Part of the reaction appeared to proceed intramolecularly, wherein the secondary amine and CO_2 were produced directly:



Most of the amine products were shown to proceed by intermolecular displacement on carbon:





In Dyer and Newborn's study (67) of the biscarbamate of benzyl alcohol and MDI, pyrolysis at 300° gave the following mole percentages of products: 84% CO_2, 25% ϕCH_2OH, 5% ϕCH_3, 1% ϕCHO, and 80% nitrogenous residue. The formation of pseudourea linkages in the residue was not explicitly claimed in this paper, but in light of later work it was very likely. Again, the composition of the volatile products has little relevance to the composition of the nitrogenous residue. Besides the comparative studies mentioned earlier, a few other papers are relevant.

The review and original work of Ngoc Son (46, 89, 90) are still the most important references in this area. The model compound ethylene bis(N-phenyl carbamate) was degraded at temperatures between 180° and 215°, under such conditions that the volatile products were recovered as soon as formed. The products included CO_2, H_2O, aniline and other aromatic amines, and several urea and carbamate derivatives. The

polymer obtained from TDI and ethylene glycol was also degraded in N_2. The volatile products were mainly CO_2, H_2O, ethylene glycol, ethylene oxide, and toluene diamine. The residue appeared to consist of polyurea and polypseudourea, the latter arising via carbodiimide. This work will be discussed later in Chapter II, dealing with midrange infrared spectroscopy.

Unfortunately, because much of the interest in the degradation of commercial PU's is connected with their extreme fire hazard, many of these degradation papers dealing with N-aryl-O-alkyl carbamates are concerned only with the gaseous products obtained at very high temperatures. One of the most thorough studies of the volatile products is that of Hileman et al. (91). Further discussion of the papers which deal with the residues of the N-aryl-O-alkyl structure will be deferred until Chapter II, since IR spectroscopy plays such a crucial role in structure elucidation.

For the N-benzyl-O-aryl and N-benzyl-O-benzyl substitution patterns, no thermal degradation studies have been reported. For the N-benzyl-O-alkyl substitution pattern, there have been a few studies, most notably those of Rumao and coworkers (10, 18, 72) already discussed among the comparative studies in the section of N-aryl substitution. Earlier, Reegen and Frisch (92) had treated PU's derived from m-XDI. The studies of Matuszak et al. (38, 73) have already been mentioned among the comparative studies in the section on N-aryl

substitution. Probably the earliest study was that of McKay and Vavasour (93), who reported N,N'-dibenzylurea as the only confirmed nitrogenous product of the pyrolysis at 280-300° of N-benzyl-O-cholesteryl carbamate.

The substitution patterns N-alkyl-O-aryl and N-alkyl-O-benzyl have received no attention in the degradation literature.

The N-alkyl-O-alkyl substitution pattern has been studied by Matuszak et al. (38, 73) and Tarakanov et al. (84) as mentioned above. Dyer and Hammond (among very few other workers) studied this degradation (16). In their work pentamethylene diisocyanate and hexamethylene diisocyanate were each reacted with hexamethylene diol, and the resulting polymers were degraded at various temperatures between 232° and 280°. From the volatile product analysis of 75% CO_2 and 76% diol with only a trace of hexamethylene diamine (for the HMDI-based polymer), it appears that formation of carbodiimide was the main pathway at 280°.

2. Degradations Other Than Thermal

Since thermal degradations of PU's are much more relevant to our study than the other kinds of degradation, the many other kinds will be treated in much less detail.

Room temperature oxidation of PU's has been almost completely neglected in the open literature, no doubt because it is such a long-term process.

Thermo-oxidative degradations have received more attention. The first thorough work in this area was that of Ngoc Son (89), which treated the N-aryl-O-alkyl case. A more recent work is that of Tarakanov et al. (84) which treated the N-aryl-O-alkyl and N-alkyl-O-alkyl cases. Flaming combustion is a special case of thermo-oxidative degradation, and of course has received considerable attention. Prominent studies are those of Skidmore and Sewell (43, 94), Mapperly and Sewell (95), Wood (96), Papa and Proops (97), Boettner and Ball (98), Martin (21), Delman (99), and Backus (29). This recent surge of interest was undoubtedly stimulated by many revised fire codes which explicitly forbade certain uses of PU's.

Photolytic degradation of PU's has been studied by a few workers since the thorough work of Beachell and Ngoc Son (46, 89, 90), which covered the N-aryl-O-alkyl case. Tarakanov et al. (100) studied O-alkyl PU's based on TDI, MDI, XDI, and H_{12}MDI, covering a wide variety of N-substituents. Beachell and Chang (101) studied the N-phenyl-O-ethyl and N-benzyl-O-ethyl carbamate models. Schollenberger and Stewart (79) studied ethyl carbanilate in depth, as did Schultze (102, 103) and Osawa (104). Schultze also studied various other model carbamates, including N-benzyl and N-alkyl cases. Cheu and Osawa (105) studied MDI-based PU's containing macroglycols.

For photo-oxidative degradation of PU's, Ngoc Son (89)

did the earliest thorough work. Tarakanov, Nevskji, and Beljakov (100) studied a variety of O-alkyl PU's, based on MDI, TDI, and HMDI. A thorough study has recently been done by Schollenberger et al. (79), covering a wide variety of N-aryl, N-benzyl, and N-alkyl cases.

Somewhat related to the photodegradations are the mass spectrographic degradations of model carbamates, which have been studied by Thomson (106), Wunsche (107), and Osawa (104). These studies mostly treated the N-aryl systems, although N-methyl-O-phenyl carbamate was treated by Thomson.

Because of various PU uses in electrical insulation, building materials, and many coatings applications, the hydrolytic degradation of PU's has been investigated extensively. These studies should be separated into hydrolyses by neutral water, by aqueous acid, and by aqueous base.

Neutral water hydrolyses were studied by Reegen and Frisch (92), Gahimer and Nieske (108), Schollenberger and Stewart (109, 110), Cohen and Van Aartsen, and Vontor and Vecera (111).

Acidic hydrolysis of carbamates was reviewed by Adams and Baron (48). A wide variety of N-substituted model carbamates and model PU's was reviewed and studied by Matuszak and Frisch (38, 73). Schollenberger and Stewart (79) studied MDI-based PU's.

Basic hydrolysis was also reviewed by Adams and Baron

(48). Although O-aryl carbamates have been almost ignored in other contexts, they were studied by Brown et al. (112) and Vontor et al. (111, 113, 114). The studies by Matuszak et al. (38, 115) also covered basic hydrolyses.

Most reported chemical degradations are aminolyses, a wide variety of amine reagents having been studied. Exemplary among the model compound studies are those of Furuya et al. (116) and of Abbate, Farrissey, and Sayigh (62), and among the PU studies is that of Okuto (2). Other degradative reagents are hexamethyldisilazane for model compounds and PU's (117, 118) and hydrogen bromide for model compounds (119, 120).

D. THE AB-TYPE POLYURETHANES

1. Synthetic Approaches

As mentioned at the outset, classical PU's are of the AABB-type. Less conventional are the AB-type PU's, which may conceivably be made by the hydrogen-transfer polyaddition of ω-hydroxyisocyanates,

$$HO\text{-}R\text{-}NCO \longrightarrow \{O\text{-}R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\}_x$$

or by the polycondensation reaction of ω-aminochloroformates,

$$Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R\text{-}NH_2 \xrightarrow[(-HCl)]{} \{O\text{-}R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\}_x$$

Both of these hypothetical syntheses may be postulated by strict analogy with the preparative methods of AABB-type PU's.

Though the term "AB-type" has been used in only one preceding report on PU's (121), it is a general term referring to polymers derived from monomers that contain both required functional groups. The presence of both functional groups in the same molecule markedly simplifies attainment of exact stoichiometric balance of reactants for AB-type relative to the AABB-type polymers.

The hypothetical reagents shown above, the ω-hydroxyisocyanate and ω-aminochloroformate, contain groups that would be expected to undergo facile intra- and/or intermolecular reactions. The large majority of PU workers would agree with P. A. S. Smith (122), who stated in his review on the Curtius reaction that "Hydroxyisocyanates have never been isolated because of the interaction of the hydroxyl and isocyanate groups with the formation of cyclic and polymeric urethanes." Only two claims seem to have been made for such a coexistence. Hoover, Stevenson, and Rothrock (123) claimed the stable existence of hydroxymethylisocyanate at -50° and of other more complex α-hydroxyisocyanates at below 0°. Ulrich, in one paper (124) and several patents (125), claimed the existence in solution of meta- and para-hydroxyphenyl isocyanates. These somewhat doubtful claims will be further discussed later in this chapter, as will

enhancement of rates of hydroxyl and isocyanate reactions by catalysts.

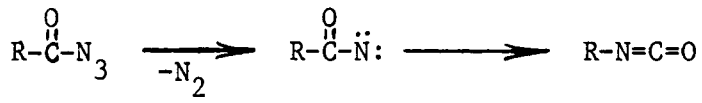
Much of the chemistry of the AB-type PU's concerns generation of the appropriate transient intermediates, such as ω-hydroxyisocyanates and ω-aminochloroformates, and all the synthetic methods known to this writer will be reviewed. Greater emphasis will be placed on those AB-types that are N-monosubstituted, since the N,N-disubstituted systems are not directly relevant to the present experimental studies.

This review will cover first those methods that use the ω-hydroxyisocyanate transient intermediate, then those that use an ω-aminochloroformate intermediate, and finally various miscellaneous methods.

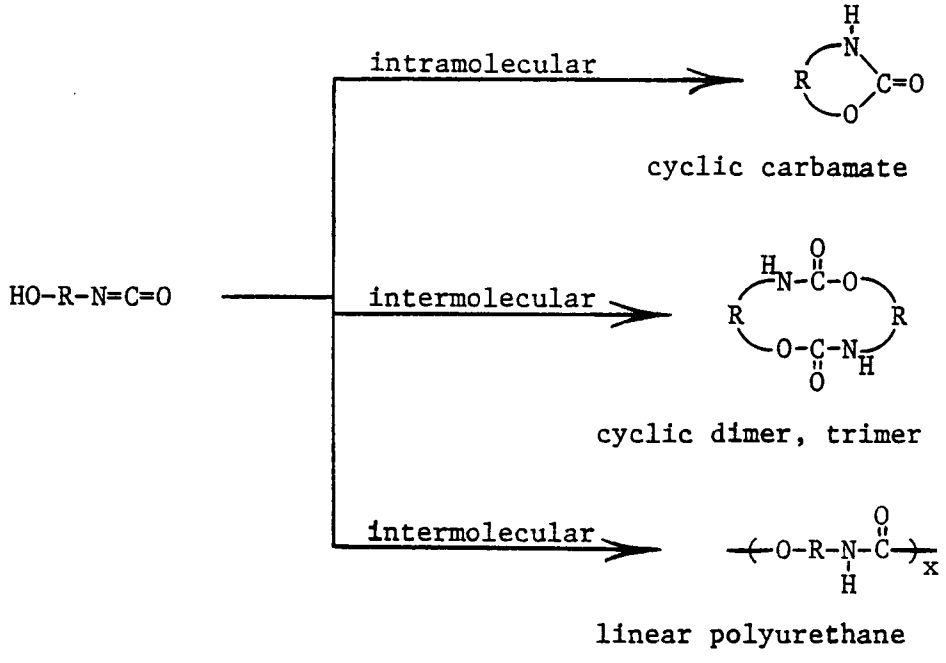
a. ω-Hydroxyisocyanate routes. Many of the methods reported for generation of isocyanates use an aqueous medium and therefore cannot be used for synthesis of AB-type PU's. Such classical syntheses as the Lossen rearrangement, the Schmidt reaction, and the Hofmann rearrangement fall into this unusable category.

For our purposes, the most important method for generation of ω-hydroxyisocyanates is the Curtius reaction.

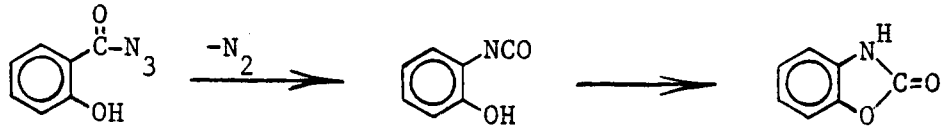
The Curtius reaction involves the thermal decomposition of an acyl azide, leading to loss of N_2 and formation of an acyl nitrene that undergoes a 1,3 rearrangement. This is illustrated schematically below. (This reaction may proceed by a more concerted-like mechanism, but this is of no concern to the present work (126).)



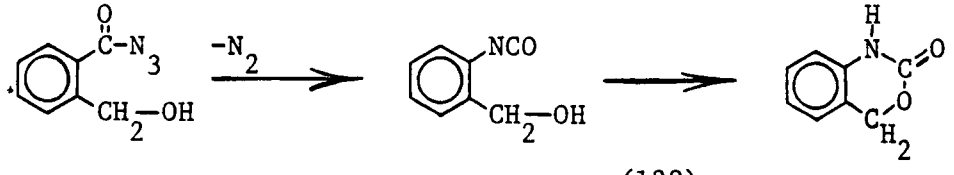
If the Curtius reaction is performed on a molecule that also contains an -OH group, the generated hydroxy-isocyanate intermediate can form various products, including cyclic monomer by intramolecular reaction and cyclic dimer and linear polymer by intermolecular reaction.



Early examples of ring formation are the following.



(127, 128, 129)



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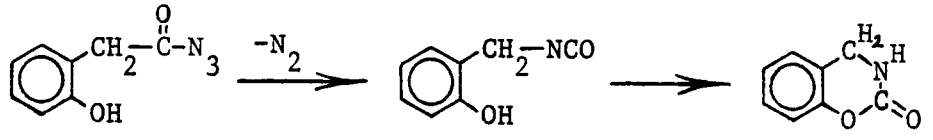

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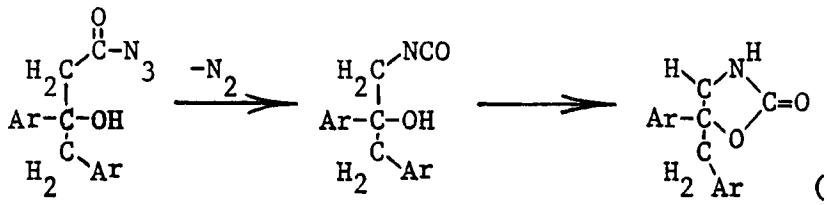
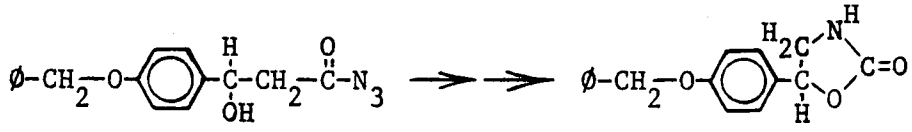


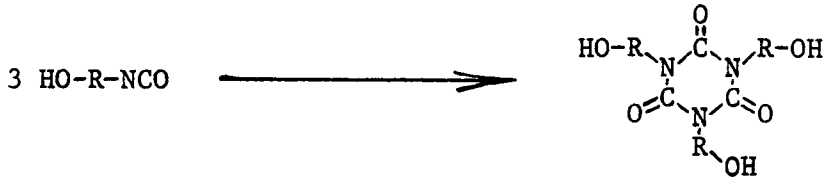
(130)



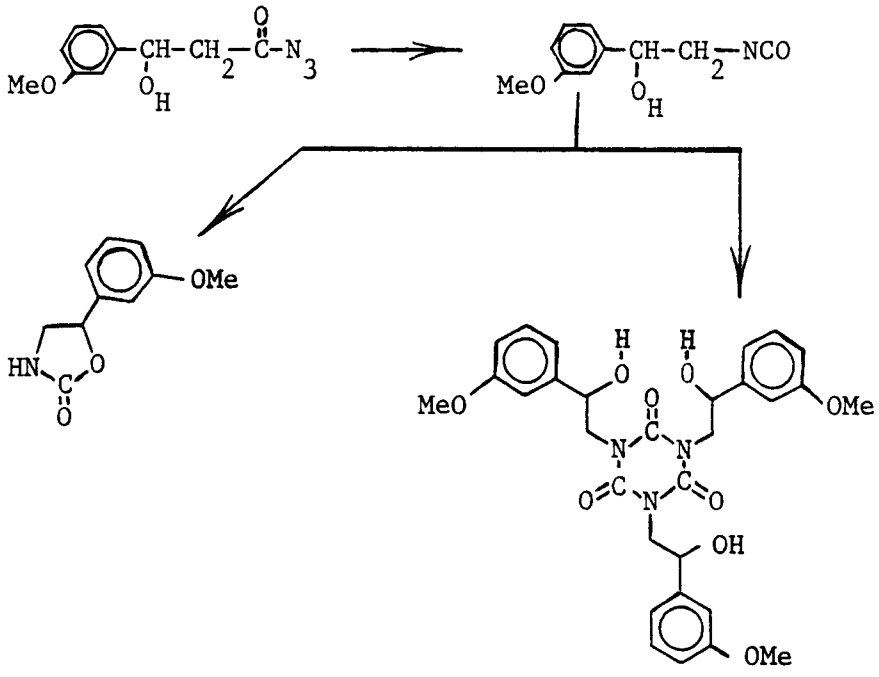
(131)

The formation of a cyclic dimer carbamate has never been reported, though it is certainly conceivable. In earlier years separation problems may have prevented its isolation, though modern liquid chromatography may now circumvent this difficulty.

Another possible reaction of hydroxyisocyanates is the formation of isocyanurates:

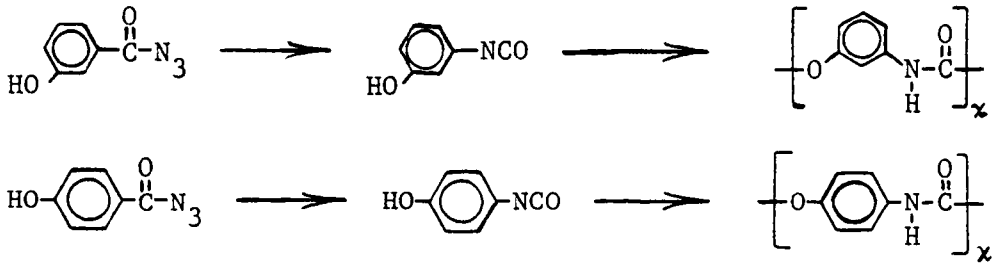


Phillips and Argabright (132) characterized isocyanurate linkages in AB-type PU's by their infrared absorptions. When Bergman and Sulzbacher (131) prepared an oxazolidone, the trimeride was also formed:

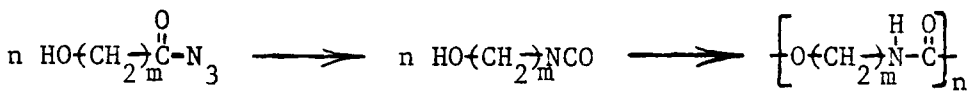


Still other byproducts are possible, and will be discussed where appropriate.

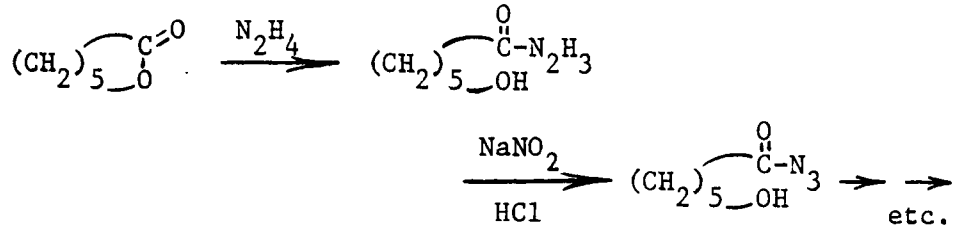
The work of Stoermer (127) contains two early examples of linear polymer formation:



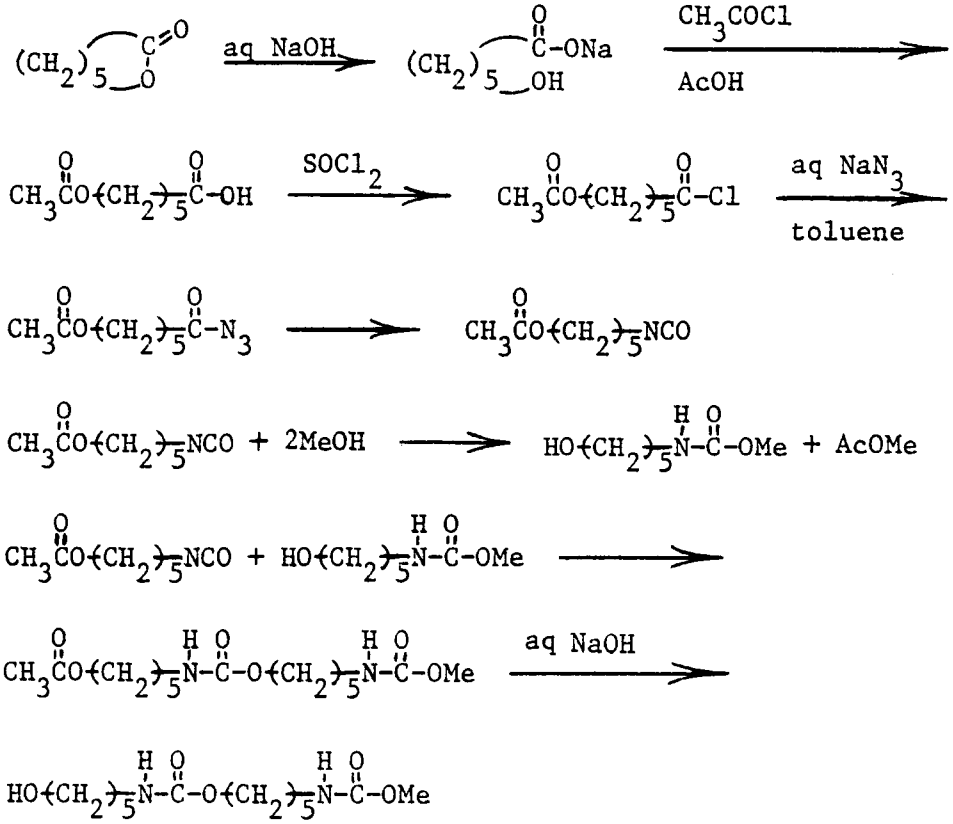
But Iwakura (133) was probably the first worker to propose the use of the Curtius reaction as a general route to AB-type PU's, "By the thermal decomposition in solution of hydroxy acid azides,"

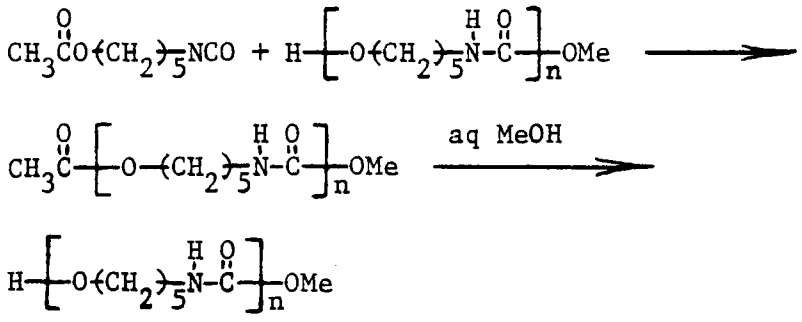


By this route, Iwakura actually made only one member of the aliphatic series, polypentamethylene urethane $-[O(CH_2)_5NH-CO]-$ from ε-caprolactone



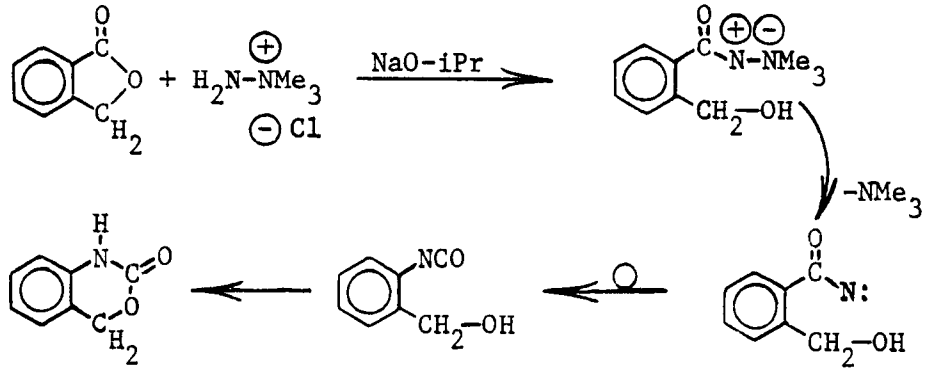
Iwakura et al. also reported the preparation of bulk amounts of this polymer much later in a more accessible journal (134). A remarkable series of oligo(pentamethylene urethanes) was also reported by Iwakura et al. (134), whose preparation utilized the Curtius reaction in each step:





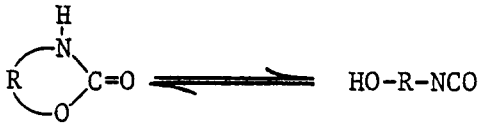
The last reaction above shows the general procedure for the synthesis of an acetoxy-oligopentamethylene urethane (n+1)-mer, which was based on the stepwise addition of a preceding hydroxy oligopentamethylene urethane n-mer with acetoxy pentamethylene isocyanate. The Curtius reaction will be met in several other contexts in this writing, as it was used extensively in the experimental work herein reported.

A reaction sequence closely related to the Curtius reaction, similar in starting materials, intermediates, mechanisms, and products, is the aminimide synthesis. At least one cyclic carbamate has been prepared in this way (135), using phthalide as the starting material.



The deliberate preparation of AB-type PU's by the aminimide route has not been reported.

Another possible way of generating ω-hydroxyisocyanates is the thermal ring-opening of cyclic carbamates



As previously noted, "splitting" of the carbamate group to isocyanate and hydroxyl moieties is a well-known reaction, and the hydrogen-transfer addition reaction is reversible at higher temperatures.

The conversion by heat alone (with no catalyst deliberately added) of cyclic carbamates to linear polymers is known in the patent literature, notably the patents of Drechsel and Hechelhammer (136, 137, 138, 139).



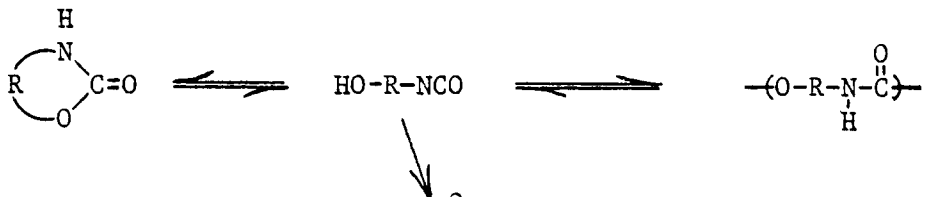
(136, 137, 138)

(137, 138, 139)

Such a polymerization of a cyclic carbamate by heat alone seems to have been reported only once in the open literature. Dyer and Read (140) prepared poly(trimethylene urethane) from tetrahydro-1,3-oxazin-2-one, repeating the work of

Drechsel (136, 137, 138).

The thermal ring-opening polymerization of cyclic carbamates is clearly expected to be an equilibrium reaction, with the ring and polymer being readily interconvertible (unlike the products of the Curtius reaction which are formed under much milder conditions). However, the intermediate may in some cases be trapped, for instance by the irreversible formation of isocyanurates. The cyclic dimer carbamate need not cause any additional complication, as it may be considered part of the polymer fraction by the criterion of nonvolatility.



The Drechsel patents (136, 137, 138) claimed that the polymerization could be accelerated by various catalysts, such as water, alcohols, and Friedel-Crafts catalysts. The Dyer and Read study (140) claimed that barium oxide speeded the polymerization. Still other papers (141, 142) claim the necessity of using certain catalysts to effect the polymerization of specific cyclic carbamates. Their review

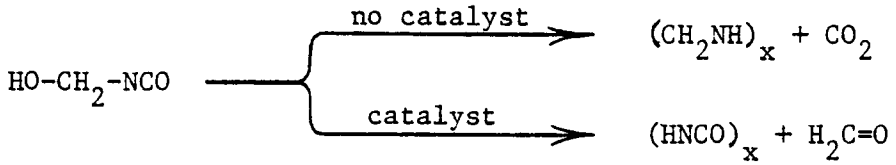
will be deferred to a more appropriate context.

A synthesis which clearly proceeds via an ω-hydroxyisocyanate is the metathetical reaction of an ω-chlorohydrin with potassium cyanate,

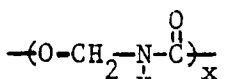
$$HO\text{-}R\text{-}Cl + KNCO \xrightarrow{DMF} \left(O\text{-}R\text{-}\underset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\right)_x$$

from which either ring or polymer or both can result, depending on the structure of the chlorohydrin. This subject was treated thoroughly by Phillips and Argabright (132), who examined the aliphatic series of chlorohydrins $HO(CH_2)_nCl$, n = 2 to 6. Ethylene chlorohydrin (n = 2) and trimethylene chlorohydrin (n = 3) gave the rings 2-oxazolidone (n = 2) and tetrahydro-2H-1,3-oxazin-2-one (n = 3) as major products, at all reagent concentrations. The amount of polymer formed from these chlorohydrins was not determined. The residual oils contained isocyanurate and urethane linkages. Tetramethylene chlorohydrin (n = 4) forms some polymeric products, but mainly yields tetrahydrofuran (56%). The polymers contained urethane, alcohol, and isocyanurate groups. Pentamethylene chlorohydrin (n = 5) forms a linear polyurethane in 63% yield, with very little isocyanurate by-product. Hexamethylene chlorohydrin (n = 6) forms a polyurethane in 84% yield, along with very little isocyanurate.

It should be mentioned that the simplest ω-hydroxyisocyanate does not form any product containing a urethane linkage. Hoover et al. (123) reported that hydroxymethylisocyanate polymerizes at temperatures below 0° with explosive violence, with the elimination of carbon dioxide in the absence of a catalyst, or with the elimination of formaldehyde in the presence of an acidic or basic catalyst.



The polymers obtained were of low MW, and were not characterized beyond their elemental analysis. None of the polymers could be represented by the structure

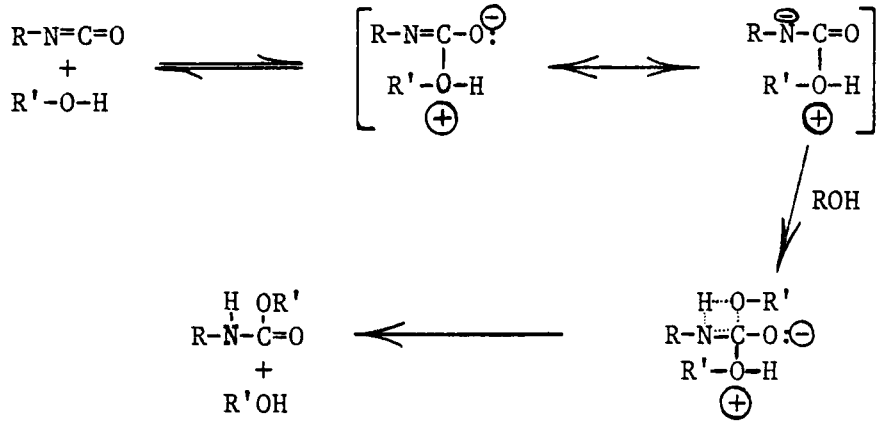


Whether α-hydroxyisocyanate was made in the first place is questionable. The general α-hydroxyisocyanates were reviewed by Smith (122, p. 350), who stated that these intermediates invariably lose cyanic acid to form aldehydes or ketones.

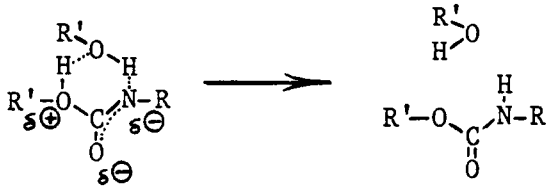


Before concluding this discussion of hydroxyisocyanates, the mechanism of the hydrogen-transfer addition

reaction between the isocyanate and hydroxyl groups, and that of catalysis, should be discussed. The reaction between the isocyanate and alcohol groups in the absence of deliberately added catalyst is well documented (143, 144, 145, p. 318). In the absence of an added catalyst, the alcohol itself is believed to act catalytically, with the complex formed between the isocyanate and alcohol involving electron-pair donation and not hydrogen-bonding (145, p. 327).



The self-catalysis scheme proposed by Lenz (146, p. 181) is similar, except that a second hydroxyl group could form two hydrogen bonds with the zwitterionic adduct to give two immediate and simultaneous proton transfers.



Presumably the function of the catalytic hydroxyl group could be fulfilled by any other group with a labile proton,

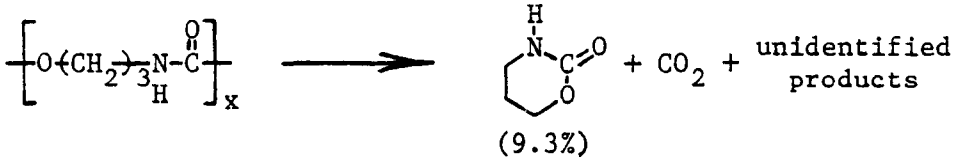
perhaps even the NH group of the product.

In most mechanistic discussions of catalysis, it is assumed that the rate determining step is the hydrogen-transfer reaction occurring after the zwitterionic adduct is formed. It should be noted that the 1,3 proton migration in the conversion of zwitterion to product is very similar to several tautomerisms familiar to organic chemists, such as the keto-enol and imine-enamine tautomerisms.

Whatever the mechanistic subtleties, the addition of isocyanate to alcohol to form a urethane is a thermodynamically favored, highly exothermic reaction. An equilibrium may exist between the urethane linkage and the component isocyanate and hydroxyl moieties, but it would be favorable to the latter only at high temperatures (147, p. 1948). It is expected that the kinds of chemical species present are much more diverse in the bulk thermal ring-opening polymerization than in the Curtius reaction, due to the more strenuous conditions in the former (higher temperature and higher concentration of reactants). In thermal polymerization, several byproducts could serve as acids or bases, even without the intentional addition of external catalysts.

In comparing the Curtius route with the thermal ring-opening route, we may expect that the former is likely to

give the kinetic product, while the latter is likely to give the thermodynamic (or equilibrium) product. The temperature of the Curtius reaction (normally refluxing benzene) is not usually high enough for appreciable "splitting" of the urethane linkage to occur. Thus whatever kind of carbamate linkage is formed first in the Curtius reaction, by intra- vs. inter-molecular reaction of the hydroxyisocyanate, is likely to so remain. These considerations are largely hypothetical, as only one test seems to have even been attempted. If the thermal polymerization of cyclic carbamates is an equilibrium process, the pyrolysis of the polymer (in a sublimator for instance) should regenerate monomer. Dyer and Read (140) attempted this conversion by pyrolysis of poly(trimethylene urethane), finding that only a 9.3% yield of cyclic carbamate tetrahydro-2H-1,3-oxazin-2-one could be obtained, carbon dioxide being lost in the process,

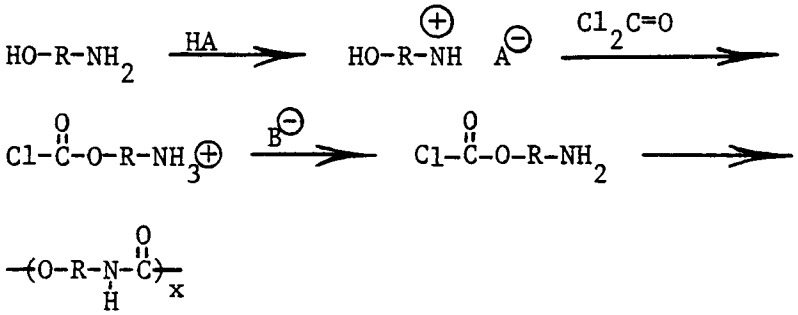


If we go beyond the uncatalyzed or autocatalyzed reaction of isocyanates with alcohols, and consider the deliberate addition of external catalysts to accelerate the reaction we find that a vast amount of work has been done and a huge literature has accumulated (51, 56, 143, 145,

148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160). Even a catalysis by light ("photoassisted" reaction) has been reported by McManus (161).

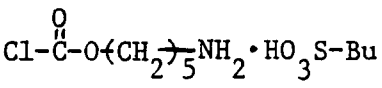
None of these studies discusses an isocyanate plus alcohol reaction that would not proceed at all in the absence of catalyst, although such reactions might proceed by a slightly different mechanism in the presence of catalysts. Since the subject of externally added catalysts is largely irrelevant to the experimental work of this writer, it will not be considered further. For detailed mechanistic considerations, the reader is referred to the cited works.

b. ω-Aminochloroformate routes. Another broadly applicable synthesis of AB-type PU's involves interfacial polycondensation of ω-aminochloroformates. The general scheme used is the following:

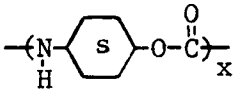


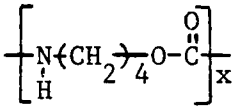
The first interfacial synthesis of this kind was reported in a 1950 French patent (162), wherein poly(pentamethylene urethane) was made by two slightly different techniques.

In one procedure, a 30% chloroform solution of the ε-ammonium chloroformate (structure shown below) was added dropwise with violent agitation to an excess of 20% aqueous K_2CO_3 at 0°.



In the other procedure, a methylene chloride solution of the hydrochloride salt of the above chloroformate was added to aqueous K_2CO_3 at -10°. Schaefgen, Koontz, and Tietz (121) have done the most thorough work in this area. They found that the amino group must be rendered unreactive early in the reaction sequence, invariably by quaternizing with a strong acid. They emphasized that the method and mechanism of the interfacial polycondensation in the AB-type monomer system differ from those in the corresponding AABB-type monomer system due to three main factors: "(1) The AB monomer is a salt; (2) both complementary functional groups are in the same molecule; (3) both functional groups are present in the organic phase." Schaefgen et al. (121) prepared several N-monosubstituted AB-type PU's by interfacial polycondensation, including those shown below.



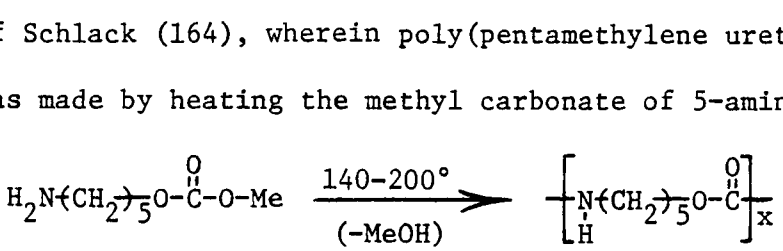


The interfacial technique is the method of choice for N,N-disubstituted AB-type PU's, for which ω-hydroxyisocyanates cannot be used. Polymers made by this technique include the two piperidine derivatives shown (121, 163).



c. Miscellaneous routes. Some AB-type PU's have been made by polycondensation processes that are difficult to classify because their mechanism is undetermined. Some of these processes may generate ω-hydroxyisocyanate intermediates by the thermal splitting reaction. In common, they all proceed via the elimination of a volatile small molecule, so they will be treated together.

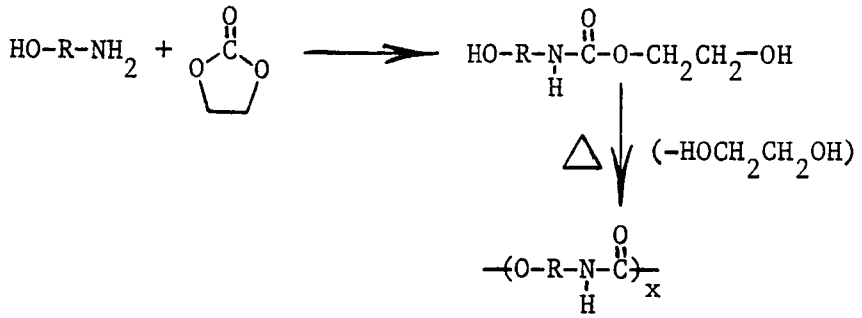
The first reaction of this type is the melt process of Schlack (164), wherein poly(pentamethylene urethane) was made by heating the methyl carbonate of 5-aminopentanol.



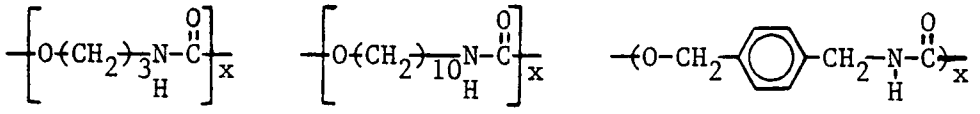
The experimental details in this patent were worded in very general terms.

Dyer et al. (140, 165) described a similar technique much more explicitly. Various aminoalcohols could be reacted with ethylene carbonate to obtain AB-type PU's directly. They found that β-hydroxyethyl carbamates were isolable

intermediates in this process

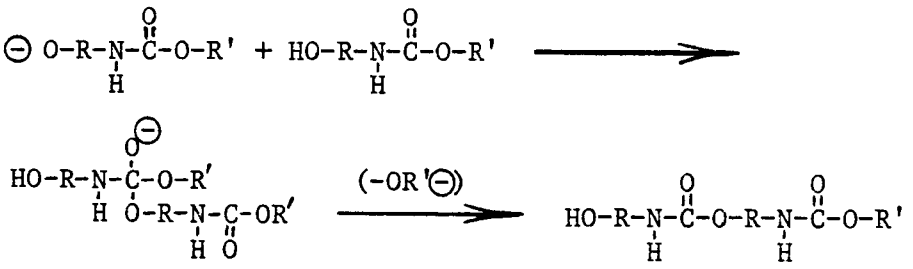


Catalysts used for these reactions were barium oxide or zinc borate, or a mixture of the two. The three polymers made by this route are shown below.



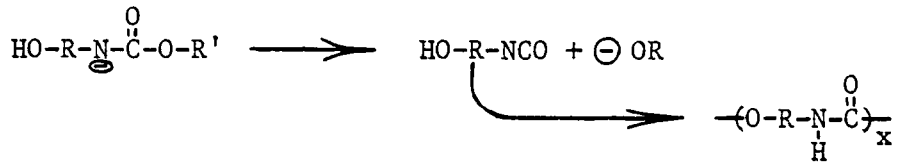
(140) (165) (165)

The catalysts used by Dyer et al. appear to function as bases, but an important question is, which proton is removed in forming the reactive species, the ω-hydroxyl or the amide proton? Initial formation of an alkoxide would probably be followed by a tetrahedral mechanism.



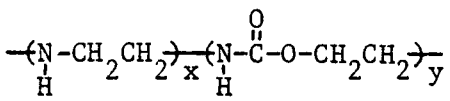
On the other hand, initial removal of the amide proton would

undoubtedly be followed by formation of an ω-hydroxyisocyanate.



The complexity of the catalysts precludes a selection of mechanism on the basis of simple Bronsted acidity.

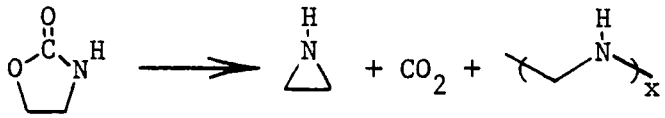
At least two poly(ethylene urethanes) have been prepared by the copolymerization of cyclic imines and carbon dioxide (166, 167). The copolymerization of ethylene imine and CO_2 was carried out in a sealed tube in the absence of solvent or catalyst (166). The reaction mechanism is not known. The product is not a homopolymeric AB-type PU but rather contains mixed units of ethylene imine and ethylene urethane:



Soga and Ikeda (167) have succeeded in preparing the corresponding N-phenyl polymer by reacting N-phenyl ethylene imine with carbon dioxide, although various catalysts (such as aluminum alkoxides) had to be used in this case.

Many workers have studied the thermal decomposition of oxazolidone (126, p. 197; 141, p. 6410; 168; 169; 170; 171; 172; 173). In general the products are carbon dioxide,

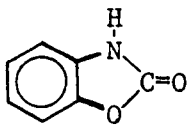
ethylene imine, and poly(ethylene imine); the polyurethane has never been detected.



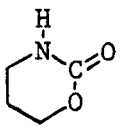
The work of Soga et al. (166, 167) suggests that eventually conditions will be found to obtain the poly(ethylene urethane) from oxazolidone.

Because polymerizations with progressively more vague mechanisms are now being considered, it is appropriate to discuss those polymerizations of cyclic carbamates that can be effected only in the presence of catalysts. For these polymerizations the mechanisms are completely unknown (141, 142).

Hall and Schneider (141) discussed the unsuccessful attempts to polymerize 2-oxazolidone and benzoxazolinone, and the successful catalyzed thermal polymerization of tetrahydro-2H-1,3-oxazin-2-one.



benzoxazolinone

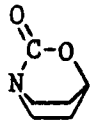


tetrahydro-2H-1,3-oxazin-2-one

The last was polymerized by sodium hydride at a temperature of 80°, in a yield of 56.7%. Since the product was not characterized beyond the determination of inherent viscosity,

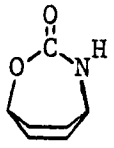
the product linkages may not be urethane.

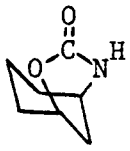
The bicyclic carbamate compound whose polymerization cannot possibly proceed via a hydroxyisocyanate is:



(142)

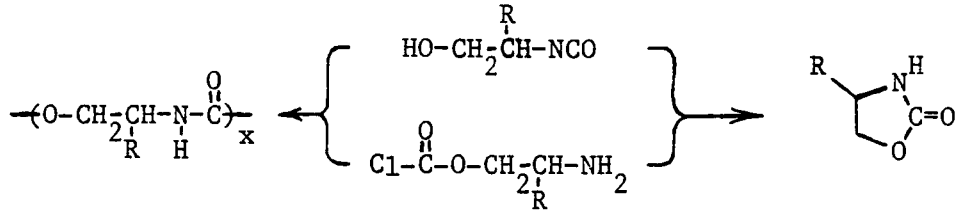
Hall reported (142, p. 6415) that the thermal polymerization of this carbamate resulted in a quantitative yield of polymer. The catalyst was not specified, beyond the implication that it could be litharge, K_2CO_3, NaH, tetraisopropyl titanate, or 2,5-dichlorobenzene sulfonic acid (142, p. 6420). The 1,4-substituted cyclohexane monomer shown below was claimed to give a 90% yield of polymer, but the corresponding 1,3-substituted monomer was recovered unchanged.



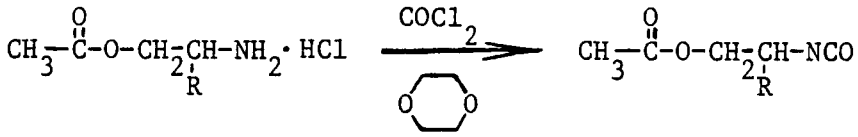


A series of AB-type oligo(ethylene urethanes) has been made for which the corresponding polymers do not exist. These AB-type oligo(ethylene urethanes) and their 1-alkyl derivatives can be made only by a stepwise procedure. If the preparation of a poly(ethylene urethane) is attempted

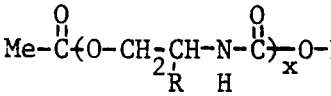
by the generation of an β-hydroxyisocyanate or β-amino-chloroformate, an oxazolidone invariably results (126):



Iwakura et al. (174) used a stepwise procedure to form such oligo(ethylene urethanes), which incorporated the following β-acetoxy isocyanate preparation.



Note that this procedure is similar to their route to the oligo(pentamethylene urethanes) mentioned earlier, except for the isocyanate preparation. With this stepwise procedure, Iwakura et al. prepared a large number of oligo(ethylene urethanes), including the following series:



R = H, x = 2 to 7 (174)

R = Me, x = 1 to 7 (175)

R = i-Pr, x = 2 to 4 (176)

R = i-Bu, x = 2 to 9 (176, 177)

R = $CH_2\emptyset$, x = 1 to 4 (175, 178)

A series of oligo(trimethylene urethanes) was similarly prepared (179). The corresponding poly(trimethylene

urethane) has been prepared in several ways by other workers (132, 136, 137, 138, 140, 141).

Since the primary emphasis of this review of the AB-type polyurethanes and of the present experimental work is the N-monosubstituted polymers, the open literature of the N,N-disubstituted polymers was not researched exhaustively. However it should be mentioned that some syntheses of the N,N-disubstituted AB-type polyurethanes have been reported (besides those previously mentioned), which have not been applied to the corresponding N-monosubstituted polymer. An example of such a synthesis is the rearrangement polymerization of N-phenyl iminocarbonate (180):



The patent literature has not been exhaustively researched.

2. Characterization of AB-Type Polyurethanes.

As expected, the characterization methods reported in the open literature are much fewer for the AB-type PU's than for the AABB-type polymers. In fact, each of the specific analyses reported can be mentioned in this section.

For structural determination, the most important characterization is undoubtedly the midrange infrared. Previous workers have reported IR spectra only for the aliphatic AB-type PU's (26, 132, 134, 165). These will be

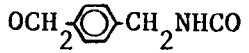
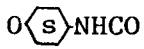
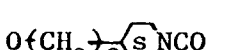
covered in Chapter II, along with other assignments and correlations by IR. A problem that should be mentioned here is the characterization of crosslinks in AB-type PU's. The formation of isocyanurate rings would not change the elemental analysis of a sample, but might drastically affect the properties of a sample, such as its solubility. These rings and the corresponding excess of pendant hydroxyl groups should be detectable by IR. The only other characterization technique which can be applied directly to such a problem is the near infrared, which will be covered in Chapter III. The near infrared has not been previously applied to any AB-type PU.

NMR seems to have been used only in the analysis of copolymer composition. The copolymers of ethyleneimine and poly(ethylene urethane) prepared by Soga et al. (166) were found to contain a maximum amount of 30.6 mole percent urethane linkages.

Inherent viscosities or relative viscosities have been traditionally reported in the open literature for all PU's. To be meaningful and reproducible, the concentration, solvent, and temperature of the viscosity measurement must also be specified. Intrinsic viscosity (limiting viscosity number) apparently has never been reported for any AB-type PU. The inherent viscosities reported for AB-type PU's are given in Table II.

TABLE II

INHERENT VISCOSITIES OF AB-TYPE PU'S

Repeat Unit In Polymer	Inherent Viscosity	Concentration[a]	Solvent	Temperature	Reference
$O(CH_2)_{10}NHCO$[b]	0.191[b]	1.0	m-cresol	25°	165
OCH_2CH_2NHCO[b]	0.183[b]	1.0	H_2O	25°	165
$O(CH_2)_5NHCO$	0.38	0.5	m-cresol	30°	134
	0.113	1.0	m-cresol	25°	165
$OCH_2CH_2N\phi CO$	0.11	0.25	90% HCO_2H	25°	167
$O(CH_2)_5NHCO$	0.94	0.5	m-cresol	30°	121
	0.08	0.5	m-cresol	30°	121
	1.25	0.5	m-cresol	30°	121
	0.81	0.5	m-cresol	30°	121

a. Concentration refers to g polymer per 100 ml solvent.

b. The originally reported relative viscosity has been recalculated as inherent viscosity.

Iwakura et al. (134) have established a precedent in using viscometry to characterize oligomers with 2 to 7 repeat units, rather low oligomers indeed. The inherent viscosity of each acetoxy-terminated oligo(pentamethylene urethane) was determined in meta-cresol at 30°, at a concentration of 1.0 g/100 ml. These inherent viscosities were plotted versus the number of repeating units, to give a monotonically rising curve, slightly concave downward (134, p. 222). The values for two hydroxy-terminated polymers were also plotted, and their curve was only slightly displaced upward. The inherent viscosities ranged from 0.03 to 0.08, requiring a viscometer with a rather long flow-time. The obvious implication of such a plot is that it provides a very convenient way to determine the number of repeat units in an oligomer. Presumably this plot could be used to determine an "average" number of repeat units in any oligomeric sample of poly(penta-methylene urethane). To precisely define what kind of average this is, would require much more work with samples containing artificially constructed size distributions of several oligomers, or containing known size distributions at any rate. So few methods are available for determining the molecular weights of oligomers, that such a convenient method should

not to be overlooked.

It appears that no other MW correlation with properties has been reported that would be adaptable to MW determinations. Variations of melting point, infrared peak intensities, and Drude equation constants with oligomer size would be highly dependant on MW distribution, for a given average MW.

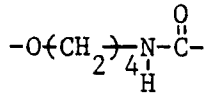
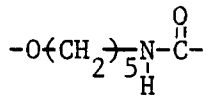
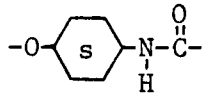
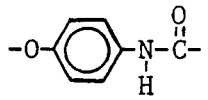
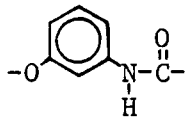
Apparently, no absolute determination of any average MW has ever been reported for any AB-type PU. Neither has any GPC "counts versus elution volume" curve ever been reported.

Almost no thermal analysis data have been reported for AB-type PU's, including DSC, DTA, TGA, and TMA. The exceptions are the studies by Nagura et al. (26, 181), where DTA and DSC thermograms were obtained for each oligomer of pentamethylene urethane, n = 2 through 10, and for the polymer. These DSC thermograms were used only to determine the melting ranges of unannealed and annealed samples.

Only a few melting points have been reported, mainly for poly(pentamethylene urethane) and the oligomers of Iwakura et al. The reported melting points of the polymers are listed in Table III.

TABLE III

REPORTED MELTING POINTS OF AB-TYPE PU'S

Polymer Structure	Melting Point	Reference
	190-196°	121
	147-149°	162
	148-153°	134
	150°	182
	155°	121
	335°	121
	300°	124, 125
	270-280°	124, 125

An X-ray study of the oligo(pentamethylene urethanes) has been done by Nagura et al. (26). A sufficiently high crystallinity of the corresponding polymer, and a sufficiently detailed diffraction pattern, were obtained to deduce a reasonable unit cell.

Studies of the annealing process were also done by the same research group, using both wide-angle (WAXD) and small-angle (SAXD) techniques (181, 183, 184).

3. Degradation of AB-Type Polyurethanes

The degradation of any AB-type PU has not yet been reported. However, on the basis of their chemical structure, we may expect rather large differences from the degradation of AABB-type PU's. The diol component of all AABB-type PU's is either small glycols alone or a combination of small glycols and macrodiols. On heating such polymers above 150°, the small glycol will be volatilized away from the decomposing bulk polymer, and the macrodiol will similarly be cleaved at the heteroatom linkages to evolve volatile products. If an ignition source is nearby, flaming combustion will result. But chemically the most important occurrence is the removal of the glycols and the macrodiol components from the polymer residue, which becomes progressively richer in the nitrogenous linkages derived from the isocyanate group.

In the AB-type monomer units investigated so far, there

are no heteroatom linkages in the chain between the isocyanate and the hydroxyl groups. Unless the whole monomer unit volatilizes away or the carbon chain cleaves somewhere, no volatile products besides H_2O and CO_2 are expected. Besides the single carbon atom in the carbamate linkage itself, all the rest of the carbon-content is expected to stay in the residue. It is the chemistry of thermal modification that makes the AB-type PU's so interesting. Analyzing the linkages that occur on thermal modification is much of the present experimental work.

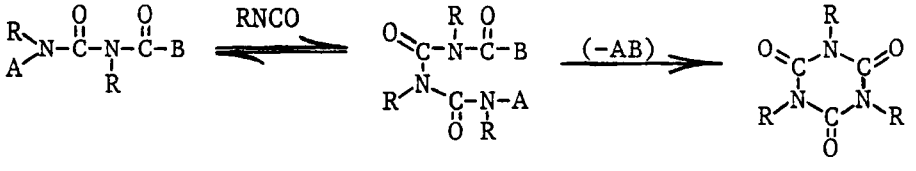
For the AB-type PU's, certain thermal modification pathways might be possible that are unknown in the AABB-type PU's. Although these pathways have not been treated by previous authors, such speculations are appropriate in this section because of their generality.

A mechanistic pathway that has been mentioned by some previous workers, but is not yet in vogue, concerns the relationship between allophanates, biurets, triurets, and isocyanurates. In conventional PU's, as the glycol component is volatilized away by heating, there certainly results an excess of isocyanate groups. As mentioned previously, these isocyanate groups might react with urethane and urea linkages to give allophanates and biurets, respectively, as thermal degradation products. But as shown by Kogon (47, 59, 185), the reaction should not stop there. Aryl isocyanates react

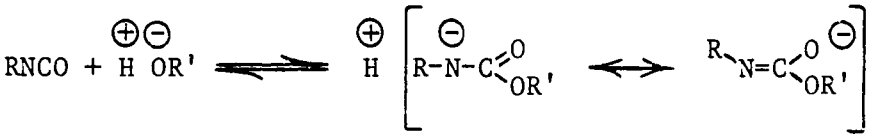
with α,γ-diarylallophanates to form triarylisocyanurates.

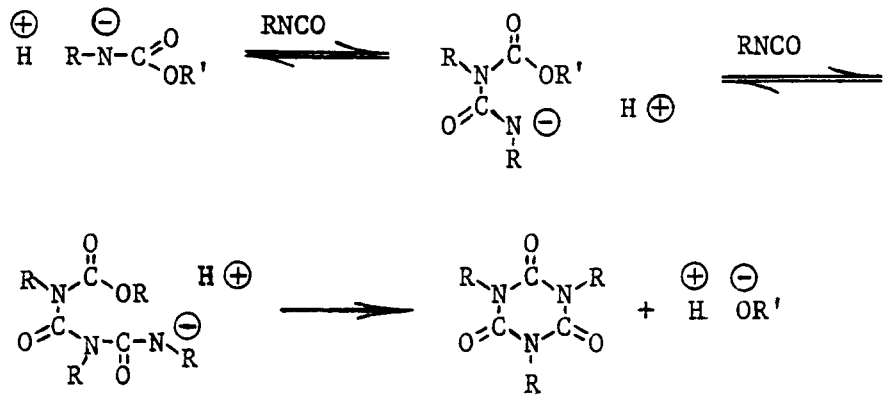


Kogon (186, p. 2254) reported that various N-alkyl substituted biurets could be prepared, but their boiling points could not be determined due to ease of decomposition (the decomposition products are presumed to be isocyanurates). Other workers have found that only α,γ-diarylallophanates are isolable, the N-alkyl allophanates being unknown (44, 45, 48). Triurets have been postulated, but do not seem to have ever been isolated. If triurets or dialkyl allophanates are ever isolated, they will no doubt be extremely labile to heat. The point was summed up nicely by Reymore (61), who explicitly showed that allophanates, biurets, and triurets are intermediates in the formation of isocyanurates. The mechanism for the generalized catalyst A-B is the following.



For catalysis by base the mechanism is probably as follows (61).



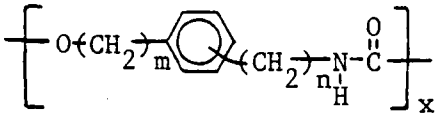


Similar considerations can be made for uretidinediones These are isolable only when R is aryl. The conversion of isocyanates to uretidinediones is reversible above room temperature, and since isocyanates are converted irreversibly to isocyanurates, the isocyanurate is favored as an equilibrium product at higher temperatures.

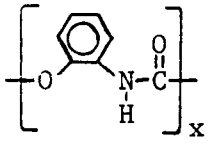
In summary, allophanates, biurets, and uretidinediones may be kinetically-controlled products at rather low temperatures for N-aryl isocyanates. For N-alkyl or N-benzyl isocyanates, one may completely forget about allophanates, biurets, triurets, and uretidinediones at all temperatures. For N-aryl isocyanates, these species are rather improbable, especially at higher temperatures. This point is made here because it is so rarely implicitly discussed in connection with the AABB-type PU's, and because the present experimental work with AB-type PU's gives no evidence for the formation of allophanates, biurets, triurets, or uretidinediones.

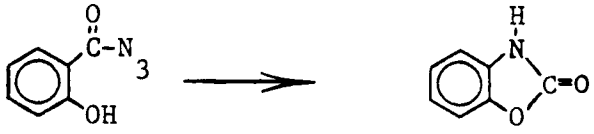
4. Considerations Specific to AB-Type Polyurethanes That Contain In-Chain Phenylene Units

a. Summary of reported syntheses. This dissertation treats the preparation and modification of AB-type PU's that contain in-chain phenylene units, illustrated schematically as:



A short summary of previous work on these systems will be presented here, following the sequence ortho, meta, and para substitution pattern.

Although Stoermer (127) did not specifically aim at poly(ortho-phenylene urethane) , he found that the Curtius reaction of salicylazide gave benzoxazolin-2-one. No by-products were reported.

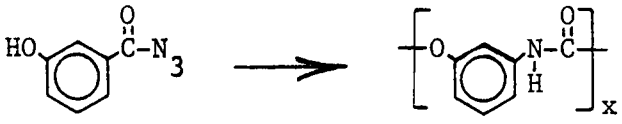


Hall and Schneider (141) attempted to prepare the PU by heating benzoxazolin-2-one in a sealed tube, with an unspecified amount of catalyst (one or more of five catalysts mentioned). No polymer product was obtained.

No other syntheses (successful or attempted) have been

reported on other PU's in the ortho series.

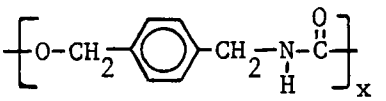
In the meta-series, only one polymer has been reported, poly(m-phenylene urethane), again by Stoermer (127) using the Curtius reaction of m-hydroxybenzoyl azide.



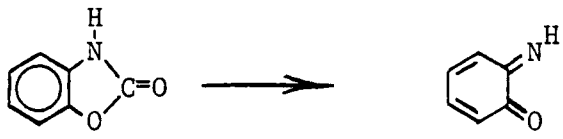
Stoermer did not characterize this polymer beyond elemental analysis.

Illari (187) and Ulrich (124) also prepared and characterized this polymer. Their studies are discussed at length in Chapter IX.

In the para series, two polymers have been previously reported. One is poly(p-phenylene urethane), obtained by Stoermer (187), Illari (187), and Ulrich (124) in the same way as its meta isomer. As in the case of the meta isomer, the characterizations of Illari and Ulrich do not agree, and most other considerations apply to this case as well.

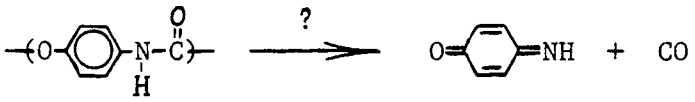
The polymer  was obtained by Dyer and Scott (165) by reacting p-hydroxymethylbenzylamine with ethylene carbonate, under heat and vacuum, and with a barium oxide-zinc borate catalyst. An inherent viscosity of 0.113 (25°, m-cresol, 1 g/100 ml) was found.

b. Side reactions during synthesis. The benzosubstituted cyclic carbamates, and the ortho- and para-phenylene linked AB-type PU's, have certain unique characteristics that should be considered. For example, we must consider the possibility of formation of quinoid species, even under nonoxidative conditions. The simplest case, benzoxazolin-2-one, might undergo a cheletropic reaction to eliminate carbon monoxide.



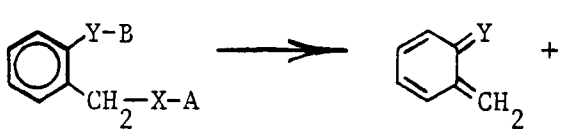
+ CO (188, p. 152).

It is more difficult to imagine this happening with the corresponding ortho- or para-linked polymer, a reaction which could not be concerted.

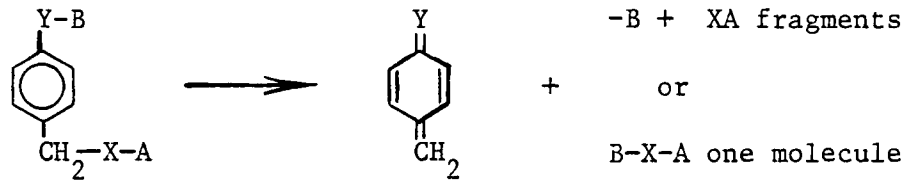


+ CO

For all the other systems, which have at least one methylene unit attached to the benzene ring, quinone methides might be formed in the general case, or quinone dimethides if Y is another methylene group (where X and Y are carbon or heteroatoms):



+ -B + -XA fragments
or
B X A one molecule



To cite specific hypothetical examples, we may consider some cyclic carbamates:



a retrograde Diels-Alder reaction



a retrograde Diels-Alder reaction

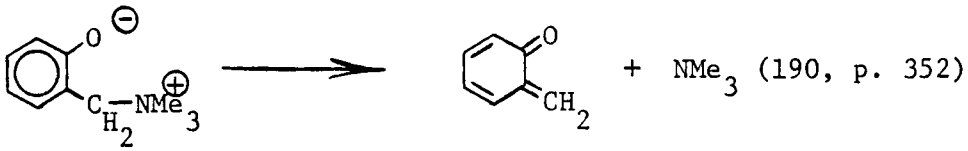


a $[\sigma 2 + \pi 2 + \sigma 2]$ cycloreversion

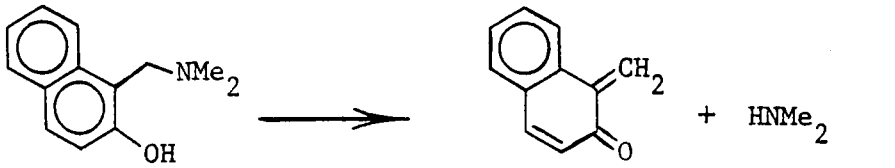
In the cyclic carbamates, the above reactions would probably be concerted if they occurred at all. In the polymers, both ortho and para, the corresponding reactions could not possibly be concerted, even if homolytic bond-cleavage occurs. The possible heterolytic bond-cleavage reactions of benzylic-heteroatom bonds ($Ar-CH_2-X$) will be considered later.

Very few analogues, or even similar reactions, of the above type have been reported to give quinone methides by homolytic cleavage. The reactions that are known

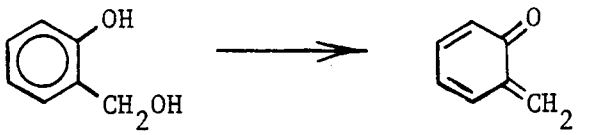
to produce quinone methides appear to be heterolytic (190, 191).



(190, p. 352)

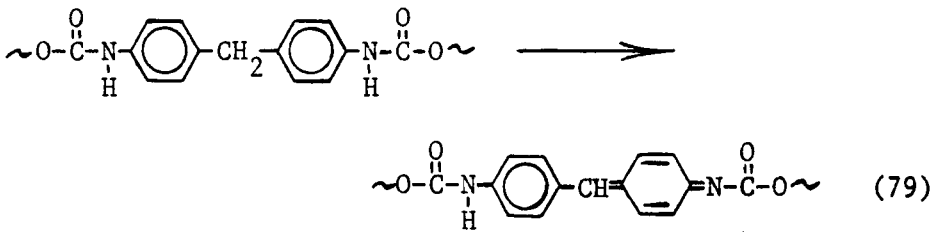


(190, p. 352; 191, p. 1172)



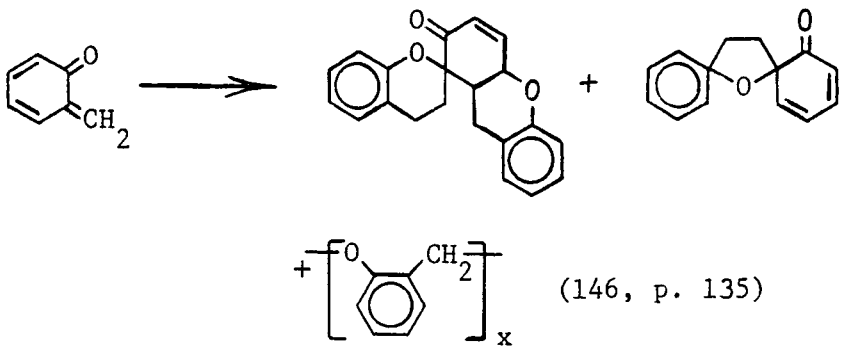
(191)

Quinoneimine methides are known, for example in the oxidation of MDI-based PU's, but these are not homolytic cleavage reactions either.



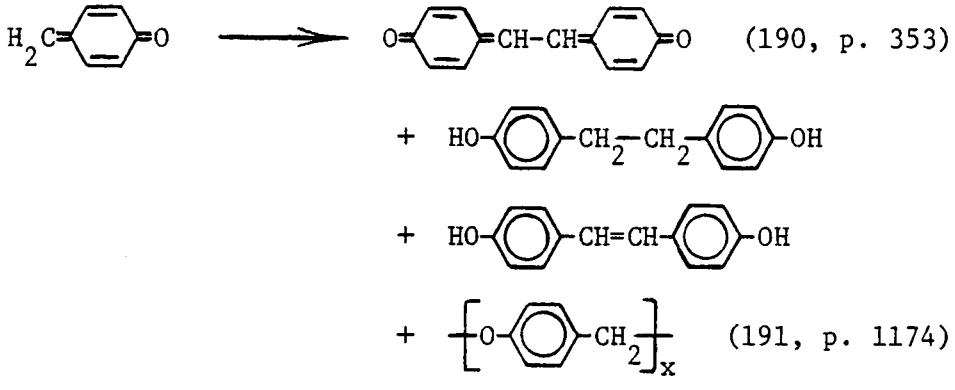
(79)

The reactions of ortho-quinone methide itself have been well explored:



(146, p. 135)

Dimers are usually formed by para-quinone methides (the first two in equal amounts by disproportionation):



(190, p. 353)

(191, p. 1174)

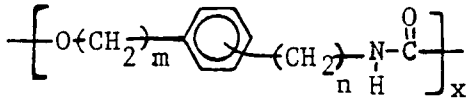
To generalize, the following four types of linkages between aromatic rings could be produced by quinone methides:

$ArCH_2OAr$ ArOAr $ArCH_2CH_2Ar$ ArCH=CHAr

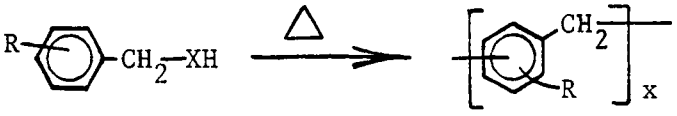
Quinone dimethides (191, p. 1145) and quinoneimine methides (79) have been investigated much less, but in the absence of further information we would postulate analogous reactions.

One salient feature of the above self-addition reactions is the absence of diarylmethane linkages in the products, $ArCH_2Ar$. This is probably because the self-additions proceed via diradical intermediates.

Some generalizations may be made about the reactivity of the hydrolysis products of the phenylene-linked AB-type PU's. The water causing the hydrolysis need not be externally added; it might be endogenously produced on heating. Hydrolysis of several such PU's, of general structure

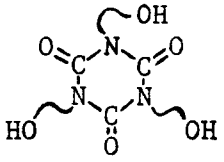
 gives rise to benzyl alcohol

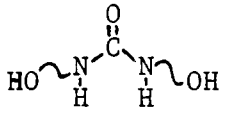
or benzylamine moieties, Ar-CH_2-XH, X = O or NH. Such benzyl-heteroatom moieties have been shown to give rise to polybenzyls on heating (83, p. 49):

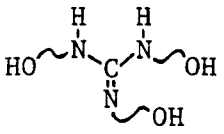


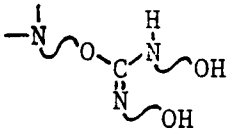
More specific considerations of such cationic intermediates should be taken up with each PU, in its appropriate chapter.

For the last generalized speculations about the heat-modification of AB-type PU's, one should inquire about the fate of the pendant hydroxyl groups. Whenever isocyanurates, ureas, or carbodiimide derivatives (guanidines, isoureas, or polymerized carbodiimides) are formed, two or three hydroxyl groups lie pendant.









If the hydroxyl group is straight-chain aliphatic, it may dehydrate or etherify. If the hydroxyl group is

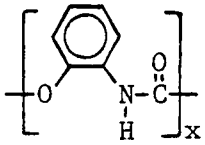
benzylic, it may condense with another benzene ring to form a diarylmethane. If the hydroxyl group is phenolic, then it may donate its proton to such basic residues as the guanidines and pseudoureas present (for example forming a guanidinium aryloxide salt).



In most of these cases, the hydroxyl group would thus contribute to crosslinking.

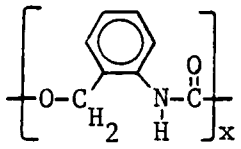
Unlike the AABB-type PU's which certainly degrade with heat to form products of negligible utility, the AB-type PU's may undergo modification with heat to form still-useful polymeric residues. Their applicability as composite resins or coatings should be studied in this respect.

c. Nomenclature. The main objective of the present experimental work was to prepare and characterize a series of ortho- and para-phenylene linked AB-type PU's, and to examine their thermal modification. The structures of the polymers, their standard nomenclature, and the abbreviated nomenclature systems used in this dissertation are listed below in the order in which they will be discussed.



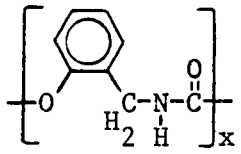
poly(oxycarbonylimino-1,2-phenylene)

polymer-ortho-00



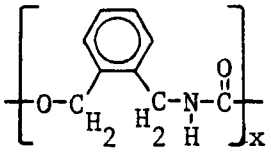
poly(oxycarbonylimino-1,2-phenylene methylene)

polymer-ortho-10



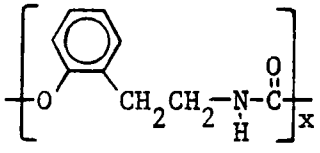
poly(oxycarbonyliminomethylene-1,2-phenylene)

polymer-ortho-01



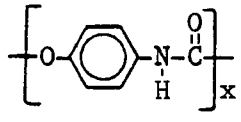
poly(oxycarbonyliminomethylene-1,2-phenylenemethylene)

polymer-ortho-11



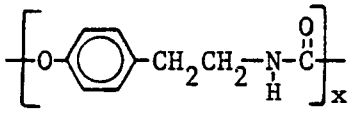
poly(oxycarbonylimino-1,2-ethanediyl-1,2-phenylene)

polymer-ortho-02



poly(oxycarbonylimino-1,4-phenylene)

polymer-para-00

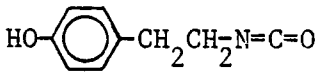


poly(oxycarbonylimino-1,2-ethanediyl-1,4-phenylene)

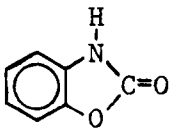
polymer-para-02

The abbreviated names are derived by specifying the substitution pattern on the aromatic unit (ortho, meta, or para), followed by the number of methylene units between O and the ring and between N and the ring, respectively. This kind of abbreviated nomenclature is applied throughout.

For example the intermediate 2-(p-hydroxyphenyl)ethylisocyanate

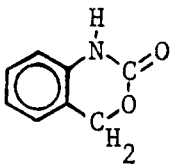


is referred to as hydroxyisocyanate-para-02; the urea derived from this intermediate, bis[2-(p-hydroxyphenyl)ethyl] urea, is referred to as urea-para-02. In the case of the benzosubstituted cylcic carbamates, the ortho substitution pattern is required, so the term ortho is not used in the abbreviated names. The relevant benzosubstituted cyclic carbamates are listed below with their standard and abbreviated names.



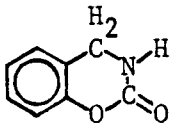
2-benzoxazolinone or 2(3H)-benzoxazolone

ring-00



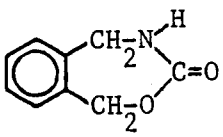
1,4-dihydro-2H-3,1-benzoxazin-2-one

ring-10



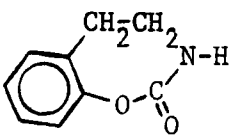
3,4-dihydro-2H-1,3-benzoxazin-2-one

ring-01



4,5-dihydro-2,4-benzoxazepin-3(1H)-one

ring-11



4,5-dihydro-1,3-benzoxazepin-2(3H)-one

ring-02

CHAPTER II

THE USE OF MIDRANGE INFRARED SPECTROSCOPY FOR CARBAMATE AND POLYURETHANE STRUCTURE ELUCIDATION

The midrange infrared is also called the sodium chloride region infrared or the ordinary infrared, and usually spans the region 2μ to 16μ (or 2000 nm to 16,000 nm, or 50,000 cm^{-1} to 625 cm^{-1}). It is distinguished from the near infrared region (0.6μ to 3μ) which lies between the visible and midrange infrared regions, and from the far infrared region (16μ to 50μ) which lies between the midrange infrared and the microwave regions. The region of overlap between the near and midrange infrared regions is thus 2μ to 3μ (2000 nm to 3000 nm, or 5000 cm^{-1} to 3333 cm^{-1}). The practical dividing line is about 2.7μ, above which pyrex glass absorbs. Below 2.7μ the near infrared is much to be preferred, because of more instrumental convenience.

The choice of wavelength (measured in micronsμ or nanometers nm) instead of frequency (measured in reciprocal centimeters cm^{-1}) as a way of reporting infrared absorptions should be discussed. The useful conversions are the following: 1 micron = 1000 millimicrons = 1000 nanometers, and (wavelength in microns)(frequency in reciprocal centimeters) 10,000 $\mu\, cm^{-1}$.

The use of frequencies is probably more natural, in that the frequency of a combination band (ν_c) is very nearly the simple sum of the frequencies of the component vibrations; i.e. $\nu_c = \nu_1 + \nu_2$. For wavelengths the relationship is more complex;

$$\frac{1}{\mu_c} = \frac{1}{\mu_1} + \frac{1}{\mu_2} \quad \text{or} \quad \mu_c = \frac{\mu_1 \mu_2}{\mu_1 + \mu_2} .$$

However the instruments used in this experimental work, for both the midrange infrared and near infrared, were calibrated linearly in wavelength. Additionally, near infrared absorptions are almost always reported in wavelength units, and since the continuity between the two spectral regions must be visualized, wavelength units will be used for both spectral regions.

For crosslinked (insoluble) and slightly-soluble polymers, the infrared (near, midrange, and far) is the only spectroscopic tool which can be routinely used for structure elucidation. This was the main reason for its emphasis in this study.

If the interferences from nujol or solvents cannot be tolerated, certainly the case in this study, then one is limited to preparation of samples as thin liquid films, thin amorphous films, or dispersions in pellets of KBr or KI. Preparing a thin liquid film is the easiest technique, but was possible in this study only for those few precursors

and model compounds that are liquid at room temperature. Some amorphous polymers were sufficiently soluble in tetrahydrofuran, or soft enough on mild heating, to allow casting or forming of thin solid films. But the vast majority of samples in this study had to be prepared as KBr or KI pellets.

A problem in the use of midrange infrared spectroscopy is the lack of certainty in the assignments of some bands due to skeletal vibrations and mixed vibrations. This problem is well known for secondary amides R-CO-NH-R' (192, p. 216). Some authors have expressed the generalization that the infrared spectrum of a carbamate is the superposition of the spectra of the corresponding amide and ester, to a first approximation (193, p. 385). It should not be a surprise to find a lack of assignments of reported carbamate bands, or rather large disagreements among the assignments by different researchers.

Although it is not presently possible to describe carbamate absorption frequencies and intensities with mathematical rigor proceeding from molecular first principles, one should still attempt to make assignments of observed bands, making the best use of previous work, the spectra of model compounds, and one's own reason. The main working principle should be to maximize the consistency among the

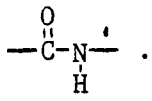
assignments of widely different structures. Realizing the inherent limitations of such assignments and rationalizations, one should attempt to establish a specific pattern of absorptions that arises from each molecular structure of interest, even if certain individual bands must remain unassigned. Establishing such a pattern, and making the correlations, should be accomplished by using a wide variety of model compounds.

In the following assignments and correlations, the spectra of amides, esters, and carbamates will be discussed before the spectra of the various degradation products and byproducts. Within the section on carbamates, the previous literature will be discussed before the proposed revisions.

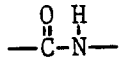
Previous amide assignments are reviewed first, as they are less ambiguous than the carbamate assignments. This discussion will be limited to secondary amides, R-CO-NH-R', as only these are relevant to the N-monosubstituted carbamate spectra.

There has been no controversy about amide assignments in the range 2.8μ to 3.5μ, in which the fundamental hydrogenic stretching bands lie. The principle bands are due to N-H stretching (3.0μ), to aromatic C-H stretching (3.25-3.30μ), and to aliphatic C-H stretching (3.35-3.5μ). The amide II first overtone contributes to the absorption

at 3.25μ (193, p. 385). The amide I band occurs in the range 5.95μ to 6.14μ, and is due entirely to carbonyl stretching (192, p. 205). Very little mixing with other vibrational modes occurs. For acyclic amides the amide II band occurs around 6.4-6.6 μ (192, p. 205; 193, p. 385; 194, p. 63; 195, p. 67; 196; 197; 198; 199). This absorption involves coupling of the N-H bending and the C-N stretching vibrations for the trans configuration,



Most lactams, possessing a cis configuration



do not show such a band, instead exhibiting a weaker band around 7.0μ (193, p. 385).

The amide III band around 7.57-7.94μ is due to a mixed vibration, with main contributions from C-N stretching and N-H in-plane bending (192, p. 220; 196; 197; 199).

The amide IV band at about 16μ is also due to a mixed vibration, mainly O=C-N bending (192, p. 205; 196; 197; 199; 200).

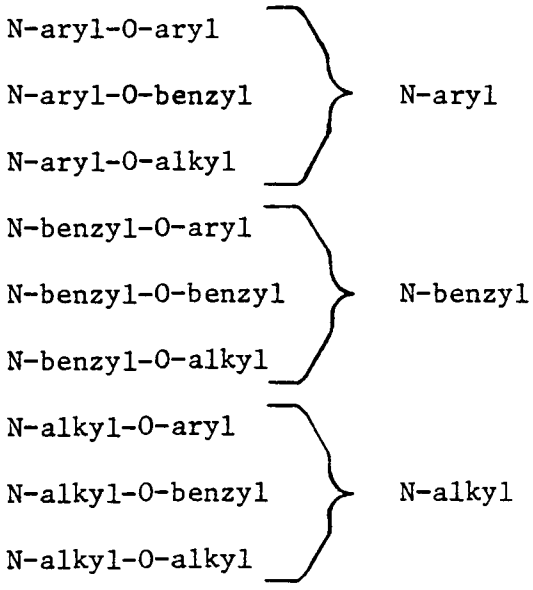
The amide V band of trans monosubstituted amides, at about 13.3-14.3μ has been assigned to N-H out-of-plane bending.

The amide VI band at about 16.7μ is due to C=O out-of-plane bending (196, 197, 199, 200).

For aliphatic amides, the R'-N stretch occurs at about 9.1μ (197), while for N-aryl amides, R-CO-NH-Ar, the Ar-N stretch occurs in the range 7.5μ to 8.0μ (193, p. 931).

For esters, the important assignments are more straightforward. The C-O single-bond stretch appears around 8.5μ (192, p. 189; 193, p. 317). The O-R' stretch appears around 9.7-10.0μ, for aliphatic R' (192, p. 189; 193, p. 317). For phenolic esters the O=C-O single-bond stretch and the O-aryl stretch give several bands in the region 8-10μ (192, p. 891), suggesting mixing of vibrational modes in such systems. From a series of phenolic esters, one may notice that bands of variable intensity appear in the regions 9.2-9.6μ and 9.8-10.0μ (192, p. 908).

The carbamates have many absorptions which correspond with those of the simpler amides and esters just mentioned. The previous assignments for N-monosubstituted carbamates R-O-CO-NH-R' will now be reviewed. As expected, the positions and intensities of the infrared bands are strongly dependent on the N and O substituents. Changing the N-substituent seems to have a greater effect than changing the O-substituent. To stress the importance of the N-substituent, the order of coverage is the following:



Whenever available, the assignments for PU's will be covered along with the corresponding model compounds in the same category. The cyclic carbamates will be covered separately, as the correlations obtainable from the open-chain carbamates do not apply to the ring forms.

There is substantial agreement among all the authors on the assignments for the region from 2.0μ to 5.6μ, the principal bands being due to N-H stretching around 3.0μ and C-H stretching between 3.2μ and 3.5μ. The more controversial region from 5.6μ to 16.0μ will be covered in more detail here.

For convenience in specifying which carbon-heteroatom vibration is meant in a carbamate molecule, the general carbamate molecule R-O-CO-NH-R' will be subdivided into the following moieties for the purposes of nomenclature:

carbamate moiety $-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$

amide moiety $-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$

ester moiety $-O-\overset{\overset{O}{\|}}{C}-$

amine moiety $-\underset{\underset{H}{|}}{N}-R'$

alcohol moiety $R-O-$

or phenol moiety

Unless otherwise noted, the samples in this review were prepared as KBr pellets or as neat films.

The system with N-aryl-O-aryl substitution has been studied only by Hayes (201) and Brumfield (202), for the model compound phenyl carbanilate. However, they mentioned only the characteristic bands due to C=O and N-H stretching.

No assignments for the system with N-aryl-O-benzyl substitution have been made.

The system with N-aryl-O-alkyl substitution is the most thoroughly studied of all. Assignments have been made by Ngoc Son (89), Backus et al. (20), Nakayama et al. (52), Matuszak (38), Schollenberger and Stewart (79), Yang (11), Nyquist (203), Ishihara et al. (204), and Paik Sung and Schneider (205, 206). The characteristic group frequencies vary insignificantly from model carbamate to high polymer, within the same

substitution pattern, so it is not necessary to specify in every case of this review the specific compounds studied. Most studies dealt with both model compounds and polymers, though the main impetus invariably was the structure elucidation of the PU's.

The strong absorption between 5.75μ and 5.9μ is agreed to be the carbonyl stretching. A medium to strong absorption between 6.2μ and 6.3μ is assigned to an aromatic ring in-plane skeletal vibration, by all PU workers except Ishihara et al. (204), who assigns the peak at 6.25μ to an N-H deformation (for the biscarbamate obtained from MDI and n-butanol). The strong absorption between 6.5μ and 6.65μ is commonly agreed to be the amide II band (called by Matuszak the "NH bend + CN stretch"), except that Nakayama et al. (52) and Ishihara et al. (204) assign a shoulder at 6.6μ to another aromatic ring in-plane skeletal vibration. A weak absorption between 6.75μ and 6.85μ is assigned by Nakayama et al. (52) and Yang (11) to a CH_2 or CH_3 deformation. A strong absorption between 6.9μ and 7.05μ is assigned to another aromatic ring in-plane skeletal vibration. The weak absorption between 7.2μ and 7.3μ is assigned to CH_2 or CH_3 deformation, by Nakayama et al. (52), Nyquist (203), and Yang (11). The medium to strong absorption between 7.45μ and 7.65μ has caused some disagreement.

Nakayama et al. (52) and Matuszak (38) assigned it to a CH_2 deformation. Yang (11) assigned it to an aryl-N stretch. Backus et al. (20) assigned it to an N-H bending. Ishihara et al. (204) assigned it to a mixed N-H bending and C-N stretching. None of these authors actually call it the amide III band.

The medium absorption between 7.8μ and 8.05μ was assigned by Nyquist (203) to aryl-N stretching. The strong absorption between 8.05μ and 8.2μ was called the amide III band by Nakayama et al. (52) and Yang (11), which is equivalent to the assignment by Nyquist (203) and Ishihara et al. (204), as a mixed N-H bending and C-N stretching. However, the papers by Nakayama et al. (52), Paik Sung and Schneider (206), and Schollenberger and Stewart (79) called it a C-O-C stretching. Ngoc Son (89) called it a C=O deformation. Much confusion thus exists about this band's assignment. The strong absorption between 8.9μ and 9.35μ has also led to some confusion. Nakayama et al. (52), Yang (11), Ishihara et al. (204), and Backus et al. (20) have called it a C-O-C stretching, whereas Paik Sung and Schneider (206), Schollenberger and Stewart (79), and Nyquist (203) have called it an O-R stretching. The weak absorption between 9.8μ and 10.0μ has been called an aryl C-H in-plane bending by Nakayama et al. (52), Yang (11), and Ishihara (204). Some weak to medium absorptions between

10.4μ and 12.2μ were assigned by several authors to aryl C-H out-of-plane bending. An absorption between 12.8μ and 12.9μ was assigned to the out-of-plane bending of the ester grouping by Nakayama et al. (52) and Yang (11). An absorption at 16μ was assigned by Nyquist (203) to the N-H out-of-plane bending. None of the authors mentioned the strong absorption due to coupled out-of-plane bending of the aryl C-H groups, which indicate the ring substitution pattern.

In assigning the various peaks between 7.45μ and 10μ, probably the only points of agreement among the various authors is the wavelength sequence of some vibrations. For instance, in order of increasing wavelength the sequence is aryl-N stretching, amide III band, O=C-O single-bond stretching, O-R' stretching, and aryl C-H in-plane bending.

No assignments for the two systems containing N-benzyl-O-aryl substitution or N-benzyl-O-benzyl substitution have been made.

Only three research groups seem to have attempted assignments in the system containing N-benzyl-O-alkyl substitution. Rumao's dissertation (10) treated polymers made from meta- and para-XDI (p. 9) and various aliphatic diols; Matuszak's dissertation (38) treated a biscarbamate made from benzyl isocyanate and ethylene glycol as well as some similar polymers made from XDI, and Argabright et al.

(207) studied metathetical reactions producing N-benzyl-O-ethyl carbamate. The various assignments are listed as follows:

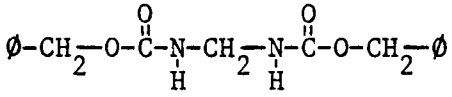
5.8-5.9μ	C=O stretching
6.2-6.3μ	N-H in-plane bending (10)
	aromatic ring in-plane skeletal vibration (38)
6.5μ	amide II (207)
6.7μ	aromatic ring in-plane skeletal vibration (10)
6.9μ	aromatic ring in-plane skeletal vibration (38)
	CH_2 scissoring (10)
7.65μ	CH_2 deformation (38)
7.85μ	N-C-O deformation (38)
8.0μ	C-O stretching (207)
8.2μ	C-O-C stretching (10)
8.9μ	C=O stretching (10)
9.4μ	C-O stretching (38)
9.75-9.8μ	C-H in-plane deformation (38)
	C=O stretching (10)
13.0μ	C-O-C deformation (10)
14.8μ	C-C wagging out-of-plane (38)

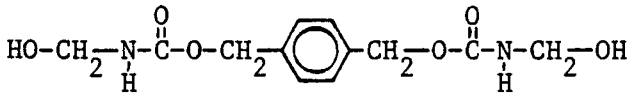
As is evident from the above listing, each author mentioned only a few of the many peaks present, so there is some disparity in the estimations of the importance of each peak. Except for the carbonyl stretching, wherever two authors

mentioned the same peak, two different assignments were made. It is assumed that the peaks at 8.9μ and 9.8μ, which Rumao (10) called "C=O stretching," are meant to be the stretching along the single bond between the carbonyl carbon and a heteroatom. For the region from 7.7μ to 16μ, the assignments reported for the N-benzyl-O-alkyl carbamates bear little resemblance to those of the N-aryl-O-alkyl carbamates reviewed before, though similar assignments would be expected.

For the system with N-alkyl-O-aryl substitution, no assignments have been made.

For the system with N-alkyl-O-benzyl substitution, only a few very special cases seem to have been studied by Takeuchi (208). The simplest of these systems are the following biscarbamates:





The entire infrared spectra are reported but only two very straightforward peaks above 5.7μ are assigned, the amide I and amide II bands. For variously substituted derivatives the carbonyl stretching ranges from 5.8μ to 5.9μ, and the amide II from 6.45μ to 6.55μ.

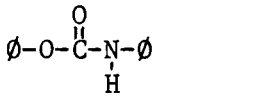
The system with N-alkyl-O-alkyl substitution has been

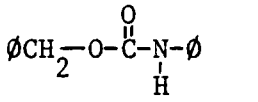
studied almost as thoroughly as the N-aryl-O-alkyl system. Assignments have been made by Cutmore and Hallam (210), Zahn and Dominik (209), Gudim and Klimenko (211), Phillips and Argabright (132), Yang (11), Matuszak (38), and Egorov (212).

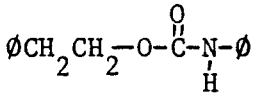
There is agreement on the assignments of the strong amide I and amide II bands, which occur respectively at 5.8-5.9μ and 6.5-6.65μ. The medium absorption at 6.75-6.85μ is variously called the CH_2 (or CH_3) bending, deformation, or scissoring — but it is certainly due to the aliphatic moieties. Zahn and Dominik (209) report a weak CH_2 deformation also at 7.05μ. A medium absorption between 7.3μ and 7.45μ was assigned as a CH_2 (or CH_3) wagging. A strong absorption between 7.8μ and 8.1μ was assigned by most as the amide III band or as a =C-N stretching (which are nearly equivalent assignments). The medium to strong absorption at 8.75-8.8μ was mentioned by five of the above authors, but was given five different assignments. The medium absorption between 9.05μ and 9.5μ was mentioned by all seven authors, but assigned variously as a C-N stretching, a C-O-C stretching, an OR' stretching, or a "carbamate group vibration." The medium absorption between 9.7μ and 10μ was called a C-C stretching, a C-O vibration, or a "carbamate group vibration." Various weak absorptions between 11.9μ and 12.5μ were mentioned but not assigned. The

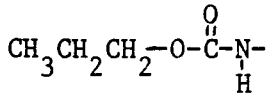
medium band at 12.8μ was called an ester group out-of-plane bending. The weak absorption between 13.3μ and 14.3μ was called a CH_2 rocking. Only Matuszak (38) mentioned a peak above 15μ, calling it an aliphatic amide vibration. For the N-alkyl-O-alkyl carbamates and PU's, there is more agreement among the various authors concerning the infrared assignments than for the other substitution patterns.

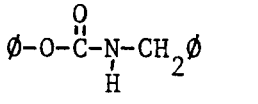
For the present research, a consistent set of assignments for the various substitution patterns has to be arrived at. Because of the extent of disagreement among previous workers, the previous assignments can be used only as rough guidelines. The main guideline used here is to achieve consistency in the assignments of the infrared bands of the following model compounds:

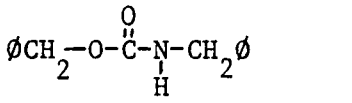

N-phenyl-O-phenyl carbamate


N-phenyl-O-benzyl carbamate

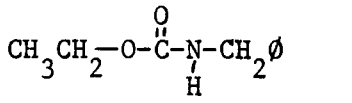

N-phenyl-O-phenethyl carbamate


N-phenyl-O-n-propyl carbamate

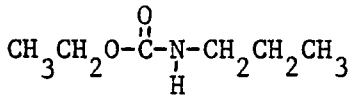

N-benzyl-O-phenyl carbamate



N-benzyl-O-benzyl carbamate



N-benzyl-O-ethyl carbamate



N-n-propyl-O-ethyl carbamate

All the above model compounds were made in the present study except N-phenyl-O-phenethyl carbamate, whose spectrum was obtained from the Sadtler collections (213, 214). The preparation of these models is described in the experimental section of this chapter. The positions and intensities of the peaks of these spectra, and several of the spectra, are attached as Appendix I.

