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I am submitting herewith a dissertation written by James Wayne Taylor, entitled "The Surface Modifications of Poly(vinyl chloride) and High Density Polyethylene using Isocyanate Chemistry." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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Vice Chancellor
Graduate Studies and Research

THE SURFACE MODIFICATIONS OF POLY(VINYL CHLORIDE) AND HIGH DENSITY POLYETHYLENE USING ISOCYANATE CHEMISTRY

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

James Wayne Taylor

June 1982

3060892

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude and deepest appreciation to Dr. James F. Kinstle for his guidance, knowledge, assistance, and encouragement during the course of this work.

Appreciation is also extended to the University of Tennessee for a teaching assistantship for three years, to the University of Tennessee PATRA Polymer Consortium for their support for two years, and to Gulf Oil Company for their support through the Gulf Oil Fellowship.

Further, the author expresses his indebtedness to Dr. Arlene Garrison and Dr. Richard Crocombe for their instructions and guidance on the use of the Fourier Transform Infrared Spectrometer which made this work possible, and to L. H. Norman for construction of the specialized glassware used in this work.

This thesis is dedicated to my wife, Teresa, whose assistance, patience, understanding, and love made this work possible.

ABSTRACT

The surfaces of poly(vinyl chloride) and high density polyethylene films were modified using isocyanate chemistry. Surface modifications were accomplished using substitution and elimination/addition reactions. Qualitative and semi quantitative characterizations were accomplished using infrared internal reflection spectroscopy.

Poly(vinyl chloride) was modified via a substitution of the chlorines using potassium cyanate solubilized into cyclohexane with 18-crown-6 ether. A carbonyl band appeared in the internal reflection spectrum intead of the isocyanate band. A nylon-1 type structure is proposed. Substitution reactions on poly(vinyl chloride)'s surface were also accomplished with potassium cyanate in the presence of a large excess of ethylene glycol. The intermediate isocyanate group was trapped to form the 2-hydroxyethyl N-poly(vinyl chloride) carbamate modified polymer. During this modification, dehydrochlorination was a competing reaction that resulted in a conjugated double bond system. Evidence for the double bonds was infrared internal reflection spectroscopy and colored films. The double bonds added chlorine quantitatively to produce colorless films. Solvolysis between allylic chlorines and ethylene glycol also occurred on the film's surface.

To accomplish substitution reactions on high density polyethylene, useable functionality was first introduced by chlorination. Comparison of infrared transmission and internal reflection spectroscopy showed the chlorination occurred predominately on the polymer's surface. Attempted substitution reactions using potassium cyanate were unsuccessful producing brown films, an indication of conjugated double bonds.

To incorporate isocyanate groups on poly(vinyl chloride) and chlorinated high density polyethylene, elimination/addition reactions were used. Both polymers were efficiently dehydrochlorinated with sodium methoxide. Isocyanate groups were then introduced onto their surfaces using two methods. The first method was an addition reaction using isocyanic acid and t-butyl hypochlorite. The second method used the pseudo halogen, chloroisocyanate. Introduction of the isocyanate group onto eliminated poly(vinyl chloride) and chlorinated high density polyethylene occurred in a higher yield using isocyanic acid and t-butyl hypochlorite than with chloroisocyanate. For eliminated poly(vinyl chloride) both methods produced colorless films; however, for eliminated chlorinated high density polyethylene, a slight yellow color remained.

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CHAPTER I

GENERAL INTRODUCTION

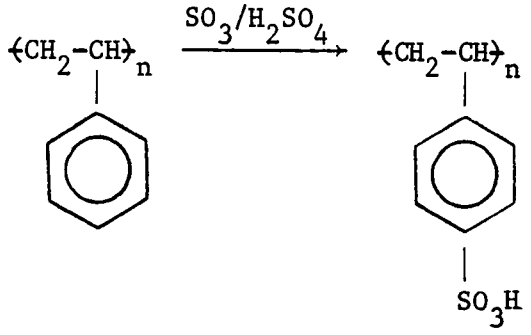
Polymers interact with their surrounding universe through their surfaces, and this interaction is greatly dependent upon the polymer's surface chemical composition. Consequently, chemical modifications of a polymer's surface can alter its adhesion,[1] wettability,[2,3] permeability,[4] dye absorption,[1] and biocompatibility.[5,6,7]

The surface of an organic polymer can be chemically modified in two ways,[8] with one being the formation of a polymer from the surface of another polymer. An example of a surface graft using polyethylene (PE) as the substrate and gaseous methyl acrylate as the grafting monomer is shown below:[9]

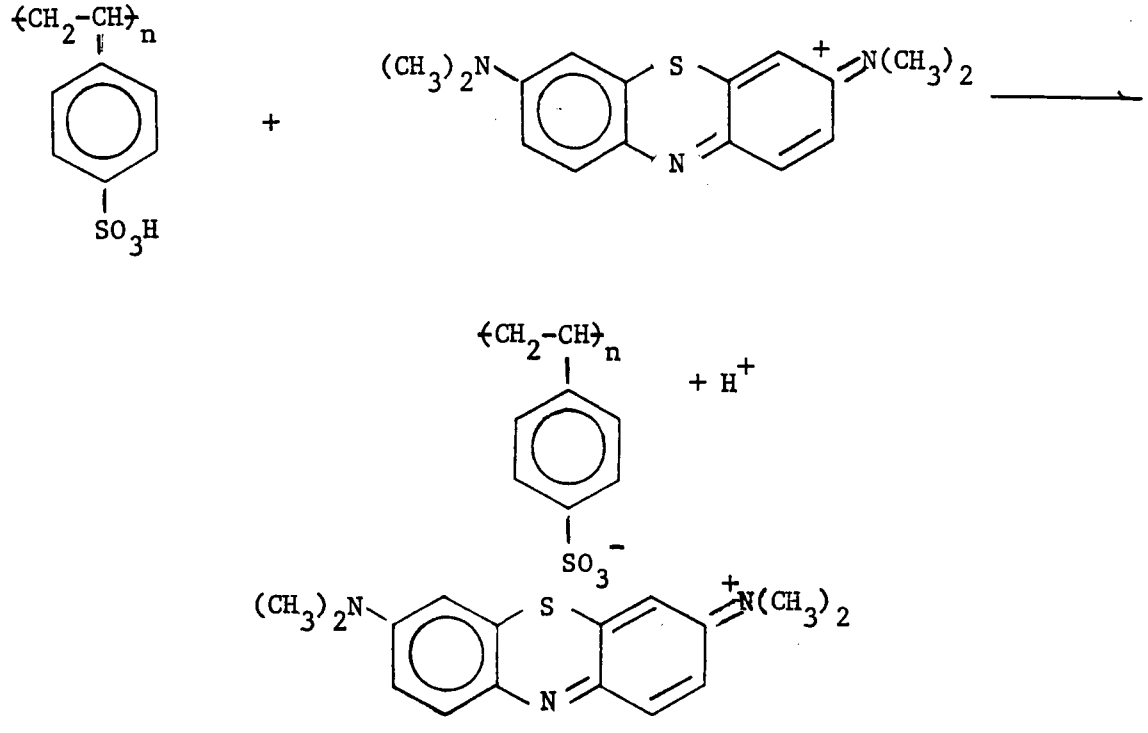
$$PE + nCH_2{=}\underset{\displaystyle CO_2CH_3}{\underset{|}{CH}} \xrightarrow{\gamma} PE\text{-}\left(CH_2\text{-}\underset{\displaystyle CO_2CH_3}{\underset{|}{CH}}\right)\sim\sim$$

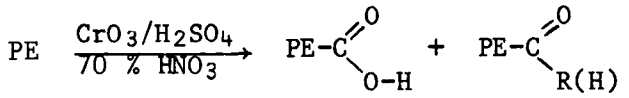
The other type of surface modification involves incorporation of a new functional group on the polymer.

New functional groups have been introduced, and existing groups altered, by a host of chemical techniques. Examples include the treatment of polymers in the presence of the plasma of various gases,[10,11] with ultraviolet radiation in the presence of various gases, [12] and with strong acids.[9,14] Gibson and Bailey[13] used fuming sulfuric acid to introduce sulfonic acid groups on the surface of polystyrene to change its functionality:



They obtained a maximum surface density of sulfonic groups of 1.54 x 10^{14} units/cm^2. The reaction depth was directly proportional to the extent of reaction and the sulfonation was diffusion controlled. The surface of the sulfonated polystyrene was then reacted with the methylene blue cation to make the dyed film:





The new functionality was composed of 60% carboxylic acid groups and 40% ketone/aldehyde groups. They obtained a maximum carboxylic acid surface density of approximately 2×10^{15} units/cm^2.

Blackwell, Degen, and Osterholtz[16] have fluorinated the surfaces of polyethylene and polypropylene using fluorine gas. The depth of fluorination was found to be proportional to the time of exposure to fluorine gas.

In the above methods of modification there are three problems in changing the functionality of polymers. First, it is desirable that any reaction used proceed in a high yield since it is impossible to separate any unwanted functionality caused by a side reaction. Secondly, characterization can be difficult because the bulk polymer must be distinguished from the polymer's surface. Third, the three dimensional spatial distribution of functional groups in the surface region is an important consideration which has no counterpart in solution chemistry. In fact, the word surface for a polymer is not straight forward. Ideally, a surface reaction is a reaction which involves those polymer chains directly on the surface. This study uses the practical definition given by Angier[8] that surface reactions are those reactions occurring predominately in the surface region, and not homogeneously throughout the polymer. The governing principle is to modify the surface chemical composition without altering the physical or mechanical properties of the substrate.

In this study, the chemistry of incorporating functional groups on the surface of polymers is stressed, rather than the final physical or mechanical properties of the products. Specifically, this study will be concerned with the incorporation of new functionality on the surfaces of two polymers: poly(vinyl chloride) (PVC) and high density polyethylene (HDPE). In particular, the goal of this work was to incorporate the isocyanate group and study its chemistry on the surfaces of these polymers.

The isocyanate group is both reactive and very versatile.[17,18,19] It is used in the synthesis of amines, ureas, amides, carbamates and many other compounds; thus, as shown in Figure 1, incorporation of this versatile group on the surface of these polymers allows a potential route to many different functional groups:

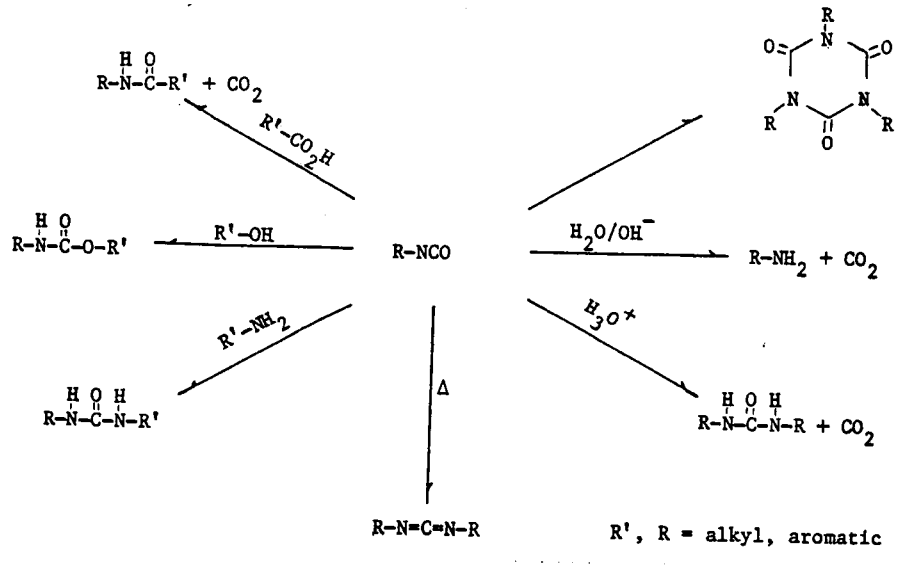


Figure 1. Possible reactions of the isocyanate group.

Two approaches were investigated. One used substitution reactions on the surfaces of PVC and chlorinated high density polyethylene (ClHDPE) using the cyanate anion. The second approach involved the elimination of HCl from the polymers and the addition of a chlorocyanate across the double bonds. These approaches are shown in Figure 2.

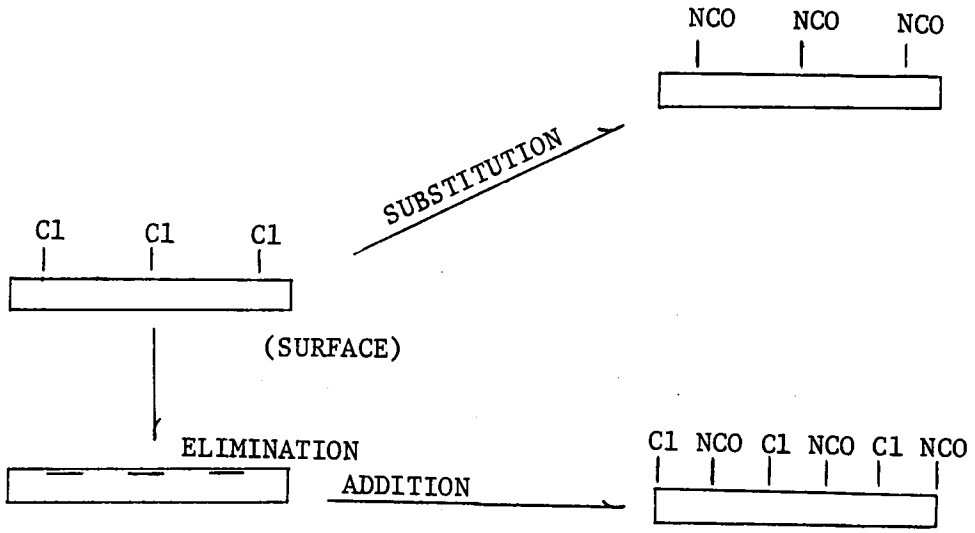
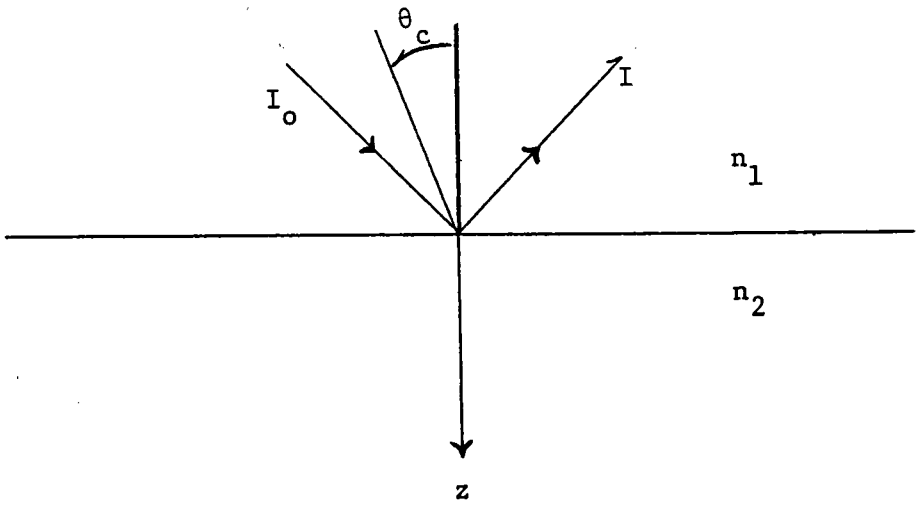


Figure 2. Possible pathways for incorporation of the isocyanate group on the surface of PVC and ClHDPE.

The method used for studying the surface of modified polymers was internal reflection spectroscopy often referred to as attenuated total reflection (ATR). This method produces an infrared spectrum of species located near the surface of the sample. It was initially proposed and developed simultaneously by Fahrentert[20] and by Harrick.[21] A brief description of its theory and the quantitative aspects of internal reflection spectroscopy will follow.[22,23,24,25]

Suppose that we have a light beam striking a surface as shown in the diagram below:



The intensity of the light beam prior to reflection is I_o and its intensity after reflection is I. The reflectivity, R, is defined by the ratio:

$$R = I/I_o \tag{1}$$

If n_2 (the refractive index of medium two) is less than n_1 (the refractive index of medium one), and if medium two is nonabsorbing, a critical angle θ_c exists which is calculated from the expression:

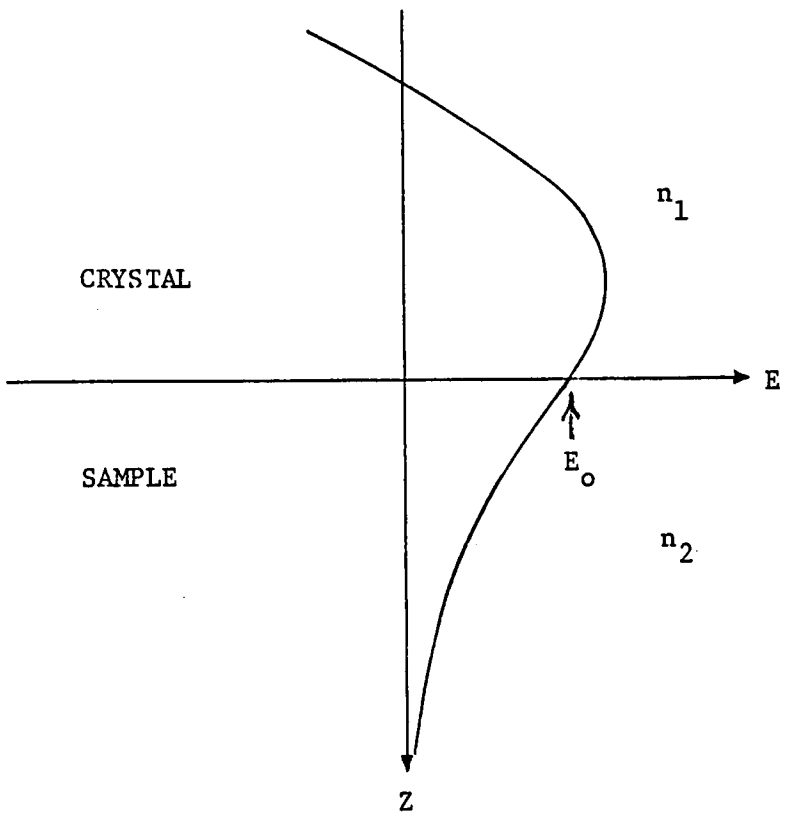
$$\theta_c = \sin^{-1}(n_2/n_1) \tag{2}$$

If the angle of the light beam is greater than θ_c, a total internal reflection occurs and

$$R = 1.0 \tag{3}$$

If medium two is absorbing, an attenuated total reflection occurs, and R is less than unit.

A total internal reflection sets up a standing wave pattern due to interference of the incoming and outgoing wave, as shown in the diagram below:



The standing wave amplitude pattern is not constant but falls off exponentially with distance z into medium two. This drop-off is not due to an absorption, but due to the fact that this is the evanescent (dissipating) field of a totally reflected wave. This exponential drop-off of the amplitude, E_o, is described by the expression:

$$E = E_o \, e^{-z/dp} \qquad (4)$$

where the two controlling parameters are E_o and dp. E_o is the value of the amplitude at the surface; dp is the depth at which the amplitude, E, has decreased to 1/e of its value at the surface. It is calculated from the expression:

$$dp = \frac{\lambda}{n_1 2\pi[\sin^2\theta-(n_2/n_1)^2]^{1/2}} \tag{5}$$

where λ is the wavelength of the incident radiation.

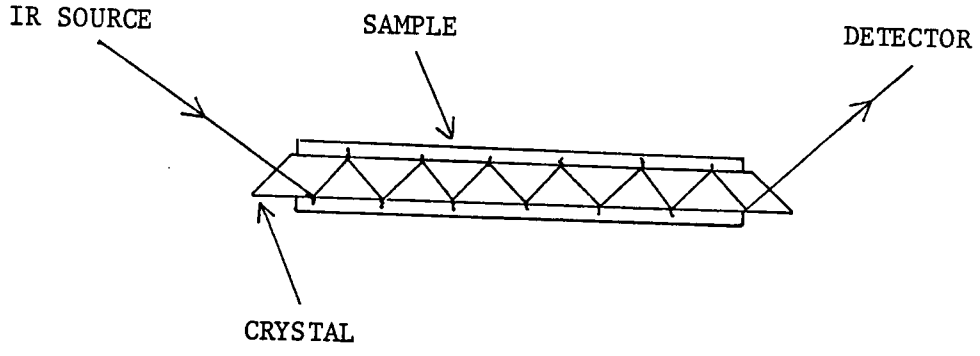
A comparison of a transmission experiment and a total internal reflection experiment shows that basic differences exist. The decrease in intensity for a transmission experiment is simply due to the amount of light absorbed. The absorption is described by the familiar Beer's Law:

$$A = \varepsilon bc \tag{6}$$

where A is the absorbance, ε the molar absorptivity, and b the path length, c is the concentration. For a transmission experiment if the material is nonabsorbing, i.e., $\varepsilon = o$, the intensity of the light beam would remain constant; however, for a total internal reflection where medium two is nonabsorbing, the intensity of the evanescent wave decreases. If medium two is absorbing, the intensity is changing because it is being absorbed, and because it is an evanescent wave.

In dealing with the quantitative aspects of internal reflection spectroscopy, the mathematics are complicated and approximations are used. The following discussion will give the important relationships necessary to understand this work.

To obtain an ATR spectrum, a trapezoid KRS-5 crystal, $n_1 = 2.4$, with a 45° cut was used.



The sample was placed on the top and bottom of the crystal. The number of reflections, N, within the crystal can be calculated from the relationship:

$$N = \ell/t \ (\tan \theta)^{-1} \tag{7}$$

where ℓ is the length of the crystal, t is its thickness and θ is the angle of incidence at the crystal's surface. For N reflections within the crystal which is in intimate contact with the sample the quantitative relationship is

$$R^N = (1-a)^N \tag{8}$$

where

$$R^N = (I/I_o)^N \tag{9}$$

and a, the absorption factor, is the absorption for a single reflection. The absorption factor is described by the relationship:

$$a = \varepsilon c d_e \tag{10}$$

where ε is the same molar absorptivity as in transmission spectroscopy and

corrected 1/14/84 JWT

$$de = \frac{\left(\frac{n_2}{n_1}\right) E_o^2 \, dp}{2 \cos \theta} = \frac{\frac{n_2}{n_1} E_o^2 dp}{2 \cos \theta} \qquad (11)$$

which is referred to as the "effective thickness," or that thickness which would give the same amount of absorption in a transmission experiment. The above expression assumes that d_e is not dependent on ε. In general, this assumption is true for $\varepsilon < 10^5$ cm^{-1}. For a larger ε, d_e is very complicated mathematically. It is important to note that because the penetration depth is proportional to wavelength, the effective thickness also increases with wavelength; thus, for two bands that are of equal intensity on a transmission experiment, the one at longer wavelength will be stronger in intensity in the internal reflection experiment. Equation 8 can be rearranged to a more convenient form similar to Beer's Law. Using Equation 9 and the approximation:

$$\ln (1-a) \underset{\sim}{} -a \qquad (12)$$

allows Equation 8 to be written as

$$N \ln (I/I_o) = -Na \qquad (13)$$

Using the identity

$$2.303 \log (x) = \ln (x) \qquad (14)$$

allows Equation 13 to be written as

$$2.303\ N \log (I/I_o) = -Na \tag{15}$$

By definition

$$A = -\log (I/I_o) \tag{16}$$

Substitution of Equation 16 into Equation 15 gives

$$A_T = N\varepsilon cd_e/2.303 \tag{17}$$

where A_T is the total absorbance observed. Thus Equation 17 can be used instead of Equation 8 provided $a < .1$. Equation 8 and Equation 17 assumes that the species of interest is homogeneous throughout the bulk of the material. Furthermore, it is assumed that intimate contact of the sample is made with the crystal. If intimate contact is not assured, a method with an internal standard can be used. With this method an absorption band unaffected by surface modification is used as a reference. If we assume that the reference species extends uniformly through the thick sample then

$$A_r = N\varepsilon_r c_r d_{er}/2.303 \tag{18}$$

where d_{er} is the effective depth for the reference sample. If we divide equation 17 by Equation 18 we form the ratio

$$\frac{A}{A_r} = \frac{\varepsilon cd_e}{\varepsilon_r c_r d_{er}} \tag{19}$$

corrected 11/14/84 JWT

According to Tompkins,[6] if the index of refraction is assumed to be the same throughout the sample then the relationship can be written as

$$\frac{A}{A_r} = \frac{\varepsilon\ c\ \lambda}{\varepsilon_r c_r \lambda_r} \tag{20}$$

where λ is the wavelength of the band of interest and λ_r is the wavelength at the reference band. It should be noted that this ratio method is based on the approximation as shown by Equation 12, and the error due to this approximation is large if $a > .1$.

The previous discussion considered absorbing species which were distributed homogeneously throughout the substrate. For an absorption caused by a species that is not distributed uniformly, i.e., $c = c(z)$ so that the concentration varies with the depth, z, Tompkins[26] derives the following equation

corrected 1/14/84 JeT

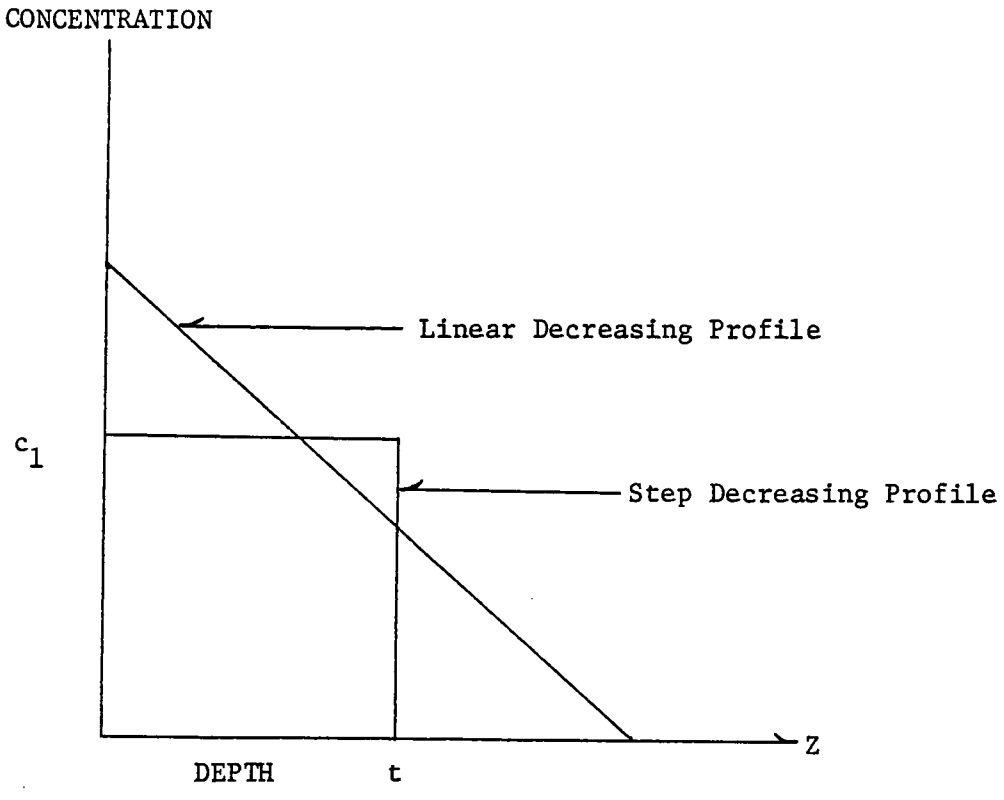
$$a = \frac{n_2/n_1 \; E_o^2}{\cos \theta} \int_0^\infty c(z) e^{-2z/dp} \, dz \qquad (21)$$

where the variable z describes the depth into the sample, a is the absorption at λ and the other terms are the same as defined previously. Tompkins then makes the following assumptions: (1) the depth profile is a step function, (2) a reference band can be located for another absorbing group that is uniformly distributed throughout the sample, and (3) the sample is assumed to be thick relative to infrared radiation. Further, Tompkins ignores the differences in electric field amplitude for equal incident amplitudes of perpendicular and parallel polarization. This field difference actually leads to a different relative thickness in isotropic media for perpendicular and parallel polarization. As long as a calibration or reference band is used in a ratio-type determination, the polarization effects can be neglected.

The step profile is defined as

$$c = \begin{cases} c_1 & z \leq t \\ 0 & z > t \end{cases} \qquad (22)$$

where t is the depth of penetration of the absorbing species. This step profile is shown in the diagram below:



Tompkins argues that, although equations can be derived for linear decreasing concentration and a step decreasing concentration, in practice the normal experimental uncertainty is greater than the different equations. He then derives

$$\frac{A}{A_r} = \frac{\varepsilon\, c_l\, \lambda}{\varepsilon_r c_r \lambda_r} \left[1-e^{-2t/dp}\right] \qquad (23)$$

which gives an expression for the absorbance of the unknown band, A, scaled by A_r, the absorbance of the reference band. He then goes through a rather complex mathematical procedure to find t.

An easier procedure based on Equation 23 has been developed by Blackwell[16] and was used in this work. If measurements are made at two angles, a ratio can be found. This ratio is described mathematically as

$$\frac{R(\theta_1)}{R(\theta_2)} = \frac{(A/A_r)_{\theta 1}}{(A/A_r)_{\theta 2}} = \frac{1-e^{-2t/dp_1}}{1-e^{-2t/dp_2}} \qquad (24)$$

where the ratio depends on the depth, t, and the known dp values at θ_1 (dp_1) and θ_2 (dp_2). For any two angles, a curve can be calculated for the ratio $R(\theta_1)/R(\theta_2)$ as a function of t. The experimental ratio should then lie on the curve at its proper value of t. Any two angles should give the same results for a given sample as long as the critical angle is not approached too closely. It is important to note that t can be found using Equation 24 without knowing the value of ε or ε_r.

Once t has been calculated then c_1 can be calculated from Equation 23 if ε_r and c_r are known. If they are not known, then the equation

$$A_T = A(ATR) = N\varepsilon d_e c_1/2.303\ [1-e^{-2t/dp}] \qquad (25)$$

can be used to calculate c_1 if a calibration curve has been made. This was the procedure in this work. It should be noted that for calculations involving Equations 24 and 25, t is in terms of the reduced wavelength λ_1, where

$$\lambda_1 = \frac{\lambda}{n_1} \qquad (26)$$

CHAPTER II

A SUBSTITUTION REACTION ON THE SURFACE OF POLY(VINYL CHLORIDE) USING POTASSIUM CYANATE AND A CROWN ETHER PHASE TRANSFER AGENT

A. INTRODUCTION AND BACKGROUND

In 1973 Takeishi, Naito, and Okawaro[27] modified PVC powder using sodium azide and tetra-n-butyl ammonium chloride or bromide salt as a phase transfer agent to obtain the azidated PVC powder:

$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2- + NaN_3 \xrightarrow[H_2O]{[(CH_3(CH_2)_3)_4N]X} -CH_2-\underset{Cl}{CH}-CH_2-\underset{N_3}{CH}-CH_2-$$

At 80° the tetra-n-butyl ammonium cation and the associated azide anion migrated into the polymer to convert 10-11% of the chlorine sites into azide sites after 16 hr. The reaction was studied using transmission IR spectroscopy and the conversions were determined by elemental analysis. No procedure was given to minimize the likelihood of trapped salts in the polymer.

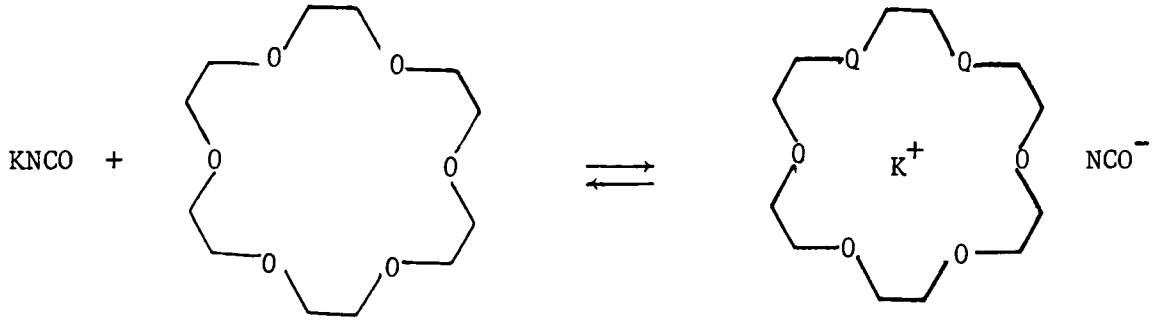
To incorporate an isocyanate group on the surface of PVC via a substitution reaction using the cyanate anion, an aprotic solvent is necessary to prevent reaction of the isocyanate group with the solvent after substitution of the cyanate anion:

$$PVC\text{-}Cl + NCO^- \rightarrow PVC\text{-}NCO + Cl^-$$

$$PVC\text{-}NCO + HX \rightarrow PVC\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}X$$

In the example above if HX is an alcohol, then a carbamate is the final product.[28,29]

To accomplish the substitution reaction potassium cyanate was chosen as the source of the nucleophile and cyclohexane as the aprotic solvent. The potassium cyanate was then solubilized into cyclohexane using 18-crown-6 ether, a phase transfer agent:[30,31,32]



This crown ether chelates the potassium cation, and allows dissolution of the salt in the nonpolar organic solvent. The cyanate anion is then unsolvated and can act as a good nucleophile.