In making assignments for the spectra of present interest, a few other guidelines are helpful, which do not directly involve the spectra of carbamate models and polymers. These guidelines may be drawn from the spectra of amides, esters, alkylamines, alcohols, anilines, and phenols. These guidelines have to do with the relative order of wavelengths, frequencies, or energies, not with their absolute positions. For the attachment of a carbonyl moiety to a nitrogen or oxygen atom by a single bond, O=C-N or O=C-O, the single bond stretching will occur at a lower wavelength (higher frequency or energy) for the C-N

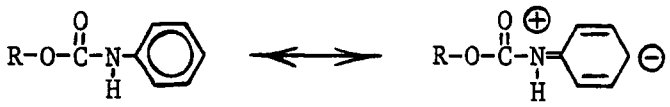
vibration than for the C-O vibration. The same holds true for the C-heteroatom vibrations of alkylamines compared with alkanols, or of anilines compared with phenols. For a given heteroatom bonded to a carbonyl carbon as compared with a methylene carbon, the carbonyl group will give rise to a single bond stretching frequency of lower wavelength than will the CH_2 group. Thus the O=C-N single-bond vibration will occur at a lower wavelength than the CH_2-O vibration. However, it is difficult to find the relative wavelength order for a given heteroatom X bonded to two different sp^2 hybridized carbons, say for O=C-X compared with Ø-X. In going down a series of model compounds, one should examine the changes of wavelength or intensity produced when only the moiety bonded to a given heteroatom X is changed from alkyl to benzyl to phenyl. The change from alkyl to benzyl should impose only a small perturbation on the C-X vibrations, but the change from benzyl to phenyl should impose a much larger perturbation. The largest change should be seen in the Ø-X stretching vibration. For the region between 7μ and 16μ, the above guidelines should be more helpful than previously attempted assignments.

One may rationalize the observation that a change in the nitrogen substituent R' has a greater effect on the infrared spectrum than a change in the oxygen substituent R

in R-O-CO-NH-R'. It is known that the carbon-nitrogen bond in the amide moiety of carbamates has partial double-bond character, due to the resonance interaction (38, p. 61)



However, the carbon-oxygen bond in the ester moiety has much less resonance interaction, and behaves more like a freely rotating single bond. An aryl substituent on the nitrogen can produce another sort of resonance interaction (38, p. 61),



which would change the character of all the nitrogen atom's bonds, relative to alkyl substituents. Changing the oxygen substituent R from alkyl to aryl would not change the character of the ester O=C-O single-bond to the same extent.

Exhaustive normal coordinate analysis studies of N-monosubstituted carbamates may someday show that the amide III band is due to a mixture of several vibrations, and that other bands in the region of 7μ to 16μ are also due to such coupled vibrations. However, at the present state of the art the best that can be done here is to plausibly and tentatively assign the main component of such a mixture. Using the general guidelines mentioned above, the N-alkyl-O-alkyl carbamates would be expected to exhibit the following

order of wavelengths for the various carbon-heteroatom single-bond vibrations in the region 7μ to 10μ:

$$\overset{O}{\overset{\|}{C}}\text{-N} < \overset{O}{\overset{\|}{C}}\text{-O} < H_2C\text{-N} < H_2C\text{-O}.$$

For a similar symmetrical substitution, N-benzyl-O-benzyl, very little change would be expected in the wavelengths or intensities. In fact the pattern for the dibenzyl substitution is very much like that for the dialkyl substitution. For the symmetrical substitution N-phenyl-O-phenyl (in the model compound phenyl carbanilate) the same wavelength order would be expected, but the absorptions might be more clustered together, by analogy with the shift from alkanol to phenol or alkylamine to aniline (193, pp. 63, 147, 573, 629). Actually the various absorptions become more spread out for the C-heteroatom single-bond vibrations. This observation may be rationalized as follows: on changing the heteroatom substituent from alkyl to aryl, the increase in effective vibrating mass outweighs any increase in bond strength. The wavelength is proportional to $\sqrt{(m/k)}$, where m is the "effective reduced mass" and k is the force constant.

In examining the series of model compounds from N-phenyl-O-phenyl carbamate to N-n-propyl-O-ethyl carbamate, fairly minor changes in the IR spectra appear for those vibrations

involving carbon-heteroatom bonds. The observed infrared bands in this series, and their changes in wavelength and intensity with substitution, will now be discussed.

For all the model carbamates, the N-H stretching appears as a sharp peak between 3.0μ and 3.1μ. A shoulder or smaller peak between 3.2μ and 3.3μ is due to the aryl C-H stretching, and appears in all models except N-n-propyl-O-ethyl carbamate. Several small peaks between 3.4μ and 3.7μ are due to aliphatic C-H stretching, and appear in all models except N-phenyl-O-phenyl carbamate. For all the models, the broad intense amide I or carbonyl band has a maximum around 5.85μ (between 5.8μ and 5.95μ), but the width-at-half-height can encompass 0.4μ. Some aromatic models have at least a small sharp peak around 6.25μ, due to an in-plane skeletal vibration of the benzene ring if one of the heteroatoms (N or O) is attached to a phenyl group. The three models which do not show this peak do not have such attachment: N-benzyl-O-benzyl, N-benzyl-O-ethyl, and N-n-propyl-O-ethyl. All models show the broad intense amide II band, with maximum between 6.45μ and 6.6μ. All the models containing an aromatic group (i.e., all models except N-n-propyl-O-ethyl carbamate) show a peak between 6.65μ and 6.75μ due to an in-plane skeletal vibration of the benzene ring. In N-benzyl-O-benzyl and N-benzyl-O-ethyl

carbamates this absorption is only a shoulder, showing that direct attachment of either the N or O heteroatom to the benzene ring is necessary for high intensity. In all models except N-phenyl-O-phenyl carbamate, a shoulder or discrete peak appears between 6.75μ and 6.85μ due to CH_2 scissoring. N-n-propyl-O-ethyl carbamate shows several peaks and shoulders between 6.7μ and 6.95μ due to various CH_2 and CH_3 deformations. All the aryl models show a sharp peak between 6.85μ and 6.95μ due to another in-plane skeletal vibration of the benzene ring. A small peak or shoulder due to a CH_2 deformation appears in all models except N-phenyl-O-phenyl carbamate between 6.95μ and 7.05μ. Small peaks between 7.15μ and 7.35μ are due to CH_2 wagging. This peak seems to be conspicuous only when a methylene group is bonded to the nitrogen atom. One or more peaks and shoulders appear in the region 7.5μ to 7.75μ, and are more intense for the N-phenyl models than for the others. Also, the N-phenyl models have the more intense peak near 7.6μ. This absorption is probably an N-H bending mode, and surely involves the nitrogen atom.

The amide III absorption appears next, in the general region 7.8μ to 8.3μ. For many carbamates, this is the strongest absorption in the spectrum. It may be split into several contiguous maxima, though it rarely shows a deep

cleft. The predominant contributor to the amide III absorption is most likely the C-N bond stretching of the amide moiety, even if the vibration is mixed. For the N-alkyl or N-benzyl carbamates, the amide III absorption appears in the region 7.8μ to 8.0μ, while for the N-phenyl carbamates the absorption appears between 8.0μ and 8.3μ. Because of the variation with structure, the amide III absorption for each model is tabulated, with the strongest peak underlined, and shoulders in parentheses, in Table IV.

An absorption of slightly longer wavelength than the amide III band can be assigned to the C-O single-bond stretching of the ester moiety. It lies between 8.2μ and 8.6μ, and its position does not correlate well with either the N or the O substituent. However, its intensity depends strongly upon whether the O substituent is phenyl or not. For O-phenyl carbamates the intensity is strong or very strong. These absorptions are listed in Table V.

A vibration which appears to be the C-N stretching of the amine moiety N-R' occurs between 9.0μ and 9.3μ for N-phenyl substituents, and between 8.6μ and 9.0μ for benzyl or alkyl substituents. Its intensity usually is medium for N-phenyl substituents, and strong for N-alkyl or N-benzyl substituents. These absorptions are listed in Table VI.

TABLE IV

C-N SINGLE-BOND STRETCHING OF AMIDE MOIETY IN MODEL CARBAMATES

N-substituent	O-substituent	Absorptions (μ)[a]
Ø	Ø	(7.9) 8.15 <u>8.3</u>
Ø	$ØCH_2$	(7.95) 8.0 <u>8.05</u> 8.15 (8.3)
Ø	$ØCH_2CH_2$	(7.85) 8.0 <u>8.2</u> 8.3
Ø	<u>n</u>-Pr	(8.0) 8.1 (8.2)
$ØCH_2$	Ø	7.95
$ØCH_2$	$ØCH_2$	7.85 <u>8.0</u>
$ØCH_2$	Et	7.8 <u>8.0</u>
$ØCH_2CH_2$	Ø	7.95
<u>n</u>-Pr	Et	(7.75) 7.85 <u>7.9</u> 8.05 (8.2)

a. The strongest peak is underlined, and shoulders are in parentheses.

TABLE V

C-O SINGLE-BOND STRETCHING OF ESTER MOIETY IN MODEL CARBAMATES

N-Substituent	O-Substituent	Absorptions (μ)[a]
Ø	Ø	8.6[b]
Ø	$ØCH_2$	<u>8.45</u>[c] 8.6
Ø	$ØCH_2CH_2$	8.6[c]
Ø	<u>n</u>-Pr	<u>8.45</u>[c] 8.6
$ØCH_2$	Ø	<u>8.2</u> 8.3[d]
$ØCH_2$	$ØCH_2$	8.2[c]
$ØCH_2$	Et	8.3[c]
$ØCH_2CH_2$	Ø	<u>8.2</u> 8.3[d]
<u>n</u>-Pr	Et	8.5[c]

a. The strongest peak is underlined, and shoulders are in parentheses.

b. Intensity is strong.

c. Intensity is medium.

d. Both peaks are very strong.

TABLE VI

N-R' SINGLE BOND STRETCHING OF AMINE MOIETY IN MODEL CARBAMATES

N-Substituent	O-Substituent	Absorptions (μ)[a]
Ø	Ø	9.3[b]
Ø	$ØCH_2$	9.0 <u>9.2</u>[b]
Ø	$ØCH_2CH_2$	9.05[b]
Ø	<u>n</u>-Pr	9.2[b]
$ØCH_2$	Ø	<u>8.6</u> 8.9[c]
$ØCH_2$	$ØCH_2$	<u>8.75</u> 8.85[d]
$ØCH_2$	Et	<u>8.75</u> 8.95[d]
$ØCH_2CH_2$	Ø	<u>8.65</u> 9.0[d]
<u>n</u>-Pr	Et	8.75[e]

a. The strongest peak is underlined.

b. Intensity is medium.

c. Both peaks have medium intensity.

d. Both peaks are strong.

e. Intensity is strong.

An absorption which undergoes less variation in position, but more variation in intensity, with the change of N-substituent lies between 9.0μ and 9.85μ and will be called an "N-associated vibration." Like the preceding vibration, this one obviously is related to the N atom. These absorptions are listed in Table VII.

The R-O stretching (the C-O stretching of the alcohol moiety) appears between 9.5μ and 10.0μ. There is no apparent correlation of absorption position or intensity with structure, though the N,O-diphenyl model and the N,O-dialkyl model do give the extremes of wavelength. These absorptions are listed in Table VIII.

Of course the above assignments and correlations of major importance between 7μ and 10μ cannot be claimed as the last word in this area. However, it seems to be the only attempt to date to correlate the absorptions of diverse N-monosubstituted carbamates in this region. This region of the infrared spectrum is crucial in detecting cross-linking moieties and by-product linkages in PU's. Knowledge of PU crosslinking will probably be limited by the extent of our knowledge of the 7μ to 10μ infrared region.

There are additional infrared bands at wavelengths above 10μ. Those carbamates which do not have a medium to strong absorption near 10.0μ (due to R-O stretching)

TABLE VII

N-ASSOCIATED VIBRATION OF MODEL CARBAMATES

N-Substituent	O-Substituent	Absorption (μ)[a]
Ø	Ø	9.85[b]
Ø	$ØCH_2$	9.45[c]
Ø	$ØCH_2CH_2$	9.3[d]
Ø	n-Pr	9.4[b]
$ØCH_2$	Ø	9.35[d]
$ØCH_2$	$ØCH_2$	9.25[d]
$ØCH_2$	Et	9.3[d]
$ØCH_2CH_2$	Ø	9.2 9.35[e]
n-Pr	Et	9.0 9.1[e]

a. The stronger peak is underlined.

b. Intensity is strong.

c. Intensity is very strong.

d. Intensity is medium.

e. Both peaks have medium intensity.

TABLE VIII

R-O STRETCHING OF ALCOHOL MOIETY OF MODEL CARBAMATES

N-Substituent	O-Substituent	Absorption (μ)[a]
Ø	Ø	10.0[b]
Ø	$ØCH_2$	9.75[c]
Ø	$ØCH_2CH_2$	9.75 <u>9.95</u>[c]
Ø	n-Pr	<u>9.7</u>[c] 9.8
$ØCH_2$	Ø	<u>9.6</u>[b] 9.75
$ØCH_2$	$ØCH_2$	<u>9.5</u>[c] 9.7
$ØCH_2$	Et	<u>9.65</u>[b] 9.75
$ØCH_2CH_2$	Ø	9.6 <u>9.8</u>[c] 9.9
n-Pr	Et	<u>9.5</u>[b] 9.75

a. The strongest peaks are underlined.

b. Intensity is strong.

c. Intensity is medium.

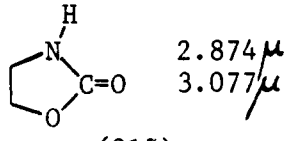
invariably show a weak to medium peak or shoulder between 9.95μ and 10.05μ due to aryl C-H in-plane bending. The weak to medium peak or shoulder invariably present between 10.2μ and 10.5μ is due to an aryl C-H bending, either in-plane or out-of-plane. A similar absorption always present between 10.9μ and 11.1μ is due to an aryl C-H out-of-plane bending. If a weak absorption is present between 11.3μ and 11.5μ, it is due to CH_2 rocking. A weak to medium peak between 11.6μ and 12.0μ is due to the out-of-plane bending of an isolated aryl C-H group. A similar peak between 12.0μ and 12.5μ is due to the out-of-plane bending of two adjacent aryl C-H groups. A medium to strong peak between 12.6μ and 13.0μ is due to the out-of-plane bending of the ester moiety, and is conspicuous in all the model compounds. Shoulders or weak peaks in this region are due to the out-of-plane bending of three adjacent aryl C-H groups. One or more strong peaks between 13.0μ and 13.8μ are due to the out-of-plane bending of four or five aryl C-H groups. In the models containing aliphatic moieties, a weak to medium peak around 13.3μ is due to CH_2 rocking. A medium to very strong peak between 14.1μ and 14.8μ is due to the out-of-plane bending of the aromatic ring. A very broad absorption of medium intensity between 14.5μ and 16μ is due to an out-of-plane bending of the entire amide moiety, or to a similar

vibration of the N-H group.

This concludes the spectral assignments of the open-chain (linear or nonheterocyclic) model carbamates used in this work. These assignments should apply to those PU's heretofore studied. However these assignments do not apply to most cyclic carbamates. The accessible knowledge of the infrared spectra of cyclic carbamates is even more chaotic than that of the linear carbamates.

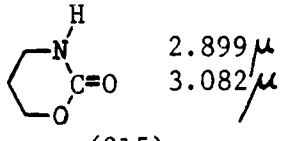
For the cyclic carbamates, previous assignments will be reviewed first, then assignments and correlations will be attempted. Special emphasis will be placed on the three cyclic carbamates used in the present study (rings-00, 10, and 01).

Most infrared studies of cyclic carbamates have made only the most straightforward assignments for each ring, such as N-H or C=O stretching. The N-H stretching of cyclic carbamates often appears at substantially higher wavelengths than in the corresponding open-chain systems. The free N-H (lower wavelength) and the H-bonded N-H peaks of various compounds are illustrated below (the sampling medium, when known, is also given).



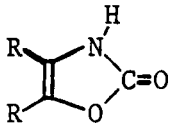
2.874 μ
3.077 μ

(215)



2.899 μ
3.082 μ

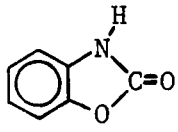
(215)



in liquid film
3.115μ
3.215μ

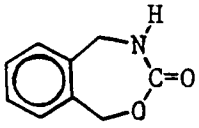
R = i-Pr, i-Bu, etc.

(216)



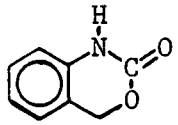
3.115μ
3.215μ

(217)



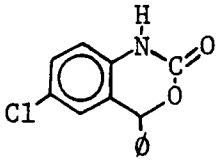
in $CHCl_3$
3.076μ

(218)



in KBr 3.125μ
(219) 3.225μ

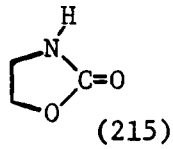
in nujol 3.174μ
(220) 3.236μ



3.076μ
(221) 3.145μ
3.205μ

in KBr 2.945μ
(222) 3.115μ

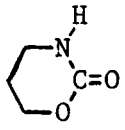
The carbonyl absorption of the following cyclic carbamates has similarly been reported.



(215)

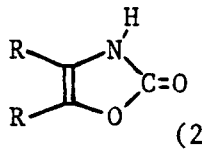
in CCl_4 5.61μ

in $CHCl_3$ 5.68μ



in KBr 5.89μ

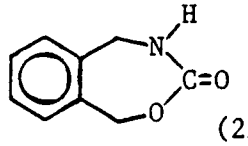
in CCl_4 5.74μ



(216)

R = i-Pr, i-Bu, etc.

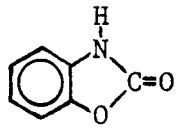
in liquid film 5.72μ



(218)

in $CHCl_3$ 5.92μ

in nujol 5.88μ
5.97μ



(217) in $CHCl_3$ 5.7μ

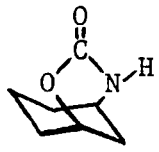
(223) 5.65 5.80μ

in $CHCl_3$ 5.58μ

(192) 5.70μ

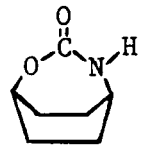
in KBr 5.66μ

(224) 5.79μ



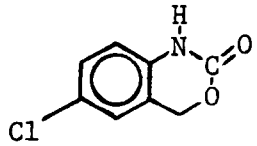
in CCl_4
5.80μ

(215)



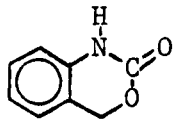
in CCl_4
5.82μ

(215)



in KBr
5.865μ

(222)



(221) 5.795μ

(219) 5.78μ

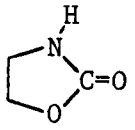
in nujol 5.81μ

(220)

Assignments like the above (N-H and C=O stretching) are quite similar for both open-chain carbamates and cyclic carbamates, and thus pose little ambiguity. Most of the other assignments of the infrared peaks arising from the carbamate heteroatom vibrations are greatly different for the cyclic and open-chain systems. Thus, when attempting to assign and to correlate the peaks in such compounds, one should bear in mind that these cyclic systems have three additional perturbations imposed on their vibrations: (1) strained bond angles due to imposition of ring conformation, (2) much less freedom of motion or much greater rigidity, and (3) the fixed cis conformation of the N-H and C=O groups.

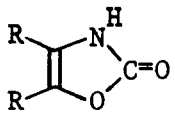
Two assignments which are expected for a wide range of cyclic carbamates are (1) the absence of the amide II band (at about 6.5μ) that is characteristic of trans N-H and C=O, and (2) the presence of a medium peak around 7.0μ to 7.1μ, characteristic of cis N-H and C=O, which we may call a "cis amide II" band (193, p. 385). Very few other generalities may be stated concerning the infrared assignments of cyclic carbamates. Assignments which apply to specific cyclic carbamates will now be discussed.

Mecke et al. (225) have made assignments for the cyclic carbamate 1,3-oxazolidine-2-one,



in terms of symmetry elements alone. They reasoned that vibrations were not localized to a pair of adjacent atoms, but that the entire system of 7 atoms vibrated in unison, or that the vibrations of all atoms were strongly coupled. This assumption is quite plausible for small ring compounds; more than for large ring compounds or open-chain compounds. Only three correspondences can be made with traditional assignments; a carbonyl stretching at 5.8μ, an N-H out-of-plane bending at 14.3μ, and an N-H in-plane bending at 6.5μ. The last corresponds to an amide II band, a very unorthodox assignment. This kind of symmetry treatment seems not to have been applied to any other cyclic carbamate, before or since that study.

Gompper and Herlinger (216) studied a series of seven 2-oxazolones, differing only in the alkyl substituents in positions 4 and 5:



R = Et, n-Pr, i-Bu, n-pentyl, n-hexyl, n-nonyl

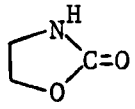
The N-H and C=O stretching peaks have already been mentioned. The peak at 5.88μ was assigned to the C=C double-bond

stretching, the peak at 7.27μ to the amide III vibration, and the peak at 10.25μ to a ring deformation ("ω ring").

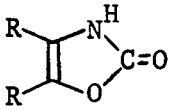
The absorptions of benzoxazolinone (ring-00) have been assigned by several workers and are listed in Table IX (for those absorptions above 6μ).

Only a few other infrared bands have been assigned for cyclic carbamates. Testa and Fontanella (219), studying ring-10, assigned a peak at 13.33μ to out-of-plane bending. Pifferi et al. (218) studied the homologous compound ring-11 in $CHCl_3$ solution, and assigned a peak at 8.93μ to the C-O stretching and a peak at 13.46μ to the aromatic C-H out-of-plane bending. This concludes a review of the infrared assignments of cyclic carbamate peaks made by previous workers.

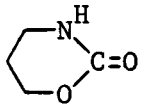
To attempt further assignments of cyclic carbamates, the complete infrared spectra of several compounds had to be used. The spectra of only three cyclic carbamates could be obtained from the literature, 2-oxazolidinone (225, 228), diethyl-2-oxazolone (216), and 1,3-oxazin-2-one (229).



2-oxazolidinone



diethyl-2-oxazolone



1,3-oxazin-2-one

The two aliphatic rings were studied as liquid films, the olefinic ring in a KBr pellet.

TABLE IX

INFRARED ASSIGNMENTS OF BENZOXAZOLINONE (RING-00)

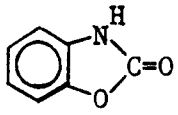
Wavelength (μ)	Intensity	Assignment	Reference
6.15	m	aromatic ring band[a]	226, 227
6.3	m	aromatic ring band[a]	217
6.74	s	aromatic ring band[a]	227
7.143	s	cis amide II	193
7.50	m	C-N vibration	227
7.63	s	C-N stretching	217, 227
7.94	s	ether group vibration	227
8.69	s	ether group vibration	227
9.08	m	cyclic system vibration[b]	227
9.89	m	aromatic ring band[a]	226, 227
10.87	w	aromatic absorption	226
11.14	m	ether group vibration	227
		aromatic absorption	226
11.49	w	aromatic C-H vibrations[c]	226, 227
11.70	w	aromatic C-H vibrations[c]	226, 227
13.10	s	aromatic C-H vibrations[c]	226, 227
13.32	s	aromatic C-H vibrations[c]	226, 227
13.48	s	aromatic C-H vibrations[c]	226, 227
13.86	s	aromatic C-H vibrations[c]	226, 227

a. Skeletal in-plane vibration of aromatic ring.

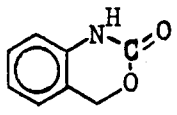
b. Skeletal vibration of entire cyclic system.

c. Extraplane C-H deformation of aromatic ring.

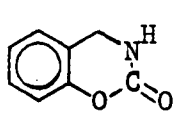
The other four infrared spectra used were those of the benzo-substituted rings of primary interest in this study:



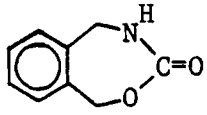
ring-00



ring-10



ring-01



ring-11

The spectra of the first three were taken in KBr pellets (see experimental section). Spectra of the last were kindly supplied by Pifferi (218), but the media used were CH_2Cl_2 and nujol. These two spectra were replotted on the same chart paper by hand, attempting to eliminate the unwanted nujol and CH_2Cl_2 interferences, and to artificially reconstruct the hypothetical KBr pellet spectrum. An authentic sample of ring-11 could not be obtained or prepared by this author, as discussed in the M.S. thesis (317, p. 103).

For these seven cyclic carbamates, the spectral region of major interest is the C-heteroatom stretching region between 7μ and 11μ, for which the proposed correlations will be given in greater detail.

The N-associated band around 7.6μ appears in roughly the same positions as in the open-chain forms (Table X). The main anomalies would be 2-oxazolidinone and ring-11 where this band is much more intense than usual (intensity comparable to amide III).

TABLE X

N-ASSOCIATED BAND OF CYCLIC CARBAMATES

Compound	Wavelength (μ)	Intensity
2-Oxazolidinone	7.5	m
Diethyl-2-oxazolone	7.5	s
1,3-Oxazin-2-one	7.4	m
Ring-00	7.65	m
Ring-10	7.6	m[b]
Ring-01	7.5	m
Ring-11	7.6[a], 7.7	s

a. Designates the stronger peak.

b. Appears as shoulder.

The amide III band, due to the C-N stretching of the amide moiety (refer to p. 81), is undoubtedly the strong peak nearest 8μ, conspicuous in every ring (Table XI).

The C-O stretching of the ester moiety is rather variable in intensity, though not in position (Table XII).

The C-N stretching of the amine moiety is variable in both position and intensity. One cannot assign this peak without referring to the corresponding open-chain structures, where this correlation is more straightforward (Table XIII).

Assignment and correlation of the next two absorptions, the "N-associated" peak between 9μ and 10μ and the O-R stretching peak around 10μ, are more doubtful than for the previous four absorptions. Only for the two rings with the least restriction of motion, 1,3-oxazin-2-one and 2,4-benzoxazepin-3-one, is the pattern in this region similar to the corresponding open-chain cases. The correlations for these absorptions have to be made using trends discussed later. Obviously the N-associated peak (Table XIV) is highly variable in both position and intensity, and so is the O-R stretching peak (Table XV).

It is fortunate that the spectra of ring-11 and the three simpler rings were available, as otherwise the task of correlating the various peaks would have been hopeless. In the two rings where the restriction of motion is least,

TABLE XI

AMIDE III BAND

Compound	Wavelength (μ)	Intensity[a]
2-Oxazolidinone	7.9, 8.0	strong
Diethyl-2-oxazolone	8.0, 8.15	strong
1,3-Oxazin-2-one	7.7, 7.8	strong
Ring-00	7.95, 8.0, 8.2, 8.35	strong, several shoulders
Ring-10	7.7, 7.9, 8.0	strong
Ring-01	7.9, 8.1	strong
Ring-11	8.0	strong

a. The wavelength of the stronger peak is underlined.

TABLE XII

C-O STRETCHING OF ESTER MOIETY

Compound	Wavelength (μ)	Intensity[a]
2-Oxazolidinone	8.1, 8.2	strong
Diethyl-2-oxazolone	8.3	strong
1,3-Oxazin-2-one	8.15, 8.3	strong
Ring-00	8.7	medium
Ring-10	8.2	medium
Ring-01	8.4	strong
Ring-11	8.3	strong

a. The wavelength of the stronger peak is underlined.

TABLE XIII

R'-N STRETCHING OF AMINE MOIETY

Compound	Wavelength (μ)	Intensity[a]
2-Oxazolidone	9.2, 9.3	strong
Diethyl-2-oxazolone	9.2, 9.3	strong
1,3-Oxazin-2-one	8.8, 8.9	strong
Ring-00	9.1	medium
Ring-10	9.4	strong
Ring-01	8.95	medium
Ring-11	8.8, <u>8.9</u>	strong

a. The wavelength of the stronger peak is underlined.

TABLE XIV

N-ASSOCIATED PEAK

Compound	Wavelength (μ)	Intensity
2-Oxazolidone	9.8	strong
Diethyl-2-oxazolone	10.0	medium
1,3-Oxazin-2-one	9.2	strong
Ring-00	9.9	medium
Ring-10	9.7	medium
Ring-01	9.1	medium
Ring-11	9.1	strong

TABLE XV

O-R STRETCHING PEAK

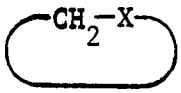
Compound	Wavelength (μ)	Intensity
2-Oxazolidone	10.3	medium
Diethyl-2-oxazolone	10.2	strong
1,3-Oxazin-2-one	10.0	medium
Ring-00	10.7	strong
Ring-10	9.9	medium
Ring-01	10.0	medium
Ring-11	9.7	strong

1,3-oxazin-2-one and ring-11 (2,4-benzoxazepin-3-one), the pattern of absorptions between 7μ and 11μ is most like that of the open-chain analogs discussed earlier and the assignments are the same. On going from the aliphatic ring 1,3-oxazin-2-one to its lower homolog 2-oxazolidinone, we find a drastic change in pattern, in both position and intensity, although a correspondence between the various peaks can still be made. On going from 2-oxazolidinone to its unsaturated counterpart diethyl-2-oxazolone, and further to ring-00 (benzoxazolone), involves a simple structural change at each step. Each small change in structure produces drastic changes in the infrared spectra, in both position and intensity, but the sequence of peaks preserves a one-to-one correspondence. Although the spectral patterns of ring-11 and 1,3-oxazin-2-one are very much alike, one could not assign the peaks of ring-00 from the assignments of ring-11 alone. Each of the simpler rings 2-oxazolidinone, diethyl-2-oxazolone, and 1,3-oxazin-2-one constitute a link in the chain of correlations.

The assignments for the two six-membered rings, ring-10 and ring-01, are more ambiguous, as they have to be made with reference to the open-chain models as well as the other rings.

There are other anomalies in the spectra of these cyclic carbamates, by comparison with the open-chain models and

polymers. The three simpler rings without fused benzo- moieties should be covered first. The 2-oxazolidinone and 1,3-oxazin-2-one rings have CH_2 scissoring peaks at anomalously low wavelengths. In the open-chain model N-n-propyl-O-ethyl carbamate a maximum occurs at 6.8μ and 6.85μ, with shoulders at 6.7μ and 6.9μ. In the five-membered ring 2-oxazolidinone the major peaks (strong intensity) occur at 6.7μ and 6.75μ, and a lesser maximum (medium intensity) at 6.5μ. In the six-membered ring 1,3-oxazin-2-one, the strong peaks occur at 6.7μ and 6.85μ, and a medium peak at 6.5μ. The unsaturated model diethyl-2-oxazolone shows no absorption between 6.2μ and 6.7μ, only one at 6.85μ due to the extracyclic ethyl groups. Thus the absorptions at 6.5μ are most likely anomalous CH_2 scissoring peaks, given by CH_2 groups in a small aliphatic ring next to a heteroatom X.



None of the benzo-substituted rings shows an absorption near 6.5μ. The "cis amide II" absorption for 2-oxazolidinone has maxima at 6.95μ, 7.05μ, and 7.1μ; for 1,3-oxazin-2-one at 7.0μ and 7.2μ; and for the diethyl-2-oxazolone model at 6.95μ and 7.2μ.

The aliphatic carbamate rings show C-C stretching peaks between 10.5μ and 11.0μ, and CH_2 rocking peaks between 11.0μ and 11.6μ. The C=C double bond stretching absorption for diethyl-2-oxazolone is a broad shoulder between 5.9μ and 6.1μ. The absorptions between 12μ and 16μ for these rings present problems. The ring 2-oxazolidinone has two broad intense bands in this region, the ring 1,3-oxazin-2-one has three, and the ring diethyl-2-oxazolone has one. The typical amide band usually ascribed to N-H out-of-plane bending has maxima at 14μ, 14.6μ, and 14.5μ for each of the three rings, respectively, although the width of the band extends over about 1μ in each case. The position of the out-of-plane bending of the ester moiety remains a mystery. In 2-oxazolidinone the peak at 13μ can account for it, while in 1,3-oxazin-2-one there are two similar great absorptions and in diethyl-2-oxazolone there are none. Bands of such magnitude are difficult to explain away.

In the benzo-substituted rings the more controversial peaks have been covered already. All four rings have a "cis amide II" peak between 7.0μ and 7.2μ. Those peaks between 10μ and 12μ which have not already been mentioned are due to aryl C-H in-plane and out-of-plane bendings. The out-of-plane bending of four adjacent aryl C-H groups is very strong for all four rings in this region, reaching a maximum around 13.5μ.

In ring-00, ring-10, and ring-01 the out-of-plane bending of the ester group presents a problem, unless it is a shoulder around 13.0μ to 13.2μ. In ring-11 it appears at 12.5μ and 13.0μ. The out-of-plane bending of the aromatic ring appears between 14.0μ and 14.5μ. The out-of-plane bending of the amide moiety or N-H group appears above 14.5μ in ring-00 and ring-10, as broad shoulders. In ring-01 and ring-11 it is probably off scale, beyond 16μ.

B. INFRARED SPECTRA OF POLYURETHANE DEGRADATION PRODUCTS

The present experimental work is not directly concerned with the volatile products of PU degradation, but rather is mainly concerned with the nonvolatile residues which may still have useful polymer properties.

The relevant infrared literature of previous carbamate and PU degradation research will be reviewed first. The various additional guidelines for detecting certain structures and linkages by midrange infrared methods will be outlined, and will be used in the experimental work of later chapters.

Unfortunately almost all of the previous thermolysis studies which used midrange infrared methods were done with N-aryl PU's and model carbamates.

We should be very careful about extending the results of these studies to N-alkyl and N-benzyl systems, since some

of the thermolysis products which have been proposed for the N-aryl systems are completely unknown for non-aryl nitrogen substituents (such as uretidinediones and triurets), while others are highly unstable (such as biurets and allophanates).

Before directing our attention to specific linkages, the general problem of band overlapping should be emphasized. This problem is especially troublesome in the carbonyl region. Most of the proposed thermolysis products contain a carbonyl group, as do ureas, biurets, allophanates, isocyanurates, and uretidinediones. The uretidinedione peak if present would show a carbonyl peak at 5.62μ to 5.72μ (76, 80) which could easily be seen. But all of the other kinds of carbonyl group absorb in the region 5.75μ to 5.62μ, with considerable overlapping (Table XVI). It should be obvious that one cannot prove the presence of allophanate or biuret using only the carbonyl region, because those absorptions could easily be accounted for by a suitable combination of carbamate, isocyanurate, and urea (230, p. 196). However, those infrared studies which report the formation of allophanate and biuret structures as thermolysis products use the carbonyl peaks alone (38, 89). The single exception is the work of Brumfield (202), but David and Staley (230) have raised serious questions about the scope and generality of Brumfield's analyses.

TABLE XVI

CARBONYL ABSORPTIONS FOR N-ARYL SUBSTITUENTS

Functional Group	References		
	(76, 80)	(38)	(230, p. 259)
Urethane	5.81-5.92μ	5.78μ	5.75-5.88μ
Urea	6.10-6.20μ	5.99-6.13μ	5.99-6.13μ
Allophanate	5.71-5.85μ 5.85-6.06μ	5.71-5.81μ 5.81-5.93μ	5.71-5.81μ 5.81-5.90μ
Biuret	5.81-5.92μ	5.81-5.94μ 5.85-6.05μ	5.81-5.92μ 5.85-6.05μ
Isocyanurate	5.81-5.92μ	5.86-5.94μ	5.85-5.92μ
Uretidinedione	5.62-5.72μ	5.62-5.63μ	5.61-5.65μ

Because the carbonyl region is a poor indicator of isocyanurate presence, at least one other characteristic absorption is needed as evidence. Isocyanurates have a characteristic ring frequency around 7.00μ to 7.15μ, and this region should be examined before the carbonyl absorption to determine the likelihood of isocyanurates. All the conclusions of Ngoc Son (89) concerning products of PU thermal degradation are questionable, because his thermolysis residues invariably showed a strong peak in this region.

Of course the problem of overlapping is not confined to the carbonyl region, in the detection of crosslinking moieties and thermolysate linkages, though the carbonyl region illustrates the problem well. The point to be made is that we should not confine our attention to a small region of the infrared spectrum, but instead should consider simultaneously as many different regions as possible, in both the midrange and near infrared regions. Ngoc Son (89), for instance, found that the carbamate peaks at 8.2μ, 9.4μ, and 13.0μ (for N-aryl-O-alkyl carbamates) were more useful for monitoring the presence of carbamate than the 5.8μ peak.

Probably a minor limitation of the present work is the lack of infrared data in the far infrared region from 16μ to 50μ (625 cm^{-1} to 20 cm^{-1}) due to difficult access to suitable equipment. Correlations in this region have been

well documented (231), and ascertaining the presence or absence of diagnostic bands would have been helpful.

Various infrared studies dealing with specific thermolysis and crosslinking structures will now be covered. Particular emphasis will be placed on those peaks considered characteristic of a certain structure, even if the vibrational modes of such peaks are unassigned.

Allophanate and biuret linkages should be considered together, as they arise from the reaction of isocyanate groups with urethane and urea groups respectively, and are allegedly formed under the same conditions.

The earliest thorough study of allophanate crosslinking in PU's is probably that of Ngoc Son (89). A linear PU made from 2,4-TDI and ethylene glycol was reacted with further TDI. This allophanate cross-linked polymer showed the following infrared peaks (89, p. 73): 3μ, 3.4μ, 5.75-6.0μ, 6.23-6.3μ, 6.5-6.8μ, 6.95μ, 7.1μ, 8.2μ, 9.4μ, 11.5μ, 12.3-12.4μ, 13.0-13.2μ.

Although Ngoc Son (89) mentioned the possibility of isocyanurate formation, he did not seriously consider triarylisocyanurate linkages as probable products of thermal degradation. In light of later work (47, 59, 61, 185, 186), the formation of isocyanurates from allophanates and isocyanates seems to be an important if not dominant reaction.

ALLOPHANATE + ISOCYANATE ⟶ ISOCYANURATE + ALCOHOL

Spectra of diarylallophanates do not show a significant peak near 7.1μ (202), but Ngoc Son's spectrum of the allophanate crosslinked polymer showed a major peak at 7.1μ (89, p. 211), characteristic of triarylisocyanurates. Surprisingly, although Ngoc Son claimed to have made polymeric allophanate and urea structures, he did not claim to detect biuret structures in his polymers.

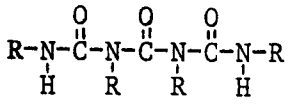
Merten et al. (76, 80) and Matuszak (115) emphasized that both allophanates and biurets have a double carbonyl peak (Table XVI), in which the shorter wavelength is the more intense. However, they did not discuss characteristic absorptions outside the carbonyl stretching region. Other studies of the carbonyl absorption of N-aryl allophanates are those of Kogon (59, 185) and Matuszak and Frisch (73). The carbonyl absorption of biurets has also been studied by Nakayama (52).

More complete infrared spectra of allophanates have been discussed by Kopusov and Zharkov (53) (including characteristic peaks at 7.25μ, 7.63μ, and 7.81μ), by Brumfield (202), and by David and Staley (230). The last two works also treated the absorptions of biurets outside the carbonyl region.

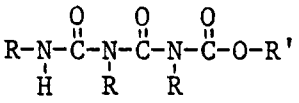
None of the aforementioned works have used midrange infrared spectroscopy to convincingly argue for the presence of either allophanate or biuret linkages in PU's, even when the preparation of high concentrations of such polymer linkages is attempted (as in Ngoc Son's work).

One need not be concerned with the infrared spectra of N-benzyl or N-alkyl allophanates and biurets, because of their extreme instability.

The presence of triurets,



or carbamoyl allophanates,



in any polymer has not been demonstrated by any method, nor has any attempt been made.

The detection of urea linkages by midrange infrared spectroscopy is a different story. Both the low-temperature synthesis of PU's and their thermolysis can give rise to urea linkages, as shown very convincingly by Ngoc Son for N-aryl systems (89).

Unfortunately Ngoc Son's work (89) illustrates another problem. One can make a polyurea in a seemingly straightforward

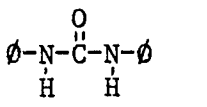
manner, by mixing equimolar quantities of diisocyanate and diamine. Ngoc Son did this with toluenediamine and TDI, and the product spectrum had peaks at 3μ, 3.4μ, 6.05μ, 6.25-6.3μ, 6.5-6.8μ, 6.9μ, 7.1μ, 8.2μ, 11.5μ, 12.3-12.4μ, and 13.3μ (89, p. 73). The peak at 7.1μ is very conspicuous, but no highly purified diarylurea model compound has a peak at 7.1μ, suggesting the substantial presence of triarylisocyanurate in Ngoc Son's sample of polyurea. In fact Skidmore and Sewell (43) made the same polyurea by the same reported method. However their reported spectrum did not contain a peak at 7.1μ, but a deep trough (43, p. 140).

Unfortunately, this kind of problem is encountered all too often in literature involving the infrared assignments of model compounds and polymers. The use of polymer reference spectra can be fraught with dangers; small model compounds highly purified should be used for model infrared spectra, whenever possible.

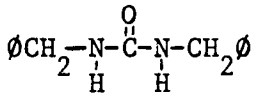
Ngoc Son determined that urea linkages were a major (or the main) component in the thermolysis residues (89, p. 72). Pyrolysis of the allophanate-crosslinked PU (89, p. 73) also gave a residue very similar to the polyurea (89, p. 213). Peaks characteristic of the polymeric diarylurea structure were 6.0-6.1μ and 13.2-13.3μ.

Others have studied the formation of diarylurea linkages from N-aryl PU's. Skidmore and Sewell (43) showed by IR that particles from the yellow smoke produced by high-temperature pyrolysis of a TDI-based polymer were almost identical to the synthetic polyurea. The very thorough pyrolysis work of Merten et al. monitored the urea peak at 6.1μ (80, p. 267).

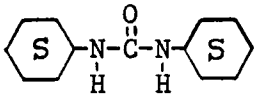
The three important systems, N-aryl, N-benzyl, and N-alkyl model compounds and polymers, were pyrolyzed by Matuszak (38), and the N,N'disubstituted ureas were found to be major products in each case. The three model compounds used by Matuszak were the following, with their characteristic carbonyl absorption:



6.06μ



6.21μ



6.21μ

Few urea assignments have been made other than the obvious N-H, C-H, and C=O stretching bands (192, p. 223). The study by Jose (232) is noteworthy for attempting correlation of prominent bands in two widely different symmetrical N,N'-disubstituted ureas, shown in Table XVII.

TABLE XVII

INFRARED ASSIGNMENTS FOR N,N'-DISUBSTITUTED UREAS

Assignment	Dimethylurea	Diphenylurea
Amide I	6.16μ vs	6.08μ s
Amide II	6.33μ sh 6.53μ sh	6.45μ s
Amide III	7.84μ s	7.59μ m 7.69μ m
N-CO-N Out-of-plane Deformation	12.82μ m	13.51μ s

The cyclic dimers and trimers of isocyanates, the uretidinediones and the isocyanurates, will be covered together because many authors treat them in the same article, and because they have somewhat similar infrared spectra. The infrared evidence for the presence of isocyanurate linkages in polymers is overwhelming, but no researchers have produced convincing evidence for the presence of significant amounts of uretidinedione linkages in any polymer. Uretidinediones with N-alkyl or N-benzyl substituents are still unknown, and if ever prepared are expected to be extremely unstable with respect to isocyanurate formation.

Nicholas and Gmitter (233) set an early precedent for minimizing the importance of isocyanate dimers in rigid N-aryl isocyanurate foams: "All samples showed the characteristic peak at 5.83μ. Dimer peak at 5.6μ and isocyanate peak at 4.45μ were absent or barely detectable." A reported spectrum showed very clearly the strong peak at 7.1μ, though only the carbonyl peak was mentioned. Tilley (76, 80) emphasized the ring frequencies of dimer (7.04-7.14μ), and stressed that dimer formation could be disregarded if the absorption at 5.62-5.72μ was negligible.

The early work of Ngoc Son (89) on the thermolysis of N-aryl-O-alkyl PU's provided good infrared evidence for the isocyanurate linkage in pyrolysis residues, as shown by peaks at 5.9μ and 7.1μ (89, p. 72, 73, 207). Urea linkages were

undoubtedly also present, but were overemphasized by Ngoc Son at the expense of isocyanurates (46, 89, 90). Ngoc Son (89) did state that a main difference between the linear PU and the cross-linked PU was a deeper band at 7.1-7.2μ (89, p. 80), which in retrospect we would ascribe to the isocyanurate linkages.

Actually Kogon (59) had set an early precedent for the infrared detection of triaryl isocyanurates, showing that various substituted compounds had the following characteristic carbonyl peaks:

$\phi_3N_3C_3O_3$	5.90μ
$(o\text{-}MeC_6H_4)_3N_3C_3O_3$	5.90μ
$(p\text{-}MeC_6H_4)_3N_3C_3O_3$	5.68μ, 5.86μ, 5.94μ
$(p\text{-}MeOC_6H_4)_3N_3C_3O_3$	5.70μ, 5.83μ, 5.95μ

Kopusov and Zharkov (53) discussed the characteristic frequencies of the phenylisocyanate trimer at 5.81μ and 7.01μ.

Use of infrared spectroscopy to detect isocyanurates in the thermolysis of PU's was used by Tilley et al. (76, 80).

David and Staley (230) discussed a wide range of triaryl-isocyanurates, generalizing that tri-ortho-substituted trimers absorbed at 5.87-5.90μ, and that tri-para-substituted trimers absorbed at 5.66-5.70μ, 5.83-5.86μ, and 5.94-5.95μ.

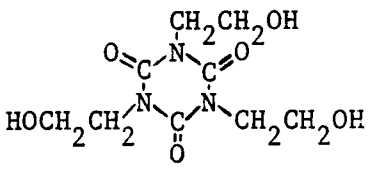
Alaminov et al. (78, 234, 234, 236, 237) discussed many triarylisocyanurate-containing polymers which had no urethane or urea linkages.

A wide range of unsymmetrical isocyanurates was studied by Argabright and Phillips (238), who emphasized another isocyanurate characteristic frequency at 13.33-13.16μ.

The infrared analysis of N-aryl PU's, using the spectra of dimer and trimer model compounds, has been reported by Sheridan and Haines (28) and by Matuszak (38, 73).

Apparently no assignments have been made for tribenzyl-isocyanurates, although the closely related compound triallyl-isocyanurate has been studied (239, 240). Vorotyntseva et al. (240) assigned peaks at 6.85μ, 10.64μ, and 12.90μ as triazine ring vibrations, with symmetries E', A_1', and A_2'' respectively.

No assignments seem to have been made for simple trialkyl-isocyanurates. But a good model isocyanurate for ω-hydroxy-alkylisocyanurates has also been studied by Vorotyntseva (240), trihydroxyethylisocyanurate.

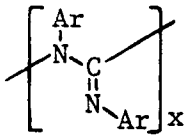


The free and bonded OH stretching bands appeared at the expected positions (2.85μ and 2.94μ). Only the peaks at 6.78μ and 12.90μ were assigned to triazine ring vibrations.

Cyanic acid itself ($H_3N_3C_3O_3$) shows characteristic triazine ring absorptions at 6.78μ, 7.12μ, and 9.48μ (241). Only the peaks at 6.78μ and 7.12μ are not greatly perturbed by the N-substituent on changing among alkyl, allyl, and aryl. The aforementioned treatments do not discuss any isocyanurate absorption bands between 6μ and 16μ as due to a vibration localized between two atoms, undoubtedly because the high symmetry of these triazine systems makes the vibrational symmetry treatment more appropriate.

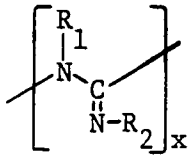
Some papers have reported the presence of isocyanate or carbodiimide peaks in PU infrared spectra, between 4μ and 5μ. Since none were found in the present experimental work, these infrared studies will not be reviewed. However, several reaction products of carbodiimides were likely, including polymerized carbodiimides, guanidines, pseudoureas, and the phenolate salts of the last two. These will be covered in the order mentioned.

Merten et al. (76, 80) appear to be the only workers who discussed the infrared spectra of N-aryl linear "poly-carbodiimides"

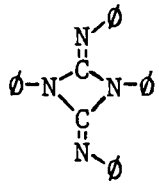


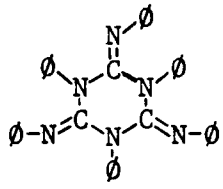
which absorbed at 6.2μ, 6.28μ, and 6.6μ.

Robinson (75) stated that N-alkyl linear polymerized carbodiimides absorbed at 6.134-6.06μ, 7.352μ, 8μ, and 9.37μ.



The spectra of the N-phenyl dimeric and trimeric cyclic compounds





were mentioned by David and Staley (230, p. 262), who reported only the C=N double-bond stretching peaks (or "carbonyl" peaks), respectively at 5.95μ and 5.99μ. Tsuzuki and Iwakura (242) reported the dimer absorption at 5.917μ. Further infrared characterization of these polymerized carbodiimide structures (linear or cyclic) is not available through the open literature. No one has reported whether the corresponding N-benzyl or N-alkyl cyclic oligomers can be made, or whether the N-alkyl

polymers (linear or cyclic) are more or less stable than the N-aryl structures.

A few standard reference spectra of various non-salt guanidines have been published, though the spectra have very rarely been discussed in the open literature. Pickard and Polly (243) mentioned the C=N stretching absorptions of triphenyl guanidine and sym-diphenyl guanidine, as 6.11μ and 6.10μ respectively. Representative reference spectra are the following:

1,3-diphenyl guanidine	$C_{13}H_{13}N_3$	(193, p. 963E)
1,3-di-o-tolyl guanidine	$C_{15}H_{17}N_3$	(193, p. 963G)
1,2,3-triphenyl guanidine	$C_{19}H_{17}N_3$	(193, p. 963F)

Most reported spectra are those of guanidine salts, with one equivalent of mineral acid (see structure; p. 71).

A little more has been said about non-salt (or free base) pseudoureas. Ngoc Son (46; 89, p. 74) studied the polypseudourea prepared from TDI and ethylene glycol, and reported infrared peaks at 3μ, 3.4-3.5μ, 6.2-6.3μ, 6.65-6.7μ, 7.2μ, and 8.0μ. Dyer and Newborn (67) had previously reported only the peaks at 3μ, 3.5μ, 6.2μ, and 6.65μ for the polypseudourea obtained from MDI and benzyl alcohol. Matuszak (38, p. 80, 83) made the following polymeric pseudourea assignments, apparently for the generalized N-substituent

(aryl, benzyl, or alkyl):

2.92-2.98μ N-H stretching

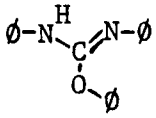
6.02-6.17μ C=N stretching

8.93-9.03μ C-O-C stretching

9.17-9.34μ (unassigned)

The infrared studies of pseudourea model compounds should be segregated according to the heteroatom substituents, whether the N or the O atom is substituted by aryl or alkyl (N- or O-benzyl substituents seem to be unreported).

1. N-Aryl-O-Aryl Model Pseudoureas. For the model compound 1,2,3-triphenyl pseudourea,



Forman et al. (246) reported the following assignments:

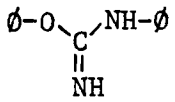
2.98μ N-H stretching

6.0μ C=N stretching

9.03μ, 9.31μ C-O-C stretching

7.53μ C-N stretching

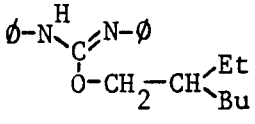
No other assignments have been reported, although the interesting compound 1,3-diphenyl pseudourea,



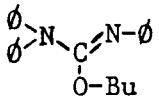
is found in the Sadtler grating collection. Its absorptions in the carbon-heteroatom stretching region (some of which are actually benzene ring vibrations) are as follows: 6.25μ, 6.289μ, 6.369μ, 6.711μ, 6.803μ, 6.97μ, 7.22μ, 8.13μ, and 8.197μ. Noteworthy is the difference in the C-N stretching wavelengths for the two models above, 6.0μ vs. 6.25μ.

2. N-Aryl-O-Alkyl Model Pseudoureas

Forman et al. (246) reported two model compounds of this type,

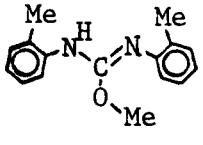


and



The assignments given for these compounds are listed in Table XVIII.

Bycroft and Cotton (248) reported for the model compound

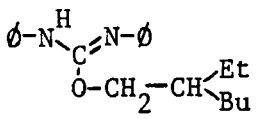
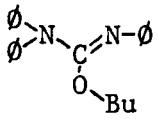


the following assignments:

N-H stretching	2.923μ
C=N stretching	6.00μ
C-N stretching	7.42μ

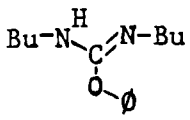
TABLE XVIII

INFRARED ASSIGNMENTS FOR N-ARYL-O-ALKYL PSEUDOUREAS

Assignments		
N-H stretching	2.97μ	-------
C=N stretching	6.03μ	6.08μ
C-O-C stretching	8.95μ and 9.23μ	8.95μ and 9.31μ
C-N stretching	7.64μ	7.66μ

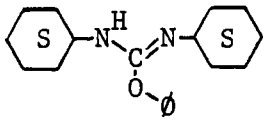
3. N-Alkyl-O-Aryl Model Pseudoureas

Forman et al. (246) reported the following assignments for the model compound



N-H stretching	2.95μ, 3.15μ
C=N stretching	5.96μ
C-O-C stretching	8.95μ, 9.1μ, 9.28μ
C-N stretching	7.75μ

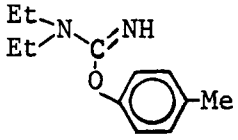
Vowinkel and Wolff (249) studied the model compound



making the following assignments

N-H stretching	2.915-2.994μ
C-N stretching	5.94-6.00μ
C O C stretching	8.130-8.333μ

The model compound



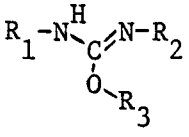
has doubtful relevance to this substitution pattern, but its spectrum (250) has the following strong peaks, which occur at about the same wavelength as the corresponding peaks of the

other two models: 6.1μ (vs), 7.1μ (s), 7.75μ (s), 8.1-8.3μ (vs), 9.1μ (s), and 9.2μ (s).

4. N-Alkyl-O-Alkyl Model Pseudoureas

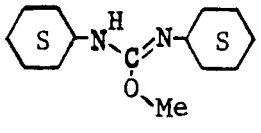
Forman et al. (246) studied four pseudoureas with this substitution pattern, wherein the alkyl groups were butyl, cyclohexyl, or 2-ethylhexyl. The various substituents gave very little difference in wavelength for the characteristic absorptions. The assignments and wavelength ranges were the following:

N-H stretching	2.90-3.05μ
C=N stretching	6.00μ
C-O-C stretching	8.9-9.0μ, 9.05-9.2μ, 9.25-9.4μ
C-N stretching	7.70-7.75μ

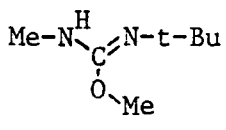


R_1, R_2, R_3 = butyl, cyclohexyl, or 2-ethylhexyl

Bycroft and Cotton (248) made a few assignments for the two model compounds,



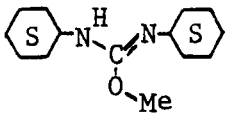
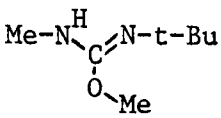
and



listed in Table XIX.

TABLE XIX

INFRARED ASSIGNMENTS FOR N-ALKYL-O-ALKYL PSEUDOUREAS

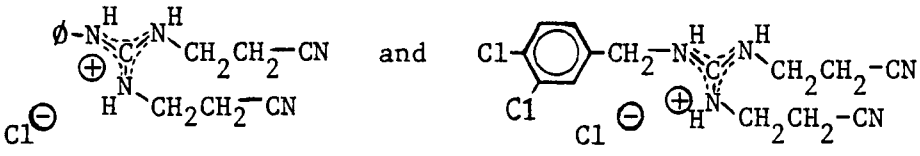
Assignment		
N-H stretching	2.90μ	2.90μ
C=N stretching	6.00μ	6.024μ
C-N stretching	7.575μ	7.462μ

Since guanidines and pseudoureas are much more stable in their salt forms than as the free bases, one would expect to find a larger literature on the infrared assignments of the salt forms. Many standard reference infrared spectra of guanidine salts and pseudourea salts are available, but assignments have scarcely been attempted, probably because of the additional perturbations and interferences introduced by the acid moiety.

For those salt forms whose infrared spectra are reported, the acid moiety is invariably a mineral acid or an organic sulfuric acid. The acid moiety is never phenolic, which would be of much greater relevance to the present research. In fact, such simple mineral acid moieties as the hydrohalic acids (HCl, HBr, and HI) are rare among the reported spectra, which makes the lack of reported assignments understandable.

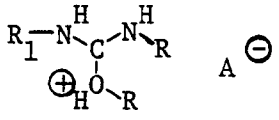
Concerning the spectra of guanidinium salts, only one generalization seems to have been made. Bellamy (251, p. 302) stated that the C=N frequencies are raised a little above normal, on going from the free base to its salt form (i.e., a free base absorption at 6.10μ would be shifted to about 6.00μ in the salt form).

Kreling and McKay (252) reported assignments for two relevant models,

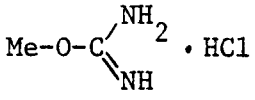


listed in Table XX.

The infrared spectra of trisubstituted pseudouronium salts



have not been discussed in the available literature, though Hashimoto and Arakawa (253) mentioned two characteristic absorptions for the monosubstituted pseudouronium hydrochloride,



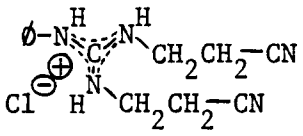
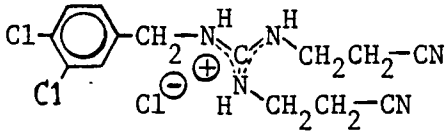
An absorption at 5.91μ presumably corresponds to the C=N stretching vibration; they also pointed out a band at 6.329μ.

5. Melamines

Melamines are also possible reaction products of carbodiimides, and their spectra have been studied fairly well (254, 255, 256). However, melamines are likely reaction products only when the hydroxyl moiety or the diol component is removed almost completely by volatilization and/or cleavage

TABLE XX

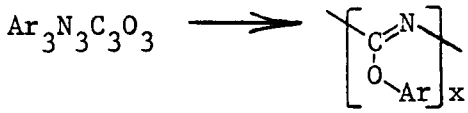
INFRARED ASSIGNMENTS FOR GUANIDINIUM SALTS

Assignment		
N-H stretching	3.081μ	3.105μ, 3.175μ, 3.279μ
C=N stretching	6.090μ	6.024μ
N-H stretching	6.233μ, 6.381μ	6.338μ, 6.439μ

to volatile products, so as to leave only nitrogenous functional groups in the residue. This degradative pathway (formation of melamines) is highly improbable for AB-type PU's, so the infrared spectra of melamines need not be considered here.

6. Polycyanates

Polycyanates should be taken more seriously, as they have been proposed as the main degradation products of isocyanurates (78). For the polycyanate which was presumably derived from a triarylisocyanurate, the following infrared assignments are given:

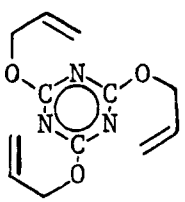


C=N stretching 6.135μ

C-N stretching 7.194μ, 7.596μ

Linear polycyanates are very difficult to obtain, but cyclic trimeric cyanates are more accessible, and should have very similar infrared absorptions.

The spectrum of triallyl cyanurate,



has been discussed by Gillham and Mentzer (239), and it should resemble closely the spectrum of the tribenzyl cyanurate. The spectra of symmetrical tris-O-substituted cyanurates, where the substituent is methyl, hexyl, or allyl, have been discussed thoroughly by Vorotyntseva et al. (255).

7. Diarylmethanes

For several AB-type PU's, diarylmethane linkages are important thermolysis products. The infrared literature of diarylmethanes is rather large, but not readily generalizable for a wide variety of substituents, including hydroxyl, amino, and alkyl. Thus the previous studies should be cited in those chapters where each study is most relevant.

From the above discussion, the reader should notice the amusing paucity of assignments and reported peaks for wavelengths above the carbonyl region, from 6.4μ to 16μ. Using the carbonyl region alone, it would be very difficult to pin down a few thermolysis products, and one could claim the possibility of several fanciful products. This is the unfortunate state of crosslinked PU analyses.

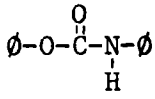
To make any progress in this area, workers will have to establish several correlations outside the carbonyl region, especially between 7μ and 11μ. It would be very desirable here to examine the effect of the N-substituent (aryl, benzyl, or alkyl) on the spectra (beyond the carbonyl region) of

ureas, guanidines, pseudoureas, phenolate salts of guanidines and pseudoureas, and isocyanurates, using many standard reference spectra as well as specially prepared model compounds. Similarities and differences in infrared peak positions and intensities should be studied. An exhaustive study of this kind would not be presently possible in its entirety, due to lack of reference spectra and suitable model compounds. Even an attempt to make such comparisons among different N-substituents would expand the bulk of this dissertation beyond all propriety. Further generalizations outside the carbonyl region for noncarbamates will therefore be limited to individual substitution patterns (N-aryl-O-aryl, for instance), and will be discussed in the appropriate chapter.

C. PREPARATION OF CARBAMATE MODEL COMPOUNDS

The preparation of the four benzo-substituted cyclic carbamates is discussed in the appropriate chapters. The preparation of the open-chain model carbamates will be outlined here.

1. Preparation of N-Phenyl-O-phenyl Carbamates

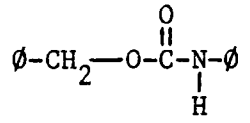


phenyl carbanilate

The preparation and properties of phenyl carbanilate have been reported by Hofmann (257, 258), Crosby and Niemann

(259), Hayes et al. (201), Christenson (260), Bloodworth and Davies (3), and Lateef et al. (39). Phenyl carbanilate was prepared by the author simply by adding phenylisocyanate (0.1 mole, 11.91 g, 10.87 ml) dropwise with stirring to phenol (0.1 mole, 9.41 g), with a catalytic amount (1 drop) of pyridine. The reaction mixture was warmed in a water bath at 60° for 5 min, whereupon crystals appeared. The hot mixture was diluted with 10 ml benzene, then 10 ml hexane. After cooling overnight, the mixture was filtered, washed with hexane, recrystallized from heptane, and dried in a vacuum desiccator (yield 184.4 g, 86.5%, mp 126-127°), lit 123° (39), 124-126° (261), 126-127° (116). The above procedure closely resembled that of Shriner, Fuson, and Curtin (262, p. 246, 299). The procedures of Pasto and Johnson (263, p. 359) and of Boots (264) are similar. Infrared absorptions were reported by Lateef et al. (39) (5.69μ) and by Hayes et al. (201) (5.83μ and 6.53μ).

2. Preparation of N-Phenyl-O-benzyl Carbamate



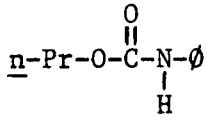
benzyl carbanilate

The preparation and properties of benzyl carbanilate have been reported by Bergstrom and Martell (265), Ben-Ishai and Katchalski (266), Fletcher and Ness (267), Mukaiyama and Hoshino (147), Mukaiyama and Iwanimi (88), Pierce and Joullie

(1963), Caldwell et al. (269), Ben-Ishai and Berger (119), and Gaylord and Sroog (270).

Benzyl carbanilate was prepared in this laboratory much like phenyl carbanilate. Benzyl alcohol (1 mole, 108.14 g, 103.5 ml), 1 ml pyridine, and 600 ml dry benzene were placed in a 1.5 l beaker, and the mixture was vigorously stirred and heated to boiling. Phenyl isocyanate (1 mole, 119.12 g, 108.7 ml) was added dropwise. The mixture was slowly boiled down to a volume of 300 ml (approximately 3 hr). Hexane (100 ml) was added, and the mixture allowed to cool overnight. The product was filtered, washed with hexane, recrystallized from hexane, and dried in a vacuum desiccator. The yield was 186.4 g (82%), mp 75-76°, lit 75-76° (270), 77-78° (261). This preparation most closely resembled that of Boots (264).

3. Preparation of N-Phenyl-O-n-propyl Carbamate



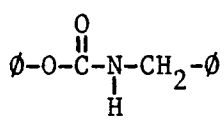
n-propyl carbanilate

This compound was prepared instead of the better known ethyl carbanilate because of the ready availability of anhydrous n-propanol. Phenylisocyanate (0.5 mole, 59.56 g, 54.35 ml) was added dropwise to a heated (80°) mixture of 225 ml n-propanol (3 mole, 180.3 g) and 1 ml pyridine, with vigorous stirring. The excess n-propanol was distilled off, until the

boiling temperature of the mixture reached 105°. On cooling to room temperature a homogeneous oil remained, which was then triturated with 100 ml pentane (no precipitation) and chilled in a dry ice bin. On standing overnight the product crystallized, and was then filtered while cold, washed with pentane, and dried in a vacuum desiccator, yield 51 g (57%). Although the reported melting point (271, p. 2678) is 57-59°, the product melted sharply at 50-51°. This melting point was not changed on recrystallization from n-hexane (with chilling in a dry ice bin).

4. Preparation of N-Benzyl-O-phenyl Carbamate

The preparation and properties of N-benzyl-O-phenyl carbamate,

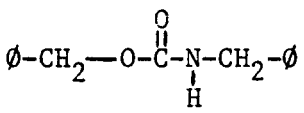


have been reported by Johnson (272, p. 523). A novel preparation using the Curtius reaction was attempted several times, using phenylacetic acid hydrazide and phenol, but all attempts were unsuccessful. The reagent phenylchloroformate had to be used (273, p. 318), following the procedures of Crosby and Niemann (259) and Hutchins and Fife (274). Benzylamine (0.2 mole, 21.43 g, 21.9 ml) was added dropwise to a vigorously stirred solution of phenylchloroformate (0.1 mole, 15.66 g) in 20 ml ether. After the mixture was stirred for 2 hr, 100

ml of 2N HCl was added to dissolve the amine hydrochloride. The mixture was extracted with ether (3 portions of 100 ml), and the ether solution was washed first with 50 ml of 2N HCl, then with 50 ml H_2O. The ether solution was dried with sodium sulfate. After the ether evaporated on standing, the product was recrystallized from hexane. The yield was 14.25 g (62.5%), mp 80-81°, lit 83-85° (272). On scaling up to mole quantities, equimolar amounts of benzylamine, phenyl chloroformate, and pyridine were used. The yield was lower, but the purity was about the same (mp 80-81°).

5. Preparation of N-Benzyl-O-benzyl Carbamate

The preparation and properties of this model compound,



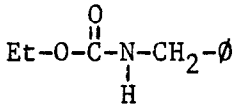
have been described by Ben Ishai (119, 266). The preparation in this laboratory was first attempted using the Curtius reaction of phenylacetic acid hydrazide. Decimolar amounts of the Curtius reagents were used: 15.0 g acyl hydrazide, 55 ml 2N HCl, 7.7 g $NaNO_2$. To the solution of phenylacetic acid azide in dry benzene (1 l) was added a mole of benzyl alcohol (108.1 g) and the mixture brought to reflux. On removing benzene (gas jet evaporation) and benzyl alcohol (vacuum distillation), a solid product remained, which was recrystallized from hexane. A very small yield of this model compound

was obtained, yield 0.96 g (4%), mp 61-63°, lit 64° (119, 266).

Another preparation was attempted using the metathetical reaction of Argabright et al. (207), in which the benzyl isocyanate intermediate is generated in DMF solution by reaction of benzyl chloride with potassium cyanate, in the presence of an alcohol, thus forming the carbamate. This attempt failed, though the method succeeded with another model compound, N-benzyl-O-ethyl carbamate.

The only successful preparation of bulk amounts of N-benzyl-O-benzyl carbamate employed benzyl chloroformate ("carbobenzoxy chloride") (273, p. 59; 275, p. 109). To a vigorously stirred ice-bath-cooled mixture of benzyl chloroformate (0.5 mole, 85.3 g), 500 ml ether, and 250 ml of 2N aq NaOH was added dropwise a solution of benzylamine (0.5 mole, 53.58 g) in 100 ml ether. The aqueous basic layer was discarded, and unreacted amine was extracted with 100 ml 1N HCl. The ethereal layer was then washed with two 100 ml portions of water, dried with sodium sulfate, and evaporated to dryness. The resulting solid was then recrystallized from hexane, yield 61.5 g (51%), mp 58-62°, lit 64° (119, 266). This Schotten-Baumann procedure is similar to those of Bergstrom (265), Ben-Ishai and Berger (119), Mukaiyama and Hoshino (147), and Blaha and Rudinger (120).

6. Preparation of N-Benzyl-O-ethyl Carbamate



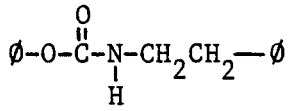
The preparation and properties of this compound have been described by Gutsche and Johnson (276), Garbrecht and Herbst (277), Argabright et al. (207), and Basterfield et al. (278).

The methathetical reaction of Argabright et al. (207) was tried. A 100 ml 3-necked flask fitted with mechanical stirrer, condenser, and N_2 bubbler was charged with 6.07 g (75 mmole) of KNCO, 3.9 g (85 mmole) dry ethanol, and 40 ml DMF. The mixture was heated to 100° and 6.33 g (50 mmole) of benzyl chloride in 5 ml DMF was added dropwise. Heating was continued for 2 hr after completion of addition. The salt was removed by filtration, and the filtrate was vacuum distilled to remove unreacted starting material and solvent. The residue was triturated with ether and filtered. Slow evaporation of the ether gave the model carbamate, yield 1.6 g (18%), mp 43-44°. The following melting points have been reported: 41.5-42° (207), 44° (278), 45-47° (276), and 48.5° (277).

The procedure of Gutsche and Johnson (276) was followed exactly, and was found to give a better yield. The following quantities were used: benzylamine (100 g, 0.933 mole, 102 ml), ethyl chloroformate, each portion (52.5 g, 0.483 mole, 38.7

ml), and NaOH (1 mole, 40 g). The yield was 72 g (43%), mp 43-44°.

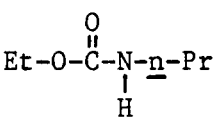
7. Preparation of N-β-Phenethyl-O-phenyl Carbamate



This compound does not seem to have been previously reported, but its preparation was straightforward, using phenyl chloroformate (273, p. 318).

A solution of phenyl chloroformate (1 mole, 156.6 g), 81 ml pyridine (1 mole, 79.1 g), and 500 ml ether was placed in a 2 l beaker cooled by an ice bath, stirred vigorously by an overhead stirrer. To this a solution of 125.7 ml (1 mole, 121.18 g) of β-phenethylamine was added dropwise. Stirring was continued for 4 hr with the temperature gradually rising to 25°. Amines were removed by extraction with 500 ml 2N HCl, followed by 250 ml 2N HCl. The ethereal solution was washed with three 500 ml portions of water, dried with sodium sulfate, and evaporated to dryness with a gas jet. The residue was recrystallized twice with hexane, yield 94 g (39%), mp 92-93° (no literature mp found).

8. Preparation of N-n-Propyl-O-Ethyl Carbamate



The preparation and properties of this aliphatic

carbamate have been reported by Shreiner (279) and by Nirdlinger et al. (280).

This procedure using ethyl chloroformate (275, p. 364) was exactly the same as the one reported by Hartman and Brethen (281) except for the substitution of propylamine for methylamine (the amine was neat rather than in aqueous solution). The molar quantities were the same: propylamine (2 mole, 118.22 g, 166 ml), ethyl chloroformate (2 mole, 217 g, 191 ml). The product distilled at 110° at 61 mm; yield 82.5 g (63%), lit 191.5-192.5°/758 mm (271, p. 1413).

CHAPTER III

THE NEAR INFRARED SPECTROSCOPY OF AB-TYPE POLYURETHANES

A. GENERAL CONSIDERATIONS

The near infrared region lies between 600 nm and 3000 nm (0.6μ to 3μ, 6000 Å to 30,000 Å, 16,667 cm^{-1} to 3333 cm^{-1}). It overlaps the visible region from 600 nm to 750 nm, and overlaps the midrange infrared region from 2000 nm to 3000 nm. For the purpose of the present work, the useful range is 1000 nm to 2650 nm. Below 1000 nm even the thickest (non-opaque) polymer films absorb too weakly, and above 2650 nm the most convenient cell material, pyrex glass, absorbs strongly.

The early work in near infrared spectroscopy was thoroughly reviewed by Wheeler (282). That review is still the best simple exposition of the basic theory and instrumentation. However Wheeler generally neglected the region from 2μ to 3μ (2000 nm to 3000 nm), and deemphasized combination bands. Wheeler very thoroughly covered the overtone stretching vibrations, whose wavelengths are nearly integral submultiples of the fundamentals (282, p. 637). More recently the organic applications have been reviewed by Whetsel (283), treating the spectral region from 700 nm to 2700 nm. The combination bands were treated thoroughly, as well as the overtones.

Both the Wheeler and Whetsel reviews were invaluable to the present study.

Correlation charts, which are so familiar and useful in the midrange infrared, have very little value in the near infrared. One of the few such compilations is that of Goddu and Delker (284). From this chart, it may be seen that widely different compounds can have rather similar patterns of absorption positions. The great differences lie in the pattern of absorption intensities, which are difficult to report in chart format.

The near infrared studies of small carbamates are rather few. Noteworthy are those of Kogon (47, 186) and Barca et al. (285). Related amide studies are those of Bath and Ellis (286), Fraser (287), Foster et al. (288), Goddu (289), Krikorian and Mahpour (290), and Krikorian et al. (291). An important isocyanate study is that of David (292). Relevant amine studies are those of Whetsel (293, 294), Krueger (295), Hambly and O'Grady (296, 297), Liddell and Wulf (298), and Strait and Hrenoff (299).

It appears that the only accessible near infrared studies of PU's are those of Gudim and Klimenko (211, 300) and of Vatulev (301, 302). These Russian workers showed much enthusiasm about the future of the near infrared in PU research.

The near infrared absorptions for various carbamate rings and linear model carbamates, ureas, isocyanurates, amines, etc., are given in Appendix II of this study. All positions of peak maxima and shoulders are noted, as well as peak intensities, but not peak breadths or areas. The probable assignments are included where relevant. The use of these model spectra will be discussed mainly in the appropriate chapter. Only rather general considerations will be mentioned here.

Materials generally have much smaller molar absorptivities in the near infrared than in the midrange infrared, so sample preparations are somewhat different, in that thicker sample layers are utilized. Whereas pyrex glass absorbs strongly in several midrange infrared regions, it is an excellent film support in the near infrared (below 2650 nm). Sodium chloride (or KI) offers no advantages as a film support in this region. Although dispersions in KBr or KI pellets can be used in the near infrared (mainly above 1900 nm), it is difficult to make them thick enough or concentrated enough to provide sufficient absorbing compound, and still maintain transparency. Because of extreme difficulties in sample preparation, KBr or KI pellets were eliminated from consideration in this near infrared work.

Though all solvents absorb to some extent in the mid-range infrared, carbon tetrachloride is completely transparent throughout the entire region from 600 nm to 3000 nm, and is the solvent of choice for all crystalline model compounds in this work. Matched quartz cells containing solvent and solution were used with CCl_4. For the more soluble solid model compounds, 1 cm cuvettes could easily be used. For the less soluble solids, such as the cyclic carbamates, ureas, and isocyanurates, 10 cm cells had to be used. For solids of very low solubility, such as 1,3-benzoxazin-2-one (ring-01) and N,N'-dibenzylurea, a scale expansion by a factor of 10 had to be used as well as 10 cm cells, to obtain a useful spectrum.

Unfortunately CCl_4 reacts with amines, so the spectra of aniline and benzylamine had to be obtained with the neat liquids, using capillary films of 0.5 mm thickness (1 cm cells with 9.5 mm spacers).

The spectrum of a compound like o-aminobenzyl alcohol, which is a solid and also an amine, should ideally be obtained as a melt. Because of the high expense of such a disposable cell, an alternative was improvised. It was found that the compound could be melted between two hot pyrex discs, and a translucent film resulted on cooling. A satisfactory spectrum was obtained from this film of "neat solid." Spectra were

also obtained from "neat solid" films of dibenzylurea and 1,3-benzoxazin-2-one, compounds which had been difficult to run as solutions. It was found that the peak positions remained very nearly the same, but that the intensities were somewhat different, in comparing the solution and the "neat solid" spectra. As the wavelength decreased, the intensities were progressively lowered relative to the solution spectra, apparently due to the greater scattering losses at lower wavelengths. The films of "neat solid" were obviously inhomogeneous due to crystallinity.

Polymer film samples were routinely prepared using a 30 ml pyrex beaker. The polymer film was either liquefied by heat to cover the beaker bottom, or else cast from solution — an extremely simple and straightforward process.

The instrument used in this work was a Cary Model 17I, which was always purged with dry nitrogen for 4 hours prior to use, and purging was continued during use. The scanning speed was routinely 0.1 nm/sec, and the chart spacing 30 nm/inch.

As a broad overview, the absorption bands in the near infrared region result from "harmonic overtones of fundamental bands and combination bands often associated with hydrogen atoms" (303, p. 171). In other words, almost all absorptions are hydrogenic, arising from OH, NH and CH groups

(which also accounts for the transparency of pyrex and CCl_4). At least one component of a combination band is invariably hydrogenic, but another component can be a high-intensity carbonyl stretching or aryl ring vibration. Prominent non-hydrogenic vibrations (exceptions to the hydrogenic rule) in the near infrared are the second overtone of the aromatic in-plane ring vibration (fundamental band near 6.9μ) around 2650 nm and the second overtone of the carbonyl stretching near 2000 nm.

Unlike absorptions in the midrange infrared, an isolated absorption ("taken out of context") in the near infrared is meaningless. All assignments are made with reference to the midrange infrared spectrum of the same compound. Only the stronger midrange peaks are likely to give rise to near infrared peaks. The frequency of a near infrared peak is usually not an exact integral multiple or arithmetic sum of component midrange frequencies, but is generally somewhat lower (283, p. 4). A literature assignment relating a frequency greater than the value calculated arithmetically should be regarded with grave suspicion; such assignments were common in the older literature. Each peak must be considered in the context of other present or absent absorptions, and relative intensities are all important. The value of the near infrared region is largely due to the ease of working

with intensities. The calibration of the Cary 17I chart in absorbance units simplifies the calculation of relative intensities.

The method of determining intensities is important. Because of the massive amount of data to be processed, peak heights rather than areas will be used in this study. Below 1800 nm (in the "overtone region") the baseline is rather obvious, because the absorptions are widely separated. Above 2000 nm (in the "combination region") there is an extensive overlap of the successive peaks, so the "single-point" method must be applied. The absorption of the baseline (considered horizontal for the entire region from 2000 nm to 2500 nm) is taken to be the value of the deepest minimum between 1750 nm and 2000 nm. Almost invariably this contrived baseline is an obvious extension of the more "natural" baseline below 1800 nm, considering all three criteria: ordinate, slope, and curvature. The few cases where this technique is suspect involve excessive scattering, where the baseline rises sharply toward lower wavelengths, due to the "inverse fourth-power" scattering law,

$$(\text{intensity scattered light}) \propto \frac{1}{(\text{wavelength})^4}$$

In these extreme cases all intensities are suspect anyway,

and only the wavelengths of absorption maxima are of interest. For the use of the near infrared in this work, it is fortunate that most polymer samples were noncrystalline, as crystallinity contributes greatly to the scattering problem. Even for those homopolymeric PU's which are highly crystalline, the nonvolatile thermolysis residues have much lower crystallinity.

Those compounds containing an aromatic ring provide a form of "internal standard" for measuring intensities. The strong peak near 2460 nm is the second overtone of the aromatic ring skeletal vibration near 6.9μ (6900 nm). The main exception in this study is the heterocycle benzoxazolin-2-one (ring-00), for which the peak at 2398 nm is the second overtone of the corresponding peak at 6.75μ, a shift apparently due to the aromaticity of the fused five-membered ring. Because this peak is independent of the number or kind of C-H bonds, and because it is often the strongest peak in the near infrared spectrum, it is arbitrarily assigned an intensity value of 10 and all other intensities are expressed relative to it.

The average absorptivity of this reference peak may be calculated from the data of Goddu and Delker (284) as about 5 1/mole cm. Actual absorptivities of all peaks would be more useful, but the determination of these for polymer samples would be much more difficult than the extra utility warrants, because the polymer film thicknesses are not uniform. Because the polymers have such a strong adhesion to glass, they invariably form a highly curved meniscus.

Assigning the 1460 nm peak an intensity value of 10 for aromatic compounds is probably the closest one can come to making most of the spectra comparable with one another. It is quite possible that the 1460 nm peak may play a more important quantitative role in the future, in that its intensity may be directly proportional to the molar concentration of benzene rings, at least within certain aromatic substitution patterns. Determining the full scope of the intensity variations of this absorption is not a proper objective of the present study.

For those few aliphatic compounds which contain no benzene rings, a similar convenient reference peak is not available, and fortunately such aliphatic compounds have a minor importance in this study. For these compounds, the strongest peak below 2500 nm was arbitrarily assigned an intensity value of 10, and this peak occurred at widely different places for the different aliphatic compounds.

In comparing the near infrared spectra of a series of aliphatic model compounds with which to elucidate the spectrum of an aliphatic polymer sample, one must first select an absorption whose molar absorptivity is most nearly the same in both model and polymer, that is an intensity which is least likely to change with molecular weight. A C-H combination band of a polymethylene chain might give such a peak, for

instance near 2380 nm (287), 2340 nm (287), 2310 nm (211, 292), 1730 nm (211; 282, p. 638), or at 1210 nm (288). The selected absorption is used as a standard, and the intensities of all other peaks are expressed relative to it. In this way the variation of the carbonyl and amide NH absorptions may be followed in polymer samples, and compared with the intensities in model compounds.

The same technique may be used for the aromatic polymers, if one desires not to use the aryl ring peak at 2460 nm as a standard.

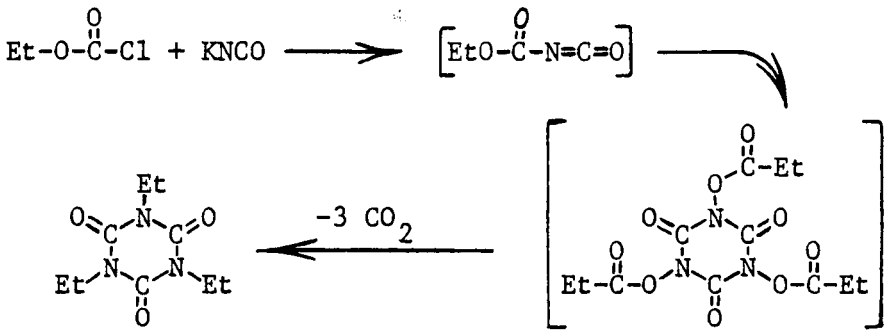
The spectra of the model compounds are placed in the appendix because each spectrum applies to more than one chapter. However, the polymer near infrared spectra are discussed in the particular chapter devoted to each particular type. Certain model compounds were unavailable commercially, and had to be prepared specifically for the near infrared spectral study. These preparations will be described briefly in the following experimental section.

B. EXPERIMENTAL SECTION; SYNTHESIS OF ADDITIONAL MODEL COMPOUNDS

1. Preparation of Isocyanurates

a. Preparation of 1,3,5-triethylisocyanurate

Triethylisocyanurate was prepared by the method of Wurtz and Henniger (304).



Potassium cyanate (0.20 mole, 16.22g) and ethyl chloroformate (0.26 mole, 28.2g, 24.8 ml), were placed in a 200 ml flask fitted with an air-cooled reflux condenser and magnetic stirrer, and heated for 24 hr with an oil bath at 180° (bath temperature).

The reaction mixture was triturated with 400 ml 95% ethanol, and about 5 g of white insoluble residue (cyanuric acid and KCl) was discarded. The solution was boiled down to 50 ml, whereupon a white solid crystallized from 30 ml ethanol, followed by sublimation at 90°, giving a yield of 8.1 g (19%), mp 93.5-94°, lit 95° (305, p. 404).

b. Preparation of 1,3,5-tribenzylisocyanurate

Tribenzylisocyanurate was prepared by the method of Argabright et al. (207). Benzyl chloride (0.2 mole, 25.32 g, 23 ml) and potassium cyanate (0.2 mole, 16.22 g) and 200 ml DMF were placed in a 500 ml round-bottom flask fitted with reflux condenser and magnetic stirrer, and heated by an oil bath. The mixture was heated at 100° and stirred for 5 hr.

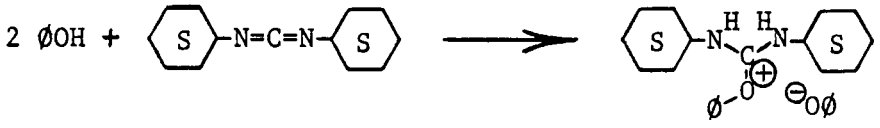
Upon stripping off the DMF with a rotovac and pouring the paste into water, a white powder was obtained by filtration. Residual solvent was removed in a vacuum oven. Upon recrysallization from ethanol, a yield of 22 g (27.5%) was obtained, mp 163-164°, lit 165° (305, p. 411).

b. Preparation of 1,3,5-triphenylisocyanurate

Triphenylisocyanurate was prepared by simply heating phenylisocyanate in the presence of a catalyst, according to Smolin and Rapoport (305, p. 410). Phenylisocyanate (0.2 mole, 23.82 g, 21.75 ml) was mixed with dry triethylamine (50 ml) and pyridine (20 ml) in an Erlenmeyer flask fitted with reflux condenser and magnetic stirrer. Upon bringing the stirred mixture to reflux, the solution quickly turned cloudy. Refluxing was continued for two hr, and solvent removed with a rotovac. The resulting paste was triturated with water, filtered, and dried in a vacuum oven. The product was recrystallized from ethanol, yield 21.7 g (91%), mp 277-278°. It is curious that the reported melting points of this compound range widely, from 274° to 293°: 274° (306), 278° (307), 280° (308), 280-281° (59), 281° (305), 284-286° (309), 293.5° (310).

2. Preparation of N,N'-Dicyclohexyl-O-phenylpseudouronium Phenolate

A simple addition reaction was used in this preparation:



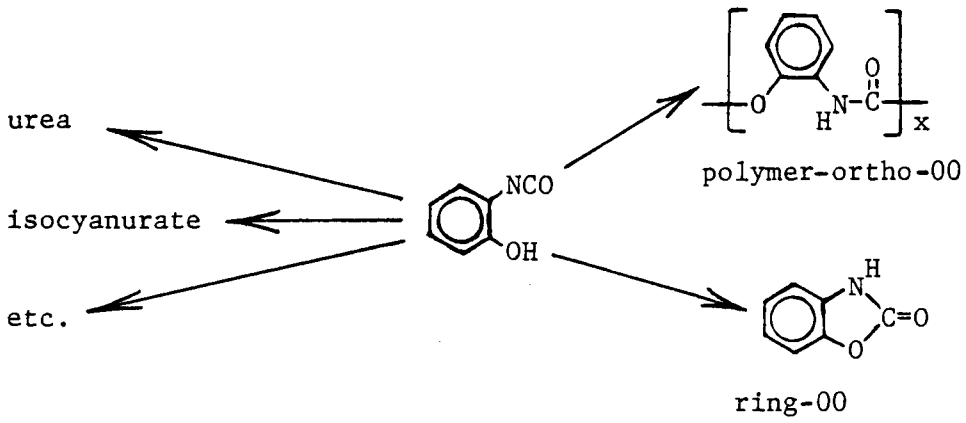
Dicyclohexylcarbodiimide (0.1 mole, 20.6 g) and anhydrous phenol (0.2 mole, 18.8 g) were placed in an Erlenmeyer flask fitted with a magnetic stirrer and a reflux condenser (protected with a drying tube). The mixture was heated to 180° for 60 min. Upon cooling a very viscous but homogeneous liquid remained, which was characterized only by its mid-range and near infrared spectra. The carbodiimide peak at 4.75μ and the phenol peaks at 8.2μ and 2.9μ disappeared. New very strong peaks at 6.9μ and at 6.15-6.6μ appeared. This preparation is very similar to that of Vowinkel and Wolff (249).

CHAPTER IV

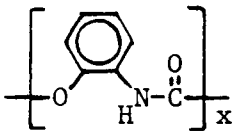
THE SYSTEM-ORTHO-00

A. GENERAL CONSIDERATIONS

This chapter is concerned with the chemistry of those compounds obtained from the hypothetical intermediate ortho-hydroxyphenylisocyanate:

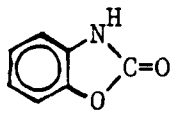


The relevant systematic Chemical Abstracts names are the following:



poly(oxycarbonylimino-o-phenylene)

poly(oxycarbonylimino-1,2-phenylene)

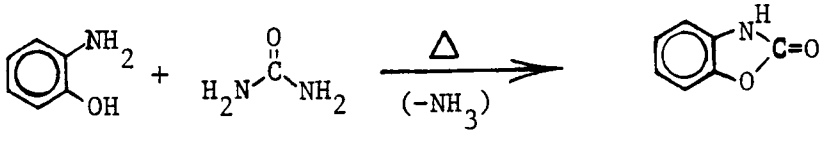


2-benzoxazolinone

2(3H)-benzoxazolone

Whenever convenient the linear polyurethane will herein be referred to as "polymer-ortho-00" and the cyclic carbamate as "ring-00."

Many syntheses of ring-00 have been devised, and these have been well reviewed (223, 311). The simplest and most practical preparation involves the reaction of o-amino-phenol with urea under moderate heat.



Several variants of this procedure have been reported (312, 313, 314, 315, 316), and the one found most convenient in this laboratory was described in detail in the author's M.S. thesis (317, p. 39).

Deliberate attempts to synthesize the linear polymer-ortho-00 have been unsuccessful. In 1958 Hall and Schneider (141) reported that attempted polymerization of ring-00 by heat and catalysts had failed, in a paper that claimed the successful polymerization by catalyzed thermal ring-opening of many other heterocycles. Their method, applied to the entire range of heterocycles, was described in very general terms:

> The monomer, 2 to 4 grams, was heated with catalyst [unspecified], 0.1 gram, in a long glass tube under a nitrogen atmosphere. Heat was supplied by refluxing

> liquid-vapor baths [unspecified]. Heat was continued until the molten monomer had become very viscous or had solidified. The tube was cooled and broken open. The polymer was freed of monomer by extraction with appropriate solvents.

Unlike the attempt by Hall and Schneider, the present research investigated the polymerizability of the heterocycles by heat alone (no catalyst deliberately added). In view of the high boiling point of ring-00 (variously reported between 335° (312) and 360° (311)) at which the compound reportedly distils unchanged at atmospheric pressure, a high degree of thermal stability is expected for this ring. This is consistent with the findings of Hall and Schneider concerning its lack of polymerizability.

B. THERMAL POLYMERIZATIONS OF RING-00

1. Preparation and Characterization of Residue IV-1.

In this study, heating the pure ring-00 (anhydrous form, mp 140°-141°) at temperatures ranging from 180° to 220° for periods of up to 3 days failed to produce any polymer, pure starting material being recovered after each attempt. On heating the ring for 6 days, the temperature being raised from 220° to 245°, 50 mg of polymer was obtained from 1 gram of starting material (polymer by criterion of nonvolatility). The experimental procedure was described in minute detail in the author's M.S. thesis (317, p. 43-45).

The DSC trace of this material (under N_2 at 10°/min using the Perkin Elmer DSC-1B) showed slight decomposition at 367° followed by extensive decomposition at 390°.

The main absorptions in the infrared spectrum of this residue (called residue IV-1) are given in Table XXI.

2. Preparation and Characterization of Residue IV-2.

Other attempts to polymerize ring-00 were made by heating about 1 g in a silica tube sealed under vacuum, at various temperatures for 24 hr. The preparation of these tubes is described in the author's M.S. thesis (317, p. 48). Three methods of heating these tubes were tried: (1) using a tube furnace with temperatures measured by a calibrated thermocouple, (2) using a fused-salt bath consisting of the sodium acetate-potassium acetate binary mixture (46.3:53.7 mole ratio), and (3) using a hydrogenation bomb with high-pressure capabilities. Because the sealed tubes frequently blew up (invariably at all temperatures above 300°), the first two heating methods mentioned above were eventually abandoned, though the lower temperature data obtained with them is considered valid.

The heating temperature and yield of each of several 24 hr runs is tabulated below. The product is the amount of nonvolatile material obtained on sublimation at 170°.

TABLE XXI

INFRARED ABSORPTIONS OF RESIDUE IV-1

Wavelength (μ)	Intensity	Assignments
2.9	s	N-H stretching
2.95	vs	N-H stretching O-H stretching
3.2	vs	aryl C-H stretching
3.3	s	aryl C-H stretching
3.45	s	NH + stretching
3.55	m	NH + stretching
5.7	m	C=O stretching of oxazolone moiety
6.1	vs	C=O stretching of carbanilide
6.3	vs	2-arylbenzoxazole carbanilide
6.5-6.65	s	2-arylbenzoxazole carbanilide
6.85	vs	skeletal vibration of benzene ring
7.0	s	possible isocyanurate
7.1	m	possible isocyanurate
7.2	m	possible pseudourea
7.3-7.4	m	2-arylbenzoxazole
7.75-7.9	m	oxazolone moiety 2-arylbenzoxazole
8.0	vs	oxazolone moiety 2-arylbenzoxazole
8.2	s	2-arylbenzoxazole carbanilide
8.4-8.7	s	oxazolone moiety
9.0-9.1	m	
9.2-9.7	m	2-arylbenzoxazole
9.95	w	2-arylbenzoxazole
10.2	w	2-arylbenzoxazole
10.95	w	carbanilide
12.5	w	
13.3	s	oxazolone moiety
13.5	vs	2-arylbenzoxazole
14-16	m	2-arylbenzoxazole carbanilide

The percentage of product by weight is also given in Table XXII. The volatile material obtained from the crude thermolysis product by sublimation was shown to be almost entirely ring-00 by infrared analysis.

All these nonvolatile products, called residue IV-2, showed very similar infrared spectra. A representative spectrum is that of the product obtained at 290-295°, absorptions from which are given below. Because of the broadness of most absorptions, it was desirable to list the ranges at successively higher intensities for some peaks. Several of these absorptions must be approximated by step functions. The infrared absorptions of residue IV-2 are given in Table XXIII. The spectra of residues IV-1 and IV-2 are rather similar in appearance, and thus likely contain similar linkages in similar amounts. Both residues are slightly soluble in tetrahydrofuran, and can dissolve completely (about 0.1 g in 100 ml). Crosslinking and/or high branching are very unlikely considering the chemistry of the formation process and the low molecular weight of the product (discussed below).

The most obvious clues to the products come from the carbonyl region. Peaks corresponding to ring-00 (5.6-5.8μ) and to a diarylurea (carbanilide absorbs at 6.1μ) are apparent, but an aryl carbanilate peak is comparatively weak

TABLE XXII

YIELDS OF RESIDUE IV-2

Temperature (°C)	Starting Weight (g)	Product Weight (g)	Yield[a] (%)
260	0.63	0.031	4.9
260	0.72	0.038	5.3
260-265	0.56	0.028	5.0
280-285	0.85	0.047	5.5
285-290	0.82	0.057	7.0
290-295	0.93	0.062	6.7

a. Percent by weight of product.

TABLE XXIII

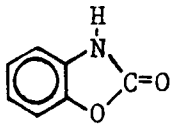
INFRARED ABSORPTIONS OF RESIDUE IV-2

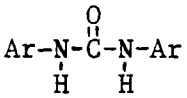
Absorption Strength at Wavelengths (μ)				Assignment
Weak	Medium	Strong	Very Strong	
		2.8		
			2.9	N-H stretching
			3.1	O-H stretching
		3.3		aryl C-H stretching
	3.3			
	3.6			$+NH_3$ stretching
		5.6		
			5.7	C=O stretching of oxazolone moiety
		5.8		
	5.9			C=O stretching of aryl carbanilate
	6.0	6.0		
			6.1	C=O stretching of carbanilide group
			6.35	2-arylbenzoxazole
		6.45		carbanilide linkage
		6.65		carbanilide linkage
			6.9	aromatic ring skeletal vibration
		7.2		possible isocyanurate
	7.5			
	7.8			
		8.05		oxazolone moiety, 2-arylbenzoxazole
8.2	8.2			
	9.1			oxazolone moiety
9.2				aryl carbanilate possible
	9.65			2-arylbenzoxazole
	9.95			oxazolone moiety, 2-arylbenzoxazole
10.45				2-arylbenzoxazole
11.0				carbanilide linkage

TABLE XXIII (CONTINUED)

Absorption Strength at Wavelengths (μ)				Assignment
Weak	Medium	Strong	Very Strong	
	9.65			2-arylbenzoxazole
	9.95			oxazolone moiety, 2-arylbenzoxazole
10.45				2-arylbenzoxazole
11.0				carbanilide linkage
	11.6			polymerized carbodiimide
12.0				
	12.05			
12.2				
12.4				
12.6				
	13.1			
		13.2		
			13.5	oxazolone moiety, 2-arylbenzoxazole
		13.7		oxazolone moiety
	13.8			
14.1				
	14.3			oxazolone moiety, 2-arylbenzoxazole
14.8				
14.9				
	15.1			carbanilide linkage
15.3				
	15.8			
	16.0			carbanilide linkage

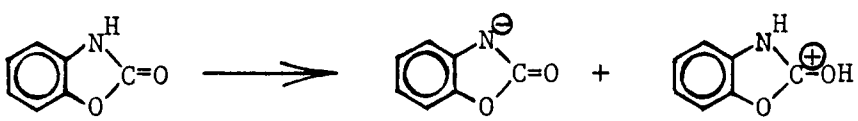
(5.8-5.9μ). Any linkages of polymer-ortho-00 are unlikely, while both of the following moieties are very likely:



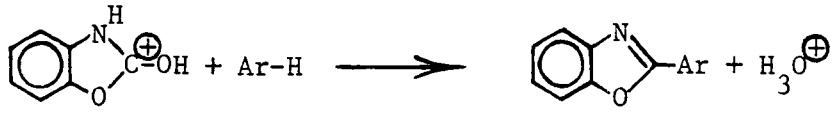


Ring-00 itself is quite volatile, so if the oxazolone ring is present the fused benzene ring must be substituted.

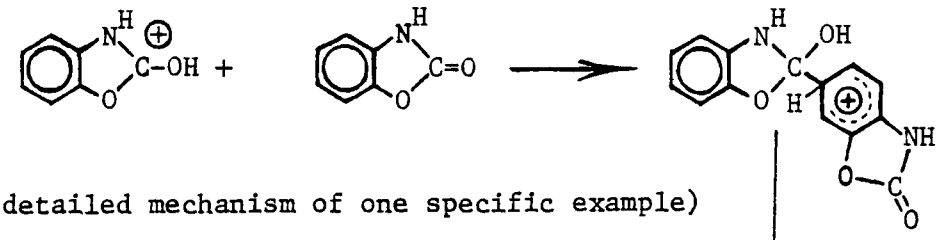
Without invoking highly transient intermediates arising from the loss of CO or CO_2 from ring-00 (discussed later), more conventional mechanisms leading to familiar structures can explain the likely products. A crucial mechanistic proposal is the autoionization of ring-00:



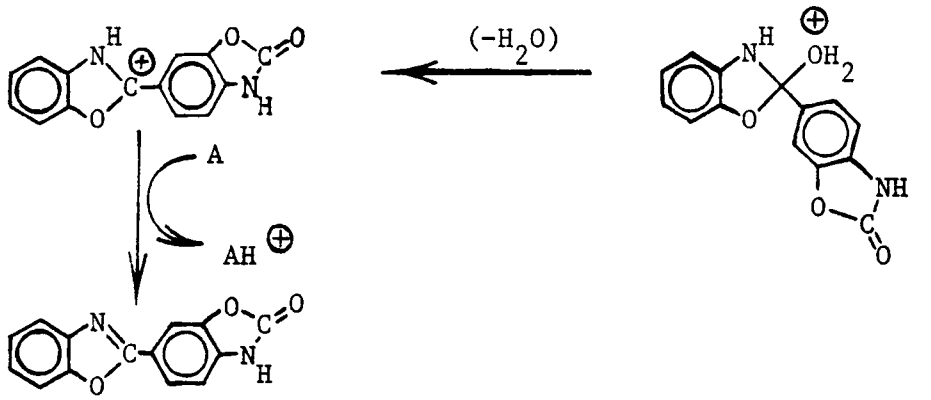
The basicity of the compound is well known (223) and the carbonyl group is a well known proton-acceptor, so the proposal of at least a small degree of autoionization seems reasonable, especially above 250°. The cation can then attack the benzene ring of ring-00 to give 2-arylbenzoxazoles (well known compounds for which several model spectra are available):



(overall result)

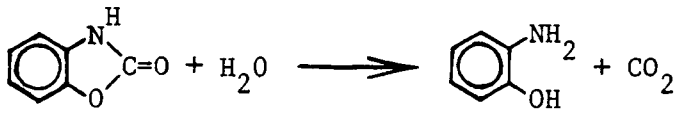


(detailed mechanism of one specific example)

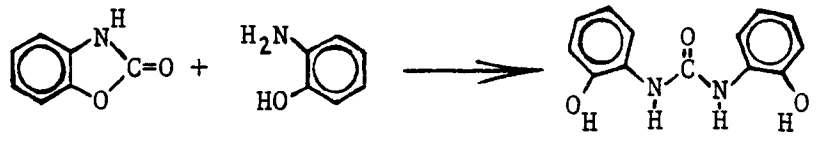


(substitution para to the O atom is also likely)

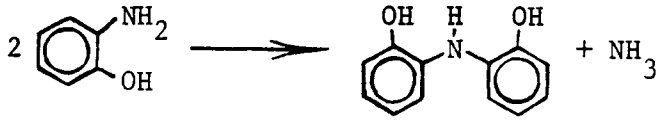
The above process would give a molecule of water as byproduct, which at high temperatures (>250°) would immediately cause the hydrolysis of a ring-00 molecule:



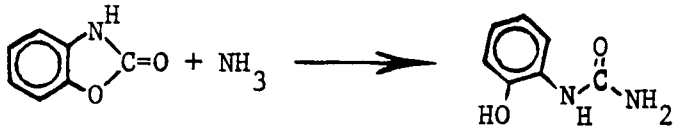
Like other anilines, the resulting o-hydroxyaniline would then react with a molecule of ring-00 to give a carbanilide derivative (223).



Two o-hydroxyaniline molecules could also react to form a diarylamine (another well-known reaction)(318, p. 773):

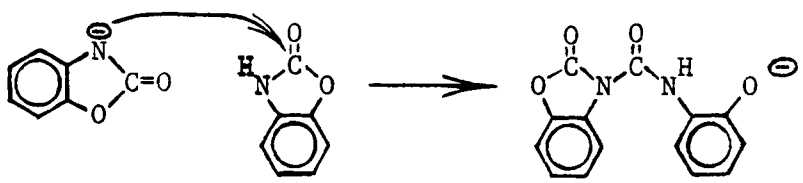


The ammonia would likely attack ring-00 to give a substituted urea:



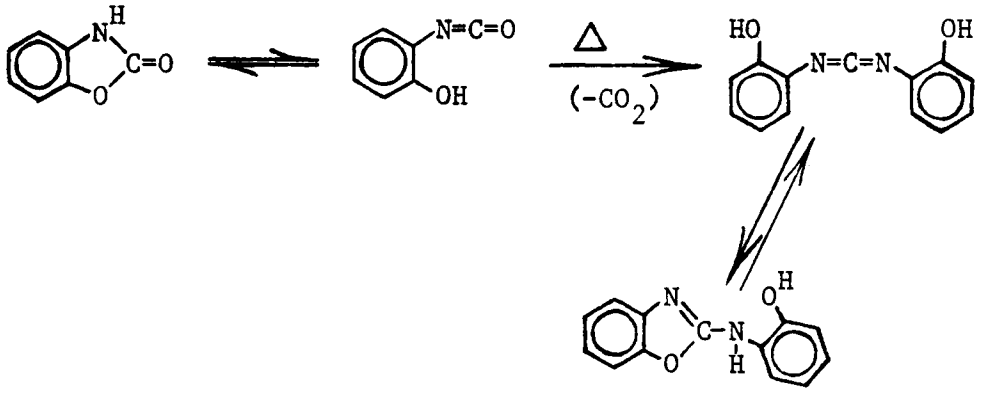
The above products are more likely to undergo attack by the protonated ring-00 than is ring-00 itself, because NH_2 or OH groups are more activating than amide or ester groups.

As for the anion of ring-00, there seems to be no driving force for it to attack an aromatic ring to give nucleophilic substitution. However it might conceivably attack the carbonyl carbon of ring-00 to give an allophanate derivative via a tetrahedral intermediate.



The dimeric arylate anion might then attack another molecule of ring-00 to give a linkage of polymer–ortho-00.

Another mechanism which leads to the formation of a 2-substituted benzoxazole as well as a pendant hydroxyl group proceeds via the condensation of two isocyanate groups to give an intermediate carbodiimide (discussed later in further detail).



This sequence of reactions is a variant of the classical pseudourea formation. The equilibrium steps should be quite reversible at elevated temperatures.

The spectra of several model compounds are available for each of the linkages postulated above, most useful being 2-arylbenzoxazoles and carbanilides (cf. Aldrich and Sadtler collections).

The spectra of the residues IV-1 and IV-2 appear to be compatible mainly with the carbanilide linkage (193, p. 950B; 319; 320; 321). Some intact oxazolone ring is very likely to be present (5.7μ, 8μ, and 13.2μ), as well as

2-arylbenzoxazole (193, p. 1111A; 322)(6.2-6.3μ, 9.5-9.6μ). The possible existence of a small amount of polymer-ortho-OO linkages is shown by absorptions at 8.15μ, 8.3μ, and 8.6μ (typical of phenyl carbanilates), though this claim is much more tenuous than the others. Certainly there is no substantial amount of open-chain carbamate linkages.

A sufficient amount of residue IV-2 was accumulated to give a near infrared spectrum, of which the measurable maxima are given in Table XXIV. The near infrared spectrum supports the midrange infrared assignments. In particular the phenolic hydroxyl peak stands out clearly at 1410 nm, although it cannot be distinguished from the NH stretching peak in the midrange infrared. Because of the substantial presence of this hydroxyl group, the initial loss of CO_2 from ring-OO is ruled out as a significant polymerization pathway (discussed later). The presence of the oxazolone moiety is indicated by absorptions at 2530-2550 nm, 2400 nm, 2297-2310 nm, 2170-2190 nm, and 1700-1750 nm. The presence of the carbanilide structure is shown by absorptions at 2455 nm and 2276 nm. Phenolic groups are apparent at 2040 nm and 1410 nm. Other absorptions have contributions from two or more structures.

An elemental analysis of residue IV-2 (pooled products) was made. The average of duplicate analyses is reported in Table XXV, as well as the calculated analyses of the three

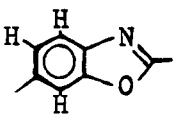
TABLE XXIV

NEAR INFRARED ABSORPTIONS OF RESIDUE IV-2

Maximum (nm)	Relative Intensity	Probable Assignment
2550	11.0	characteristic of ring-00
2540	10.7	characteristic of ring-00
2530	10.7	characteristic of ring-00
2455	8.0	2nd overtone 6.9μ (phenols and carbanilides)
2400	10.0	2nd overtone 6.75μ (ring-00)
2310	8.0	characteristic of ring 00
2297	8.7	ring-00 combination (2xC=O + 1010 cm^{-1})
2276	9.3	carbanilide combination (2xC=O + amide III)
2190	4.0	ring-00 combination (2xC=O + 1150 cm^{-1})
2180	4.0	ring-00 combination (2xC=O + 1150 cm^{-1})
2170	4.0	ring-00 combination (2xC=O + Amide III)
2145	6.0	aromatic C-H combination
2040	2.0	phenol combination (3400 cm^{-1} + 1600 cm^{-1})
2030	2.0	carbanilide 2nd overtone C=O
1990	0.7	ring-00 2nd overtone C=O
1750	0.7	ring-00 1st overtone aromatic C-H
1730	1.3	ring-00 1st overtone aromatic C-H
1700	1.9	ring-00 1st overtone aromatic C-H
1690	2.0	aryl rings 1st overtone aromatic C-H
1675	3.2	aryl rings 1st overtone aromatic C-H
1663	3.1	aryl rings 1st overtone aromatic C-H
1495	0.7	carbanilide 1st overtone N-H
1410	1.3	1st overtone phenolic O-H

TABLE XXV

ELEMENTAL PERCENTAGE COMPOSITIONS

Compound or Moiety	C	H	N	O[a]
residue IV-2	67.81	4.76	9.23	18.20
ring-00	62.22	3.73	10.37	23.68
urea-00	63.91	4.95	11.47	19.67
	71.79	2.58	11.96	13.67

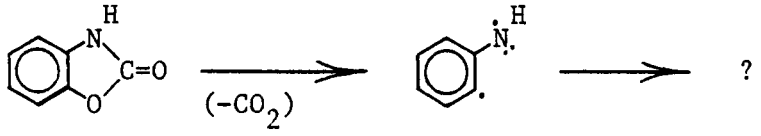
a. By difference; i.e. %O = 100% - (%C + %H + %N)

structures under consideration. Based on these data, it is very unlikely that CO or CO_2 was lost in forming the polymer (increase in C content, decrease in N content). Since the O content markedly decreased, it is more likely that some H_2O was lost, hence the likelihood of 2-arylbenzoxazole linkages. But the bulk of the material seems to have retained the composition of ring-OO, which implies three structures: ring-OO, isocyanurate, and polymer-ortho-OO.

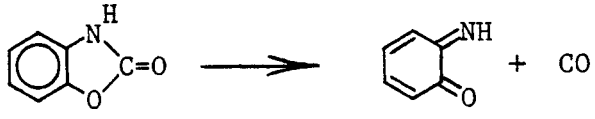
The above sequence of reactions proposed to have formed the nonvolatile residue, could well be self limiting, in the absence of deliberately added Lewis acid. The production of ammonia, arylamine, and diarylamine groups could cause the protonation of the ring-OO carbonyl group to cease, because instead the much more basic amine molecules would be protonated. With present data we cannot even guess the effect of different heating times at constant temperature.

Even though some of the data lead one to believe that it is not the major mechanistic pathway, it is possible that CO or CO_2 may be lost in the initial thermolysis step, especially at temperatures above 350° (the normal boiling point at 1 bar).

If CO_2 were lost in an initial step, an amino radical would probably be formed, but its subsequent fate is open to speculation.



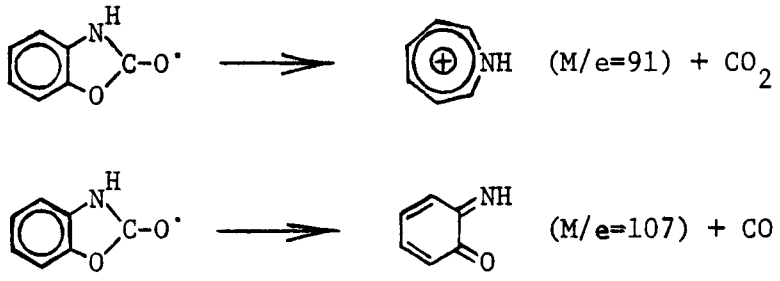
If CO were lost in a cheletropic reaction, the initially formed species would be an orthoquinonemonoimine.



The reactions which such a species could undergo are too numerous to mention here, but are covered well by Finley and Tong (323).

The mass spectrum of ring-00 has doubtful relevance in this connection, but may shed some light on the preferential loss of CO or CO_2 from ring-00. The mass spectra (at 20, 50, and 70 ev) invariably showed a peak at M/e 44, corresponding to $CO_2^{\oplus}$, but the peak at M/e 28 was obscured by background, so one cannot determine whether $CO^{\oplus}$ was produced. Peaks at 135, 107, and 91 were also invariably present, corresponding to P (parent), P-CO, and P-CO_2,

respectively. The peak at 91 (loss of CO_2) was consistently stronger than the one at 107 (loss of CO) by a factor of 35 at 70 eV and 25 at 20 eV.



But the ease of loss of CO_2 from the radical cation of ring-00 may not reflect a corresponding ease of losing CO_2 from the neutral molecule.

The disintegration of ring-00 above 300° to form gaseous small molecules may be chemically significant. The invariable rupture of the silica tubes above 300° is puzzling. The type of tube prepared is capable of withstanding 50 bar of internal pressure (324). The minute fraction of ring-00 converted to polymer is not sufficient to account for the tremendous internal pressure of 50 bar (considering vapor pressures of ring-00, H_2O, NH_3, and CO_2 combined). The yields of polymer (that is, residues IV-1 and IV-2) would not likely be above 10% on extrapolation to 300°. Therefore 300° probably represents the onset of a completely new process of degradation. A large fraction of the ring-00 starting material would have to be converted

to small gaseous molecules to provide enough pressure to rupture the silica tube. Though the evolution of CO or CO_2 is not an important process below 300°, it might be important above 300°.

The residue IV-2 was obtained in sufficient quantity to characterize in a few other ways. An X-ray diffraction pattern obtained from the pelletized powder of residue IV-2 showed the material to be completely amorphous (experimental procedure discussed in Chapter VII).

Two molecular weights were obtained by an isopiestic method (the technique of using droplets in a capillary tube is discussed in the experimental section). A sample obtained at 260°-265° showed a number-average MW (M_n) of 515, while a sample obtained at 290°-295° had an M_n of 585. The standard deviation in both cases was about 40, for five determinations. These averages correspond roughly to tetramer and pentamer, so the MW is too low for the subject of "linear-vs.-branched" polymers to have any significance. These materials are polymers by the criterion of nonvolatility, but not by any other criterion. The conclusion of Hall and Schneider (141) regarding the nonpolymerizability of ring-00 is substantiated to a certain extent.

Unfortunately TGA equipment was not available for analyzing residue IV-1, though one sample of residue IV-2

was analyzed by TGA. With a nitrogen atmosphere and a scanning rate of 10°/min, 10% volatilized at 263°, 25% at 310°, and 50% at 380°. At 500°, 30% of the original weight remained. Two steep portions of the curve could be discerned, the first with an inflection point at 32% and 330°, the second with an inflection point at 64% and 460°. Such TGA data will henceforth be reported in a table, like Table XXVI. The thermal stability of residue IV-2 compared very favorably with the other polymers of this study, but unlike the others, this TGA scan was not as amenable to mechanistic interpretation. A more explicit tabular comparison of the above data with that of the other polymers will be made in the last chapter.

The corresponding TGA scan of ring-00 was obtained in both nitrogen and air (Table XXVII). These data show the high volatility of ring-00. The TGA curves for the different atmospheres were nearly superimposable.

3. Preparation and Characterization of Residue IV-3

Another method of heating ring-00 was devised to circumvent the pressure buildup. The ring was dissolved in refluxing paraffin, heated by a bath of molten solder (Sn-Pb/50-50), the temperature rising gradually over a 5-day period from 260° to 370° (as the lower paraffin fractions

TABLE XXVI

THERMOGRAVIMETRIC ANALYSES OF RESIDUE IV-2 UNDER NITROGEN

Temp at wt loss[a]			Residue (%)	1st Inflection		2nd Inflection	
10%	25%	50%	at 500°	% Vol[b]	Temp	% Vol[b]	Temp
263	310	380	30	32	330	64	460

a. Abbreviation for "Temperature at weight loss."

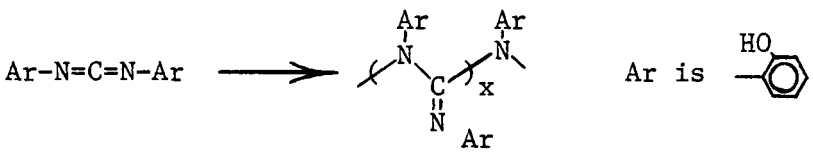
b. Abbreviation for "Percent volatilized."

TABLE XXVII

THERMOGRAVIMETRIC ANALYSES OF RING-00

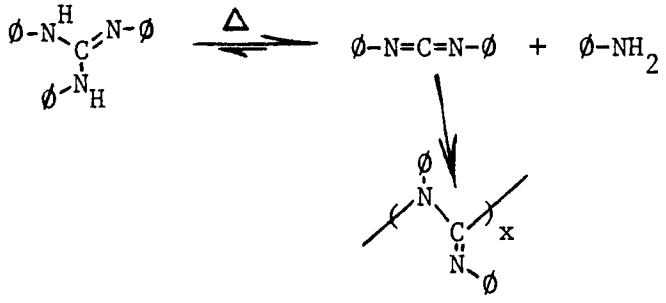
Atmosphere	Temp at wt loss			Residue (%)	Inflection	
	10%	25%	50%	at 500°	% Vol	Temp
Nitrogen	180	200	215	2	90	230
Air	185	205	220	2	90	235

were removed). The nonvolatile product was obtained in 16% yield, and designated residue IV-3. It was black and insoluble in THF. It appeared to consist of the polymerized carbodiimide, a substance which contains N-aryl guanidine moieties, as illustrated below (the aryl group is o-hydroxyphenyl).

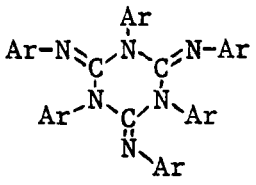


The diarylcarbodiimide would arise via the hydroxyisocyanate with loss of CO_2, as shown on p. 182. Although the formation of polymerized carbodiimide would entail the evolution of CO_2 (the CO_2 being lost subsequent to ring-opening and a cycloaddition reaction) this process still might not account for the buildup of high pressure above 300°, since still other processes might occur to give only gaseous products. The intramolecular pseudourea formation is expected to be more

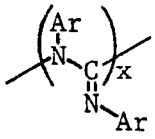
reversible than the addition polymerization of the carbodiimide. The infrared spectrum of the product, residue IV-3, was almost identical to that of polymerized diphenylcarbodiimide, a similarity which strongly suggested the structure. The main difference was a band at 8.1-8.2μ in the spectrum of residue IV-3, due to phenolic hydroxyl. The sample of polymerized diphenylcarbodiimide was obtained from triphenylguanidine at 370° in refluxing paraffin, as described in the experimental section.



In residue IV-3, there is a question about whether some pendant hydroxyl groups would ionize to phenolate ions, given the close proximity of the strongly basic guanidine moieties. In this case the phenolic groups do not appear to be appreciably ionized, as the strong C-O stretching peak is closer to 8.2μ than to 7.9μ. The guanidinium ion is probably not formed to a significant extent. Because of the weakness of the 5.9μ peak in the product, the cyclic carbodiimide trimer appears to be in much lower concentration than the linear polymer (230, p. 262).



cyclic trimer



linear polymer

Subjecting triphenylguanidine to this refluxing paraffin treatment at 370° gave an intractable black material whose midrange infrared spectrum had a few broad peaks: 2.8-3.4μ, 6.8-7.4μ, 11.5-11.7μ, 13.3-13.8μ, and 15.0-15.2μ. The rest of the spectrum consisted of steps rather than peaks, though the positions of these steps were quite characteristic and reproducible for the purpose of matching spectra. For products subjected to temperatures above 300°, as much attention was paid to steps as to peaks.

It is therefore necessary to devise a system for reporting such steps (or shoulders) in the midrange infrared spectra, which seems to have little precedent. A single absorption of this type is conventionally reported as a shoulder, though the spectra of the very high temperature thermolysis products consist of a long series of "shoulders." A step is approximated by the intersection of a horizontal line and a sloping line, and only a vertes which is convex toward increasing absorption is herein reported as a step.

For the sample of polymerized diphenylcarbodiimide prepared from triphenylguanidine, steps are reported for absorptions increasing or decreasing with increasing wavelength. Because of the larger number of short steps, it would be highly impractical to adapt this "step function" to tabular form, as in Table XXIII. The decreasing steps are the following: 3.55μ, 3.85μ, 7.35μ, 7.65μ, 8.1μ, 8.5μ, 9.2μ, 9.4μ, 9.7μ, 10.05μ, 10.4μ, 10.75μ. There are five increasing steps: 5.85μ, 5.95μ, 6.1μ, 6.2μ, 6.75μ.

For the thermolysis residue of ring-00 obtained at 370°, broad peaks occurred at the following positions: 2.8-3.1μ, 6.2μ, 6.85-7.35μ, 8.1-8.2μ, 11.6μ, 12.5-12.9μ, 13.4-13.8μ, 15.0-15.2μ. The decreasing steps are the following: 3.55μ, 3.85μ, 7.8μ, 8.75μ, 9.2μ, 9.35μ, 9.8μ, 10.1μ, 10.4μ, 10.8μ, 14.3μ. There are four increasing steps: 5.9μ, 6.1μ, 6.4μ, 6.7μ.

The spectra of the residues of thermolysis at 370° from triphenylguanidine and from ring-00 are very similar. The differences may be ascribed to the pendant phenolic hydroxyl groups in the latter, which give absorptions around 8.1μ and 14.3μ.

C. POLYMER DERIVED FROM ORTHO-HYDROXYPHENYL ISOCYANATE BY THE CURTIUS REACTION

1. Preparation and Characterization of Residue IV-4.

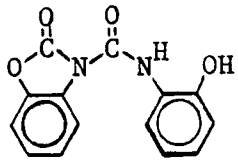
Another attempt to make polymer ortho-00 used the Curtius reaction. The meta and para analogs, polymer meta-00 and polymer-para-00, have been made by this route (127), but the Curtius reaction of salicyl hydrazide has been reported to give only ring-00 (127, 129). Because an unexpected byproduct might have been polymeric, this Curtius reaction was repeated as described in the author's M.S. thesis (317, p. 46-48). A very low yield of nonvolatile product was obtained (less than 100 mg from 12.5 g salicylhydrazide), which did have some interesting absorptions, shown in Table XXVIII. The carbonyl absorption is much closer to that of phenyl carbanilate than to that of ring-00, which would suggest the presence of polymer-ortho-00 (the diarylurea and triarylisocyanurate are ruled out by the absence of characteristic absorptions). However the amide III band seems to be misplaced, as well as the Ar-N and Ar-0 stretching peaks. The structure of this product remains unclear, although the presence of polymer-ortho-00 is more likely in this sample than in the thermal polymerization samples. Possibly some type of allophanate could be the major product. The

TABLE XXVIII

INFRARED ABSORPTIONS OF RESIDUE IV-4

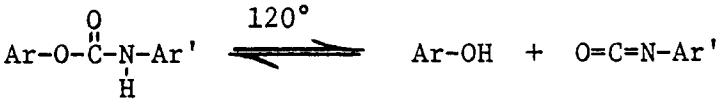
Absorption (μ)	Intensity	Proposed Assignment
3.0-3.25	s	stretching bands of N-H, O-H, C-H
5.8	s	C=O stretching (allophanate?)
6.25	m	aromatic ring skeletal vibration
6.85	m	aromatic ring skeletal vibration
7.7-7.9	s	
8.8-8.95	m	
9.3	m	
13.5	s	oxazolone moiety

simplest such allophanate,

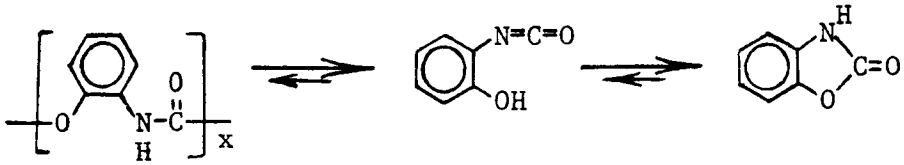


would be very difficult to synthesize in pure form, because of its expected thermal lability, and its infrared spectrum is difficult to predict from model compound spectra.

It may be highly relevant that the workup of the Curtius product never involved temperatures higher than 80°, so that the kinetic product may have been obtained rather than the thermodynamic product. Even if a pure sample of polymer-ortho-00 could be made, it is unlikely that it could remain as such at temperatures higher than 120°. This corresponds to the splitting temperature of aryl carbanilates (39, 81, 85, 325):



The equilibrium product is thus expected near 120°, which means the highly stable ring-00 (the driving force is the formation of the strain-free ring):



D. EXPERIMENTAL DETAILS

For heating at temperatures above 250° an oil bath could not be used, due to excessive smoking and flashing. Molten salt baths of potassium bisulfate or sodium acetate-potassium acetate eutectic were tried, but the glass or quartz tubes frequently exploded, breaking the hot bath containers and causing incredible messes. Baths of mercury or Wood's metal were convenient but highly toxic. Reliably constant and homogeneous baths were attained with molten solder (50% Pb-50%Sn by weight), whose use became routine in this study. The solder was confined in a heavy iron crucible, insulated with asbestos sheet and ribbon, and shielded with asbestos sheet.

White paraffin wax was used as an inert solvent (or dispersing medium) up to 370°. The refluxing paraffin quickly dissolved or suspended all organic materials. Its use minimized air oxidation, allowed homogeneous heating of the thermolyzed material, and prevented the loss of most organic solids by sublimation.

The mass spectra of ring-00, and of all other rings and models in this work, were made with a Hitachi Perkin-Elmer RMU 6E Mass Spectrometer. Solid samples were volatilized at 200° inside the instrument by radiative heating from a hot copper block. The sample vapor was bombarded with electrons at energies of 20, 50, and 70 eV. In addition, a sample of perfluoroalkane was bombarded at 70 eV to obtain

with electrons at energies of 20, 50, and 70 eV. In addition, a sample of perfluoroalkane was bombarded at 70 eV to obtain mass markers, and a background spectrum was also obtained. Thus a total of five film strips were obtained for each sample submitted, and each film strip gave a spectrum at three different attenuations. Unfortunately every background scan showed a very strong peak at an M/e value of 28, corresponding to the cation of carbon monoxide, so the loss of CO from ring-OO cannot be demonstrated by a peak at this M/e value.

The molecular weights of various polymeric samples of this study were determined by the isopiestic method of Barger (326). This and similar techniques have been studied more recently by Parrette (327) and by Pals and Staverman (328). In principle, this technique is a kind of membrane osmometry, in which the membrane is a vapor space permeable only to solvent molecules. The technique has been lucidly described in exhaustive detail in Barger's paper (326), to which the reader is referred.

The Barger method requires capillary tubes of small uniform internal diameter. The glass capillary tubes (0.7 mm ID, 1.0 mm OD) were obtained from Sargent Welch Scientific Co. The chief difficulty of this technique was filling the capillaries with minute drops of the right size and spacing.

For this purpose a capillary tube of 50 cm length was fitted inside the tip of a Pasteur disposable pipette (Fisher Scientific Company), and the concentric tubes joined with epoxy sealant (easypoxy repair kit, Conap, Inc.). This arrangement made it possible (but not easy) to control the drop size and spacing with finger pressure. The tubes were filled with at least 7 drops of alternating solutions, according to Barger's recommendation (326). For preliminary trials, a Bausch and Lomb 7X magnifier with superimposed measuring scale (graduated in 0.1 mm, readable to nearest 0.05 mm) was used. The equivalence of osmolarities could be determined with this magnifier, but only with considerable eyestrain. The reflecting microscope of a Tukon hardness tester (Wilson Mechanical Instruments Co., New York, N.Y.) was found much more satisfactory. This device used a Bausch and Lomb optical system, with a 10X objective and 12.5X Ramsden eyepiece with a Filar micrometer. This micrometer was ruled at intervals of 1.0 mm, and one revolution of the micrometer drum was equivalent to 1 mm. Estimates could be made to 0.001 mm (1μ), or 1 Filar unit. On calibration, a Filar unit equalled 1.06μ in this instrument.

Azobenzene (MW 182.23) was used as the osmometry standard, stock solutions of various concentrations (from 0.0002

to 0.1 mole/l) being made up. Pure tetrahydrofuran was not used as solvent, but rather a mixed solvent made by adding 5 ml water to 100 ml commercial tetrahydrofuran (Fisher certified grade) at 30°, a solvent herein called "hydrous tetrahydrofuran." The desirability of adding a fixed amount of water to an organic solvent is due to the well-known hygroscopicity of tetrahydrofuran (329, p. 704) and of the PU's (24, 330). A large amount (2 gal) of this solvent was made up at the same time, to insure homogeneity of solvent among all samples (a peroxide inhibitor is added to the commercial solvent). In this molecular weight method, the use of mixed solvents is permissible, unlike the stringent requirements for obtaining reliable data from VPO instruments.

The procedure is simple but time-consuming. At least a dozen capillary tubes must be made, each with different concentrations of standard or unknown, for each MW determination. Either the concentration of unknown (in grams/l) or of standard (in moles/l) may be varied. A difference in concentrations of 0.0003 mole/l appears to be detectable. The repeatability of successive determinations is troublesome, as the values may range widely, so a standard deviation (SD) of several determinations should be reported, along with the number of determinations (N).

$$SD = \sqrt{\sum_{i=1}^{N}(x_i - \bar{x})^2/(N-1)} \qquad \bar{x} = \sum_{i=1}^{N} x_i/N$$

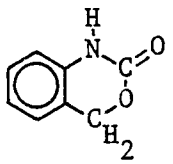
An obvious drawback of this method, in its simplest form, is that it makes no provision for "extrapolation to zero concentration" to correct for variations in activity coefficients. However, this isopiestic method is not recommended for high polymers (327, 328), and it has been found suitable for oligomers or low polymers, for which few other methods are available. A check was made with tristearin (MW 891.45), for which a molecular weight of 820 (SD 110) was found. For another polymer of greater inherent importance, and with sufficient solubility, a further check with the Rast camphor method (331, p. 36) would be desirable. However, more PU's are soluble in THF than are soluble in camphor, so the Rast camphor method cannot be used routinely, as simple and time-tested as it is.

CHAPTER V

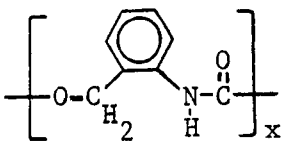
THE SYSTEM-ORTHO-10

A. GENERAL CONSIDERATIONS

The systematic name of ring-10 is 1,4-dihydro-2H-3,1-benzoxazin-2-one and of polymer-ortho-10 is poly(oxycarbonylimino-o-phenylenemethylene) or poly(oxycarbonylimino-1,2-phenylenemethylene).



ring-10



polymer-ortho-10

The cyclic carbamate, ring-10, has been made by several routes, most being esoteric and impractical (135, 219, 221, 264, 332, 333). Four of these routes are discussed in the M.S. thesis; two were actually used (317). One of the latter routes (220), using the reagent trichloroacetyl chloride to provide the carbonyl moiety, was discussed in minute detail (317, p. 53-57). The only really practical preparation known to this author is the Curtius reaction route of Lindemann and Schultheis (128), for which the sequence of steps beginning with phthalide was described thoroughly in the M.S. thesis.

Polymer-ortho-10 had not been reported prior to the work of this author. Its preparation was attempted via the thermal ring-opening of ring-10 and via the Curtius reaction. The polymers formed were characterized in detail, including reassignment of many infrared peaks.

B. THERMAL POLYMERIZATIONS OF RING-10 AND CHARACTERIZATION OF THE POLYMERS

Several methods were utilized to effect the thermal ring-opening polymerization of ring-10. For those methods which confined the ring in an evacuated closed tube, heat was applied by one of three ways: using a vacuum oven, a tube furnace, or an oil bath. The evacuated closed tube, called the "PZN tube", is described in the M.S. thesis (317, p. 43). Heating by oil bath was clearly superior to heating by the tube furnace or by vacuum oven (because of temperature gradients in the latter two methods), but in retrospect the method could have been much improved by using a molten metal bath (solder, Wood's metal, or mercury), mainly because molten metals are much less prone to seep through ground glass joints than is hot oil (molten metals are more viscous than oil and have a lower interfacial tension with glass -- both of which oppose the capillary effect). Moreover the heated oil presented a charring, volatilization, and polymerization problem -- besides the typical fire hazard (flashing occurred several times).

The procedures of using the evacuated closed tube and the workup of the products are described in the M.S. thesis (317, p. 64), including the removal of oil that had seeped into the tube by trituration with boiling heptane. The results of these bulk polymerizations were described in the M.S. thesis (317, p. 65-73), and are summarized here in Table XXIX.

The midrange infrared spectra of the polymeric products merit detailed discussion. As the polymerization temperature increased beyond 170°, the soluble fraction showed an absorption at 6.0μ which increased relative to that at 5.8μ. This 6.0μ absorption is undoubtedly due to the urea (or carbanilide) linkage. Above 190° no soluble fraction was formed at all, the insoluble polymer yield was above 60% (by weight), and the IR spectrum of the crosslinked polymer was quite different from that of the ring. Most conspicuously the carbamate linkages were completely absent (no peaks at 5.8μ or 9.4μ).

All the crosslinked polymers formed between 190° and 220° are very hard and very difficult to grind into a powder. Consequently the KBr or KI pellets give poor IR spectra; though a prominent band is apparent at about 6μ, the peaks are generally low broad humps due to severe scattering. At low polymer concentrations the pellet becomes opaque. The spectrum is obviously superimposed on a typical scattering curve ($I \propto 1/\lambda^4$), where the baseline shows a high absorbance at lower wavelengths.

TABLE XXIX

POLYMERS FROM HEATING RING-10 IN BULK

Temperature (°C)	Yield (%)[a]		Predominate Linkages			
	Soluble	Insoluble	Carbamate	Urea	Isocyanurate	Diarylmethane
154	5	0	√			
160-165	7		√			
		5	little	√	√	
165-170	8		√			
		11	little	√	√	
176-185	10		little	√	√	
		40		√	√	√
193-198	0					
		60		√	√	√
207-211	0					
		81			√	√
216[b]	0					
		83			√	√

a. Yield is percent nonvolatile based on initial weight.

b. This sample was heated 48 hr in tube furnace, all others were heated in oil bath.

Increasing presence of the IR peak at 6.0μ correlates well with increasing crosslinking, a fact to be discussed later.

The characteristic or diagnostic peaks of various by-products should be mentioned. The urea linkage has characteristic peaks at 6.0μ, 6.9μ, 7.6μ, and 8.1μ. The triphenylisocyanurate group shows strong absorptions at 5.9μ, 6.7μ, and 7.1μ. Diarylmethane structures have characteristic absorptions at 8.4-8.5μ and at 9.6-9.7μ. In particular, methylenedianiline derivatives give diagnostic peaks at 6.15μ, 6.9μ, 7.25μ, and 7.7-7.9μ.

Another method for effecting thermal ring-opening polymerization of ring-10 is to dissolve the ring in a refluxing high-boiling solvent. The escape of the volatile ring is thereby minimized, and oxidation or hydrolysis does not occur to any greater extent than when oil-bath immersion is used. Typically, 1 g of ring is mixed with 30 ml of "inert" solvent with bp above 130°. The mixture is quickly heated to reflux, and refluxing is continued for 1 week. The effects of varying time of reflux or concentration of ring have not yet been studied, as the primary objective was to try a wide range of solvents.

Obviously no solvent should be used which might degrade the carbamate linkage, or which might react with either the isocyanate or hydroxyl groups in the intermediate. Not so

apparent is the need to avoid halogenated aliphatic solvents, as these cause extensive haloalkylation of the polymer. Several common solvents with benzylic hydrogens were used, and in some cases these also gave alkylation to a small extent. Since temperatures exceeding 130° and reflux times of 1 week were used, otherwise inert solvents might react with the ring, its polymer, or any of their degradation products.

In the workup of the polymer product, the solvent was stripped off by vacuum distillation. All remaining solvent was removed in a vacuum oven. The residue was then subjected to sublimation at 120° and 0.1 mm for 48 hr. The resulting nonvolatile residue was considered polymeric. The results of using the various solvents are given in Table XXX.

An apparent difference between the polymers made in the closed tube and those made in the refluxing solvents is the greater amount of soluble fraction in the latter at almost all temperatures. We may assume that the refluxing solvent approach might favor the formation of linear or branched polymers over crosslinked or gelled polymers, due to a dilution effect by the solvent.

As in the case of those samples of polymer-ortho-10 prepared by the oil-bath immersion technique, the samples prepared in the refluxing solvents showed midrange infrared spectra very similar to those of ring-10. In fact, the polymer

TABLE XXX

POLYMERS FROM HEATING RING-10 IN REFLUXING SOLVENTS

Solvent	Bp	Yield (%)[a]		Linkages in Soluble Fraction[b]				
		Sol	Insol	Solvent	PU	Isocyanurate	Urea	Diarylmethane
C_6H_5Cl	132	10	-		√	little		
C_6H_5Et	136	32	-	√	√	little	√	
$(n\text{-}Bu)_2O$	142	21	-		√	√	√	√
o-xylene	144	40	-		√	√		√
$Cl_2CHCHCl_2$	146	91	25	√	√	√		√
cumene	152	150	-	√	√	little		
anisole	154	10	-		√	√	√	
cyclohexanone	156	95	-	√	√	√		
C_6H_5Br	156	63	-		√	√		
$(n\text{-}Pr)_3N$	156	72	10		little		√	√
mesitylene	164	43	-		√	√	√	√
phenetole	170	63	-		√	√	√	√
m-dichlorobenzene	173	82	-		√	√	√	√
s-butylbenzene	173	78	-	√	√	√	√	√
p-cymene	177	70	-	√	√	√		

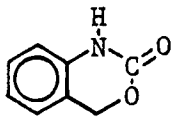
TABLE XXX (Continued)

Solvent	Bp	Yield (%)[a]		Linkages in Soluble Fraction[b]				
		Sol	Insol	Solvent	PU	Isocyanurate	Urea	Diarylmethane
tetramethylurea	177	45	8		little	√	√	√
o-dichlorobenzene	181	72	-		√	√	√	√
n-butylbenzene	183	95	-	√	√	√	√	√
pentyl ether	187	88	-		√	√	√	√
durene	190	93	-		little	√	√	√
dimethylaniline	193	123	-	√	none	√	little	√
veratrole	206	76	-	√	none	√	√	√
tetralin	207	89	-	√	none	√	√	√
tributylamine	216	84	-		none	√	√	√
quinoline	237	82	-		none	√		√

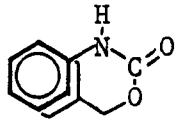
a. Yield is percent nonvolatile based on initial weight.

b. Solvent designation signifies chemical incorporation of solvent into product.

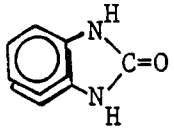
spectra resembled the ring much more closely than they resembled the model compound, O-benzyl carbanilate. The most prominent difference between the spectra of the polymer and of the model compound is the absence of the amide II band at 6.5μ in the spectrum of the polymer, an absorption expected due to a presumed trans configuration between the carbonyl group and the N-H group. These groups are probably cis in the polymer as well as in the ring, because successive aromatic rings along the polymer chain are very likely stacked above one another (like pancakes). Even those polymer samples containing substantial amounts of urea show little absorption at 6.5μ, suggesting a similar stacking of successive aromatic rings.



ring-10



likely stacking
in PU segments



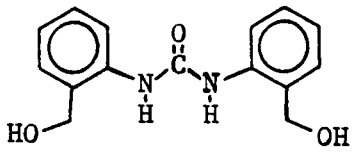
likely stacking
in urea segments

Such stacking arrangements are not easily amenable to X-ray analyses, because the solids are entirely amorphous (according to wide angle X-ray diffractions of powdered samples).

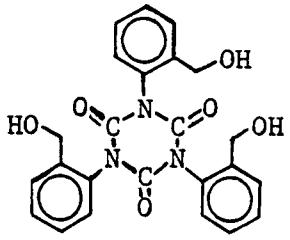
The near infrared spectra were more useful in detecting non-carbamate structures, and shed little light on the carbamate linkages.

It should be noted that each urea molecule arising from

the monomer will have two pendant benzyl alcohol groups, while each isocyanurate molecule will have three such groups:

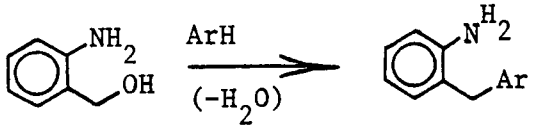


urea moiety



isocyanurate moiety

These hydroxymethyl groups are activated by the ortho nitrogen, and should condense with suitable aromatic rings to form diarylmethanes. Any o-aminobenzyl alcohol arising from the monomer by hydrolysis should very easily form such diarylmethanes, or methylenedianilines, in a well-known reaction (334, p. 496). In this study o-aminobenzyl alcohol was heated for two days in refluxing decalin to provide reference spectra in the midrange and near infrared.



The formation of diarylmethanes from urea groups in this system is probably the reason that a good correlation exists between the intensity of the absorption at 6.0μ and the amount of crosslinked product in the closed-tube polymerizations.

It is easy to rationalize the inclusion of such solvent molecules as veratrole and dimethylaniline in the polymer product, as such activated benzene rings could easily be attacked by the benzyl alcohol groups. More difficult to rationalize is the inclusion of alkyl benzene solvents such as cumene, cymene, ethylbenzene, tetralin, and the butylbenzenes. A common feature of these solvents is the presence of a secondary or tertiary benzylic hydrogen, which would give rise to benzyl alcohol groups by oxidation during prolonged refluxing, or could undergo other free radical abstraction-coupling reactions.

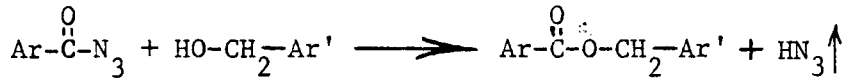
The formation of diarylmethane linkages would of course require the production of water. This was examined by using decalin (commercial cis-trans mixture, bp 192°) as the refluxing solvent (50 ml were used with 5 g of ring-10) with a Dean-Stark trap below the reflux condenser. In the usual reflux apparatus, small water droplets collected on the condenser bore above the ring of solvent condensation. On occasion violent bumping would be caused by a water drop falling into the boiling solvent. Because of the volatility of the ring, a Dean-Stark trap was not used routinely to remove water from the system.

C. POLYMER-ORTHO-10 FROM THE CURTIUS REACTION AND FURTHER CHARACTERIZATIONS OF POLYMERS

As mentioned in the M.S. thesis (317, p. 73-75), the Curtius reaction that produces ring-10 also gives a PU by-product, in rather low yield and questionable purity. Because of the cheapness and availability of the starting material phthalide, this Curtius reaction was studied in more detail than any of the other Curtius reactions.

Various modifications of the Curtius procedure were tried, such as extracting the azide into various solvents or adding different solvents to the benzene extract prior to refluxing. When the azide was heated in a 1:1 mixture of ether and benzene (with all the ether being lost within 30 min, nearly pure PU was formed, but in 0.8% yield. Heating the azide in a high-boiling solvent like bis(ethoxyethyl)ether or dimethylformamide resulted in a 12% yield of nonvolatile product, which had almost no carbamate linkages. Instead mostly urea, with some isocyanurate and diarylmethane linkages, was shown by the IR spectrum. Most Curtius products showed some ester absorption at 5.6μ, due to the elimination of hydrazine or hydrazoic acid (discussed in Chapter I) by the hydrazide or azide:

$$Ar-\overset{O}{\overset{\|}{C}}-N_2H_3 + HO-CH_2-Ar' \longrightarrow Ar-\overset{O}{\overset{\|}{C}}-O-CH_2-Ar' + N_2H_4\uparrow$$



Compared to the thermal ring-opening methods, the Curtius reaction is certainly a less feasible way of producing polymer-ortho-10.

Two methods of working up the Curtius product could be used to obtain the polymer. In the first method, all the mother liquors and washing solvents from the workup of the ring are pooled, the solvents stripped off completely, the dry residue subjected to sublimation at 120° and 0.1 mm Hg for 48 hr, and the nonvolatile material recovered. In the second less convenient method, the crude product of the Curtius reaction is stripped of all solvent and subjected to sublimation. The sublimate is worked up to produce ring-10, and the nonvolatile material is recovered. In both workup procedures, the nonvolatile residue is a brittle, dark brown material, amounting to a small fraction of the total yield (less than 6% for the usual conditions). The sublimate is mostly ring-10, with a little phthalide. The nonvolatile residue has the structure of polymer-ortho-10 predominately, as shown by its infrared spectrum, which agrees in large part with the spectrum of samples of polymer-ortho-10 produced by thermal polymerization.

An attempt was made to quantitatively determine the amount of isocyanurate present by infrared spectroscopy.

Since isocyanurate and carbamate are only two of several possible linkages in the polymers, a more realistic effort was directed toward finding the mole ratio of isocyanurate to carbamate. Conceivably, this might be done by using a prominent peak of the isocyanurate, where nothing else absorbs, and a similar peak of the carbamate. One would then form a ratio of the absorbances of these two peaks which appear in the same spectrum. The ratio of the absorbances should bear a monotonic relation with the mole ratio of the linkages present. The monotonic relation, or "calibration curve," should be determined by using known molar ratios of pure model compounds, assuming that the molar absorptivities of the model compounds are the same as those of the corresponding linkages in the polymer. The expected advantage of such a method would be extreme simplicity and convenience, making it routinely useful for a large number of samples. Still, the method was beset by a number of theoretical and practical difficulties. One obvious disadvantage is that it would give only relative values, since no attempt would be made to obtain reproducibility of sample thicknesses or concentrations.

Another problem concerns peak areas vs. peak heights. Since a peak is usually broadened on going from small molecule to macromolecule (for identical numbers of a functional group), peak areas should be employed, the area being:

$$\int (\text{absorbance})\, d(\text{wavenumber})$$

All infrared spectrometers available to this writer (these were many, but the Beckman IR-5A was selected for convenience) were calibrated in a linear transmittance scale, making it much more convenient to use peak heights rather than peak areas.

A related problem is that of baseline. The method of drawing tangents at the basal extremities of the peak can be used if the nearby peaks do not overlap, or if their overlap is proportional to peak height. Because of the highly variable composition of the polymers, this is seldom the case here. About the only minimum absorption that was consistent throughout all the spectra was in the triple bond region (4μ to 5μ), where no peaks were observed. Therefore a horizontal tangent was drawn through the minimum absorption in this region, serving as the baseline for all the peaks between 5.8μ and 9.6μ. This "single point method" is less conventional for the midrange infrared than for the near infrared. The transmittances of the baseline and of the peak maximum were converted to absorbances, and the difference between these two values was considered the height of the peak. The ratio of the heights of two characteristic peaks was used to plot the ordinate of a point on the calibration curve (ratio of peak heights vs. mole

ratio). Even the "single point method" (used as a last resort) fails when the spectrum is obviously superimposed on a scattering curve ($I \propto 1/\lambda^4$) due to an excessively large particle size (characteristic of hard, highly-crosslinked samples). Only a few polymer infrared spectra did not have a perceptible scattering curve.

For the present system-ortho-10, it was decided to use N-phenyl-O-benzyl carbamate as a suitable model for polymer-ortho-10, triphenylisocyanurate as a model for the polymeric isocyanurate linkages, and N,N'-diphenyl urea as a model for the 2,2'-bis(hydroxymethyl)carbanilide. The peak at 9.4μ was fairly strong in the carbamate but absent in the isocyanurate and urea. Both the ring-10 and the model benzyl carbanilate have negligible absorptions at 7.1μ, and the peaks at 5.8μ and 9.4μ have the same ratio, so these two compounds could probably be used interchangeably as models in this system.

The infrared spectrum of triphenylisocyanurate was very different from those of triethylisocyanurate and tribenzylisocyanurate, as far as the intensities of the characteristic isocyanurate peaks were concerned. Obviously the nitrogen substituent was most important in choosing the appropriate model.

Because the ratio of isocyanurate to carbamate peak heights varied from small (0.3) to large (250), this ratio was plotted on the log scale of semilog graph paper with the

mole ratio on the linear scale, and the calibration curve was plotted. Because there was considerable vertical scatter in plotting each point of the calibration curve, only an accuracy of ±11% could be claimed in subsequently determined molar ratios. For polymers made below 170° (having a sufficiently small amount of urea), the amount of isocyanurate varied between 10% and 30%, exclusive of any urea or diarylmethane structures. This was true for those polymers made in a closed tube and for those made in refluxing solvents. A similar range of isocyanurate compositions, or perhaps slightly lower, was found for the polymers made by the Curtius reaction.

The near infrared spectra of the above-mentioned polymers (thermal and Curtius products) should be discussed. To obtain an NIR spectrum, a translucent film of the polymer must be formed, which is not always possible. Only for those polymers obtained in yields greater than 0.3 g was NIR spectroscopy even attempted.

Only one bulk thermal polymerization product (soluble fraction made at 176-185°) was examined by NIR. Seven polymers made in refluxing solvents were examined, including those made in o-oxylene, bromobenzene, cyclohexanone, mesitylene, phenetole, s-butylbenzene, and n-butylbenzene. In general, the overall spectrum of each product bore more resemblance to that of ring-10 than of the open-chain model benzyl carbanilate.

However, the region from 2270 nm to 2410 nm invariably had much more intense absorptions in the polymers than in the ring-10. For one polymer, that made in cyclohexanone, this anomaly could be explained by incorporation of solvent (probably as the enamine). Solvent incorporation could not cause a similar anomalous intensity in the other polymers, because the intensity bore an inverse correlation with the aliphatic content of the solvent. The region from 2270 nm to 2410 nm is usually associated with aliphatic structures, but it is not likely that aromatic rings are lost unless the quinoneimine methide intermediate (arising by a retrograde Diels-Alder reaction) is taken seriously.

On examining various relevant model compounds, the only one which shows strong peaks in the region 2270 nm to 2410 nm is o-aminobenzyl alcohol. These peaks are undoubtedly due to the intramolecularly hydrogen-bonded aminoalcohol system. The combination of the strong midrange infrared peak at 10μ (1000 cm^{-1}) due to C-O stretching with the strong O-H stretching peaks from 2.9μ to 3.2μ would account for the various strong absorptions seen in the near infrared between 2270 nm and 2410 nm. The ortho nitrogen atom provides a suitable electron donor for the intramolecular hydrogen bond which completes a six-membered ring. It is unlikely that any other combination would account for the high intensity of this near infrared region. A carbonyl group bonded to the nitrogen atom might also be an electron

donor for hydrogen bonding with the pendant methylol group. The large width of the O-H stretching band in the midrange infrared is due to hydrogen bonding, which in turn gives rise to the wide range of near infrared frequencies. Intramolecular hydrogen bonding is probably required to account for the high intensity of the near infrared absorptions, as benzyl alcohol itself does not give any peaks of comparable magnitude in that region (2270 nm to 2410 nm).

The typical benzyl alcohol peak at about 1410 nm (first overtone O-H stretching) also appears at rather low intensity (0.1 to 0.5) in all these polymer samples. The corresponding peak in benzyl alcohol itself has an intensity of 2.6. It is tempting to calculate the mole percentage of methylol groups from such figures, but the 1410 nm peak accounts for only the free OH groups (not H-bonded). The hydrogen-bonded OH groups have a first overtone around 1490 nm, which overlaps with the N-H stretching first overtone. We can conclude with certainty only that the pendant methylol groups are present. The nitrogen atoms are undoubtedly tied up in the various amide forms (carbamate, isocyanurate, or urea) as the N-H stretching first overtone is weak in the polymer spectra.

It should be asked whether the carbonyl second overtone below 2080 nm might help distinguish between carbamate, urea, and isocyanurate linkages. One problem is the lack of precise demarcations for these wavelengths. All certainly absorb

below 2100 nm and above 1950 nm. Triphenylisocyanurate shows only three weak peaks in this region, at 2015 nm, 2070 nm, and 2095 nm. At least the 2015 nm peak should be considered the carbonyl second overtone, which has an intensity of 0.1. Comparing the region 2010-2050 nm in a polymer NIR spectrum with various model compounds should give a clue to distinguish among urea, carbamate, and isocyanurate linkages, which have marked intensity differences. The weakness of absorption in this region for the polymers made in the refluxing solvents o-xylene, cyclohexanone, mesitylene, s-butylbenzene, and n-butylbenzene suggests a substantial isocyanurate composition. The strong absorption in the bromobenzene polymer suggests a high urea composition. The intermediate cases are probably high in carbamate. These estimates are slight refinements of the grosser estimates obtained from the midrange spectra. Differential scanning calorimetry (DSC) of system-ortho-10 polymers gave information only about degradation temperatures (usually only the onset). It was not useful for detecting glass transition temperatures (T_g) or melting temperatures (T_m). The DSC results remained substantially the same as reported in the M.S. thesis (317, p. 78).

Wide-angle X-ray diffraction patterns of powdered samples of polymer-ortho-10 (three samples considered most likely to have this structure) showed the complete lack of crystallinity in these samples.

No further GPC work was done was done on these polymers beyond that reported in the M.S. thesis (317, p. 75-77).

The inherent viscosities of several polymers in system-ortho-10 were determined (m-cresol, 30°, 1 g polymer in 100 ml solvent). The viscosities of three bulk polymers, one Curtius polymer, and five refluxing solvent polymers were measured. These values are given in Table XXXI.

Three molecular weights were determined by Barger's isopiestic method. Two samples made in chlorobenzene and one made in ethylbenzene (refluxing solvent polymerizations) were selected. The two chlorobenzene polymer samples had molecular weights of 1215 and 1435, with standard deviations of about 260 and 290 respectively. The ethylbenzene polymer had a molecular weight of 1460, with a standard deviation of 315. Assuming a PU structure, these molecular weights correspond to a degree of polymerization of 8 to 10.

D. THERMAL MODIFICATION OF SYSTEM-ORTHO-10 POLYMERS

Because the polymers formed from ring-10 have widely different structures, depending on the temperature of formation, it is desirable to examine the changes produced in a given polymer sample by heating under various conditions. One should attempt to determine whether the various structures are produced only from the ring or whether one or more polymer

TABLE XXXI

INHERENT VISCOSITIES OF POLYMERS IN SYSTEM-ORTHO-10

Polymer Preparation Technique	Inherent Viscosity (η_{inh})[a]
Bulk Thermal Polymerization	
160-165°	0.22
165-170°	0.19
176-185°	0.20
Refluxing Solvent Polymerization	
chlorobenzene	0.28
chlorobenzene	0.35
ethylbenzene	0.37
o-xylene	0.24
bromobenzene	0.21
Curtius Reaction Product	
refluxing benzene[b]	0.16

a. For a concentration of 1 g polymer in 100 ml m-cresol at 30°.

b. The intermediate azide was extracted from aqueous solution into dry benzene.

structures are intermediate products of thermolysis. Or, can a given thermolysis product be produced by both the ring and some polymer derived from the ring? Of course we are also concerned with the possible utility of these polymers, and the maintenance of useful polymer properties at elevated temperatures.

A preliminary study of the thermolysis of the polymers of ring-10 was made using the heating device of a differential scanning calorimeter (Perkin Elmer DSC-1B). The aluminum sample pans (for volatile samples) were charged with pelletized material, and the instrument was purged with dry nitrogen for 30 min prior to heating. The temperature of the sample pan was raised quickly to the desired level, maintained at a steady value for 1 hr, and then quickly dropped. This arrangement was used for preliminary studies because minute samples were required (which nevertheless gave sufficient residues for IR spectra), because a fairly short time of isothermal heating could be controlled exactly, and because the nitrogen purging minimized oxidation.

It was found that heating a PU sample above 220° led to a buildup of internal pressure which invariably ruptured the sample pan (which can withstand 30 psia).

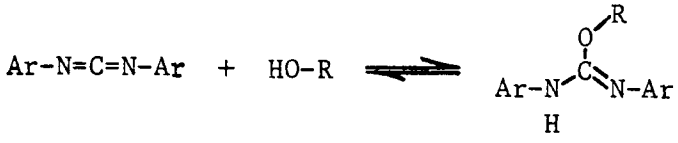
Several urethane-containing polymers from ring-10 were heated for 1 hr at temperatures ranging from 200° to 500°, at intervals of 50°. It was noticed that a white solid (largely

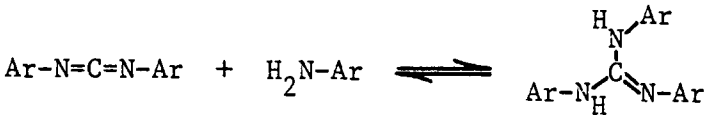
ring-10 by IR) accumulated on the window of the sample compartment, especially for temperatures of 300° and lower. Above 300° dark oils were evolved, probably methylenedianilines (by IR).

On heating at 200°, a rather complex IR spectrum was produced. Some carbamate remained, shown by substantial absorptions at 5.8μ and 9.4μ. Considerable amounts of urea, isocyanurate, and diarylmethane were present as well.

After heating at 250° neither carbamate nor urea remained. Isocyanurate and diarylmethane structures seemed dominant. A guanidine moiety also appeared likely, due to absorptions at 7.6μ, 8.0μ, and 14.4μ. This appearance may be deceptive, because instead of being discrete guanidine groups, the guanidine moiety may be part of a polymerized carbodiimide. Actually both groups are possible at 250°. The urea and carbamate linkage would dissociate into the isocyanate group and amino or hydroxyl groups. The isocyanate groups would then form either or both of two thermally stable linkages, the isocyanurate or carbodiimide.

The fate of the carbodiimide is very much open to question. If it adds an amine or alcohol group to form a guanidine or pseudourea, respectively, these linkages are probably formed only on cooling, since these additions are quite reversible at elevated temperatures (giving preparative methods for carbodiimides in many instances):





For the system-10, guanidine formation is more likely than pseudourea formation, simply because the hydroxymethyl groups are used up at much lower temperatures in forming diarylmethanes. It is certain that no carbodiimide is present in the cooled thermolysis product, because of the complete absence of an infrared peak near 4.7μ. Thus either guanidines are formed on cooling, or else the carbodiimides are polymerized while hot, or both processes may occur.

From 300° to 500° (heating time 1 hr) the amount of isocyanurate steadily decreased, though some did remain up to 500°. The diarylmethane structures also remained. The guanidine group appeared to remain, but its infrared evidence is more likely due to its presence in the structure of polymerized carbodiimides.

A difficult-to-explain phenomenon arose in the low frequency end of the infrared spectrum. On thermolysis at 200° the large bands with maxima at 13.2μ and 14.3μ dominated the spectrum (due mainly to aryl hydrogens). These bands

decreased steadily in size up to 450°, at which point they collapsed to nothing. On the other hand, an absorption at 15.1μ, which appeared as a small shoulder at 200°, steadily increased in size up to 500°, relative to all other peaks. At 500° it became one of the strongest peaks in the spectrum. This peak is proposed to be characteristic of the polymerized carbodiimide structure, as it is clearly present in the spectra of the pyrolysates of triphenylguanidine, di-o-tolylguanidine, diphenylguanidine, and dicyclohexylcarbodiimide (heating these compounds at 370° in solutions of refluxing paraffin).

In searching a collection of far-infrared spectra (231), it was found that several compounds which contain a highly conjugated guanidine, pseudourea, or pseudothiourea structure exhibit a peak between 15.0μ and 15.6μ. It is reasonable to propose a skeletal (non-hydrogenic) vibration, involving several nitrogen and carbon atoms of the polymerized carbodiimide grouping. It is the strong band at 15.1μ that argues against graphitization as a thermolysis product at 500° or lower. Polycyclic aromatic compounds of the benzenoid "chickenwire" type do not have a very strong infrared band at this wavelength (many examined model compounds with graphite-like structures do not).

Temperatures of thermolysis higher than 500° were not used, so graphitization at still higher temperatures cannot

be refuted. Conley (77, p. 358) proposed a degradation pathway of carbodiimides which would lead to such graphite-like residues or carbon chars:

$$Ar\text{-}N{=}C{=}N\text{-}Ar \xrightarrow{\Delta} Ar\text{-}N{=}C: + Ar\text{-}CN + :N\text{-}Ar$$

$$Ar\text{-}N{=}C: + Ar\text{-}H \longrightarrow Ar\text{-}Ar + HCN$$

$$Ar\text{-}CN + Ar\text{-}H \longrightarrow Ar\text{-}Ar + HCN$$

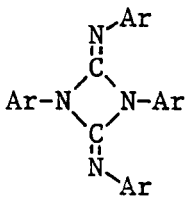
Experimental details for the formation of such products were not accessible to this author.

As discussed in the introduction, all the following linkages should give carbodiimides on heating above 300°: isocyanate, carbamate, urea, guanidine, pseudourea, and isocyanurate. Carbodiimides in turn should polymerize by addition across the C=N double bond. Whether cyclic or linear polymers are formed, or the proportion of each, probably depends on the N-substituent — and is a rather important question.

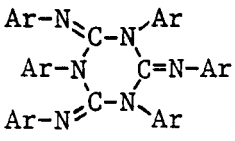
The infrared absorptions of the polymerized carbodiimides also constitute a very important problem. Alaminov and coworkers (78, 234, 235, 236, 237) studied the pyrolysis products of isocyanurates at 500°, and found these gave broad peaks at 6.15μ, 7.2μ, and 7.6μ. Although Alaminov and Proynova (78) supposed these absorptions to arise from the

polycyanate structure, the very similar polymerized carbodiimide structure is much more likely, for reasons discussed in the introduction.

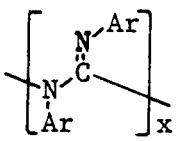
Almost all of the past infrared work has been done on the polymers from N,N'-diarylcarbodiimides. David and Staley (230, p. 262) reported that the dimer and trimer had a C=N double bond stretching absorption at 5.95μ and 5.99μ, respectively.



5.95μ (230)
5.917μ (242)



5.99μ (230)



6.2μ or 6.28μ (76, 80)

Merten et al. reported that the linear polymer absorbs at 6.2μ or 6.28μ. Tsuzuki and Iwakura (242) reported that the dimer had the double-bond stretching frequency at 5.91μ. The only infrared study of such polymers containing non-aryl N-substituents seems to be that of Robinson (75), who also worked with unsymmetrical carbodiimides, but considered only the linear polymers. The reported infrared absorptions were the following:

6.06μ to 6.134μ	C=N stretching
7.352μ, 8.0μ	C-N stretching
9.37μ	backbone N-Me stretching

No absorptions at wavelengths higher than 9.5μ have been reported for any polymerized carbodiimide.

The dimer, trimer, and linear polymer of a carbodiimide bear a close resemblance to the corresponding polymers of an isocyanate. For hexaphenylisomelamine, the C=N double-bond stretching peak (5.99μ) lies very close to the corresponding carbonyl peak of triphenylisocyanurate (5.90μ). It is expected that the ring frequencies of the carbodiimide trimer will be even closer to those of the isocyanurate (335), because in both cases there is negligible distortion from the ideal bond angles and the entire molecule is planar. The four membered rings obviously do not provide the ideal bond angles for sp^2 hybridization, and the linear polymers obviously do not have the same steric requirements, so such a close correspondence is not expected. On purely theoretical grounds, then, the following ring vibrations are expected for the diphenyl carbodiimide trimer:

6.7μ, 6.9μ	benzene ring
7.1μ (7.0-7.2μ)	triazine ring
7.8μ	triazine ring

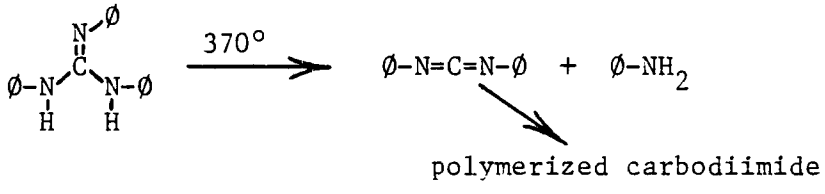
8.2μ triazine ring

9.3μ triazine ring

9.7μ benzene ring

The band at 7.1μ is expected to be the strongest of the ring frequencies, by far.

The sample of polymerized diphenyl carbodiimide discussed in Chapter IV, which was made by heating triphenylguanidine at 370° in refluxing paraffin, is a suitable model for this system also.



The product has prominent absorptions at 6.0μ and at 6.2μ (the latter is about twice as strong), though neither is a discrete peak. The small absorption at 5.9μ may be due to the dimer. The strongest absorption, from 6.8μ to 7.3μ, is undoubtedly due to the merging of the benzene ring frequency at 6.0μ, the isomelamine ring frequency at 7.1μ (7.0μ to 7.2μ) and the C-N vibration at 7.2μ (open-chain polymer). Shoulders at 7.6μ and 7.8μ are quite apparent, assigned to linear and ring forms respectively. Several lesser shoulders were mentioned previously. Most conspicuous is the strong peak from 14.95μ

to 15.2μ. A small peak at 11.5-11.7μ is characteristic of all polymerized carbodiimides.

The 500°-thermolysis residue of polymer-ortho-10 was quite similar to the above sample of polymerized diphenylcarbodiimide, with the one notable exception being the absence of a strong broad band around 13.5μ (due to 4 or 5 adjacent aryl C-H bonds). A strong band around 13.5μ was present in the 400°-thermolysis residue, and in those obtained at lower temperatures, but this band had almost disappeared on 450°-thermolysis.

This disappearance can only mean a disappearance of one or more aryl hydrogens. After the formation of methylene bridges between benzene rings, only three aryl hydrogens are available, on the average, for each benzene ring. We may rationalize the disappearance of the 13.5μ band at 500° by invoking a free radical coupling of adjacent benzene rings,

$$\text{Ar-H} + \text{H-Ar'} \longrightarrow \text{Ar-Ar'} + \text{H}_2\uparrow$$

with the evolution of some hydrogen gas, to further decrease the number of aryl hydrogens. Some aryl hydrogens do remain at 500°, as shown by a substantial absorption at 3.3μ, but these probably do not occur in groups of more than three adjacent hydrogens. Besides this difficulty at 500°, the

chemistry of the thermolyses is explainable in terms of more classical condensation and addition reactions, giving ureas, diarylmethanes, isocyanurates, guanidines, and polymerized carbodiimides for the system-ortho-10. Further thermolysis studies of this system provide elaborations of this scheme.

Because heating the samples of polymer-ortho-10 caused the aluminum DSC sample pans to rupture at such a low temperature (<220°), it was thought that heating should be done in a sealed silica tube for a period longer than 1 hr. The same type of sealed silica tube described in Chapter IV was used, along with the same heating device (a hydrogenation bomb). Heating was done for 24 hr. The arrangement was only slightly better than the DSC sample pans, because the silica tubes invariably burst above 240°. Nevertheless, thermolyses were carried out at 200° and 230° for polymeric samples of system-ortho-10. The nonvolatile residues (sublimation at 120 and 0.8 mm) were examined by IR. The 200°-thermolysate showed a little carbamate, but predominately urea, isocyanurate, and diarylmethane. The 230°-thermolysate showed no carbamate, little urea, and predominately isocyanurate and diarylmethane. A small 15.1μ peak was visible, ascribed to polymerized carbodiimide. For polymers made below 185°, the composition of the thermolysis residue (nonvolatile portion) did not depend on the method of making the polymer. These results with the sealed silica tubes make highly plausible the idea that polymers

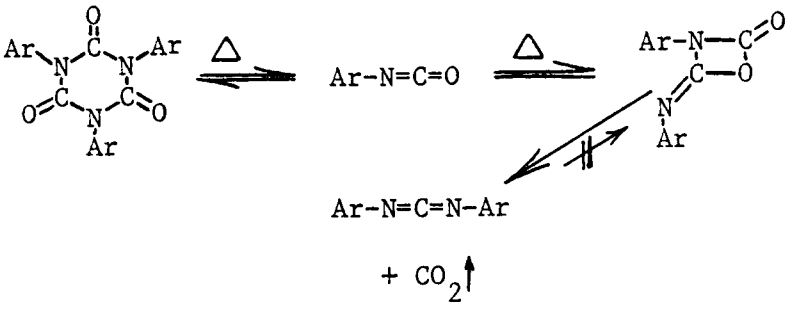
are formed at a lower temperature (directly from the ring). These results also raise another question, which would be more difficult (tedious and time consuming) to test; concerning whether the composition of the final product depends only on the time and manner of heating at the highest temperature of processing, and not on previous history at lower temperatures. For lack of data, this latter question has been left unanswered.

Because the evolution of much volatile material on heating produced enough pressure to rupture silica, a series of thermolyses was done during the application of vacuum (at most 1 mm). The simultaneous application of heat and vacuum over a 24 hr period was sufficient to remove all carbamate linkages at 180°, though less than half the polymeric carbamate linkages were lost as volatilized ring-10 (collected on a sublimator cold-finger). Mass balances on sublimates and residues, combined with the initial carbamate/isocyanurate ratio obtained by IR (discussed earlier), usually showed less than 25% conversion of PU linkages to cyclic carbamate linkages. For thermolyses below 230° it is assumed that the balance of the isocyanate groups was converted to isocyanurate and urea, rather than carbodiimide, and that the lost mass is due to removal of water. Such quantitative estimates must remain crude, because the urea component of the starting material

must be small enough to be neglected (a questionable assumption).

Thermolysis at 200° under vacuum gave much more isocyanurate than urea. At 280°, guanidine was more prominent than isocyanurate, with a small amount of polymerized carbodiimide. At 370° isocyanurate and guanidine were negligible relative to polymerized carbodiimide. In fact, the residue was almost entirely in the form of the linear polymer, according to the weakness of an absorption around 6.0μ. The steric bulk of the diarylmethane structures probably destabilizes the cyclic oligomers of the carbodiimide, relative to the linear polymer. The correspondence between the spectrum of this residue and the spectrum of polymerized diphenyl carbodiimide (obtained from triphenylguanidine) was quite striking. The only noticeable differences were that the residue derived from ring-10 had a lower absorption at 6.0μ and a stronger absorption at 7.3μ. The definite peak at 7.3μ was the strongest absorption in the spectrum. Only the nitrogenous linkages have been discussed, as the diarylmethane linkages seemed to remain throughout the series. Compared with the series of thermolyses done without vacuum (actually under pressure), the thermolyses done with vacuum give greater relative amounts of carbodiimide products (guanidine or polymer). This effect is due to the greater ease of removing CO_2 from the system, which favors the carbodiimide products relative to the isocyanate products

(mainly isocyanurate).



For a polymer made from ring-10 in refluxing bromobenzene (bp 156°), the weights of the residues on vacuum thermolysis at several temperatures were measured, and the percentage of original weight calculated (24 hr heating):

97.5% at 170°

94.6% at 180°

90.6% at 200°

73.3% at 280°

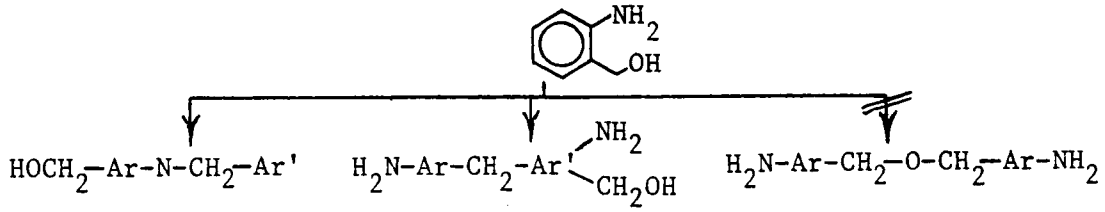
41.1% at 370°

For temperatures up to 200°, the heating was done in a sublimation apparatus (well submerged in an oil bath). Above 200°, a tube containing the sample was continuously evacuated and heated with a molten solder bath.

The sample thermolyzed at 200° under vacuum was subjected to hydrolysis by 10% NaOH at 60° for 24 hr. The slurry was neutralized, filtered, and washed with water. From the dried precipitate, two organic fractions were obtained, one soluble

in benzene and one insoluble. Below 7.5μ the infrared spectra of these fractions were almost identical. Surprisingly, the benzene insoluble fraction had more distinct peaks than the soluble fraction in the region above 7.5μ, especially in the "fingerprint region." The soluble fraction had the stronger peaks at 7.65-8.05μ, 11.3-11.7μ, and 13.0-13.5μ, but the weaker peak at 13.0-13.5μ. Both fractions seem to be a mixture of isocyanurate and diarylmethane (methylenedianiline), but the differences between the infrared spectra of the fractions are not easily rationalizable.

In order to obtain the infrared data from a model polymer, o-aminobenzyl alcohol was itself polymerized thermally, in refluxing bromobenzene. The product had a negligible absorption at 9.9μ, showing the loss of the C-O bond, presumably from the methylol group. Thus, N-benzyl aniline or diarylmethane linkages could be formed, but clearly not dibenzyl ether linkages.

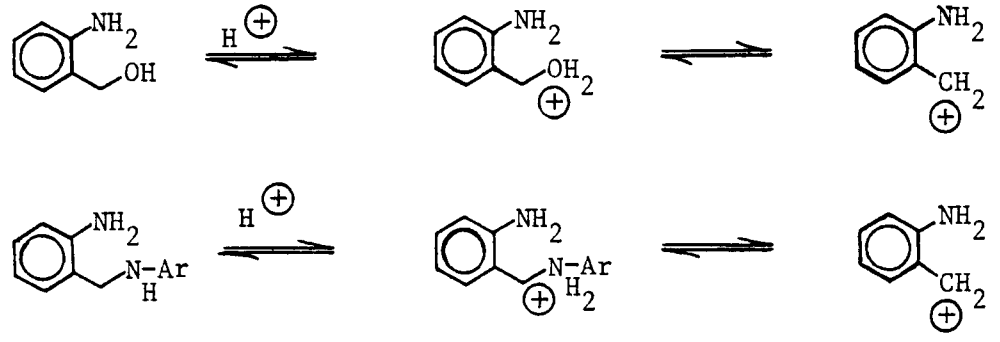


N-benzyl aniline diarylmethane dibenzyl ether

The infrared spectrum corresponds much more closely to the methylenedianiline structure (336) than to the N-benzyl

aniline structure (193, p. 630G). The reaction was reported by Conley (334, p. 496) but useful details were not readily accessible, nor was the type of methylene bridging in the product specified.

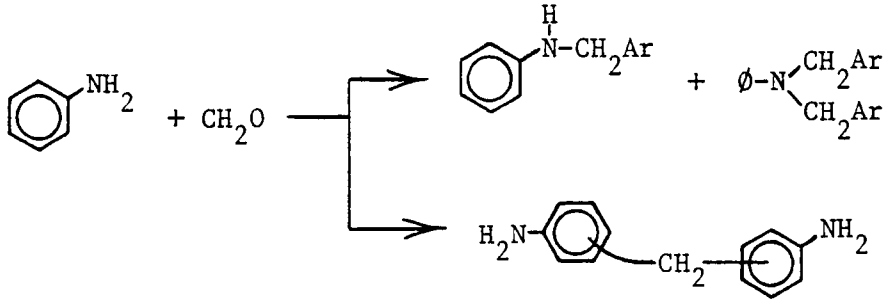
A trace of acid might be required to catalyze the condensation to methylenedianilines, but this could easily arise by autoxidation giving anthranilic acid. If the N-benzyl aniline products were first formed, they too would probably give methylenedianilines on further heating, because the aniline molecule is also a good leaving group:



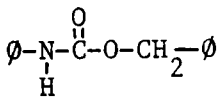
The utility of this model polymer was that it showed clearly that none of the polymers derived from ring-10 by heating was composed largely of such diarylmethane linkages, and that the hydrolysis of ring-10 to o-hydroxymethyl aniline was an insignificant pathway in the thermal polymerizations.

Another series of model polymers was prepared by condensing aniline with various amounts of formaldehyde, a reaction also reported by Conley (334, p. 496). This reaction is more

likely to produce N-benzyl aniline and N,N-dibenzyl aniline linkages than diarylmethane linkages.



The infrared spectra of this series of model polymers had very little in common with the spectra of any polymers obtained from ring-10, or with the spectrum of thermally polymerized o-aminobenzyl alcohol. It is concluded that N-benzyl aniline or N,N-dibenzyl aniline linkages can be removed from consideration in trying to elucidate the structures of the polymers obtained from ring-10. Though apparently a digression, this work was necessary because of the results reported by Dyer and Wright (42), which dealt with the open-chain model compound N-phenyl-O-benzyl carbamate,



a model for ring-10 and polymer-ortho-10. This paper mentioned the reversibility of the thermal dissociation of the carbamate, with which the work of this chapter is in complete agreement. But the present work is not in agreement with the reported

yields of N-benzyl aniline and N,N-dibenzyl aniline that were obtained by thermolyzing the model compound. The implications of the chemistry of the above secondary and tertiary amines, as applied to system-ortho-10, was discussed at length in the M.S. thesis (317, p. 29, 30, 72, 73).

Very little near infrared work on the thermolysis of these polymers was done. The polymer made in refluxing cyclohexanone was vacuum-thermolyzed at 170° for 12 hr, and the polymer made in refluxing n-butylbenzene was vacuum thermolyzed at 180° for 24 hr. The former showed increased absorptions at 2360 nm, 2345 nm, and 2296 nm, and the latter showed increases at 2525 nm, 2425 nm, 2305 nm, 2167 nm, and 2145 nm (see Appendix IV). These changes are rather insignificant. The former would suggest an increasing aliphatic content, or an increasing content of o-hydroxymethyl aniline groups, both of which are difficult to rationalize.

Some informative thermogravimetric analysis (TGA) data were obtained. The quantities of most interest are the temperature by which 10%, 25%, and 50% weight loss had occurred, the residue weight at 500°, and the temperatures and weight losses at the first and second inflection points, or steep portions. The rings showed only one region of rapid weight loss (one inflection point) or steep part, as did several polymers. Some polymers, however, showed two regions of rapid weight loss (two inflection points), and their significance will be discussed

where appropriate. All TGA's were recorded at a scan rate of 10°/min. Most scans were done in a nitrogen atmosphere, but some were done in air, so the atmosphere must be specified.

Ring-10 and three polymers of system-ortho-10 were scanned under nitrogen (Table XXXII). Ring-10 and two polymers of system-ortho-10 were scanned in air (Table XXXIII). Unfortunately some TGA's of the polymers were not recorded to sufficiently high temperatures to give the second inflection point. One polymer sample (bulk polymerization at 160-165°) showed three inflection points on degradation in air. Each steep part corresponds to a distinct mode of degradation, and each flat part corresponds to a polymer more stable than the one before it. The first steep part, for thermolysis under nitrogen, probably comprises three steps in succession: splitting of urea groups, loss of CO_2, and formation of carbodiimides. The second flat part is likely due to the stability of isocyanurates and carbodiimide products (guanidines or polymers). The second steep part is probably due to the conversion of isocyanurates to polymerized carbodiimides. If a third steep part is seen under nitrogen, it will probably correspond to the formation of biaryls and diarylamines, at temperatures higher than 500°.

Degradation in air would add several complications. Benzyl alcohol groups could be oxidized to benzoic acids, and

TABLE XXXII

THERMOGRAVIMETRIC ANALYSES OF SYSTEM-ORTHO-10 MATERIALS UNDER NITROGEN

Compound	Temp at wt loss			Residue (%)	1st Inflection		2nd Inflection	
	10%	25%	50%	at 500°	% Vol	Temp	% Vol	Temp
Ring-10	185	210	228	0	65	242	--	--
Polymer-ortho-10 (bulk 160-165°)	210	330	465	30	16	238	61	477
Polymer-ortho-10 (bulk 176-185°)	246	360	485	43	11	250	50	485
Crosslinked polymer (refluxing quinoline)	260	312	378	34	37	340	>66	>500

TABLE XXXIII

THERMOGRAVIMETRIC ANALYSES OF SYSTEM-ORTHO-10 MATERIALS IN AIR

Compound	Temp at wt loss			Residue (%)	1st Inflection		2nd Inflection	
	10%	25%	50%	at 500°	% Vol	Temp	% Vol	Temp
Ring-10	196	220	238	6	70	248	--	--
Polymer-ortho-10 (bulk 160-165°)	219	427	525	55	13	235	37	474[a]
Crosslinked polymer (refluxing quinoline)	275	323	490	49	25	323	>51	>500

a. A third inflection occurs at 90% weight loss and 560°.

diarylmethanes to benzophenones. The benzoic acids would condense with aniline groups to form N-arylbenzamides, and with benzene rings to form benzophenones. The main result of these conversions probably would be to add the weight of the oxygen atoms to the residue otherwise obtained.

Because such a high percentage of the original weight is retained upon degradation in air, it is tempting to pursue another line of investigation in this direction, as the residues might retain retain useful polymeric properties to extremely high temperatures. However, because so many additional reactions can occur, this topic will not be treated in further detail here.

The most obvious result of the above TGA data is the much lower volatilization of any polymer compared to ring-10, by all standards of comparison. This is expected "by definition" because of the volatility criterion of polymer properties.

Another obvious result for any specific substance above is that the residual weight in oxygen is always greater than the corresponding residual weight in nitrogen at the same temperature. The above TGA scans will be compared with the TGA scans of other rings and polymers in the last chapter.

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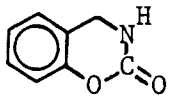
CHAPTER VI

THE SYSTEM-ORTHO-01

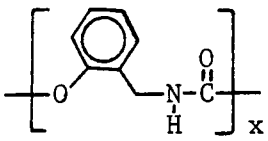
A. GENERAL CONSIDERATIONS

The cyclic carbamate herein called "ring-01" is more systematically named 3,4-dihydro-2H-1,3-benzoxazin-2-one, according to Chemical Abstracts nomenclature.



ring-01

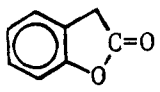
The corresponding open-chain AB-type PU has the systematic names poly(oxycarbonyliminomethylene-o-phenylene) and poly-(oxycarbonyliminomethylene-1,2-phenylene) but will more conveniently be called polymer-ortho-01 in this work.



polymer-ortho-01

The three general methods for preparing ring-01 have been discussed in the author's M.S. thesis (317, p. 80-82). Only one of these methods has preparative value, the other two being very hazardous. The Curtius reaction was used in the present research. This application of the Curtius reaction was first reported by Lindemann and Schultheis (128),

and an improved procedure was reported in the M.S. thesis (317, p. 90-93). The starting material coumaranone



is costly, so several preparations of this compound in bulk quantities were tried. The Erlenmeyer azlactone synthesis was found to be the best (275, p. 443; 337; 338; 339; 340, p. 207; 341; 342). The most successful procedure for preparing this compound was given in detail in the M.S. thesis (317, p. 85-89).

B. THERMAL POLYMERIZATIONS OF RING-01 AND CHARACTERIZATION OF THE POLYMERS

Bulk thermal polymerizations of ring-01 were carried out in evacuated closed tubes (317, p. 43), like the bulk polymerizations described in the previous chapter. The heating of the ring and the workup of the product were described in the M.S. thesis (317, p. 94). The resulting product yields and compositions (317, p. 95-97) are presented in Table XXXIV. The yields are given as percent by weight based on starting material. All these polymers were prepared by heating in an oil bath except the one at 194° (marked with superscript b) which was prepared in a vacuum oven. The gross differences in the product yields and compositions are difficult to

TABLE XXIV

POLYMERS FROM HEATING RING-01 IN BULK

Temperature (°C)	Yield (%)		Predominate Linkages				
	Soluble	Insol	PU	Isocyanurate	Urea	Isourea	Diarylmethane
170-176	20	0	√	little			
180-185	30	0	√	√	little		
190-194	47		√	√	√		
		a		√		√	
194[b]	14	0	√	√			
206-209	16		√				
		52		√		√	little
227-230	<1		√		√		
		~70		√		√	little

a. Undetermined amount

b. This sample was prepared by heating in a vacuum oven; all the rest by heating in an oil bath.

explain, in comparing the oil bath heating at 190-194° with the vacuum oven heating at 194°.

In the presence of the carbamate peaks of polymer-ortho-01, it is possible only to discern the presence or absence of the corresponding isocyanurate, rather than to quantitate the amount of isocyanurate, because the isocyanurate peak at 5.95μ overlaps strongly with the carbamate peak at 5.80μ. It is a strange coincidence that every other peak which appears in the IR spectrum of tribenzylisocyanurate, also appears in the spectra of either ring-01 or the model compound N-benzyl-O-phenyl carbamate. Diarylmethane linkages show characteristic absorptions at 8.4-8.5μ and at 9.6-9.7μ (common to most diarylmethanes), as well as at 7.3μ, 7.5μ, 8.1μ, and 8.25μ, shown by methylenediphenols (343). In spite of these analytical difficulties, it can be stated with a high degree of certainty that the closed-tube polymerizations of ring-01 gave slightly higher yields of PU in purer form, when compared with those from ring-10 at the same temperatures.

As in the case of ring-10, refluxing solvent polymerizations were also carried out on ring-01. The general trend was formation of lesser amounts of polymer from ring-01 than of polymer from ring-10 under equivalent conditions, although the polymer formed had a higher proportion of carbamate linkages. Again, appreciable amounts of "solvent" were incorporated,

especially for preparations made in cyclohexanone and in aromatic hydrocarbons with benzylic H's. As in the previous chapter, the yields of soluble fraction of polymer are generally higher than in the bulk (closed tube) polymerization, probably because of the dilution effect of the solvent. Although highly branched polymers are likely products in the refluxing solvents, gelled or crosslinked products are not likely. The overall results for the refluxing solvent polymerizations are given in Table XXXV.

For the polymers of system-ortho-01, a large proportion of the urea linkages detected by infrared spectroscopy may in fact be isoureas. In the presence of both urea and carbamate linkages, isourea linkages would be very difficult to detect. As discussed in Chapter II, the N,N'-dialkyl-O-aryl isoureas are characterized by absorptions at 6.0-6.1μ, 7.1μ, 7.75μ, 8.1-8.35μ, and 8.95-9.25μ (246, 249, 250). In the presence of phenolic hydroxyl groups, these isoureas would be largely converted to isouronium phenolate salts, which would shift the above infrared absorptions to lower wavelengths. What is observed is a broadening of the above wavelengths to the left.

Various polymer samples of system-ortho-01 were examined by near infrared spectroscopy. Most of these NIR spectra supported the presence of isocyanurate as the main by-product rather than urea. All of the samples examined were prepared

TABLE XXXV

POLYMERS FROM HEATING RING-01 IN REFLUXING SOLVENTS

Solvent	Bp	Yield (%)[a]		Linkages in Soluble Fraction[b]				
		Sol	Insol	Solvent	PU	Isocyanurate	Urea	Diarylmethane
C_6H_5Cl	131	5	-		√	little		
C_6H_5Et	136	20	-		√	little		
(n-Bu)$_2$O	142	5	-		√	little		
o-xylene	144	15	-		√		√	
cumene	152	110	-	√	√		√	
anisole	153	6	-		√		√	
cyclohexanone	156	132	-	√	√		√	
C_6H_5Br	156	5	-		√	little		
mesitylene	164	7	-		√	little		
phenetole	170	18	-		√		little	
s-butylbenzene	173	32	-	√	√	√	little	
p-cymene	177	81	-	√	√	√	little	
tetramethylurea	177	29	-			√	√	
o-dichlorobenzene	180	6	-		√		little	
n-butylbenzene	183	82	-	√		√	√	

TABLE XXXV (Continued)

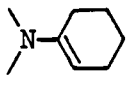
Solvent	Bp	Yield (%)[a]		Linkages in Soluble Fraction[b,c]				
		Sol	Insol	Solvent	PU	Isocyanurate	Urea	Diarylmethane
pentyl ether	187	54	-		√	√	√	
dimethylaniline	193	116	-	√	little	√	√	
veratrole	206	71	12	√	little	√	√	
tetralin	207	110	-	√	little	√	√	
$(Bu)_3N$	216	94	-				√	√
quinoline	237	21	40				√	√

a. Yield is percent nonvolatile based on initial weight.

b. Solvent designation signifies chemical incorporation of solvent into product.

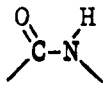
c. The infrared peaks characteristic of the urea linkage may instead be due to isourea linkages; in the presence of carbamate peaks the two are indistinguishable.

in refluxing solvents. The polymer prepared in cyclohexanone was clearly anomalous, due to the incorporation of a large amount of aliphatic material, presumably as cyclohexenylamine moieties.



This structure was specifically supported by absorptions at 2162 nm, 2152 nm, and 2141 nm, which are due to the cis-olefin structure (282, p. 641; 283, p. 28; 292). The very strong absorptions in the regions 2400-2283 nm and 1810-1710 nm were partly due to the aliphatic structures.

The overall spectra resembled the spectrum of ring-01 rather than that of the corresponding open-chain model compound N-benzyl-O-phenyl carbamate. This is probably due to the cisoid conformation of the carbamoyl group



in the polymer. Almost all the samples showed strong absorptions in the region 2400-2270 nm. The methylene combinations alone cannot account for the gross disparity between the strong absorptions in the carbamate and isocyanurate models and the rather low absorption in the urea model (N,N'-dibenzyl urea). For models of this system (N-benzyl, O-phenyl

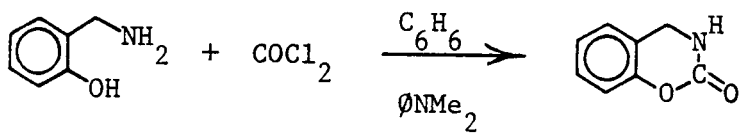
substitution), the absorptions in the region 2400-2270 nm are due also to another combination, that of (1) either the carbonyl first overtone (2x1700 cm^{-1}) or the N-H stretching (3300 cm^{-1}) and (2) various strong peaks in the region from 12.5μ to 8μ (800 cm^{-1} to 1250 cm^{-1}). N,N'-Dibenzyl urea has only medium or weak absorptions in this region, which give rise to rather low absorptions in the near infrared region at 2400-2270 nm. At any rate, the intensity of absorption in this region in the polymer spectra (all samples except that made in cumene) would favor either the carbamate or isocyanurate structures over the urea structure.

A stronger indication of the presence of substantial isocyanurate is the weakness of the absorptions in the region 2050-1950 nm. A third indication is the weakness of absorption around 1480 nm, due to the amide N-H group. The absorption of phenolic OH does not appear as a discrete peak around 1417 nm, but instead as a very broad hump in the region 1400-1460 nm. The near infrared spectra of the various polymer samples (made in cumene, cyclohexanone, s-butylbenzene, p-cymene, tetramethylurea, dimethylaniline, and tributylamine) are given in Appendix V.