B. RESULTS AND DISCUSSION

PVC film was reacted with potassium cyanate using 18-crown-6 ether in cyclohexane for 7 hr at 60°. After the reaction the colorless film was extracted with anhydrous diethyl ether for 18 hr then vacuum dried at 47° for 24 hr. The ATR-IR spectrum in Figure 3 reveals two carbonyl absorption bands. As shown in Figure 4, closer examination reveals an absorption band at 1725 cm^{-1} and a smaller band at 1754 cm^{-1}. Furthermore, no isocyanate absorption at 2260 cm^{-1} was detected. Further extraction with methanol for 18 hr, then vacuum drying at 47° for 24 hr, did not reduce the carbonyl peak's intensity. The appearance of the transmission spectrum in Figure 5 shows that the reaction occurred predominately on the film's surface. No weight

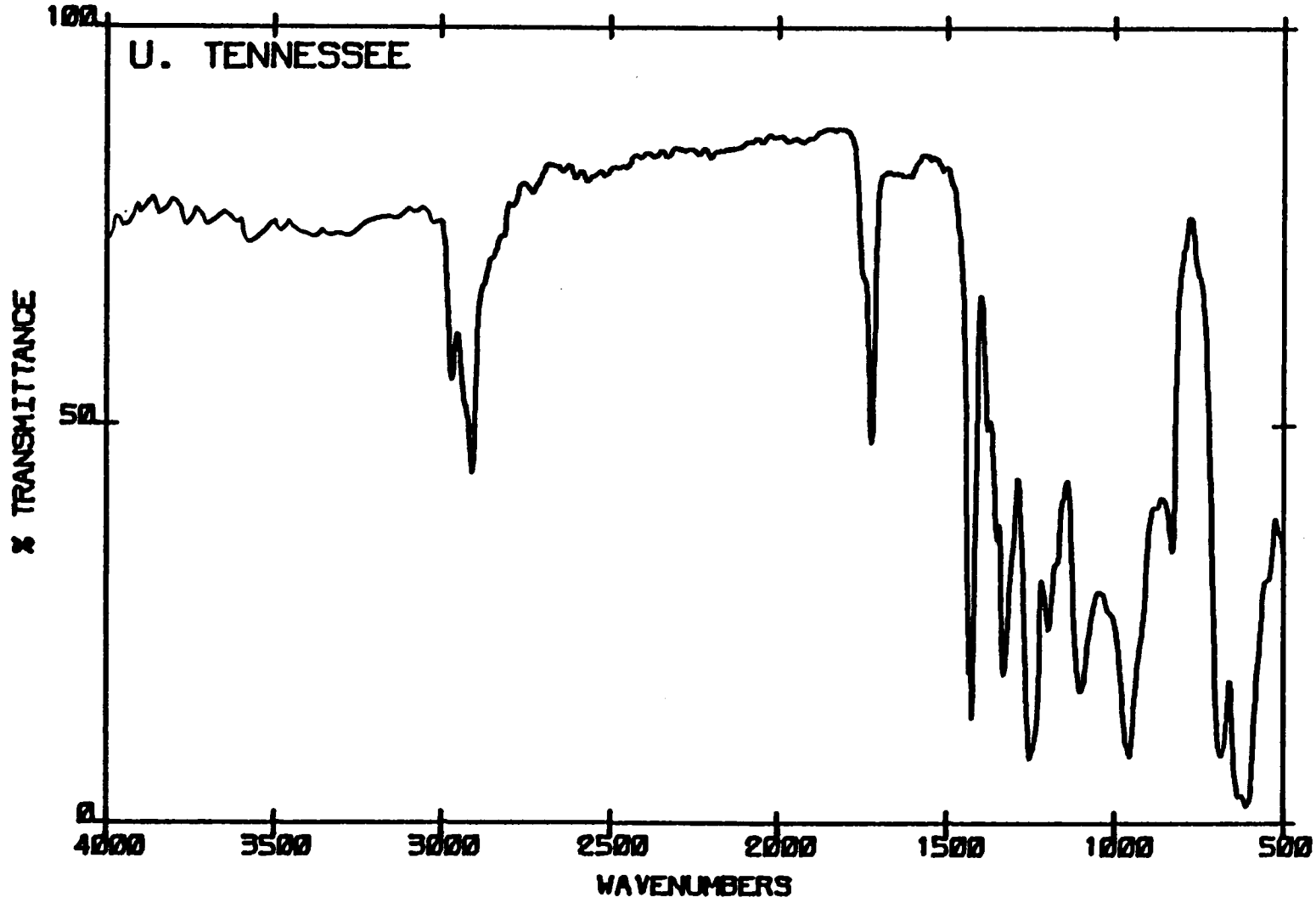


Figure 3. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions: 18-crown-6 ether, 0.146M; KNCO, saturated; solvent, cyclohexane; reaction temperature, 60°; reaction time, 7 hr.)

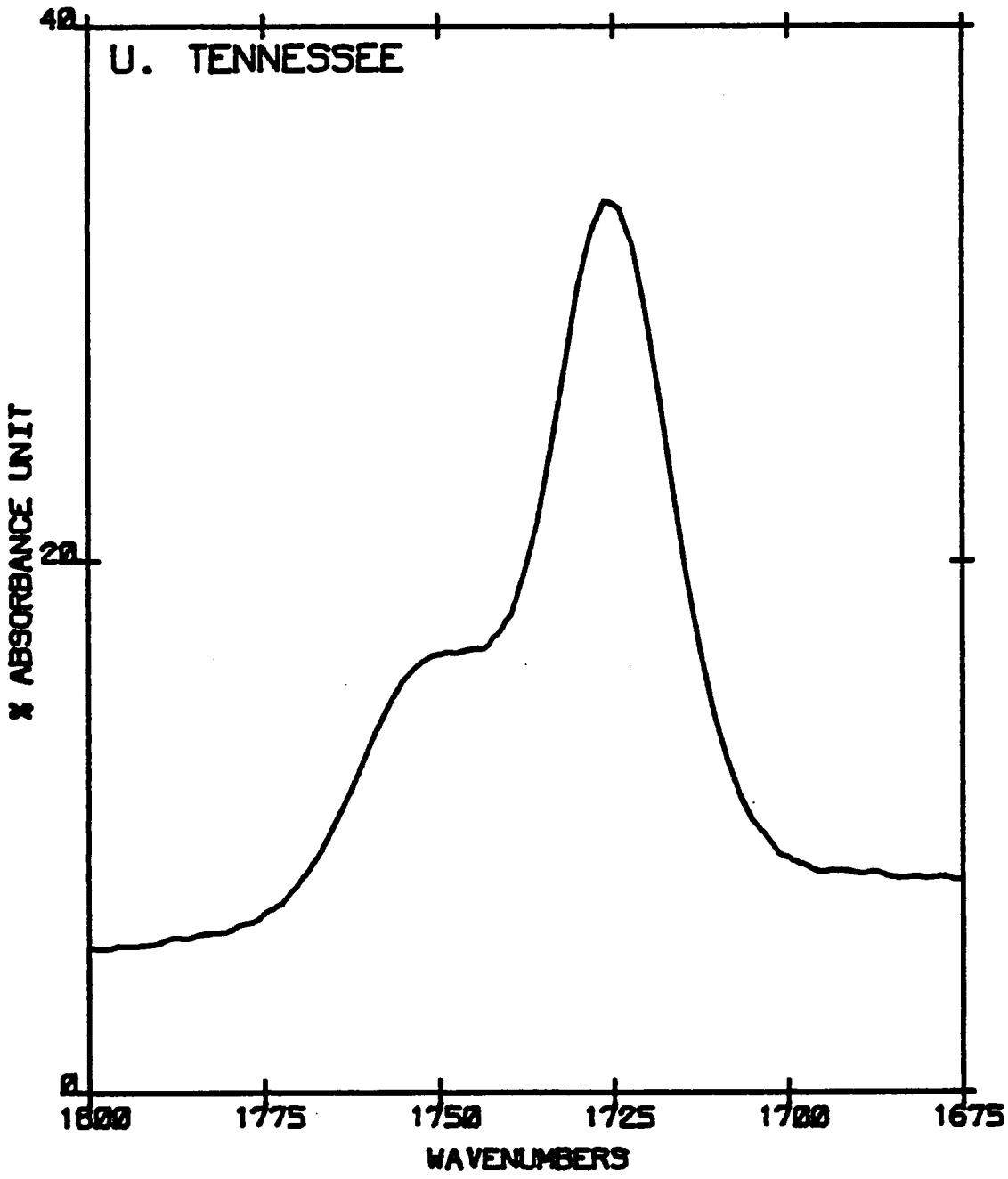


Figure 4. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Closer examination of part of spectrum shown in Figure 3.)

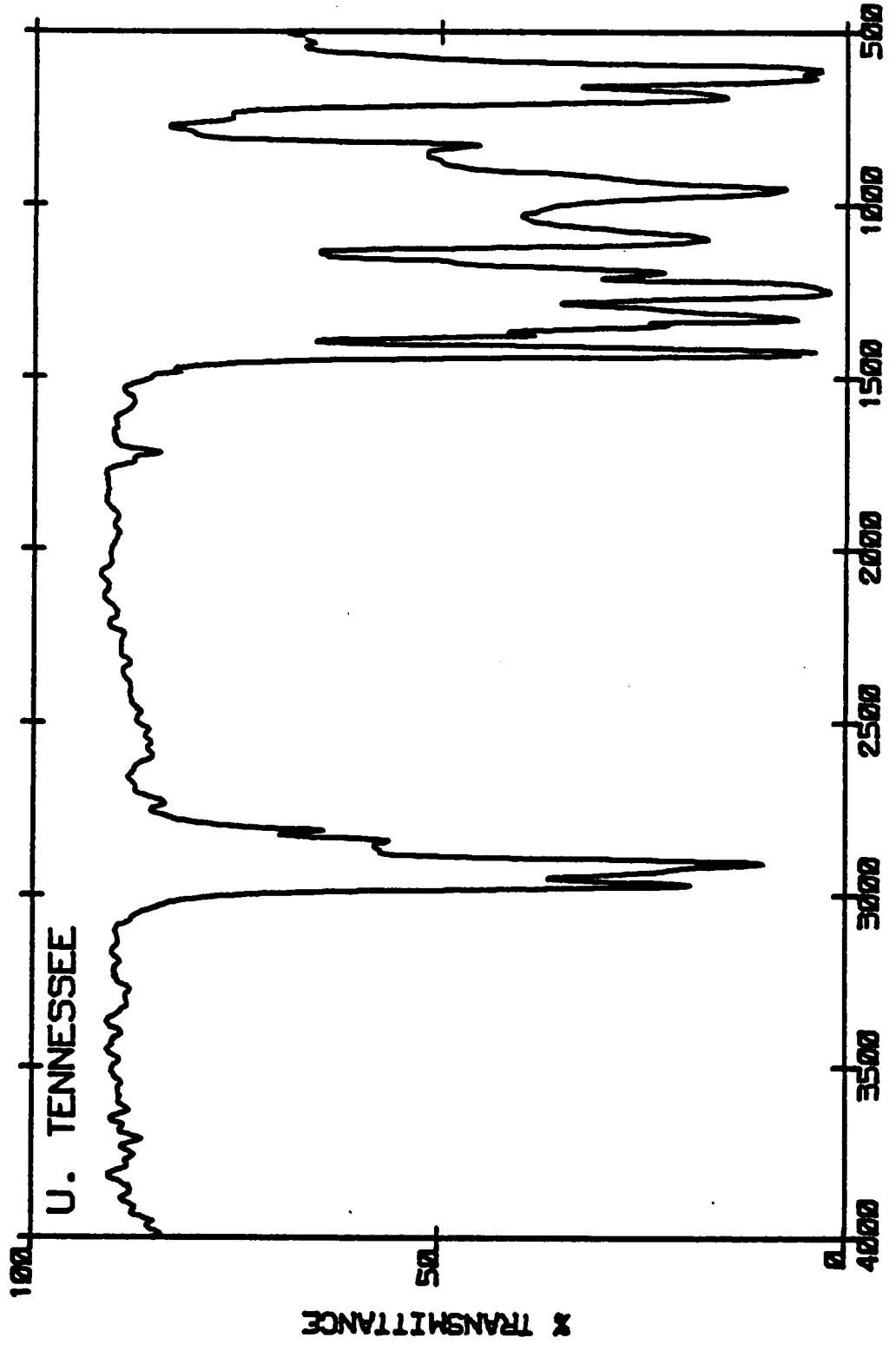
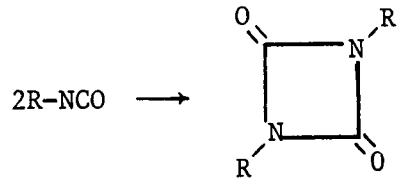


Figure 5. Transmission IR spectrum of modified PVC film taken in vacuum. (Same film as used for spectra in Figures 3 and 4.)

change (± .0003g) was detected after the reaction, and the depth of reaction was determined by depth analysis, using internal reflection spectroscopy, to be approximately 1 μ.

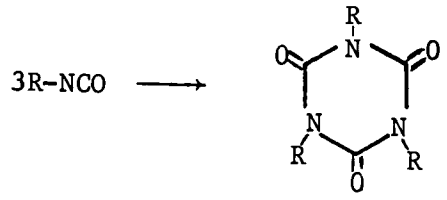
To determine if the absorption bands were from trapped salts, the films were dissolved in tetrahydrofuran, precipitated in methanol, then vacuum dried. A new film was then cast from tetrahydrofuran, extracted with methanol under argon for 18 hr, then vacuum dried at 47° for 24 hr. This procedure resulted in a pink opaque film; however, the transmission infrared spectrum again revealed the same two carbonyl absorption bands.

At least three possible structures can rationalize the carbonyl peaks. The isocyanate group may dimerize to form a 1,3-disubstituted uretinedione:[17,18,33]



This reaction is known if R contains a phenyl group attached directly to the nitrogen atom, but is unknown if R is an alkyl group.[18]

Another possibility is the formation of a 1,3,5-trisubstituted isocyanurate:[28,34]



In the above reaction R can be an aromatic or alkyl group. This

structure is unlikely for two reasons: first, three isocyanate groups would have to be properly oriented to form a 1,3,5-trisubstituted isocyanurate compound and secondly, the infrared absorption of isocyanurate carbonyls is normally from 1700 cm^{-1} to 1680 cm^{-1}.[35]

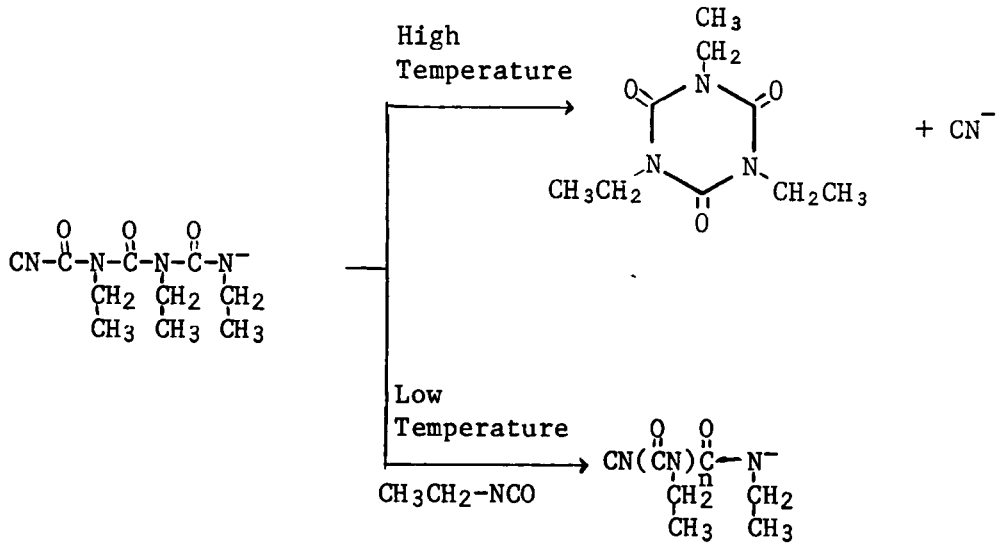
The most likely structure is a nylon-1 type structure. In 1960, Shashoua, Sweeney, and Tietz[36] reported the polymerization of alkyl isocyanates to nylon-1 structures using sodium cyanide in aprotic solvent mixtures. The infrared spectra of their nylon-1 showed a carbonyl absorption at 1709 cm^{-1} and a C-N stretch from 1389 cm^{-1} to 1282 cm^{-1}. They suggested that the organic isocyanates polymerized anionically to form the nylon-1 structures. For example, in the polymerization of ethyl isocyanate, the initiation step can be considered as an attack of the cyanide anion on the isocyanate group:

$$CH_3CH_2\text{-}NCO \xrightarrow{CN^-} CH_3CH_2\bar{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CN$$

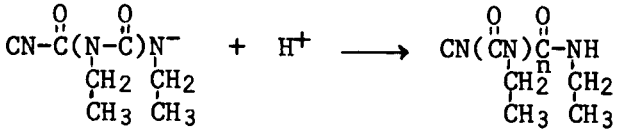
The propagation step is believed to proceed through the isocyanate group to form the trimer product or the linear polymer:

$$CN\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{CH_3}{|}}{\underset{|}{N^-}}\text{-}\underset{\underset{CH_3}{|}}{CH_2} \;+\; \underset{\underset{CH_3}{|}}{\underset{|}{NCO}}\text{-}\underset{\underset{CH_3}{|}}{CH_2} \;\rightarrow\; CN\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{CH_3}{|}}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{CH_3}{|}}{\underset{|}{N^-}}\text{-}\underset{\underset{CH_3}{|}}{CH_2}$$

$$CN\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{CH_3}{|}}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{CH_3}{|}}{\underset{|}{N^-}}\text{-}\underset{\underset{CH_3}{|}}{CH_2} \;+\; \underset{\underset{CH_3}{|}}{\underset{|}{NCO}}\text{-}\underset{\underset{CH_3}{|}}{CH_2} \;\rightarrow\; CN\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{CH_3}{|}}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{CH_3}{|}}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{CH_3}{|}}{\underset{|}{N^-}}\text{-}\underset{\underset{CH_3}{|}}{CH_2}$$



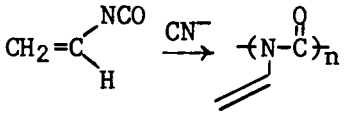
In general, high temperature favors formation of the trimer and low temperature favors formation of the linear polymer. The termination step in the polymerization occurs by reaction of the anionic nitrogen with a proton from the reaction medium:



The proton comes either from small amounts of water present in the reaction medium or from the addition of methanol.