C. POLYMER-ORTHO-01 FROM THE CURTIUS REACTION AND FURTHER CHARACTERIZATIONS OF POLYMERS

Samples of polymer-ortho-01 were also made as a byproduct of the same Curtius reaction used to make ring-01. The isolation and purification was described in the M.S. thesis (317, p. 97). A yield of about 6% was obtained in each of two runs, and the polymer had a small amount of isocyanurate linkages but no urea linkages. Variations in the procedure of the Curtius reaction, in order to optimize the yield or purity of polymer-ortho-01, were not tried because of the expense of coumaranone.

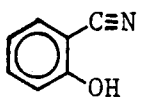
In an attempt to work out a more direct synthesis of polymer-ortho-01 (or of ring-01), the author studied the reaction of salicylamine (o-hydroxybenzylamine) with various reagents which supply the carbonyl moiety, such as phosgene, diethyl carbonate, ethylene carbonate, ethyl chloroformate, and dimethyl carbonate. The successful application of such a reaction, in the synthesis of ring-01, has been reported in one patent (344).



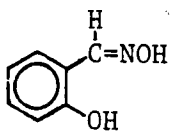
The foremost difficulty was the preparation of salicylamine itself, preferably in pure anhydrous form. The

preparation of this compound was claimed in several papers (345, 346, 347, 348, 349). The disparity of the reported melting points (ranging from 114° to 130°) indicates difficulties in purification.

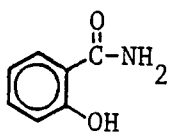
The preparations of salicylamine attempted in this laboratory were the electrolytic reductions of salicylonitrile, salicylaldoxime, and salicylamine which were all readily available.



salicylonitrile



salicylaldoxime



salicylamide

The electrolytic reduction technique was suggested by the highly successful preparation of o-aminobenzyl alcohol from anthranilic acid in this laboratory (317, p. 54; 350). Expectation of a successful preparation of salicylamine was reinforced by ample precedent in the reduction of benzonitriles (351, 352, 353), benzaldoximes (354; 355; 356, p. 86; 357; 358), and benzamides (356, p. 80; 359; 360; 361; 362) to benzylamines.

The reductions of salicylonitrile and salicylaldoxime were completely unsuccessful, whereas a 16% yield of impure salicylamine could be obtained from salicylamide. The electrolytic apparatus and electrolysis procedure were the same as

those used for o-aminobenzyl alcohol (317, p. 54). However, the anolyte and catholyte were slightly different, because of the insolubility of salicylamide in non-alcoholic solutions. The catholyte used was the following: 100 g salicylamide (0.72 mole), 600 g 95% ethanol, 350 g H_2SO_4, 100 g H_2O. The anolyte was 30% H_2SO_4. The reduction was continued for 10 hr following the disappearance of the salicylamide (undissolved portion). The catholyte solution was withdrawn, added dropwise to 130 g sodium hydroxide pellets, and neutralized with sodium bicarbonate. All residual residual solvent was removed by gas jet evaporation followed by vacuum oven drying (60°). The salicylamine was extracted from the solid mass with ether, using a large capacity Soxhlet extractor, and the ether was then stripped off. The yield of product was 14.2 g (16.1%), mp 111-190° (reported values range from 114° to 130°, see above). The infrared (Appendix V) and nmr spectra were consistent with the salicylamine structure (no spectra previously reported).

The infrared spectrum showed a broad very strong absorption from 3.2μ to 4.4μ, and a strong absorption from 4.6μ to 5.0μ. The other sharper peaks were as follows: 6.2μ (s), 6.25μ (vs), 6.4μ (vs), 6.5μ (vs), 6.75μ (vs), 6.9μ (vs), 7.3μ (m), 7.5μ (m), 7.7μ (vs), 8.0μ (vs), 8.35μ (m), 8.7μ (m), 8.85μ (vs), 8.95μ (s), 9.25μ (m), 9.6μ (w), 10.3μ (w), 10.8μ (w), 11.65μ (m), 13.35μ (vs), 13.75μ (s). The

salicylamide strong peaks at 6.0μ, 7.4μ, and 11.9μ were completely absent, and the saligenin strong peak at 9.95μ was also absent. No other impurities were expected or found. The nmr spectrum (solvent $CDCl_3$, TMS internal) showed the expected resonance signals.

3.15-3.5δ (max 3.3δ) diffuse hump (3H) OH and NH_2

4.65δ sharp singlet (2H) CH_2

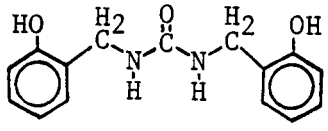
6.6-7.3δ (strongest at 6.75δ and 7.05δ) multiplet (4H) ArH

Phosgenation of salicylamine was tried using a Schotten-Baumann technique, according to the method of Pifferi et al. (218) for the analogous preparation of ring-11. However, neither ring-01 nor any polymer (nonvolatile on sublimation at 120° and 0.8 mm) could be isolated.

For the other condensation reactions of salicylamine with each of four "carbonyl" reagents (diethyl carbonate, dimethyl carbonate, ethylene carbonate, and ethyl chloroformate), equimolar amounts of salicylamine and the reagent (0.05 mole each) and 5 ml triethylamine were refluxed for 24 hr, after which volatile materials were first removed by vacuum distillation (1-1.2 mm, at most 100°) followed by sublimation (0.3-0.5 mm, 120° 48 hr). The product from dimethyl carbonate was liquid at room temperature, even after further prolonged heating in a vacuum oven at 170°, so this nonvolatile product was not characterized further. On working up the various distillates and sublimates, the volatile ring-01 could not be

isolated (nor any other solid product). Three of the products (from diethyl carbonate, ethylene carbonate, and ethyl chloroformate) were nonvolatile solids.

All three of these products showed a strong dibenzyl urea presence at 6.1μ, 6.2μ, and 9.7μ. The product from diethyl carbonate did not show any other carbonyl absorption, and was almost exclusively the urea "dimer,"



The carbonate linkage was notably lacking in all samples; only the sample made from ethyl chloroformate could have a small amount (shoulder at 5.6-5.7μ). Only the sample made from ethylene carbonate could have a substantial amount of carbamate linkage (peak at 5.8μ), while the sample made in ethyl chloroformate had a small amount (definitely more carbamate than carbonate). The sample likely to have the highest molecular weight was the one made in ethylene carbonate, as the other two samples had much too little carbamate or carbonate composition. Molecular weights were not determined, but the inherent viscosities showed this trend. Viscosities were determined in a Ubbelohde viscometer (Cannon instruments), using m-cresol at 30°. A concentration of 1.0 g/100 ml was used (Table XXXVI).

TABLE XXXVI

INHERENT VISCOSITIES OF POLYMERS FORMED FROM REAGENTS SUPPLYING THE CARBONYL MOIETY

Reagent	Inherent viscosity[a]
ethylene carbonate	0.065
ethyl chloroformate	0.058
diethyl carbonate	0.049

a. At a concentration of 1 g polymer per 100 ml m-cresol at 30°.

These inherent viscosities were much lower than the values given by samples of polymer-ortho-01, typically in the range 0.23 to 0.61 (1.0 g/100 ml m-cresol at 30°). Attempts to optimize the molecular weight by adjusting reaction conditions would probably greatly improve the above inherent viscosities.

There is some precedent for the formation of PU's from ethylene carbonate and ω-hydroxyamines; specifically that of Dyer et al. (140, 165). Carbamate linkages rather than urea linkages are formed, because the reaction proceeds through the isolable intermediate 2-hydroxyethyl carbonate. Not surprisingly, ethylene carbonate in the present work gave the polymer with the largest proportion of carbamate. Most "carbonyl moiety" reagents are expected to give the urea linkage, since the amino group is much more nucleophilic than the hydroxyl group. If both of the heteroatom moieties attached to the carbonyl group are readily displaceable, the amino groups will react first to form urea linkages and the remaining carbonyl moiety should form carbonate linkages. Apparently with the present compounds, the phenolic hydroxyl group was not sufficiently nucleophilic to form the carbonate linkages in an amount equivalent to the urea product. Furthermore, once the amino group of the o-aminomethyl phenol has reacted, then the mobility of each phenolic moiety is restricted, which would further decrease their reactivity.

Further characterization of the various products of system-ortho-01 should be covered. As with the polymers of system-ortho-10 (Chapter V), none of the polymers of system-ortho-01 showed melting points or glass transitions by DSC, only various modes of decomposition (317, p. 98, 99). The glass transition probably occurs over such a broad range as to be nondiscernable. No melting peak was observed, which is consistent with the noncrystallinity of the samples as shown by X-ray diffraction.

Viscometry was done on several samples having a high proportion of carbamate linkages. The highest inherent viscosities were given by samples made by bulk thermal polymerization. The samples made at 170-176° and at 180-185° showed inherent viscosities of 0.61 and 0.58 respectively. Polymers made in refluxing ethylbenzene and dibutyl ether showed inherent viscosities of 0.23 and 0.41 respectively. A Curtius reaction polymer gave an inherent viscosity of 0.49. As usual, these inherent viscosities were determined in m-cresol at 30°, at a concentration of 1.0 g polymer in 100 ml solvent.

Isopiestic molecular weights (Barger's capillary tube method) were in turn done on two of these polymers. The polymer made in bulk at 170-176° had a molecular weight of 2080, with a standard deviation of 565. The polymer made in refluxing dibutyl ether had a molecular weight of 1630, with a standard deviation of 510.

D. THERMAL MODIFICATION OF SYSTEM-ORTHO-01 POLYMERS

Thermal stability and thermal modifications of polymer-ortho-01 were of high interest, and these thermolyses showed several contrasting features with those of polymer-ortho-10. A preliminary thermolysis series was done at 200°, 250°, and 300°, by heating with the DSC-1B under nitrogen. At 200°, a sample of polymer-ortho-01 showed almost no change, a small amount of urea being produced (IR pellet of residue). Upon 250° thermolysis, no carbamate or urea linkages remained. Instead isocyanurate (5.9μ, 7.05μ, and 7.55μ) and isouronium phenolate (6.1-6.5μ, 7.9μ, and 8.7μ) predominated. Some polymerized carbodiimide was definitely present (6.2μ, 11.6μ, and 15.1μ). Upon 300° thermolysis, these three components were all present, but with more polymerized carbodiimide.

A series of thermolyses was also carried out under constant vacuum, each thermolysis for 24 hr. At 200° surprisingly little change was produced in the sample, either in the infrared spectrum or in the weight loss (16%). The isocyanurate component appeared to increase (5.9μ). The urea composition did increase slightly. A small blip at 15.1μ due to polymerized carbodiimide was detectable.

At 280° under vacuum, much more change was produced, most obviously in the carbonyl region. Some isocyanurate

was present, but isouronium phenolate structures (6.1-6.4μ, 7.5μ, and 7.9μ) predominated. A definite peak at 15.1μ was present, indicating polymerized carbodiimide. Unionized phenolic groups were also evident (8.1-8.4μ). The weight loss was 24.1%.

Upon thermolysis at 370° under vacuum, the changes were drastic. A little isocyanurate remained (5.8μ), but polymerized carbodiimide was dominant. There was no apparent isouronium phenolate. Neither a phenolate ion C-O stretching peak appeared (at 7.9μ), nor the phenolic stretching peak (8.1-8.4μ), surprisingly. Even more surprisingly, the aryl C-H deformation band at 13.4μ almost disappeared, as in the case of system-ortho-10 (Chapter V). Perhaps the disappearance of both the phenolic and phenolate C-O stretching (7.9-8.4μ) and the aryl C-H deformation (13.4μ) could both be explained by an elimination of water under these extreme conditions, to give a coupling reaction.

$$\text{Ar-OH} + \text{H-Ar}' \longrightarrow \text{Ar-Ar}'$$

At 370° the weight loss was 57.2%.

A single near infrared spectrum of a thermolysate was obtained. The sample made in dimethyl aniline was heated under vacuum at 200° for 24 hr. The only significant change was a decrease in the absorptions from 1990 nm to 2050 nm, corresponding to an increase in the isocyanurate content.

Salicylamine itself was polymerized in two refluxing solvents (bromobenzene and o-dichlorobenzene) to obtain the product infrared spectra. Spectra were taken of the crude product, and of the fractions soluble and insoluble in THF. Dibenzylamine linkages were shown by a strong peak at 9.0-9.1μ, and diarylmethane linkages by a strong peak at 9.6-9.8μ. Because of various strong peaks in these products in the region from 8μ to 10μ, these spectra of polymerized salicylamine showed no resemblance to the various products obtained from ring-01 or polymer-ortho-01. Little hydrolysis occurs in the polymerizations to give salicylamine. This was checked by running two refluxing solvent polymerizations (bromobenzene and o-dichlorobenzene) with Dean-Stark traps to collect water, and fitted with drying tubes to keep out atmospheric water. No water was collected. System-ortho-01 gave rise to much less diarylmethane product than did system-ortho-10 (Chapter V).

A few thermogravimetric analyses were run on some materials of system-ortho-01. Samples were run at 10°/min in nitrogen (Table XXXVII) and in air (Table XXXVIII). Ring-01 was also run in both atmospheres.

In both nitrogen and in air, the TGA scans of ring-01 were almost identical. Below 280°, the TGA scans of polymer-ortho-01 were almost superimposable. From 280° to 480° the

TABLE XXXVII

THERMOGRAVIMETRIC ANALYSES OF SYSTEM-ORTHO-01 MATERIALS UNDER NITROGEN

Compound	Temp at wt loss			Residue (%) at 500°	1st Inflection		2nd Inflection	
	10%	25%	50%		% Vol	Temp	% Vol	Temp
Ring-01	195	220	235	~0[a]	75	245	--	--
Polymer-ortho-01 (bulk 180-185°)	220	245	275	34	66	250	>70	>580
Soluble fraction (bulk 206-209°)	267	307	362	38	44	350	>62	>500
Crosslinked polymer (refluxing quinoline)	240	375	---	60	7	200	>40	>500

a. This sample had a residue of 6% at 300°.

TABLE XXXVIII

THERMOGRAVIMETRIC ANALYSES OF SYSTEM-ORTHO-01 MATERIALS IN AIR

Compound	Temp at wt loss			Residue (%) at 500°	1st Inflection		2nd Inflection	
	10%	25%	50%		% Vol	Temp	% Vol	Temp
Ring-01	200	220	240	~0[a]	90	255	--	--
Polymer-ortho-01 (bulk 180-185°)	215	240	270	33	31	250	84	540
Crosslinked polymer (refluxing quinoline)	217	428	---	57	13	250	>43	>500

a. This sample had a residue of 6% at 300°.

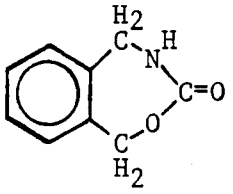
residue of polymer-ortho-01 was greater in air than in nitrogen, but above 500° the residue fell sharply to zero in air. In nitrogen, a 30% residue remained even at 500°. The crosslinked polymers obviously had high stability. In the series of thermolyses in the DSC-1B, it was noted that the residues from 300° to 500° formed highly tenacious films.

CHAPTER VII

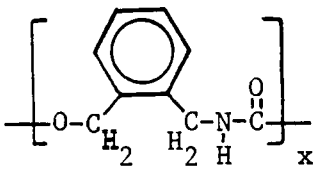
THE SYSTEM-ORTHO-11

A. GENERAL CONSIDERATIONS

The cyclic carbamate ring-11 has the systematic name 4,5-dihydro-2,4-benzoxazepin-3(1H)-one. The corresponding PU, called polymer-ortho-11 herein, has the systematic names poly(oxycarbonyliminomethylene-o-phenylenemethylene) and poly(oxycarbonyliminomethylene-1,2-phenylenemethylene).



ring-11



polymer-ortho-11

The synthesis of ring-11 was first reported by Pifferi and coworkers in 1972 (218). Attempts by this author to repeat their synthesis with phosgene failed. The problems associated with the preparation of the intermediate o-hydroxymethylbenzylamine are detailed in the M.S. thesis, as well as the problem of hydrolysis during the phosgenation step (317, p. 103-107). The thermal conversion of ring-11 to polymer-ortho-11 was therefore not investigated by this author.

B. POLYMER-ORTHO-11 FROM THE CURTIUS REACTION AND CHARACTERIZATION OF THE POLYMERS

Polymer-ortho-11 was successfully made by the Curtius reaction from 3-isochromanone, which was in turn made from indene. This entire sequence is detailed in the M.S. thesis (317, p. 107-117), as well as the characterization of o-hydroxymethylphenylacetyl hydrazide (317, p. 110-112), a new compound. The sequence of reactions starting with 3-isochromanone is more concisely described in the paper by Kinstle and Sepulveda (363).

The yield of polymer-ortho-11 from the hydrazide was typically 70%, and it was the sole carbamate product. Ring-11 could not be separated from the Curtius products by sublimation at 120° and 0.5 mm. A by-product of the Curtius reaction was N,N'-bis(o-hydroxymethylbenzyl)urea, obtained in about 25% yield. The partial characterization of polymer-ortho-11 was given in the M.S. thesis (317, p. 115-117) and in the Kinstle and Sepulveda paper (363). Some additional characterization has been done.

Unlike polymer-ortho-10 and polymer-ortho-01, the infrared spectrum of polymer-ortho-11 did have an amide II band at 6.45μ to 6.6μ, due to a trans conformation of the O and H atoms in the amide moiety. The infrared spectrum of polymer-ortho-11 resembled much more closely the spectrum of

the open-chain model compound N-benzyl-O-benzyl carbamate than that of the benzoxazepinone ring-11 (spectrum kindly supplied by Pifferi). Since the carbamate absorbs at 5.9μ, isocyanurate as a minor component cannot even be detected by the use of its carbonyl at 5.95μ. The isocyanurate methylene absorption at 7.55μ might be used with confidence. Such a small peak is present in the spectra of all samples of polymer-ortho-11. The urea linkage is clearly absent from the polymer samples (6.1-6.2μ).

For every nitrogen atom involved in an isocyanurate or urea moiety, there must be a pendant methylol group. At processing temperatures (less than 120°), it is unlikely that methylol groups would lead to diarylmethane linkages , since the benzene rings are not activated by oxygen or nitrogen substituents. Since the methylol group absorbs strongly at 10μ, its presence would be readily apparent. The spectra of most samples do not show such a peak, and bands due to diarylmethane linkages are also absent. So, either the isocyanurate and urea must be minimal, or the methylol groups react in ways other than forming diarylmethanes.

For those few samples which did show a small peak around 10μ, an attempt was made to quantitate the amount of isocyanurate. Tribenzylisocyanurate and N-benzyl-O-benzyl carbamate were used as model compounds, synthetic mixtures of various mole percentages being constructed. The peak at 7.55μ was

considered characteristic of the isocyanurate structure, while the peak at 8.7-8.8μ was considered characteristic of the carbamate structure (this method is substantially the same as that described in Chapter V). The highest isocyanurate compositions were between 10% and 25%. Because of the considerable vertical scatter in the calibration curve, the range cannot be further narrowed.

Because of the high crystallinity of polymer-ortho-11, it was difficult to obtain a translucent film thick enough to provide a near infrared spectrum. A marginally satisfactory NIR spectrum was obtained (Appendix VI). The spectrum did not closely resemble either that of the model N-benzyl-O-benzyl carbamate or of N-n-propyl-O-ethyl carbamate, but rather appeared to be between the two. The strength of the absorptions from 2295 nm to 2405 nm ruled out the presence of urea, and the strength of the absorptions at 2020 nm and 2045 nm ruled out the isocyanurate presence. The remarkable strength of a peak at 1405 nm might be attributed to pendant hydroxymethyl groups, but it could also be enhanced by water. The strength of this peak remains enigmatic.

The X-ray diffraction pattern was obtained both on a photographic film and on a diffractometer stripchart. Unlike the other ortho-linked polymers, polymer-ortho-11 showed very high crystallinity. The following d-spacings in the crystal lattice were calculated: 6.11 Å, 4.44 Å, 4.17 Å, and 4.08 Å.

The scattering at 2θ = 20° (d_{hkl} = 4.44 Å) was certainly the strongest, while that at 2θ = 14.5° (d_{hkl} = 6.11 Å) was clearly the sharpest.

A sample which was purest in PU was examined by DSC for a melting transition. None could be observed, though much decomposition was apparent by 18°. Though highly crystalline, this polymer appears to decompose before it melts, at a fairly low temperature.

Probably because of its high crystallinity, this polymer was not sufficiently soluble in tetrahydrofuran to give an isopiestic molecular weight (Barger's method). However, it was soluble enough in m-cresol at 30° to give an inherent viscosity, 0.46 at a concentration of 1 g/100 ml, for the sample purest in PU.

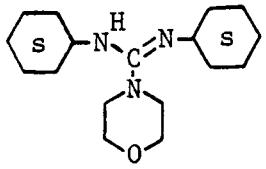
C. THERMAL MODIFICATION OF SYSTEM-ORTHO-11 POLYMERS

In the study of the thermal stability of polymer-ortho-11, the use of the DSC-1B as a heating device was unsatisfactory, because of the facile gas evolution by this polymer. Nevertheless samples were heated for 1 hr at 200° and 250°, with the sample pan rupturing at both temperatures. Though the material showed frothing and liquefaction at 200°, the infrared spectrum of the thermolysis residue showed surprisingly little change. The isocyanurate composition did increase slightly, and the polymerized carbodiimide absorption appeared at 15.1 μ. On

250° thermolysis (1 hr) the isocyanurate and polymerized carbodiimide structures were definitely present, and possibly the diarylmethane linkages (9.6-9.8μ). Certainly the pendant methylol groups were not conspicuous (10.0μ). Though pseudourea groups may be present (6.2μ), their characteristic absorptions would overlap with those of the polymerized carbodiimide structures.

The thermolyses with continuously applied vacuum were more informative, as the pressure buildup by generation of volatile products caused no problems. As low as 150° some change was shown in the infrared spectrum, which can be accounted for by the formation of isocyanurate (7.1μ and 7.55μ) and diarylmethane (8.4μ and 9.6μ) moieties, with essentially no pendant methylol groups. At 200° these changes were a little more pronounced, and the polymerized carbodiimide peak appeared (15.0-15.2μ). The overall changes were drastic, the spectrum having no resemblance to the polymer-ortho-11 or the corresponding urea. The predominant linkages appear to be isocyanurate, polymerized carbodiimide, and diarylmethane. Thermolysis at 370° under vacuum did not give enough residue to make a single KI pellet. The polymer was completely converted to volatile materials. The weight losses in the vacuum thermolyses (24 hr) were 30.4% at 150°, 43.9% at 200°, 87.2% at 280°, and 100% at 370°.

The most informative near infrared data were obtained from the thick film, more transparent than unthermolyzed material, that remained after 200° vacuum thermolysis. The most noticeable changes in the spectrum occurred in the region from 2030 nm to 2200 nm, which underwent a marked increase. This is most easily attributed to the polymerized carbodiimide component, whose closest model compound, the aliphatic guanidine,



absorbs in this region (second overtone of C=N stretching) more strongly than does the carbamate, isocyanurate, or urea (second overtone of the C=O stretching).

The subject of thermolyses is closely related to the conversion of polymer to ring -- it is the reverse of ring-opening polymerization. This reverse conversion should be facile if a true equilibrium is involved. Below 230° only liquid volatile products could be obtained by pyrolysis in a sublimator under vacuum. At 250° a small amount of white solid deposited on the sublimator cold finger, but a DSC scan of this deposit did not show any melting endotherm near 161°, the reported melting point of the ring. The infrared spectrum

showed a small carbonyl peak at 5.95μ, but not the cyclic carbamate peaks at 8.0μ and 9.5μ. Some isocyanurate in this material was likely, but a much larger second component was not identified. Thermolysis at 280° produced an almost instantaneous sublimate with an off-white color, whose infrared spectrum was almost identical to that of the previously mentioned sublimate. No ring-11 was detected among the products of any thermolysis.

Thermogravimetric analyses were made of three polymers in this system-ortho-11. The TGA scan depended strongly on heat treatment. A sample produced directly from the Curtius reaction showed rather low stability. Almost identical TGA curves were produced in nitrogen and in air (Table XXXIX). Such large early weight losses are most likely due to decarboxylations of some sort, combined with elimination of water to form diarylmethanes or new benzyl-nitrogen linkages. The second large weight losses beginning at 250° must be due to cleavage of the benzyl-heteroatom bonds to give volatile products. A negligible fraction remained at 400°.

Treatment at 130° in a sublimator under vacuum conferred some thermal stability, but only up to about 250°. Two such samples were subjected to thermogravimetric analyses under N_2 (as usual at 10°/min), and the resulting curves were almost

TABLE XXXIX

THERMOGRAVIMETRIC ANALYSES OF POLYMER-ORTHO-11

Atmosphere	Temp at wt loss			Residue (%)	1st Inflection		2nd Inflection	
	10%	25%	50%	at 500°	% Vol	Temp	% Vol	Temp
nitrogen	137	167	280	2	25	167	67	300
air	137	167	260	6	30	175	74	305

superimposable (Table XL). Only one region of rapid change (one inflection point) was apparent for these "heat-treated" samples.

Polymer-ortho-11 is clearly the least thermally stable of all the polymers examined, probably because of having two relatively labile benzyl-heteroatom linkages in each repeat unit, neither of which readily leads to diarylmethane linkages with relatively unactivated aromatic rings.

D. EXPERIMENTAL; X-RAY DIFFRACTION

Only two relevant experimental procedures were not discussed in previous chapters, the X-ray diffractions using photographic film and using a goniometer with a strip-chart recorder.

The sample was prepared by pulverizing 200 mg polymer, then compacting this powder at 12,000 psi in a KBr-pellet die (~1 mm diameter). This pelletized solid sample was the ideal size for both X-ray diffraction techniques.

The X-ray photographs were taken with a Philips Electronics diffractometer (Mt. Vernon, N.Y.), using a nickel filter. One hr exposures were made, at 15 milliamps and 35 kilovolts. The film used was Eastman Kodak "No-Screen" medical X-ray film (NS54T, 8.3 x 10.2 cm).

The charts giving the intensity of the diffracted X-rays versus the value of 2θ were obtained with a General Electric

TABLE XL

THERMOGRAVIMETRIC ANALYSES OF HEAT TREATED SAMPLES OF POLYMER-ORTHO-11

Temp at wt loss			Residue (%)	Residue (%)	Residue (%)	Inflection	
10%	25%	50%	at 350°	at 400°	at 500°	% Vol	Temp
273	287	297	4	2.5	2	40	292
278	288	297	4	2.5	2	40	292

XRD5 diffractometer, coupled with an Ortec counting circuit. The values of 2θ, and hence the d-spacings, were obtained much more easily with this device. The photographic method was used as a quick screening test, to determine which samples were crystalline.

The values of the d-spacings were calculated by the Bragg relationship (364, p. 414),

$$\lambda = 2d_{hkl}\sin\theta$$

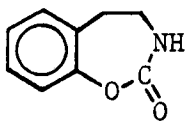
The values of 2θ so obtained with these instruments for the sample of poly(pentamethylene urethane) agreed with the literature values, thereby showing the present equipment and methods to be trustworthy (26, 181, 183).

CHAPTER VIII

THE SYSTEM-ORTHO-02

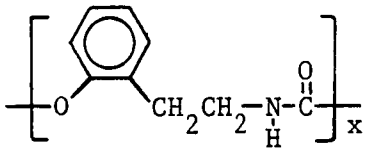
A. GENERAL CONSIDERATIONS

The cyclic carbamate which would be called ring-02 or 4,5-dihydro-1,3-benzoxazepin-2(3H)-one is unknown.



ring-02

The corresponding PU, polymer-ortho-02, seems not to have been reported before, although closely related Curtius reactions have been reported (365). This polymer has the systematic name poly(oxycarbonyliminoethylene-o-phenylene) or poly(oxycarbonylimino-1,2-ethanediyl-1,2-phenylene).

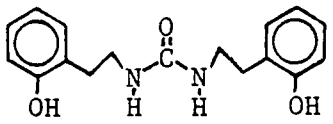


polymer-ortho-02

B. POLYMER-ORTHO-02 FROM THE CURTIUS REACTION AND CHARACTERIZATION OF THE POLYMERS

The preparation of this polymer from the commercially available hydrocoumarin by the Curtius procedure, was described in detail in the M.S. thesis (317, p. 118-122). None of the corresponding cyclic carbamate ring-02 could be

isolated from the product mixture, although the urea-ortho-02

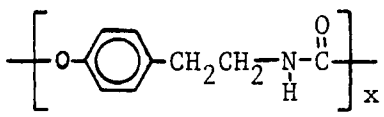


was produced in about 8% yield (317, p. 121-122). The infrared spectra of the urea and the PU were reported in the M.S. thesis (317, p. 123, 124). However the polymer was not characterized further in that work.

An elemental analysis of the product showed 66.61% C, 5.69% H, and 8.36% N (calc 66.24% C, 5.56% H, 8.58% N).

Further comments on the infrared spectrum of polymer-ortho-02 are in order, especially concerning some noncarbamate linkages. The carbonyl peak has a shoulder at 5.7μ, suggesting the presence of ester linkages. The urea is definitely present in minor amount, showing the triad of peaks at 6.1μ, 6.2μ, and 6.3μ (also the order of increasing intensity). The isocyanurate is probable, due to a peak at 7.5μ and shoulders at 7.05μ and 13.05μ. The pendant groups are obvious by the absorption at 8.1μ.

Overall the spectrum bears much resemblance to that of another polymer prepared by the Curtius reaction and discussed in Chapter X, the corresponding para-linked polymer-para-02



The spectrum of the model compound N-phenethyl-O-phenyl-carbamate (Chapter II) shows several differences from that of polymer-ortho-02, but these differences can all be ascribed to the urea, isocyanurate, and phenolic groups, and to the ortho-disubstitution in the polymer.

An attempt was made to quantitate the amount of isocyanurate, by the infrared method discussed in Chapter V. The isocyanurate-characteristic peak at 7.5μ and the carbamate-characteristic peak at 8.2μ were used for calibration purposes, with the model compounds triethyl isocyanurate and N-phenethyl-O-phenyl carbamate. The isocyanurate composition appeared not to be above 25%, usually slightly above 10%. The same calibration curve was used for polymer-ortho-02 and polymer-para-02.

Just as with the polymer-ortho-11 (Chapter VII), the open-chain carbamate N-phenethyl-O-phenyl carbamate is a very poor model compound for polymer-ortho-02 in near infrared spectroscopy. Much better models are ring-01 and the corresponding para-linked polymer, polymer-para-02, discussed in Chapter X. Apparently these better models have about the same kinds of aliphatic and aromatic hydrogens, and more similar numbers of each kind, as well as other similar structural features. In the "combination region" from 2150 nm to 2750 nm, the open-chain model carbamates have been

consistently poor models for the PU's in near infrared spectroscopy, for whatever reason.

A most noticeable feature of the two near infrared spectra of polymer-ortho-02 (Appendix VII) is the weakness of the phenolic absorption around 1490 nm, which means a low concentration of urea and isocyanurate groups. The N-H absorption appears around 1490 nm, but is broadened in these solid-state systems by hydrogen bonding. In other regions the spectrum is quite similar to that of ring-01, for probably the same reasons.

X-ray diffraction of various samples of this polymer showed its completely amorphous nature, in marked contrast to its highly crystalline isomers, polymer-ortho-11 and polymer-para-02.

The glass-transition probably occurs over too broad a range to be detected with the DSC-1B. A melting transition was of course not observed, but the DSC scans did show the onset of decomposition in nitrogen at 220-230°.

C. THERMAL MODIFICATIONS OF SYSTEM-ORTHO-02 POLYMERS

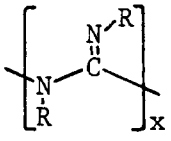
Polymer-ortho-02 could not be produced from the corresponding heterocycle, because the cyclic carbamate has never been made. However it was natural to attempt the reverse reaction, the conversion of polymer to cyclic carbamate by applying heat. On vacuum thermolysis in a sublimator up to

160°, only liquid products could be obtained. Below 120° the small amount of distillate collected appeared to be dihydrocoumarin by infrared. Above 150° the predominant distillate appeared to be dihydrobenzofuran, also by infrared analysis alone. Above 200° a small amount of solid was collected, which consisted in part of isocyanurate. Other components would not be separated or even qualitatively identified. The off-white sublimate obtained at 280° contained even less isocyanurate. At no temperature was a carbamate apparent in the distillate or sublimate IR spectra. Attempts by this author to displace the (possible) equilibrium from polymer to ring were unsuccessful.

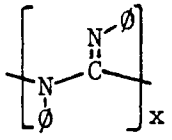
Samples of polymer-ortho-02 were heated for 1 hr at 200°, 250°, and 300° with the DSC-1B instrument, in a nitrogen atmosphere. At 200°, the only noticeable change was an increase in the amount of urea linkage (6.1μ, 6.2μ, and 6.3μ). At 250°, some carbamate appeared to be still present, surprisingly (5.8μ, 8.2μ, and 8.6μ). However the isouronium phenolate structure seemed present in large amount (6.1-6.4μ, 7.3-7.4μ, 7.9μ and 9.0μ). The polymerized carbodiimide peak was noticeable at 15.0-15.2μ. The isocyanurate presence (5.95μ, 7.05μ, and 7.5μ) appeared unchanged. At 300°, the carbamate and urea compositions were negligible, but isocyanurate linkages were definitely present. The isouronium phenolate structure appeared dominant, while the polymerized

carbodiimide structure (11.6μ and 15.0-15.2μ) increased.

A series of vacuum thermolyses was also run at 200°, 280°, and 370° for 24 hr each. At 200° considerable carbamate remained but isocyanurate and urea were predominant. Polymerized carbodiimide was present in minor amount (11.6μ and 15.1μ). At 280° isocyanurate was present, but polymerized carbodiimide appeared dominant (6.1-6.4μ, 11.6μ, and 15.0-15.2μ). Some of the phenolic hydroxyls were definitely ionized, judging from the absorption at 7.9μ, so that some guanidine moieties in the polymerized carbodiimide were really guanidinium ions. The model for N-alkyl polymerized carbodiimide



was obtained by pyrolyzing dicyclohexyl carbodiimide in refluxing paraffin at 370°. This model polymer had absorptions surprisingly similar to those of polymerized diphenyl carbodiimide,



especially the conspicuous peaks at 11.6μ, 13.2-13.5μ, and 15.0-15.2μ.

The residue obtained by thermolysis of polymer-ortho-02 at 370° consisted almost entirely of polymerized carbodiimide. This residue is by far the hardest and toughest of all the thermolysis residues of this study.

The various residues of vacuum thermolysis (in terms of weight percent based on starting material), were 94.1% at 200°, 47.6% at 280°, and 6% at 370°.

A few thermogravimetric analyses of polymer-ortho-02 were made, both in nitrogen and in air (Table XLI), at a heating rate of 10°/min. All of these various curves were quite similar, for different Curtius reaction products. All of these polymers showed only one inflection point, or region of rapid change. The volatilization of the polymer is almost complete at 500°, but the small residue (around 10%) is expected to remain up to extremely high temperatures.

Isopiestic molecular weights and viscosities were determined for two samples of polymer-ortho-02, and turned out to be rather low. The procedure for obtaining both samples analyzed was the same as that described in the M.S. thesis (317, p. 120-122). As usual, the inherent viscosities were determined in m-cresol at 30°, at a concentration of 1 g/100 ml (Table XLII).

TABLE XLI

THERMOGRAVIMETRIC ANALYSES OF POLYMER-ORTHO-02

Atmosphere	Temp at wt loss			Residue (%) at 400°	Residue (%) at 500°	Inflection	
	10%	25%	50%			% Vol	Temp
nitrogen	262	288	320	15	11	54	325
nitrogen	245	269	296	10	8	46	291
nitrogen	257	283	312	10	8	40	300
air	253	278	308	17	14	40	295

TABLE XLII

ISOPIESTIC MOLECULAR WEIGHTS AND INHERENT VISCOSITIES

OF POLYMER-ORTHO-02

Molecular Weight	Standard Deviation	Inherent Viscosity[a]
1320	310	0.31
1190	270	0.26

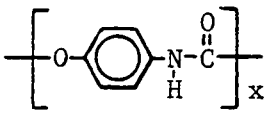
a. Determined in m-cresol at 30°, at a concentration of 1 g per 100 ml.

CHAPTER IX

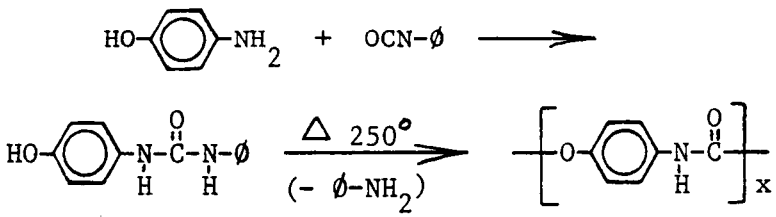
THE SYSTEM-PARA-00

A. GENERAL CONSIDERATIONS

The systematic names of this PU are poly(oxycarbonyl-imino-p-phenylene) or poly(oxycarbonylimino-1,4-phenylene).



This polymer was first reported by Stoermer (127), who in fact prepared it by the same Curtius procedure used in this study. As characterization, Stoermer reported only the structural formula, with the comment "viel höheren molekulargewicht." Illari et al. (187) made this polymer by reacting p-aminophenol with phenylisocyanate to form p-hydroxycarbanilide, and pyrolyzing this compound to eliminate aniline.

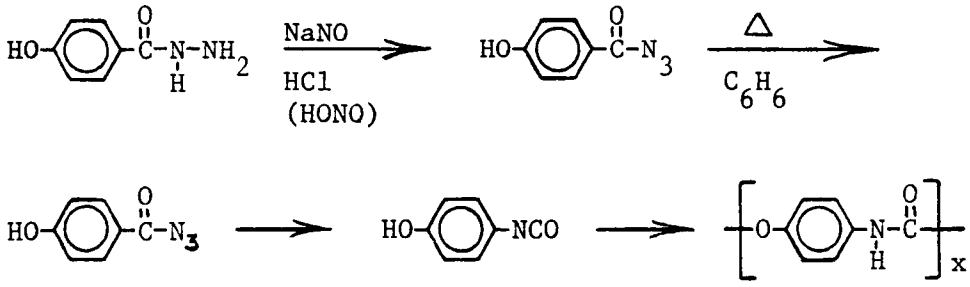


Illari et al. reported a melting point of 240° and a good elemental analysis.

Ulrich (124) reported the preparation of polymer-para-00 from p-hydroxyphenyl isocyanate, which he claimed was stable in solution. Experimental details were omitted, but these claims were referenced to a patent (125). According to this patent, p-isocyanatophenol was obtained by treating p-aminophenol with phosgene in a "highly aprotic solvent." It was claimed that the monomer p-hydroxyphenyl isocyanate distills around 80° at 0.05 mm. However, it seems never to have been proved that this compound exists in monomer form in solution, although its existence in the vapor state is highly plausible.

B. POLYMER-PARA-00 FROM THE CURTIUS REACTION AND CHARACTERIZATION OF THE POLYMERS

The preparation of polymer-para-00 from the commercially available (Aldrich) p-hydroxybenzoyl hydrazide is described in the experimental part. Three runs were made, with yields of 80.4%, 84.7%, and 88.3%.



An elemental analysis of the product showed 61.92% C, 3.88% H, 10.19% N (calc 62.22% C, 3.73% H, 10.37% N).

The infrared spectrum of the polymeric material is given in Table XLIII, with the likely assignments. The soluble and insoluble polymer fractions (solvent THF) had almost identical infrared spectra, except that the isocyanurate peaks were slightly stronger in the insoluble fractions.

Quantitative estimation of isocyanurate was attempted with the method discussed previously (Chapter V) using the isocyanurate peak at 7.1μ and the carbamate peak at 8.3-8.4μ. The model compounds were triphenylisocyanurate and phenyl carbanilate. For the THF-soluble fractions of polymer-para-00, the mole fraction of isocyanurate was between 10% and 15%, and for the THF-insoluble fractions the mole fraction of isocyanurate was between 15% and 25%.

The near infrared spectrum of this polymer bore a rather good resemblance overall to that of phenyl carbanilate. Some peaks between 2300 nm and 2040 nm are stronger in the polymer spectrum, and may be accounted for by certain combinations of strong peaks, given in Table XLIV.

The relative weakness of the absorption around 2010 nm due to the carbonyl second overtone is probably due to the presence of isocyanurate linkages in the polymer.

The N-H first overtone around 1500 nm is broadened due to hydrogen bonding, the bonded form occurring at 1505 nm and the free form near 1480 nm. The rather large absorption between 1400 nm and 1440 nm is due to phenolic OH groups in the

TABLE XLIII

INFRARED ABSORPTIONS OF POLYMER-PARA-00

Wavelength (μ)	Intensity	Assignment
3.05	s	N-H stretching
3.25	sh	aryl C-H stretching
5.75	sh	carbamate C=O stretching
5.85	vs	carbamate, isocyanurate C=O stretching
5.95	sh	isocyanurate C=O stretching
6.1	m	urea C=O stretching
6.2	s	in-plane aromatic ring stretching
6.5	vs	amide II
6.65	vs	in-plane aromatic ring stretching
6.8-7.0	m	in-plane aromatic ring stretching
7.1	s	isocyanurate ring stretching
7.6	m	N-associated vibration
8.1-8.2	vs	amide III
8.35-8.45	vs	amide III
8.55	sh	ester moiety =C-O stretching
9.0	m	N-Ø stretching
9.3-9.4	w	N-associated vibration
9.9	s	O-Ø stretching
10.45	w	aryl C-H in-plane bending
10.7	w	aryl C-H out-of-plane bending
10.8	w	aryl C-H out-of-plane bending
11.75	w	aryl C-H out-of-plane bending
11.9-12.0	m	aryl C-H out-of-plane bending
13.1	w	O=C-O out-of-plane bending
13.3	w	O=C-O out-of-plane bending
13.5	w	O=C-O out-of-plane bending
14.4	w	N-H out-of-plane bending
14.8	m	N-H out-of-plane bending
15.2	m	N-H out-of-plane bending

TABLE XLIV

PROMINENT NEAR INFRARED ASSIGNMENTS OF POLYMER-PARA-00

Wavelength (nm)	Frequency (cm^{-1})	Probable Assignments
2270	4405	2x1720+1010 and 3300+1170[a]
2180	4587	2x1720+1170[a]
2150	4651	2x1720+1220[a]
2060	4854	2x1700+1420 (isocyanurate)
2050	4878	2x1720+1450 and 3300+1620[a]
2040	4901	2x1720+1500 and 3300+1620[a]

a. The assignments for these carbamate frequencies may be found in Table XLIII; examples of their μ equivalents are: 3.05μ = 3300 cm^{-1}, 5.85μ = 1720 cm^{-1}, 6.2μ = 1620 cm^{-1}, 6.9μ = 1450 cm^{-1}, 7.1μ = 1420 cm^{-1}, 8.2μ = 1220 cm^{-1}, 8.5μ = 1170 cm^{-1}, 9.9μ = 1010 cm^{-1}.

polymer, arising from either isocyanurate or urea linkages.

Because the two melting points reported for this polymer, 240° (187) and >300° (124), are not consistent, it was desired to check the melting transition by DSC. However the scan made with the DSC-1B machine showed only a gradually increasing loss of volatiles, first noticeable around 125°. No melting transition was seen at all, although "sublimation" was severe at 250°. This interesting behavior merits later discussion, since a large polymer molecule cannot really sublime.

An x-ray diffraction powder pattern showed high crystallinity. The crystalline reflections lay at the angles of 2θ = 20.7°, 22.5°, 23°, 27.5°, and 40°. The corresponding d-spacings are the following: 4.29 Å, 3.95 Å, 3.87 Å, and 2.25 Å.

Due to its high crystallinity, polymer-para-00 was almost insoluble in THF, so an isopiestic MW measurement could not be made. It was also not soluble enough in m-cresol to give a concentration of 1 g/100 ml, to permit a comparison with the other viscometries of this study. At a concentration of 0.2 g/100 ml in m-cresol (30°), the inherent viscosity was 0.073.

C. THERMAL MODIFICATION OF POLYMER-PARA-00

The behavior of polymer-para-00 on heating is highly unusual among polymers, and in fact severely strains the volatility criterion of the polymeric state.

The polymer was first heated at 200°, 250°, and 300° in a DSC-1B machine, under nitrogen for 1 hr. Heating at 200° gave a rather small residue, but this residue showed little change from the original polymer. The small changes were increases at 6.1μ, 6.2μ, and 7.9μ due to isouronium phenolate structures, and increases at 11.6μ (shoulder) and 15.2μ due to polymerized carbodiimide structures. The isocyanurate composition did not noticeably increase. At 250°, the amount of carbamate decreased further, shown by the decline of peaks at 5.8-5.9μ, 8.5μ, and 9.0μ, but much carbamate was still present. Some isocyanurate and polymerized carbodiimide were present, but isouronium phenolate accounted for most of the residue.

At 300° polymerized carbodiimide and isouronium phenolate accounted for all of the residue. This residue is extremely hard and tough, very difficult to pelletize with KI.

The usual series of vacuum thermolyses was done at 200°, 280°, and 370°. At 200° only a slight amount of carbamate remained. The small residue contained mainly isocyanurate and isouronium phenolate, though some polymerized carbodiimide was definitely present. At 280° isocyanurate and polymerized carbodiimide account for all of the residue, while at 370° only polymerized carbodiimide is present.

Thermogravimetric analyses of polymer-para-00 were made in nitrogen and in air, at the usual scanning rate of 10°/min.

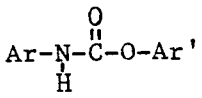
The results are given in Table XLV. Only one region of rapid change (inflection point) is shown. The only really stable residual product is polymerized carbodiimide, which would probably graphitize before it volatilized away.

The residual weights for the three vacuum thermolyses were the following (24 hr heating); 49.5% at 200°, 27.3% at 280°, and 12.5% at 370°.

The sublimate which formed on the cooler part of the thermolysis tube, a yellowish-white solid, was shown by the infrared spectra to be polymer-ortho-00. This polymer contained a slight amount of isocyanurate (less than 10%).

It is safe to say that the thermal behavior of polymer-para-00 resembles that of no other PU, with the possible exception of polymer-meta-00 (which was not studied in the present work).

It was mentioned in the introduction that phenyl carbanilates



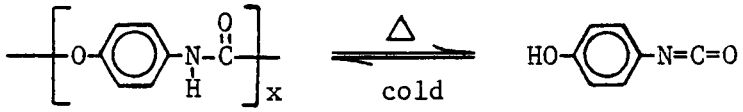
undergo very facile thermal dissociation into their isocyanate and hydroxyl components. Polymer-para-00 is of course such a compound. It should come as no surprise that heating polymer-para-00 causes its dissociation to the volatile

TABLE XLV

THERMOGRAVIMETRIC ANALYSES OF POLYMER-PARA-00

Atmosphere	Temp at wt loss			Residue (%) at 350°	Residue (%) at 500°	Inflection	
	10%	25%	50%			% Vol	Temp
nitrogen	197	248	285	20	15	47	280
air	200	258	297	25	19	52	300

compound p-hydroxyphenyl isocyanate which reforms the polymer on a cooler surface.



It is ironic that this study which relies so heavily on the polymer nonvolatility criterion would encounter one of the few conceivable examples where the criterion is dubious.

D. EXPERIMENTAL DETAILS

The experimental procedure given here in detail for the preparation of polymer-para-00 is very similar to the Curtius reactions reported by Lindemann and Schultheis (128) and those given in the M.S. thesis (317) and in the Kinstle and Sepulveda paper (363). The reaction was undoubtedly performed in a very similar way by Stoermer (127), but was not reported in detail. The modification involving extraction of the azide into benzene was adapted from P.A.S. Smith (122).

The starting material p-hydroxybenzoyl hydrazide was purchased from Aldrich Chemical Co. (Milwaukee, Wis).

The hydrazide (5.07 g or 0.0333 mole) was stirred with 18.4 ml 2N HCl, and the suspension was filtered and washed with 40 ml water (the insoluble material is largely the diacylhydrazide contaminant). The filtrate (with washings) was placed

in a tall, very narrow 2 l beaker (basal area about 50 cm^2), equipped with magnetic stirring and surrounded by an ice bath. Benzene (800 ml) was layered over the aqueous solution. While maintaining the temperature at 5°, the layers were vigorously stirred as a solution of 2.6 g of sodium nitrite in 20 ml of water was added over a five minute period. The benzene layer was decanted, the aqueous layer was extracted with three 100 ml portions of benzene, and the combined benzene solutions were dried over $MgSO_4$. The solution of azide in benzene was filtered into a 2 l round bottom flask equipped with a reflux condenser, thermometer, magnetic stirrer, and hot water bath. The filter cake of $MgSO_4$ was washed with 100 ml dry benzene; this benzene was also added to the flask.

While stirring, the temperature of the azide-benzene solution was quickly raised to 70°, whereupon vigorous evolution of nitrogen commenced. The temperature of the solution was raised to 80° and maintained for 2 hr.

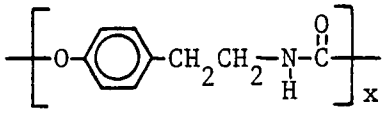
The suspension of product in benzene was transferred to a beaker and evaporated to dryness. It was necessary to scrape the sides of the flask, as much of the product had adhered to the glass surfaces. Nonpolymeric volatile materials were removed by heating in a vacuum oven at 100° for 4 days. Three runs were made on this scale, the yields being 3.62 g, 3.81 g, and 3.97 g (80.4%, 84.7%, and 88.3% respectively). Some polymer was undoubtedly lost during the vacuum-oven treatment.

CHAPTER X

THE SYSTEM-PARA-02

A. GENERAL CONSIDERATIONS

The polymer designated here as polymer-para-02 has the standard names poly(oxycarbonyliminoethylene-p-phenylene) and poly(oxycarbonylimino-1,2-ethanediyl-1,4-phenylene).



Although it is derived in a straightforward way from the commercially available (Aldrich) para-hydroxyphenylpropionyl hydrazide, the polymer appears not to have been previously reported.

B. POLYMER-PARA-02 FROM THE CURTIUS REACTION AND CHARACTERIZATION OF THE POLYMERS

The Curtius reaction to prepare this polymer was performed in the same way as for polymer-para-00. For a run starting with 5 g hydrazide (0.0278 mole), 15.3 ml of 2 N HCl and 2.14 g $NaNO_2$ (0.0308 mole) were used. Proportional quantities of the above reagents were used for each of three other runs starting with 1.80 g hydrazide, for which the yields of the polymer were 1.25 g, 1.27 g, and 1.28 g (76.7%, 77.9%, and 78.5% respectively).

Since this polymer did not show the troublesome behavior of reversible thermal dissociation, a higher temperature could be used to remove volatile materials by distillation or sublimation (120° at ~1 mm).

The elemental analysis of the yellow solid product showed 65.92% C, 5.79% H, 8.27% N (calc 66.24% C, 5.56% H, 8.58% N).

The infrared spectrum of this polymer showed the absorptions given in Table XLVI. The overall spectrum of polymer-para-02 bears a good resemblance to the spectra of the model compound N-phenethyl-O-phenyl carbamate and of the polymer-ortho-02 (treated in Chapter VIII).

The amount of isocyanurate was estimated by the method discussed in Chapter V, using the model compounds N-phenethyl-O-phenyl carbamate and triethylisocyanurate. The carbamate peak at 7.95μ and the isocyanurate peak at 7.05μ were used as the characteristic peaks. The isocyanurate was estimated to be present in less than 12 mole percent.

Because of the high crystallinity of polymer-para-02, it was difficult to get near infrared spectra from it. Four rather unsatisfactory spectra were obtained (Appendix IX). Although the combination region (2600-2150 nm) of the near infrared spectra resembled those of polymer-ortho-02 more than that of the model compound N-phenethyl-O-phenyl carbamate, the deviations from the model compound spectrum were less drastic than those of the ortho-linked polymer.

TABLE XLVI

INFRARED ABSORPTIONS OF POLYMER-PARA-02

Wavelength (μ)	Intensity	Assignment
3.05	s	N-H stretching
3.3	m	aromatic C-H stretching
3.45	m	aliphatic C-H stretching
5.75	s, sh	carbamate C=O stretching
5.8-5.85	vs	carbamate and isocyanurate C=O stretching
5.95	m, sh	isocyanurate C=O stretching
6.05	m	urea C=O stretching
6.2	m	urea C=O stretching (H-bonded)
6.25	m, sh	aromatic ring in-plane stretching
6.5	vs	amide II
6.65	vs	aromatic ring in-plane stretching
6.9	m	aromatic ring in-plane stretching
7.05	m	isocyanurate ring vibration
7.3	m	aliphatic CH_2 bending
7.65	m	isocyanurate ring vibration
7.75	m	N-associated vibration
7.85	m	N-associated vibration
7.95	s	amide III band
8.15-8.25	vs	amide III band
8.35	vs	C-O stretching of ester moiety
8.55	s	N-R stretching
9.05	m	N-associated vibration
9.35-9.6	w	N-associated vibration
9.8	m	O-aryl stretching
10.1-10.25	m	aromatic C-H in-plane bending
10.45	w	aromatic C-H out-of-plane bending
11.8-12.2	m	para linkage (2 adjacent H)
13.1-13.2	w	out-of-plane deformation of ester group
14.0-15.5	m	N-H out-of-plane bending

Overall the near infrared spectrum is about what would be expected of a homopolyurethane. No characteristic urea or isocyanurate intensities are apparent, nor are phenolic OH intensities. The N-H first overtone is somewhat broadened around 1475 nm, which is expected due to H-bonding.

Rather than improving the transparency of the sample, heating under vacuum at 160° for 24 hr lowers the quality of the near infrared spectrum. A spectrum so obtained is given in Appendix IX.

No melting transition was seen by DSC. Instead a decomposition region began around 225°.

X-ray diffraction showed the polymer to be highly crystalline. The angles (2θ) of the diffracted beam were found to be 20°, 21°41', 25°30', and 28°30', corresponding to d-spacings of 4.44 Å, 4.10 Å, 3.49 Å, and 3.13 Å, respectively. The sharpest and most intense reflection was that 20°. The broadest and weakest (hardly detectable) was that at 28°30'.

The high crystallinity of polymer-para-02 did not allow sufficient solubility in tetrahydrofuran to obtain isopiestic molecular weights. Inherent viscosities were obtained for two samples (m-cresol, 30°), but at a concentration of only 0.5 g/100 ml; these values were 0.175 and 0.158. A solubility of 1 g/100 ml in m-cresol could not be obtained.

C. THERMAL MODIFICATION OF POLYMER-PARA-02

Thermolysis under nitrogen was carried out in the heating compartment of a DSC-1B machine, for a period of 1 hr at 200° and 250°. Heating at 200 increased slightly the amount of isocyanurate (5.95μ, 7.05μ, and 7.5μ). The largest change was the formation of isouronium phenolate (6.1-6.5μ, 7.4-7.6μ, 7.9μ, and 8.7μ). Another minor change was the formation of polymerized carbodiimide (11.6μ and 15.0-15.2μ). Much carbamate clearly remained. At 250°, all carbamate linkages were converted to isocyanurate, isouronium phenolate, and polymerized carbodiimide, the isouronium phenolate appearing to predominate.

Another more informative series of thermolyses were run for 24 hr under continuous vacuum, at 200°, 280°, and 370°. At 200° under vacuum, only a small amount of carbamate remained. Some isocyanurate and polymerized carbodiimide were present in the residue, but the main component was isouronium phenolate. At 280° under vacuum, isocyanurate and isouronium phenolate were minor components, and polymerized carbodiimide predominated. At 370° under vacuum, polymerized carbodiimide was the only apparent component in the residue.

The following weight percentages of starting material remained on each of three vacuum thermolyses: 79.2% at 200° 33.8% at 280°, and 9.4% at 370°.

As in the cases of the thermolyses of polymer-ortho-02 and polymer-para-00, the vacuum thermolysis products of polymer-para-02 at 280° and 370° were extremely hard and tough. These materials could not be removed from the walls of a pyrex vessel without removing glass slivers. The adhesion was also extreme on silica surfaces and aluminum surfaces.

Thermogravimetric analyses were made of this polymer, in nitrogen and in air, at a scanning rate of 10°/min. This polymer showed only one region of rapid change (inflection point), after which little residue is left. The curves were quite similar in nitrogen and in air (Table XLVII).

TABLE XLVII

THERMOGRAVIMETRIC ANALYSES OF POLYMER-PARA-02

Atmosphere	Temp at wt loss			Residue (%) at 400°	Residue (%) at 500°	Inflection	
	10%	25%	50%			% Vol	Temp
nitrogen	247	283	317	17	14	48	314
air	247	283	323	27	21	45	315

CHAPTER XI

POLY(PENTAMETHYLENE URETHANE)

A. SYNTHESIS AND CHARACTERIZATION

Poly(pentamethylene urethane) is by far the best known of the AB-type PU's. The many ways it has been prepared have been reviewed in the introduction. Even the use of the Curtius reaction to prepare this polymer was reported long ago by Iwakura et al. (133, 134).

The polymer was prepared in the present work mainly to obtain its near and midrange infrared spectra, and to investigate its thermolyses. These properties of the wholly aliphatic poly (pentamethylene urethane) should then be compared with the corresponding properties of the various phenylene-linked PU's, to provide a more comprehensive picture of structure-property relationships in AB-type PU's.

The preparation of ϵ-hydroxycaproyl hydrazide was performed according to the method of Allen and Magder (366). This hydrazide was converted by the normal Curtius procedure to the ϵ-hydroxycaproyl azide and thence to the poly(pentamethylene urethane) (133, 134). It was purified by Iwakura's method of washing with hot methanol.

The product so obtained was examined by DSC. A melting transition was observed from 140° to 145° (reported mp 148-153°) (134).

A wide-angle X-ray diffraction pattern was made of this polymer, giving diffraction angles (2θ) of 20.2°, 24.5°, and 40° (weak and broad). These angles 2θ correspond to d-spacings of 4.39 Å, 3.63 Å, and 2.25 Å, respectively. These data correspond with that of Nagura et al. (181), providing a check on the diffractometer angles used for other polymers of this study.

A carefully prepared and purified sample gave an inherent viscosity of 0.29 in m-cresol at 30° (conc = 0.5g/100 ml). The corresponding value determined by Iwakura et al. (134, p.214) was 0.38.

Due to its high crystallinity, the sample was not sufficiently soluble in tetrahydrofuran to give an isopiestic molecular weight.

Having been satisfied that the sample was reasonably polymeric and that it conformed with previous data, it was further characterized and used for comparisons.

The first task was reporting and assigning the various absorptions. Iwakura et al. (134, p. 221) reproduced the entire infrared spectrum (polymer in nujol) ot poly(pentamethylene urethane), but did not attempt most assignments. His spectrum agrees substantially with the one obtained in this study.

Phillips and Argabright (132) attempted a few assignments:

3.076 μ	N-H stretching
5.90 μ	C=O stretching

6.43μ	amide II
7.97μ	O=C-O moiety
9.37μ	=C-O-C moiety

Using the currently obtained infrared spectrum of poly-(pentamethylene urethane) in a potassium iodide pellet, the wavelengths are reported and assignments attempted in Table XLVIII.

The estimation of mole percent in these polymers was attempted, using the model compounds N-n-propyl-O-ethyl carbamate and triethylisocyanurate. The most characteristic isocyanurate absorption, that at 7.05μ, was not a discrete peak in the various samples, but rather a shoulder on the 6.95μ peak. By comparing the height and contour of this shoulder with the height of the 7.9μ carbamate peak (amide III band), the amount of isocyanurate in most samples could be bracketed between 12.5% and 75% (averaging 30 mole percent as an estimate), assuming the transferability of peak positions, heights, and shapes from the synthetic mixtures of model compounds to the polymers of interest. Because of the additional assumptions concerning nonvariability of peak shapes and contours, this estimate is even less reliable than the previous ones.

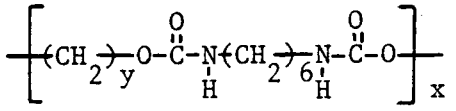
Because of the high crystallinity of poly(pentamethylene urethane), it was difficult to get a good near infrared spectrum, because sufficient thickness and sufficient transparency are mutually exclusive.

TABLE XLVIII

INFRARED ABSORPTIONS OF POLY(PENTAMETHYLENE URETHANE)

Wavelength (μ)	Intensity	Assignment
3.00	vs	N-H stretching
3.40	s	aliphatic C-H stretching
3.45	s	aliphatic C-H stretching
3.50	s	aliphatic C-H stretching
5.75	m, sh	carbamate C=O stretching
5.85	s, sh	carbamate C=O stretching
5.90	vs	carbamate C=O stretching
5.95	vs	carbamate, isocyanurate C=O stretching
6.05	s, sh	isocyanurate C=O stretching
6.1-6.2	m	urea C=O stretching
6.4	m, sh	amide II band
6.5-6.55	s	amide II band
6.6	m, sh	amide II band
6.8	m	methylene scissoring
6.85	m	methylene scissoring
6.95	m	methylene scissoring
7.05	m	isocyanurate ring vibration
7.15	m	isocyanurate ring vibration
7.30	m	methylene wagging
7.70	m	N-associated peak
7.90	s	amide III band
8.15	m	amide III band
8.25-8.4	w	ester moiety C-O stretching
8.65-8.95	m	N-R stretching
9.4-9.5	w	N-associated band
9.65-9.95	m	O-R stretching
10.5	w, sh	O-R stretching
12.75-12.9	w	ester moiety out-of-plane bending isocyanurate ring vibration
13.7	w	polymethylene rocking
14.8	w, sh	amide moiety out-of-plane bending
15.05	m	amide moiety out-of-plane bending
15.5-16	m	amide moiety out-of-plane bending

This particular near infrared spectrum is probably the most interesting one of all those studied, because a connection may be made with previous work. Gudim and Klimenko (300) reported the near-infrared spectrum of the PU's of the generalized structure,



y = 3 to 10 inclusive

Although this is an AABB-type PU, its near infrared spectrum should be very similar th that of poly(pentamethylene urethane), because the same bond types are present in both structures.

Unfortunately it is very difficult to discern relative intensities from the data of Gudim and Klimenko (300). The intensities in this author's spectrum are assigned relative to the strongest peak at 2290 mm, given a value of 10. Those assignments suggested by Gudim and Klimenko are starred and several additional assignments are attempted in Table XLIX.

The near infrared spectrum of poly(pentamethylene urethane) appears to be very much like the spectra of the aliphatic AABB-type PU's studied by Gudim and Klimenko (300). It is also remarkably similar in both absorption wavelengths and intensities to the spectrum of the model compound N-n-propyl-O-ethyl carbamate (solution spectrum in CCl_4). The main difference between the spectrum of the polymer and that of the model carbamate is broadening of the first overtone of the N-H stretching band around 1480 nm, due to hydrogen bonding in the solid film.

TABLE XLIX

NEAR INFRARED ABSORPTIONS OF POLY(PENTAMETHYLENE URETHANE)

Wavelength (nm)	Frequency (cm^{-1})	Relative Intensity	Assignments
2545	3929	4.8	N-H combination (3300 + 600)
2515	3976	6.0	N-H combination (3300 + 680)
2489	4018	5.8	N-H combination (3330 + 700)
2455	4073	6.1	urethane combination (2x1700 + 680)
2440	4098	6.5	urethane combination (2x1700 + 680)
2400	4167	6.3	ester moiety combination (2x1700 + 780)
2380	4202	7.4	methylene combination (2900 + 1370)
2350	4255	6.9	methylene combination (2900 + 1470)
2340	4274	6.7	methylene combination (2900 + 1470)
2305	4338	7.2	* CH combination (2315 nm) methylene combination (2950 + 1470)
2290	4367	10.0	methylene combination (2950 + 1470)
2273	4399	7.9	characteristic of polymethylene chain
2183	4581	3.7	* C=O stretching + urethane group vibration (2188 nm) (2x1720 + 1140 or 3300 + 1270)
2130	4695	1.4	urethane combination (2x1700 + 1270)
2075	4819	1.1	urethane combination (3300 + 1540)
2055	4866	3.8	* NH stretching + deformation (2062 nm) urethane combination (3330 + 1540)
1988	5030	0.8	* not assigned C=O second overtone (3x1700)
1935	5168	0.3	* OH stretching + deformation (1923 nm) urethane combination (3550 + 1650)

TABLE XLIX (Continued)

Wavelength (nm)	Frequency (cm^{-1})	Relative Intensity	Assignments
1835	5450	0.2	
1810	5525	0.3	
1790-1770	5587-5650	0.4	first overtone C-H stretching
1750	5714	0.8	* CH stretching (1751 nm)
1714	5834	1.3	* CH stretching (1724 nm)
1705	5865	1.0	first overtone C-H stretching
1600-1575	6250-6349	0.1	first overtone N-H stretching
1536	6510	0.4	first overtone H-bound N-H stretching
1500-1480	6667-6757	0.2	* NH stretching (1506 nm) first overtone free N-H stretching
1420-1390	7042-7194	0.1	first overtone free O-H stretching
1220	8197	0.1	* OCH stretching (1235 nm) first overtone C-H stretching (next to O)
1210-1180	8264-8475	0.15	first overtone C-H stretching

a. Numbers in parentheses have units of cm^{-1}, unless otherwise noted.

Another difference is the presence of the hydroxyl group in the polymer, which shows a broad low-intensity band from 1390 nm to 1420 nm, the first overtone of the O-H stretching. The second overtone of the carbonyl stretching is also weaker in the polymer (at 2012 nm and 2030 nm), undoubtedly due to the isocyanurate linkages.

B. THERMAL MODIFICATION OF POLY(PENTAMETHYLENE URETHANE)

Samples of poly(pentamethylene urethane) were thermolyzed at 200° and 250° in the heating compartment of a DSC-1B machine, for 1 hr under nitrogen. On thermolysis at 200°, the chief result was the conversion of some carbamate to isourea (6.15μ), isocyanurate (6.0μ, 7.05μ, and 7.15μ), and polymerized carbodiimide (6.2μ, 11.6μ, and 15.1μ), though most of the carbamate linkages remained. The pendant hydroxyl group was clearly present (9.4-9.65μ). On thermolysis at 250°, some carbamate still appeared, though the amide II band decreased considerably relative to the 5.95μ carbonyl peak. Isocyanurate was clearly present to a large extent (7.05μ and 7.15μ. Isourea (6.15μ) and polymerized carbodiimide (11.6μ and 15.0-15.2μ) were also present, in lesser amounts. Surprisingly, the residue at 250° was a viscous liquid.

Another series of thermolyses was made under continuous vacuum for 24 hr at 200°, 280°, and 370°. The residue at 200° showed little change from the original PU, though the amount

of isocyanurate (7.05μ and 7.15μ) obviously increased. A small amount of polymerized carbodiimide (11.6μ and 15.0-15.2μ) also appeared. The absorption of the pendant hydroxyl groups did not increase significantly.

At 280°, the residue was a viscous liquid, unlike the solids obtained for all the other polymers of this study. The infrared spectrum showed surprisingly little change from the one obtained for the 200° thermolysate. All remaining carbamate was converted largely to isourea. Isocyanurate and polymerized carbodiimide were present. The most obvious change was a large relative increase in the absorption at 6.75-7.0μ. The pendant hydroxyl group was conspicuous (2.9-3.0μ and 9.4-9.5μ).

At 370°, the infrared spectrum of the thermolysis residue was essentially the same, though the liquid product was even less viscous than the one obtained at 280°.

The sample thermolyzed at 200° under vacuum formed a translucent solid film, amenable to near infrared analysis. This spectrum did show fairly drastic changes from the unthermolyzed sample. In the region 2310-2500 nm, the spectrum showed a broad flat absorption of high intensity, quite unlike the many discrete peaks in the unthermolyzed sample. This would indicate an increasing aliphatic content of the residue, at the expense of the heteroatom (O or N) content. This increase in the aliphatic content is also shown by the strength of the absorptions from 1705 nm to 1825 nm.

The first overtone region of the H-bound and free N-H stretching (1480 nm to 1600 nm) also shows greater strength in the thermolysate, affirming the presence of nitrogen. In contrast the OH overtone peaks from 1390 nm to 1420 nm are nearly unchanged. These results only indicate the loss of CO_2 from the original linkages, but do not clearly indicate the main product formed, guanidine, isourea, or polymerized carbodiimide. A serious problem remains to explain the abnormal strength of the absorptions from 1987 nm to 2170 nm in the 200° thermolysate. Certainly the dialkyl urea or trialkylisocyanurate linkages would not account for this intensity. Unfortunately model compounds for the aliphatic-substituted pseudourea or polymerized carbodiimide linkages are not yet available for near-infrared spectroscopy.

Residual weights in the vacuum thermolyses were obtained, as for the previous polymers: 96.1% at 200°, 80.5% at 280°, and 0.07% at 370°. The polymer did not appreciably decompose at 280°, but was almost completely volatilized at 370°. This undoubtedly meant that the heteroatoms O and N were split from the polymethylene chain to give olefins, between 280° and 370°, which volatilized rather than undergoing addition polymerization.

Thermogravimetric analyses were obtained in nitrogen and in air. The usual data were extracted from these two TGA scans, given in Table L. Thus, although this aliphatic PU shows high

TABLE L

THERMOGRAVIMETRIC ANALYSES OF POLY(PENTAMETHYLENE URETHANE)

Atmosphere	Temp at wt loss			Residue (%) at 400°	Residue (%) at 500°	Inflection	
	10%	25%	50%			% Vol	Temp
nitrogen	323	343	355	>1.5	>1	60	359
air	313	338	356	6	3	60	360

thermal stability, it forms only a small amount of thermolysis residue above 360°, and almost all of its thermolysis residues appear to be of little practical use.

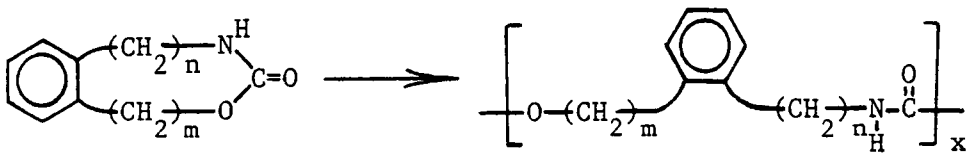
CHAPTER XII

COMPARISONS AND CONTRASTS AMONG THE AB-TYPE POLYURETHANES

This chapter will attempt to compare and contrast the more important properties of the eight polymers discussed in earlier chapters. The name used in this work, the AB-type PU repeat unit, and the corresponding chapter are given in Table LI.

The first five ortho-substituted PU's were those of principal interest in this work. The two para-substituted PU's and the aliphatic PU were of interest mainly as extreme cases, whose properties would help put the ortho series of polymers in their proper perspective.

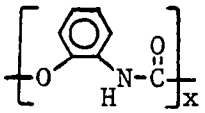
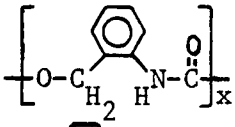
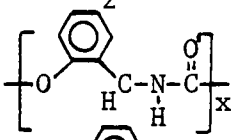
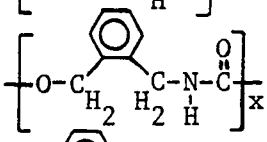
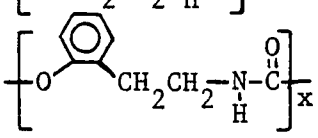
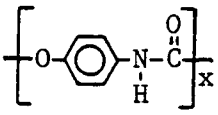
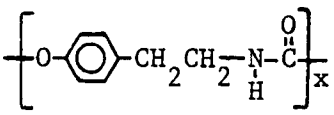
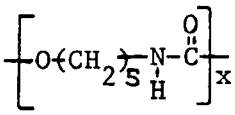
One of the aims of this work was to find which of the ortho-substituted PU's could be made by ring-opening polymerization of the corresponding cyclic carbamate.



This author was able to make only polymer-ortho-10 and polymer-ortho-01 in this manner. The attempted preparation of polymer-ortho-00 by this method failed. Some of the polymers of system-ortho-00 might be copolymers with a few linkages of the open-chain carbamate type, but clearly no homopolymer

TABLE LI

POLYURETHANES TREATED IN THIS WORK

Repeat Unit	Name	Chapter
	polymer-ortho-00	IV
	polymer-ortho-10	V
	polymer-ortho-01	VI
	polymer-ortho-11	VII
	polymer-ortho-02	VIII
	polymer-para-00	IX
	polymer-para-02	X
	poly(pentamethylene urethane)	XI

with this repeat unit was made, and for sound theoretical reasons it is very doubtful that polymer-ortho-00 will ever be made. The method could not be tried for polymer-ortho-11 and polymer-ortho-02, because of the unavailability of the corresponding heterocycles.

Another main objective was to find out which of the above AB-type PU's could be made by the Curtius reaction, in reasonably homopolymeric form. All of these polymers but the first could be prepared by the Curtius reaction, although the yield was low in some cases. The cases of low yield were polymer-ortho-10 and polymer-ortho-01, for which the ratio of yields of cyclic carbamate to linear PU was about 10:1 (disregarding the various byproducts such as ureas and lactones).

Among the characterization techniques, the midrange infrared proved the most useful by far. In order to arrive at reasonable assignments of the infrared absorptions of these polymers, it was necessary to make a systematic study of the infrared spectra of cyclic carbamates and open-chain model carbamates. It was found that the midrange infrared spectra of polymer-ortho-10 and of polymer-ortho-01 matched more closely the spectra of the corresponding rings (ring-10 and ring-01, respectively) than the spectra of the open-chain model carbamates (N-phenyl-O-benzyl carbamate and N-benzyl-O-phenyl carbamate, respectively). In particular, the expected amide II band of these polymers around 6.5μ was absent or rather

weak, indicating a cisoid conformation between the carbonyl and N-H groups in the polymer. In all other cases, the spectrum of the polymer had a close correspondence with the spectrum of the corresponding open-chain model compound. In particular, polymer-ortho-11 did not give a spectrum similar to that of ring-11, but it did have a spectrum similar to that of the model compound N-benzyl-O-benzyl carbamate. The spectra of polymer-ortho-02 and of polymer-para-02 bore a close correspondence with each other and with the model compound N-phenethyl-O-phenyl carbamate. All PU's besides the two mentioned exceptions (polymer-ortho-10 and polymer-ortho-01) showed an amide II band around 6.5μ. Qualitative detection of major or minor components in a sample by infrared spectroscopy is feasible due to the high information content of a midrange infrared spectrum. However, precise quantitative estimation of mole percentages is extremely difficult; accuracy in determining isocyanurate mole percentages cannot be better than $\pm$8-9%.

Near infrared spectroscopy is also a method that potentially gives a great amount of information. Because the general field of near infrared spectroscopy is still in its infancy, there is a lack of assignments and intensity correlations, so it yielded less information in this study than the midrange infrared. However, in distinguishing among the various hydrogenic vibrations, it was much more useful than the midrange

infrared. It was particularly useful in probing the fate of the hydroxyl moiety derived from the carbamate linkage for each polymer system.

In this study, differential scanning calorimetry (using the Perkin-Elmer DSC-1B) proved to be an unproductive characterization technique. No glass transition temperatures were detected for these polymers, and the melting temperature appeared to exceed the onset of decomposition. Thermomechanical analysis (TMA) equipment would have been highly desirable to detect the onset of flow or softening, and possibly to describe the softening in quantitative terms. Although DSC showed a vague onset of decomposition or volatilization ("T_d" or "decomposition temperature"), thermogravimetric analysis (TGA) was a much better tool to describe decomposition, and will be discussed later.

Opacity and frangibility provided good indications of crystallinity, but this was shown conclusively by X-ray wide-angle diffraction. In every case, the crystalline polymers were light colored (off-white) and had a tendency to powder, while the amorphous polymers were amber or brown and formed rigid films. The crystalline polymers were polymer-ortho-11, polymer-para-00, polymer-para-02, and poly(pentamethylene urethane), and these had exceptionally little amorphous character. All the other polymers showed no detectable crystallinity. While deformation might enhance their tendency to

crystallize, no orientation studies were carried out.

Inherent viscosities were used in these studies, largely due to heavy precedent. Meta-cresol is the traditional solvent for viscometry of PU's and was so used in this work, although the solute is not recoverable. Tetrahydrofuran evaporated too easily and was too hygroscopic. Viscometry showed that the AB-type PU's of this study were not very high polymers. The relatively low MW's probably reflect the ease of forming isocyanurate, urea, and carbodiimide linkages -- all of which upset the stoichiometric balance of the hydroxyl and isocyanate groups.

Isopiestic determinations of number-average MW, using aqueous tetrahydrofuran as solvent, were feasible only with the amorphous polymers. These MW's roughly paralleled the inherent viscosities.

One of the main incentives for studying these AB-type PU's was to examine their thermal behavior, especially the linkages produced in the residues of thermolysis or pyrolysis. For reasons detailed in the introduction, these residues are expected to be different from those derived from AABB-type PU's. Among the thermolysis products of this study, no infrared evidence was found for the existence of such linkages as allophanate, biuret, carbamoyl allophanate, triuret, and uretidinedione. Isocyanurate, guanidine, pseudourea, and polymerized carbodiimide were very likely major components of the various

residues, and these have been previously shown to be pyrolysis products in some systems of the AABB-type. Unreacted carbodiimides were definitely not found, which may be a feature of the AB-type PU's of this study. Other linkages which were found in some of these polymer systems may also be features peculiar to the present systems. These included diarylmethanes, and phenolate salts of guanidines and pseudoureas. A possibility that should not be overlooked is the formation of phenolate salts of polymerized carbodiimides, which do contain many guanidine moieties. However these very high temperature thermolysis products are so difficult to pulverize, and the particles in the KI pellets are so large, that much information is lost in the resulting infrared spectrum due to peak broadening. It would be difficult to confirm the presence of phenolate salts of polymerized carbodiimides in these residues.

Thermogravimetric analyses (TGA) gave useful quantitative data about the amount of residue remaining at various temperatures. These TGA scans were run at least once under nitrogen, and some samples were also run in air. Those samples analyzed in both atmospheres showed very similar pairs of TGA curves as a general rule. All three cyclic carbamates, ring-00, ring-10, and ring-01, showed a single mode of volatilization, which was rapid and complete. These TGA curves were perfectly sigmoid, showing no nonvolatile intermediates. In both atmospheres, the regions of most rapid change (inflection points) were all

below 260°. Some polymers of this study also showed the sudden onset of a single, rapid, and complete volatilization. One was the wholly aliphatic material, poly(pentamethylene urethane), whose inflection point at 360° corresponds to the most rapid and most complete volatilization in all the polymers studied. Another similar case was the polymer with two benzylic heteroatoms, polymer-ortho-11 (with heat treatment), which gave an inflection point around 295°. Polymers which showed almost the same behavior were polymer-ortho-02 and polymer-para-02, which were alike in so many other ways. For both these materials, the volatilization was much more gradual, spread over about 200°, and was not quite complete (residues at 500° were about 9% for the ortho polymer and about 14% for the para polymer). In both cases the inflection point lay around 300-325°. Polymer-para-00 showed behavior a little farther removed from the cyclic carbamates. This polymer might be said to show a single mode of decomposition, because the residue at 500° was only 15% (in air about 19%). However the decomposition process occurred over a temperature range of about 300° (100° to 400°), the inflection point being centered at about 280°. There is thus a smooth gradation in thermolysis behavior from the most volatile ring (ring-00) to the most refractory polymer (residue IV-3 of system-ortho-00 or "polymerized ring-00").

The aliphatic AB-type PU behaved much like aliphatic AABB-type PU's on thermolysis. For the aromatic AB-type PU's,

there is only one system which can be directly compared with the corresponding AABB-type polymer. This is polymer-ortho-10, which can be compared with the addition polymer formed with p-phenylene diisocyanate and p-xylylene-α,α'-diol (discussed in the Introduction, Chapter I). In the latter case, the diol molecule volatilizes on thermolysis, while in the former case the benzyl alcohol moiety forms diarylmethane linkages. This is the main difference in the behaviors of these polymers, and mechanistically it is a large difference.

Only a few of the possible AB-type PU's have been synthesized up to 1977; in fact, this statement is still true if the discussion is limited to only the phenylene-linked AB-type PU's. For a homologous series in which at most two methylene units may lie between the benzene ring and either heteroatom (0 to 4 total methylenes), there are twenty-seven (3x3x3) possible polymer systems: (a) three substitution patterns (ortho, meta, or para), (b) three modes of connecting the nitrogen atom to the benzene ring (aniline, benzylamine, or phenethylamine), and (c) three modes of connecting the oxygen atom to the benzene ring (phenol, benzyl alcohol, or phenethyl alcohol). Including the work reported here, only nine of these possible systems have been studied at all, and only two (polymer-meta-00 and polymer-para-00) have been studied in depth by several authors. The seven phenylene-linked systems of this study show a wide variety of behaviors. It would be a very worthwhile

goal to obtain a unified picture of the behavior of all twenty-seven above-mentioned phenylene-linked AB-type PU's.

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APPENDIXES

APPENDIX I

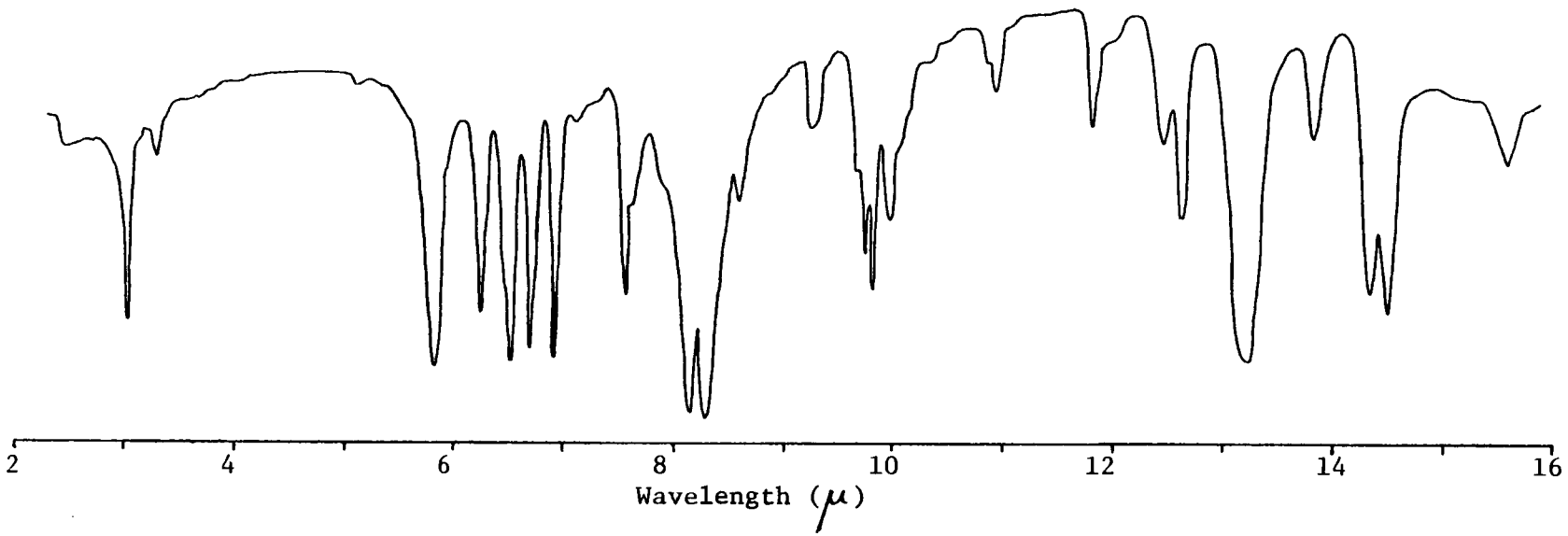


Figure 1. Midrange infrared spectrum of N-phenyl-O-phenyl carbamate.

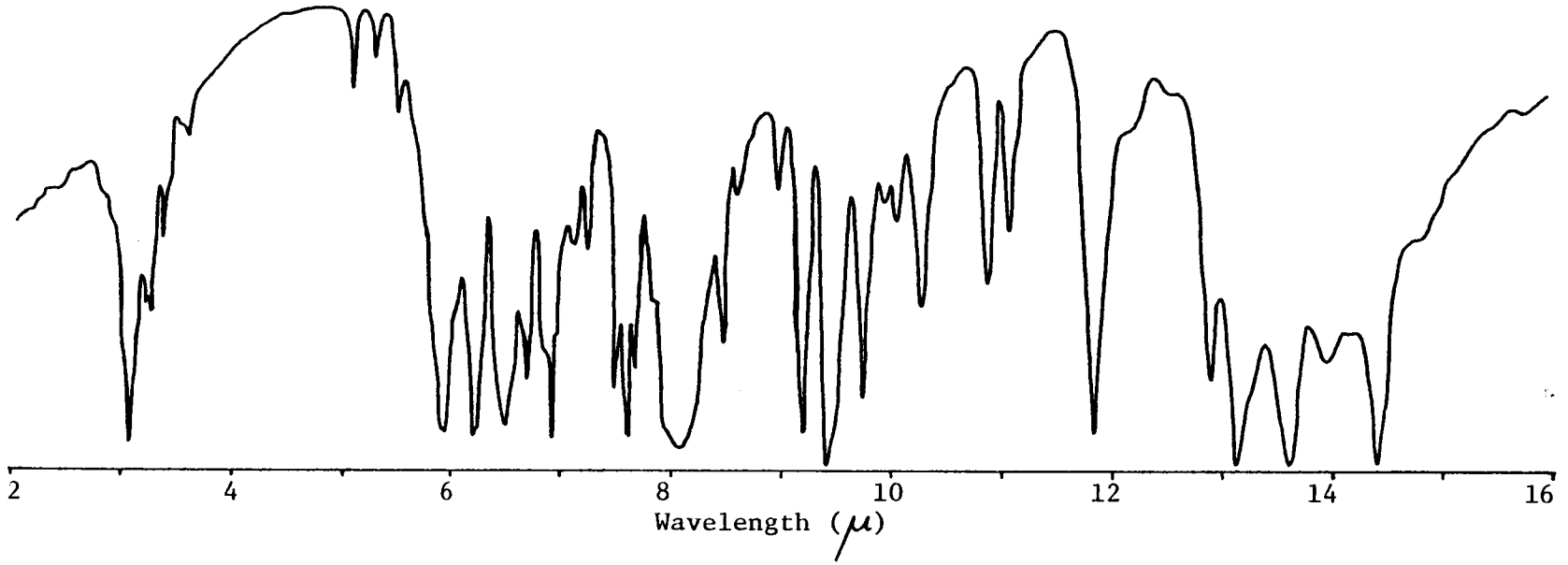


Figure 2. Midrange infrared spectrum of N-phenyl-O-benzyl carbamate.

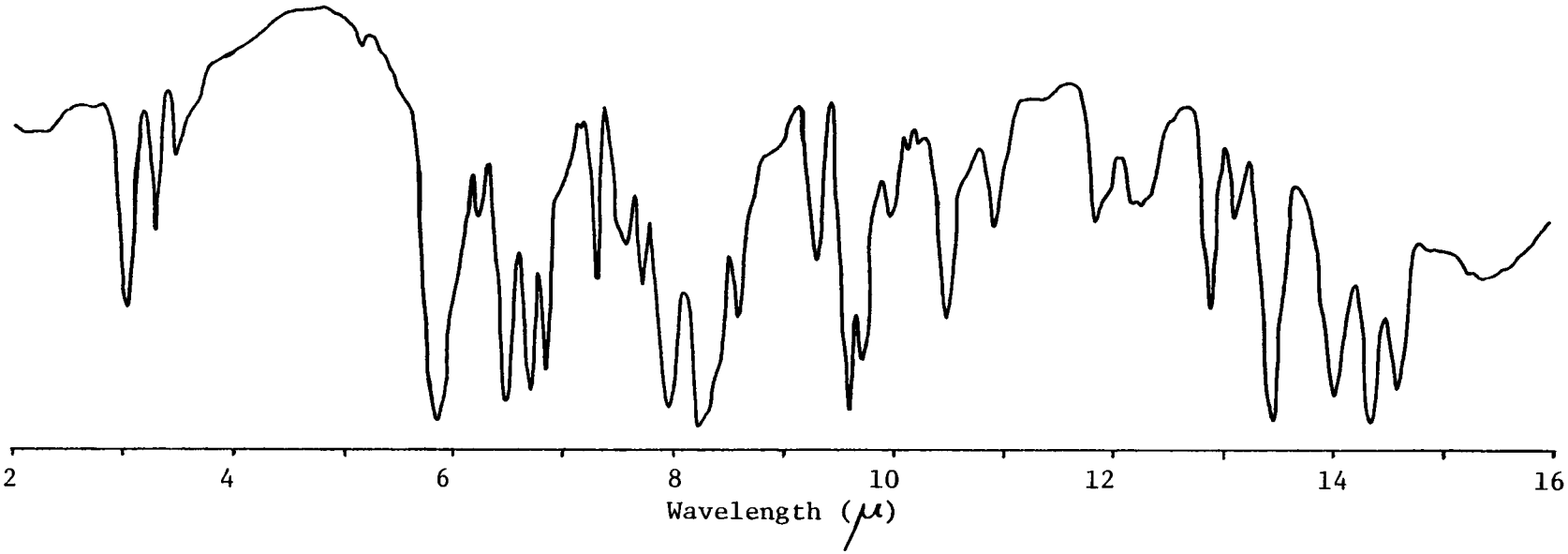


Figure 3. Midrange infrared spectrum of N-benzyl-O-phenyl carbamate.

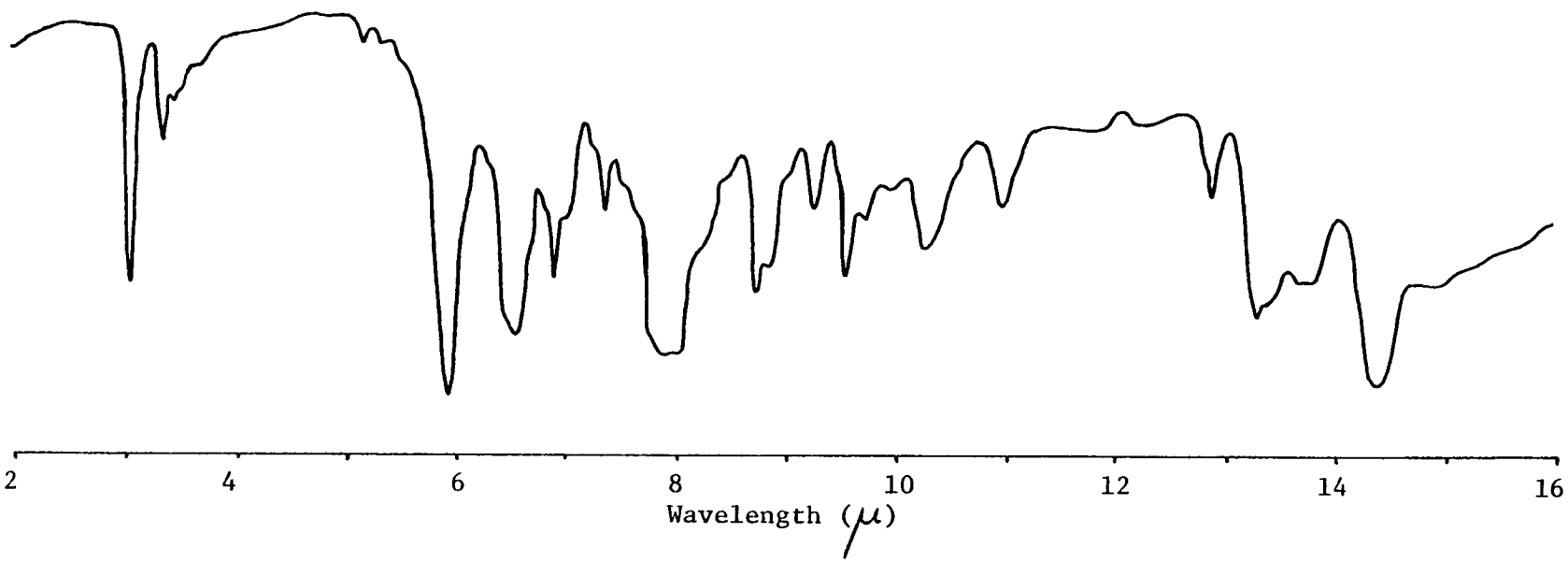


Figure 4. Midrange infrared spectrum of N-benzyl-O-benzyl carbamate.

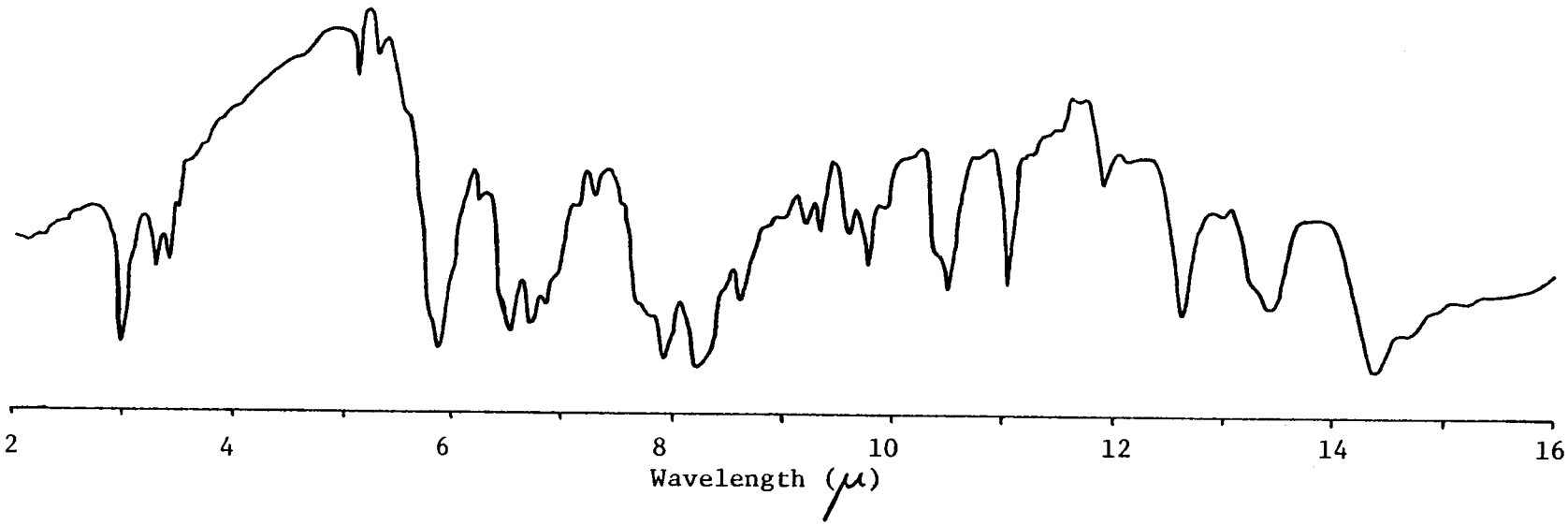


Figure 5. Midrange infrared spectrum of N-phenethyl-O-phenyl carbamate.