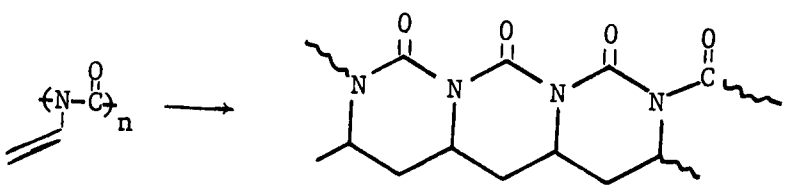
Natta, Petro, and Cambin[37] reported the polymerization of phenyl isocyanate and n-butyl isocyanate. The poly(phenyl isocyanate) gave a carbonyl band at about 1750 cm^{-1} and a band at 1270 cm^{-1} which corresponded to a C-N stretch. An unidentified band appeared at 1165 cm^{-1}. Poly(n-butyl isocyanate) gave a carbonyl band at 1698 cm^{-1} and a band at 1270 cm^{-1} which corresponded to a disubstituted amide. An unidentified band appeared at 1190 cm^{-1}.

In 1964, Overberger, Oaki, and Mukamal[38] reported the polymerization of vinyl isocyanate through the isocyanate group using sodium cyanide as the catalyst:



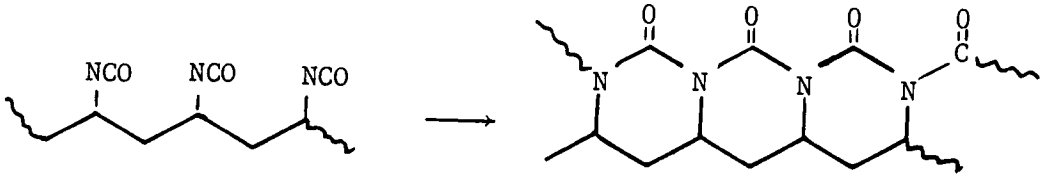
A carbonyl absorption at 1735 cm^{-1} was reported for this polymer. Absorptions at 1332 cm^{-1} and 1232 cm^{-1} (or from 1332 cm^{-1} to 1232 cm^{-1}, it is not exactly clear) were used as an indication of disubstituted amide structure.

If the above poly(vinyl isocyanate) is polymerized through its double bond using azobisisobutyronitrile and ultraviolet light in dimethyl acetamide a carbonyl absorption at 1690 cm^{-1} appears and a ladder structure is proposed:



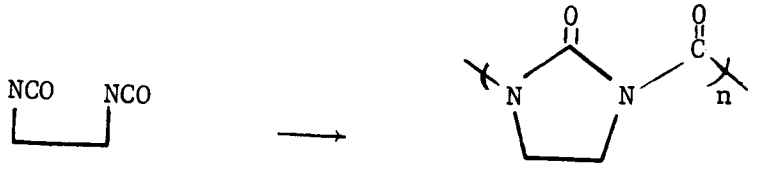
The absorption at 1690 cm^{-1} is surprising since poly(alkyl isocyanates) generally have absorptions at about 1709 cm^{-1} and when poly(vinyl isocyanate) is polymerized first through its carbon carbon double bond then through the isocyanate group using gamma radiation a

carbonyl absorption at 1730 cm^{-1} appears. A similar ladder structure is proposed:

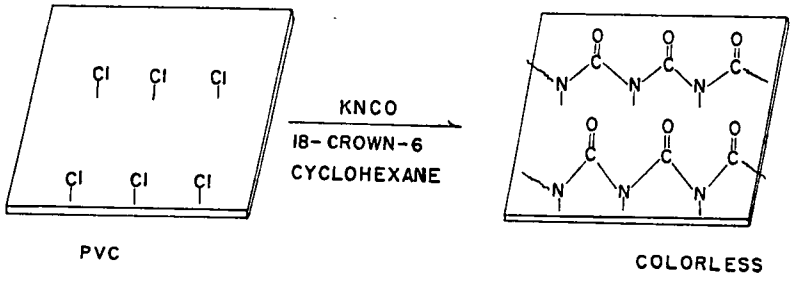


They did not interpret the differences in the carbonyl absorptions.

Strained nylon-1 structures are known to give higher carbonyl absorptions. King[39] polymerized ethylene diisocyanate and observed carbonyl absorptions at 1785 cm^{-1} and 1695 cm^{-1}:



The experimental results, along with the literature cited, are consistent with the presence of a nylon-1 type structure on the surface of PVC:



The lower carbonyl absorption at 1725 cm^{-1} is ascribed to the nylon-1 type structure from an intramolecular reaction. The higher carbonyl absorption at 1754 cm^{-1} suggests an absorption of a carbonyl under strain.

The weak to medium absorptions between 1350 cm^{-1} and 1200 cm^{-1} have been attributed to the C-N stretch in secondary amides and

are referred to as amide III absorptions.[40] The amide III absorption is not observed in Figure 3 (p 17), the ATR-IR of the modified PVC; however, if the ATR-IR spectrum of PVC is substracted from the modified polymer, the spectrum in Figure 6 is generated.[41,42] As shown in Figure 6, close examination of the difference spectrum shows a weak absorption at 1250 cm^{-1} and a doublet at 1125 cm and 1188 cm^{-1}. The absorption at 1250 cm^{-1} suggests an amide III band. Absorption bands at 1165 and 1190 cm^{-1} are shown by Natta _et al._[37] for poly(phenyl isocyanate) and poly(_n_-butyl isocyanate) respectively but are not identified.

Mechanistically, the suggested structure can be explained. It is known that the cyanate anion can catalyze alkyl isocyanate trimerization to the 1,3,5-trisubstituted isocyanurate.[28] The isocyanate anion attacks the carbonyl in the cyanate group. This results in the breaking of the nitrogen-carbon π bond in the isocyanate group and the making of σ-bonds to form the 1,3,5-trisubstituted isocyanurate. The mechanism is analogous to the formation of the cyanurate using the cyanide anion as the catalyst as previously shown.

Once on the surface of PVC, the isocyanate group motion is restricted. In other words, the mechanistic pathway to the isocyanurate is no longer possible; therefore a propagation reaction results in N-substituted nylon-1 type structures:

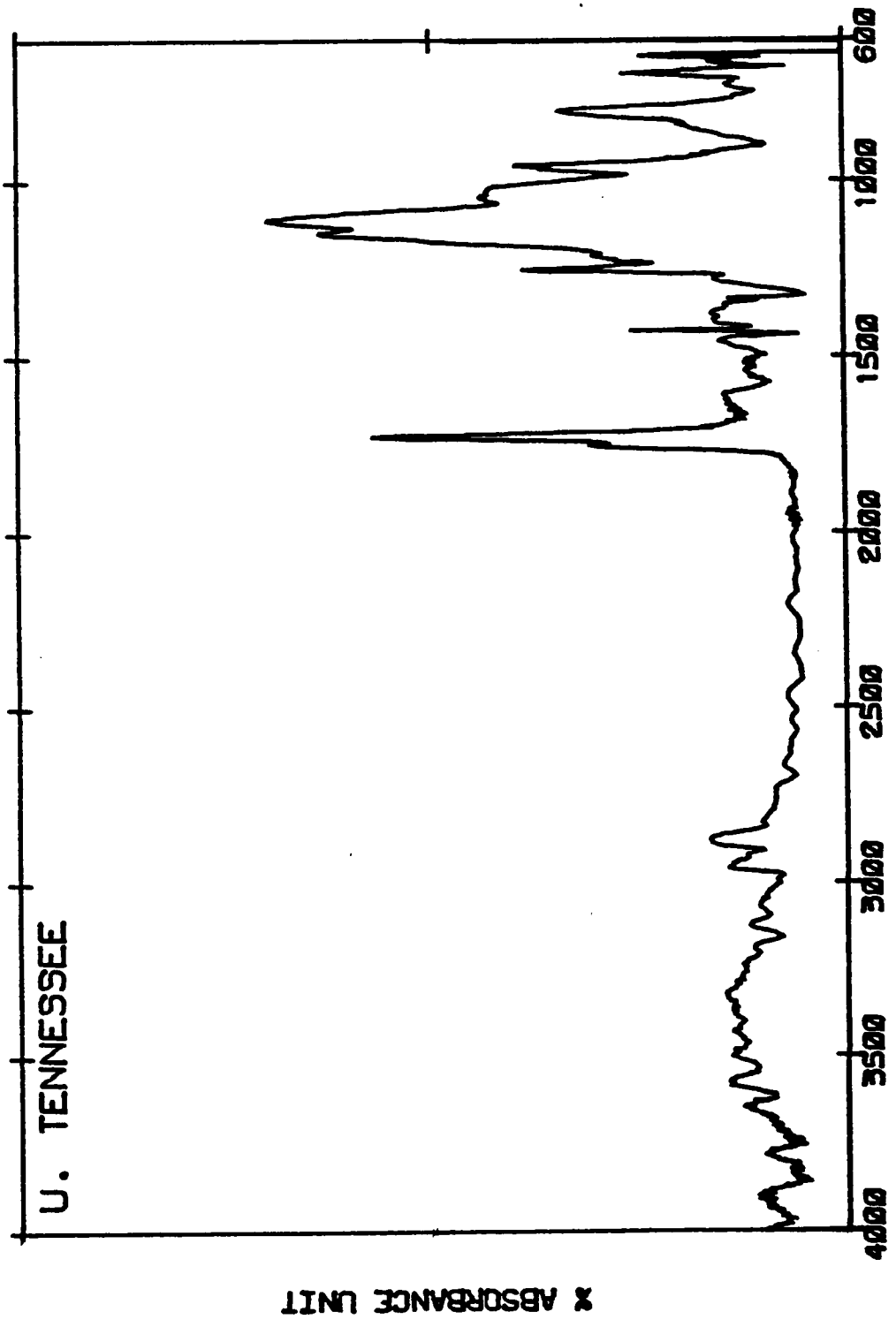
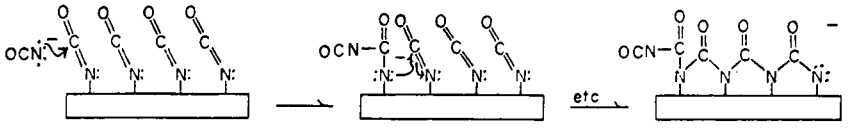


Figure 6. ATR-IR difference spectrum of modified PVC minus PVC.



The infrared absorptions at 1725 cm^{-1} and 1754 cm^{-1} suggest propagation along the main chain and from one chain to another resulting in cross-linking. The absorption at 1754 cm^{-1} supports a strained carbonyl resulting from the intermolecular reaction.

Thermodynamically, the polymerization of organic isocyanates can be understood by considering the free energy equation:

$$\Delta G = \Delta H - T\Delta S$$

where ΔH is the enthalpy change for polymerization and ΔS is the entropy change. When polymerization occurs, ΔG is less than zero. For organic isocyanates, a π bond is broken and a σ bond is formed resulting in a negative ΔH. Since the ΔH is negative, ΔG will be negative provided $\Delta H < T\Delta S$. For polymerization of small molecules, the ΔS is normally very negative since the monomer units are being locked in a growing polymer chain resulting in a more ordered state.

For a constant temperature, the free energy equation predicts an increase in ΔS. Polymerizations of isocyanates are normally run at low temperatures to minimize the $T\Delta S$ term. Reactions run at the higher temperature results in the formation of the isocyanurate; however, at least one instance of polymerizing an organic isocyanate above room temperature has been reported by Ugi and Neumann[43] who polymerized phenyl isocyanate in dimethylformamide at 50° using lithium azide as the initiator. For the modified PVC the entropy of polymerization for

an isocyanate group attached to a formed polymer backbone is less negative than the entropy of polymerization for a growing poly(organic isocyanate) in solution since the polymers bound isocyanate group should be in a less ordered state. This less ordered state minimizes the $T\Delta S$ term resulting in a $\Delta G<0$; thus, the formation of the nylon-1 is thermodynamically allowed at a higher temperature.

The above arguments support nylon-1 type structures; however, it must be noted that, in spite of the extensive purifications, etc., there is a remote possibility that the carbonyl bonds are the result of some unknown trapped salt or salts. Furthermore, it should be noted that whether nylon-1 type structures or trapped salts are present, the following discussion on the depth analysis of the absorbing species will remain valid.

To determine the depth of the absorbing species by the two angle method, 45 and 51.2 degree angles were used.[16,26] Both non absolute absorbance (peak height) and absolute absorbance (peak area) were used for comparison. The absorbance due to the methylene group in the crystalline region of the polymer at 1424 cm^{-1} was chosen as the reference species, with the base line drawn from 1480 cm^{-1} to 1400 cm^{-1}. The absorbing species at 1725 cm^{-1} was used for the depth analysis with a base line drawn from 1800 cm^{-1} to 1550 cm^{-1}. For the absolute measurement, the peak area was integrated from 1800 cm^{-1} to 1700 cm^{-1}.