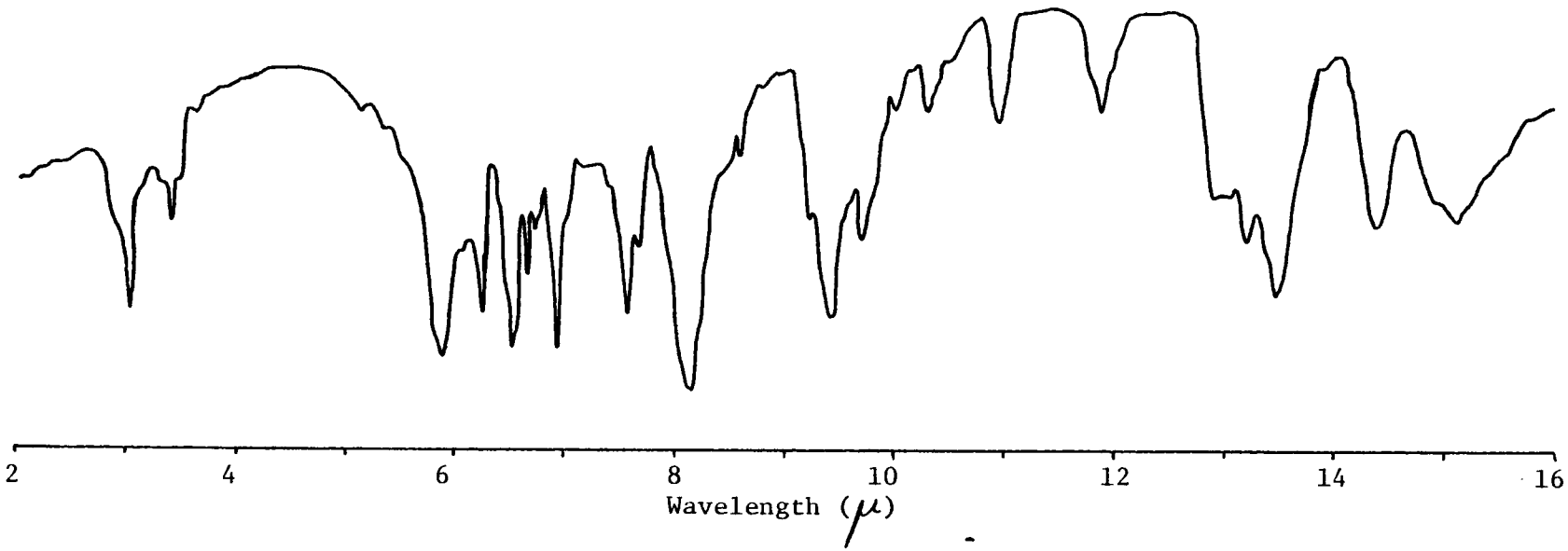


Figure 6. Midrange infrared spectrum of N-phenyl-O-n-propyl carbamate.

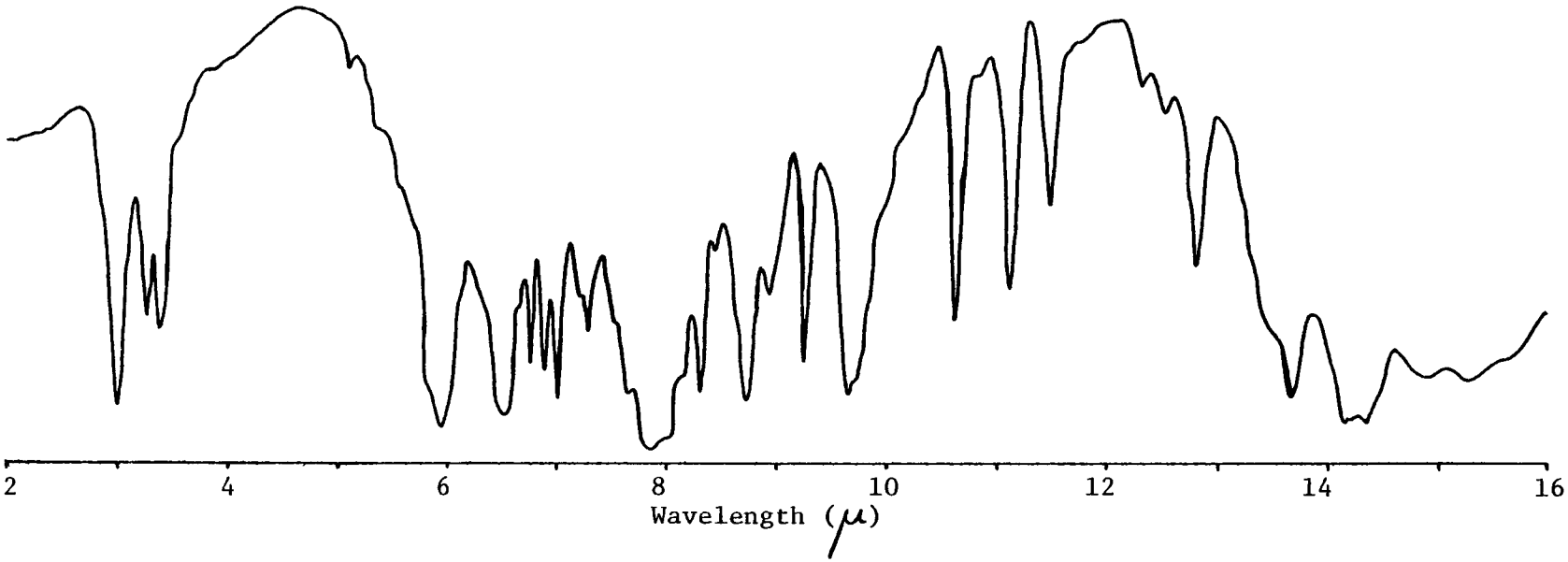


Figure 7. Midrange infrared spectrum of N-benzyl-O-ethyl carbamate.

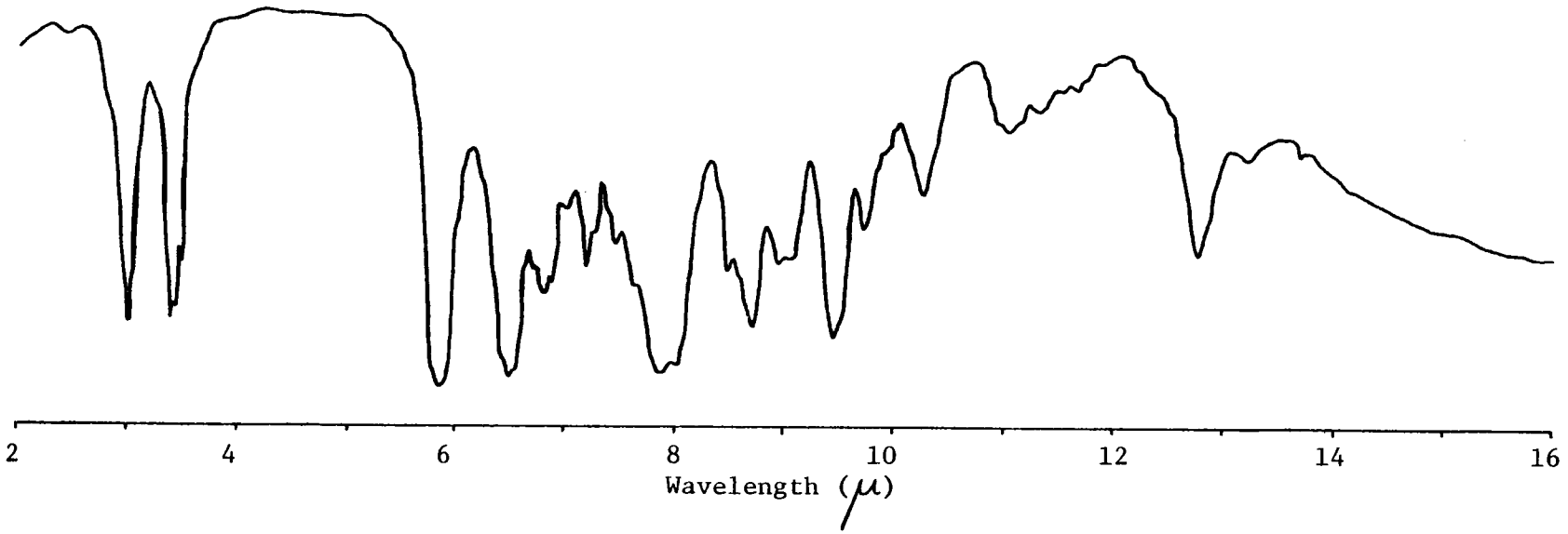


Figure 8. Midrange infrared spectrum of N-n-propyl-O-ethyl carbamate.

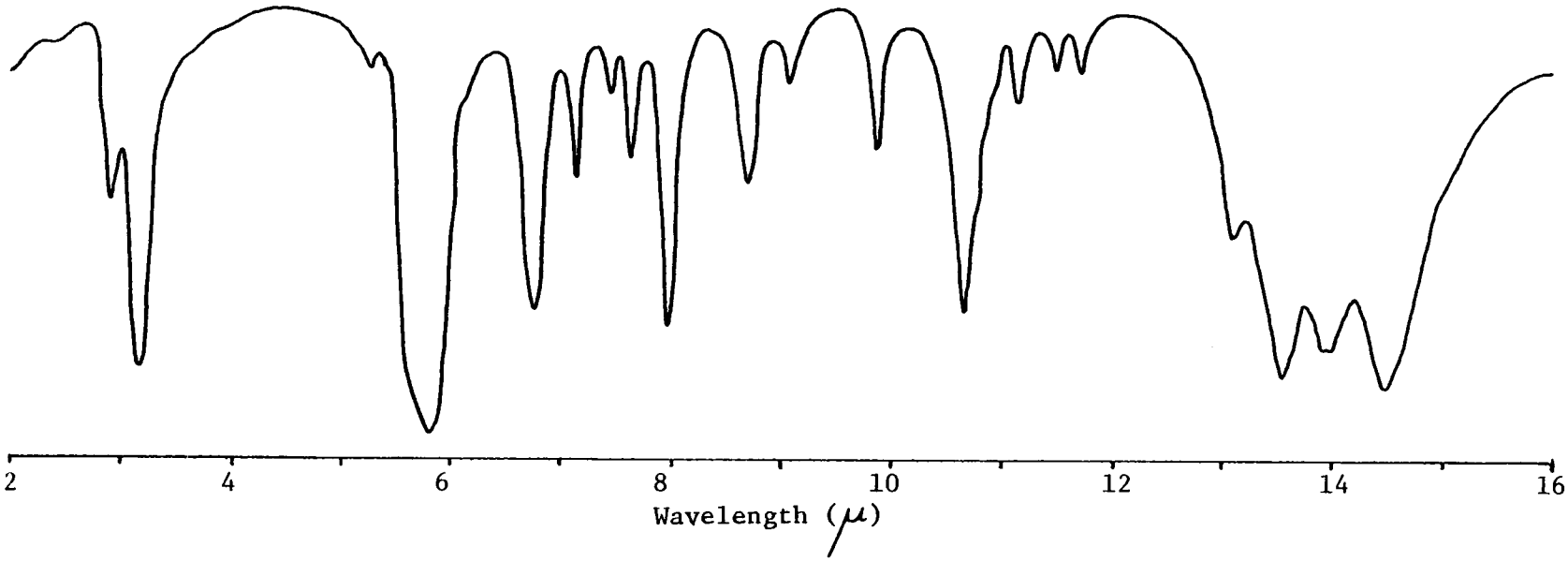


Figure 9. Midrange infrared spectrum of ring-00.

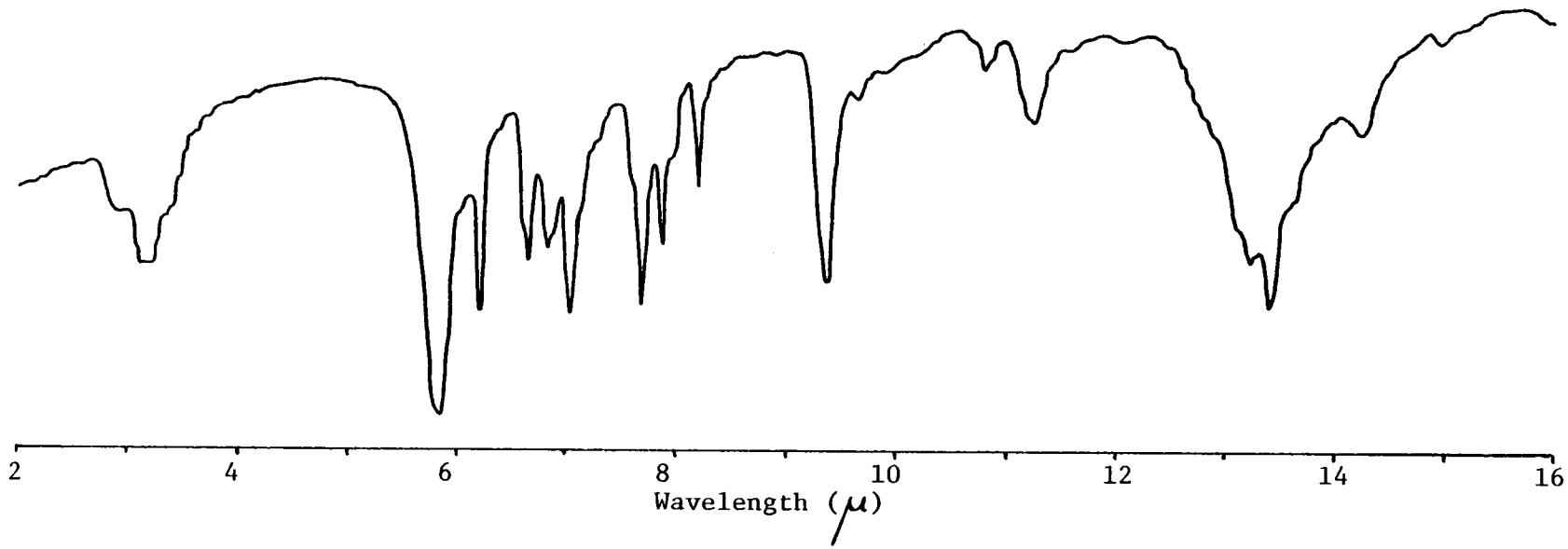


Figure 10. Midrange infrared spectrum of ring-10.

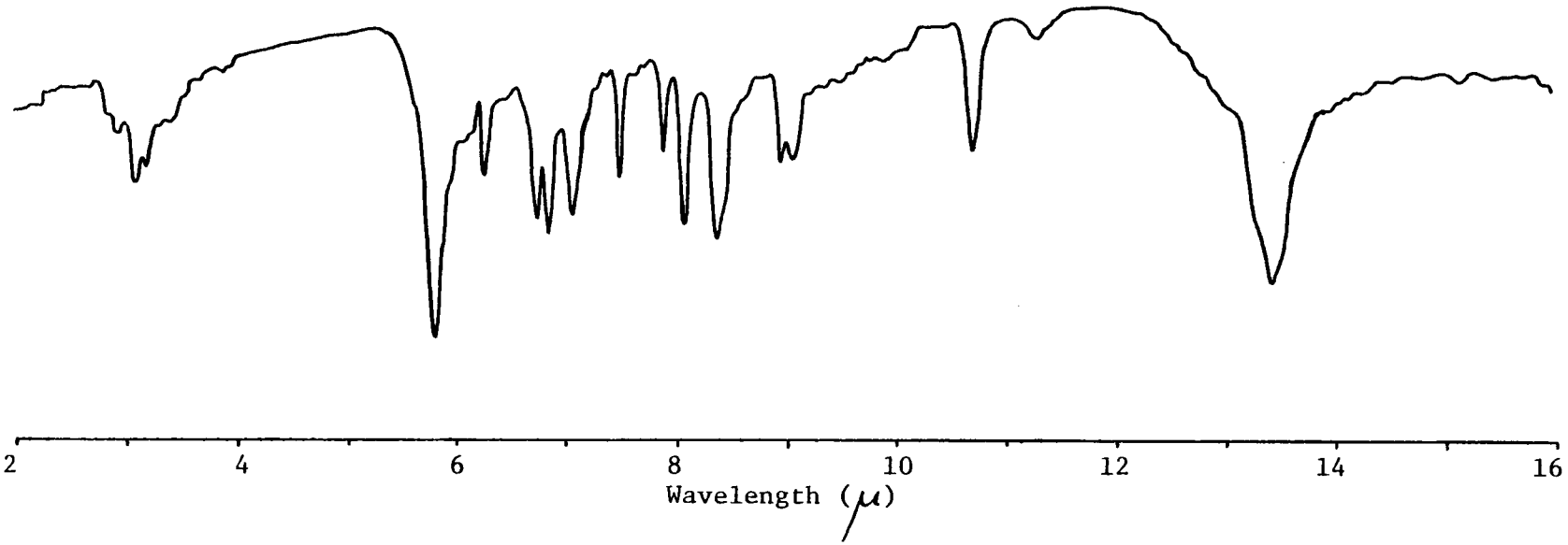


Figure 11. Midrange infrared spectrum of ring-01.

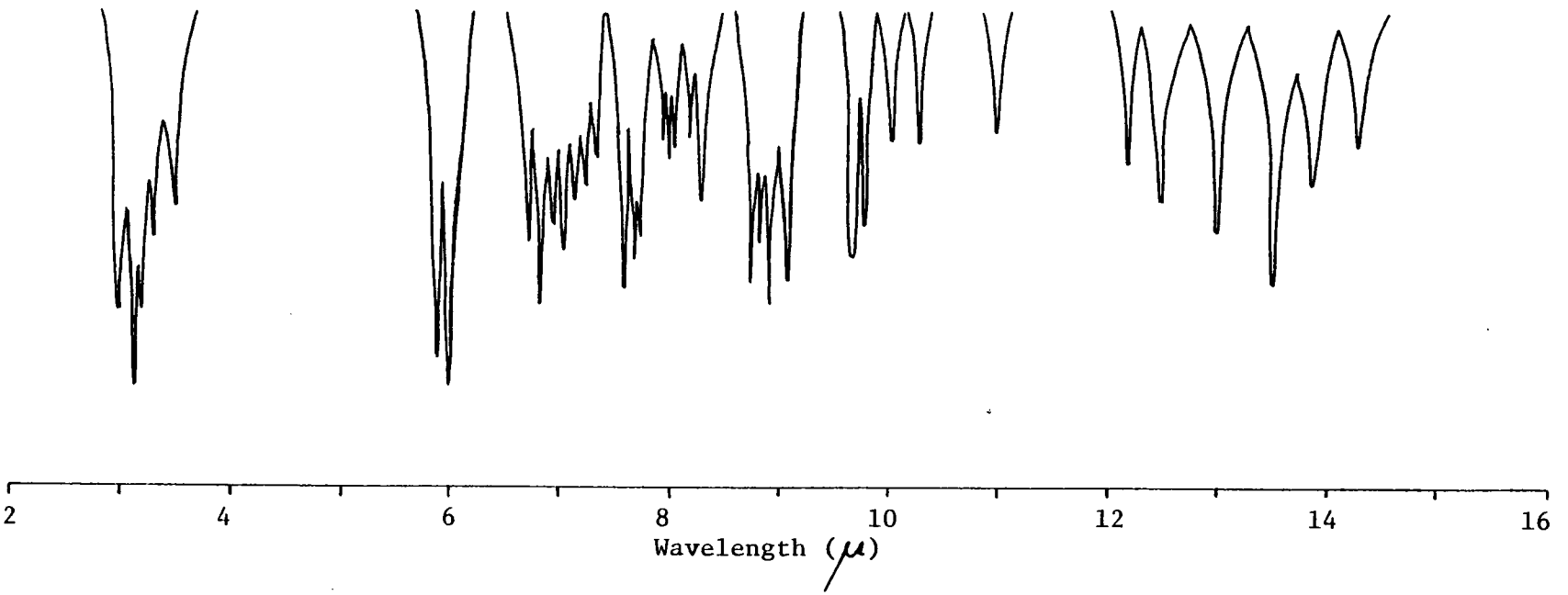


Figure 12. Midrange infrared spectrum of ring-11. Hypothetical KI pellet spectrum obtained as a composite of spectra shown in Figures 13 and 14.

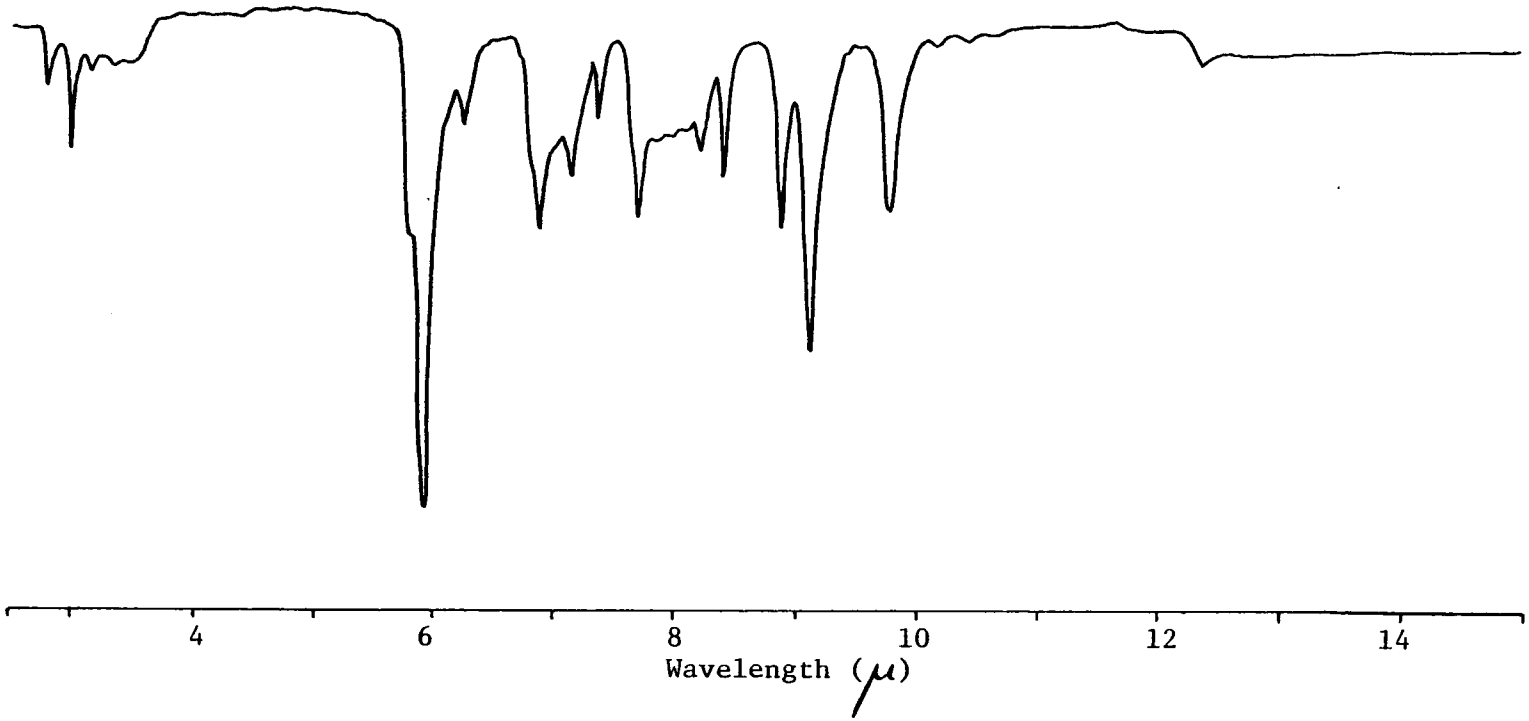


Figure 13. Midrange infrared spectrum of ring-11 in CH_2Cl_2 solution. Kindly supplied by Pifferi.

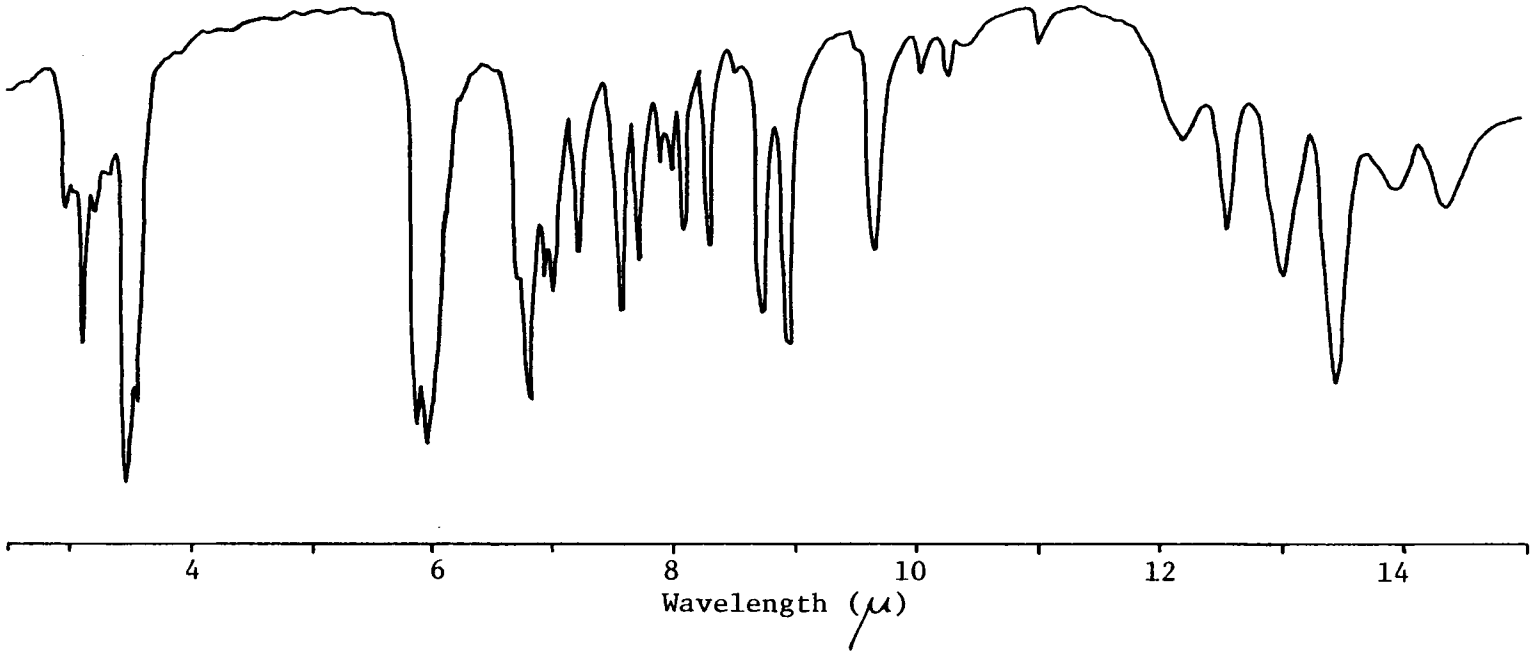


Figure 14. Midrange infrared spectrum of ring-11 in nujol mull. Kindly supplied by Pifferi.

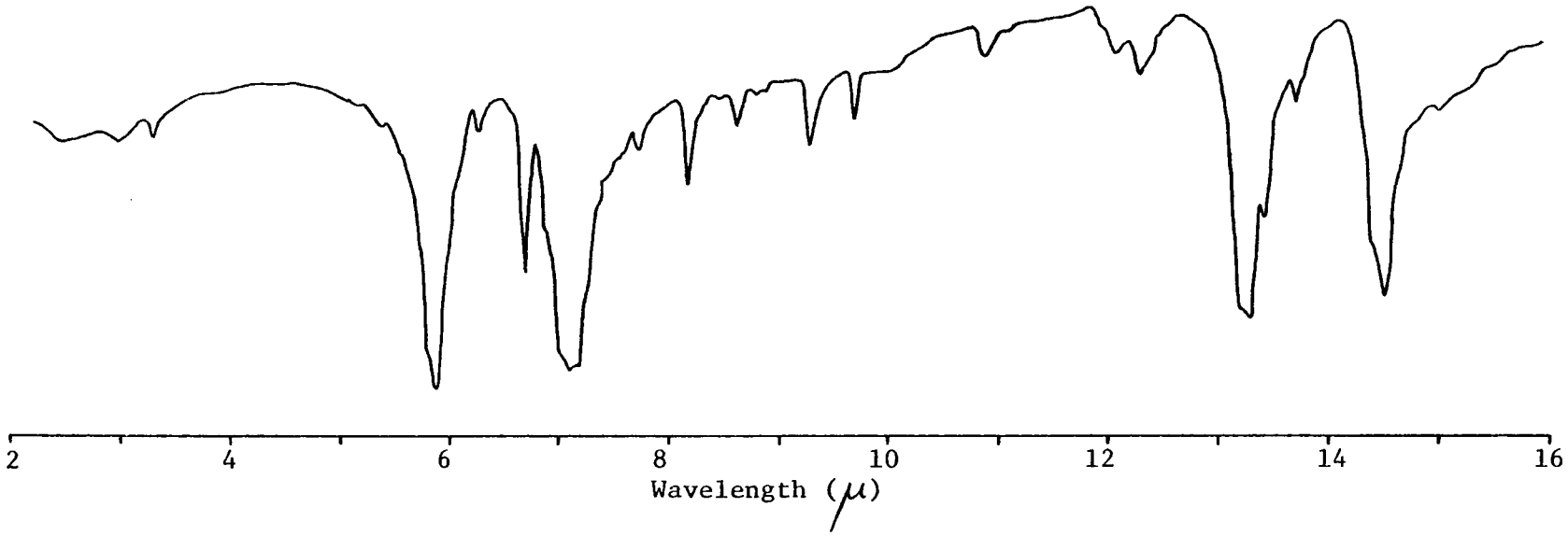


Figure 15. Midrange infrared spectrum of triphenylisocyanurate.

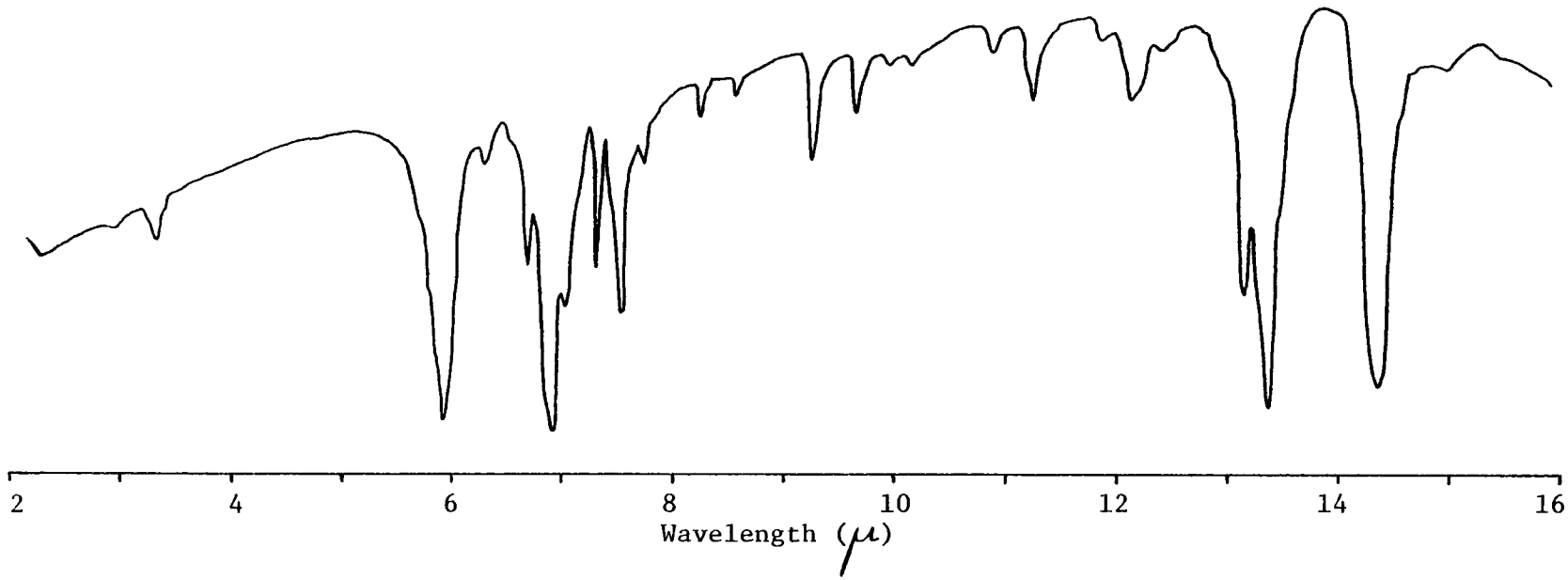


Figure 16. Midrange infrared spectrum of tribenzylisocyanurate.

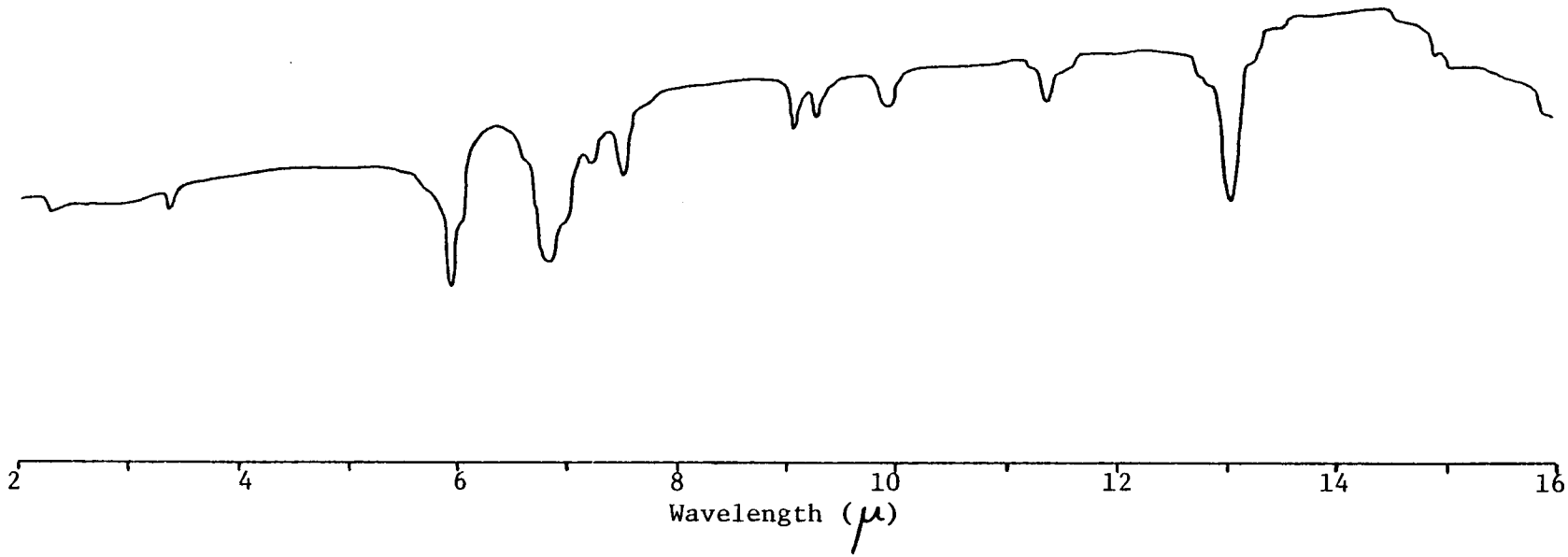


Figure 17. Midrange infrared spectrum of triethylisocyanurate.

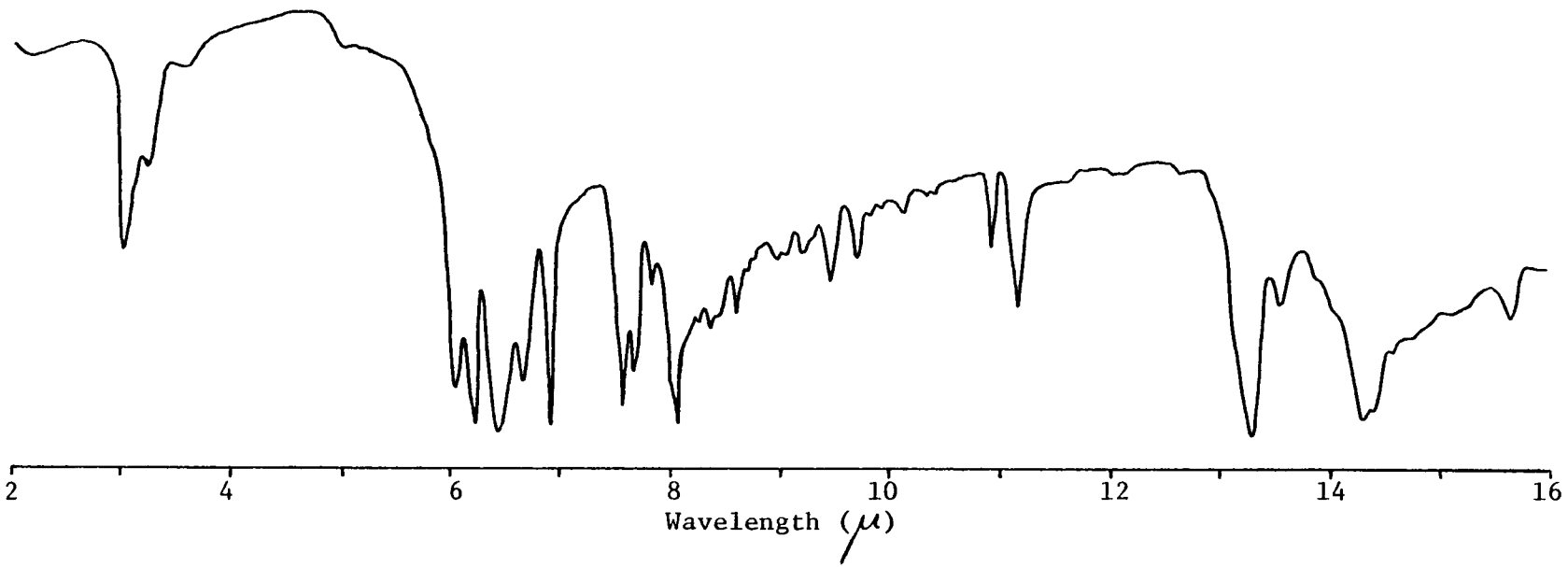


Figure 18. Midrange infrared spectrum of N,N'-diphenyl urea.

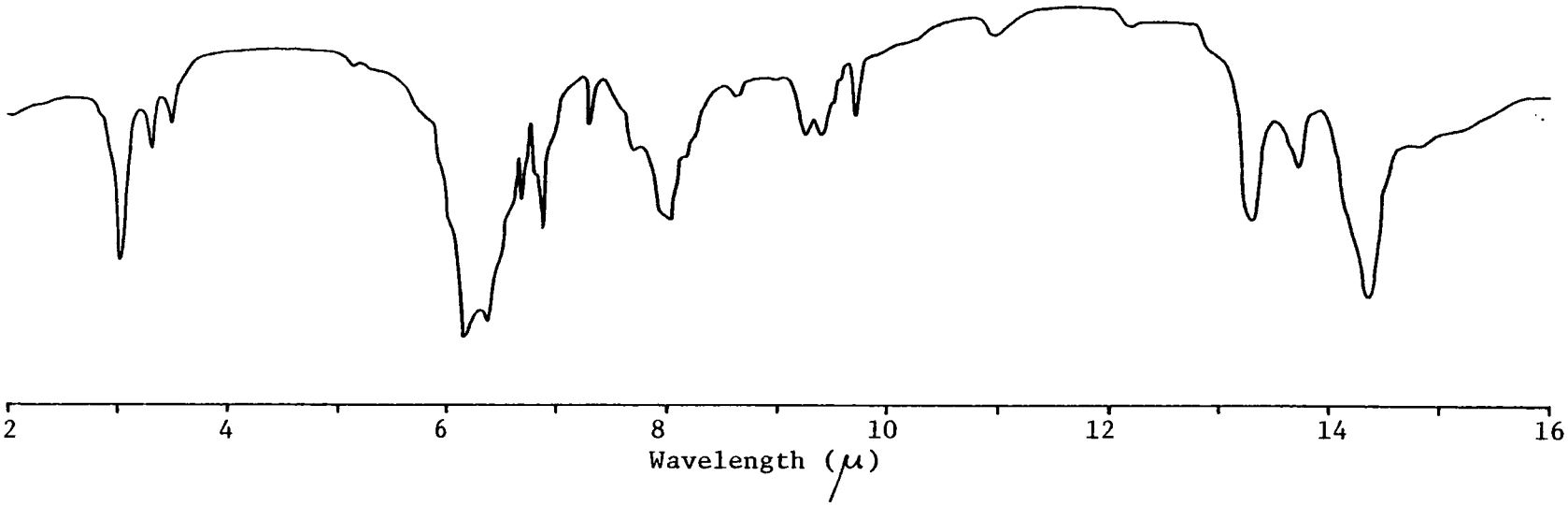


Figure 19. Midrange infrared spectrum of N,N'-dibenzyl urea.

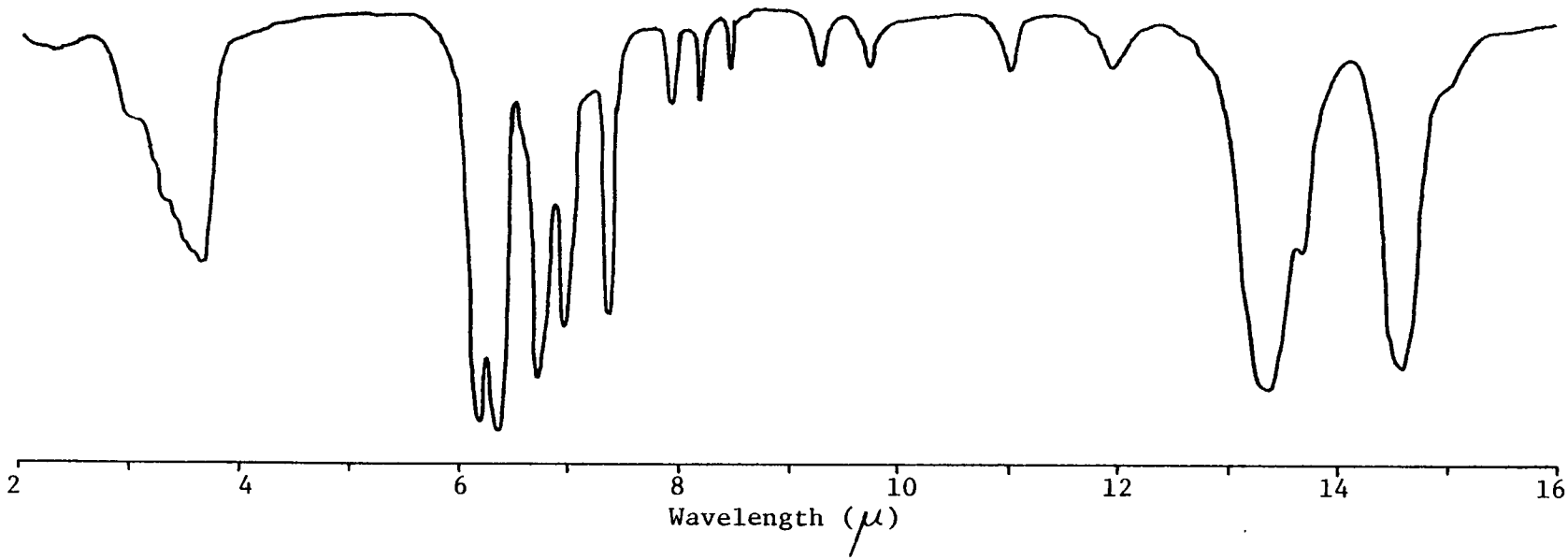


Figure 20. Midrange infrared spectrum of N,N',N"-triphenyl guanidinium hydrochloride.

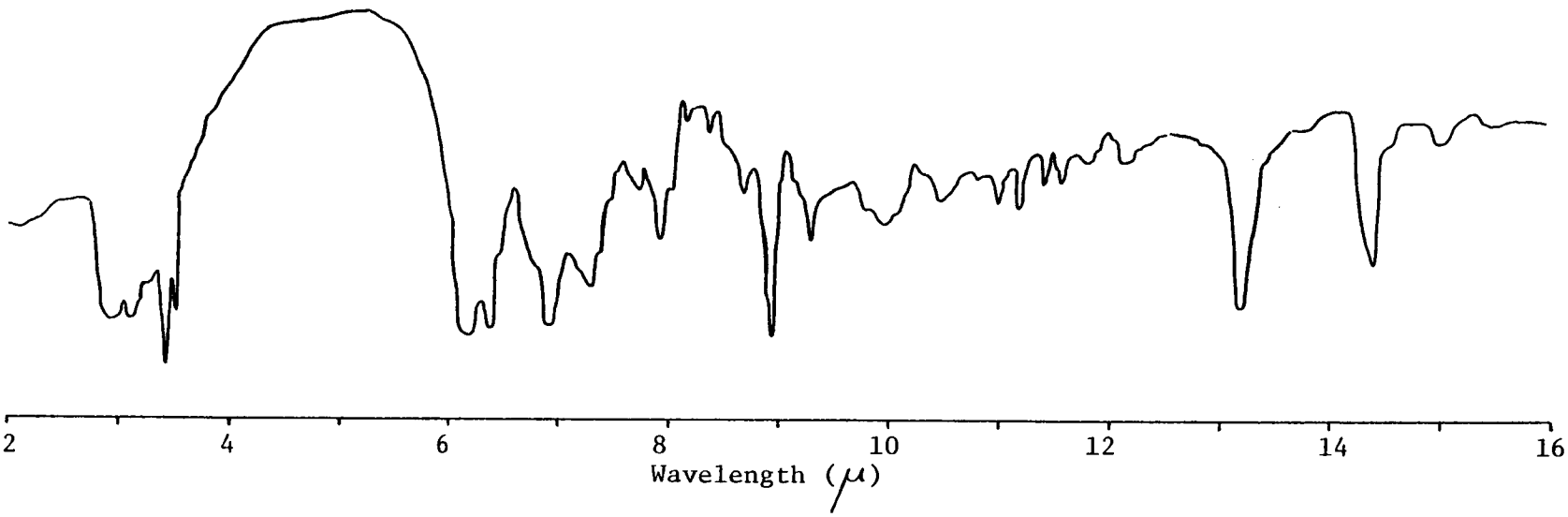


Figure 21. Midrange infrared spectrum of N,N'-dicyclohexyl-4-morpholinecarboxamidinium phenolate.

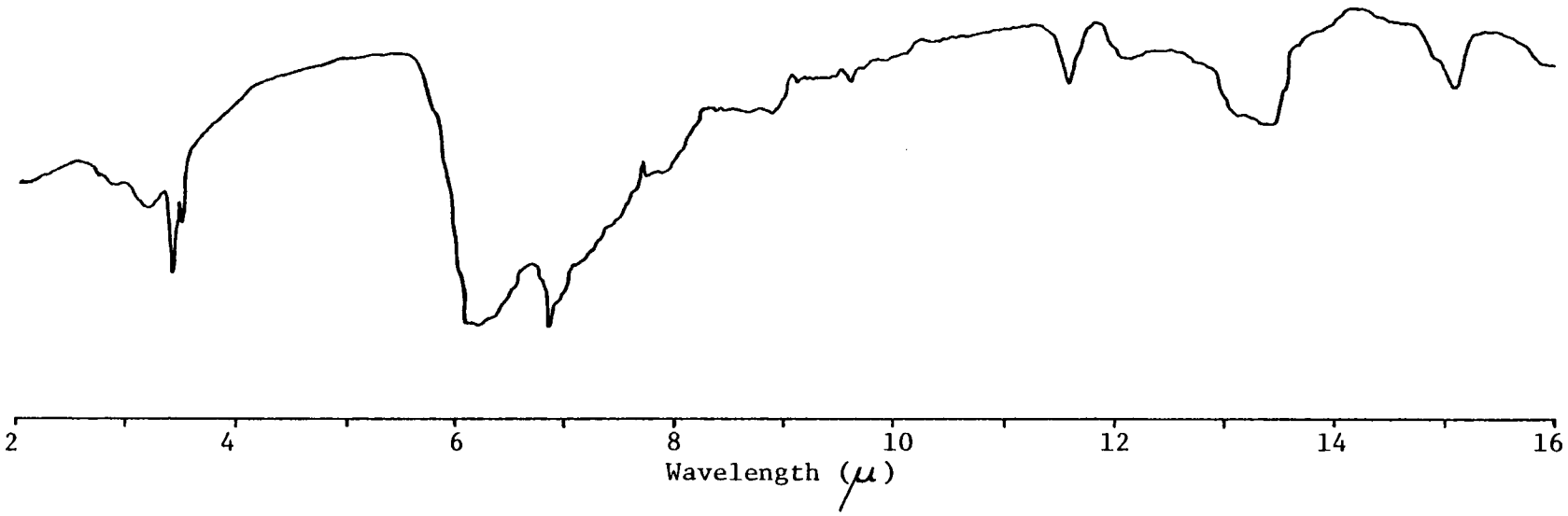


Figure 22. Midrange infrared spectrum of polymerized dicyclohexyl carbodiimide.

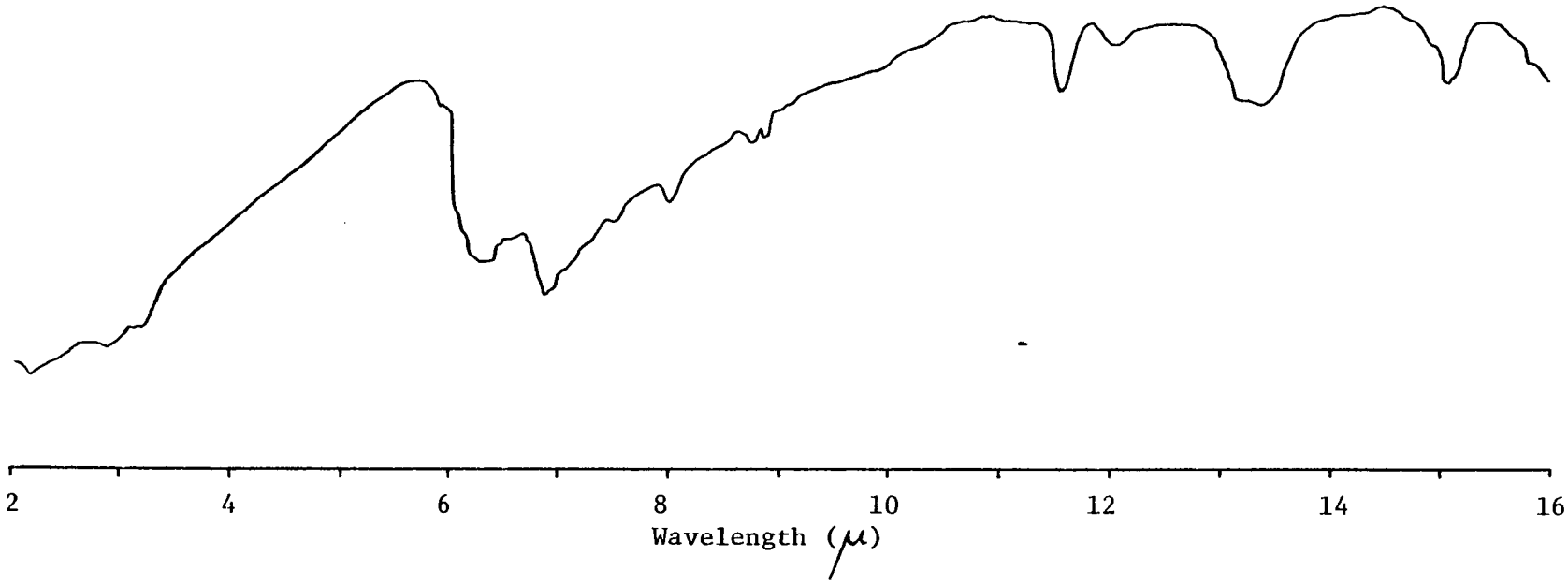


Figure 23. Midrange infrared spectrum of polymerized diphenyl carbodiimide.

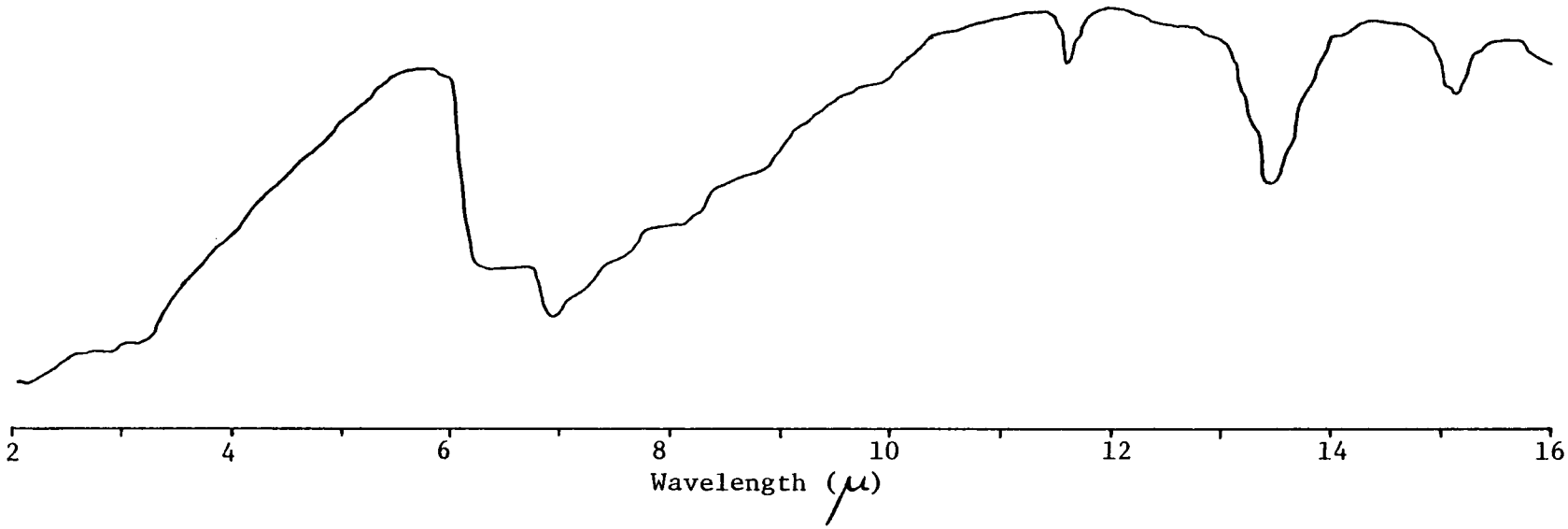


Figure 24. Midrange infrared spectrum of polymerized di-o-tolyl carbodiimide.

APPENDIX II

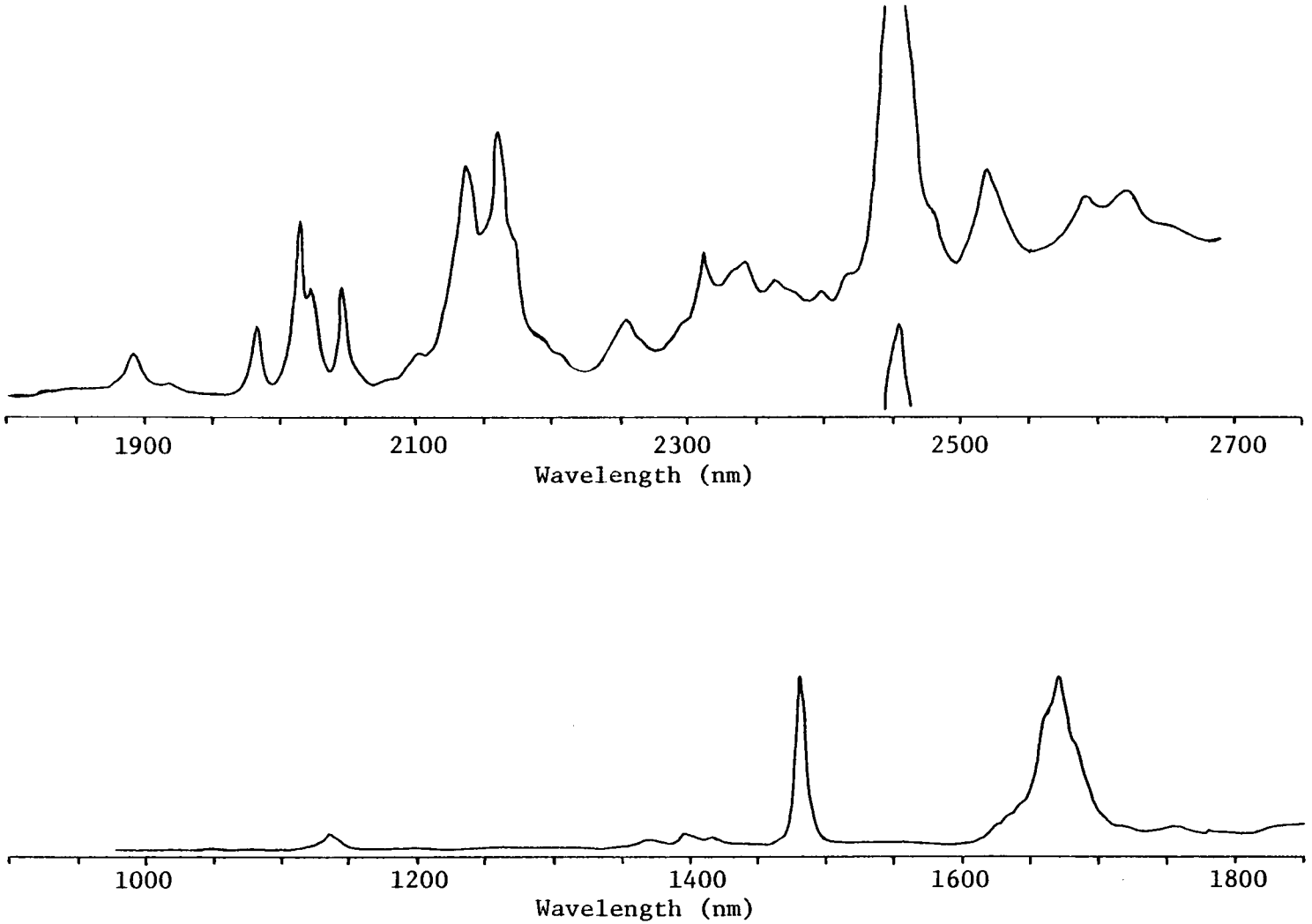


Figure 25. Near infrared spectrum of N-phenyl-O-phenyl carbamate.

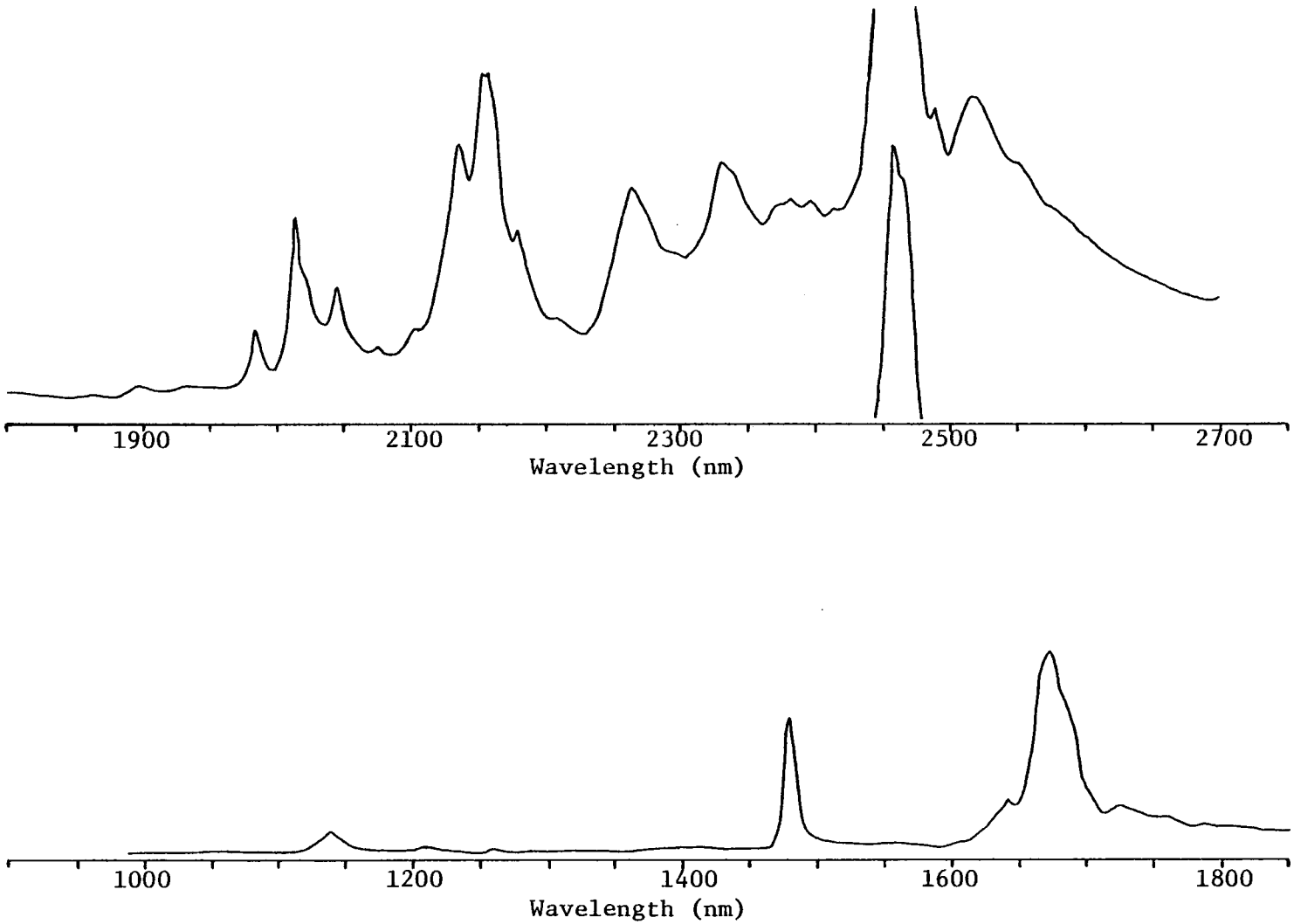


Figure 26. Near infrared spectrum of N-phenyl-O-benzyl carbamate.

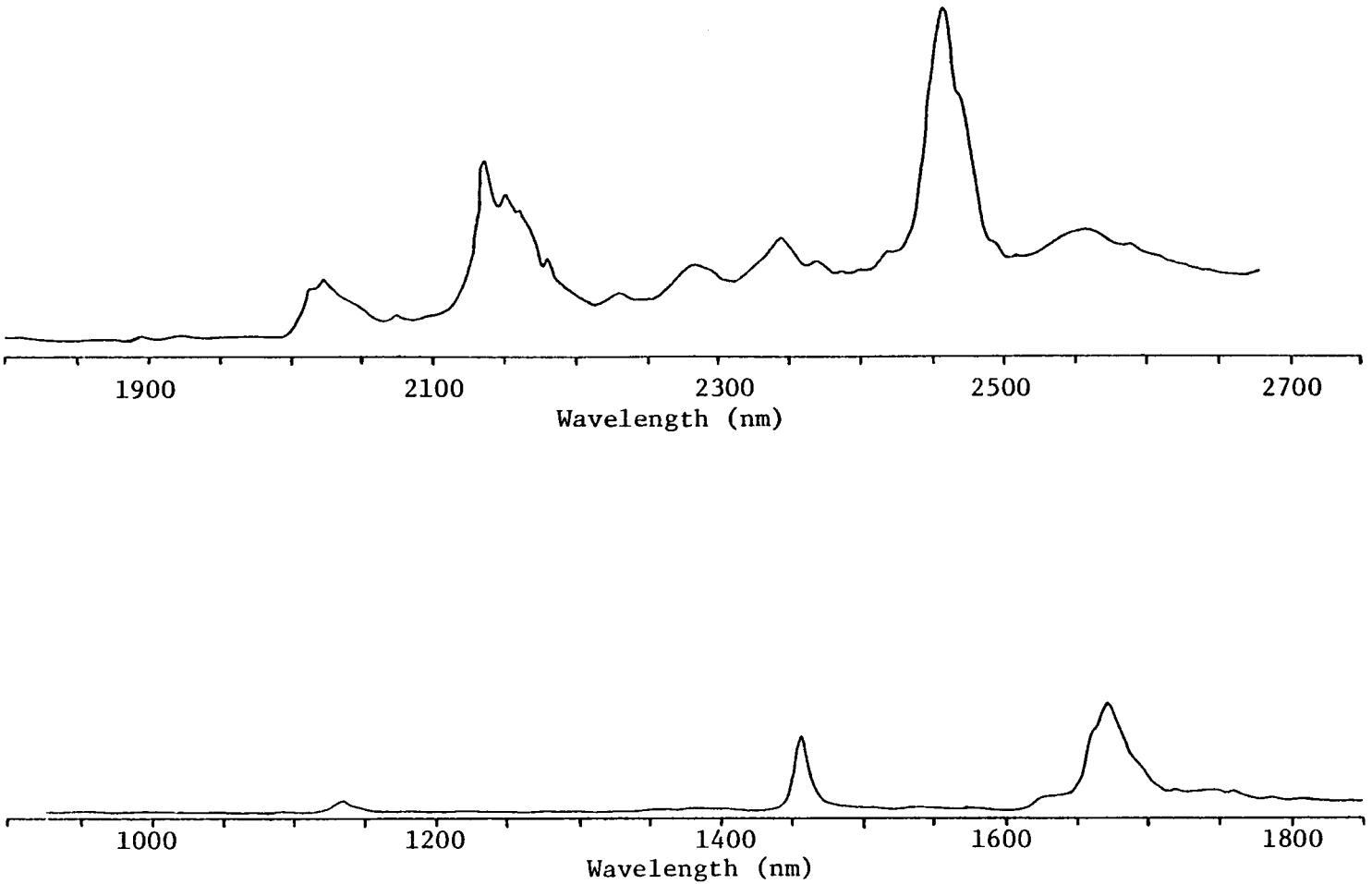


Figure 27. Near infrared spectrum of N-benzyl-O-phenyl carbamate.

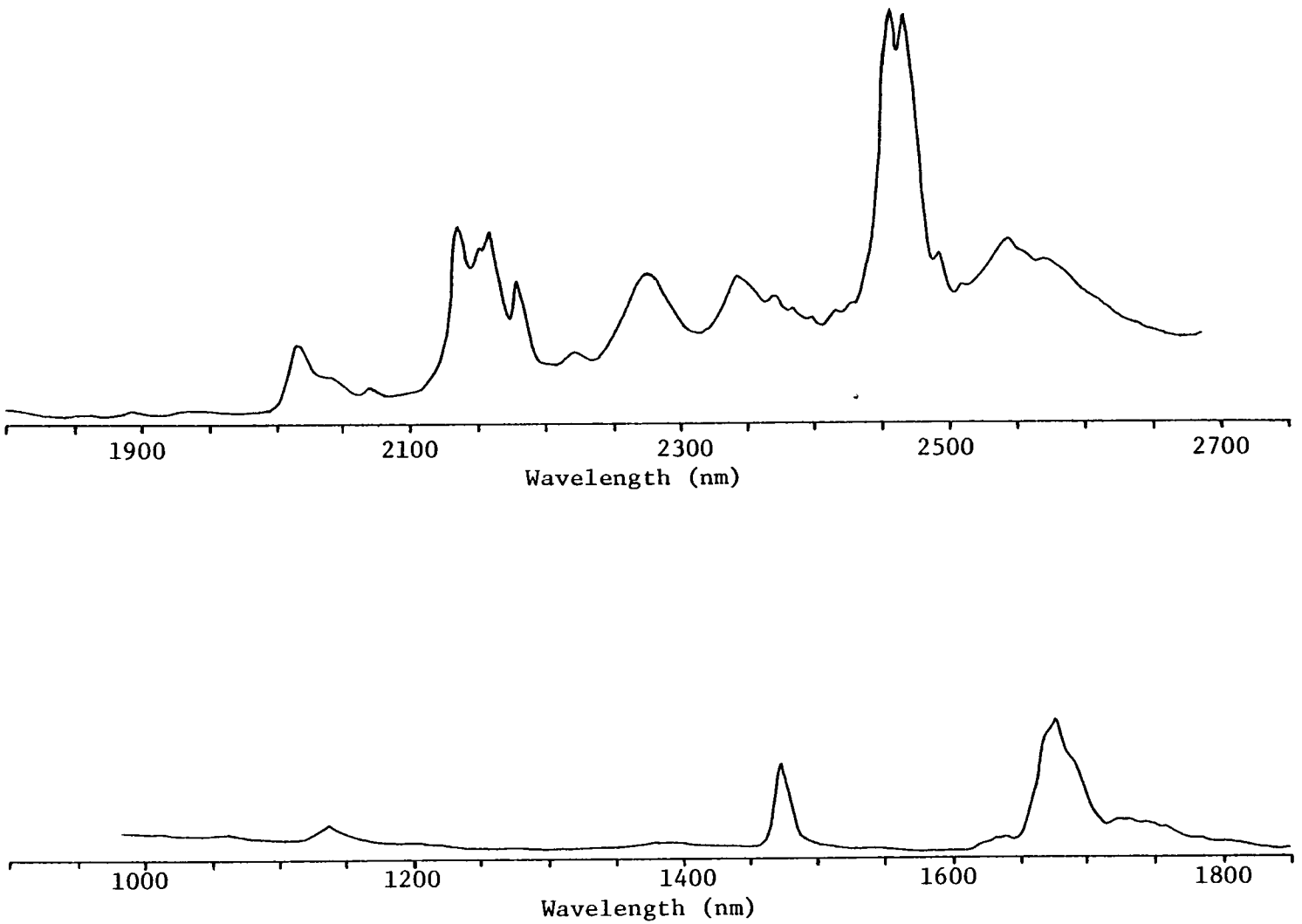


Figure 28. Near infrared spectrum of N-benzyl-O-benzyl carbamate.

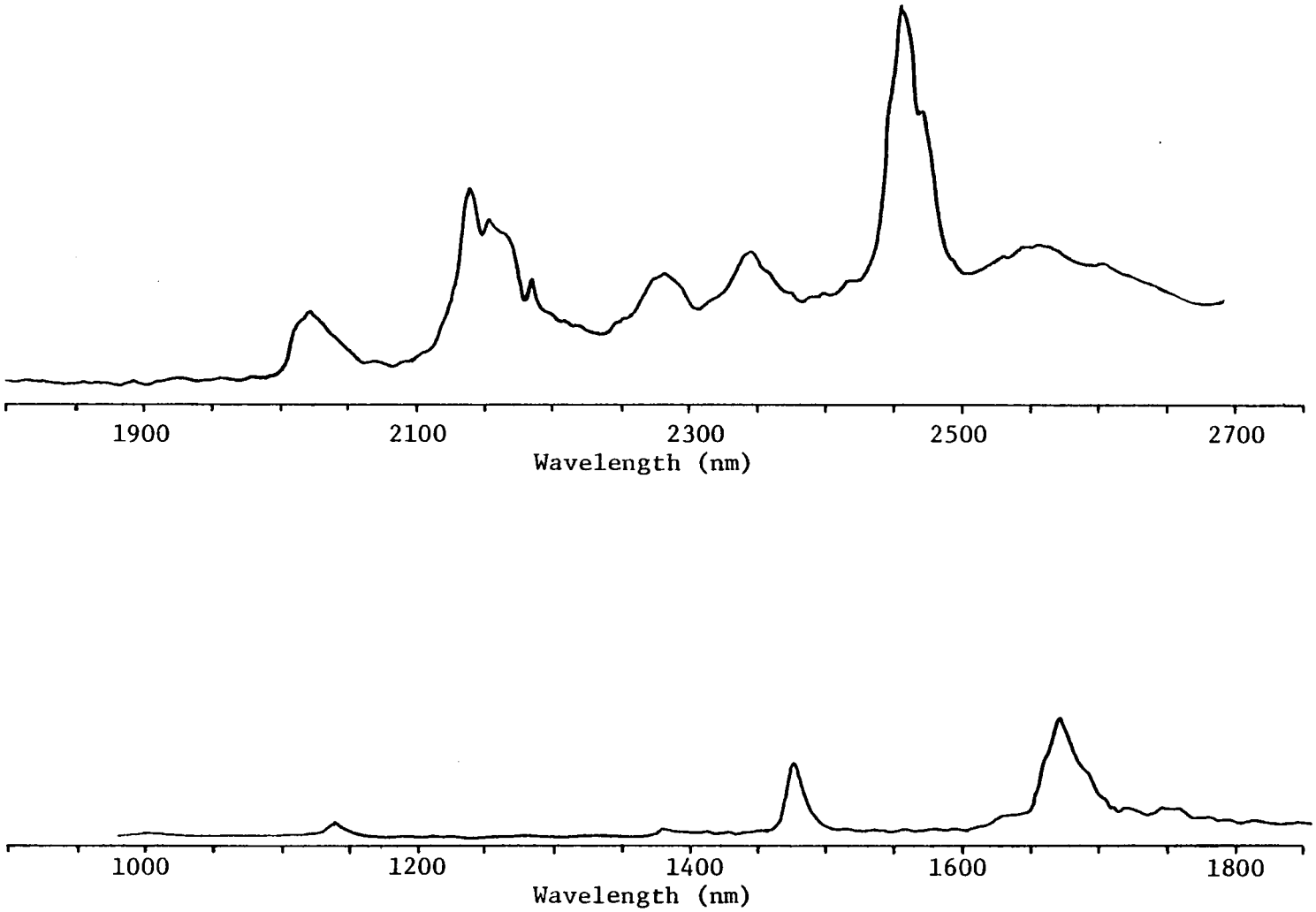


Figure 29. Near infrared spectrum of N-phenethyl-O-phenyl carbamate.

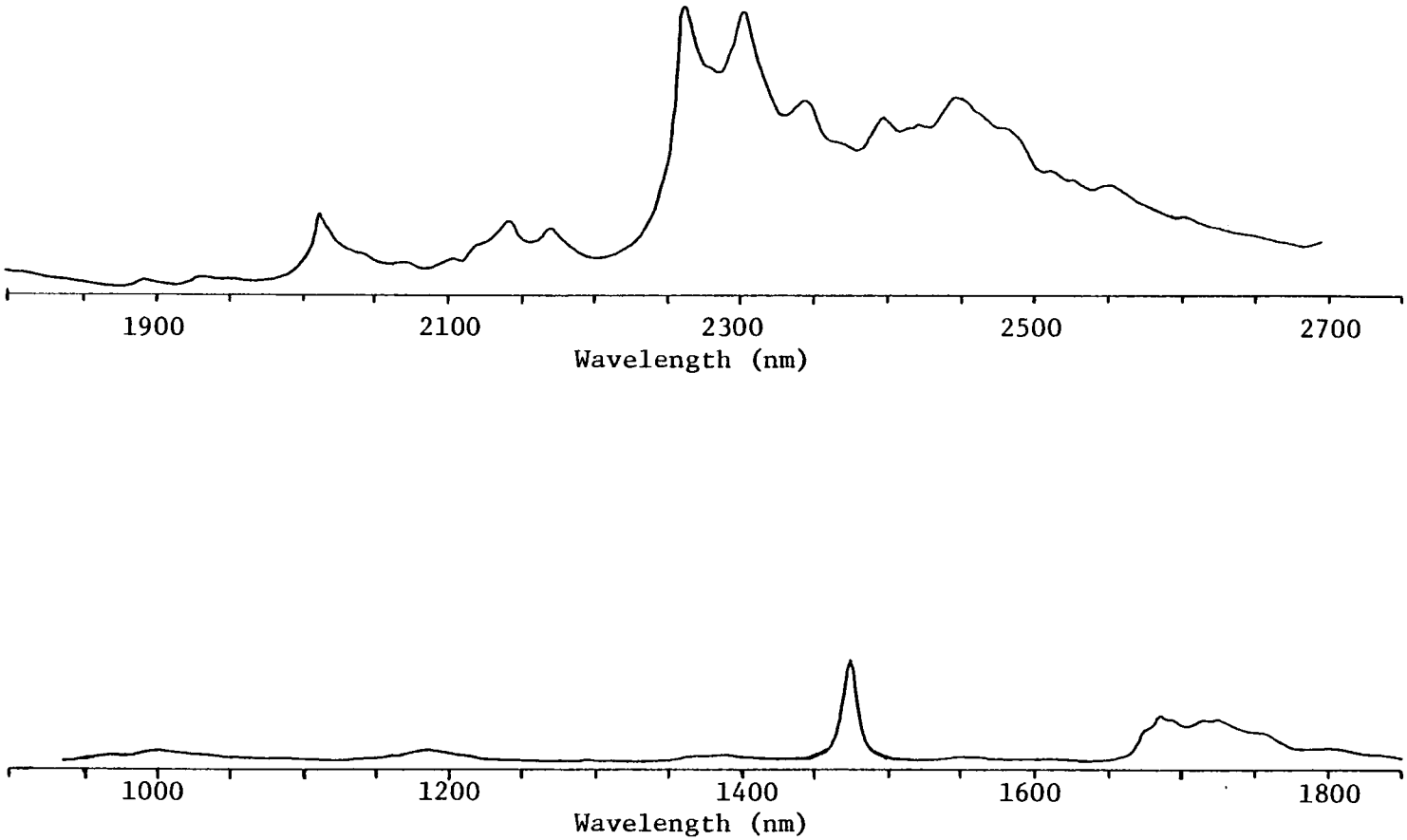
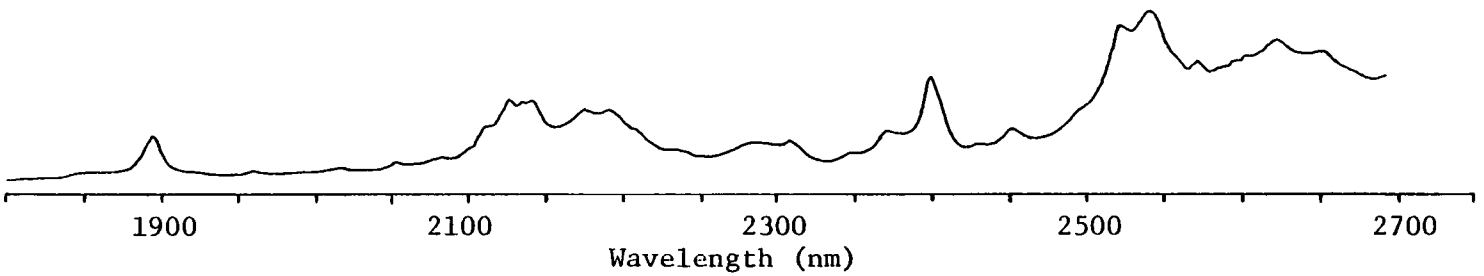


Figure 30. Near infrared spectrum of N-n-propyl-O-ethyl carbamate.



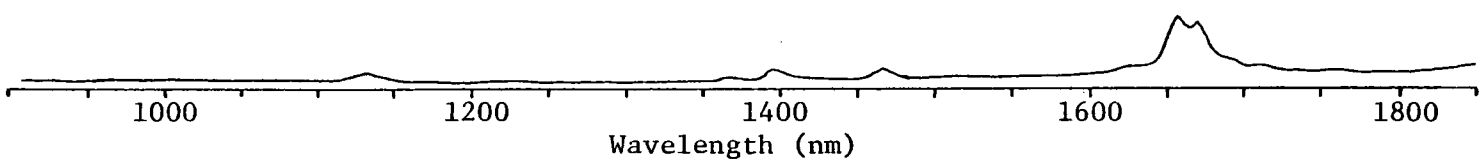


Figure 31. Near infrared spectrum of ring-00.

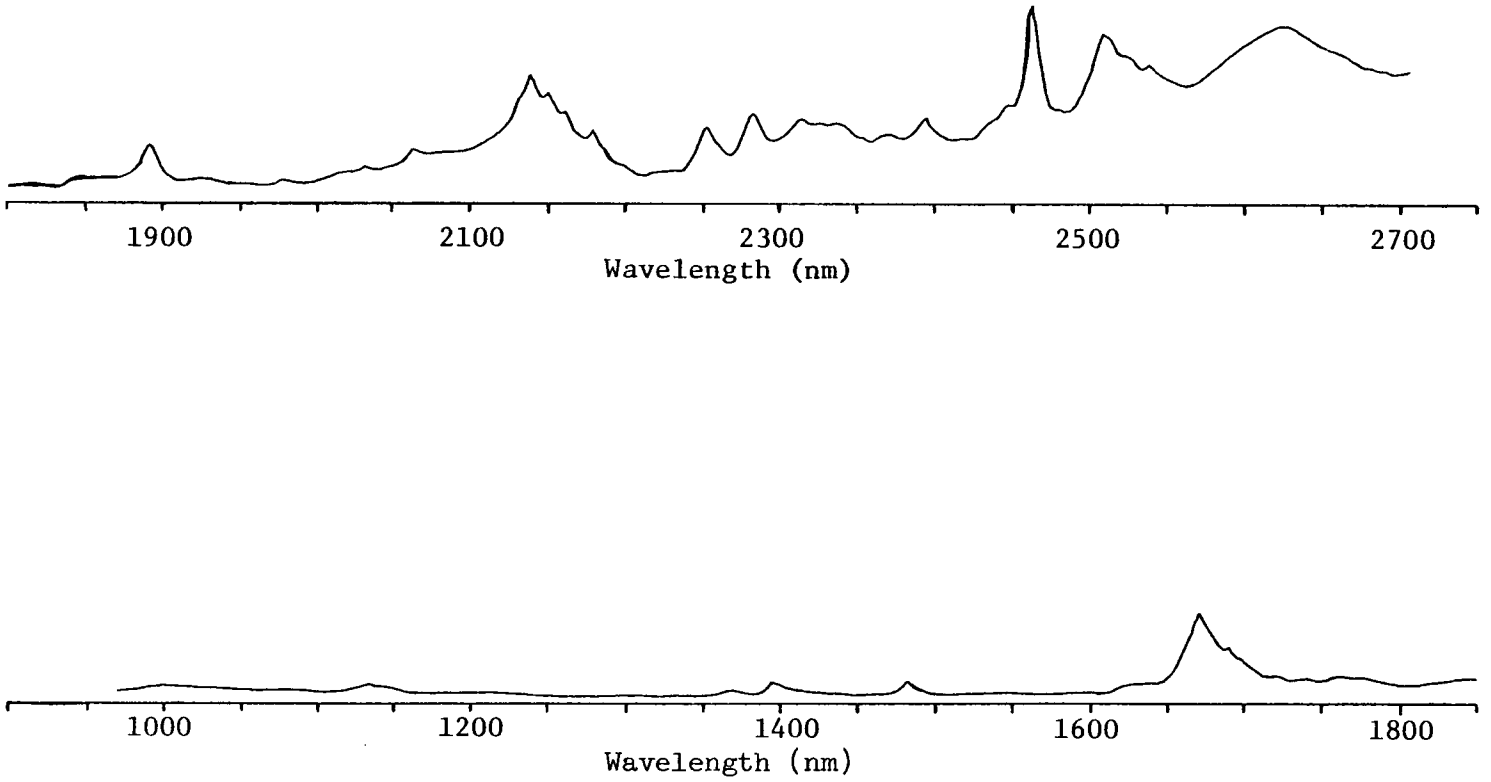
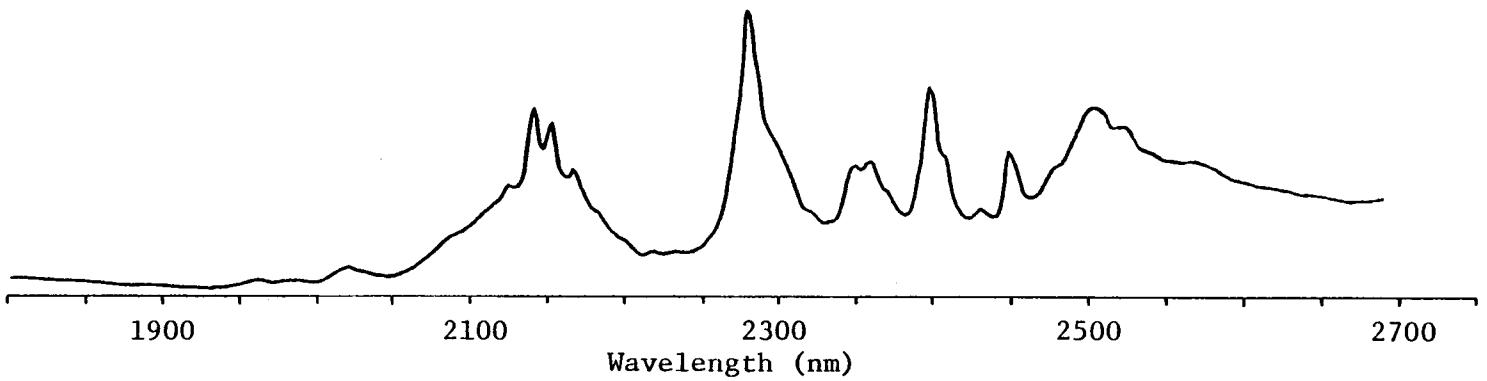


Figure 32. Near infrared spectrum of ring-10.



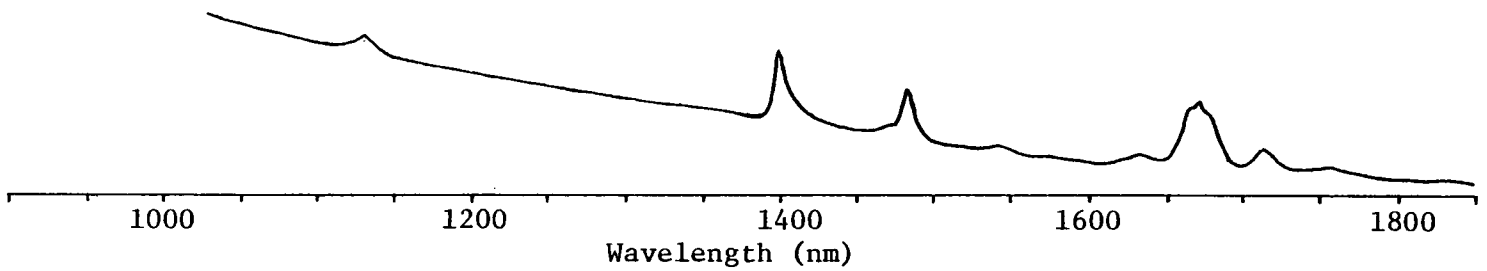


Figure 33. Near infrared spectrum of ring-01.

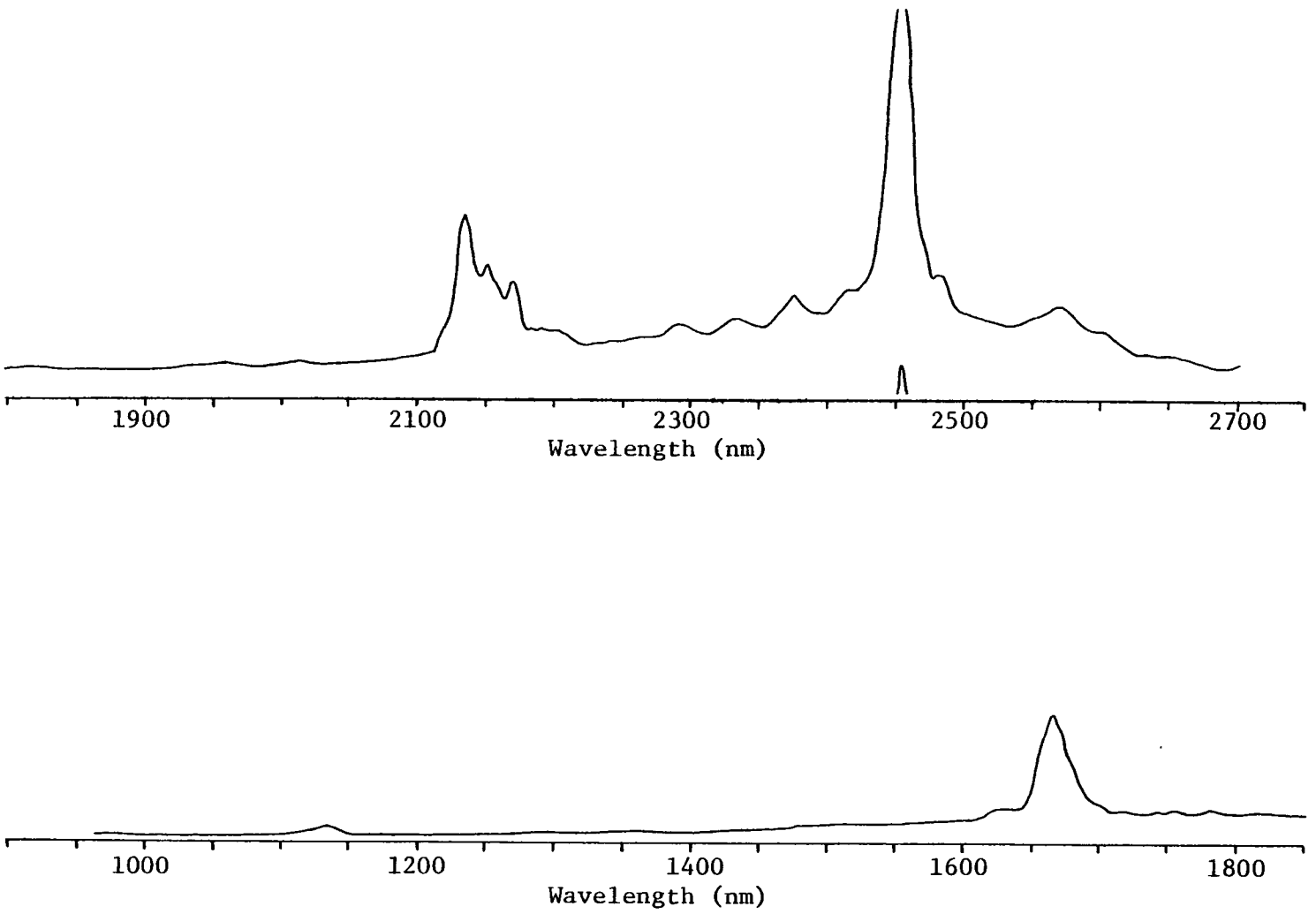


Figure 34. Near infrared spectrum of triphenylisocyanurate.

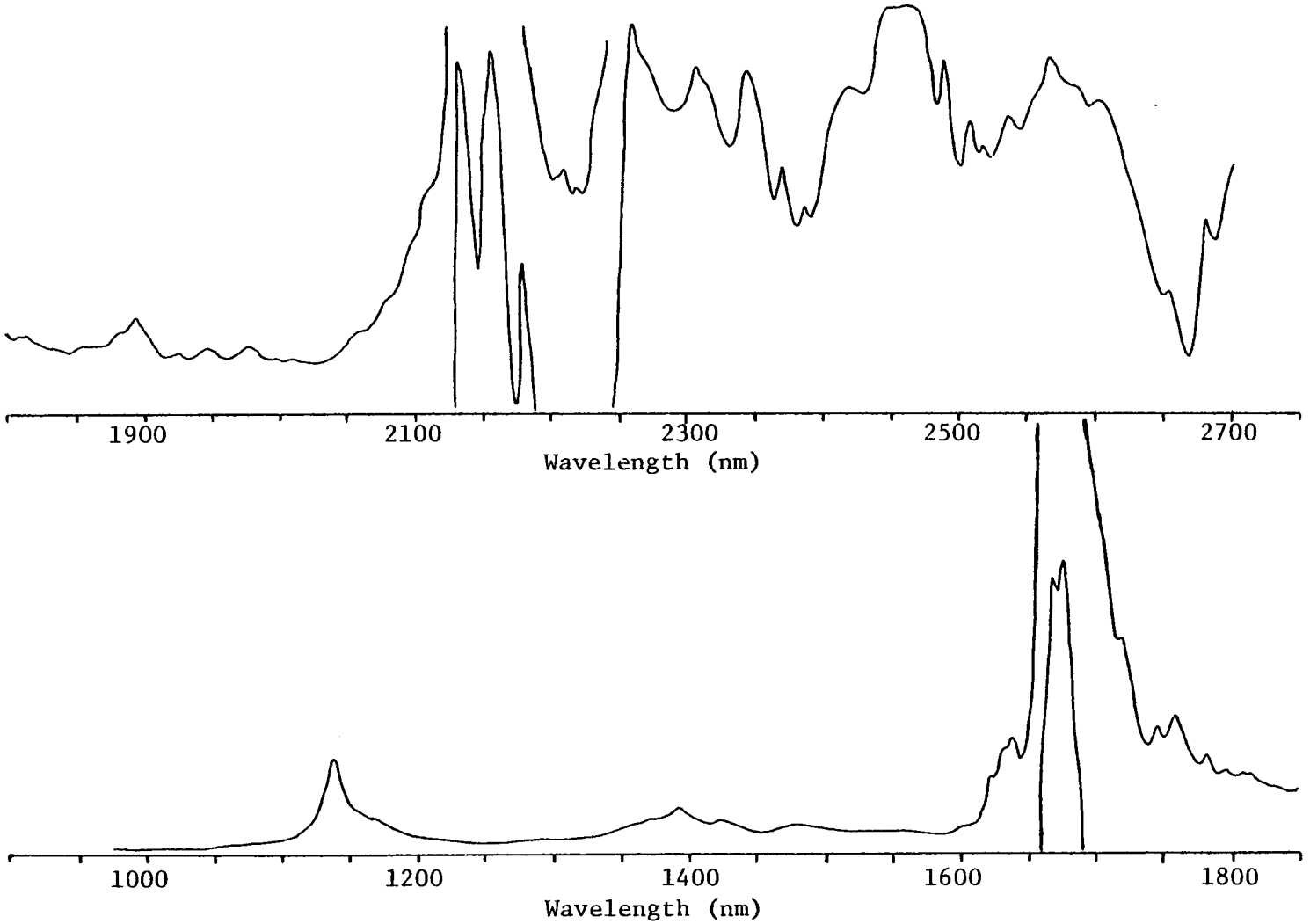


Figure 35. Near infrared spectrum of tribenzylisocyanurate.

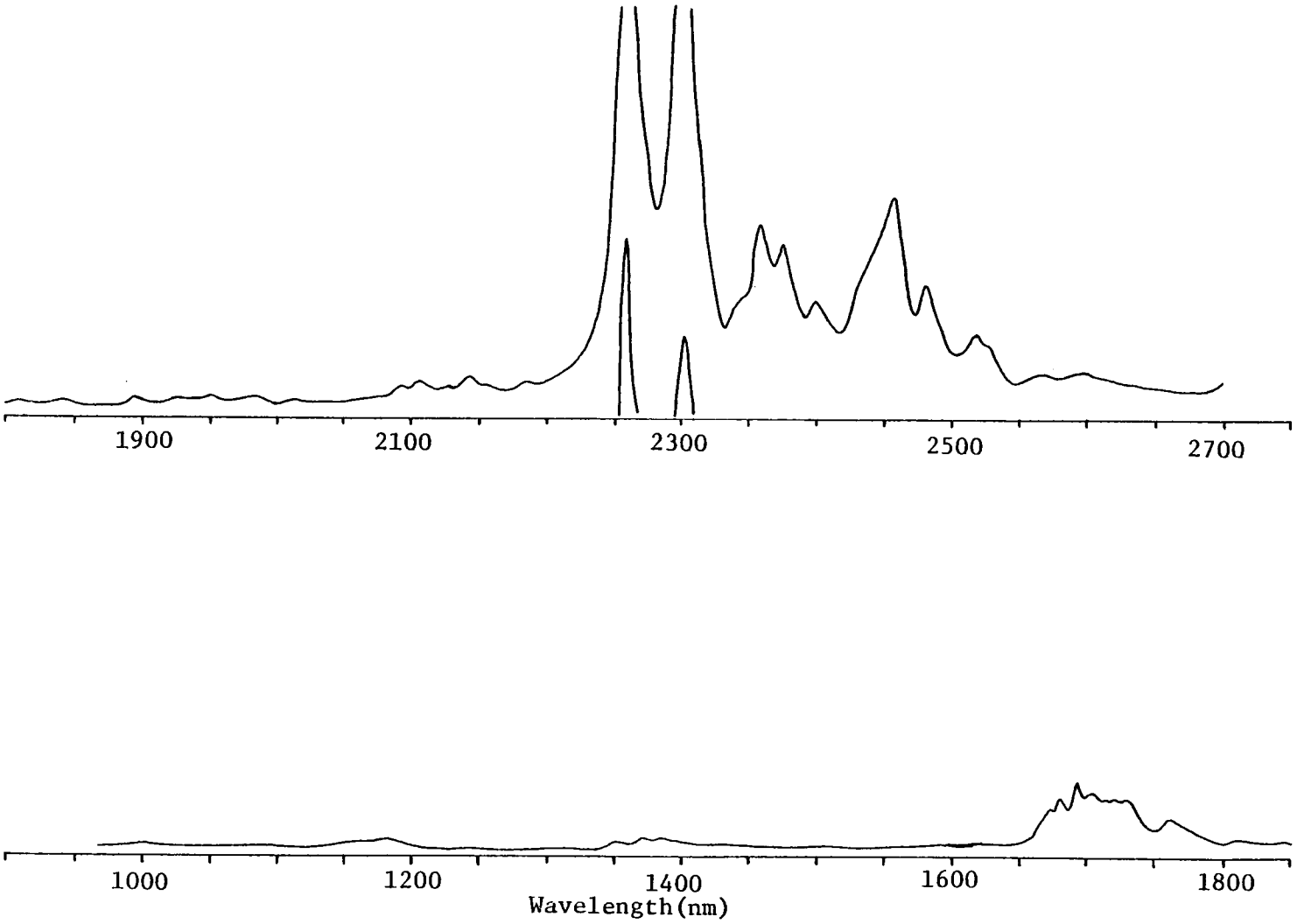


Figure 36. Near infrared spectrum of triethylisocyanurate.

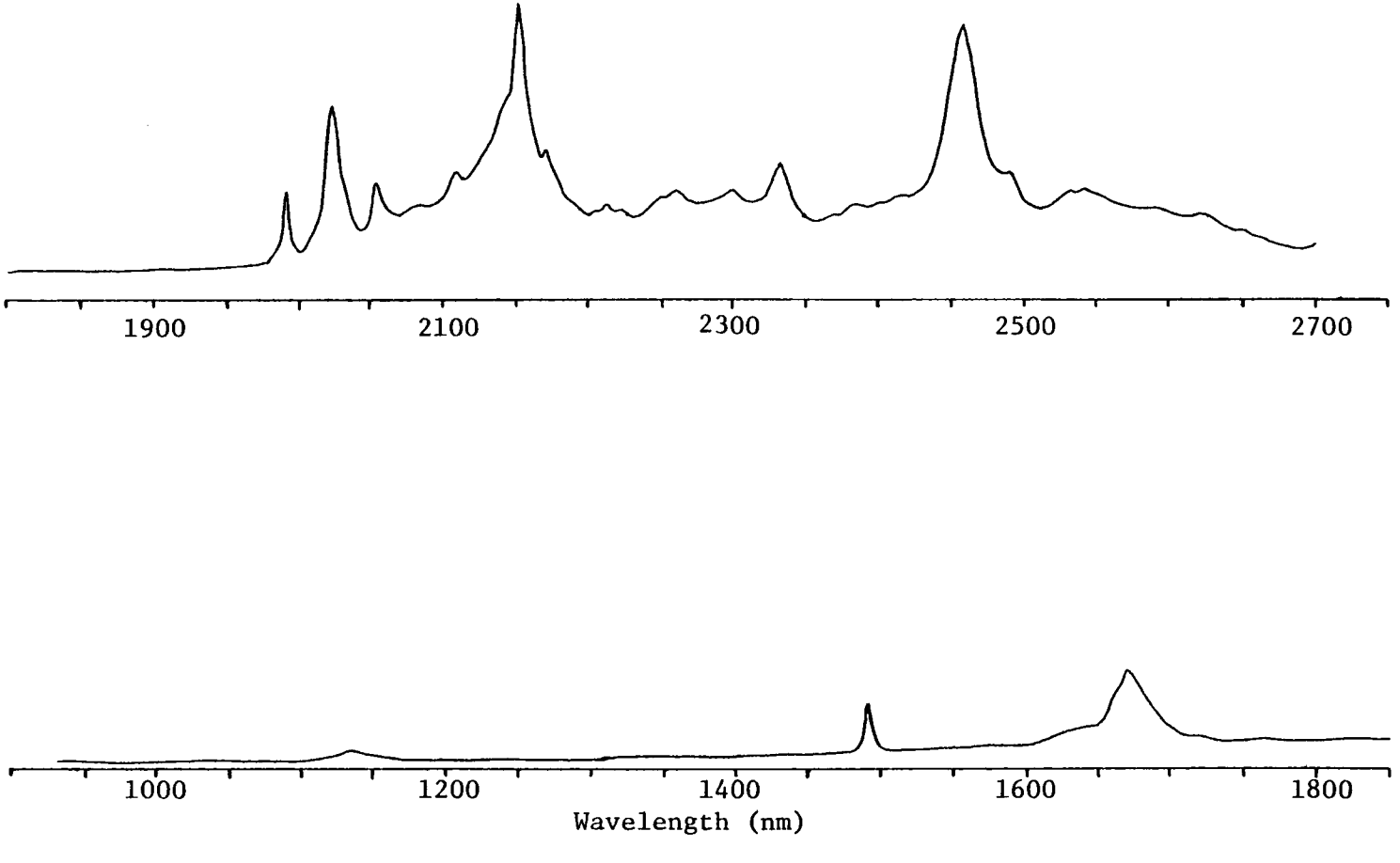


Figure 37. Near infrared spectrum of N,N'-diphenylurea.

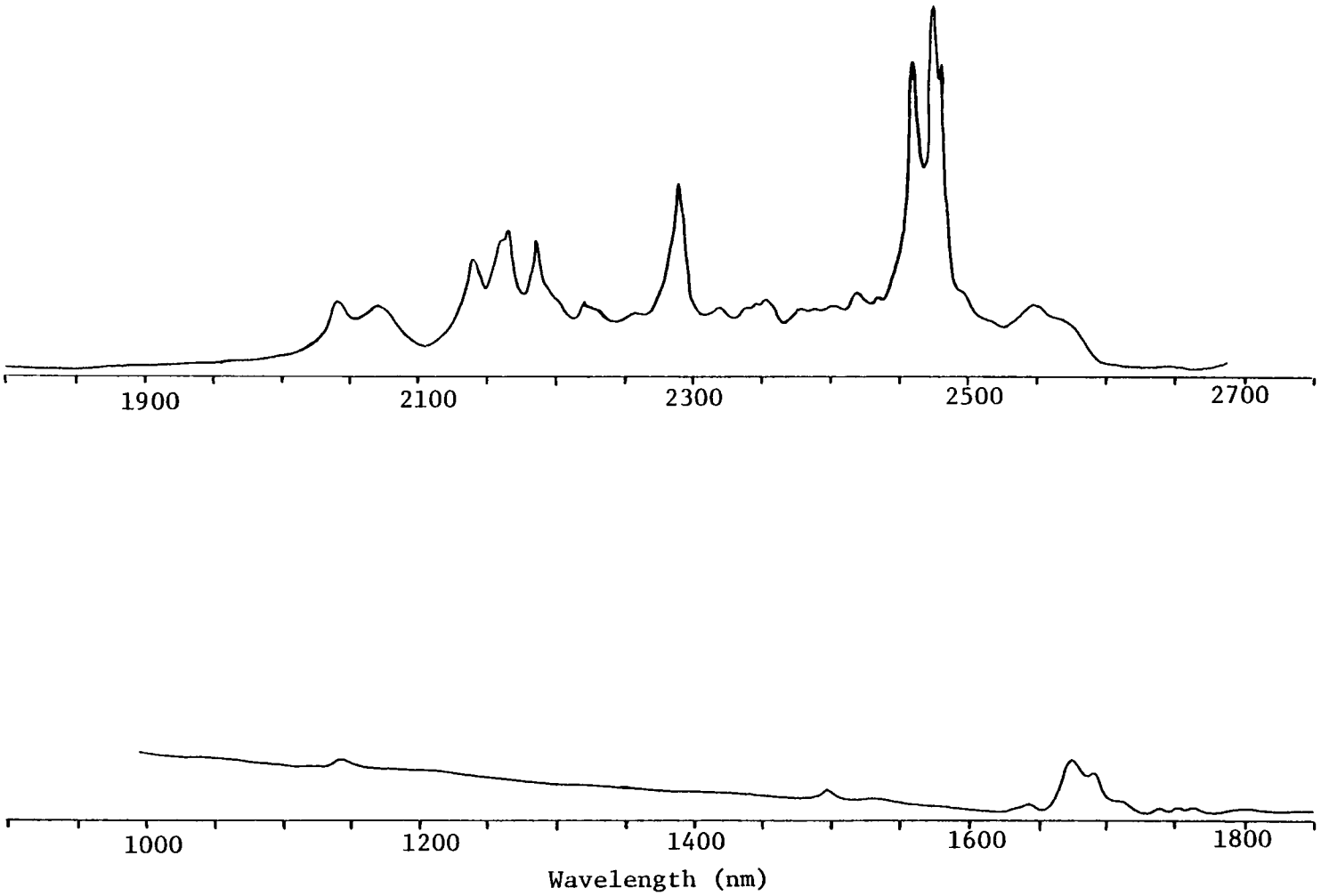


Figure 38. Near infrared spectrum of N,N'-dibenzylurea.

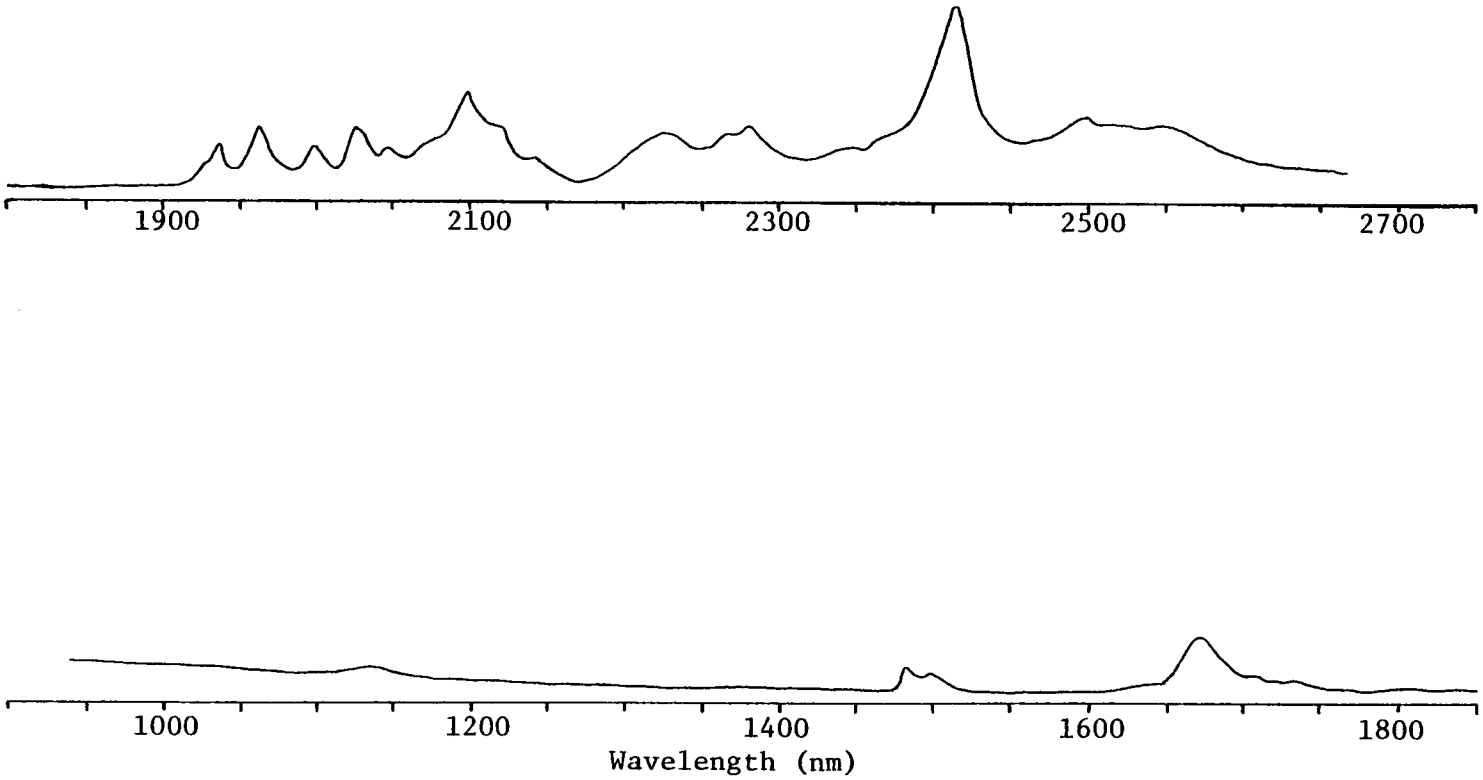


Figure 39. Near infrared spectrum of N,N',N"-triphenylguanidine.

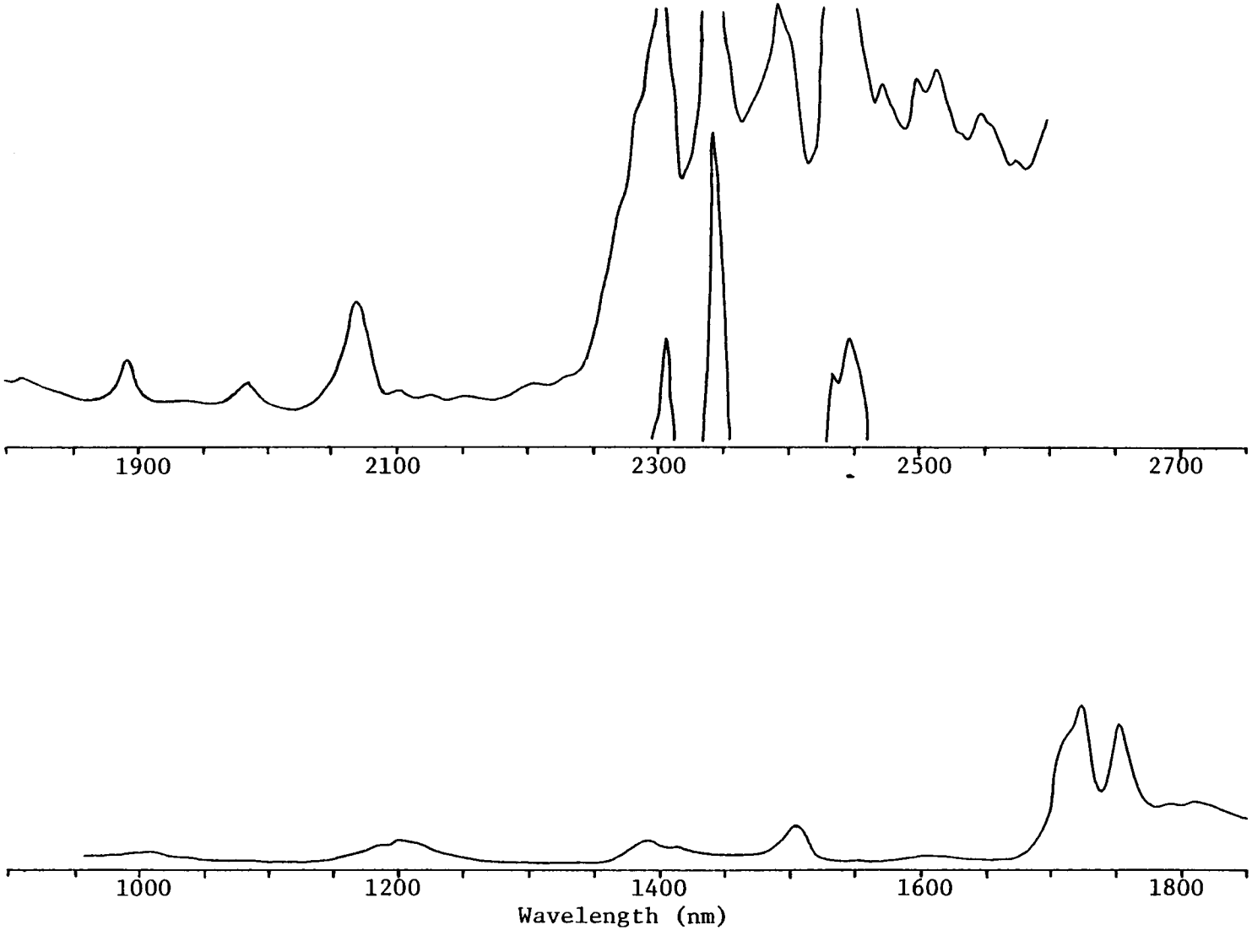


Figure 40. Near infrared spectrum of N,N'-dicyclohexyl-4-morpholinecarboxamide.

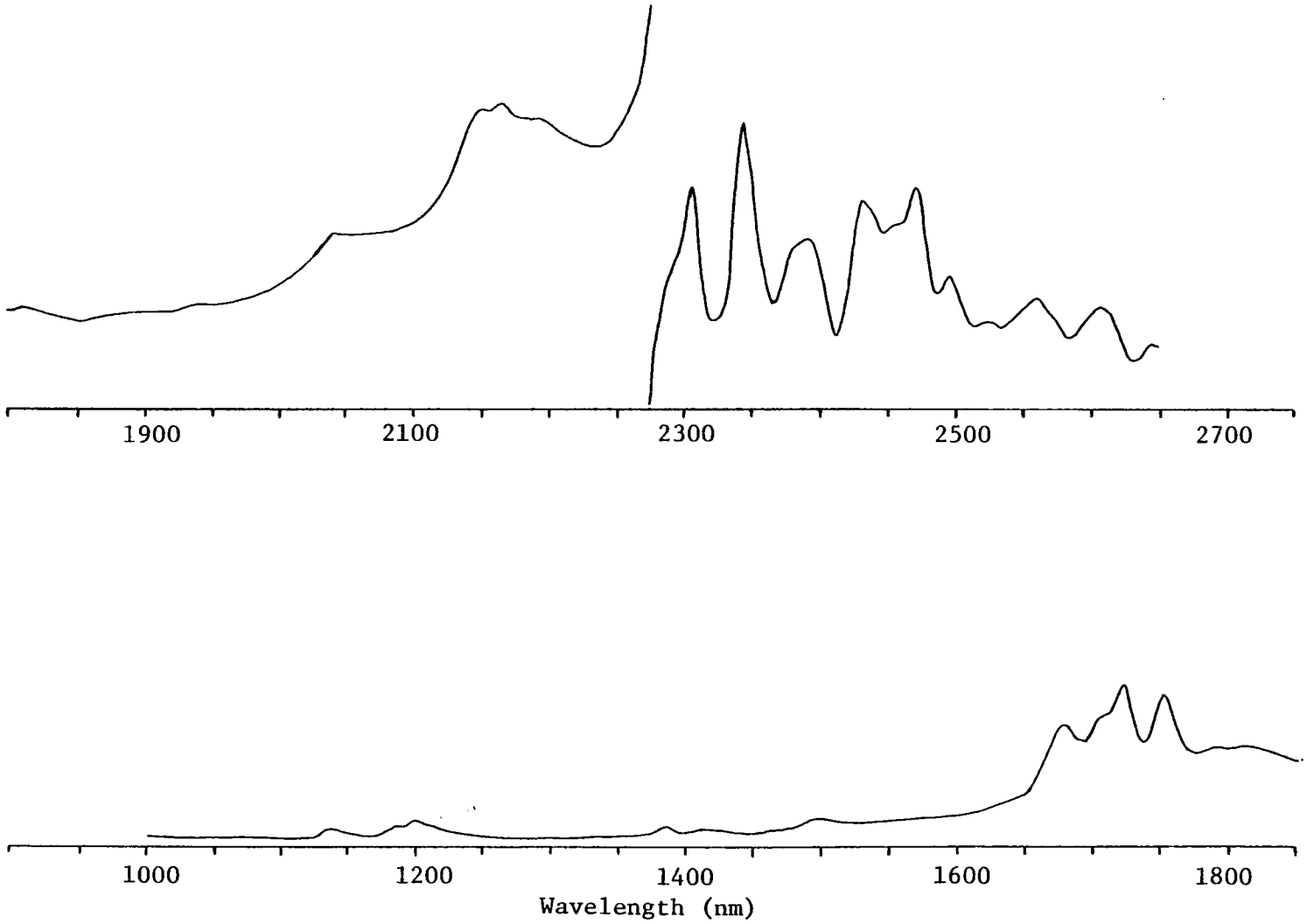


Figure 41. Near infrared spectrum of N,N'-dicyclohexyl-4-morpholinecarboxamidinium phenolate.

TABLE LII

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS - DIRECTORY

Compound	Spectrum[a]
N-phenyl-O-phenyl carbamate	A
N-phenyl-O-benzyl carbamate	B
N-benzyl-O-phenyl carbamate	C
N-benzyl-O-benzyl carbamate	D
N-phenethyl-O-phenyl carbamate	E
N-phenyl-O-n-propyl carbamate	F
N-benzyl-O-ethyl carbamate	G
N-n-propyl-O-ethyl carbamate	H
ring-00	I
ring-10	J
ring-01	K
triphenylisocyanurate	L
tribenzylisocyanurate	M
triethylisocyanurate	N
N,N'-diphenyl urea	O
N,N'-dibenzyl urea	P
N,N'-dicyclohexyl urea	Q
N,N',N''-triphenyl guanidine	R
N-morpholino-N',N''-dicyclohexylcarboxamidine	S
N-morpholino-N ,N''-dicyclohexylcarboxamidinium phenolate	T
N,N'-dicyclohexyl-O-phenyl isouronium phenolate	U
phenol	V
benzyl alcohol	W
aniline	X
benzylamine	Y
o-aminobenzyl alcohol	Z
toluene	AA
diphenylmethane	BB
triphenylmethane	CC
tetralin	DD

a. The reduced data, wavelength (nm) vs. relative intensity (R.I.), has been extracted from the near infrared spectra and presented in columnar form in the succeeding pages of this table. All spectra were obtained in carbon tetrachloride solution except for T,U,X,Y, and Z. The samples for T,U,X, and Y were prepared as neat films of 0.5 mm thickness. The sample for Z was prepared as a solid film.

TABLE LIII

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS A THROUGH D

A		B		C		D	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2625	4.3	2575	2.9	2559	3.4	2570	3.6
2593	4.3	2550	3.6	2493	3.0	2545	3.2
2520	4.8	2520	4.6	2470	7.4	2510	3.0
2480	4.0	2518	4.6	2458	10.0	2494	3.8
2460	8.9	2493	4.4	2420	2.7	2470	9.8
2456	10.0	2467	9.5	2370	2.5	2461	10.0
2450	9.3	2461	10.0	2345	3.1	2430	2.7
2420	2.7	2416	2.9	2284	2.4	2417	2.5
2400	2.2	2398	3.0	2232	1.5	2398	2.4
2380	2.2	2385	3.0	2182	2.5	2385	2.6
2364	2.5	2375	3.0	2162	3.9	2372	2.9
2344	2.9	2334	3.6	2153	4.5	2344	3.3
2337	2.8	2295	2.2	2138	5.4	2276	3.4
2313	3.1	2266	3.2	2076	0.9	2224	1.5
2300	1.7	2208	1.2	2040	1.2	2180	3.3
2265	1.3	2181	2.6	2025	1.9	2163	4.5
2255	1.7	2160	5.0	2015	1.7	2155	5.0
2208	1.0	2156	5.0	1760	0.5	2138	4.6
2185	1.4	2138	4.0	1740	0.6	2105	0.7
2170	3.7	2104	1.1	1720	0.7	2070	0.8
2160	5.7	2076	0.8	1700	0.9	2035	1.0
2152	3.7	2046	1.8	1690	1.5	2015	1.7
2137	5.0	2020	1.9	1672	3.1	1785	0.3
2103	1.2	2015	2.8	1665	2.5	1758	0.6
2046	2.5	1985	1.1	1640	0.5	1744	0.7
2024	2.4	1760	0.5	1630	0.4	1730	0.8
2014	3.8	1745	0.5	1476	2.3	1722	0.8
1984	1.7	1723	0.7	1136	0.2	1686	2.2
1894	0.5	1700	1.0			1676	3.1
1783	0.3	1675	3.0			1670	2.9
1760	0.3	1643	0.8			1640	0.4
1718	0.4	1635	0.6			1630	0.3
1700	0.7	1432	2.0			1476	2.1
1690	1.4	1138	0.3			1138	0.4
1680	2.2						
1671	3.5						
1665	2.9						
1645	0.8						
1635	0.6						
1625	0.4						
1481	3.6						
1417	0.2						
1404	0.2						
1395	0.3						
1375	0.1						

TABLE LIV

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS E THROUGH H

E		F		G		H	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2554	3.6	2600	2.2	2585	3.5	2545	3.5
2495	3.2	2550	3.0	2545	4.2	2523	3.6
2473	7.1	2520	6.5	2509	3.7	2511	4.1
2458	10.0	2480	7.4	2493	4.6	2480	5.6
2420	2.7	2463	10.0	2470	9.9	2464	6.2
2400	2.3	2450	9.1	2461	10.0	2446	6.7
2358	2.9	2420	5.9	2413	4.7	2424	5.8
2346	3.4	2387	5.4	2400	4.8	2397	6.1
2324	2.3	2370	5.1	2370	4.0	2369	5.2
2284	2.9	2344	6.5	2345	5.3	2350	6.8
2276	2.8	2334	6.5	2304	6.8	2340	6.7
2217	1.5	2317	6.3	2260	7.9	2304	9.9
2195	1.8	2300	7.4	2225	2.4	2280	7.9
2184	2.7	2267	8.0	2180	3.3	2263	10.0
2165	3.9	2190	1.4	2164	4.0	2170	2.3
2154	4.4	2170	2.8	2154	4.0	2140	2.6
2139	5.2	2154	6.1	2138	4.9	2125	1.8
2070	0.6	2130	3.5	2096	1.1	2100	1.1
2036	1.4	2103	1.5	2071	1.3	2066	1.0
2022	1.9	2067	1.2	2040	1.6	2030	2.0
2015	1.7	2045	2.6	2025	1.9	2012	2.7
1760	0.6	2020	2.8	2011	2.8	1930	0.5
1747	0.7	2013	5.0	1756	0.9	1891	0.5
1720	0.7	1983	2.2	1725	1.3	1795	0.5
1690	1.6	1750	1.1	1690	2.4	1758	1.0
1672	3.1	1730	1.3	1677	3.2	1731	1.5
1665	2.0	1695	2.0	1670	2.4	1719	1.5
1640	0.4	1684	2.5	1660	1.2	1698	1.4
1630	0.4	1673	2.6	1640	0.4	1692	1.7
1475	1.8	1642	1.0	1630	0.4	1683	1.1
1136	0.3	1480	5.0	1474	3.4	1474	3.5
		1205	0.3	1183	0.2	1205	0.2
		1185	0.3	1140	0.3	1185	0.3
		1140	0.3				

TABLE LV

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS I THROUGH L

I		J		K		L	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2623	13.2	2539	7.0	2510	9.7	2635	0.25
2572	11.2	2510	8.5	2484	9.9	2600	0.8
2541	16.0	2480	4.5	2464	10.0	2570	1.5
2521	14.8	2464	10.0	2450	10.0	2510	1.1
2500	6.7	2448	4.7	2439	6.2	2500	1.2
2450	5.6	2440	4.0	2420	7.5	2485	2.2
2429	4.0	2425	3.0	2407	9.5	2480	2.2
2398	10.0	2394	3.8	2396	12.1	2454	10.0
2369	5.2	2370	3.2	2371	9.7	2417	2.0
2346	3.6	2355	3.0	2357	8.9	2385	2.1
2308	4.8	2340	3.5	2350	9.1	2377	1.8
2283	4.4	2325	3.8	2307	11.7	2353	1.7
2234	3.6	2315	4.0	2295	9.1	2336	1.2
2207	5.6	2282	4.3	2280	11.2	2330	1.0
2193	7.2	2253	3.5	2220	3.0	2315	1.1
2175	7.2	2230	1.1	2200	3.7	2294	1.0
2142	8.0	2195	1.5	2180	4.1	2290	1.0
2135	8.0	2179	3.3	2167	5.3	2270	0.7
2126	8.0	2167	3.2	2152	4.4	2240	0.6
2115	5.6	2160	4.2	2141	4.6	2205	0.8
2085	2.8	2150	5.4	2125	3.8	2192	0.9
2055	2.4	2139	6.2	2110	3.0	2184	0.9
2018	2.0	2090	2.2	2090	3.9	2171	2.0
1960	1.6	2064	2.3	2075	3.1	2158	2.0
1764	1.0	2030	1.2	2053	4.1	2153	2.5
1754	1.0	1976	0.6	2045	2.2	2135	3.8
1714	1.4	1925	0.7	2020	2.4	2123	1.0
1694	2.0	1893	2.6	2000	2.8	2095	0.2
1685	2.2	1775	0.6	1994	2.8	2070	0.15
1671	5.2	1758	0.6	1960	1.3	2015	0.1
1658	5.6	1735	0.6	1756	1.0	1781	0.35
1625	1.2	1720	0.8	1735	1.7	1758	0.4
1467	1.4	1700	1.6	1715	1.5	1744	0.35
1395	1.0	1690	2.4	1693	2.7	1717	0.4
1370	0.4	1685	2.4	1685	3.1	1700	0.5
1130	0.4	1675	3.5	1675	3.9	1692	0.75
		1670	4.2	1670	3.5		
		1640	0.4	1665	3.4		
		1627	0.4	1634	1.3		
		1483	0.7	1479	4.4		
		1403	0.4	1195	0.3		
		1395	0.6				
		1370	0.2				
		1145	0.2				
		1136	0.3				

TABLE LVI

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS M THROUGH O

M		M		N		O	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2682	7.3	1784	1.2	2560	0.63	2625	2.3
2653	6.3	1759	1.7	2527	1.1	2545	3.2
2604	8.8	1746	1.5	2520	1.4	2534	3.2
2590	8.9	1719	2.6	2483	2.3	2491	4.0
2570	9.3	1676	8.7	2458	3.8	2460	10.0
2560	9.0	1668	8.5	2434	2.4	2416	3.2
2538	8.5	1639	1.4	2402	1.9	2405	2.8
2520	8.2	1633	1.3	2376	3.0	2385	2.6
2511	8.5	1622	0.9	2360	3.3	2370	2.3
2492	9.3	1478	0.3	2350	2.1	2333	4.6
2470	10.0	1425	0.35	2304	8.3	2300	3.3
2460	10.0	1395	0.5	2259	10.0	2260	3.3
2450	10.0	1375	0.4	2216	0.76	2255	3.2
2420	9.0	1365	0.35	2187	0.55	2223	2.6
2387	7.5	1355	0.3	2159	0.52	2214	2.8
2370	8.5	1345	0.2	2144	0.66	2172	4.9
2344	9.1	1167	0.35	2126	0.45	2153	11.0
2315	9.1	1158	0.45	2110	0.55	2110	4.0
2308	9.2	1138	1.1	2094	0.52	2090	2.6
2263	9.7			2070	0.28	2055	3.7
2240	4.8			2044	0.21	2024	6.8
2222	5.3			2015	0.21	1992	3.3
2212	5.8			1984	0.28	1720	0.2
2195	3.1			1954	0.31	1700	0.5
2181	6.8			1930	0.24	1682	1.8
2161	9.5			1894	0.28	1670	3.0
2136	9.4			1844	0.21	1640	0.9
2115	2.7			1813	0.21	1630	0.7
2100	2.0			1758	0.55	1491	2.1
2083	1.3			1727	0.9	1136	0.3
2060	0.9			1719	0.9		
2012	0.55			1703	0.97		
2000	0.6			1691	1.25		
1978	0.75			1679	0.97		
1946	0.70			1670	0.76		
1925	0.65			1454	0.07		
1894	1.1			1426	0.07		
1884	0.95			1405	0.07		
1867	0.8			1396	0.14		
1855	0.8			1386	0.17		
1834	0.8			1372	0.17		
1823	0.8			1354	1.0		
1816	0.9			1180	0.17		
1810	0.95			1170	0.14		
1800	0.95			1150	0.07		

TABLE LVII

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS P THROUGH S

P		O		R		S	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2546	1.7	2617	10.0	2547	3.9	2576	3.8
2495	2.0	2580	6.5	2500	2.7	2550	4.5
2480	8.6	2497	4.3	2490	3.4	2517	5.2
2473	10.0	2470	4.6	2465	10.0	2502	5.1
2461	9.1	2450	5.6	2420	2.9	2476	5.0
2434	1.9	2434	6.3	2400	2.4	2448	6.9
2420	2.0	2395	7.0	2390	2.2	2434	6.4
2401	1.7	2384	6.1	2334	3.4	2397	6.2
2391	2.1	2344	10.0	2319	3.2	2345	10.0
2374	2.2	2323	4.8	2276	3.2	2327	3.9
2352	1.9	2316	9.6	2260	2.4	2307	6.9
2340	1.6	2285	5.2	2193	1.7	2288	4.7
2320	1.6	2275	3.3	2170	3.4	2275	3.3
2310	1.4	2018	0.6	2148	5.4	2235	0.8
2288	5.1	1893	2.6	2124	2.7	2205	0.7
2257	1.5	1752	2.0	2097	2.2	2150	0.5
2219	1.7	1723	2.6	2075	3.4	2128	0.5
2190	2.2	1705	1.5	2047	2.4	2100	0.5
2184	3.6	1695	0.6	2024	1.5	2070	1.9
2160	3.3	1610	1.5	2012	3.4	1984	0.7
2138	3.0	1600	0.6	1987	2.4	1940	0.4
2070	1.7	1473	1.3	1980	1.5	1893	H_2O
2050	1.9	1410	0.7	1730	0.75	1830	0.8
2040	1.8	1400	0.7	1700	1.0	1812	0.9
2014	2.3	1395	0.9	1674	2.9	1795	0.8
1763	0.1	1215	0.4	1645	0.5	1772	0.9
1751	0.2	1200	0.4	1498	1.0	1754	2.0
1737	0.2			1485	1.5	1725	2.3
1710	0.3					1717	1.9
1693	3.5					1505	0.6
1688	3.5					1425	0.2
1674	1.7					1412	0.3
1645	0.5					1395	0.3
1538	0.2					1390	0.3
1523	0.2					1380	0.2
1498	0.3					1235	0.2
1482	1.8					1215	0.3
1466	1.2					1200	0.3
1405	0.7					1185	0.3
1396	1.1					1170	0.2
1147	0.7						

TABLE LVIII

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS T THROUGH W

T		U		V		W	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2550	7.1	2645	7.5	2590	4.9	2573	5.2
2510	8.0	2606	8.0	2540	6.0	2540	4.2
2500	8.6	2560	8.2	2510	2.7	2512	3.4
2474	10.0	2522	7.8	2485	5.1	2495	3.8
2450	9.7	2496	8.6	2468	10.0	2471	9.7
2440	9.4	2470	10.0	2426	2.6	2463	10.0
2394	8.4	2455	9.4	2385	1.3	2420	2.7
2345	10.9	2432	9.8	2371	1.4	2404	2.1
2306	9.3	2393	9.2	2340	1.4	2386	1.9
2204	2.3	2385	9.1	2320	2.4	2372	2.2
2168	2.4	2344	11.1	2280	0.9	2344	3.2
2153	2.3	2306	10.0	2195	1.8	2330	2.5
2070	1.9	2290	8.7	2165	4.7	2291	2.9
1986	0.7	2195	4.6	2151	4.8	2250	1.1
1800	1.2	2165	4.8	2137	5.3	2215	1.1
1754	2.0	2150	4.7	2097	3.5	2184	3.0
1724	2.4	2080	2.7	2090	4.2	2164	4.1
1715	2.2	2070	2.7	2054	1.4	2156	3.7
1690	1.2	2060	2.7	2020	2.5	2139	4.1
1680	1.0	2040	2.7	1967	1.4	2120	1.7
1650	0.3	1990	1.7	1919	1.0	2086	1.8
1502	0.4	1940	1.5	1898	0.5	2063	1.4
1410	0.15	1910	1.4	1752	0.15	2020	1.0
1386	0.15	1810	1.5	1720	0.15	2003	1.1
1210	0.2	1790	1.4	1700	0.53	1970	0.2
1200	0.3	1752	2.3	1680	2.3	1900	0.07
1190	0.2	1790	1.4	1670	2.6	1890	0.07
		1752	2.3	1635	0.35	1810	0.2
		1723	2.4	1625	0.31	1786	0.35
		1710	2.0	1417	5.3	1760	0.55
		1678	1.8	1370	0.1	1750	0.55
		1644	0.66	1355	0.1	1720	0.55
		1496	0.33	1217	0.1	1690	1.7
		1412	0.2	1136	0.31	1676	2.9
		1386	0.13			1643	0.35
		1215	0.2			1633	0.35
		1198	0.3			1625	0.2
		1185	0.2			1415	2.6
		1140	0.13			1213	0.07
						1140	0.3

TABLE LIX

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS X THROUGH AA

X		Y		Z		AA	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2650	6.4	2600	5.0	2615	6.5	2490	2.4
2620	5.9	2570	4.3	2583	12.6	2476	10.0
2595	6.0	2550	3.8	2564	11.6	2463	8.6
2550	5.5	2496	4.1	2540	8.1	2455	8.2
2528	5.3	2476	9.4	2530	7.7	2432	2.0
2510	5.3	2465	10.0	2491	7.3	2419	1.7
2478	10.0	2436	4.2	2467	7.3	2403	1.6
2461	7.6	2404	3.7	2454	7.8	2388	1.6
2440	4.6	2390	3.7	2432	10.0	2373	1.8
2390	2.6	2370	5.0	2410	7.3	2356	3.7
2370	2.1	2360	5.4	2371	7.3	2346	4.0
2315	2.5	2347	6.0	2356	7.0	2319	3.9
2284	1.9	2296	4.1	2345	7.3	2295	3.1
2260	2.0	2252	2.8	2338	6.8	2276	3.3
2215	3.6	2210	3.6	2300	5.4	2225	0.6
2203	3.5	2186	3.8	2294	5.1	2201	0.7
2181	3.7	2166	4.5	2278	3.0	2185	2.4
2167	3.2	2159	4.2	2255	3.5	2167	4.0
2159	3.5	2142	4.6	2238	5.4	2155	2.6
2140	2.9	2115	2.5	2203	5.8	2141	3.1
2093	1.4	2060	0.65	2170	6.5	2120	0.4
2024	1.4	2024	4.7	2151	4.5	2100	0.2
1986	3.6	2000	2.0	2140	4.1	2060	0.1
1865	0.3	1790	0.2	2123	5.1	2030	0.1
1812	0.25	1764	0.4	2054	2.4	2010	0.2
1750	0.25	1754	0.4	2007	4.9	1875	0.1
1723	0.2	1725	0.3	1994	3.8	1810	0.05
1710	0.4	1694	1.4	1733	0.4	1800	0.06
1690	1.3	1680	2.2	1724	0.4	1770	0.6
1680	1.2	1645	0.4	1690	1.0	1743	0.8
1672	1.3	1635	0.3	1676	1.3	1728	0.7
1643	0.3	1532	2.5	1668	1.1	1701	2.0
1635	0.3	1492	0.3	1635	0.3	1694	2.3
1520	1.1	1384	0.5	1527	1.8	1680	3.2
1505	1.5	1234	0.1	1516	1.1	1645	0.5
1470	0.3	1142	0.25	1490	0.4	1634	0.4
1380	0.4			1420	0.1	1440	0.05
1350	0.05			1140	0.3	1410	0.07
1144	0.14					1400	0.07
						1380	0.1
						1363	0.05
						1190	0.2
						1147	0.3
						1140	0.35

TABLE LX

NEAR INFRARED SPECTRA OF MODEL COMPOUNDS BB THROUGH DD

BB		CC		DD		DD	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2600	2.5	2496	2.4	2587	9.6	1795	2.2
2590	2.5	2470	9.4	2542	5.4	1784	3.2
2575	2.3	2465	10.0	2524	7.0	1774	3.4
2545	2.1	2430	2.3	2505	8.4	1758	4.6
2512	1.7	2422	2.6	2494	10.0	1750	3.8
2500	2.6	2403	1.4	2470	7.2	1734	3.2
2475	10.0	2368	2.7	2435	10.0	1720	4.2
2464	9.7	2357	2.1	2418	9.0	1703	3.2
2433	2.6	2336	1.2	2396	11.2	1694	3.8
2402	1.5	2321	1.2	2390	10.6	1686	3.4
2390	1.6	2290	0.8	2369	11.2	1678	4.2
2359	3.4	2280	0.7	2361	13.6	1662	1.3
2310	1.8	2253	0.3	2356	15.2	1653	0.7
2294	1.5	2218	0.4	2340	12.8	1640	0.6
2252	0.8	2186	2.7	2320	12.0	1635	0.5
2218	1.1	2167	3.7	2298	11.6	1435	0.2
2210	1.1	2163	3.5	2226	1.0	1420	0.3
2186	3.2	2142	4.1	2201	1.2	1400	0.3
2167	4.2	2105	0.2	2188	4.4	1383	0.3
2163	4.0	1890	0.2	2176	6.6	1220	0.5
2143	3.9	1850	0.2	2161	3.3	1212	0.6
2100	0.2	1790	0.3	2148	4.0	1200	0.6
1890	0.1	1765	0.5	2143	4.1	1187	0.4
1860	0.2	1750	0.3	2115	1.0	1147	0.3
1815	0.2	1725	0.5			1143	0.4
1790	0.25	1690	2.0				
1764	0.9	1675	3.3				
1754	0.7	1643	0.5				
1725	0.55	1635	0.5				
1690	2.2	1625	0.3				
1680	3.4						
1674	3.2						
1645	0.5						
1634	0.4						
1628	0.3						
1585	0.04						
1513	0.03						
1495	0.03						
1465	0.04						
1430	0.05						
1397	0.06						
1380	0.05						
1345	0.03						
1205	0.05						
1140	0.32						

APPENDIX III

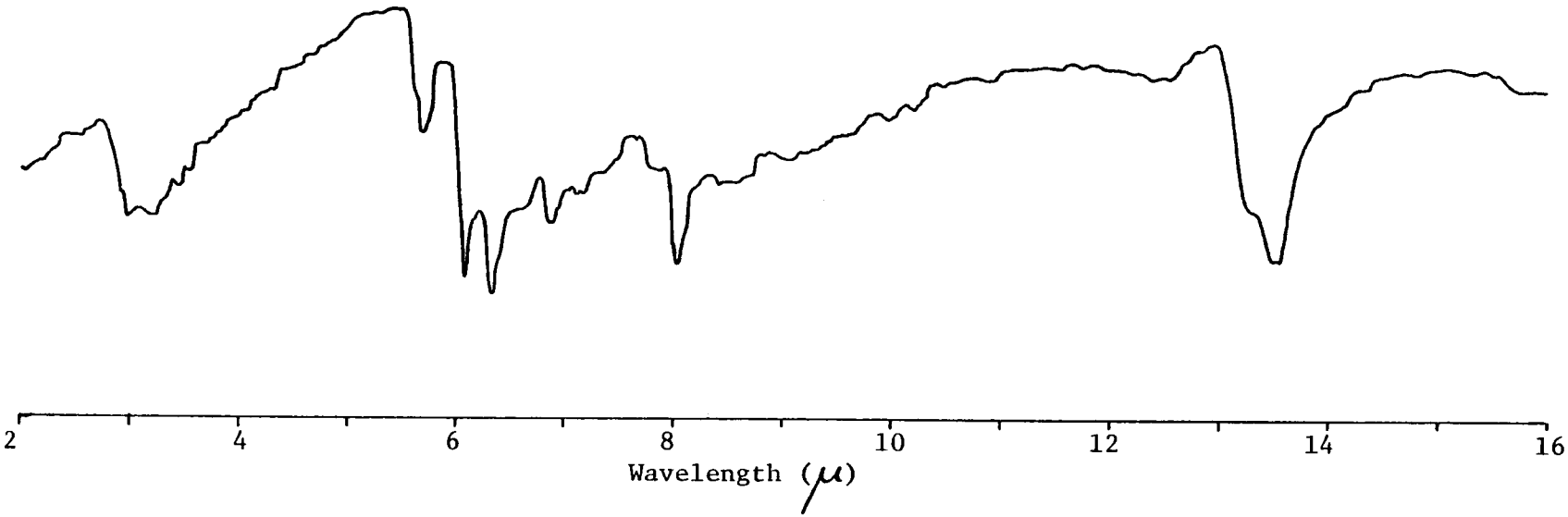


Figure 42. Midrange infrared spectrum of residue IV-1.

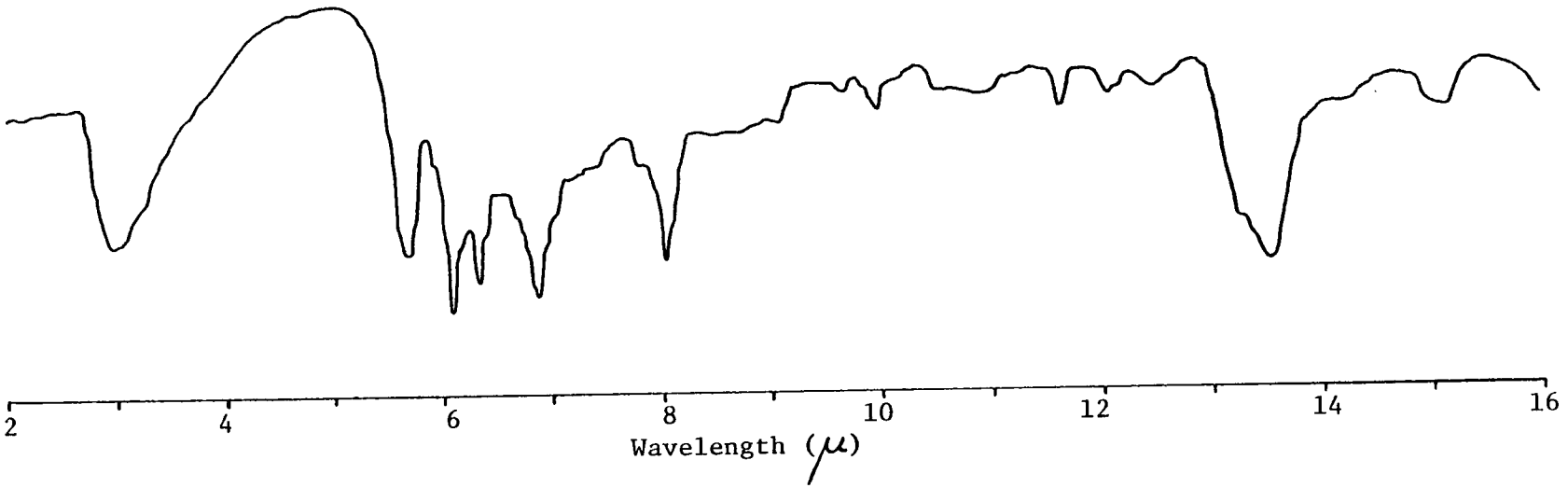


Figure 43. Midrange infrared spectrum of residue IV-2, prepared at 290-295°.

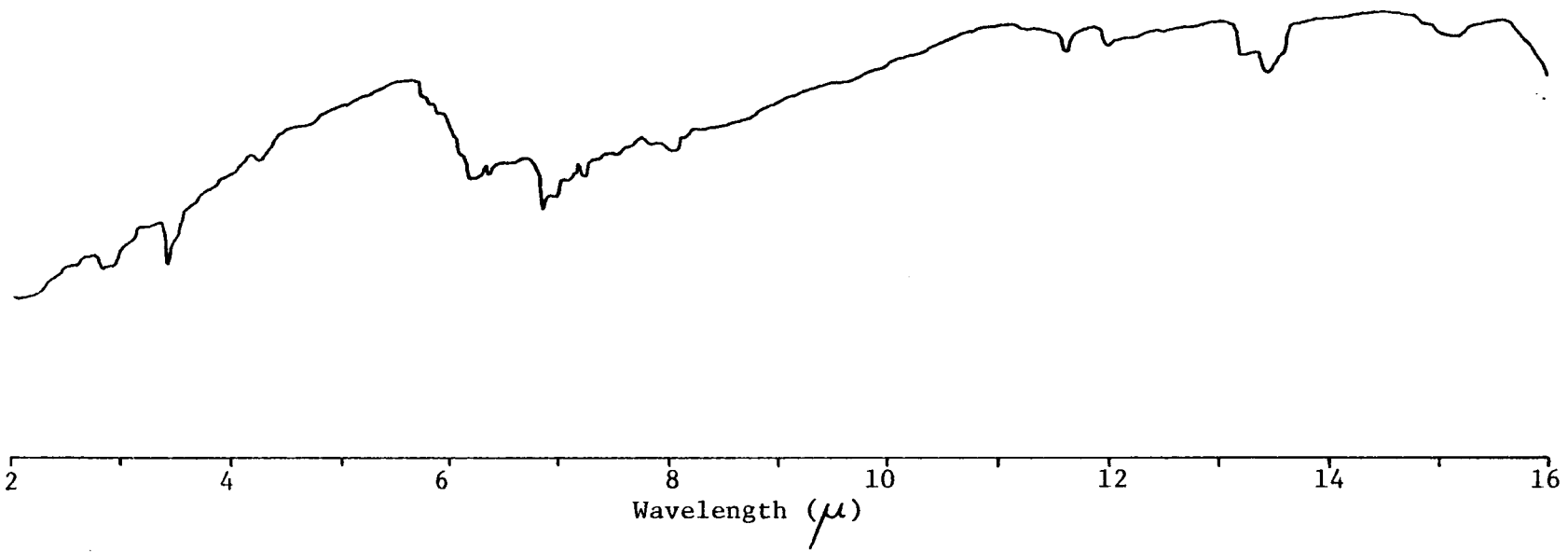


Figure 44. Midrange infrared spectrum of residue IV-3, mostly polymerized carbodiimide.

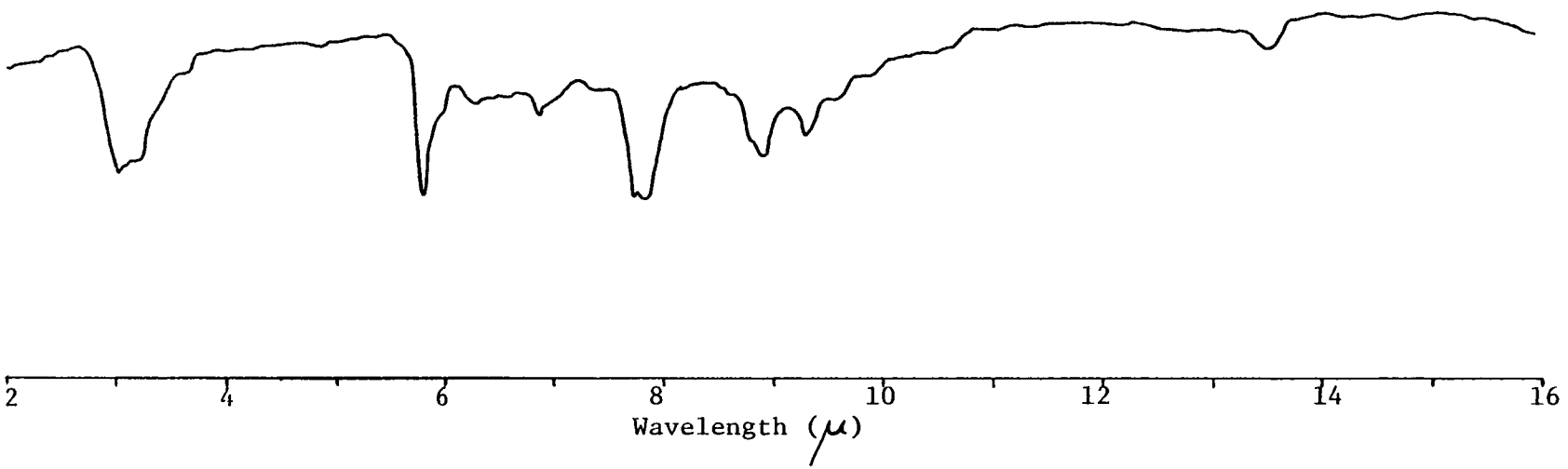


Figure 45. Midrange infrared spectrum of residue IV-4.

APPENDIX IV

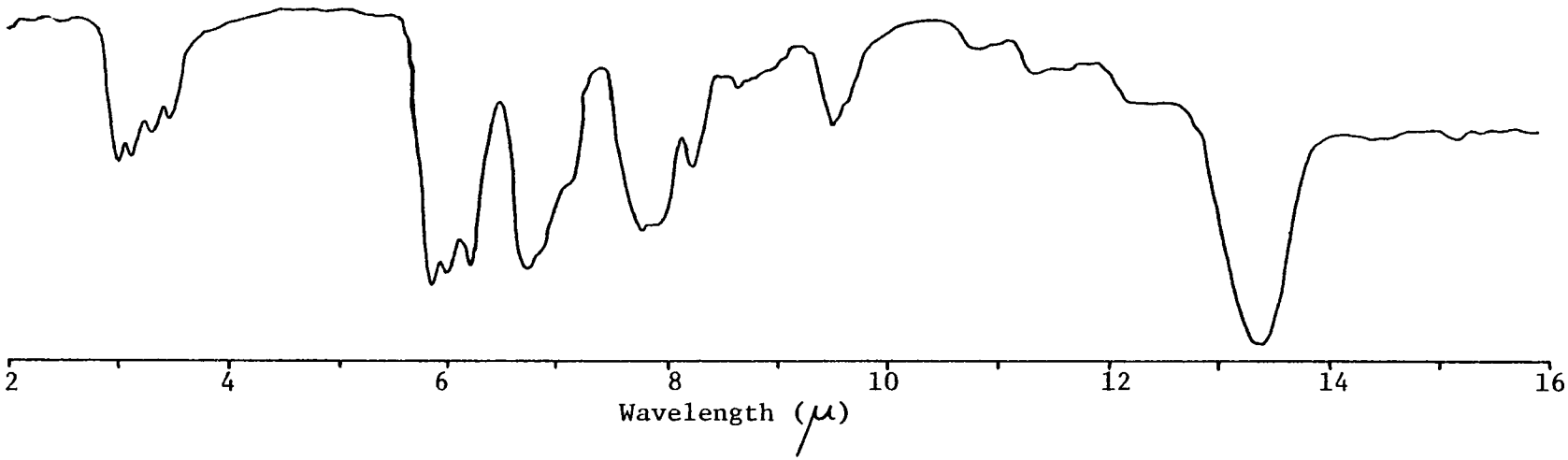


Figure 46. Midrange infrared spectrum of polymer-ortho-10, bulk polymerization at 168°. Made by heating in vacuum oven.

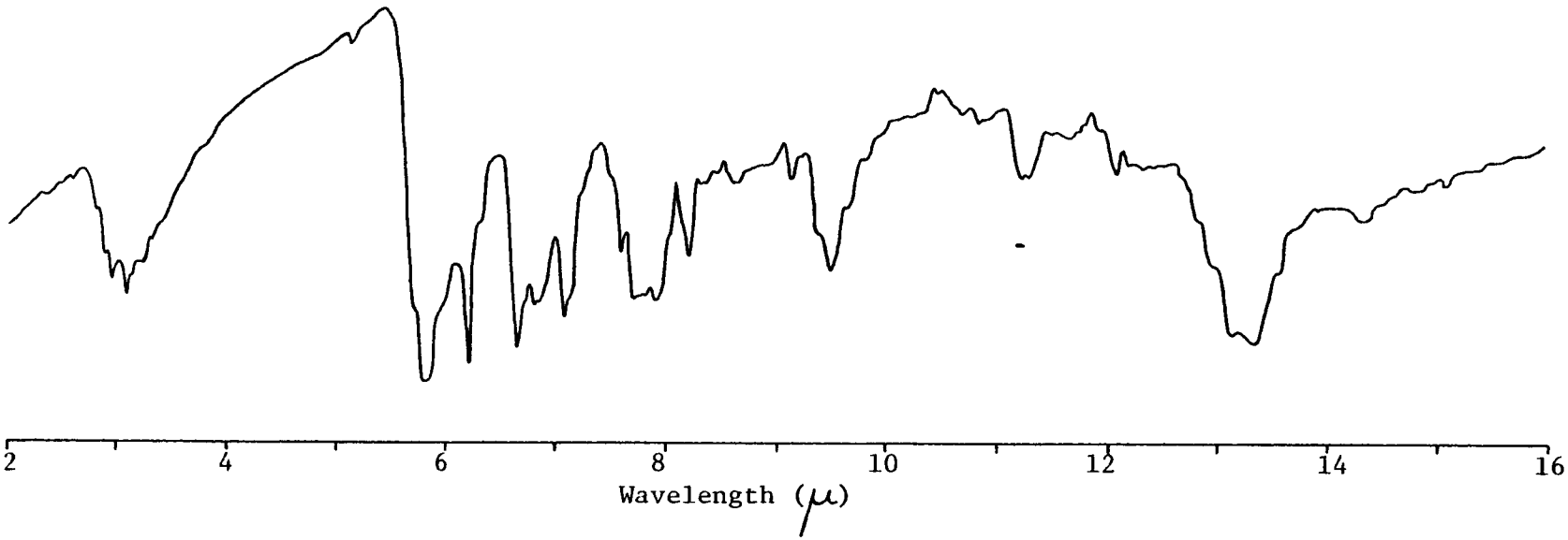


Figure 47. Midrange infrared spectrum of polymer-ortho-10, bulk polymerization at 154°. Made by heating in oil bath.

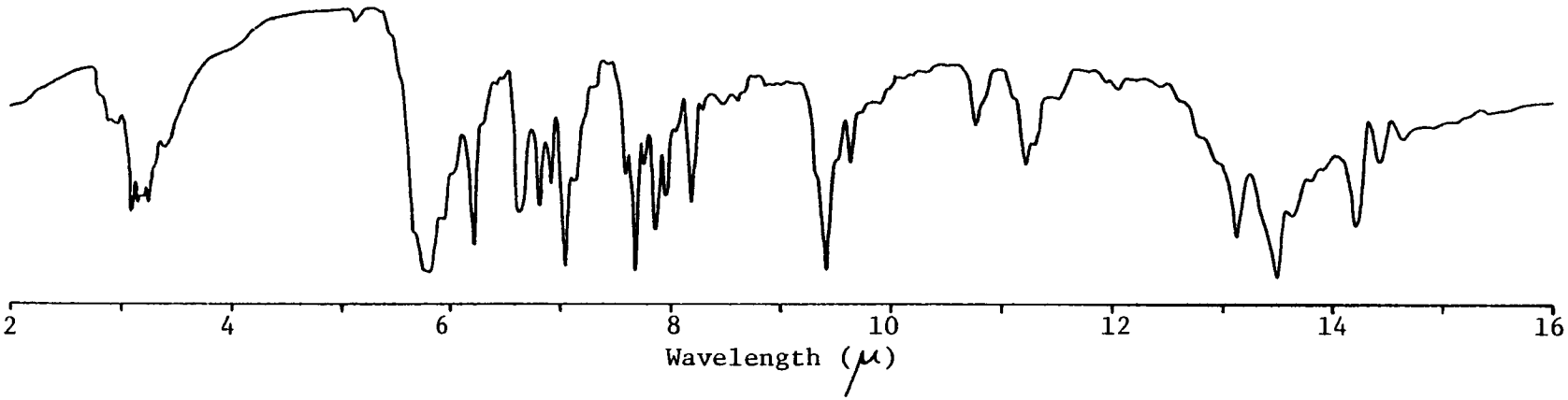


Figure 48. Midrange infrared spectrum of polymer-ortho-10, bulk polymerization at 165-170°. Made by heating in oil bath.

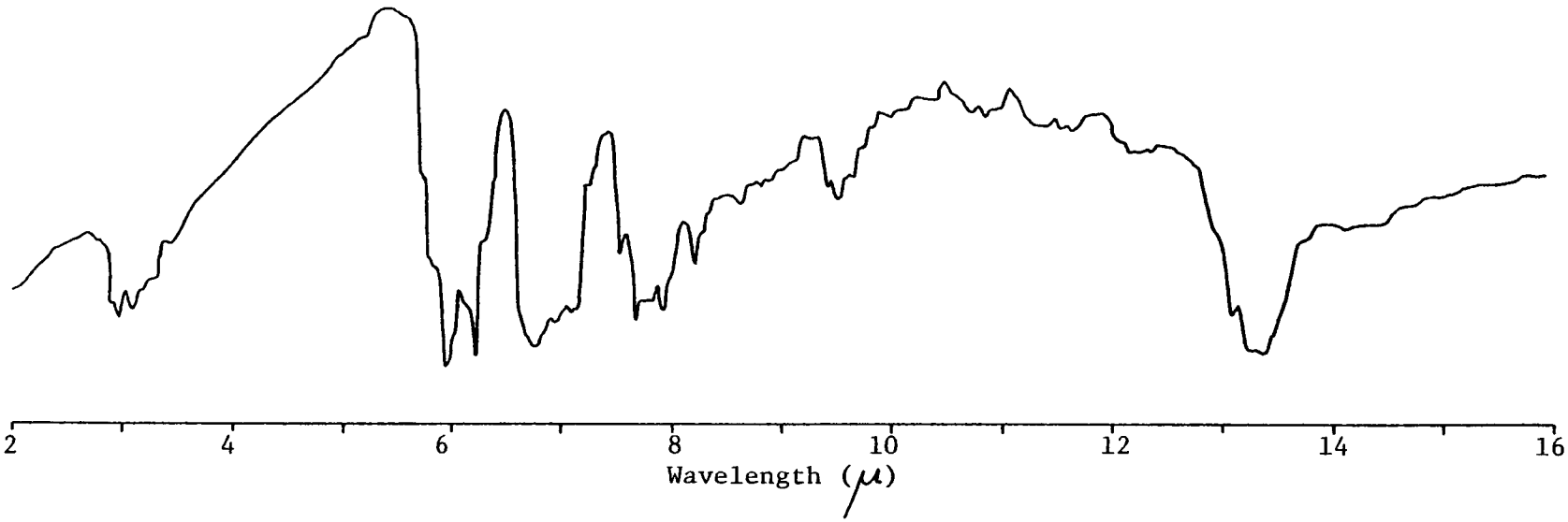


Figure 49. Midrange infrared spectrum of polymer-ortho-10, bulk polymerization at 176-185°. Made by heating in oil bath.

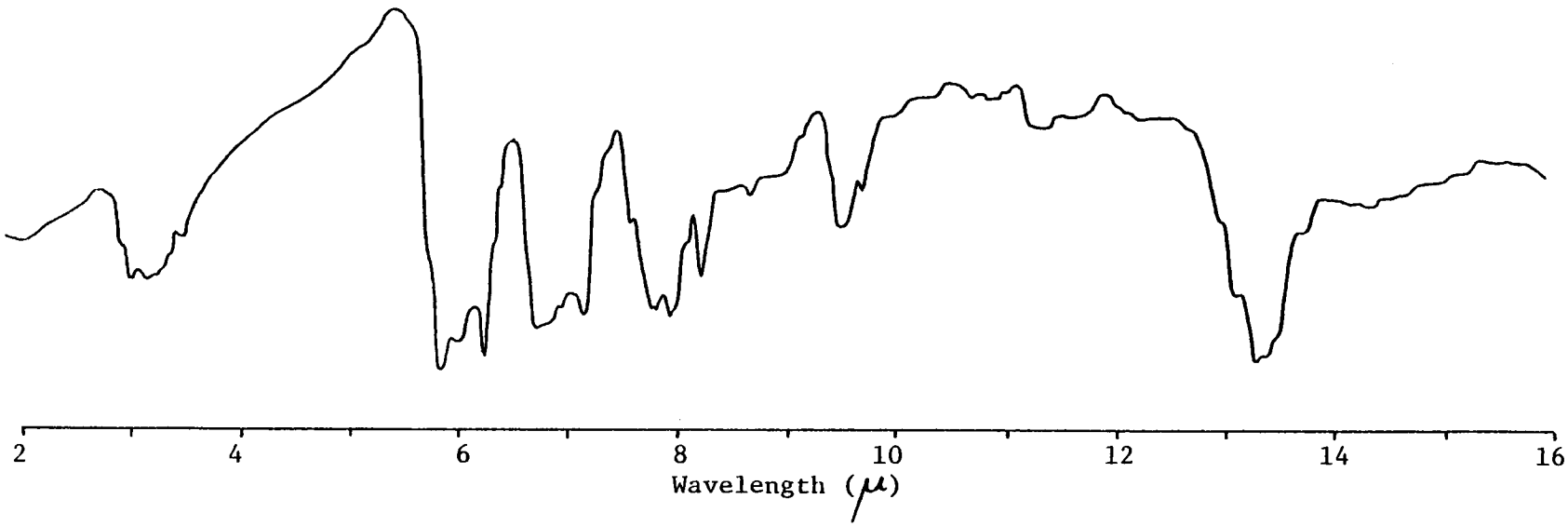


Figure 50. Midrange infrared spectrum of polymer-ortho-10, bulk polymerization at 180°. Made by heating in oil bath.

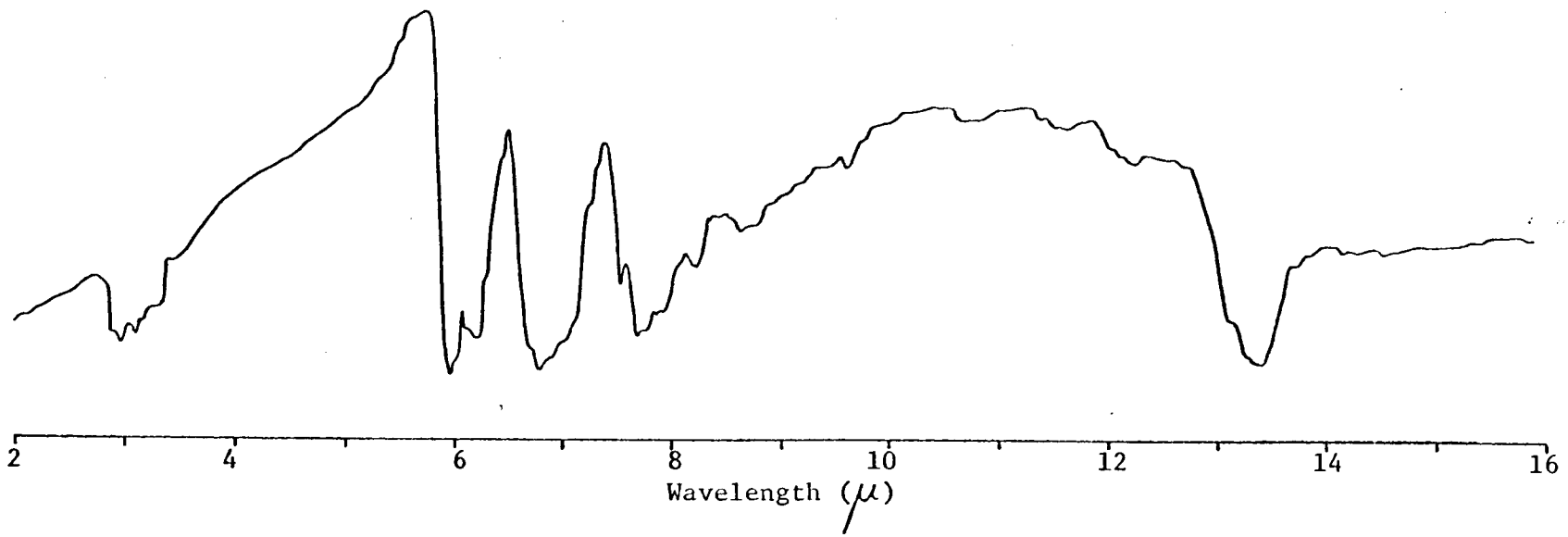


Figure 51. Midrange infrared spectrum of system-ortho-10 crosslinked polymer, bulk polymerization at 194-202°. Made by heating in oil bath.

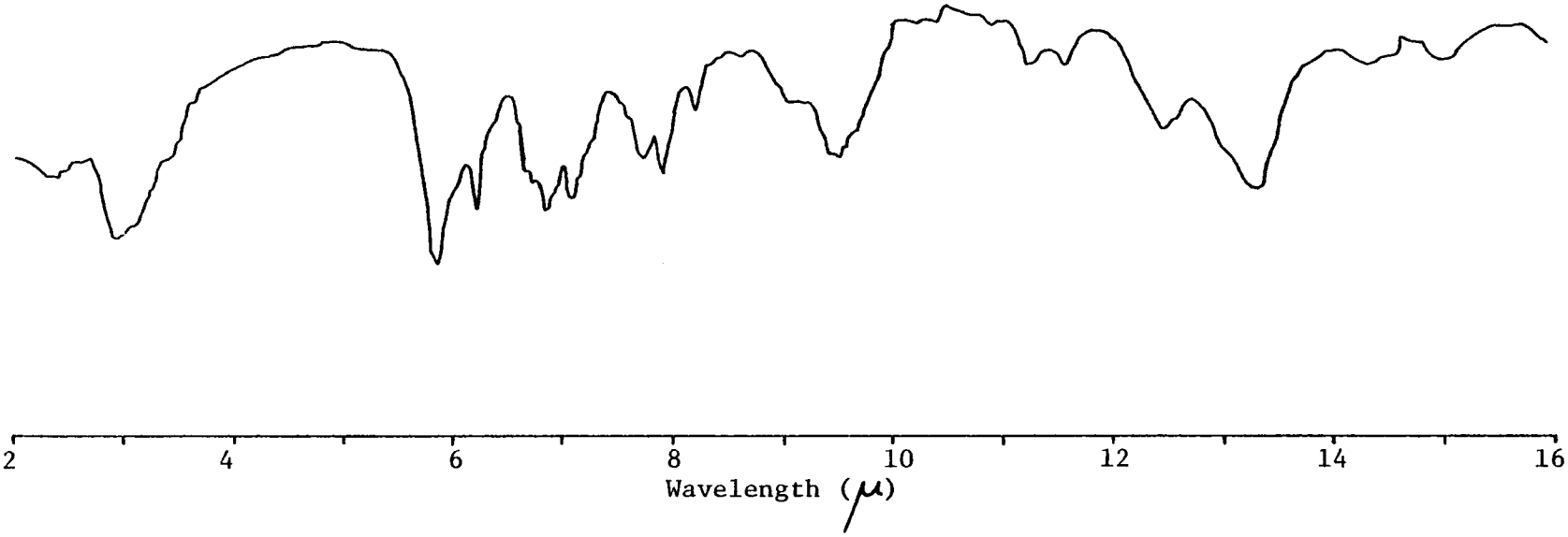


Figure 52. Midrange infrared spectrum of polymer-ortho-10, refluxing solvent polymerization at 132°. Made by heating in chlorobenzene.

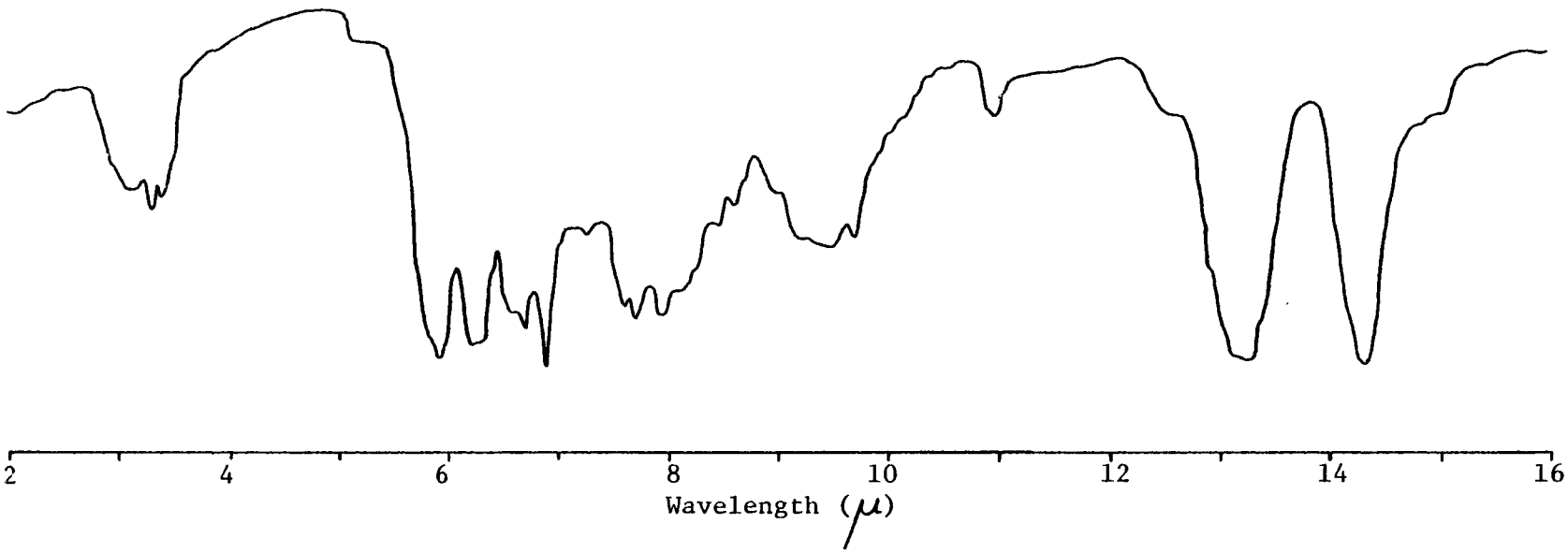


Figure 53. Midrange infrared spectrum of polymer-ortho-10, refluxing solvent polymerization at 136°. Made by heating in ethylbenzene.

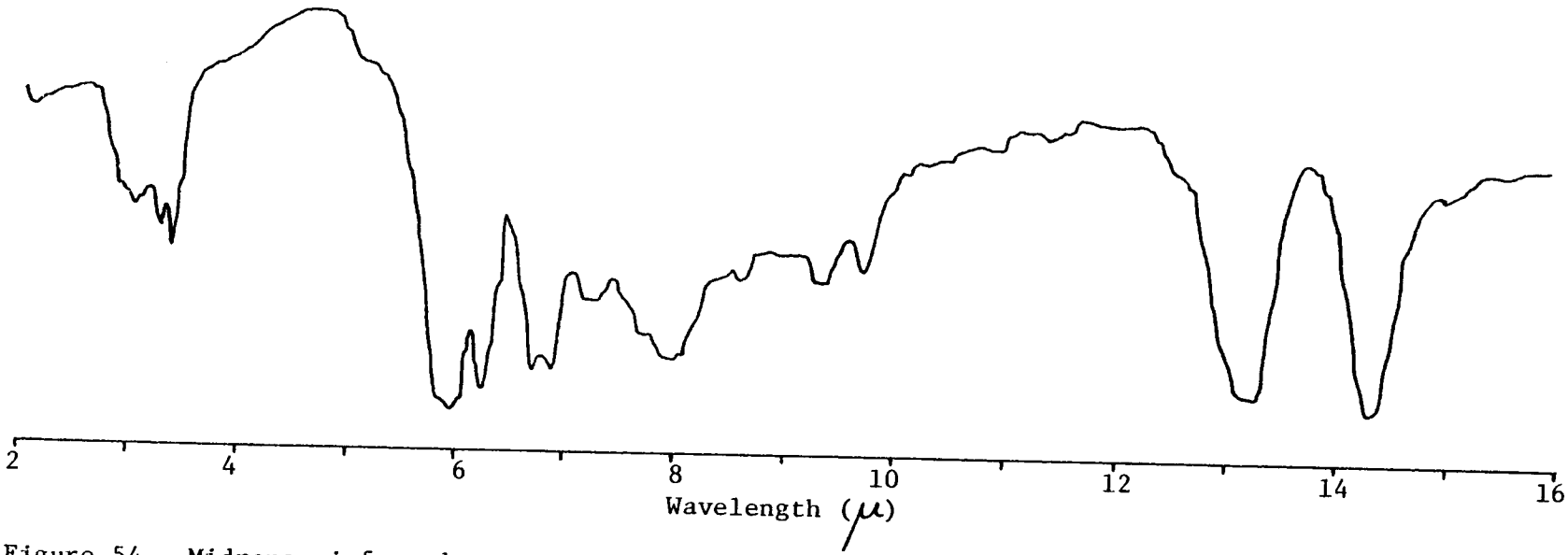


Figure 54. Midrange infrared spectrum of polymer-ortho-10, refluxing solvent polymerization at 152°. Made by heating in cumene.

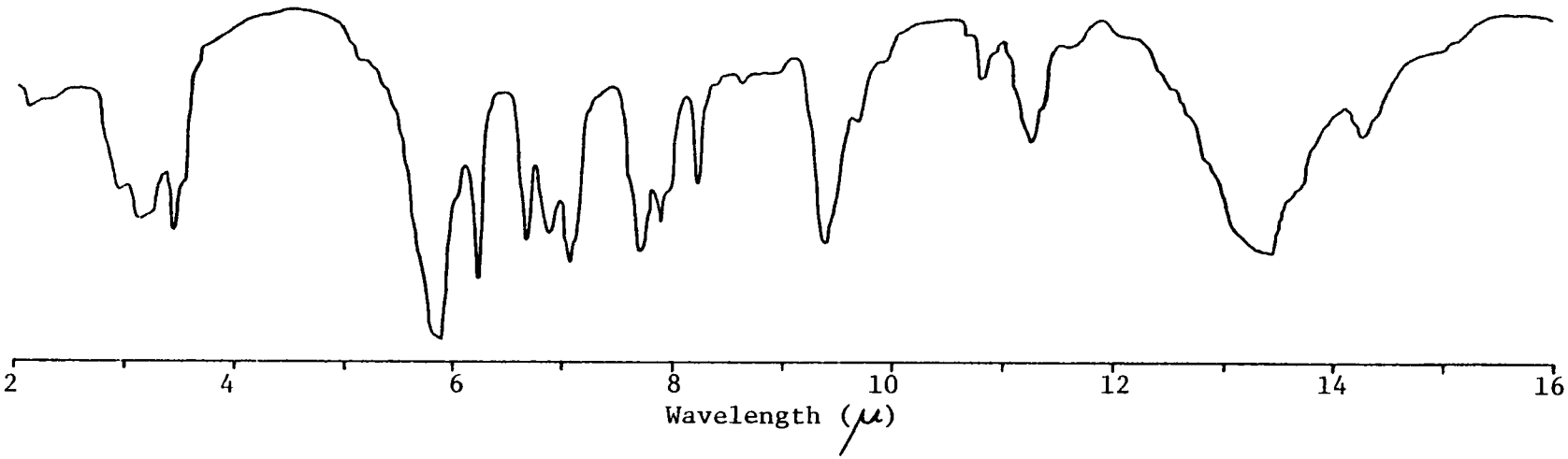


Figure 55. Midrange infrared spectrum of polymer-ortho-10, refluxing solvent polymerization at 156°. Made by heating in cyclohexanone.

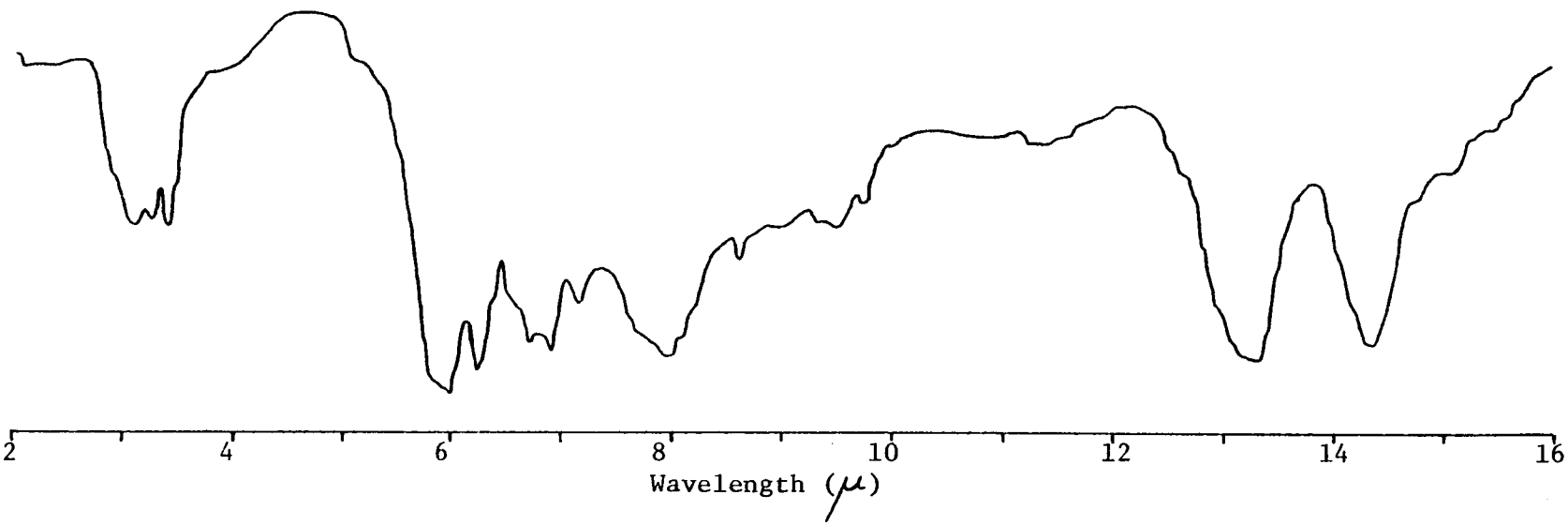


Figure 56. Midrange infrared spectrum of polymer-ortho-10, refluxing solvent polymerization at 183°. Made by heating in n-butylbenzene.

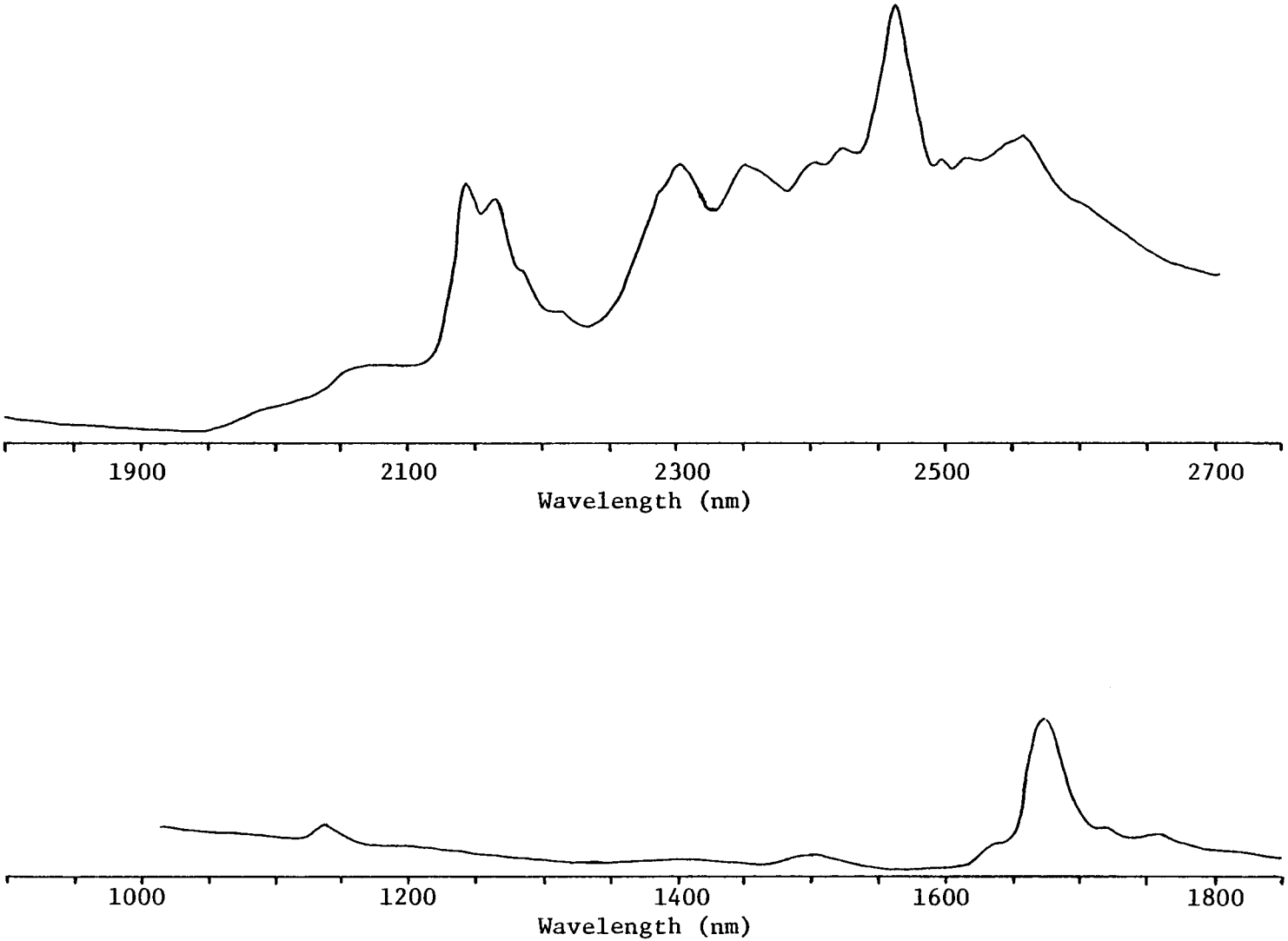


Figure 57. Near infrared spectrum of polymer-ortho-10, refluxing solvent polymerization at 183°.

TABLE LXI

NEAR INFRARED SPECTRA OF SYSTEM-ORTHO-10 POLYMERS - DIRECTORY

Polymer[a]	Spectrum[b]
soluble fraction, bulk polymerization at 176-185°	A
refluxing solvent polymerization at 144° (o-xylene)	B
refluxing solvent polymerization at 156° (cyclohexanone)	C
refluxing solvent polymerization at 156° (bromobenzene)	D
refluxing solvent polymerization at 165° (mesitylene)	E
refluxing solvent polymerization at 170° (phenetole)	F
refluxing solvent polymerization at 173° (s-butylbenzene)	G
refluxing solvent polymerization at 183° (n-butylbenzene)	H
sample C heated at 170° for 12 hr under vacuum	I
sample H heated at 180° for 24 hr under vacuum	J

a. All samples except I and J contained at least a small amount of polymer-ortho-10 according to midrange infrared data.

b. The reduced data, wavelength (nm) vs. relative intensity (R.I.), has been extracted from the near infrared data and presented in columnar form in the succeeding pages of this table. All samples were prepared as films on pyrex glass.

TABLE LXII

NEAR INFRARED SPECTRA OF SYSTEM-ORTHO-10 POLYMERS A THROUGH D

A		B		C		D	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2546	11.2	2450	10.0	2505	10.5	2515	11.3
2514	11.6	2405	10.0	2440	10.0	2450	10.0
2440	10.0	2350	9.0	2400	10.5	2405	8.7
2400	8.8	2300	10.0	2344	12.6	2370	8.0
2350	7.8	2277	11.0	2295	13.2	2320	8.7
2312	9.0	2168	5.0	2235	3.2	2285	8.7
2280	9.4	2143	6.0	2170	3.2	2220	5.3
2220	3.9	2100	1.5	2150	3.2	2175	7.3
2170	4.8	1755	1.5	1775	1.6	2160	6.0
2155	4.6	1715	2.5	1750	2.6	2150	6.0
2144	4.8	1675	5.0	1715	3.2	2100	3.3
2100	3.0	1410	0.5	1680	1.9	1984	5.3
2070	2.4			1675	1.6	1720	0.6
1980	3.4			1410	0.5	1680	2.0
1910	0.6					1510	0.7
1760	0.8					1410	0.3
1730	1.4						
1710	1.5						
1678	2.8						
1640	0.3						
1520	0.8						
1505	1.0						
1470	0.2						
1413	0.3						

TABLE LXIII

NEAR INFRARED SPECTRA OF SYSTEM-ORTHO-10 POLYMERS E THROUGH H

E		F		G		H	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
		2515	13.2				
2535	11.3	2480	10.6	2515	8.0	2518	6.4
2515	12.2	2460	10.0	2465	10.0	2498	6.3
2500	11.3	2400	9.3	2400	6.0	2465	10.0
2457	10.0	2367	8.5	2344	5.0	2425	6.6
2400	8.3	2345	8.3	2305	8.0	2405	6.3
2360	8.3	2315	8.4	2279	7.0	2354	6.2
2340	8.3	2290	8.2	2188	2.0	2290	5.6
2315	10.2	2260	6.4	2163	4.5	2213	2.8
2290	9.3	2200	5.3	2141	6.0	2185	3.8
2260	6.1	2170	7.7	1673	5.0	2166	5.5
2190	4.8	2150	8.4			2144	5.8
2165	7.0	2100	4.0			2080	1.7
2150	8.3	2060	2.4			2000	0.6
2110	2.8	1995	2.0			1787	0.5
2040	1.3	1720	1.3			1762	0.8
1770	2.5	1675	4.2			1750	0.7
1720	1.3	1640	1.0			1720	0.9
1703	2.2	1500	0.3			1676	3.5
1676	4.4	1410	0.3			1640	0.6
1500	0.5	1140	0.3			1500	0.25
1410	0.3					1410	0.1

TABLE LXIV

NEAR INFRARED SPECTRA OF SYSTEM-ORTHO-10 POLYMERS I AND J

I		J	
nm	R.I.	nm	R.I.
2500	11.0	2560	8.3
2440	10.0	2525	7.3
2400	11.0	2500	6.9
2360	13.0	2465	10.0
2345	14.5	2425	7.5
2296	15.0	2410	7.0
2170	3.5	2356	6.8
2160	3.5	2305	6.5
2150	3.5	2210	3.2
2140	3.5	2185	4.3
2110	1.5	2167	6.4
2060	1.0	2145	6.7
1780	1.5	2075	2.0
1770	2.0	2000	0.6
1760	2.5	1790	0.6
1750	3.0	1762	0.9
1740	2.5	1750	0.9
1720	3.0	1720	1.0
1710	3.0	1677	4.2
1700	2.5	1640	0.8
1680	2.0	1510	0.3
1670	1.5	1500	0.3
1410	0.3	1410	0.1
1400	0.3	1400	0.1
1200	0.6	1141	0.5
1140	0.3		

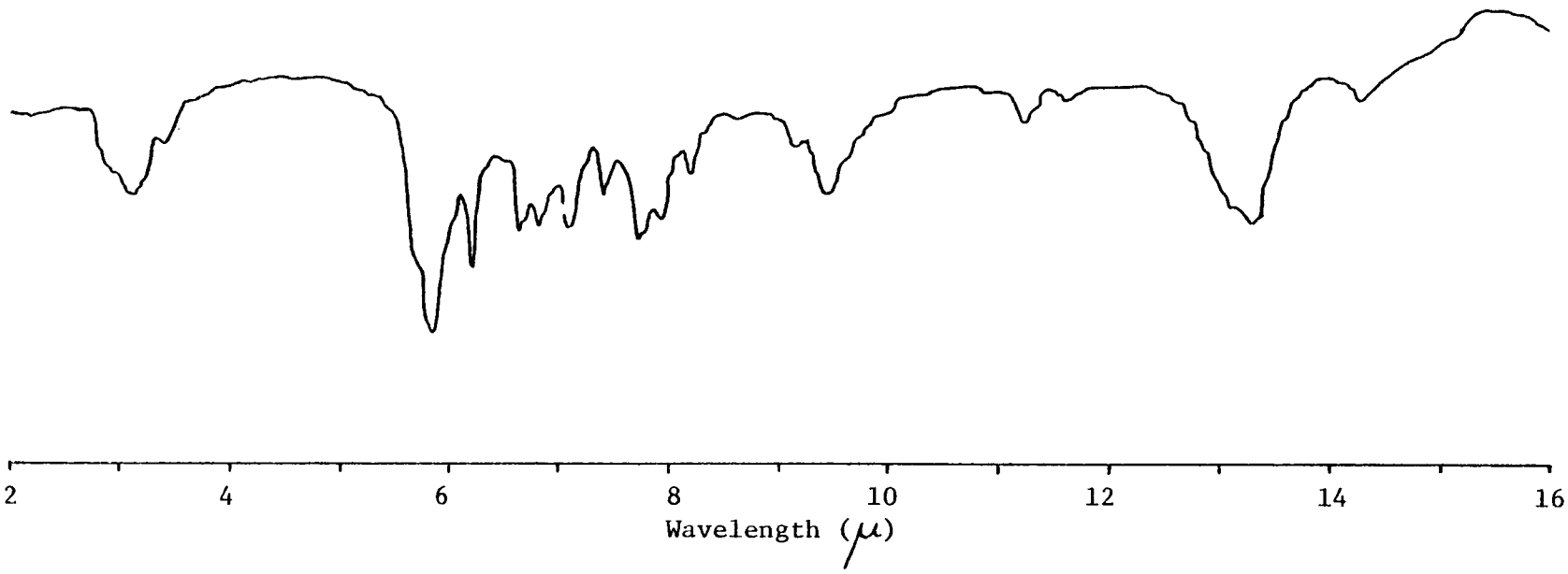


Figure 58. Midrange infrared spectrum of polymer-ortho-10, product of Curtius reaction.