Using Equation 24 from Chapter 1, a curve (shown in Figure 7) can be plotted for the ratio R(45)/R(51.2) as a function of t, the depth of reaction of the absorbing species. The depth of reaction is in terms of the reduced wavelength, λ_1, which is 2.415×10^{-4} cm at 1725

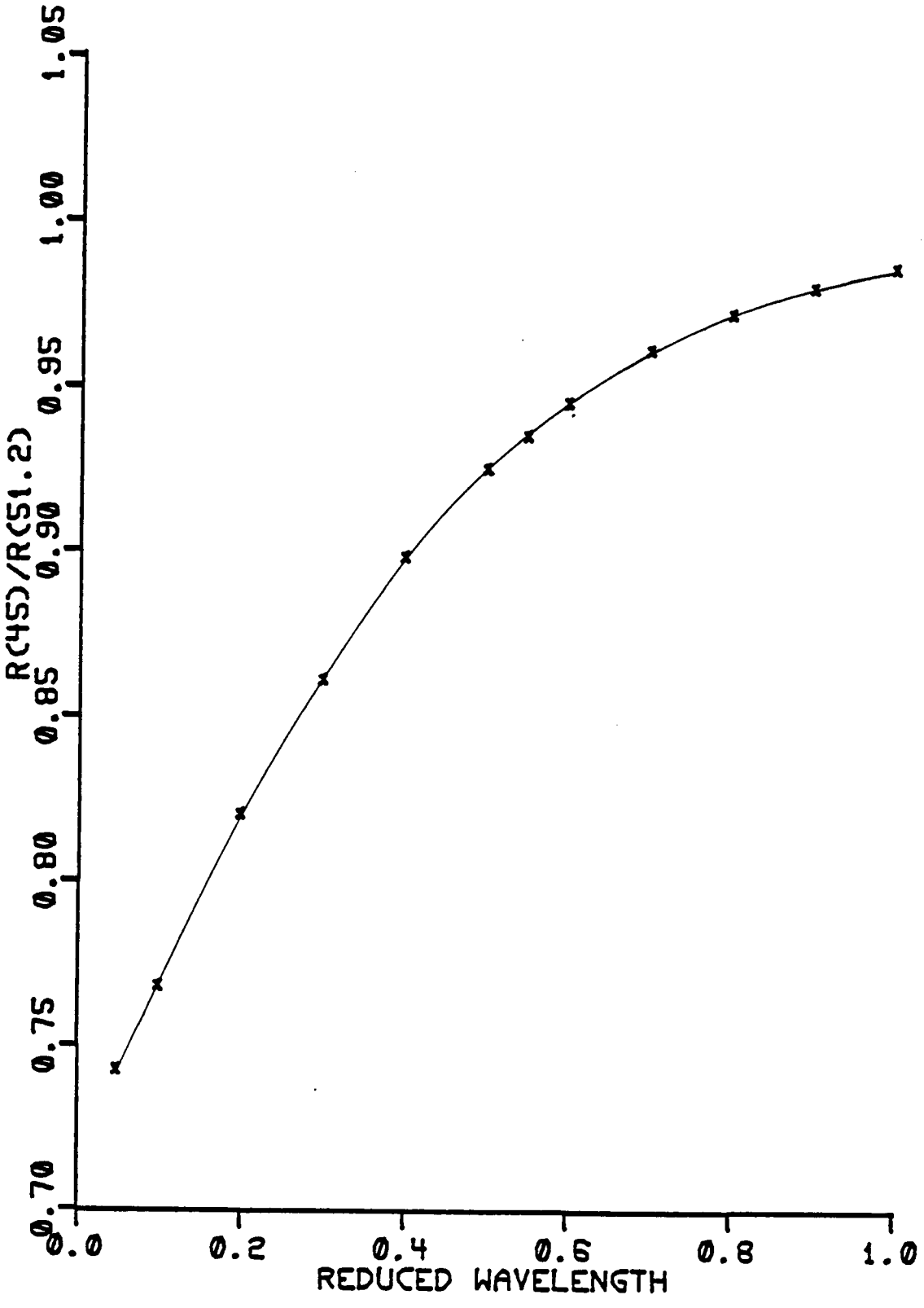


Figure 7. A two angle depth analysis curve for an absorbing species at 1725 cm^{-1}. (Plotted using Equation 24.)

cm^{-1}. As an example of how the curve is used, consider the experimentally determined R(45)/R(51.2) value of .906 (see Table I). Figure 7 gives $t = .41\lambda_1$ or a depth of reaction of 9.9×10^{-5}cm for the absorbing species at 1725 cm^{-1}.

As shown in Table I the range for R(45)/R(51.2) is large for the non absolute measurements at a 90% confidence level for the modified film; thus, from Figure 7 one can only say the depth of reaction is greater than $.2\lambda_1$. The absolute measurement gives a smaller range for the depth, $.26\lambda < t < .73\lambda_1$, at a 90% confidence level. This study found that these ranges were a result of mirror alignment which resulted in small changes in $(A/A_r)_{\theta 1}$ and $(A/A_r)_{\theta 2}$.

To check these results a new method was developed which involves measurements at only one angle. As shown by Equation 25 in Chapter I

$$A(ATR) = N\varepsilon c_1 d_e/2.303\ [1-e^{-2t/dp}]$$

Now c_1 is the average concentration in a step profile; for a light beam being transmitted through the film, c_1 can be expressed in terms of Beer's Law as

$$c_1 = \frac{A(TRN)}{\varepsilon\ t} \tag{27}$$

Substitution of Equation 27 into Equation 25 and rearrangement gives

$$\frac{A(ATR)}{A(TRN)} = \frac{Nd_e}{2.303\ t}\ [1-e^{-2t/dp}] \tag{28}$$

where dp is 1.162×10^{-4} cm, d_e is calculated from the results in

Chapter III to be 2.36×10^{-4} cm at 1725 cm^{-1}, and N is 20. Substitution of these values into Equation 28 gives

$$\frac{A(ATR)}{A(TRN)} = \frac{2.05 \times 10^{-3}}{t} \left[1-e^{-1.721 \times 10^{4} t}\right] \qquad (29)$$

This equation is plotted in Figure 8. Note that calculation of the depth, t, does not require any knowledge of ε.

For the one angle method the curve in Figure 8 shows that the accuracy of the depth measurement increases compared to the two angle method shown in Figure 7 at depths of approximately $1.0\lambda_1$. In the two angle method for depths greater than $0.5\lambda_1$, a small change in the ratio R(45)/R(51.2) results in a large depth change. In other words, a small error in the measurement of R(45)/R(51.2) results in a correspondingly large error in the depth measurement. For the one angle measurement, as the depth of reaction or the concentration of absorbing species increases, the probability increase that useful signal above the background noise can be obtained. Practically, for the absorbing species studied, meaningful signals were obtained for depths as low as about $0.4\lambda_1$ provided fringes in the spectrum could be avoided.

The one angle method depends upon two important factors: first, good film contact must be assured; however, a reference band can be used to normalize the absorbing species if a measure of the film contact has been made. For example, the d_e in Chapter III was determined from a physical blend of a carbamate standard and PVC film, total film area 16.0 cm. The methylene group at 1424 cm^{-1} was used as a measure of film contact and in this case was found to have an

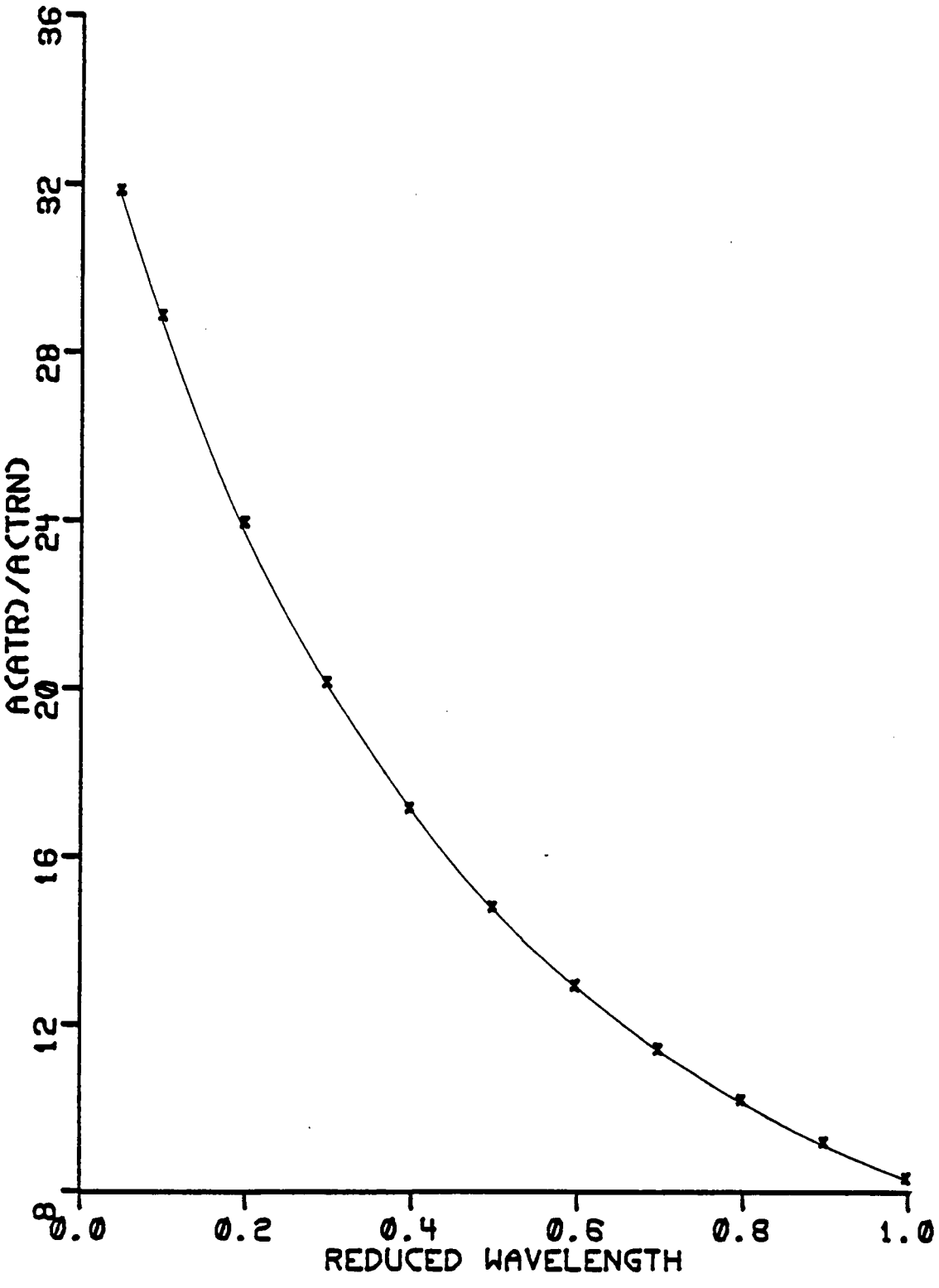


Figure 8. A one angle depth analysis curve for an absorbing species at 1725 cm^{-1}.

TABLE I

DEPTH ANALYSIS OF ABSORBING SPECIES AT 1725 cm^{-1} ON THE SURFACE OF POLY(VINYL CHLORIDE)

Method	Non Absolute Absorbance	Absolute Absorbance	Depth Using Non Absolute Absorbance	Depth Using Absolute Absorbance
$\frac{R(45)}{R(51.2)}$	0.959 ± 0.095	0.906 ± 0.059	$0.74\lambda_1$	$0.41\lambda_1$
$\frac{A(ATR)}{A(TRN)}$	17.4 ± 2.7	16.3 ± 2.9	$0.40\lambda_1$	$0.44\lambda_1$
$\frac{*A(ATR)}{A(TRN)}$	16.3	15.0	$0.44\lambda_1$	$0.49\lambda_1$

a. All $\pm$ values are at a 90% confidence level.

b. $\lambda_1 = 2.415 \times 10^{-4}$ cm, 24150 Å.

c. *The crystalline methylene band at 1424 cm^{-1} was 0.856 absorbance.

absorbance of about 0.86. Absorption band for a film in poor contact with the crystal allows the proper value of d_e to be used. Care must be taken, however, since a large change in crystallinity would give erroneous absorbance values for the absorbing species. Secondly, for a signal to be detected above the background noise in a transmission experiment with a small path length, an absorbing species with a large molar absorptivity is desirable as well as a reliable instrument. This study uses the signal averaging available in Fourier Transform Infrared Spectrometry (FTIR). Figure 9 shows the transmission absorption band at 1725 cm^{-1} (1000 scans) after the reaction on the PVC film. Since the light beam is penetrating two surfaces, the actual absorbance used in Equation 29 is 1/2 of what is observed in Figure 9. If necessary, methods for eliminating fringes are available.[44,45] The result in Table I (p 33) shows that this method agrees well with the two angle measurements. Furthermore, if a reaction occurs in which the reference band is affected, e.g., elimination in PVC, the one angle method still allows an approximate depth of reaction $\pm$ $0.1\lambda_1$ to be determined.

In conclusion, attempted substitution of cyanate for chloride did not give the expected isocyanate group. It is proposed that the cyanate anion, acting as the initiator, resulted in the polymerization of newly incorporated isocyanate groups on the surface of the polymer to form nylon-1 type surface structures. The depth of reaction can be determined with internal reflection spectroscopy using a two angle measurement or by a combination of internal reflection and transmission spectroscopy.

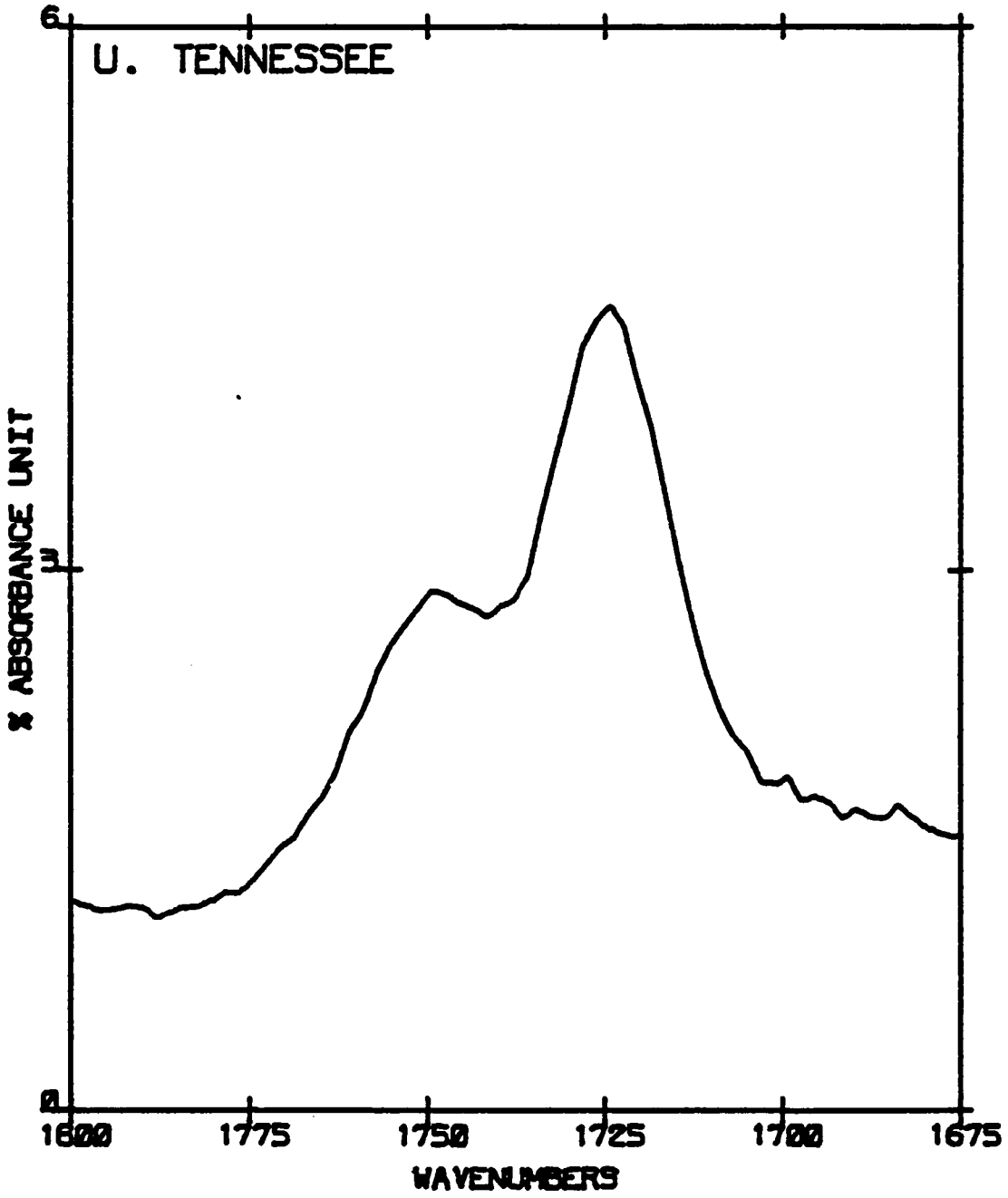


Figure 9. Transmission IR spectrum of modified PVC film taken in vacuum. (Closer examination of part of spectrum shown in Figure 3.)

C. EXPERIMENTAL

Film preparation: The literature suggests several ways of casting and drying PVC films. The procedures are varied and often vague. Ostensson and Flodin[46] dried PVC powder containing tetrahydrofuran and ethanol at an elevated temperature for 7 d. Marechal[47] washed films cast from tetrahydrofuran with methanol, then vacuum dried them. Gibb and MacCallum[48] cast their films from tetrahydrofuran, vacuum dried them for 7 d at 35°, soaked them in methanol for 24 hr then repeated their drying procedure. According to Rabek, Shur and Ranby,[49] the amount of tetrahydrofuran in freshly cast PVC film is 6-8%, and can be reduced to 3-4% by prolonged heating at 40° or by soaking the films in methanol. They reportedly removed all the tetrahydrofuran from their films by heating their samples at 80° for 6 hr, with high vacuum accelerating the process.

This study did not yield Rabek's result. Figure 10 shows the percent weight loss of tetrahydrofuran from a 50 μ thick film of PVC under vacuum at 80° after predrying the film at 47° for 90 hr. After 6 hr at 80° there is a break in the rate of tetrahydrofuran loss. The transmission spectrum (Figure 11) shows an absorption band at 1065 cm^{-1} after 12 hr at 80° under vacuum which indicates that tetrahydrofuran remains.

To cast and dry the PVC films in this study the following procedure was developed. A 5% weight solution of PVC in tetrahydrofuran was prepared under argon. The films were cast in an argon atmosphere and dried for 24 hr under a stream of argon. The films were then vacuum dried at 47° for 90 hr and at 80° for 6 hr and extracted with

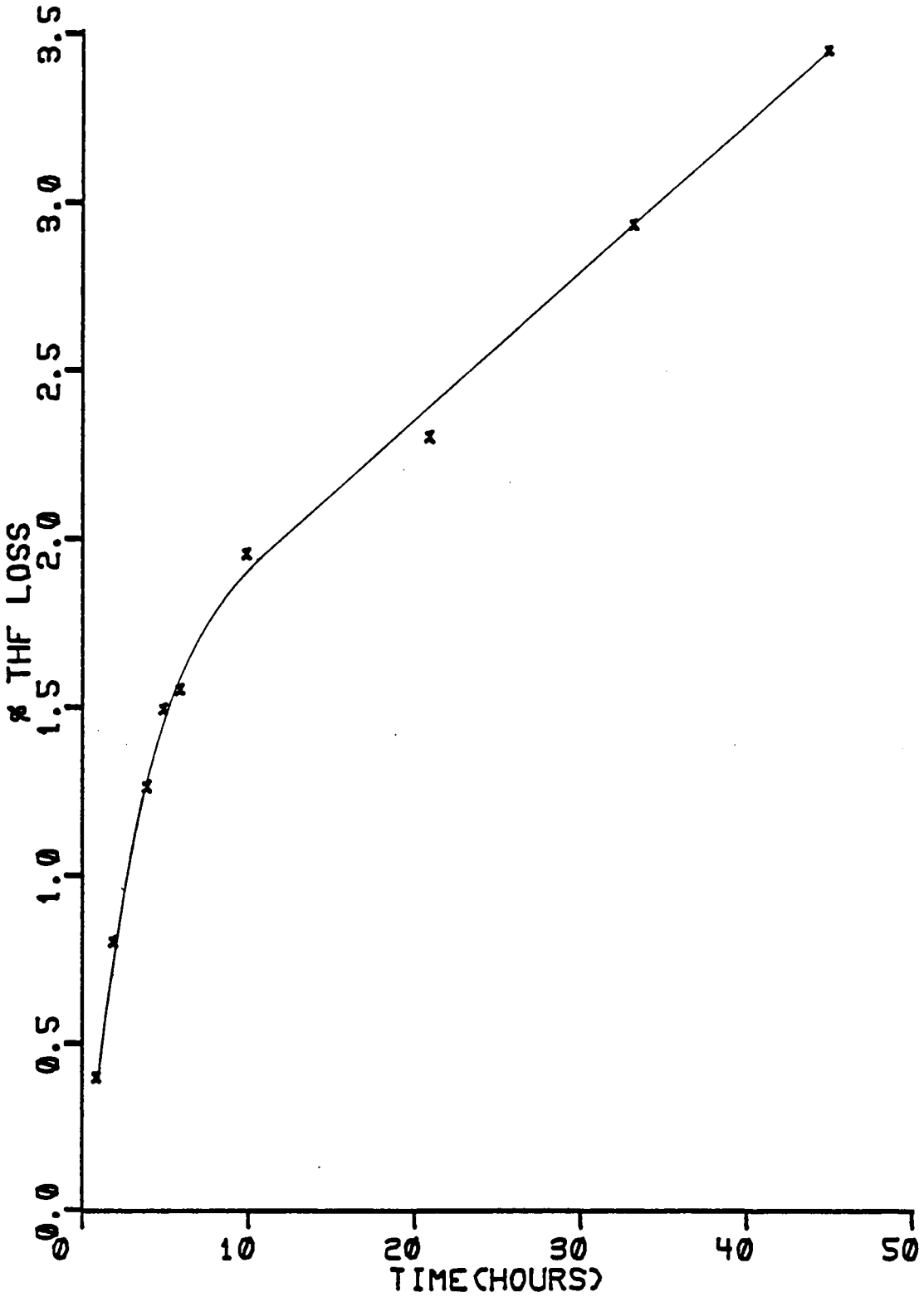


Figure 10. Percent weight loss of tetrahydrofuran from PVC film under vacuum at 80°, after predrying the 50μ thick film under vacuum at 47° for 90 hr.

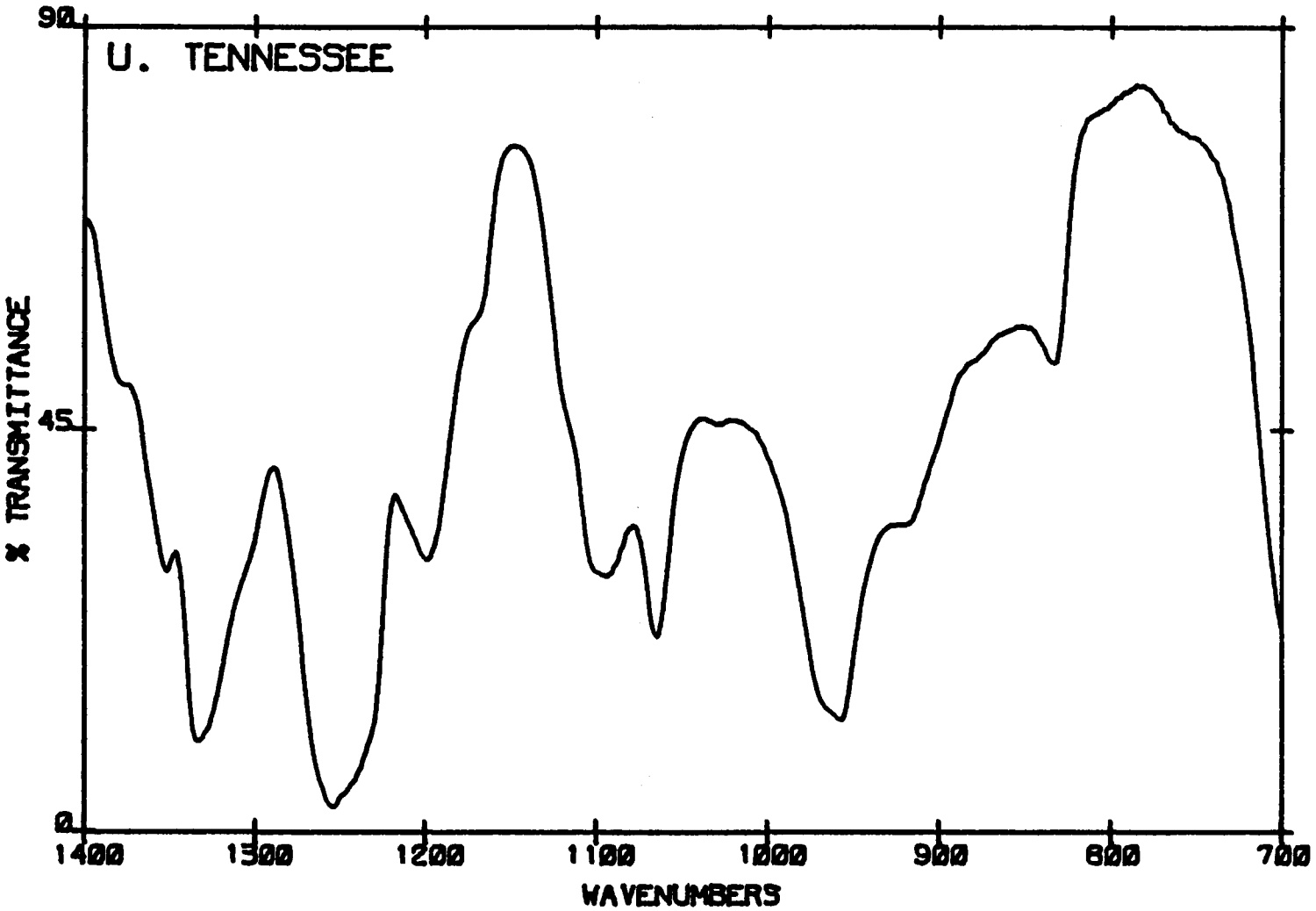


Figure 11. Transmission IR spectrum of PVC film. (Drying conditions: vacuum dried at 47° for 90 hr, then at 80° for 12 hr.)

methanol for 18 hr using a soxhlet extractor at 59-61°. The films were then vacuum dried at 47° for 24 hr and 80° for 6 hr. As shown in Figure 12, the transmission infrared absorption bands of these colorless films agreed with the literature values.[50,51] To check the above procedure a film was further extracted with methanol for 85 hr and vacuum dried to a constant weight (±0.00003 g). This colorless film had a weight loss of <0.4%.

Reaction: A sample of PVC film was cut to size (4.0 cm x 4.3 cm x 50 μ), weighed (typically 0.128 g), placed on a glass screen, and held in place by a glass weight. To a 250 ml beaker equipped with a magnetic stirrer, large stopper, and gas inlet and outlet was added 0.297 g of potassium cyanate, 0.619 g of 18-crown-6 ether and 35 ml of dried cyclohexane. The mixture was stirred for 30 min, and the magnetic stirrer removed. The gas outlet was attached to an oil bubbler and the flask flushed with dried argon gas for 15 min. The flask was then lowered into an oil bath, 60° ± 1, and the reaction mixture brought up to 60°. The film was then lowered with a glass dipper into the reaction medium. After the 7 hr reaction time, the film was removed and washed for 15 min in cyclohexane, then in diethyl ether. After these washings the film was extracted with diethyl ether from a bed of calcium hydride in a soxhlet extractor under an argon atmosphere. The film was then vacuum dried at 47° for 24 hr. The colorless film had infrared carbonyl bands at 1754 cm^{-1} and 1725 cm^{-1}. Further extraction with methanol, followed by soxhlet extraction under an argon atmosphere, followed by vacuum drying at 47° for 24 hr, produced a colorless film, still with carbonyl bands at 1754 cm^{-1} and 1725 cm^{-1}.

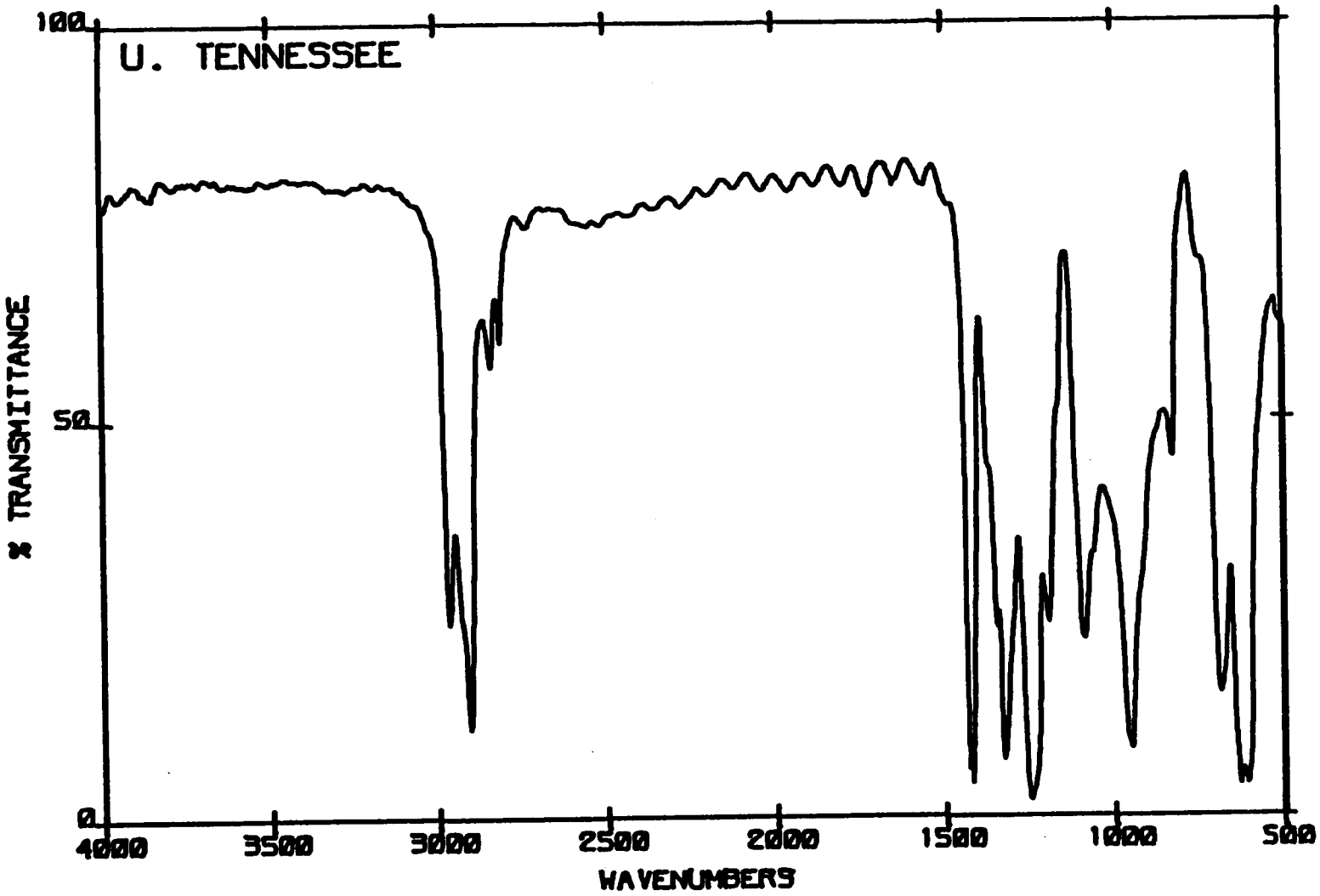


Figure 12. Transmission IR spectrum of PVC film. (Drying conditions: vacuum dried at 47° for 90 hr, at 80° for 6 hr, extracted with methanol for 18 hr, then vacuum dried at 47° for 24 hr, and at 80° for 6 hr, respectively. Note fringes between 2850 cm^{-1} and 1500 cm^{-1}.)

CHAPTER III

A SUBSTITUTION REACTION ON THE SURFACE OF POLY(VINYL CHLORIDE) USING POTASSIUM CYANATE IN THE PRESENCE OF ETHYLENE GLYCOL

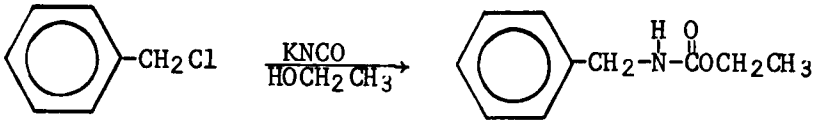
A. INTRODUCTION AND BACKGROUND

This Chapter will show that chlorines in PVC can be displaced by the cyanate anion in the presence of ethylene glycol to form the surface modified polymer, 2-hydroxyethyl N-PVC carbamate. Overall, this is a substitution reaction immediately followed by an addition reaction.

$$\text{PVC-Cl} \xrightarrow{\text{NCO}^-} \text{PVC-NCO}$$

$$\text{PVC-NCO} \xrightarrow{\text{HOCH}_2\text{CH}_2\text{OH}} \text{PVC-N(H)-C(=O)-OCH}_2\text{CH}_2\text{OH}$$

Argabright, Rider, and Sieck[28] have shown that in the presence of ethanol, alkyl chlorides react with potassium cyanate in a variety of aprotic solvents to form the ethyl N-substitutedcarbamates. For example, benzyl chloride was reacted with potassium cyanate in the presence of ethanol using dimethyl formamide to form the ethyl N-benzylcarbamate in 70% yield:



For PVC surface modification dimethyl sulfoxide was chosen as the aprotic solvent because the rate enhancement for substitution reactions using potassium cyanate in the presence of alcohols is high, and the

solubility of potassium cyanate is greater in dimethyl sulfoxide than in dimethyl formamide or N-methyl pyrrolidone. Ethylene glycol was chosen as the alcohol so that the product would have a hydrophilic surface and a reactive hydroxy group on its surface. Furthermore, the high boiling point of ethylene glycol, 198° at 760 mm, allows a wide temperature range for the reaction. Qualitatively the degree of swelling of the PVC films was controlled by varying the amounts of ethylene glycol in dimethyl sulfoxide. For a 90% v:v DMSO-EG solvent system noticeable amounts of polymer dissolved under the reaction conditions described below. In this work, the volume percent will always refer to the first solvent, e.g., DMSO. At 80% v:v DMSO-EG, there was noticeable swelling of the PVC films. At 50% v:v DMSO-EG, no swelling of the PVC films was observed.