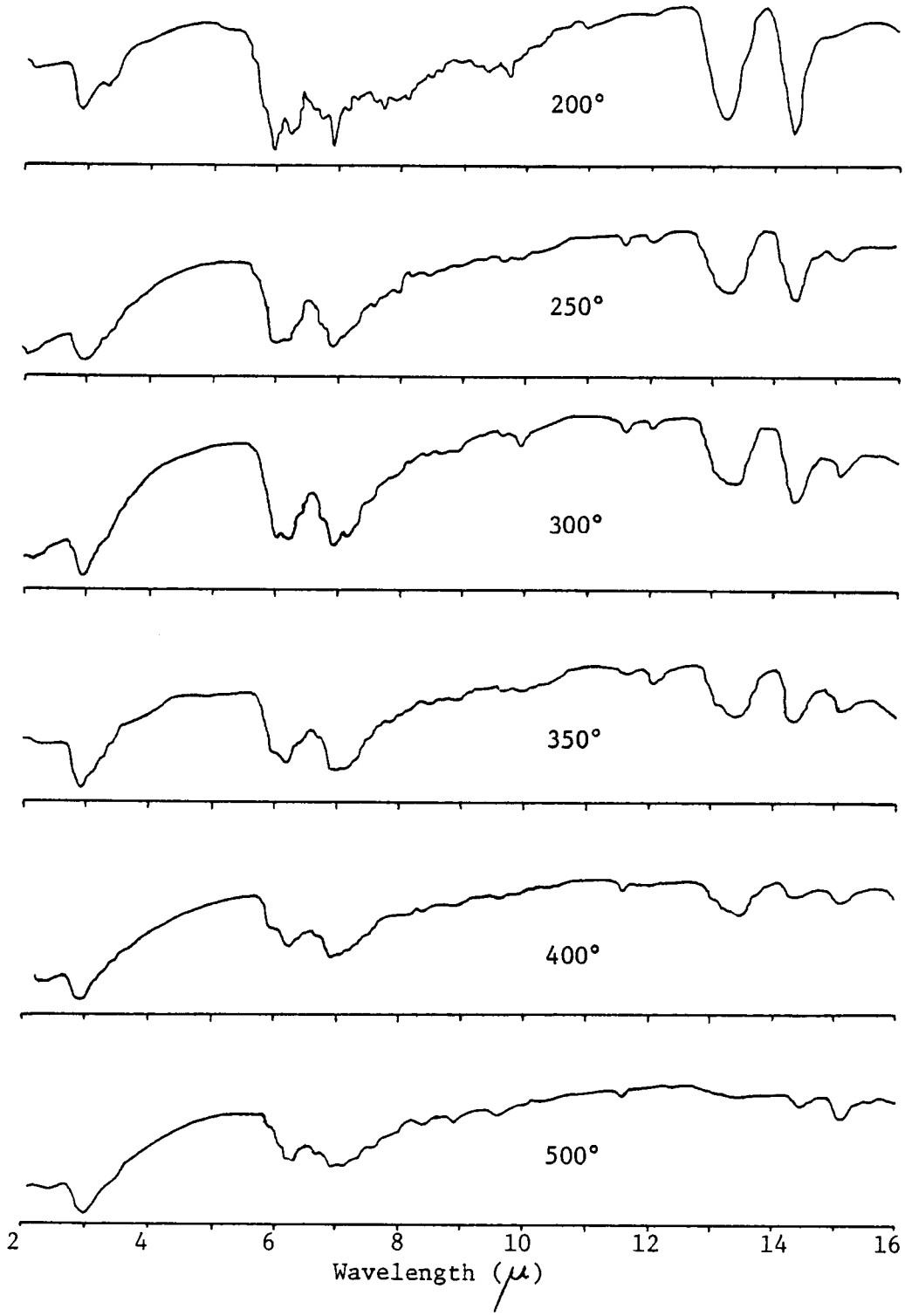


Figure 59. Midrange infrared spectra of thermolyzed samples of polymer-ortho-10. Original sample made in refluxing ethylbenzene. Heating for 1 hr in DSC sample pan.

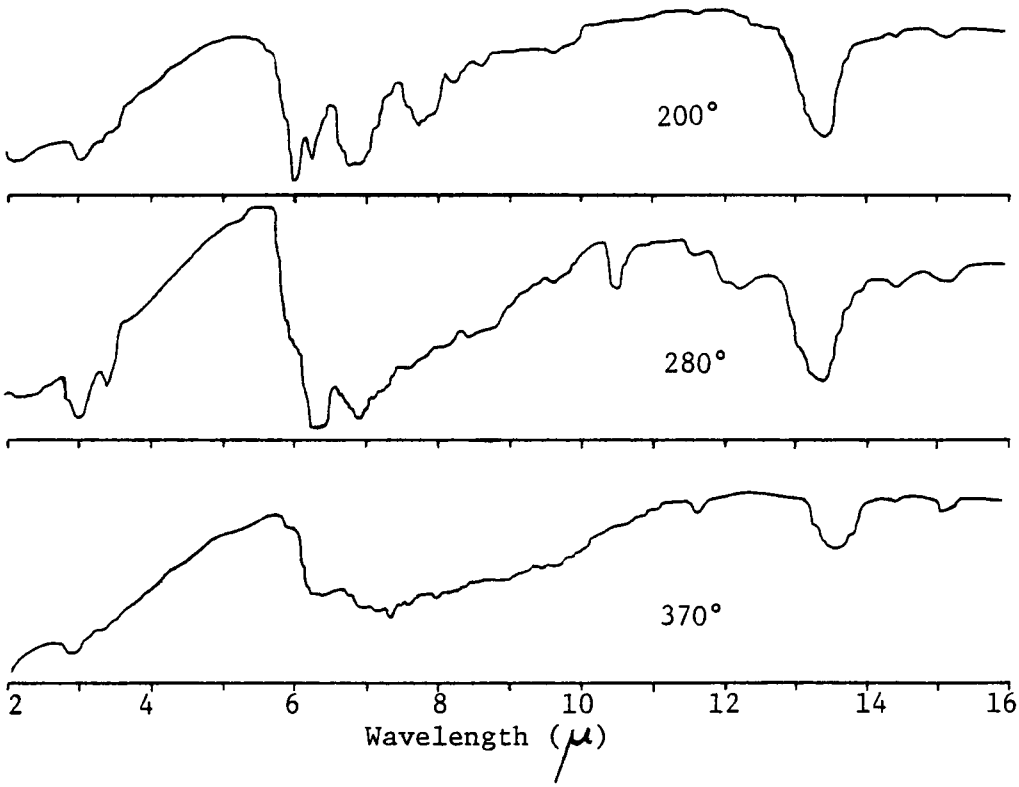


Figure 60. Midrange infrared spectra of thermolyzed samples of polymer-ortho-10. Original sample made in refluxing chlorobenzene. Heating for 24 hr under vacuum.

APPENDIX V

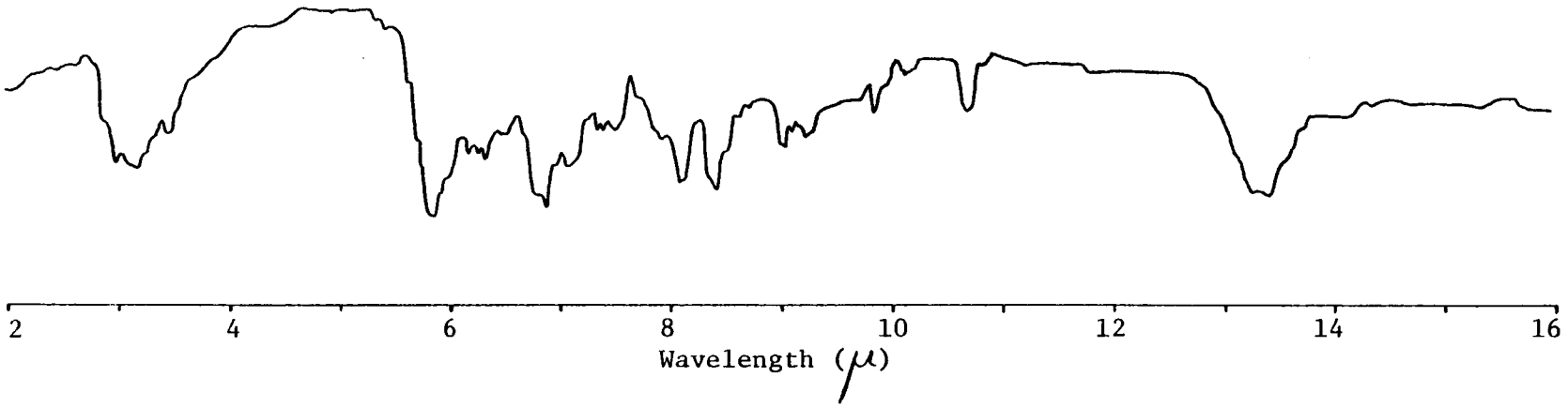


Figure 61. Midrange infrared spectrum of polymer-ortho-01, bulk polymerization at 170-176°. Made by heating in oil bath.

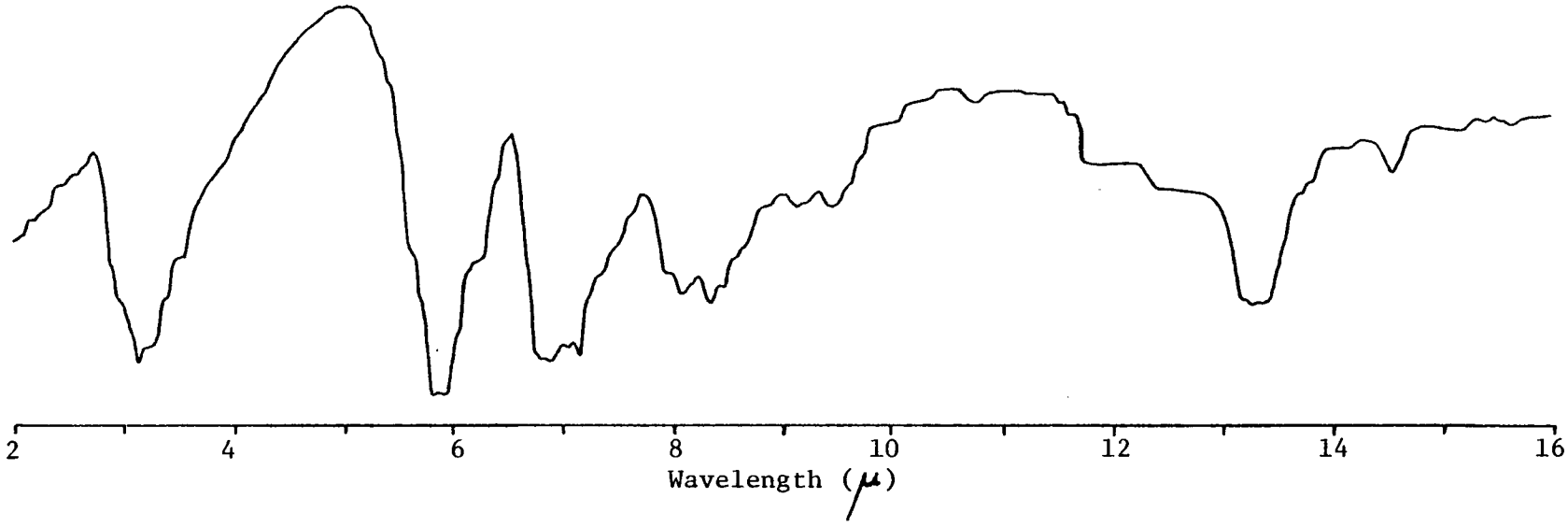


Figure 62. Midrange infrared spectrum of polymer-ortho-01, bulk polymerization at 206-209°. Made by heating in oil bath.

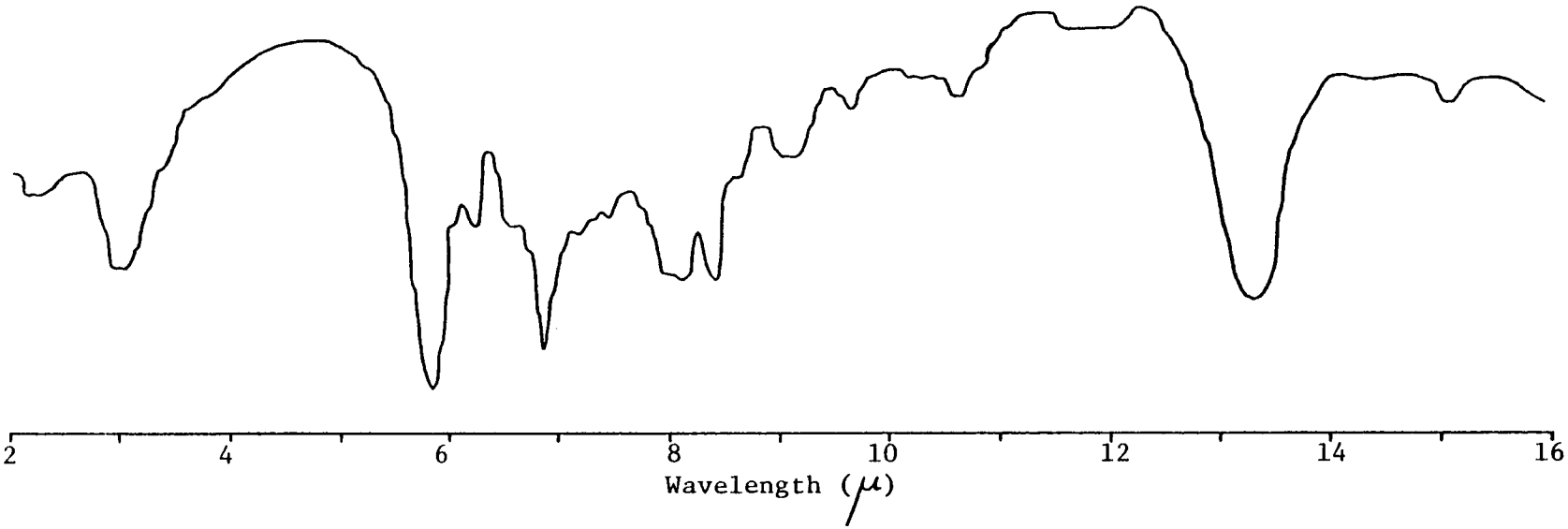


Figure 63. Midrange infrared spectrum of polymer-ortho-01, refluxing solvent polymerization at 144°. Made by heating in o-xylene.

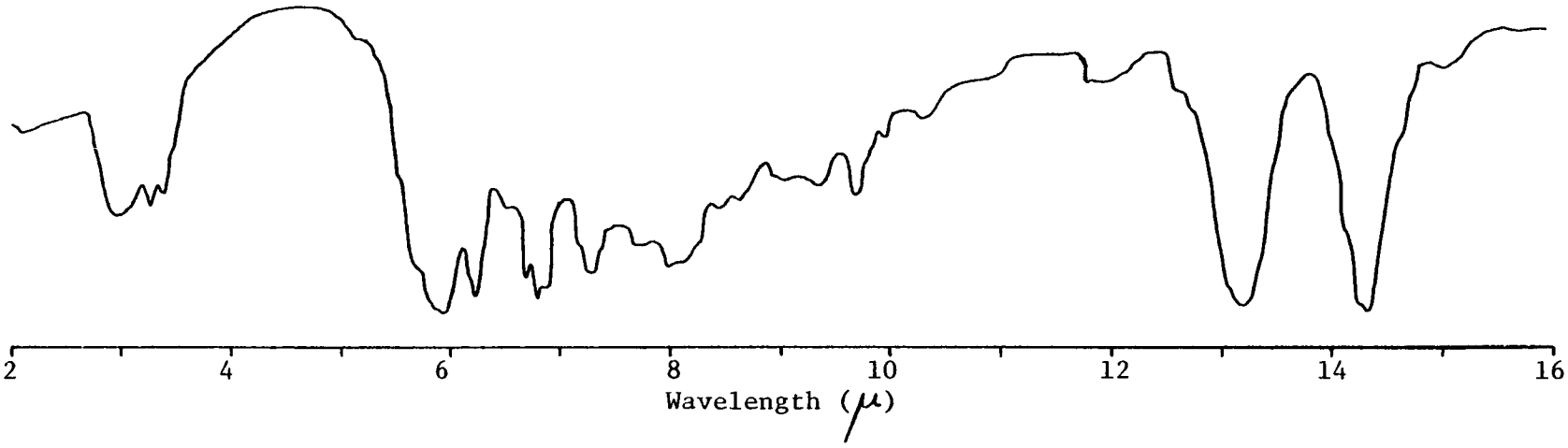


Figure 64. Midrange infrared spectrum of polymer-ortho-01, refluxing solvent polymerization at 152°. Made by heating in cumene.

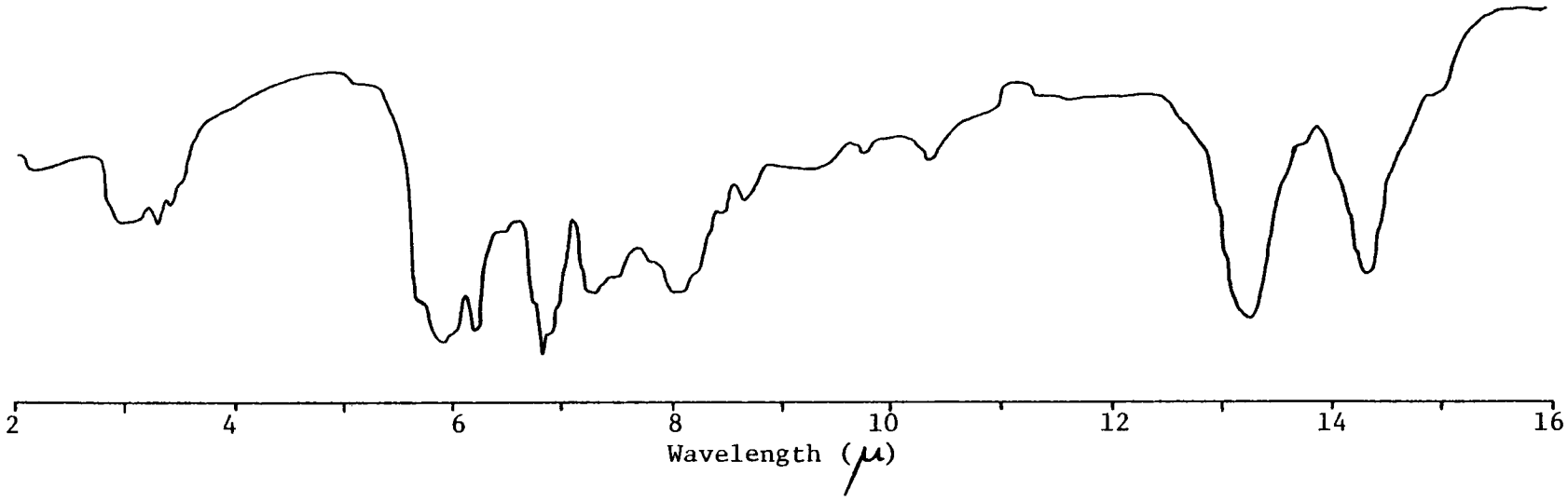


Figure 65. Midrange infrared spectrum of polymer-ortho-01, refluxing solvent polymerization at 183°. Made by heating in n-butylbenzene.

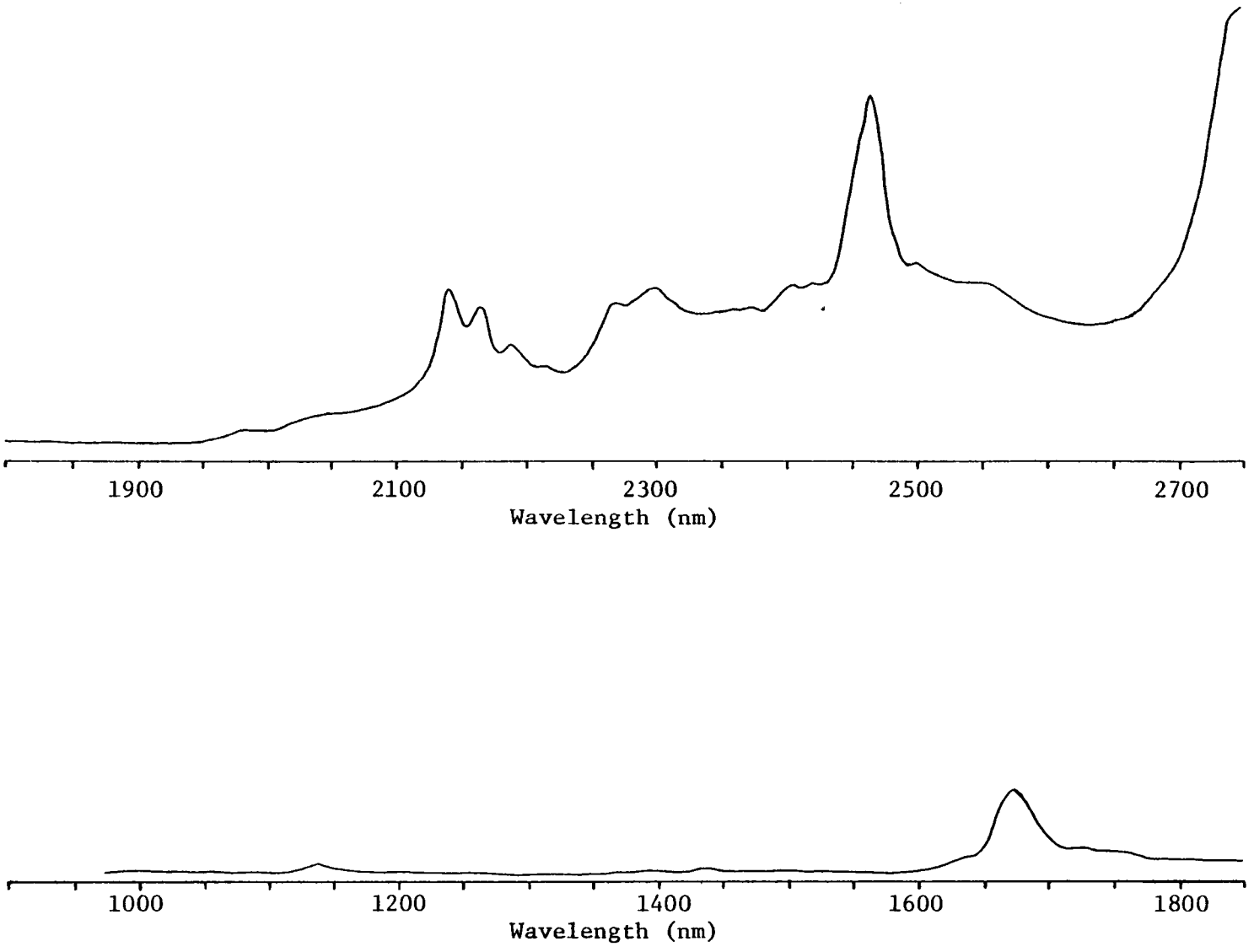
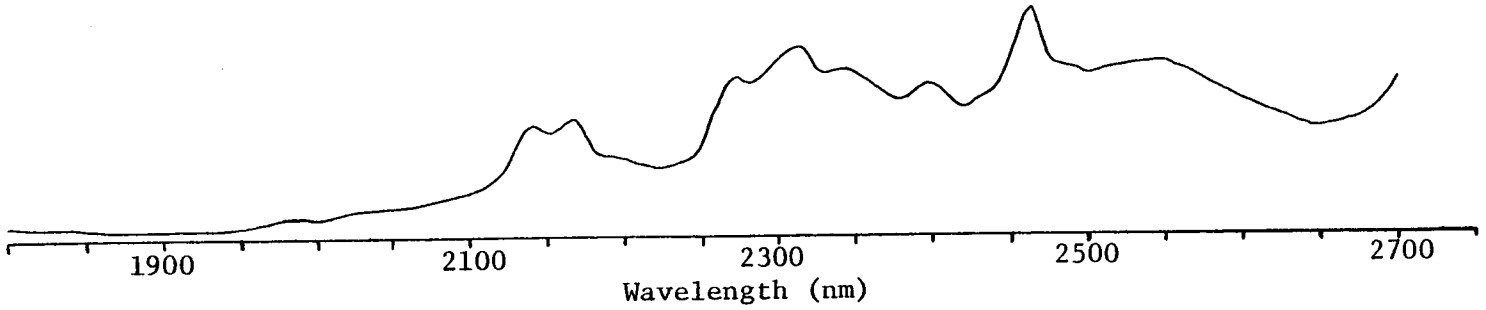


Figure 66. Near infrared spectrum of polymer-ortho-01, refluxing solvent polymerization at 152°. Made in refluxing cumene.



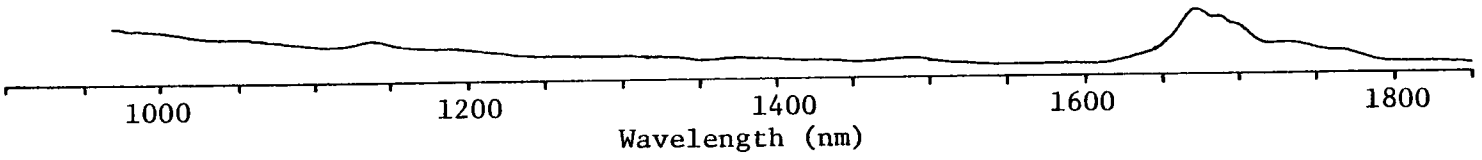
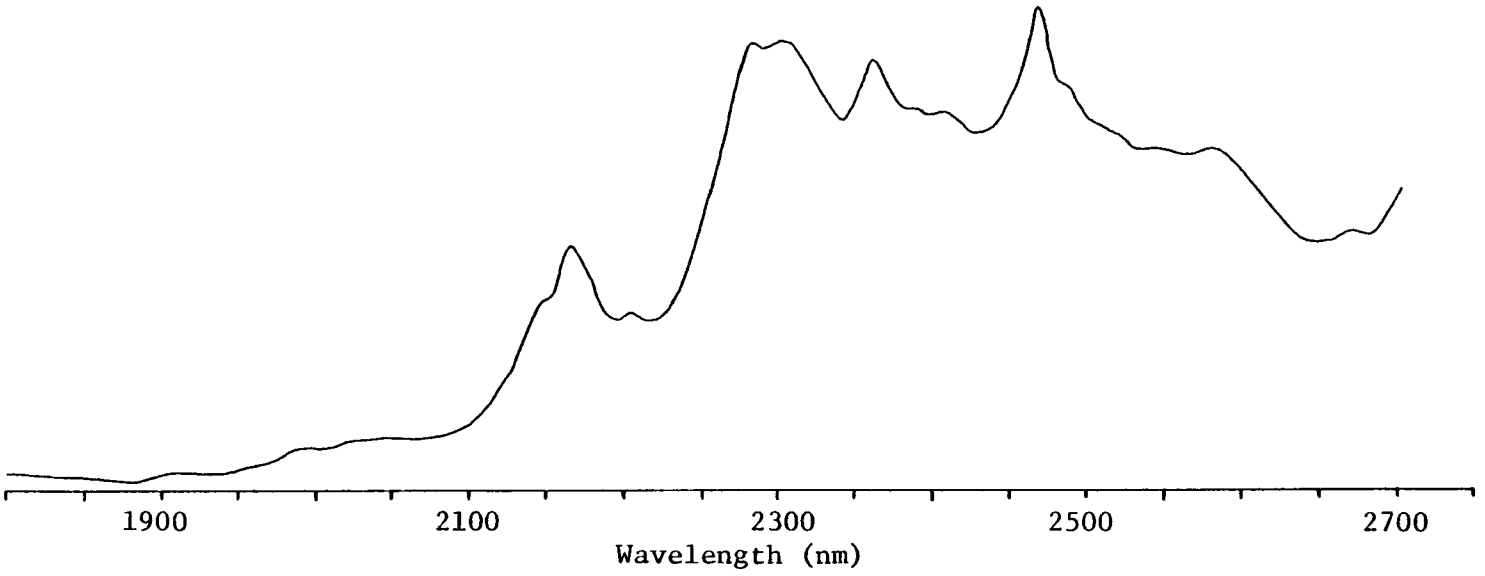


Figure 67. Near infrared spectrum of polymer-ortho-01, refluxing solvent polymerization at 177°. Made in refluxing p-cymene.



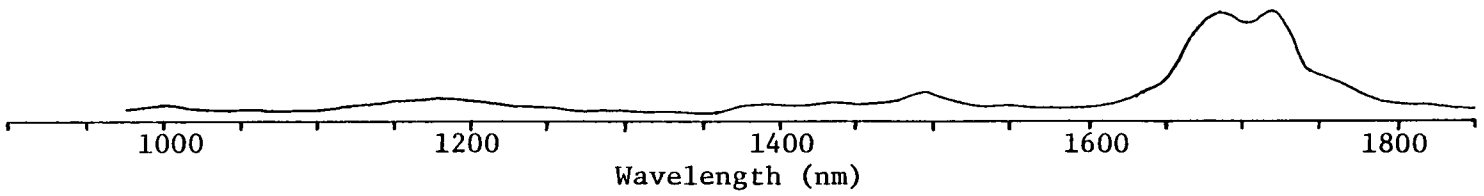


Figure 68. Near infrared spectrum of polymer-ortho-01, refluxing solvent polymerization at 193°. Made by heating in dimethylaniline.

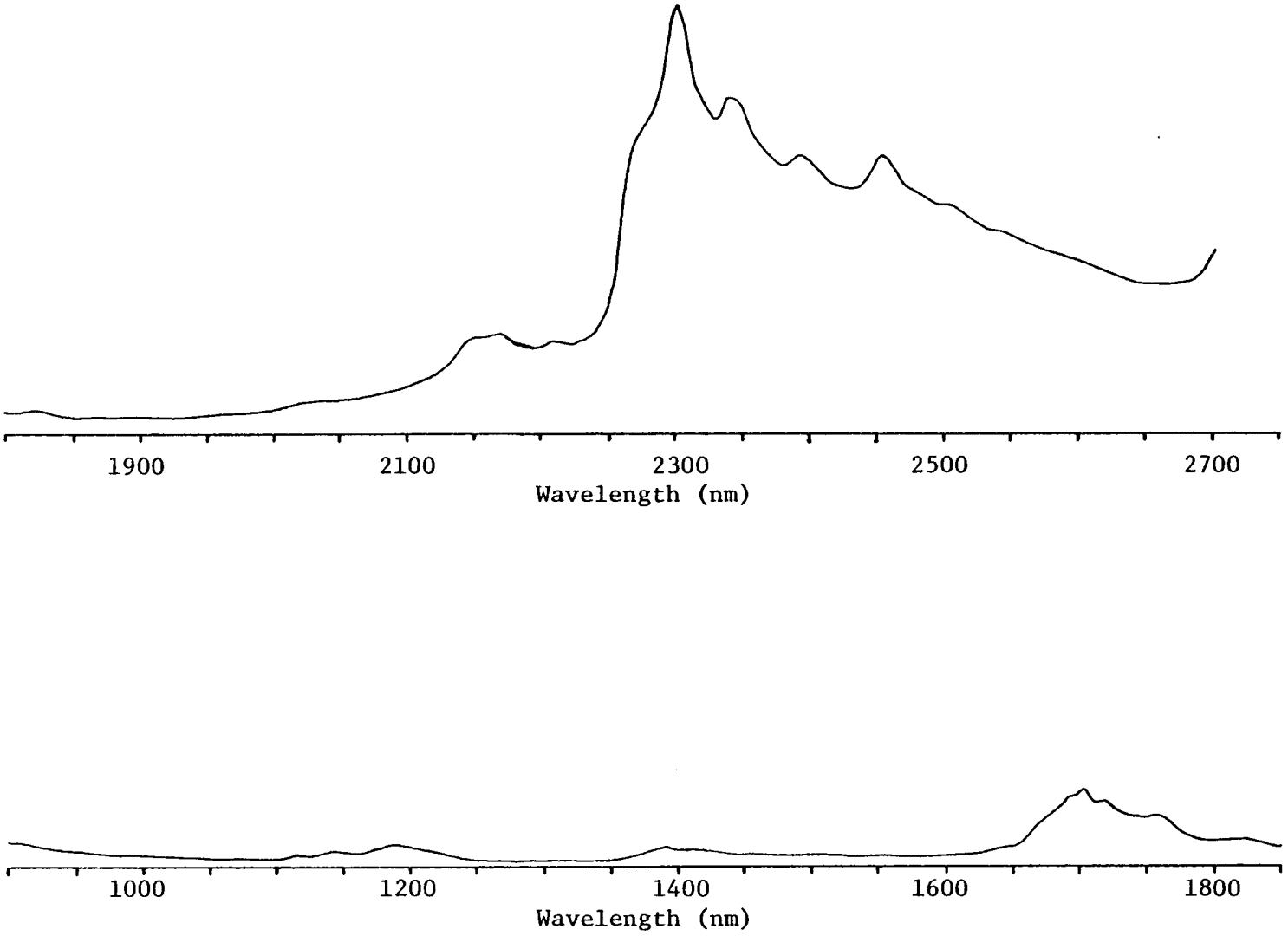


Figure 69. Near infrared spectrum of polymer-ortho-01, refluxing solvent polymerization at 216°. Made by heating in tributylamine.

TABLE LXV

NEAR INFRARED SPECTRA OF SYSTEM-ORTHO-01 POLYMERS - DIRECTORY

Polymer[a]	Spectrum[b]
refluxing solvent polymerization at 152° (cumene)	A
refluxing solvent polymerization at 156° (cyclohexanone)	B
refluxing solvent polymerization at 173° (s-butylbenzene)	C
refluxing solvent polymerization at 177° (p-cymene)	D
refluxing solvent polymerization at 177° (tetramethylurea)	E
refluxing solvent polymerization at 193° (dimethylaniline)	F
refluxing solvent polymerization at 216° (tributylamine)	G
sample F heated at 200° for 24 hr under vacuum	H
polymerized salicylamine	I

a. All samples except G and I contained at least a small amount of polymer-ortho-01 according to midrange infrared data.

b. The reduced data, wavelength (nm) vs. relative intensity (R.I.), has been extracted from the near infrared data and presented in columnar form in the succeeding pages of this table. All samples were prepared as films on pyrex glass.

TABLE LXVI

NEAR INFRARED SPECTRA OF SYSTEM-ORTHO-01 POLYMERS A THROUGH D

A		B		C		D	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2540	4.6	2540	10.9	2530	10.8	2545	7.5
2499	5.2	2502	10.5	2520	10.8	2485	7.3
2465	10.0	2445	10.0	2465	10.0	2464	10.0
2420	4.6	2434	10.5	2400	8.1	2435	6.0
2405	4.6	2400	10.6	2360	7.3	2398	6.7
2374	3.9	2387	10.7	2304	7.3	2345	7.3
2360	3.8	2348	11.1	2270	6.2	2315	8.3
2300	4.4	2336	11.2	2190	4.6	2305	8.1
2268	4.1	2297	11.3	2160	6.2	2275	6.9
2215	2.3	2283	10.8	2143	7.3	2190	3.5
2189	2.9	2200	4.3	2100	2.3	2167	5.2
2165	4.0	2162	6.2	1700	1.2	2140	4.8
2141	4.5	2152	5.5	1672	3.5	2060	1.0
2050	0.9	2141	5.7			1760	0.6
1990	0.4	2095	3.0			1730	0.9
1760	0.5	2030	1.2			1698	1.7
1740	0.5	1980	0.8			1685	2.1
1720	0.7	1810	2.3			1673	2.4
1680	2.1	1780	3.9			1640	0.3
1673	2.3	1748	4.5			1490	0.2
1640	0.4	1710	3.4			1135	0.2
1500	0.15	1675	1.2				
1440	0.15	1510	0.6				
1400	0.1	1490	0.5				
1140	0.3	1480	0.4				
		1430	0.4				
		1410	0.4				
		1390	0.3				
		1270	0.2				
		1205	0.9				
		1145	0.4				

TABLE LXVII

NEAR INFRARED SPECTRA OF SYSTEM-ORTHO-01 POLYMERS E THROUGH H

E		F		G		H	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2540	10.6	2580	7.0	2505	8.3	2580	6.8
2450	10.0	2540	7.1	2457	10.0	2540	6.9
2400	10.0	2485	8.4	2396	10.0	2510	7.4
2360	9.4	2468	10.0	2365	10.3	2485	8.4
2293	12.5	2440	7.5	2344	12.0	2469	10.0
2267	12.8	2410	7.9	2320	12.2	2405	7.8
2210	5.6	2390	8.0	2305	15.0	2390	8.0
2145	6.9	2364	8.9	2277	10.8	2362	9.1
1760	1.2	2305	9.3	2220	3.6	2305	9.6
1710	1.9	2284	9.3	2210	3.6	2285	9.4
1672	3.4	2205	3.8	2165	4.0	2203	3.6
1400	0.3	2166	5.2	2155	3.9	2165	5.2
1390	0.3	2150	4.1	2060	0.7	2150	4.0
		2125	2.5	2040	0.6	2125	2.3
		2050	1.3	1820	0.9	2050	1.0
		2025	1.2	1750	1.8	2030	0.9
		1993	1.1	1735	1.9	1990	0.7
		1760	1.2	1720	2.3	1760	1.5
		1718	1.8	1703	2.4	1718	2.0
		1690	1.8	1692	2.2	1685	2.1
		1684	1.9	1680	1.5	1675	1.8
		1675	1.7	1650	0.4	1645	0.6
		1645	0.4	1410	0.3	1490	0.6
		1490	0.5	1390	0.4	1445	0.3
		1450	0.5	1380	0.3	1390	0.2
		1440	0.3	1205	0.3		
		1400	0.2	1190	0.4		
		1390	0.2	1150	0.13		
				1140	0.13		

TABLE LXVIII

NEAR INFRARED SPECTRUM OF SYSTEM-ORTHO-01 POLYMER I

I	
nm	R.I.
2600	11.0
2550	11.0
2500	10.0
2445	9.0
2410	8.2
2325	7.7
2315	8.0
2270	9.2
2160	7.7
2145	8.0
2050	3.3
1950	1.8
1730	1.3
1705	1.4
1680	1.8
1670	1.5
1640	0.5

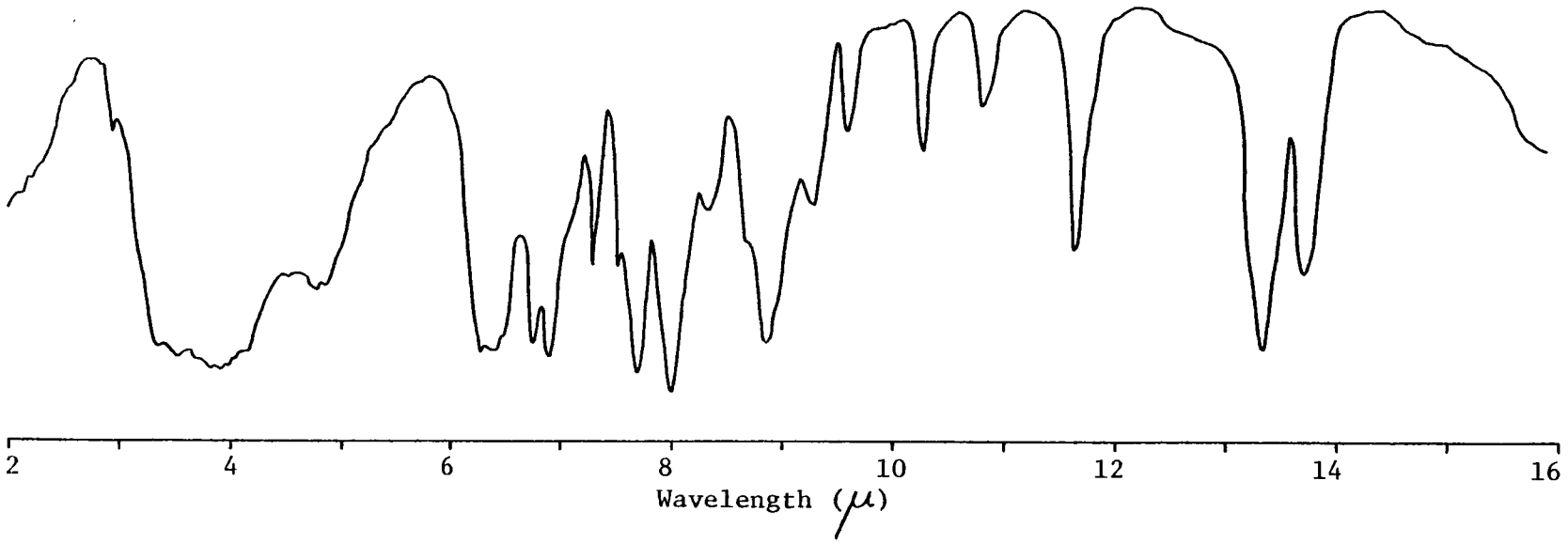


Figure 70. Midrange infrared spectrum of salicylamine.

APPENDIX VI

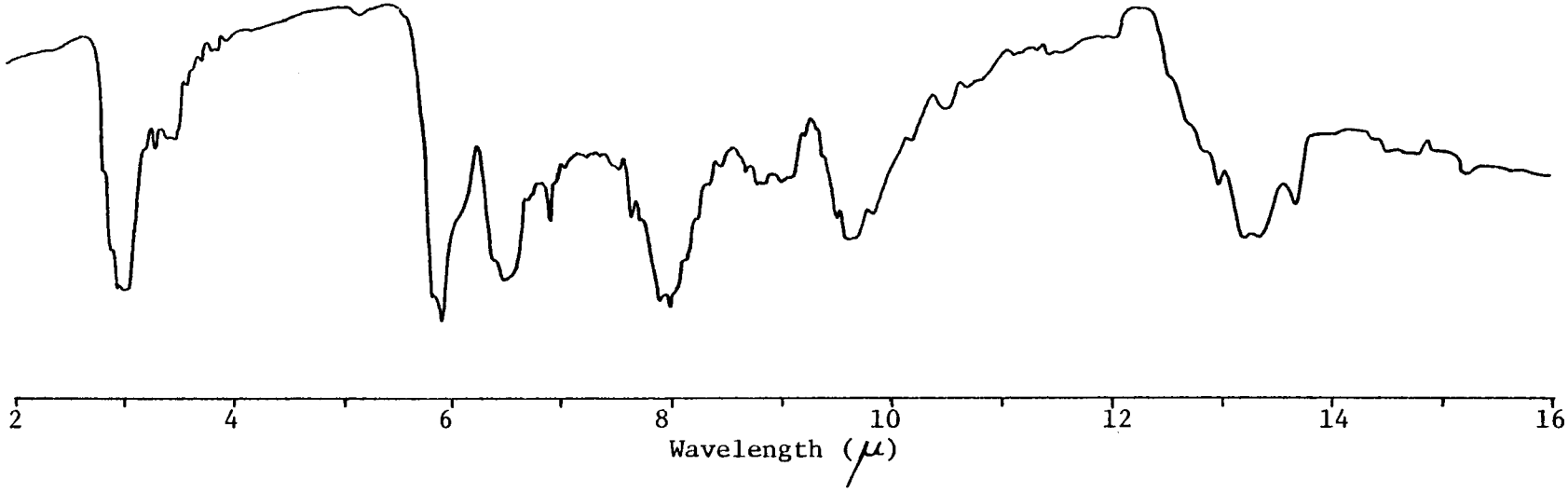


Figure 71. Midrange infrared spectrum of polymer-ortho-11, Curtius reaction product.

TABLE LXIX

NEAR INFRARED SPECTRA OF SYSTEM-ORTHO-11 POLYMERS

Polymer-ortho-11[a]		Thermolyzed sample[b]	
nm	R.I.	nm	R.I.
2505	10.7	2550	14.4
2455	10.0	2500	11.6
2405	10.0	2470	10.0
2385	9.3	2450	10.0
2313	10.0	2420	10.8
2295	10.0	2400	11.6
2275	9.3	2385	11.6
2190	3.2	2367	11.8
2170	3.9	2355	11.8
2140	4.6	2282	11.8
2085	2.1	2270	10.8
2045	2.9	2200	6.6
2020	1.8	2184	8.2
1750	1.8	2169	10.8
1740	2.5	2140	9.2
1720	2.9	2080	3.6
1700	3.9	2045	5.8
1685	4.3	2030	4.8
1670	2.1	1980	0.8
1405	5.4	1940	0.4
		1790	0.4
		1770	0.8
		1750	1.2
		1740	1.6
		1730	1.6
		1720	1.6
		1678	4.2
		1640	0.4
		1630	0.4
		1510	0.4
		1490	1.6
		1483	1.6
		1140	0.4

a. Sample prepared as thin film.

b. Heated under vacuum at 200° for 24 hr.

APPENDIX VII

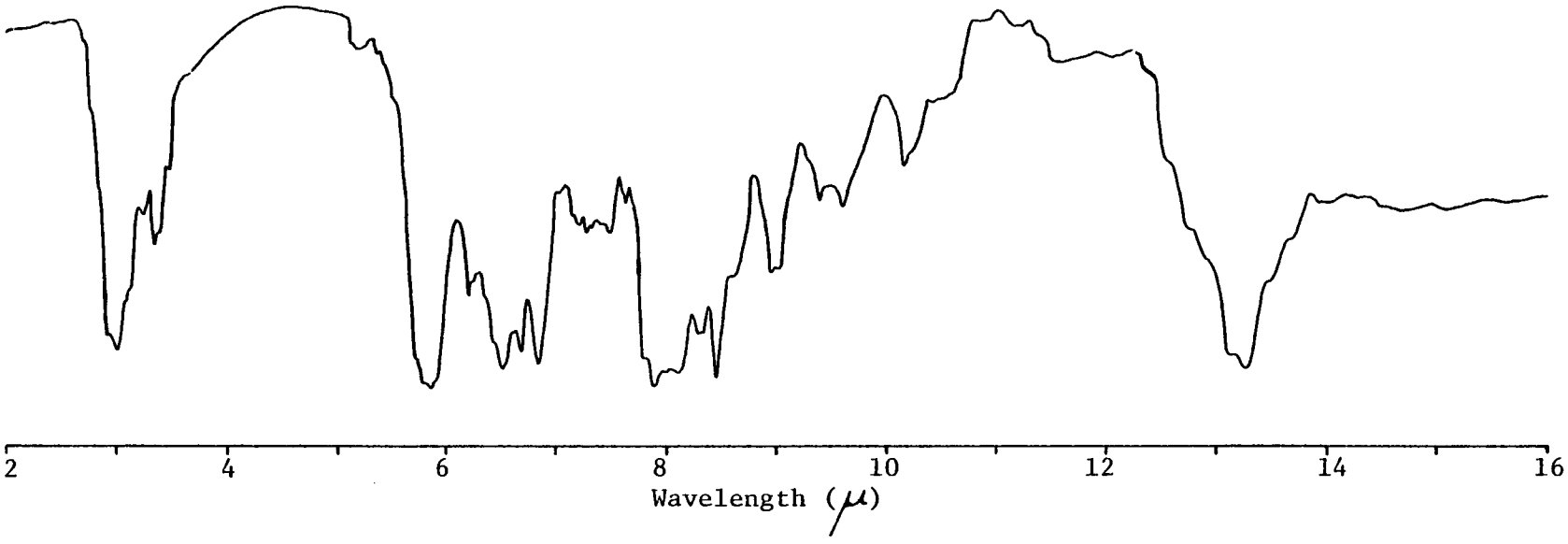


Figure 72. Midrange infrared spectrum of polymer-ortho-02, Curtius reaction product.

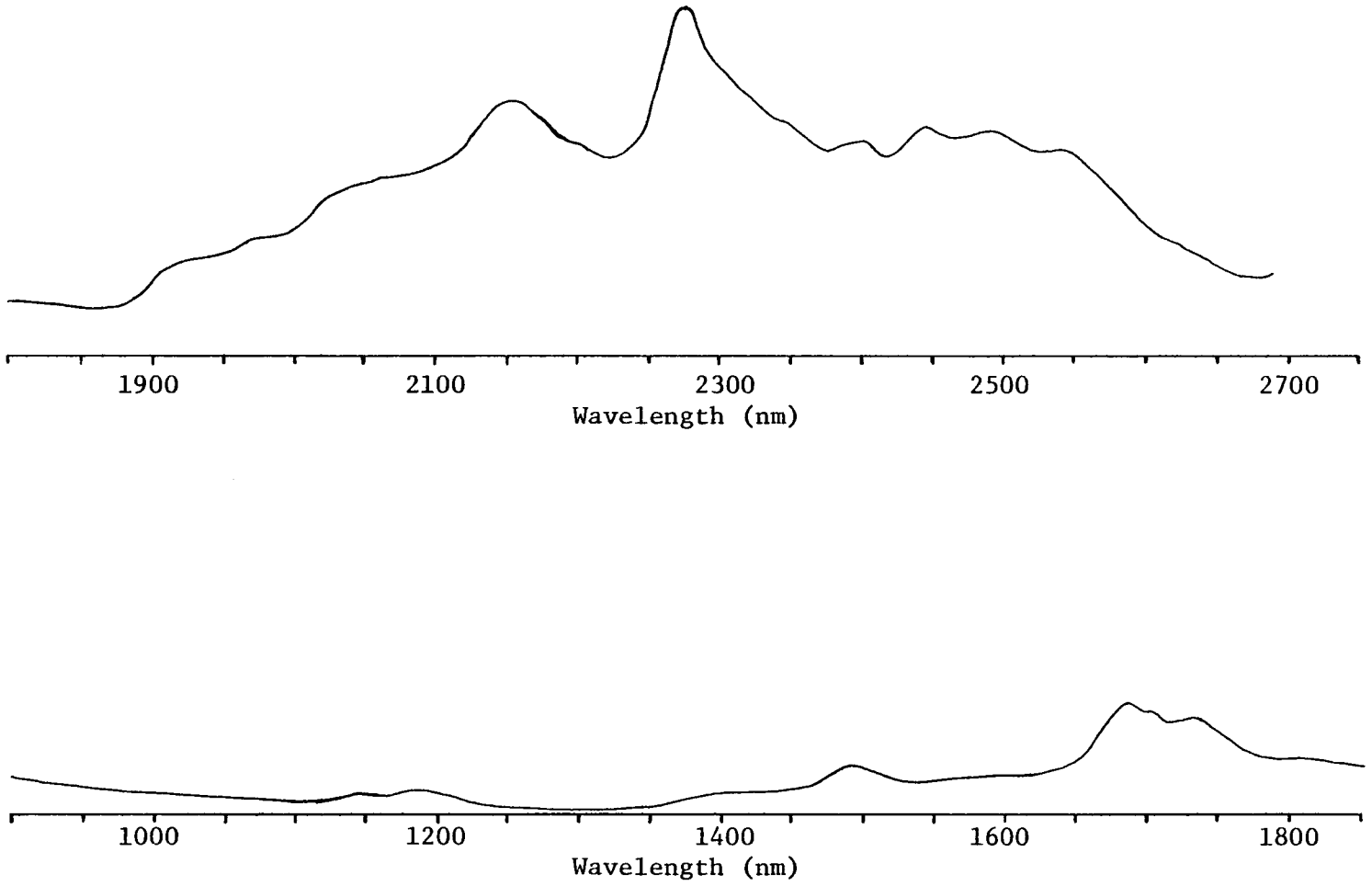


Figure 73. Near infrared spectrum of polymer-ortho-02, Curtius reaction product.

TABLE LXX

NEAR INFRARED SPECTRA OF POLYMER-ORTHO-02

Sample A[a]		Sample B[a]		Sample C[b]	
nm	R.I.	nm	R.I.	nm	R.I.
2493	9.9	2550	11.8	2520	11.6
2446	10.0	2500	10.6	2455	10.0
2402	9.4	2480	10.0	2402	9.5
2390	9.2	2444	10.4	2350	9.7
2345	10.0	2402	9.9	2320	10.0
2320	11.7	2346	8.9	2280	12.1
2277	15.5	2330	9.2	2205	7.1
2200	9.2	2314	9.5	2170	8.2
2170	10.8	2304	9.6	2160	8.7
2155	11.3	2275	13.7	2145	8.2
2070	6.7	2270	13.2	2080	3.9
2040	6.3	2235	6.6	2060	3.9
1980	4.1	2195	6.4	2030	3.2
1930	3.1	2171	8.2	1980	1.6
1810	1.2	2162	8.2	1950	1.0
1734	2.0	2152	8.2	1740	1.6
1700	2.4	2145	7.8	1700	1.8
1688	2.8	2060	4.5	1680	2.4
1640	0.8	2053	5.2	1490	1.1
1490	1.8	2040	4.0		
1440	0.8	1960	1.3		
1410	0.8	1930	1.2		
1195	0.6	1910	1.0		
1143	0.4	1770	0.5		
		1750	0.9		
		1730	1.4		
		1705	1.7		
		1690	2.1		
		1680	2.5		
		1675	2.4		
		1650	0.5		
		1640	0.2		
		1525	0.5		
		1515	0.5		
		1500	0.6		
		1487	0.7		

a. Samples A and B are Curtius reaction products.

b. Sample C was heated under vacuum at 150° for 24 hr.

APPENDIX VIII

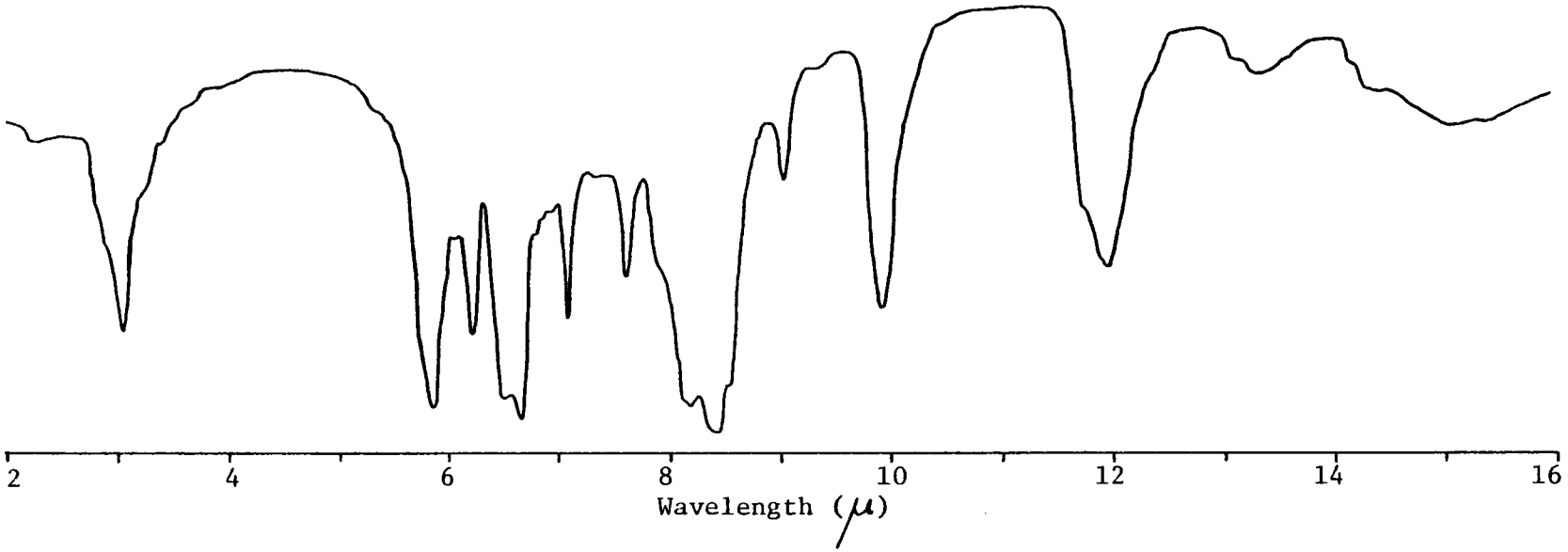


Figure 74. Midrange infrared spectrum of polymer-para-00, Curtius reaction product.

TABLE LXXI

NEAR INFRARED SPECTRUM OF POLYMER-PARA-00

Polymer-para-00[a]	
nm	R.I.
2570	5.6
2540	6.1
2500	6.7
2455	10.0
2400	4.0
2380	4.0
2320	5.6
2310	5.7
2300	5.7
2270	6.3
2180	6.0
2150	7.2
2135	6.7
2060	5.6
2050	5.6
2040	5.0
2010	2.5
2000	2.0
1980	2.0
1970	1.9
1960	1.2
1950	1.1
1940	0.8
1710	0.6
1700	1.0
1690	0.8
1680	1.4
1670	1.8
1665	2.0
1660	1.7
1650	0.8
1520	1.7
1505	2.1
1490	1.7
1480	1.2
1450	0.8
1440	0.8
1430	1.0
1420	1.0
1410	1.0
1400	0.8

a. Polymer prepared as thin film on pyrex.

APPENDIX IX

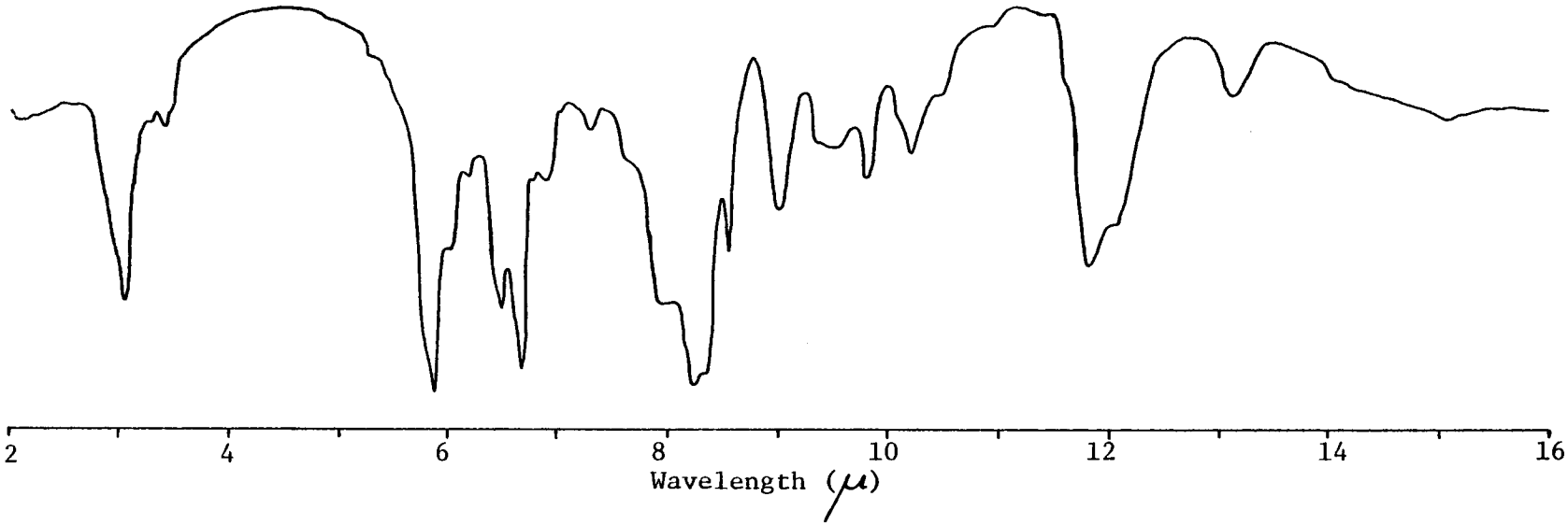


Figure 75. Midrange infrared spectrum of polymer-para-02, Curtius reaction product.

TABLE LXXII

NEAR INFRARED SPECTRA OF POLYMER-PARA-02

Sample A[a]		Sample B[a]		Sample C[a]		Sample D[b]	
nm	R.I.	nm	R.I.	nm	R.I.	nm	R.I.
2550	4.6	2540	5.0	2500	5.1	2463	10.0
2505	5.7	2500	6.1	2464	10.0	2345	6.9
2464	10.0	2464	10.0	2400	3.5	2280	7.7
2400	4.3	2400	4.8	2340	5.2	2190	6.1
2360	4.8	2340	6.1	2280	8.7	2160	7.7
2343	5.7	2280	8.3	2190	4.3	2140	6.9
2315	6.1	2190	5.4	2159	6.6	2055	4.9
2280	8.8	2158	6.9	2140	4.8	2020	3.5
2190	3.9	2140	5.6	2053	2.8	1980	2.9
2160	5.9	2050	3.5	1977	1.9	1760	1.2
2140	4.3	1975	2.2	1750	1.1	1750	1.4
2050	2.3	1770	0.4	1734	1.5	1680	1.8
1975	1.3	1750	0.7	1703	2.0	1670	2.0
1735	1.4	1735	0.9	1686	2.3		
1705	1.8	1700	1.2	1670	1.8		
1690	1.9	1685	1.4	1650	0.4		
1680	1.7	1670	1.2	1535	0.5		
1670	1.5	1530	0.4	1510	0.7		
1510	0.3	1510	0.6	1500	0.9		
1487	0.5	1490	0.6	1490	1.0		

a. Samples A,B, and C are Curtius reaction products without any heat treatment.

b. Sample D was heated under vacuum at 160° for 24 hr.

APPENDIX X

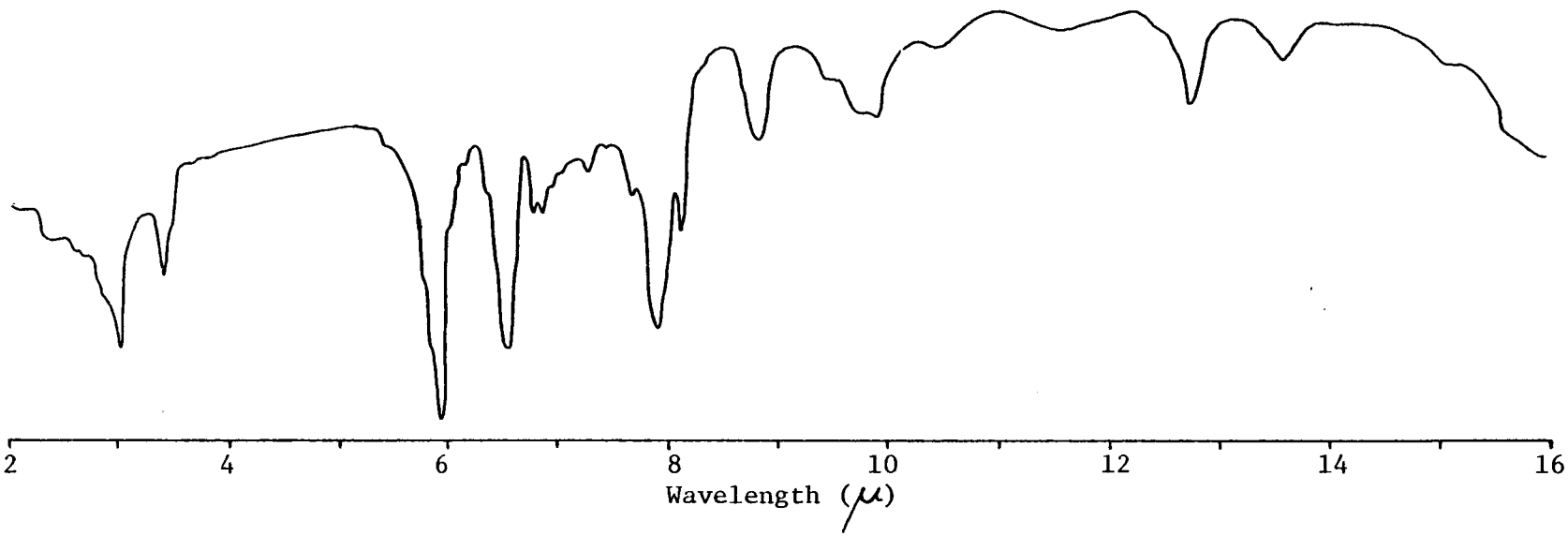
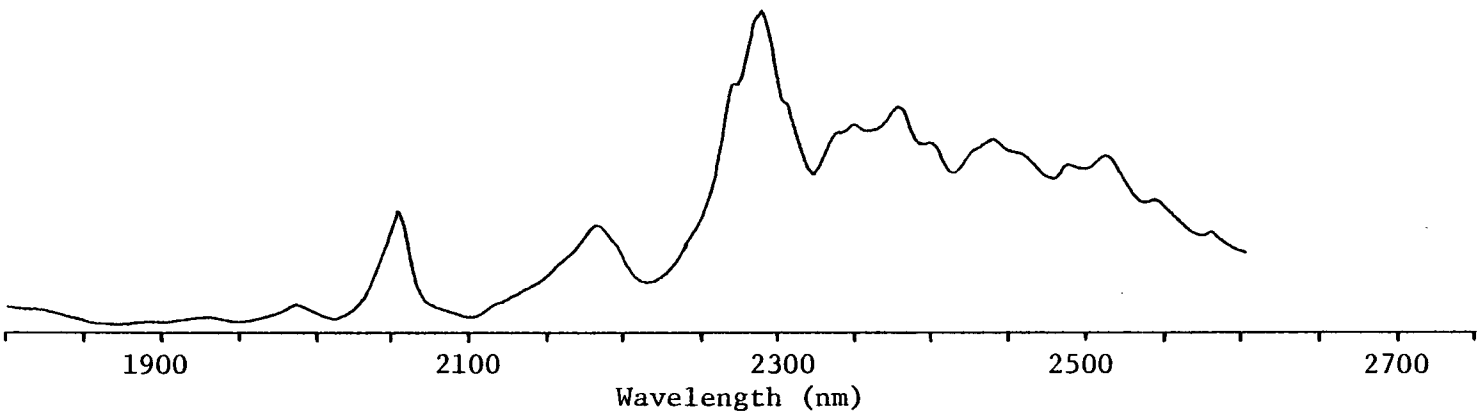


Figure 76. Midrange infrared spectrum of poly(pentamethylene urethane), Curtius reaction product.



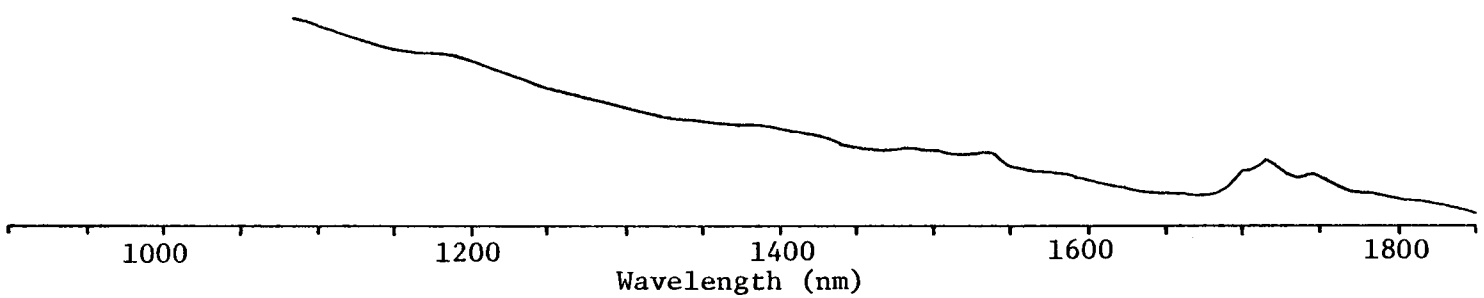


Figure 77. Near infrared spectrum of poly(pentamethylene urethane), Curtius reaction product.

TABLE LXXIII

NEAR INFRARED SPECTRUM OF POLY(PENTAMETHYLENE URETHANE)

Poly(pentamethylene urethane)[a]			
nm	R.I.	nm	R.I.
2545	4.8	1790	0.4
2515	6.0	1780	0.4
2489	5.8	1770	0.4
2455	6.1	1750	0.8
2440	6.5	1714	1.3
2400	6.3	1705	1.0
2380	7.4	1600	0.1
2350	6.9	1575	0.1
2340	6.7	1536	0.4
2305	7.2	1500	0.2
2290	10.0	1490	0.2
2273	7.9	1480	0.2
2183	3.7	1420	0.1
2130	1.4	1410	0.1
2075	1.1	1400	0.1
2055	3.8	1390	0.1
1988	0.8	1220	0.1
1935	0.3	1210	0.2
1835	0.2	1200	0.2
1810	0.3	1190	0.2
		1180	0.1

a. Curtius reaction product without any heat treatment.

APPENDIX XI

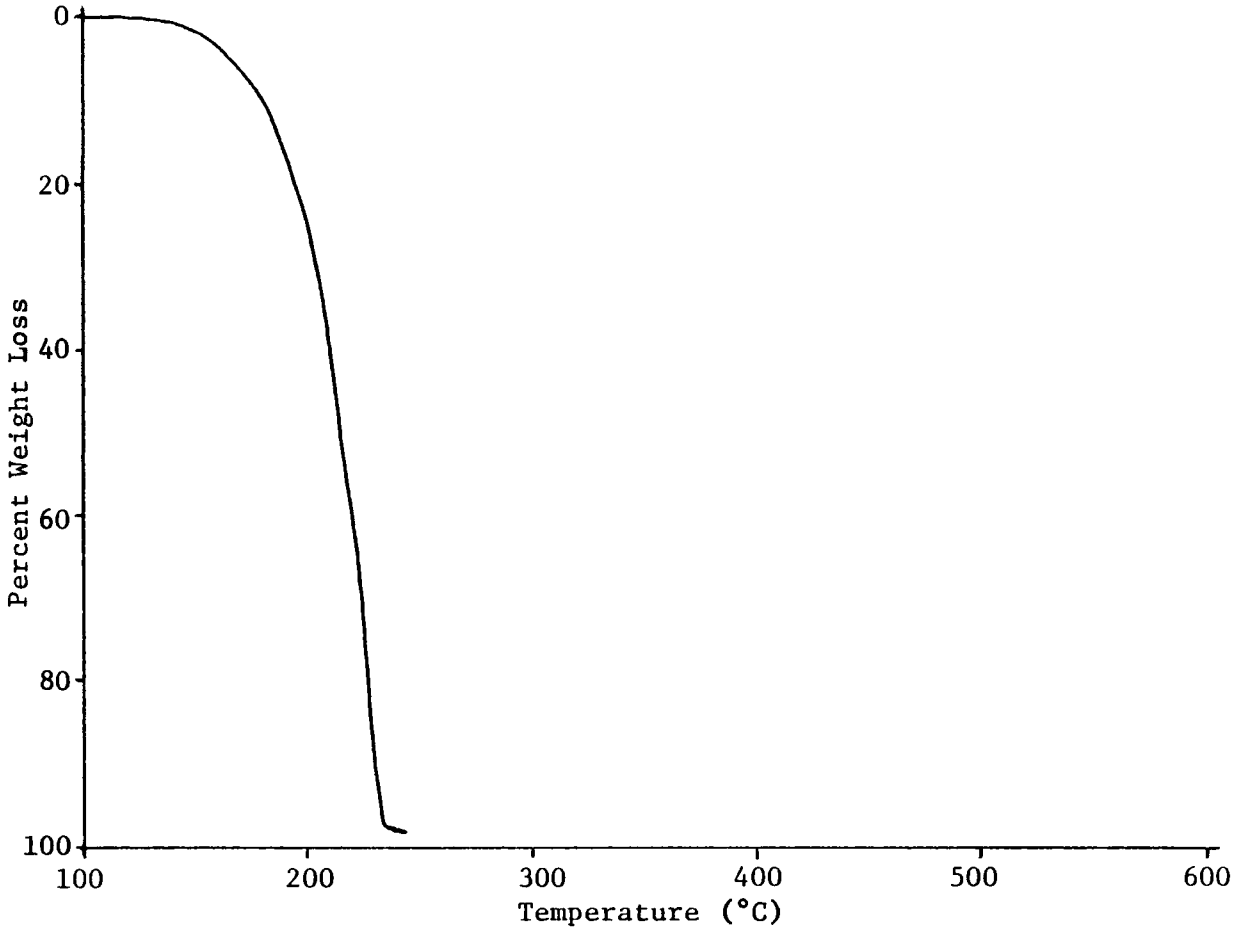


Figure 78. Thermogravimetric analysis of ring-00, under nitrogen.

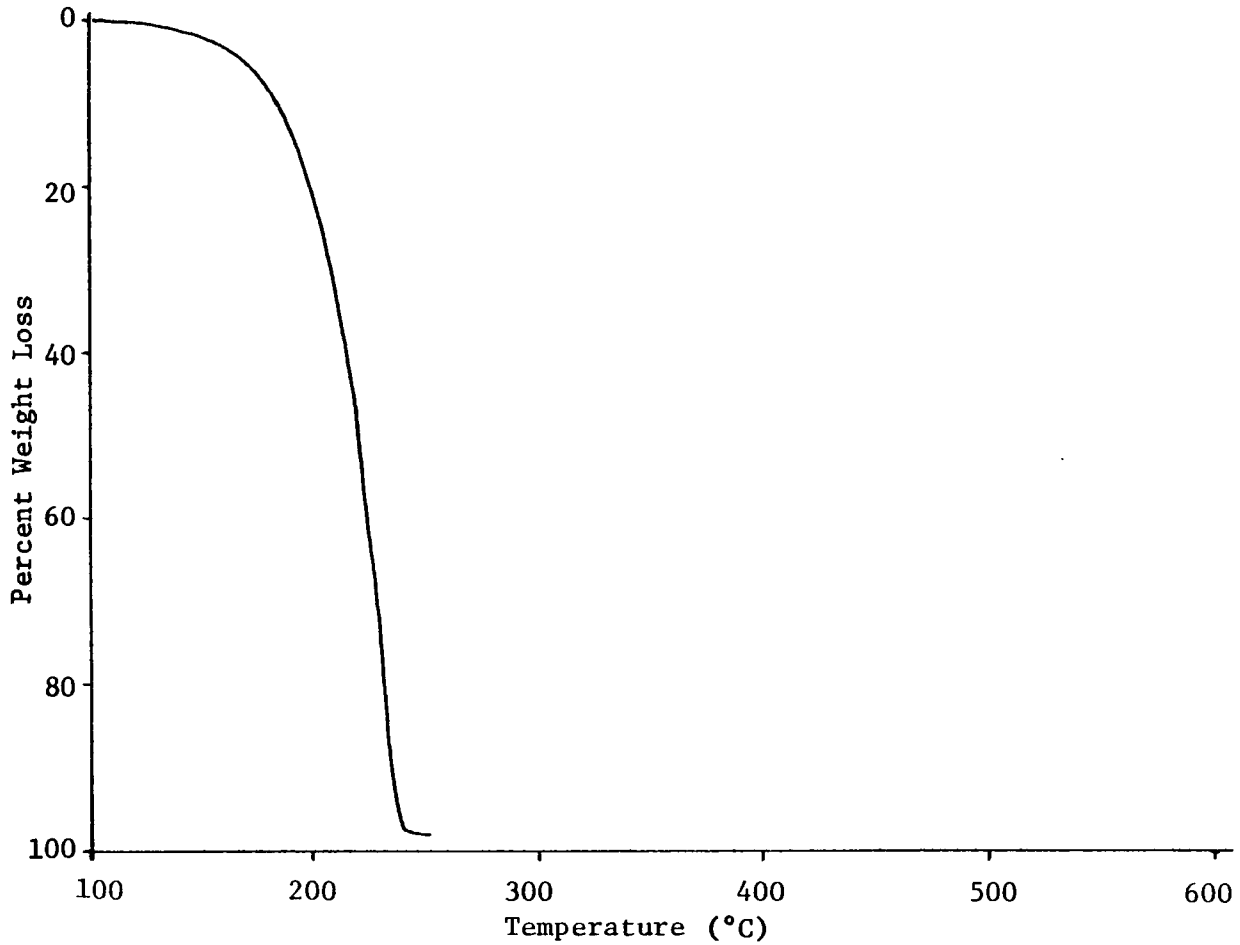


Figure 79. Thermogravimetric analysis of ring-00, in air.

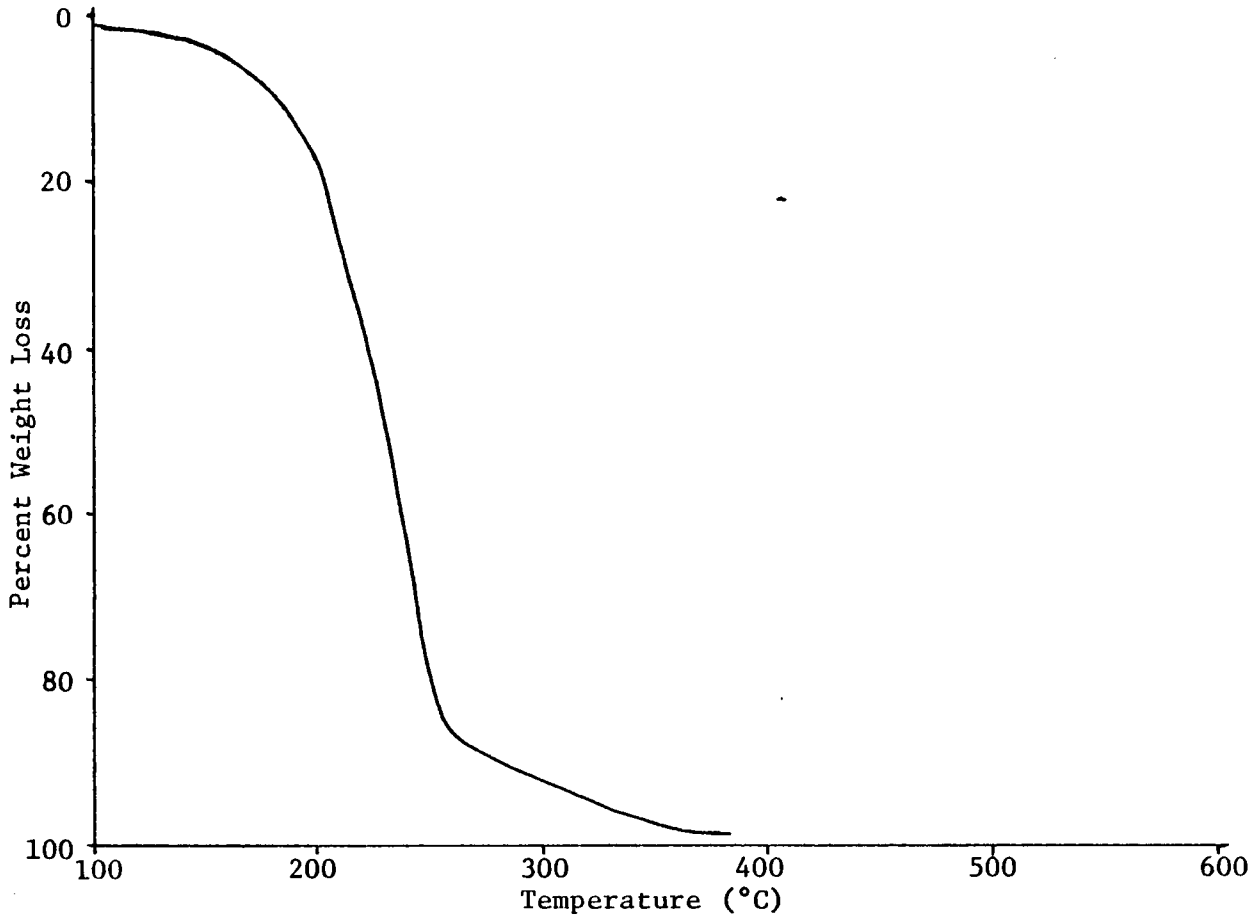


Figure 80. Thermogravimetric analysis of ring-10, under nitrogen.

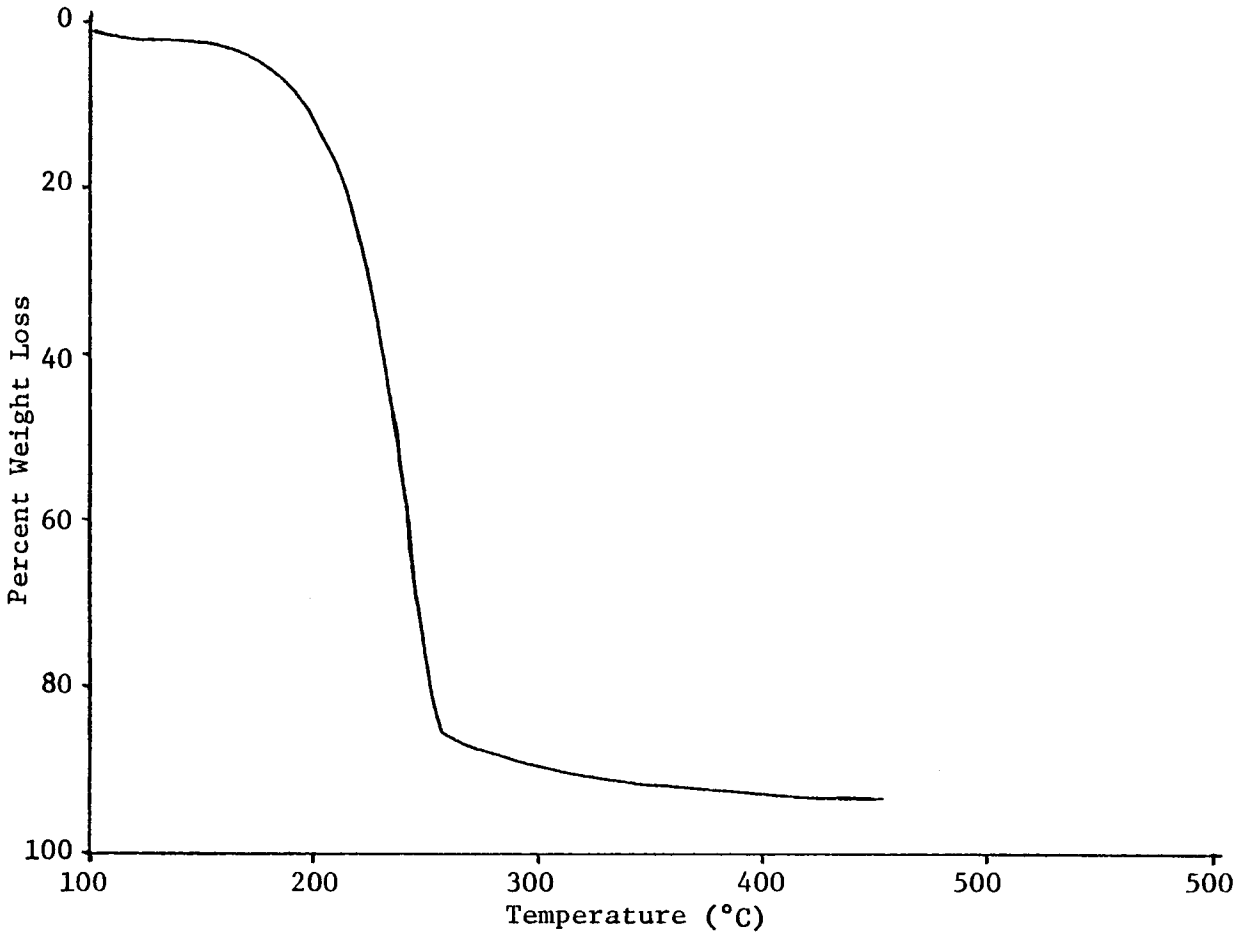


Figure 81. Thermogravimetric analysis of ring-10, in air.

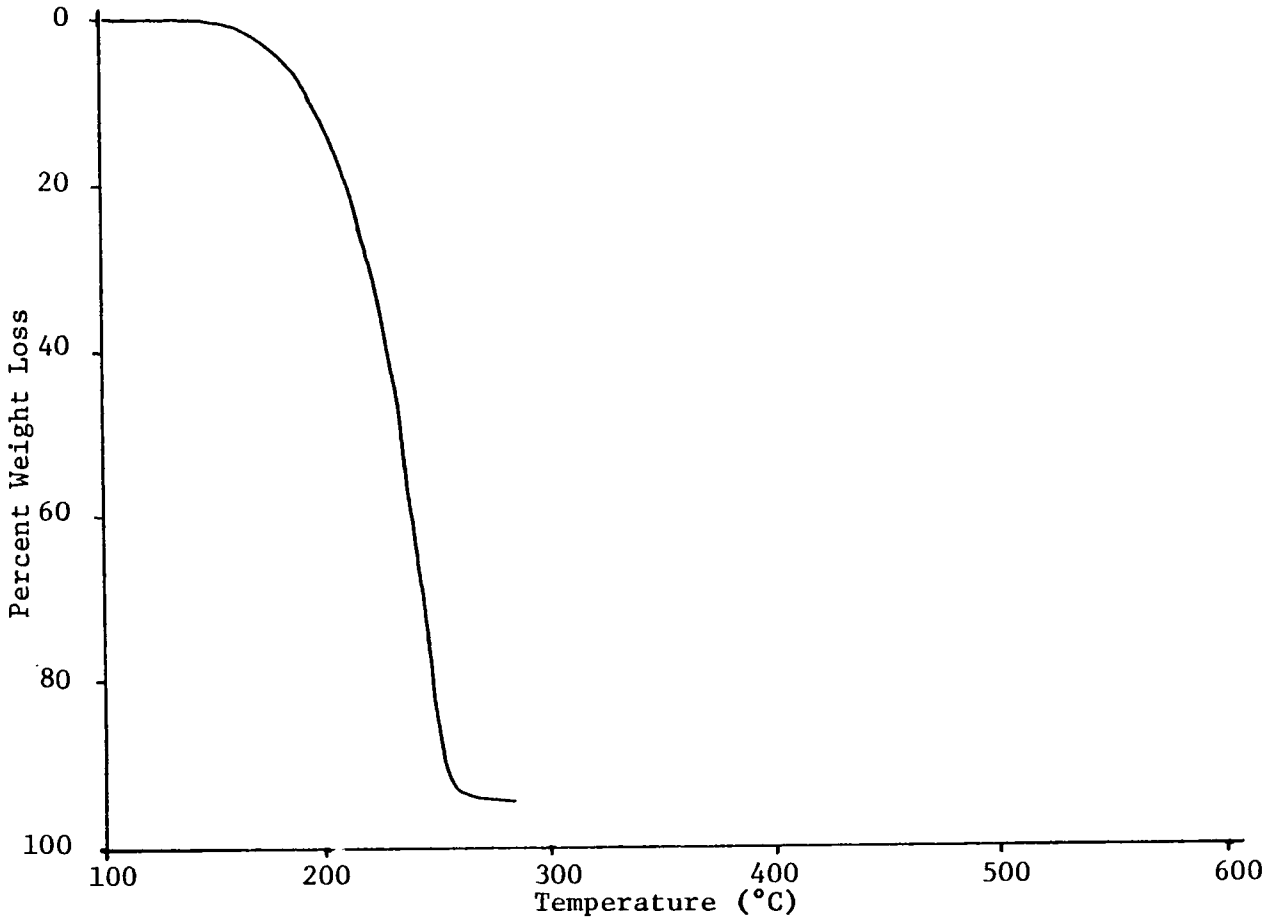


Figure 82. Thermogravimetric analysis of ring-01, under nitrogen.

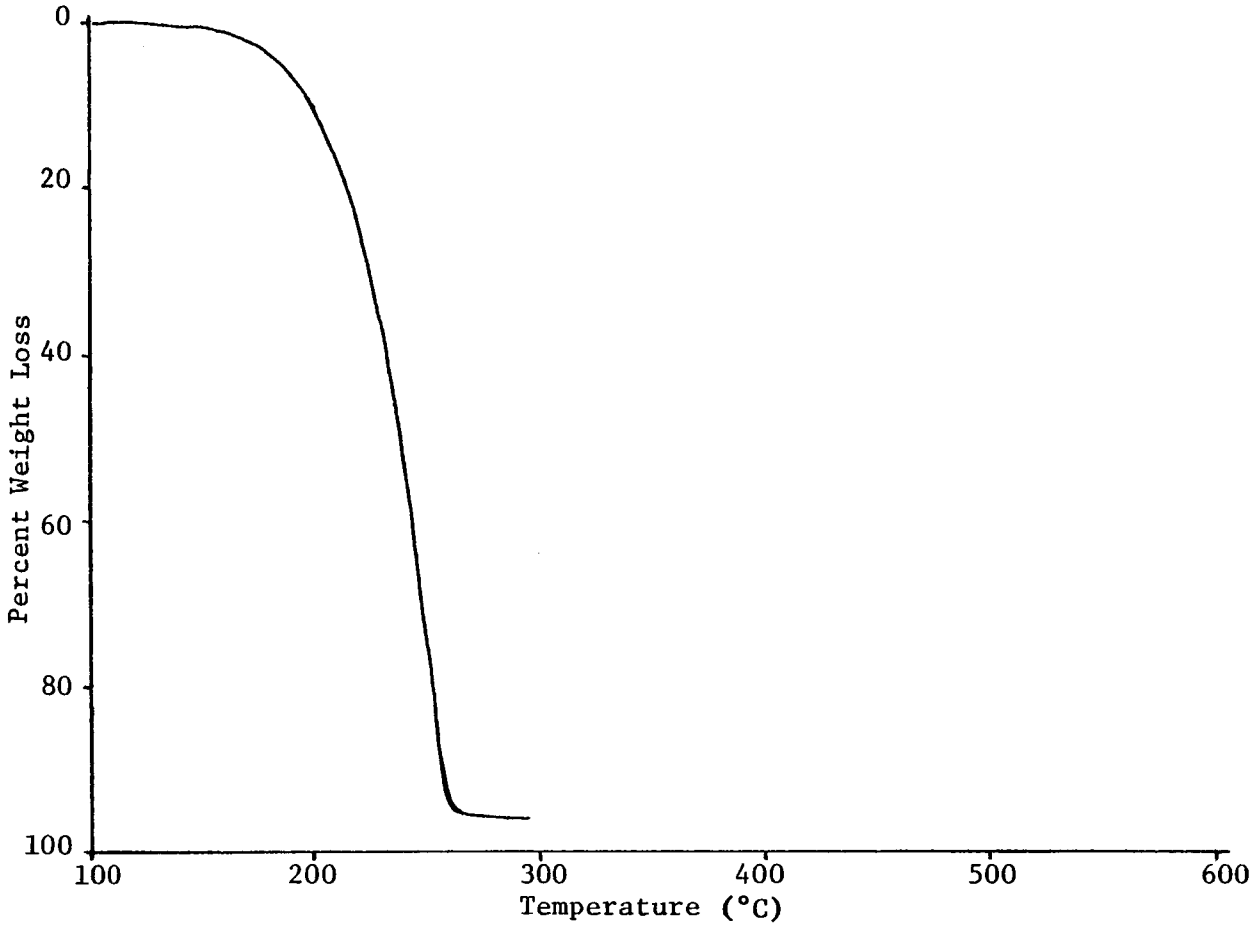


Figure 83. Thermogravimetric analysis of ring-01, in air.

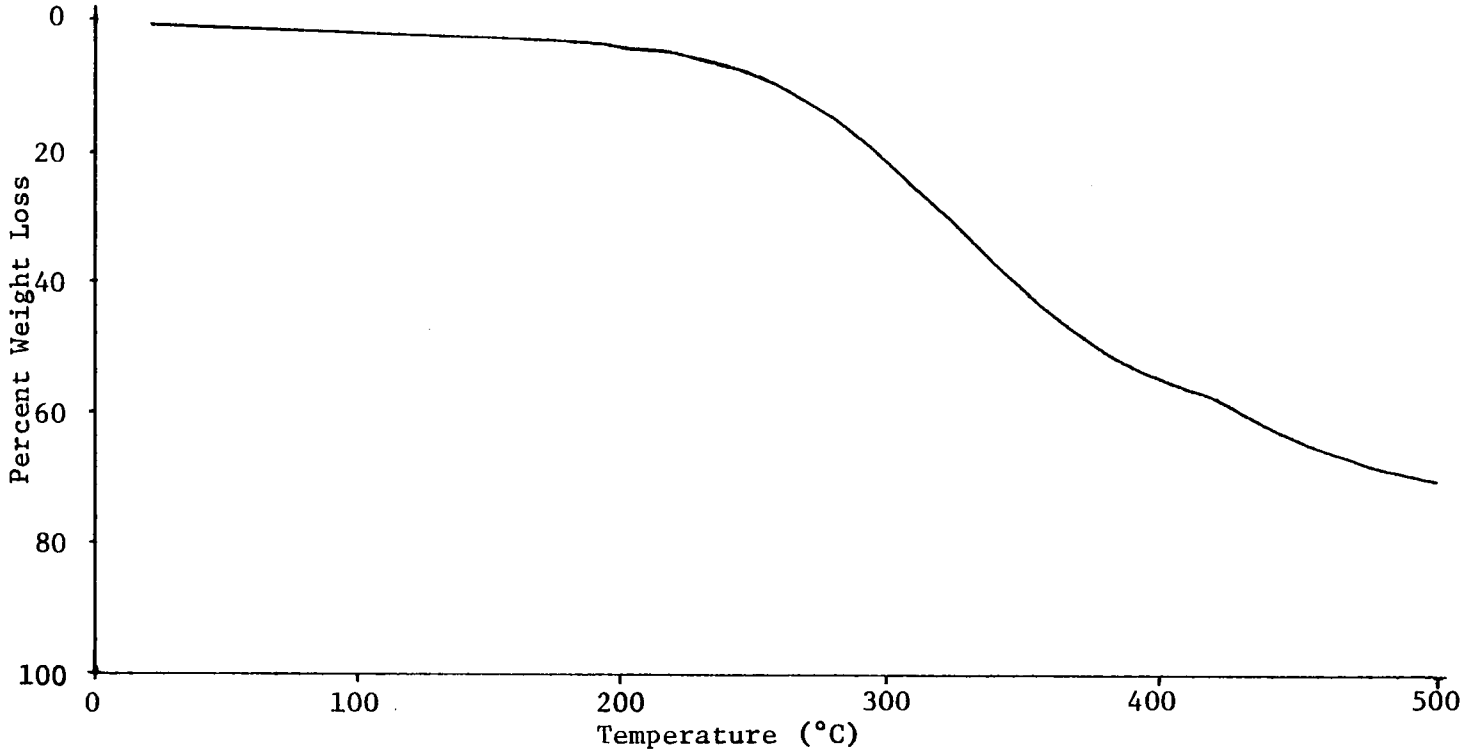


Figure 84. Thermogravimetric analysis of residue IV-1, under nitrogen.