B. RESULTS AND DISCUSSION

The reaction of PVC with potassium cyanate was done using 80% v:v DMSO-EG solution as the solvent system. At 130° the reaction proceeded rapidly producing a yellow film and an orange-red color in the reaction medium within 3 min. After 15 min in the reaction medium, the ATR-IR spectrum of the film revealed a carbonyl band and a N-H deformation (see Figure 13). As shown in Figure 14 these bands are at 1719 cm^{-1} and 1508 mm^{-1} respectively. Subtraction of the ATR-IR spectrum of PVC from that of the reacted film gives the difference spectrum in Figure 15. This spectrum shows an absorption at 1238 cm^{-1} which is indicative of a C-N stretch coupled to a N-H deformation.

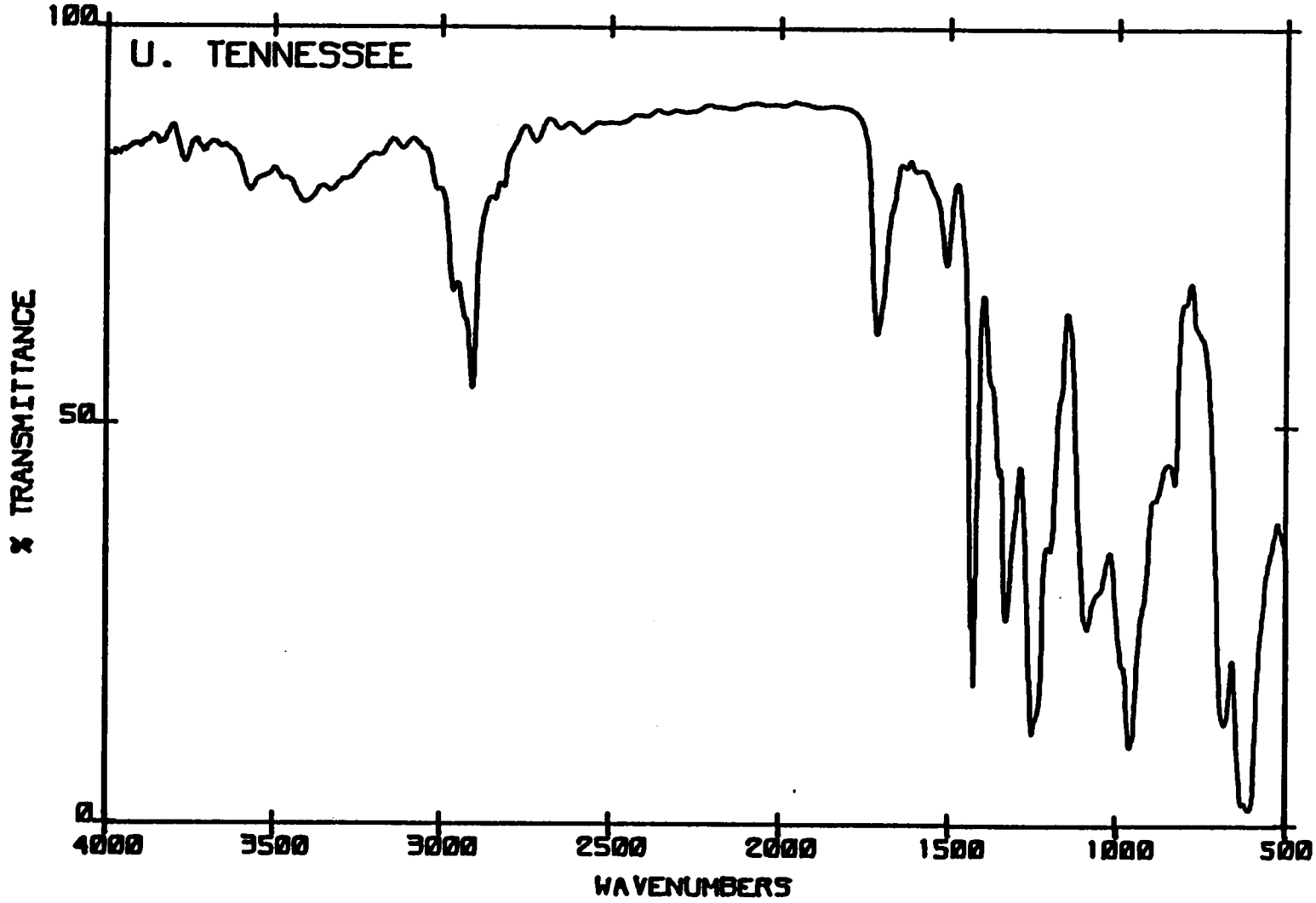


Figure 13. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions: KNCO, 0.146M (initial concentration); solvent, 80% v:v DMSO-EG; reaction temperature, 130°; reaction time, 15 min.)

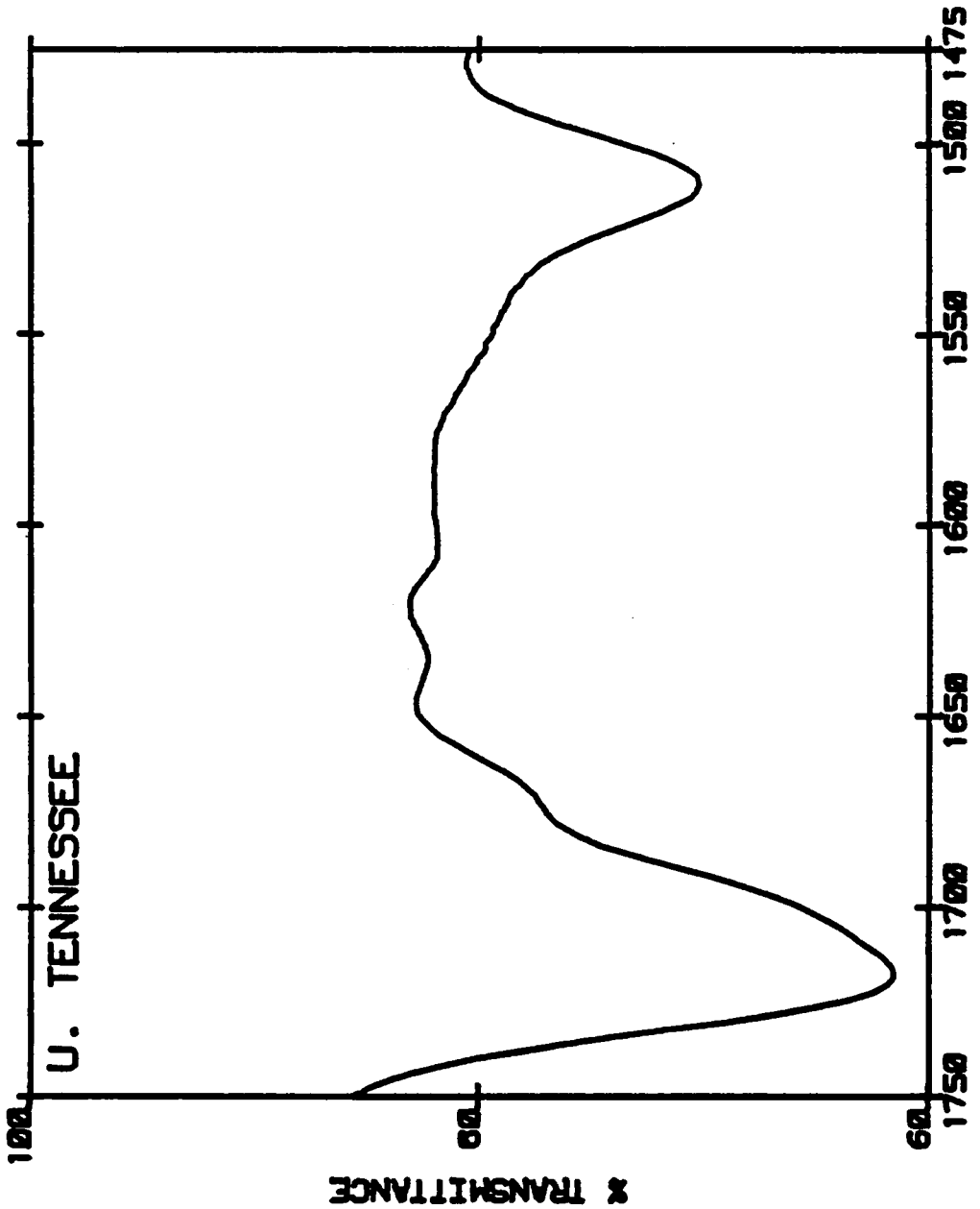


Figure 14. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Closer examination of part of spectrum shown in Figure 13.)

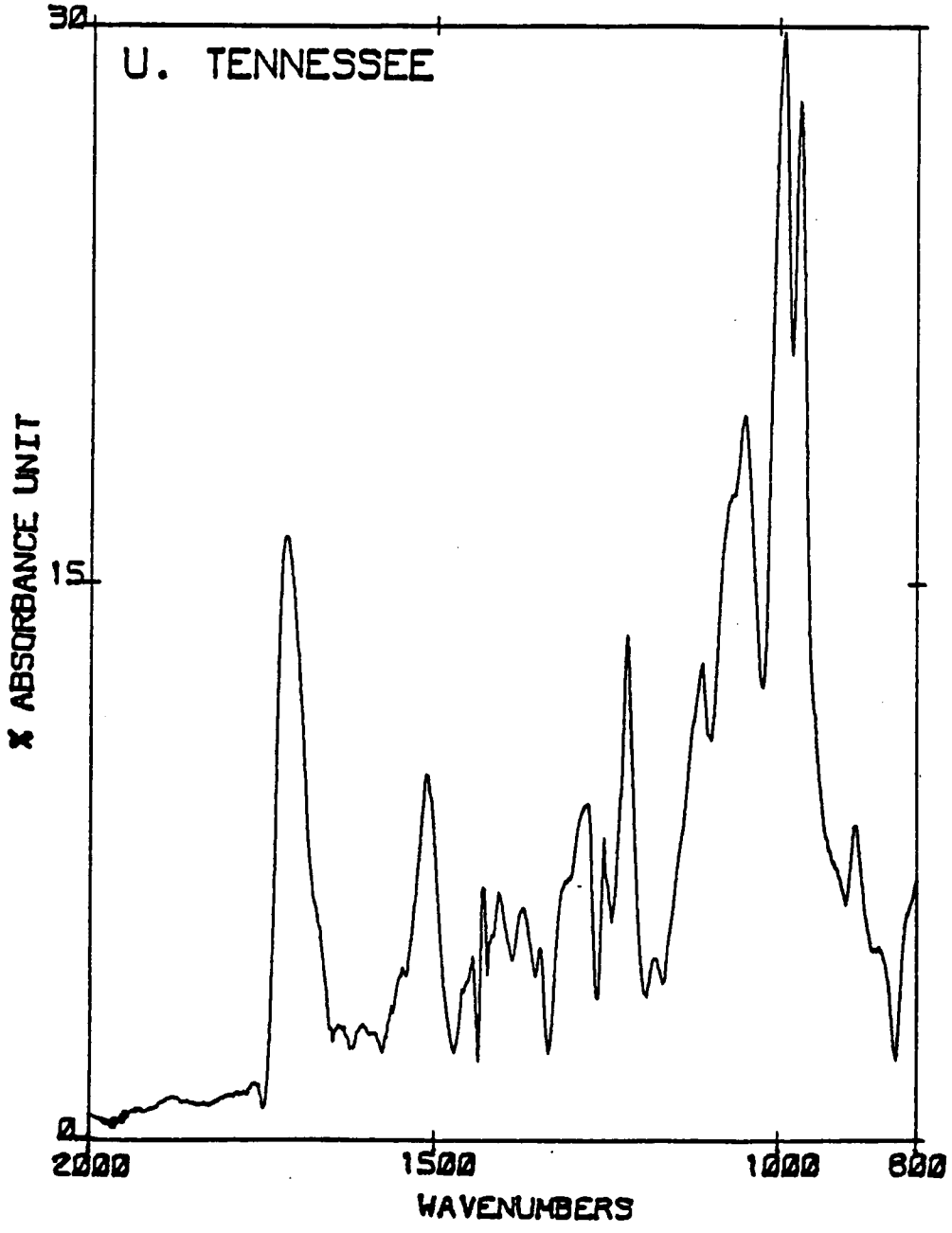
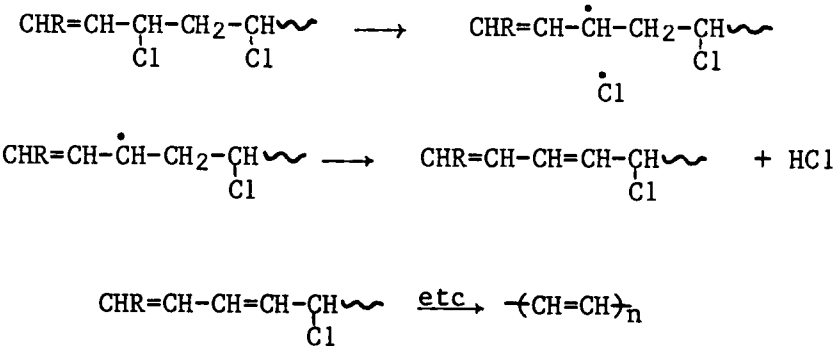


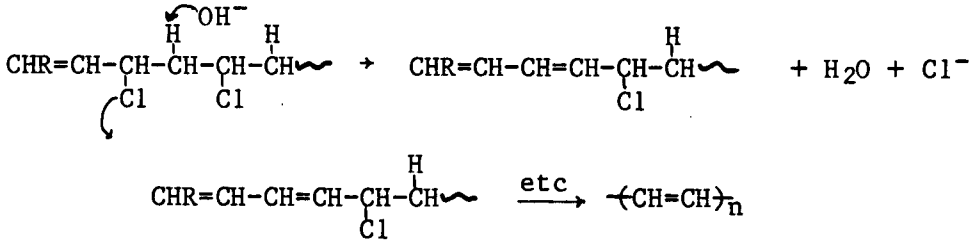
Figure 15. ATR-IR difference spectrum of modified PVC minus PVC.

After the reaction the film was highly colored and opaque, so a transmission infrared spectrum could not be obtained. The color was an indication of a conjugated double bond sequence with a length greater than five.[52] It is well known that heat[52,53,54,55] and bases[45] result in the dehydrochlorination of PVC and the formation of conjugated double bonds (polyenes).[56,57] With increasing length of these polyene sequences the light absorption of the polymer is shifted towards longer wavelength from ultraviolet to the region of visible light; therefore, the reaction can be observed visually by the color change of the polymer from yellow through orange, red, brown until black. This discoloration occurs at low degradation levels - as low as 0.1%.[52] Maddams suggests that the conjugated double bond sequence is greater than five at degradation levels less than .01% conversion.[58]

For thermal degradation, dehydrochlorination begins at approximately 100°[59] instead of the predicted 300-400°.[60] In the past,[61] the ease of elimination has been attributed to tertiary chlorine atoms at branch points in PVC and/or from random unsaturations which would give allylic chlorine atoms. Caraculacu[62,63] did not obtain any indications of tertiary chlorine atoms in PVC by spectroscopy or phenolysis. Braun and Weiss[64] confirmed these results and found that the copolymer of vinyl chloride and 2-chloropropene decomposed much faster than PVC with the same number of branch points. Thus, the low temperature dehydrochlorination of PVC results from allylic chlorine atoms (~.3%).[65] Normal PVC can have up to 15 internal double bonds for each 1000 carbon atoms.[59] For thermal degradation the proposed mechanism is usually involves radicals:



For bases the mechanism is different, but the reason for the ease of dehydrochloroination is similar. For example, PVC is easily dehydrochlorinated with potassium hydroxide dissolved in tetrahydrofuran and ethanol:



It is known that eliminated PVC can be quantitatively chlorinated in chlorohydrocarbons to give a colorless film.[46] The film reacted at 130° was swollen in chloroform, and chlorine gas was bubbled into the chloroform. The film became colorless almost instantaneously. The procedure allowed the transmission spectrum in Figure 16 to be obtained. The larger carbonyl band shows that the reaction went deep into the film. The band at 755 cm^{-1} shows that some chloroform solvent remains in the film.[66] Dissolution of the reacted film in tetrahydrofuran followed by precipitation in methanol did not decrease the intensity of the carbonyl band in the transmission spectrum.