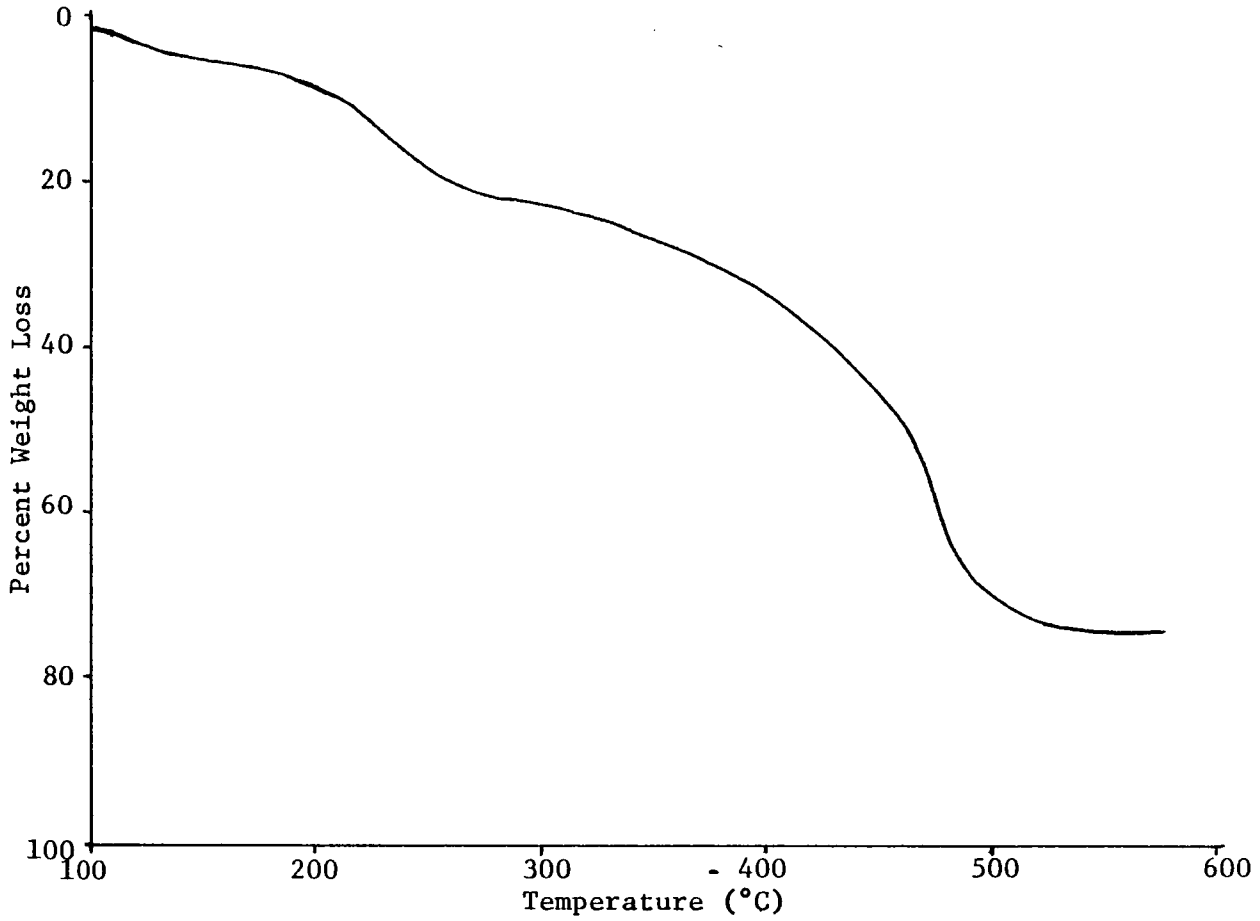


Figure 85. Thermogravimetric analysis of polymer-ortho-10, under nitrogen, bulk polymerization at 160-165°. Made by heating in oil bath.

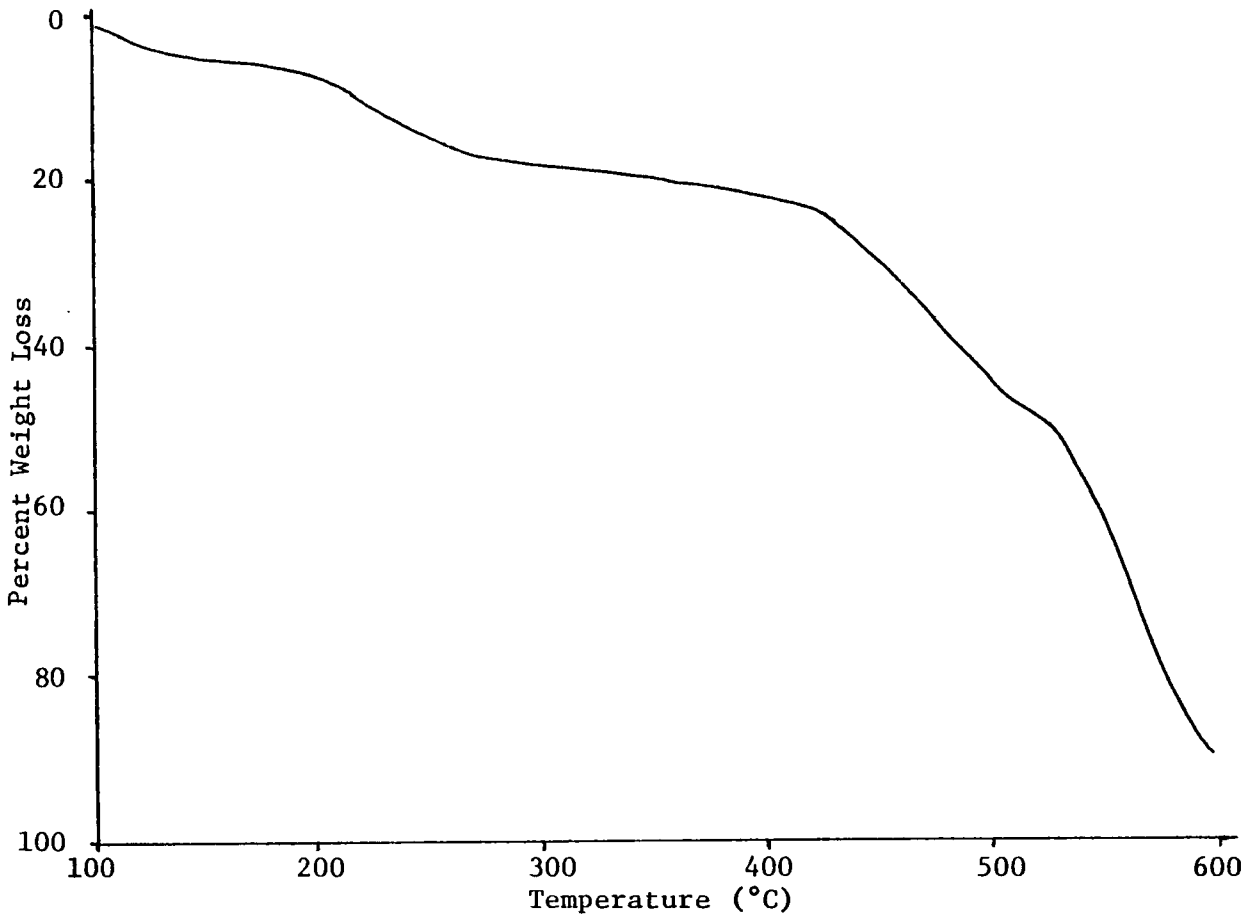


Figure 86. Thermogravimetric analysis of polymer-ortho-10 in air, bulk polymerization at 160-165°. Made by heating in oil bath.

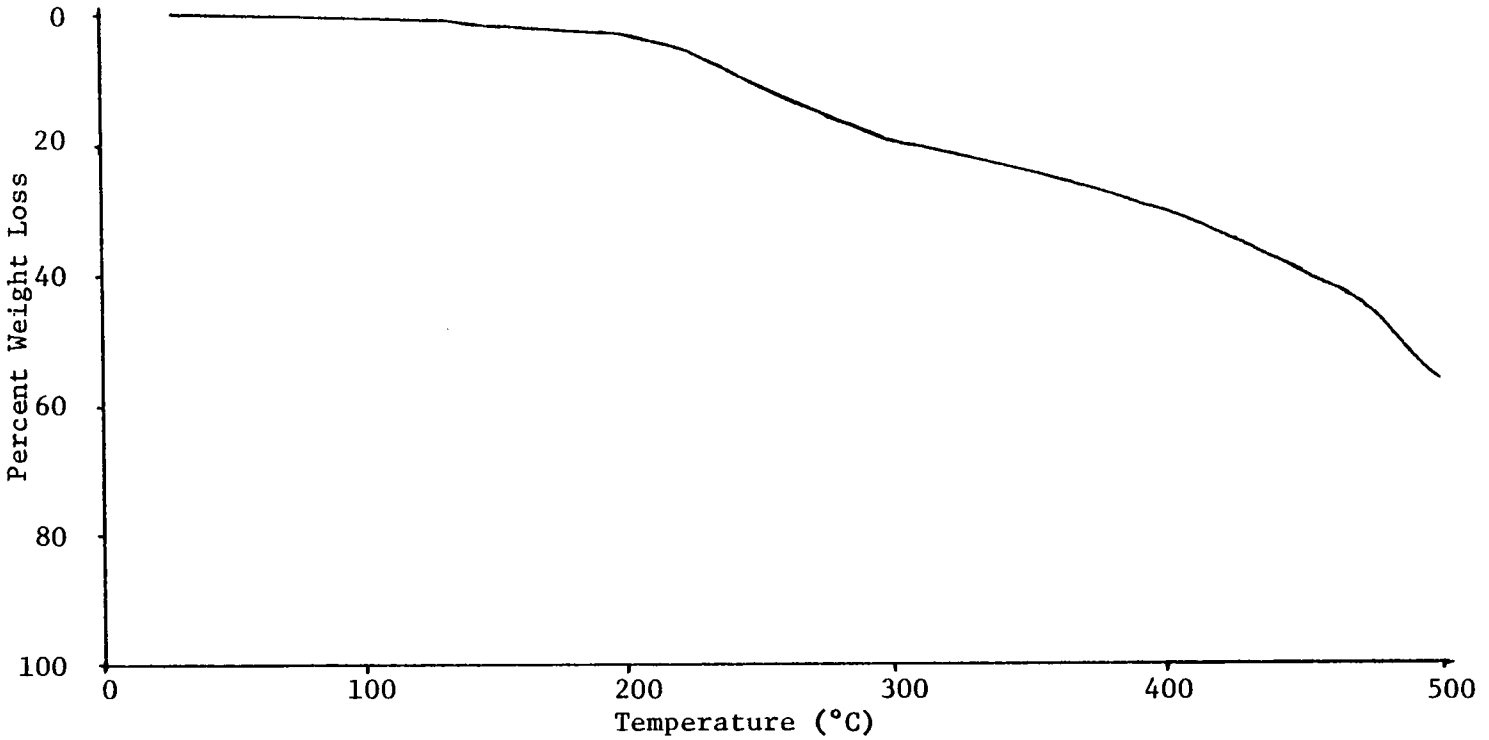


Figure 87. Thermogravimetric analysis of polymer-ortho-10 under nitrogen, bulk polymerization at 176-185°. Made by heating in oil bath.

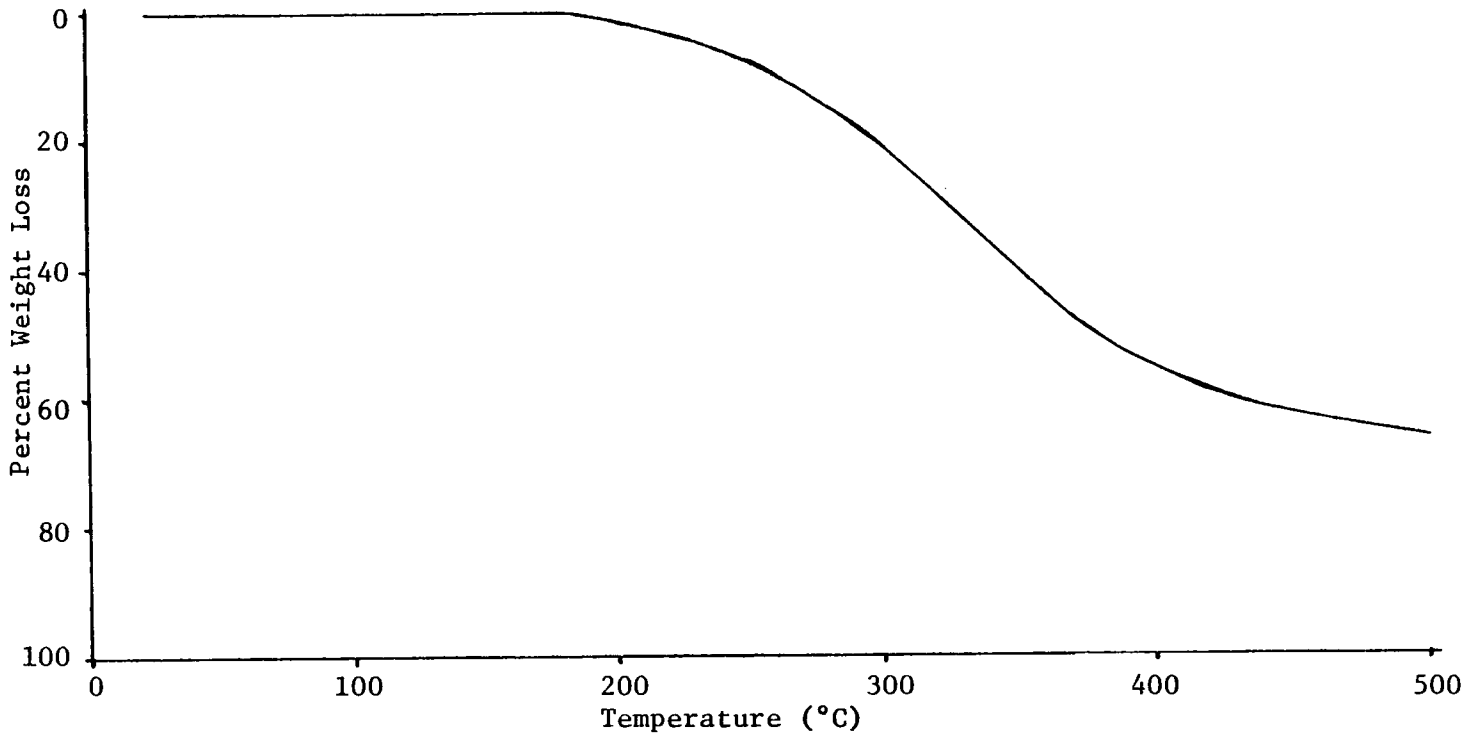


Figure 88. Thermogravimetric analysis of system-ortho-10 crosslinked polymer under nitrogen, refluxing solvent polymerization at 237°. Made by heating in quinoline.

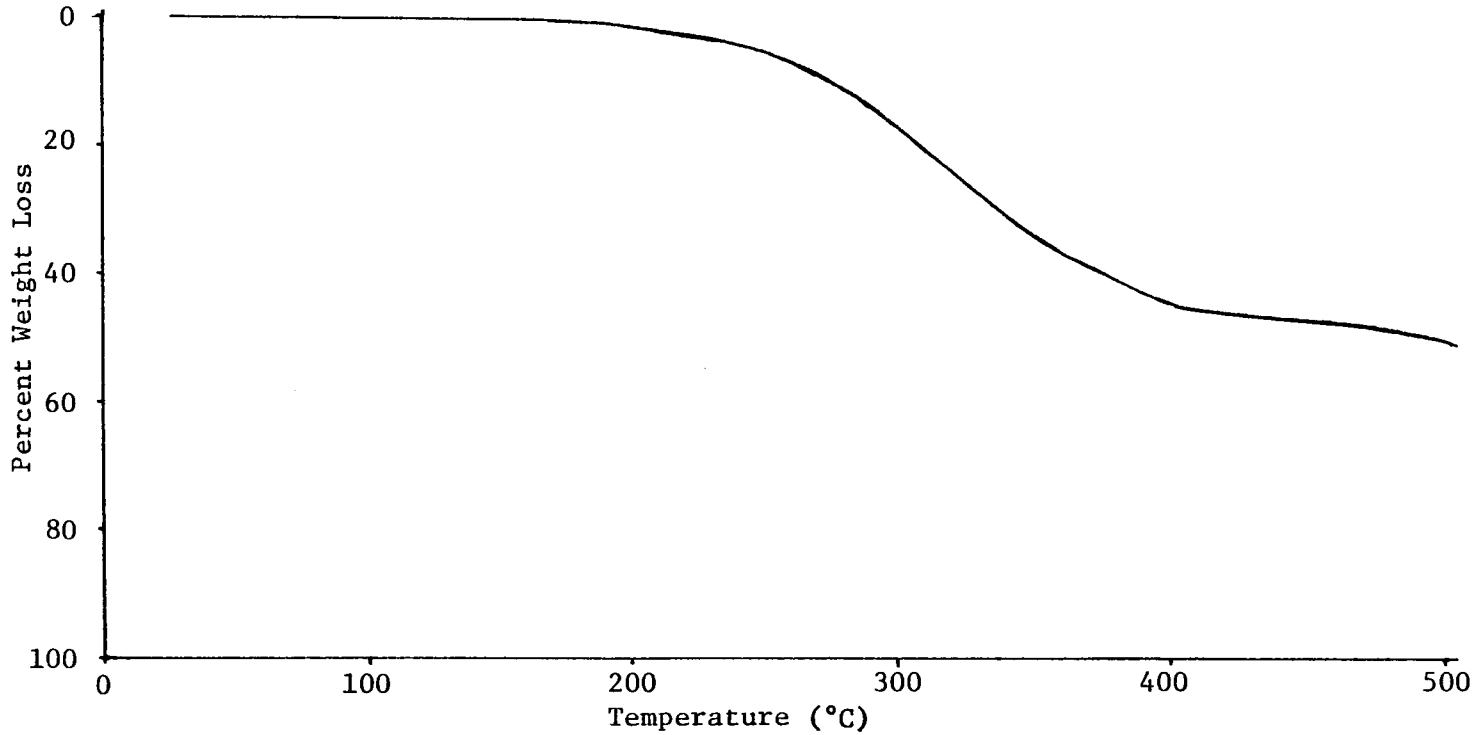


Figure 89. Thermogravimetric analysis of system-ortho-10 crosslinked polymer in air, refluxing solvent polymerization at 237°. Made by heating in quinoline.

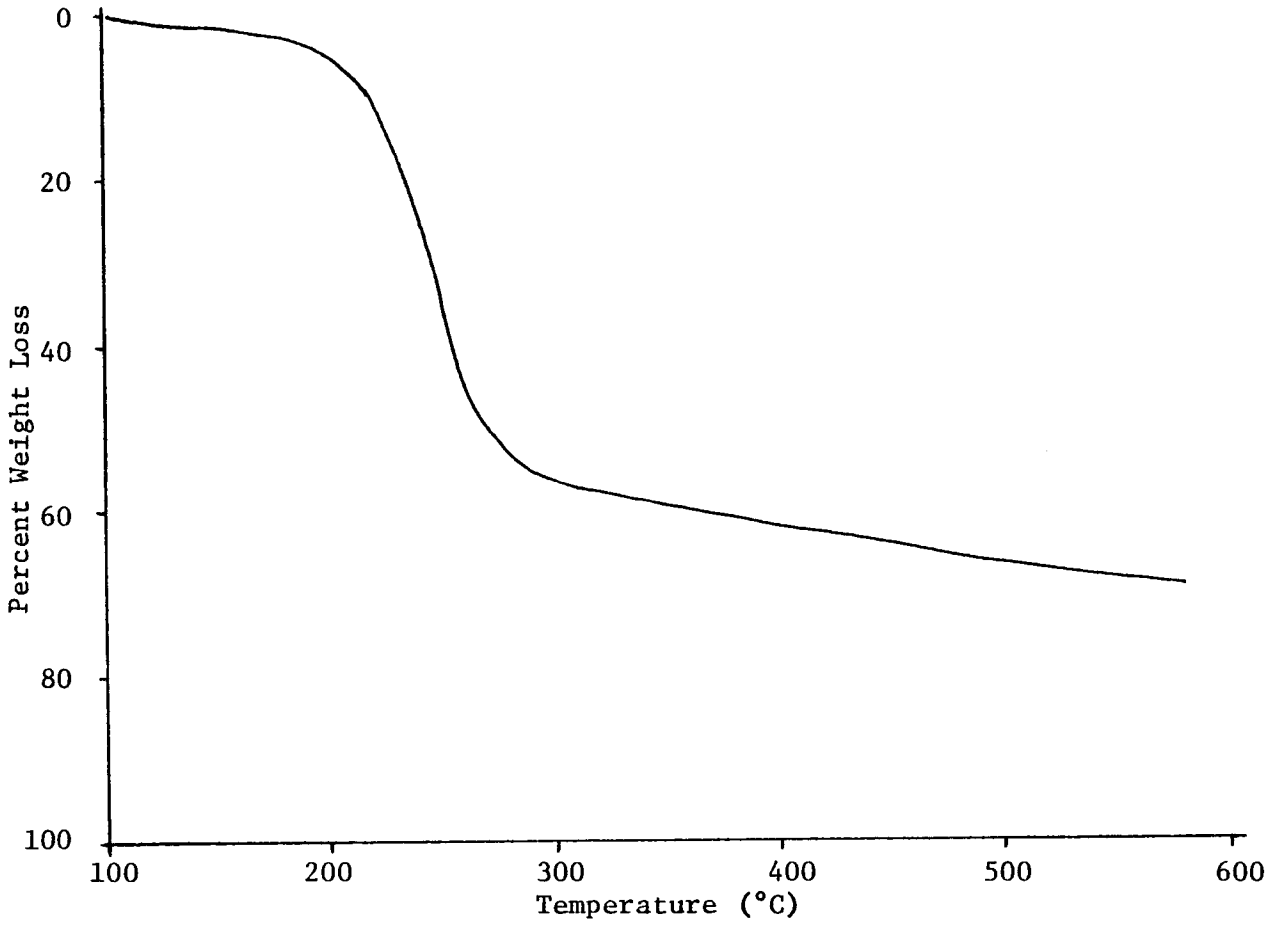


Figure 90. Thermogravimetric analysis of polymer-ortho-01, under nitrogen, bulk polymerization at 180-185°. Made by heating in oil bath.

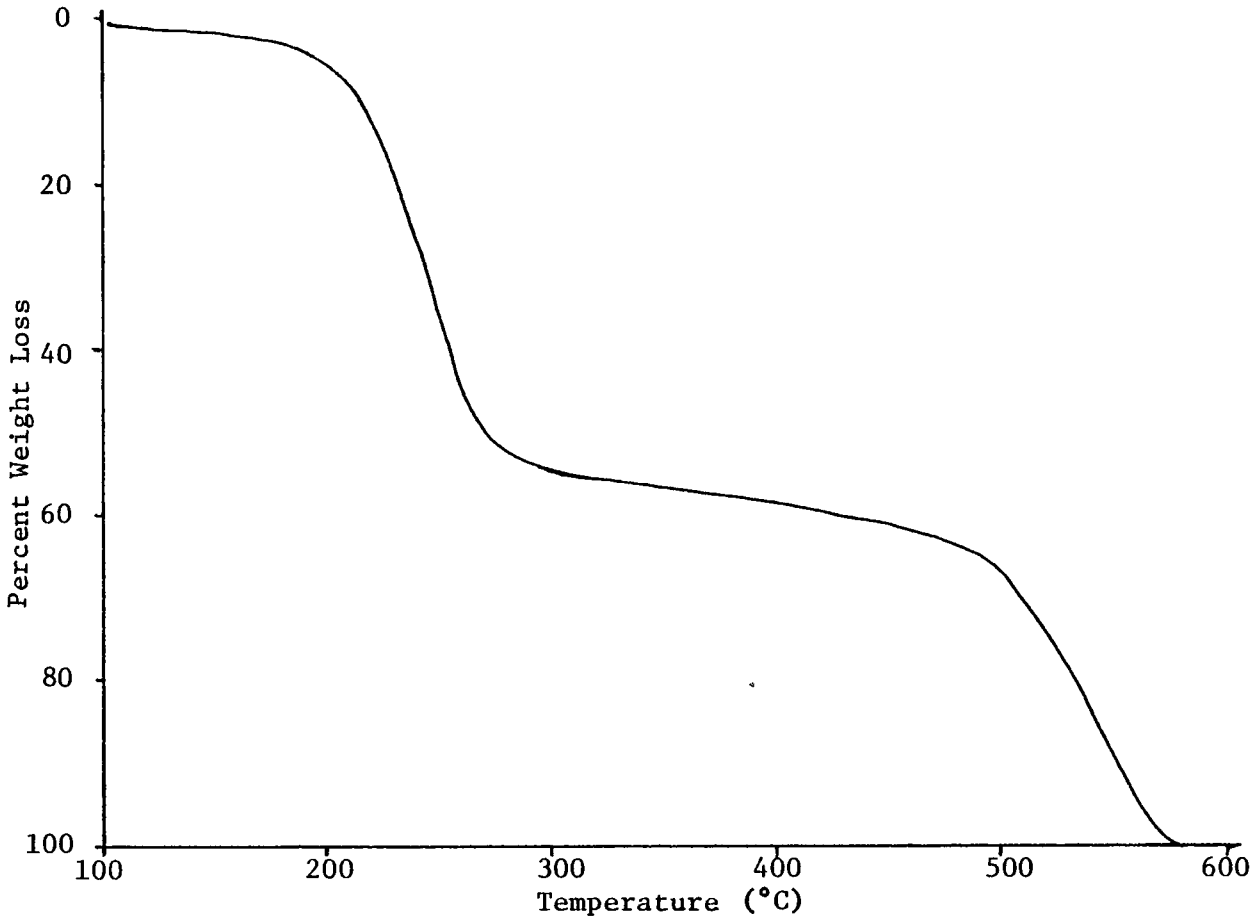


Figure 91. Thermogravimetric analysis of polymer-ortho-01 in air, bulk polymerization at 180-185°. Made by heating in oil bath.

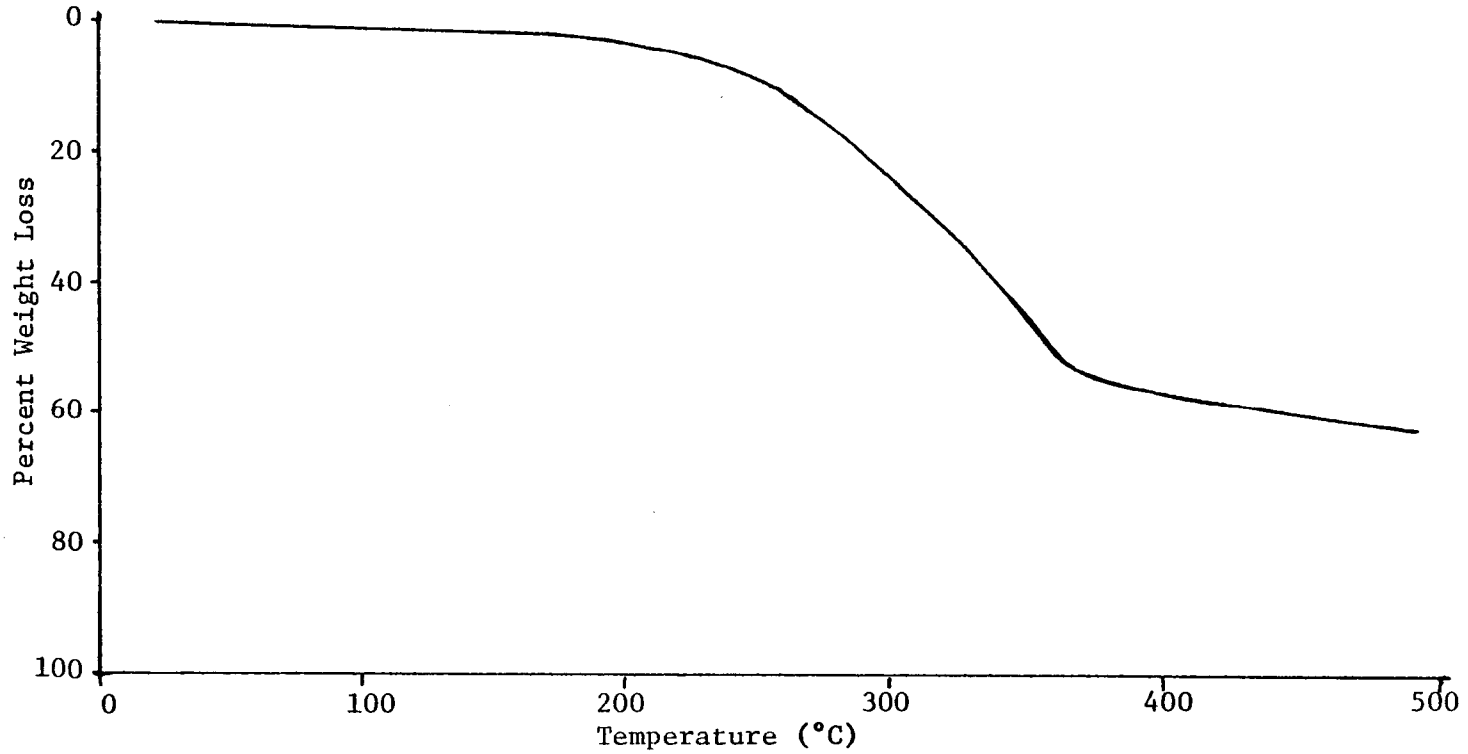


Figure 92. Thermogravimetric analysis of polymer-ortho-01 under nitrogen, bulk polymerization at 206-209°. Made by heating in oil bath.

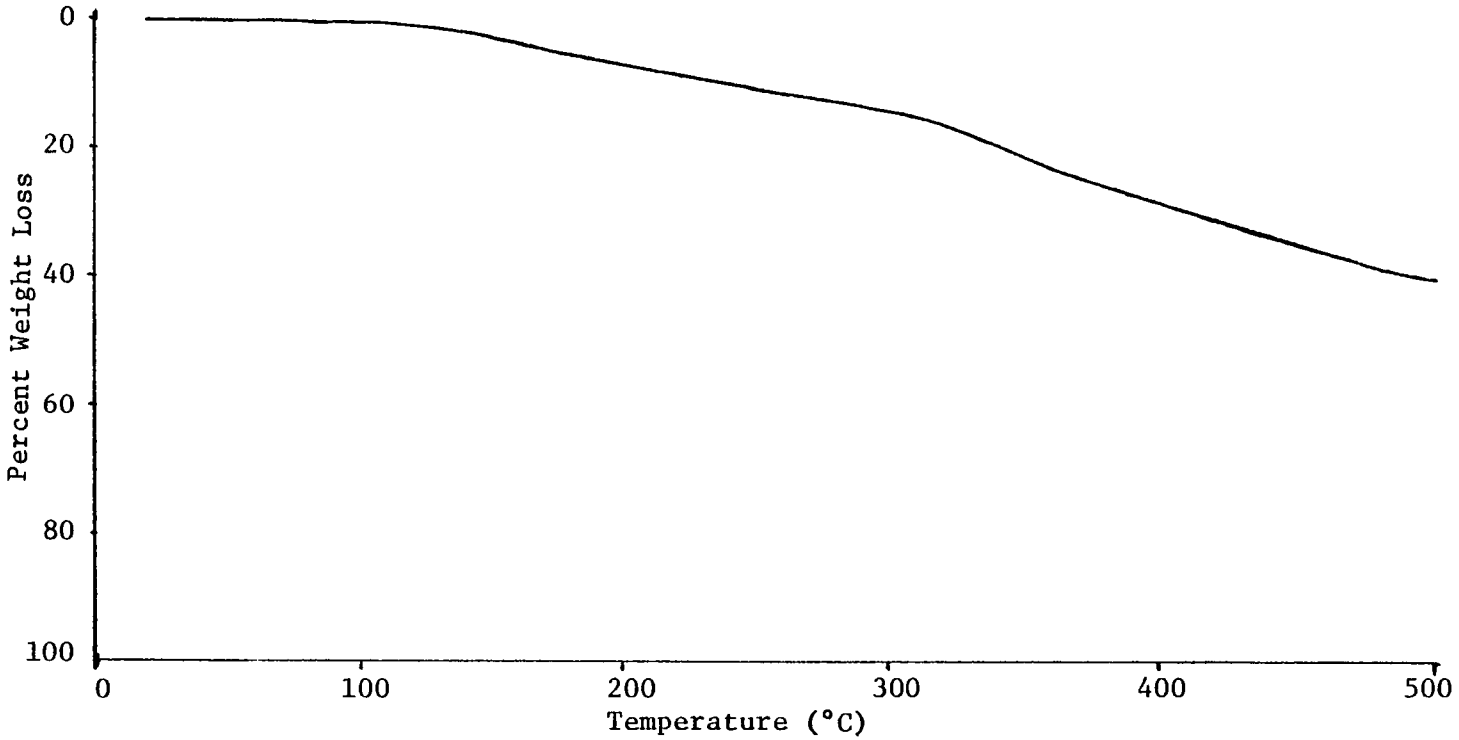


Figure 93. Thermogravimetric analysis of system-ortho-01 crosslinked polymer under nitrogen, refluxing solvent polymerization at 237°. Made by heating in quinoline.

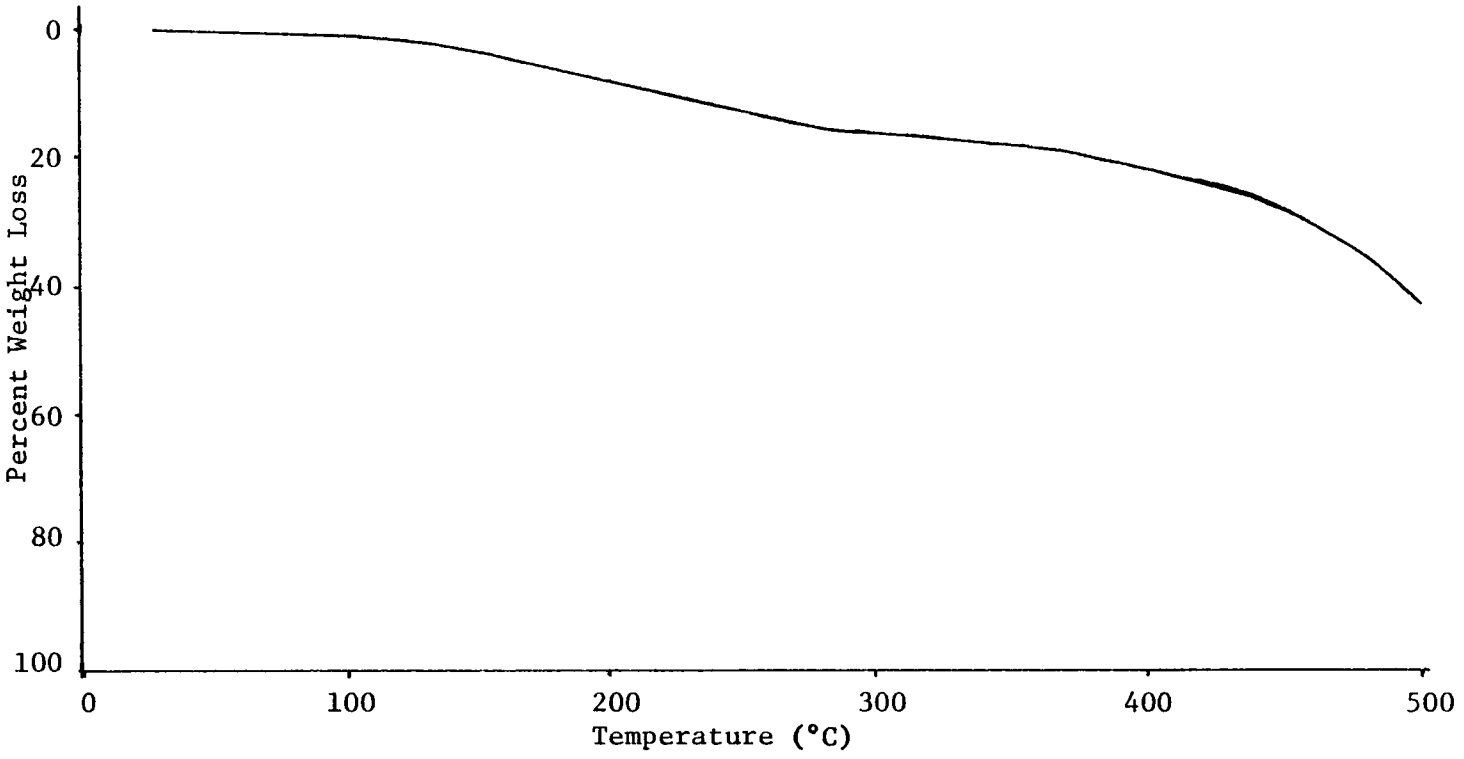


Figure 94. Thermogravimetric analysis of system-ortho-01 crosslinked polymer in air, refluxing solvent polymerization at 237°. Made by heating in quinoline.

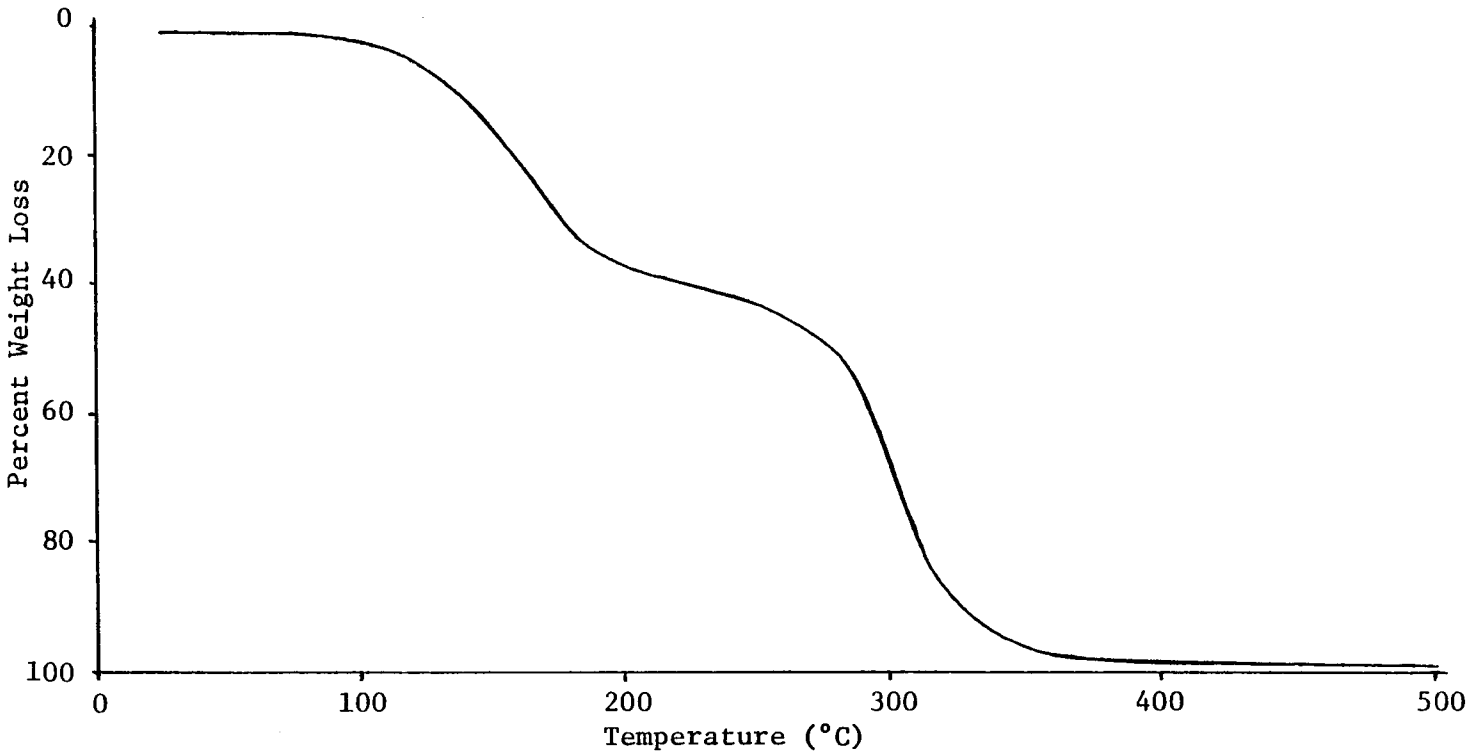


Figure 95. Thermogravimetric analysis of polymer-ortho-11 under nitrogen, Curtius reaction product without heat treatment.

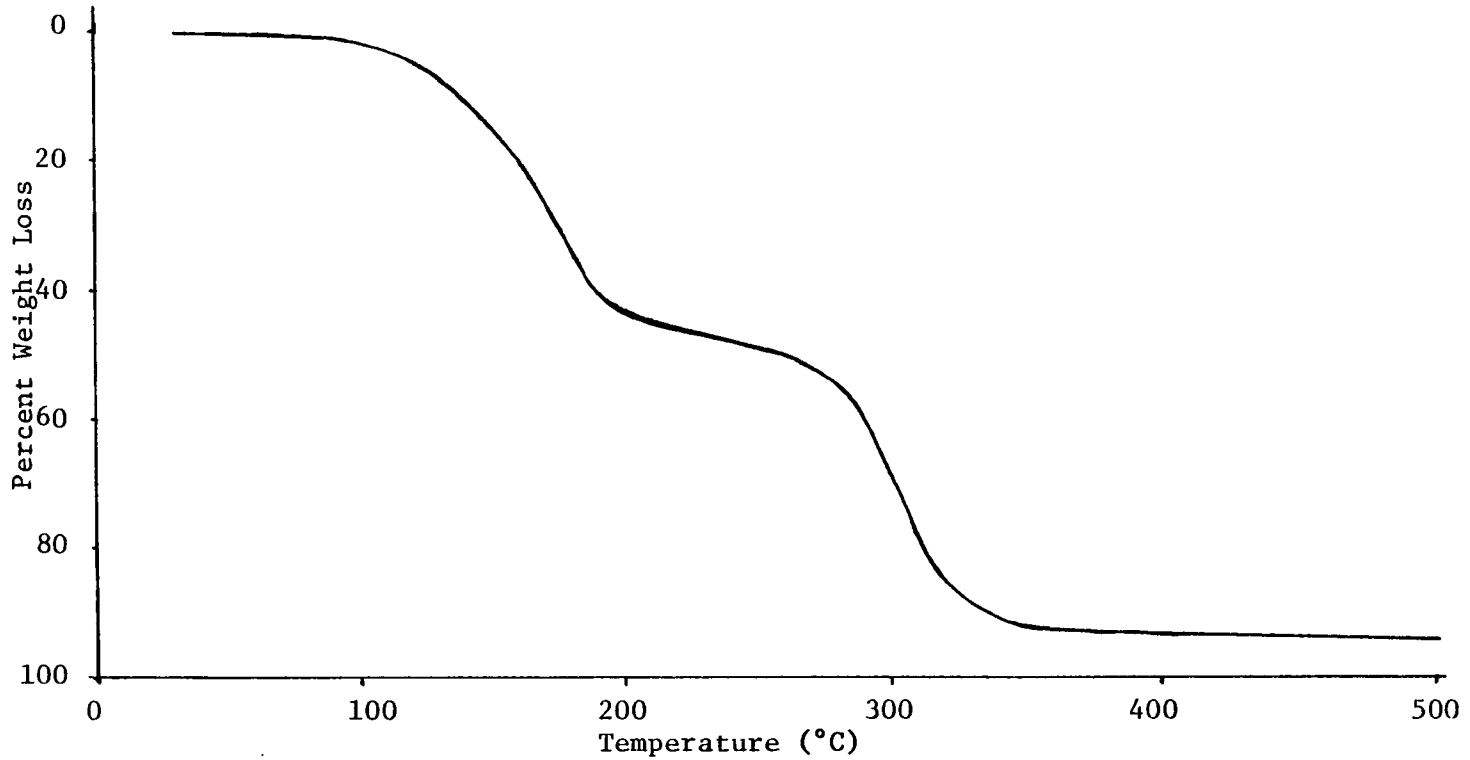


Figure 96. Thermogravimetric analysis of polymer-ortho-11 in air, Curtius reaction product without heat treatment.

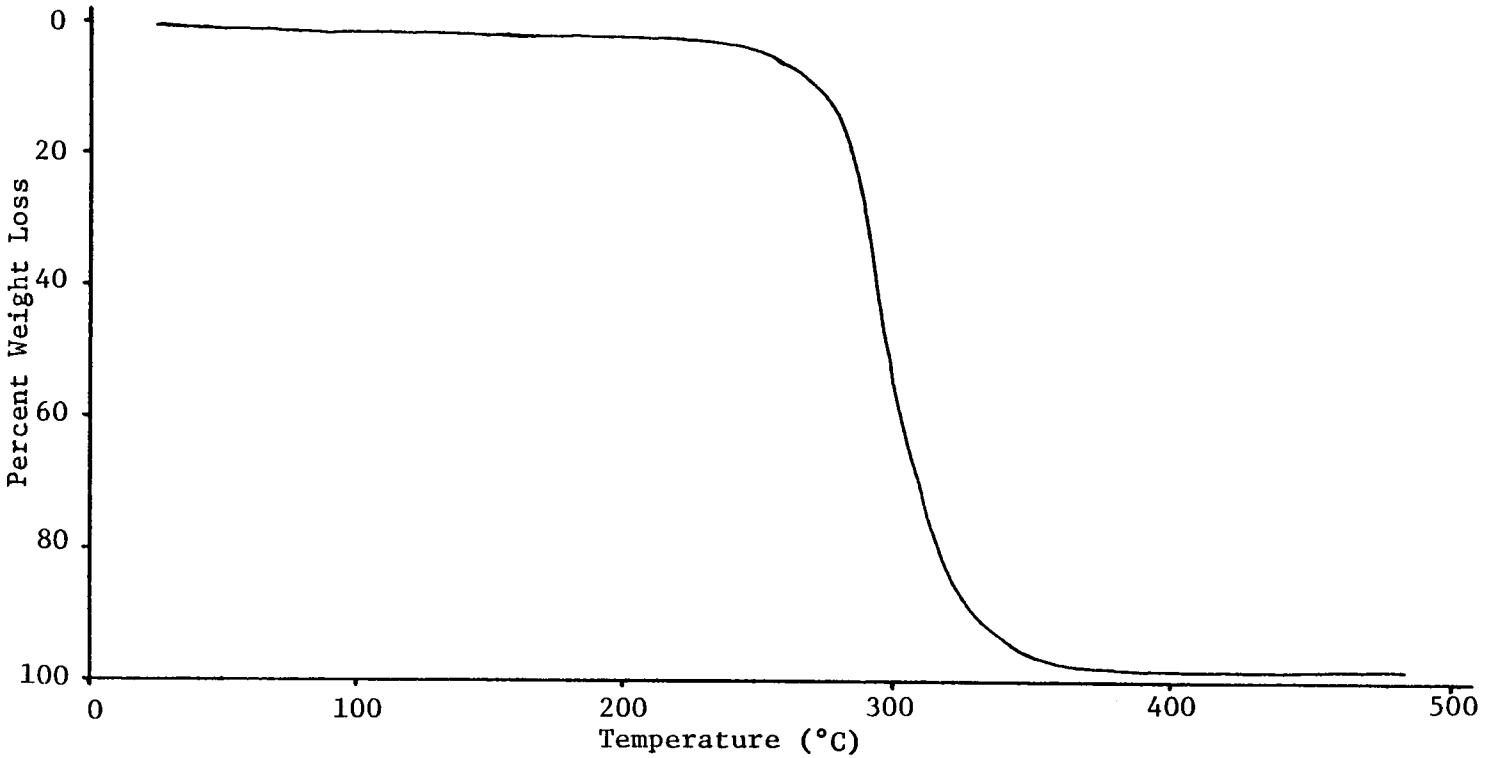


Figure 97. Thermogravimetric analysis of polymer-ortho-11 under nitrogen, Curtius reaction product with heat treatment.

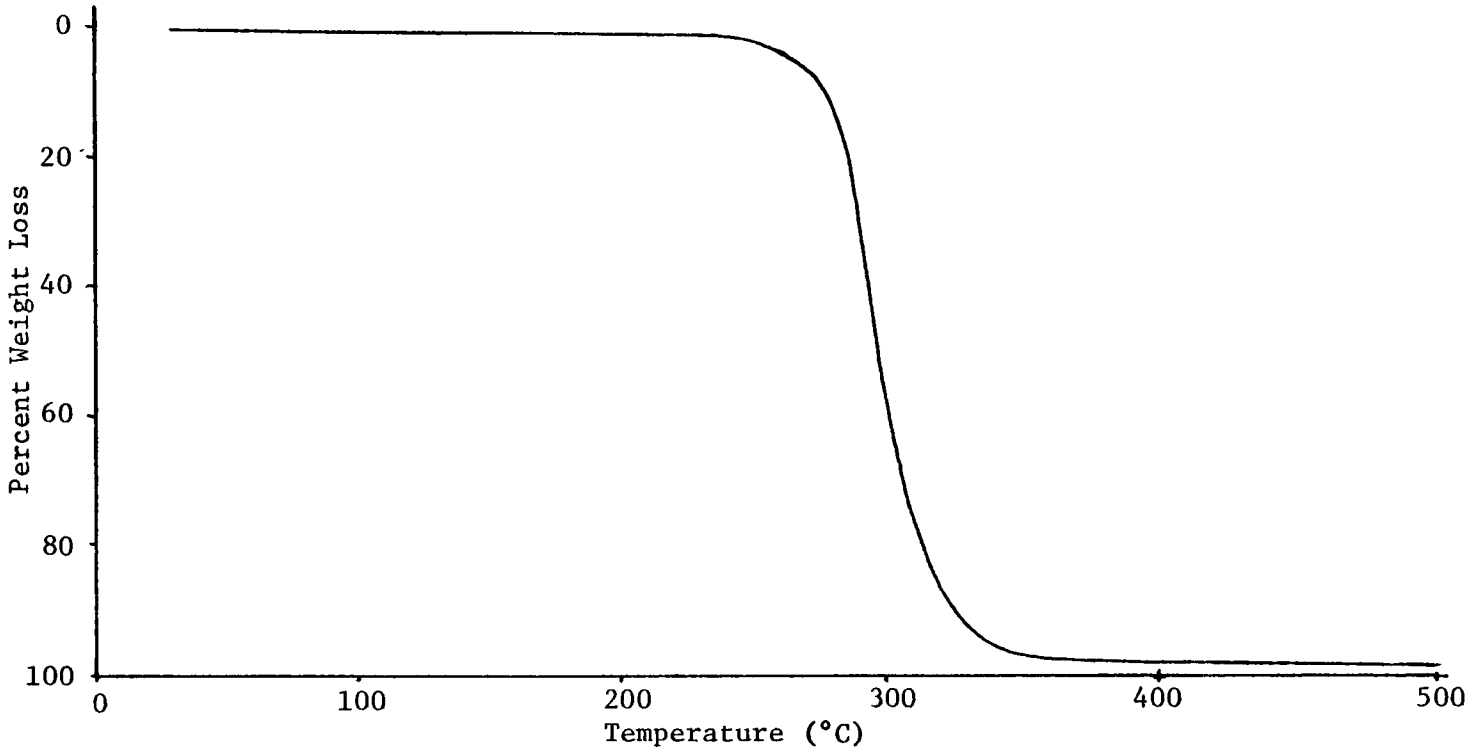


Figure 98. Thermogravimetric analysis of polymer-ortho-11 under nitrogen, Curtius reaction product with heat treatment.

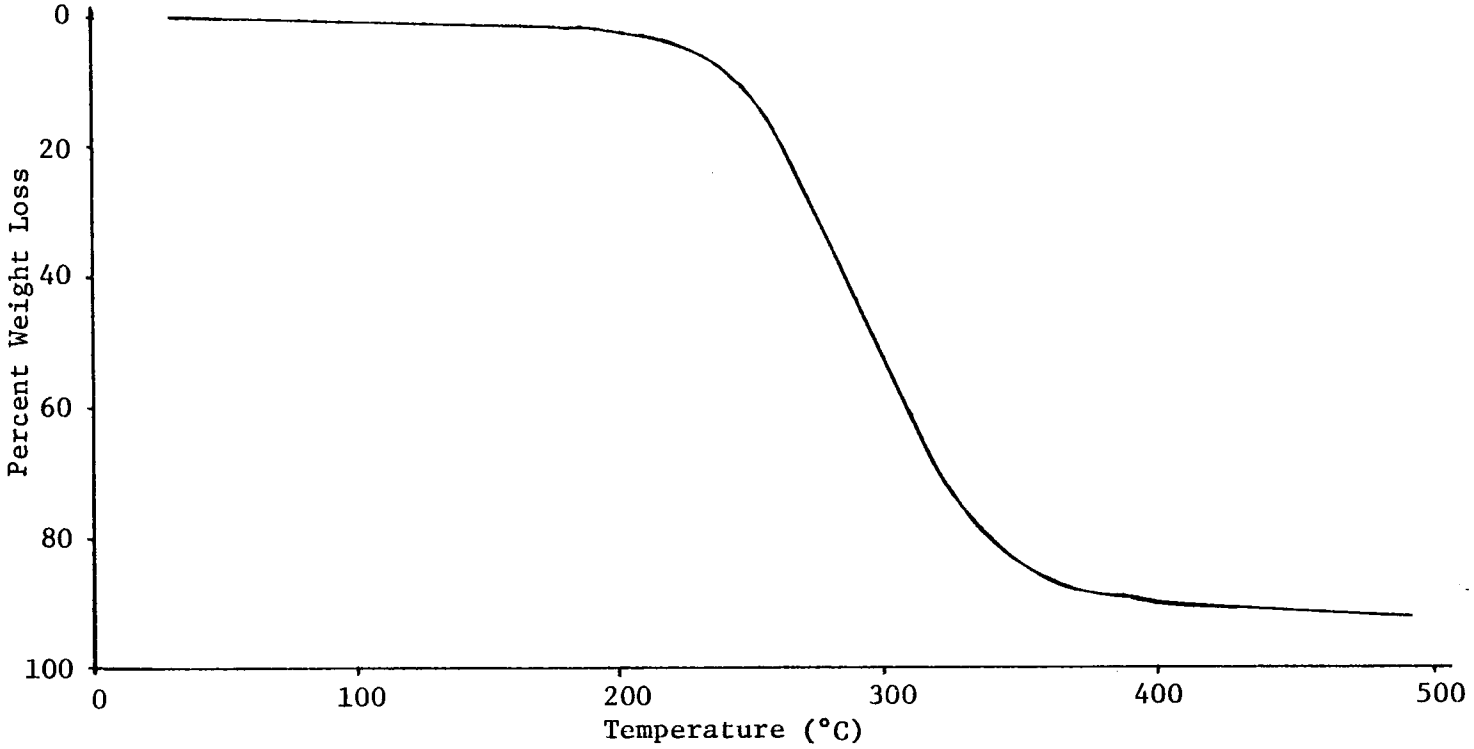


Figure 99. Thermogravimetric analysis of polymer-ortho-02 under nitrogen, Curtius reaction product.

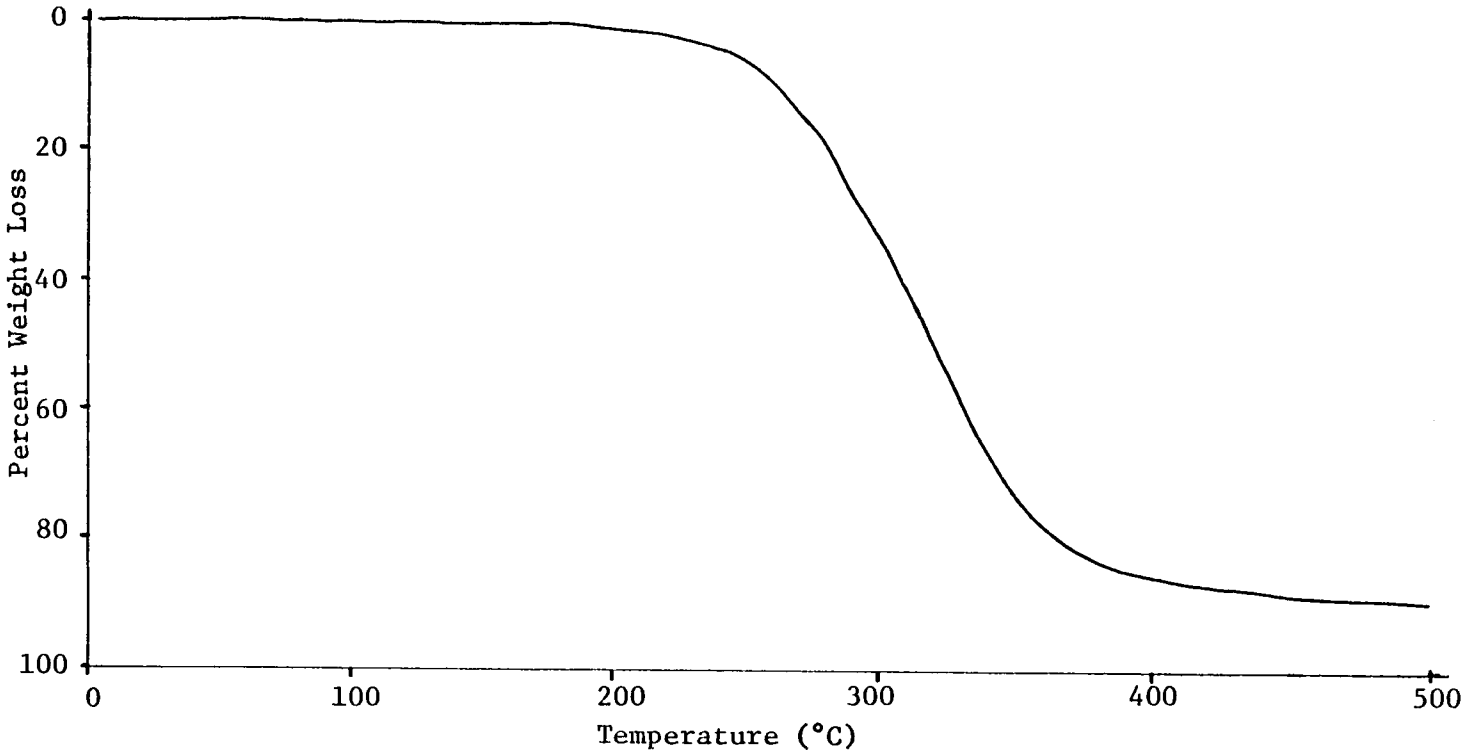


Figure 100. Thermogravimetric analysis of polymer-ortho-02 under nitrogen, Curtius reaction product.

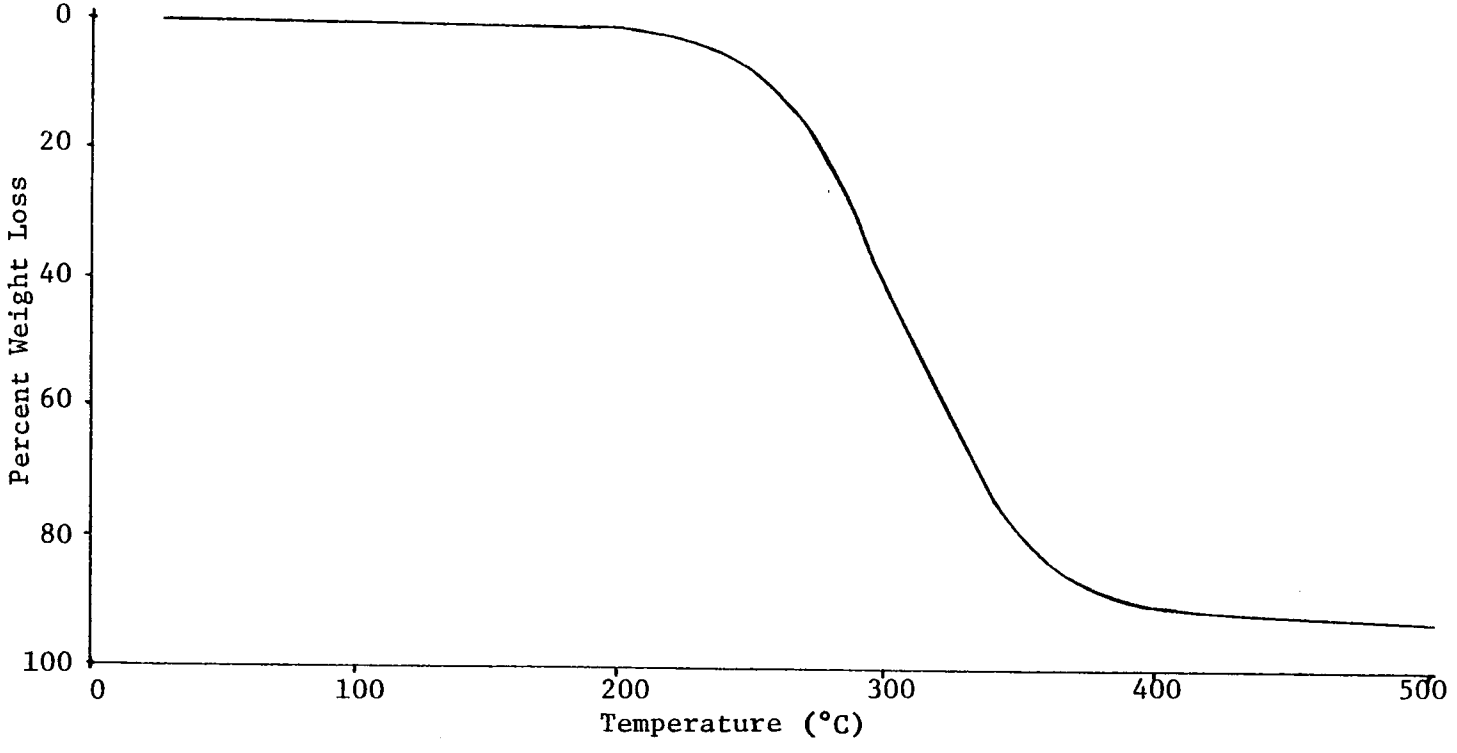


Figure 101. Thermogravimetric analysis of polymer-ortho-02 under nitrogen, Curtius reaction product.

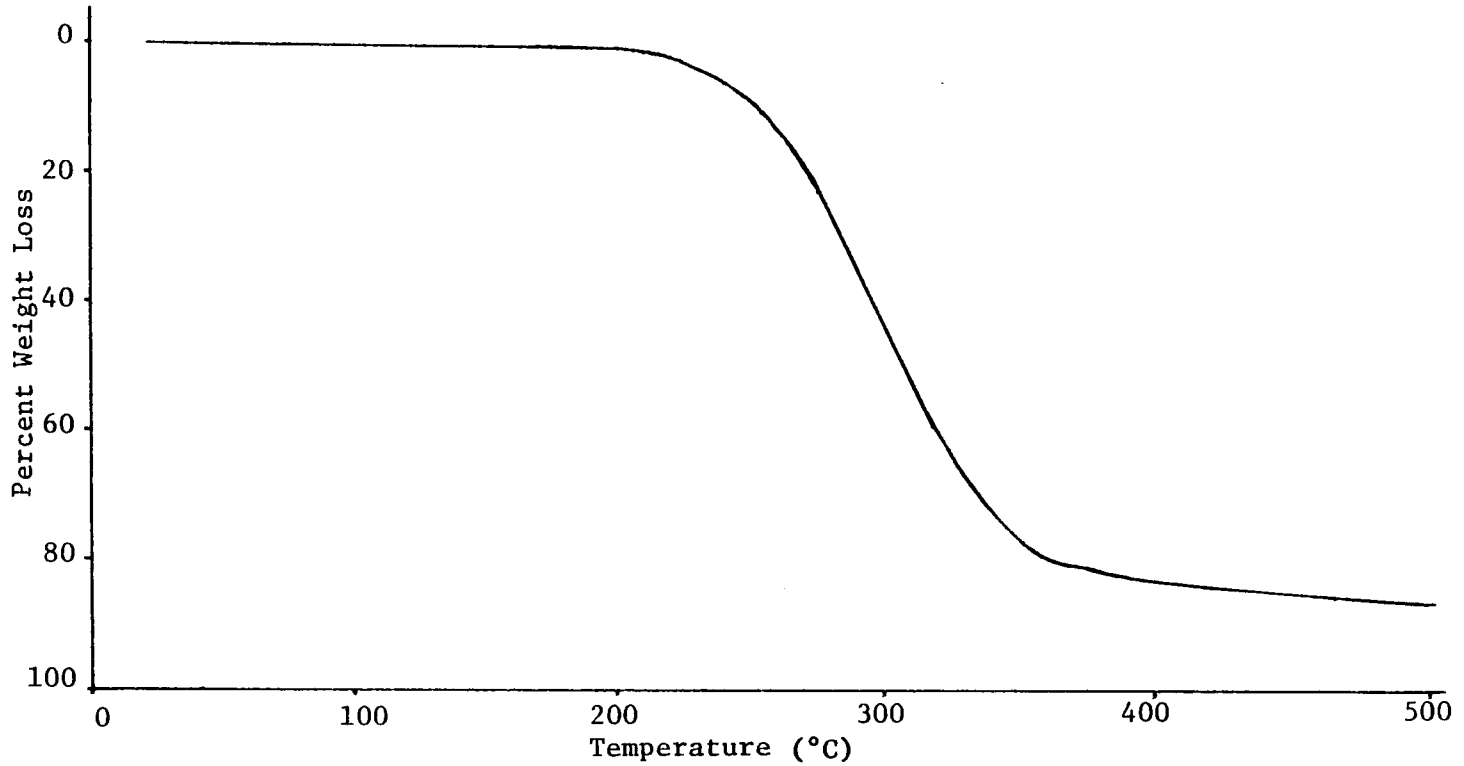


Figure 102. Thermogravimetric analysis of polymer-ortho-02 in air, Curtius reaction product.

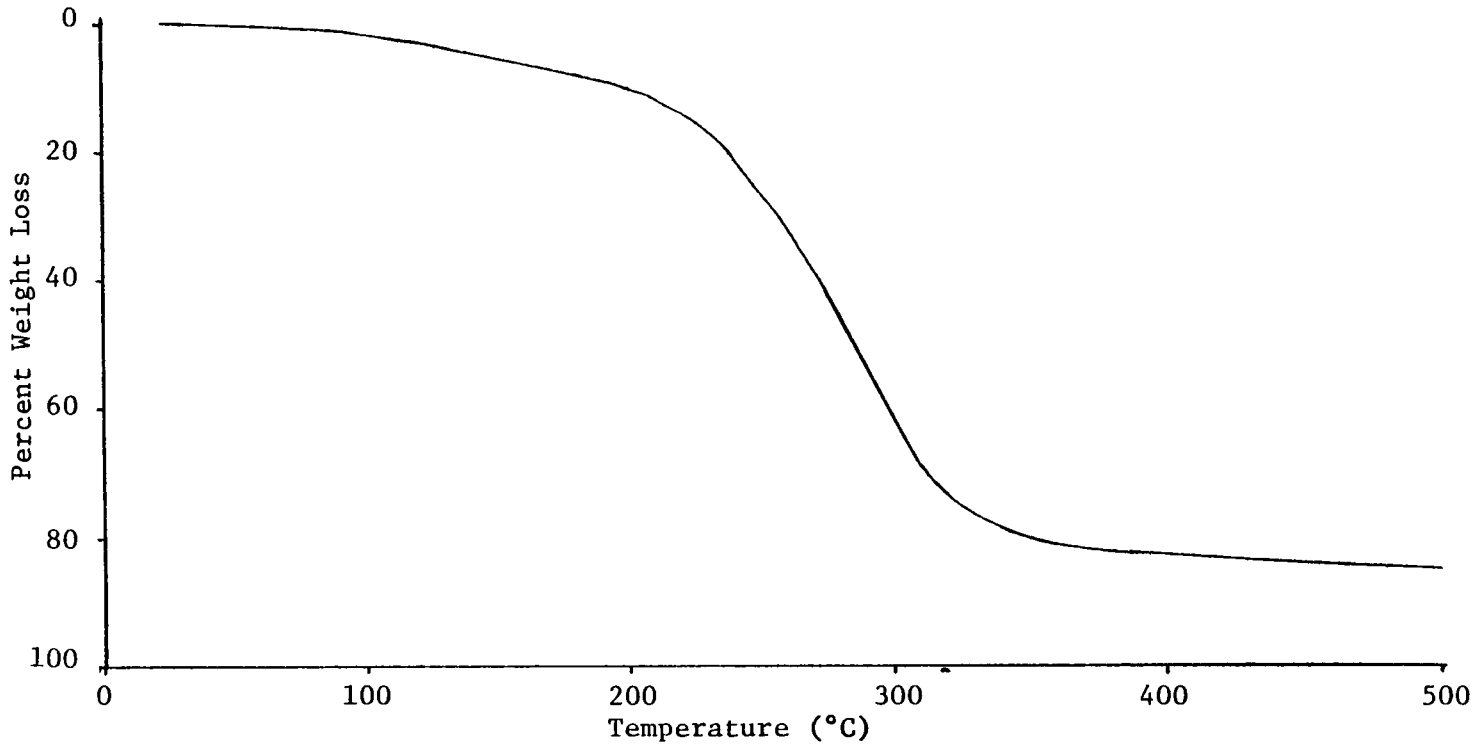


Figure 103. Thermogravimetric analysis of polymer-para-00 under nitrogen, Curtius reaction product.

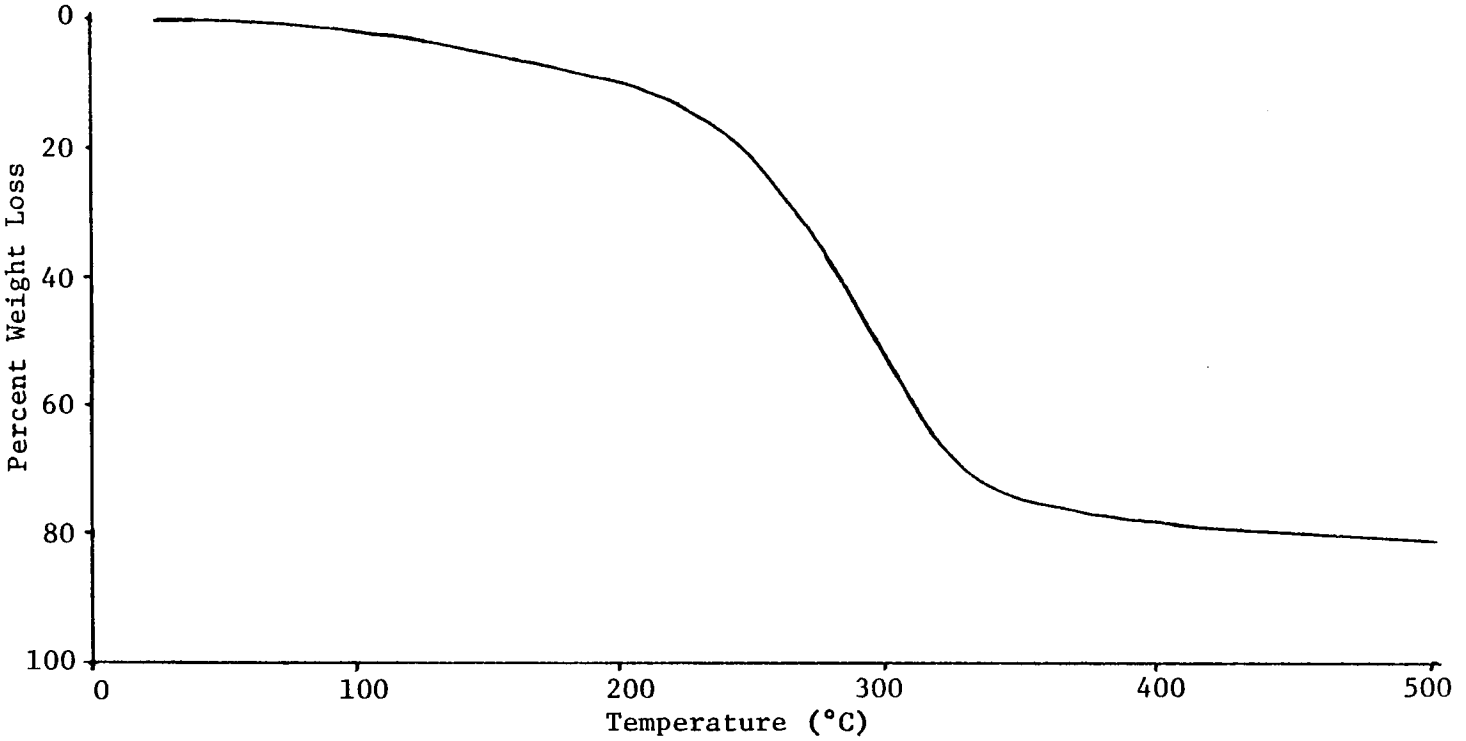


Figure 104. Thermogravimetric analysis of polymer-para-00 in air, Curtius reaction product.

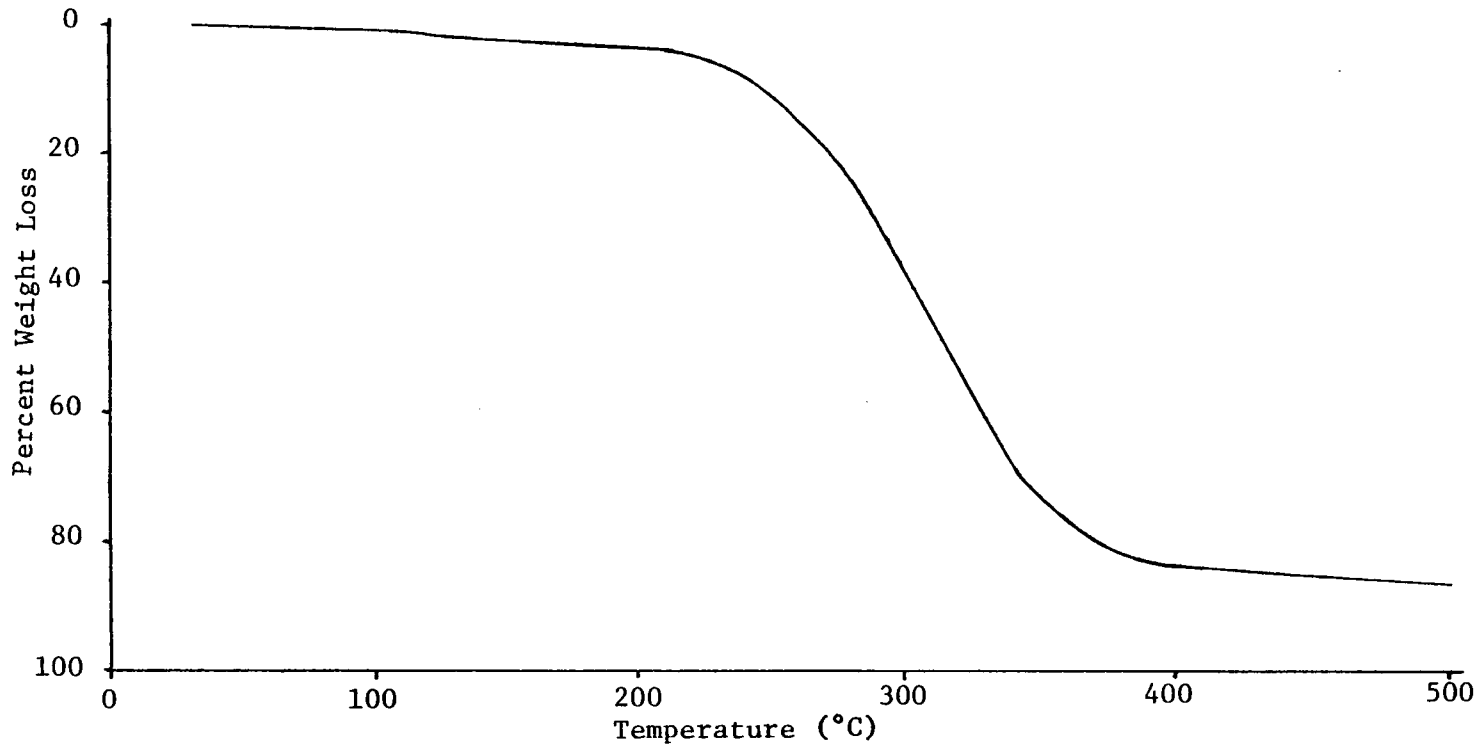


Figure 105. Thermogravimetric analysis of polymer-para-02 under nitrogen, Curtius reaction product.

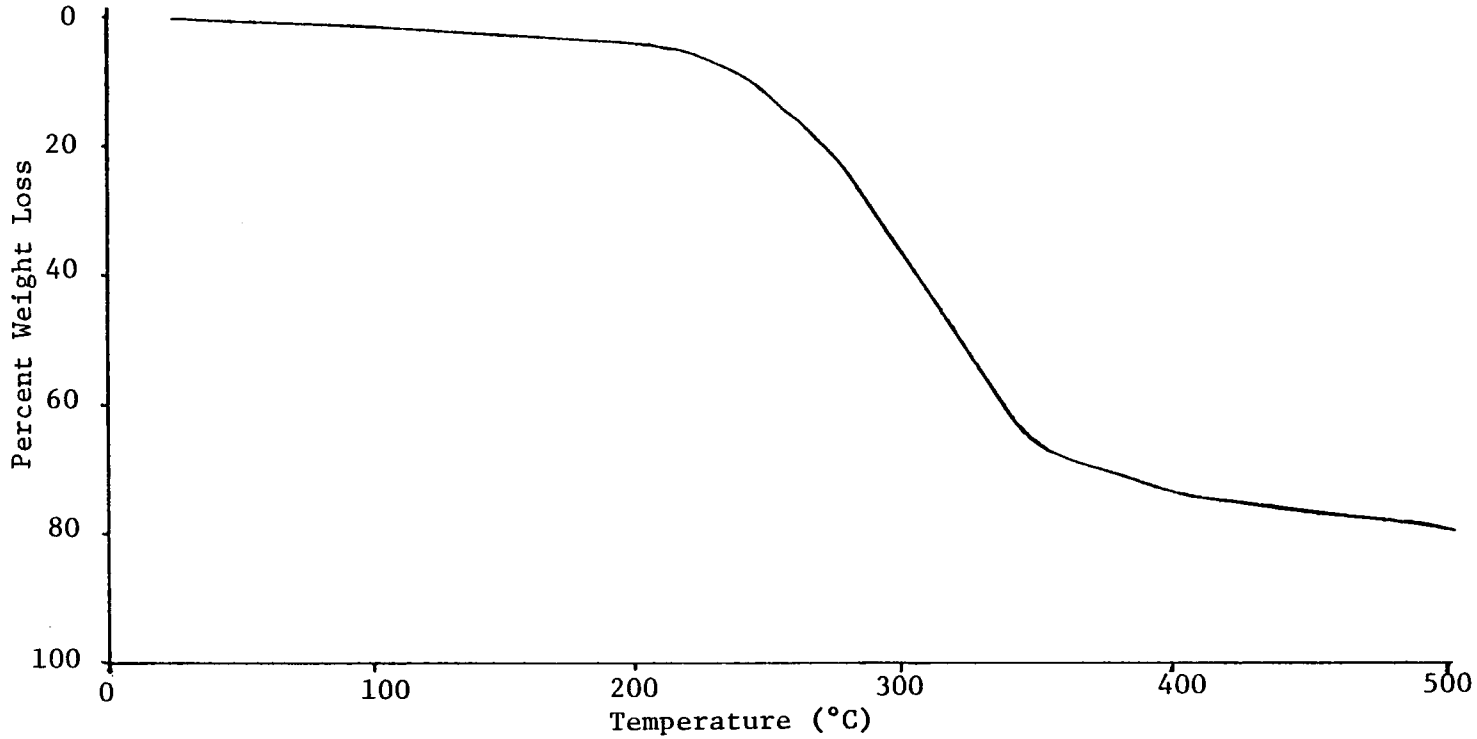


Figure 106. Thermogravimetric analysis of polymer-para-02 in air, Curtius reaction product.

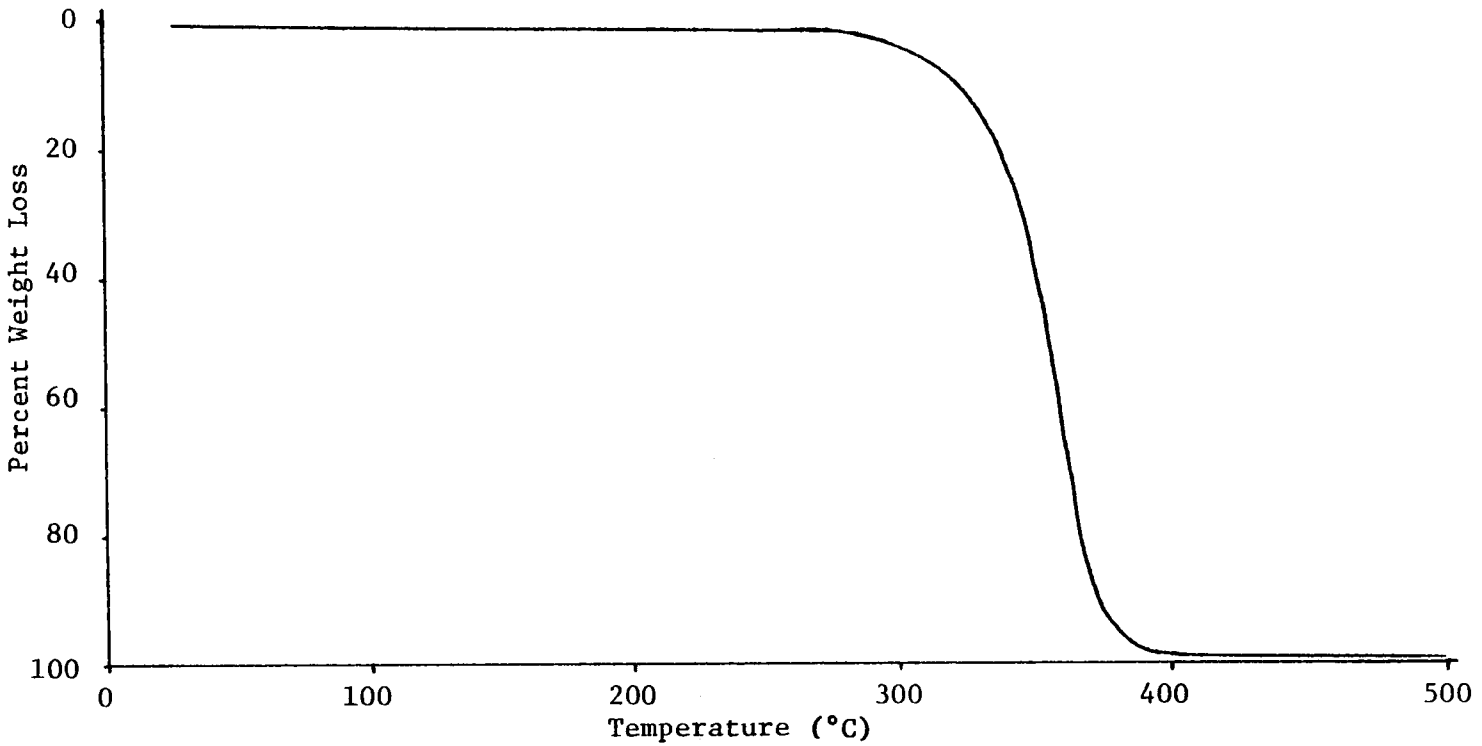


Figure 107. Thermogravimetric analysis of poly(pentamethylene urethane) under nitrogen, Curtius reaction product.

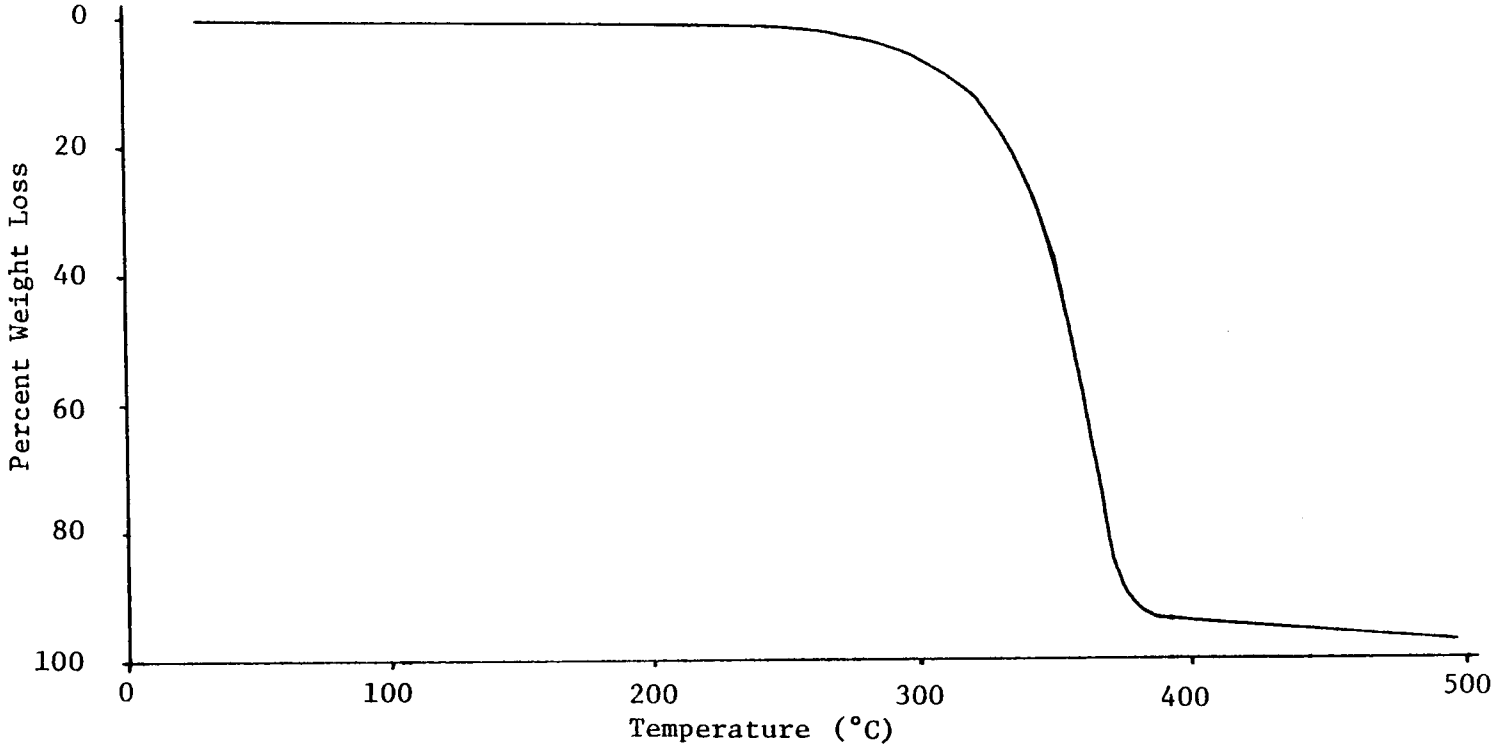


Figure 108. Thermogravimetric analysis of poly(pentamethylene urethane) in air, Curtius reaction product.

APPENDIX XII

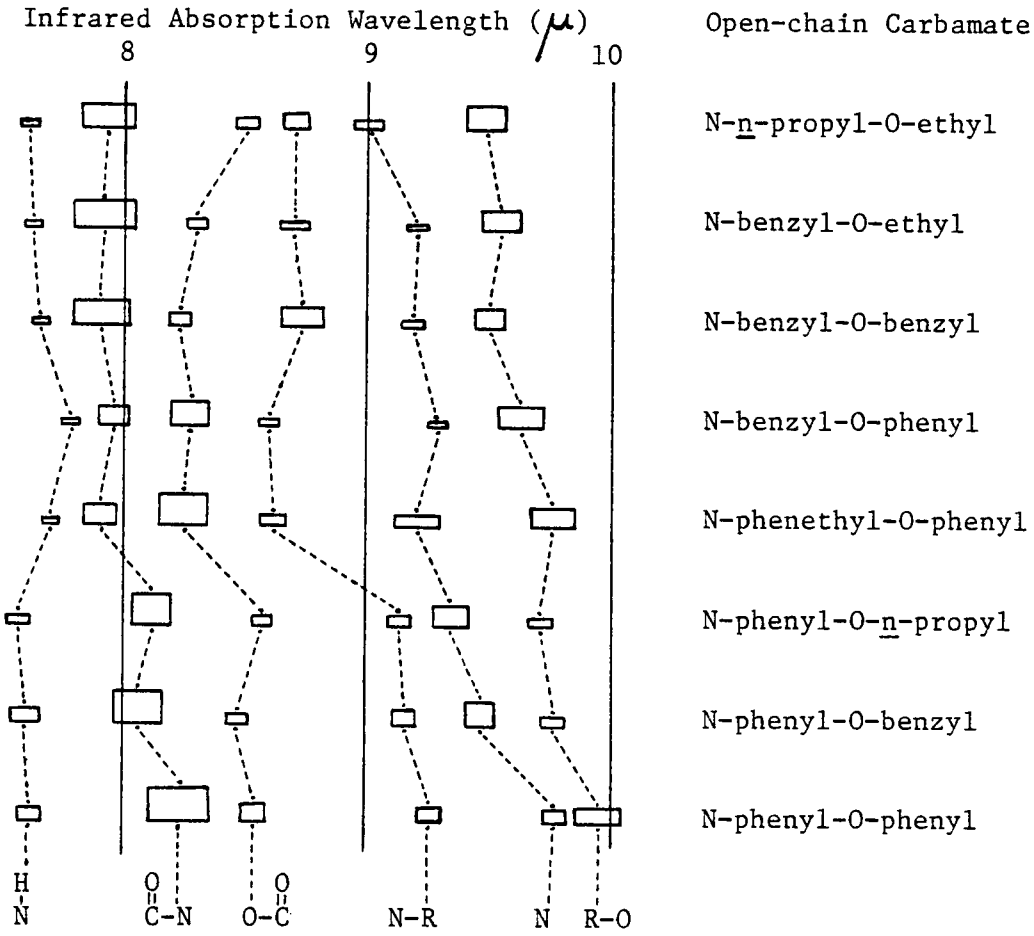


Figure 109. Correlation diagram for midrange infrared absorptions of open-chain carbamates. The moiety which predominately gives rise to each series of absorptions is shown at bottom. The relative intensity and breadth of each absorption is indicated by the dimensions of the corresponding rectangle. The molecules are arranged from top to bottom roughly in the order of increasing electronic delocalization. Tables IV through VIII give more detailed information for the above modes of vibration.

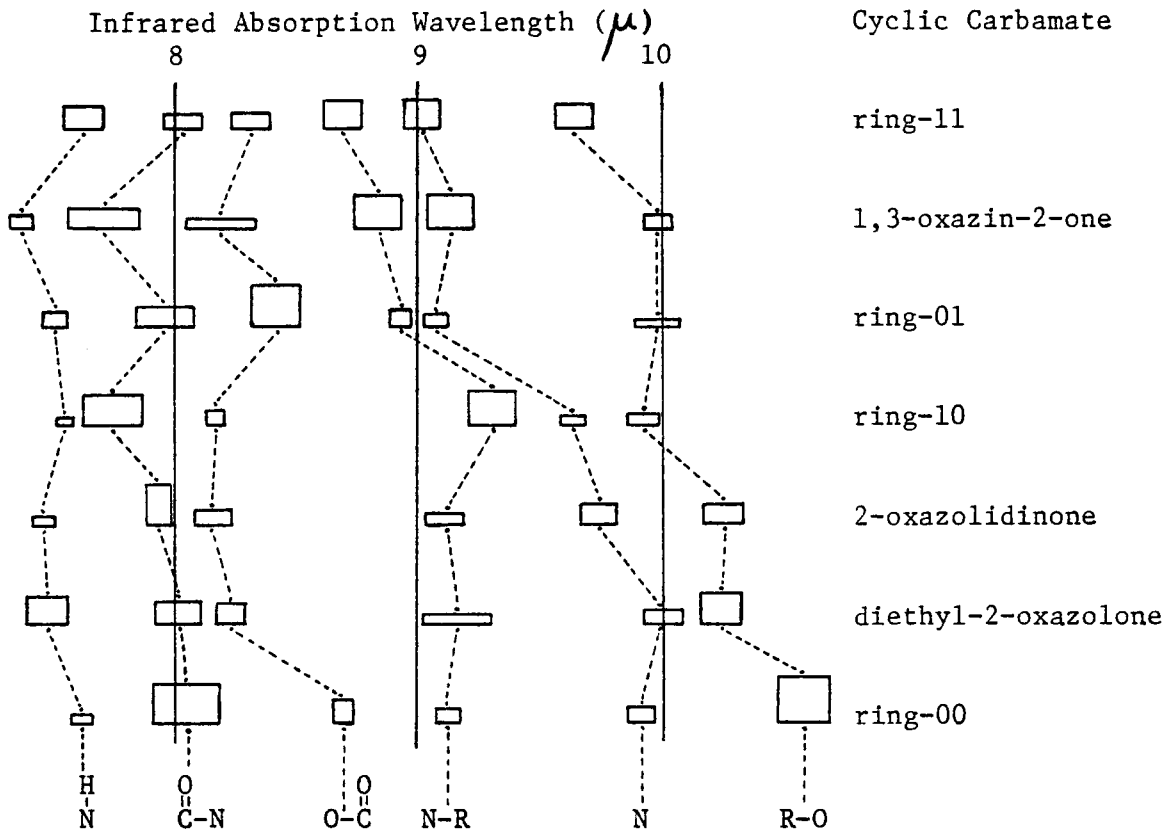


Figure 110. Correlation diagram for midrange infrared absorptions of cyclic carbamates. The moiety which predominately gives rise to each series of absorptions is shown at bottom. The relative intensity and breadth of each absorption is indicated by the dimensions of the corresponding rectangle. The molecules are arranged from top to bottom roughly in the order of decreasing ring size and increasing ring rigidity. Tables X through XV give more detailed information for the above modes of vibration.

VITA

Lorenzo Eric Sepulveda was born in Mexico City, Mexico on December 16, 1945. He attended several elementary schools in Mexico City and Martin, Tennessee, moving back and forth frequently. He attended the Martin High School for two years, and graduated from the Webb School in Bellbuckle, Tennessee. He entered Rensselaer Polytechnic Institute (R.P.I.) in September 1963, where he graduated in June 1967 with a B.S. in chemistry. During the latter two years he worked as curator of the mineral museum in the Geology Department at R.P.I. After working during the summer of 1967 as an analytical chemist for the New York State Department of Health, he completed one semester of graduate study at R.P.I. From April 1968 until November 1968 he worked as a synthetic organic chemist at the Sun Chemical Corporation in Rosebank, Staten Island, New York.

In November 1968 he entered the U.S. Army and worked as a medical laboratory technician until August 1970. During this time he attended Butler University in Indianapolis for two semesters, pursuing graduate study in chemistry. From September 1970 until June 1972 he worked with family enterprises in Weakley County, Tennessee, also sporadically taking courses at the Martin campus of the University of Tennessee. In June 1972 he began graduate study at the University of Tennessee at Knoxville, where he held teaching and research assistantships, while specializing in the Polymer Program of the Chemistry Department.

The author is a member of Alpha Chi Sigma (chemistry

professional), Phi Kappa Phi (scholastic honor society), and the ACS (American Chemical Society). To date, he has co-authored four papers, one book chapter, three ACS talks, and numerous seminars on the enclosed work. One paper on the enclosed work received the Arthur K. Doolittle 1977 award from the Organic Coatings and Plastics Division of the ACS.

After spending one quarter at the UT College of Law, the author decided to forego a career in chemical patent law. He has accepted employment with Texas Eastman Company in Longview, Texas, to engage in polymer research.