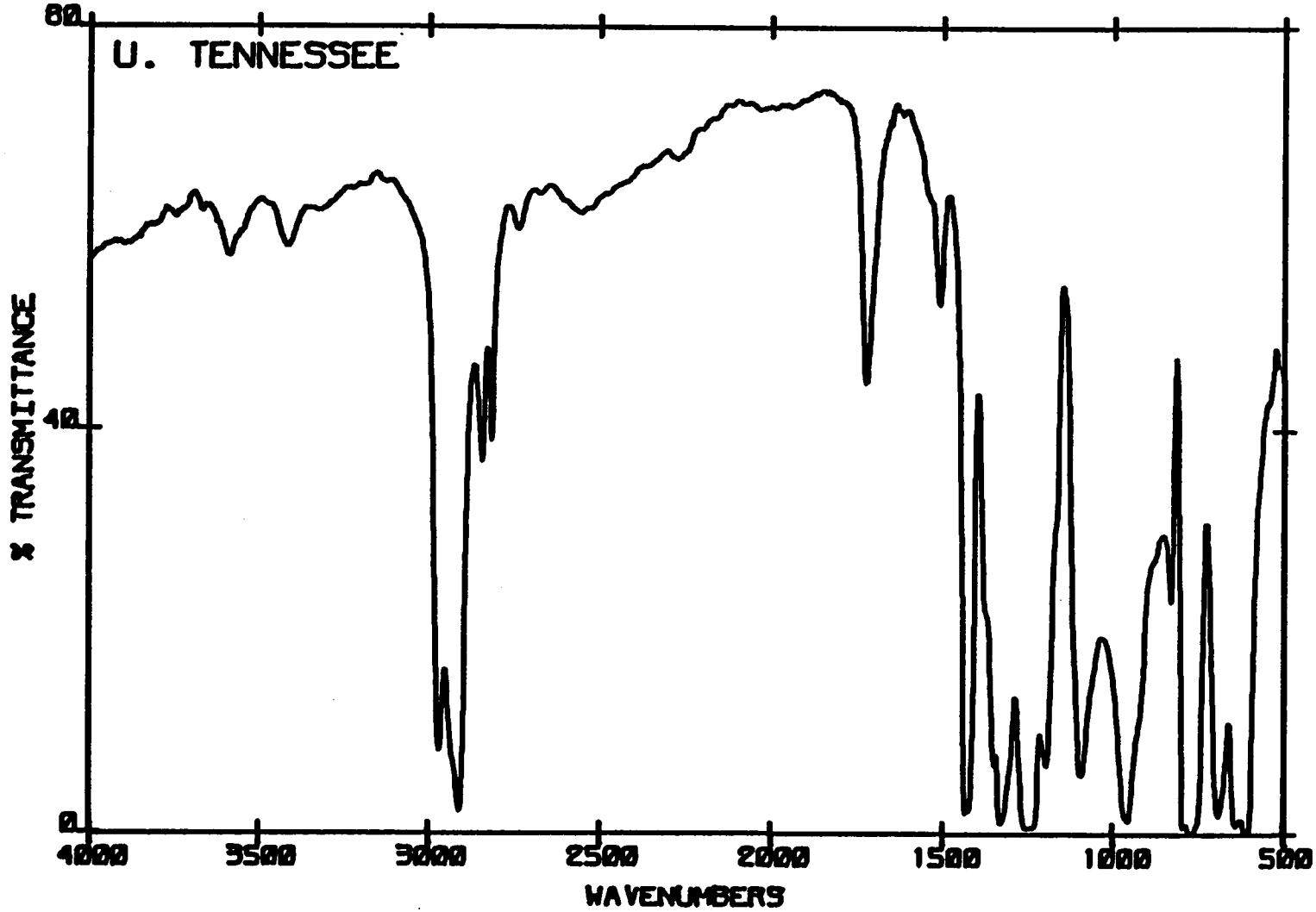


Figure 16. Transmission IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Same film as used for spectra in Figures 13 and 14.)

The reaction was tried in 50% v:v DMSO-EG and in 100% ethylene glycol at 130° at 15 min and 24 hr respectively, but resulted in elimination and no substitution. At 60° in 80% v:v DMSO-EG the PVC films turned slightly yellow in 6 hr and dark red in 18 hr. Analysis of the ATR-IR spectrum for reaction at 9, 12 and 18 hr (see Figures 17, 18 and 19, respectively) shows a carbonyl band at 1719 cm^{-1}, and a band at 1508 cm^{-1} which again indicates a N-H deformation.[67] Comparison of the transmission spectra in Figures 20, 21, and 22 shows that the reaction occurred predominately on the films' surface. After 6 hr in the reaction mixture no carbonyl bands were observed in the ATR-IR spectrum.

As the reactions at 60° proceeded, internal reflection spectroscopy revealed a band at 3016 cm^{-1}. This band was identified as a sp^2-s stretch of a carbon hydrogen bond.[68] All of the films decolorized within 12 min when chlorine gas was bubbled into a mixture of the swollen film and chloroform at room temperature. Figure 23 shows the band at 3016 cm^{-1} before and after the chlorination of the films that had been reacted at 60° for 18 hr. The disappearance of the 3016 cm^{-1} band agrees with a change from sp^2-s stretch to a sp^3-s carbon hydrogen stretch because of the addition reaction:

$$(CH{=}CH)_n \xrightarrow{Cl_2} (CHCl{-}CHCl)_n$$

In addition, figure 23 shows that the band at 2966 cm^{-1} which represents the methine sp^3-s carbon hydrogen stretch in the amorphous and crystalline regions increases in intensity after the chlorination reaction.[51]

From the band disappearance, the addition appeared to be virtually quantitative (>99%) for all the above films. As shown on the bottom

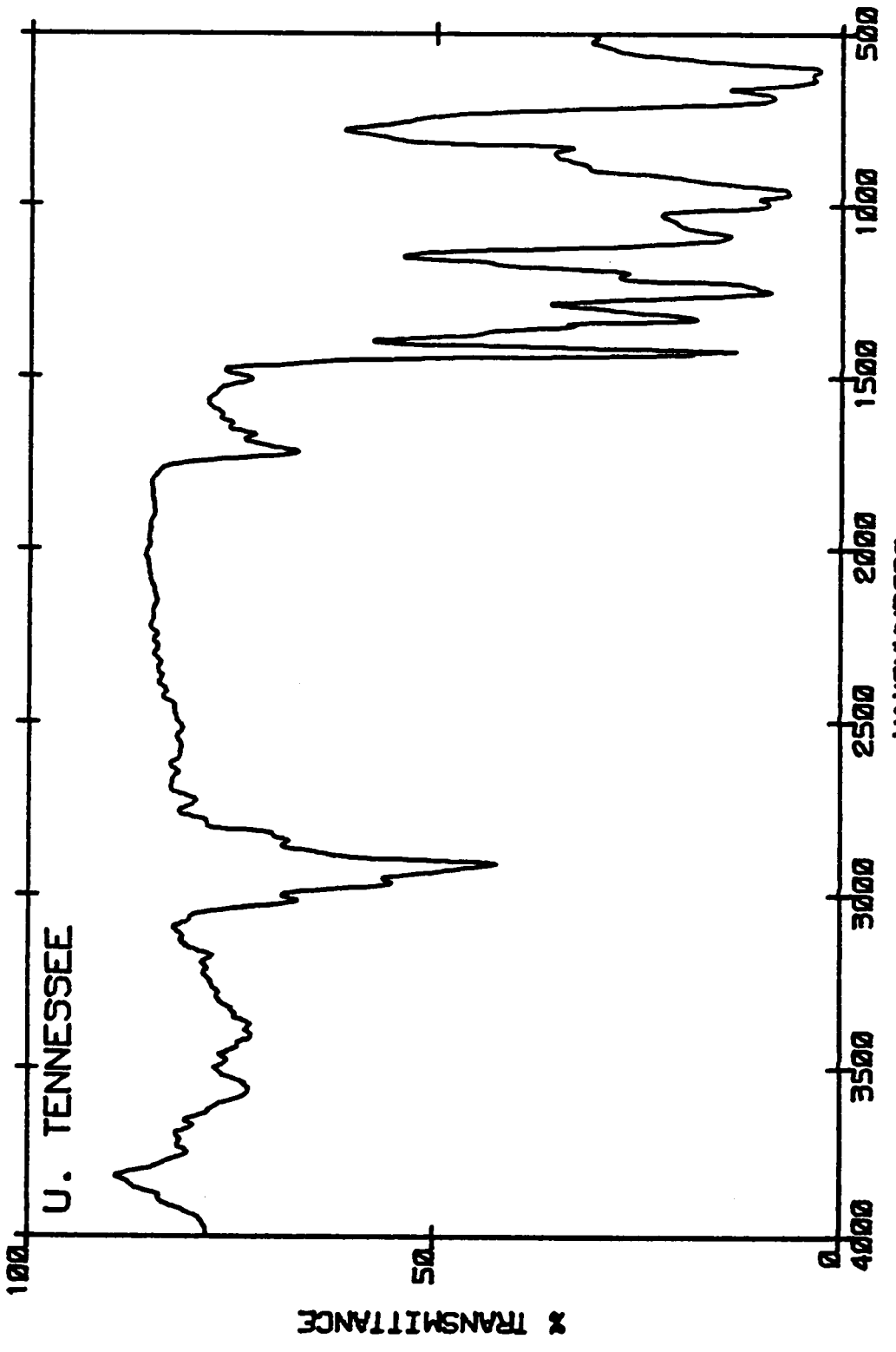


Figure 17. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions: KNCO, 0.146M (initial concentration); solvent, 80% v:v DMSO-EG; reaction temperature, 60°; reaction time, 9 hr.)

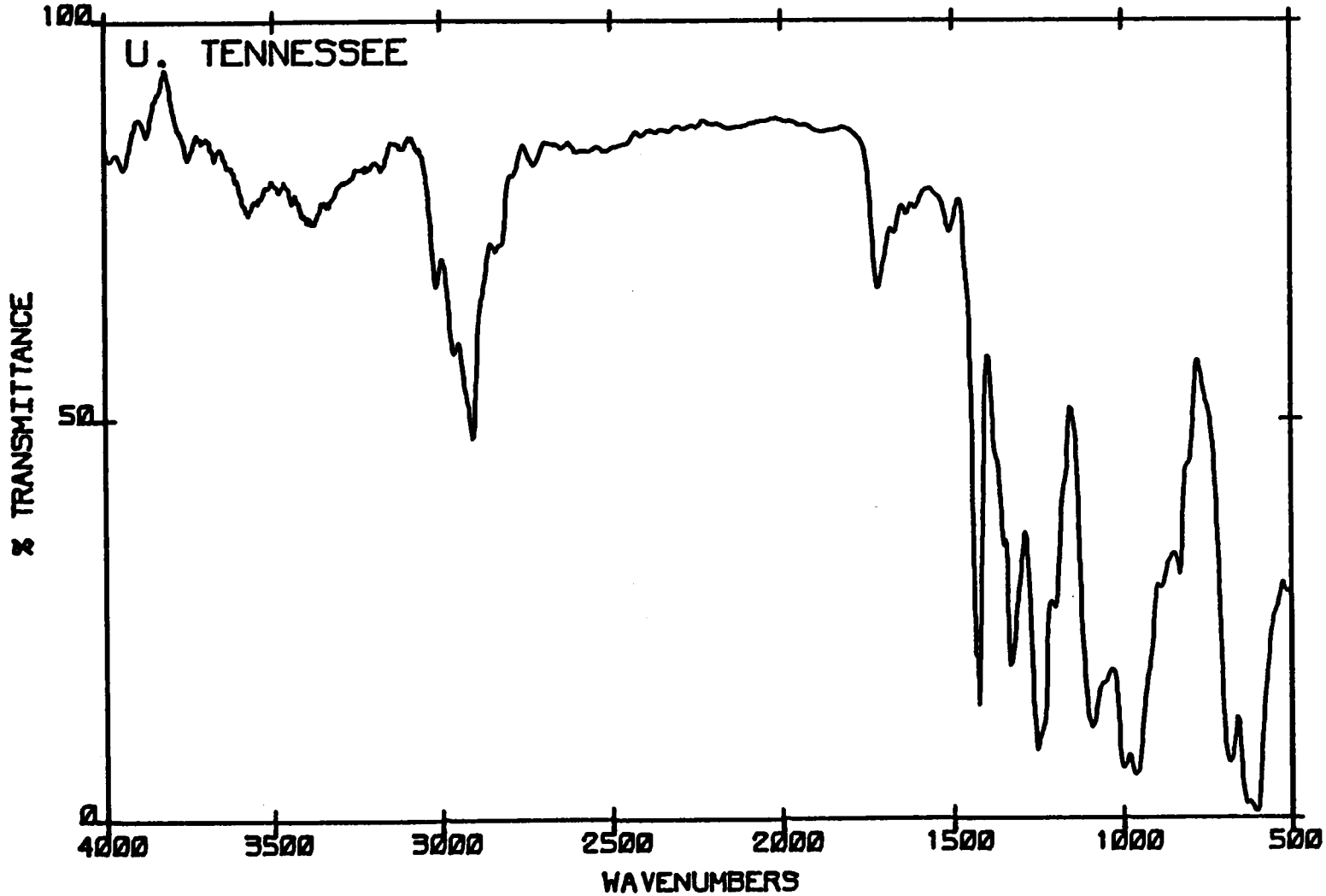


Figure 18. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions; KNCO, 0.146M (initial concentration); solvent, 80% v:v DMSO-EG; reaction temperature, 60°; reaction time, 12 hr.)

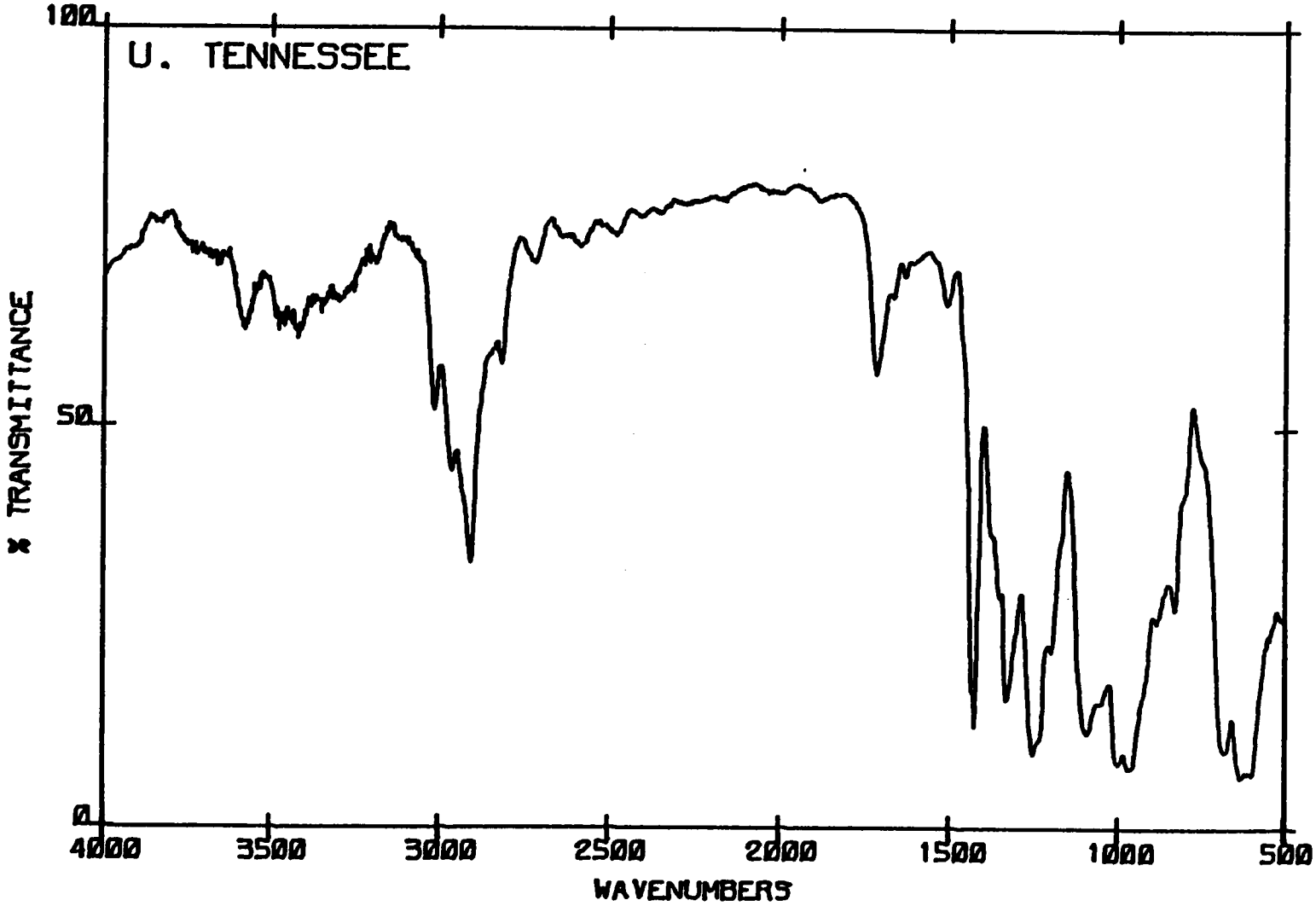


Figure 19. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions: KNCO, 0.146M (initial concentration); solvent, 80% v:v DMSO-EG; reaction temperature, 60°; reaction time, 18 hr.)

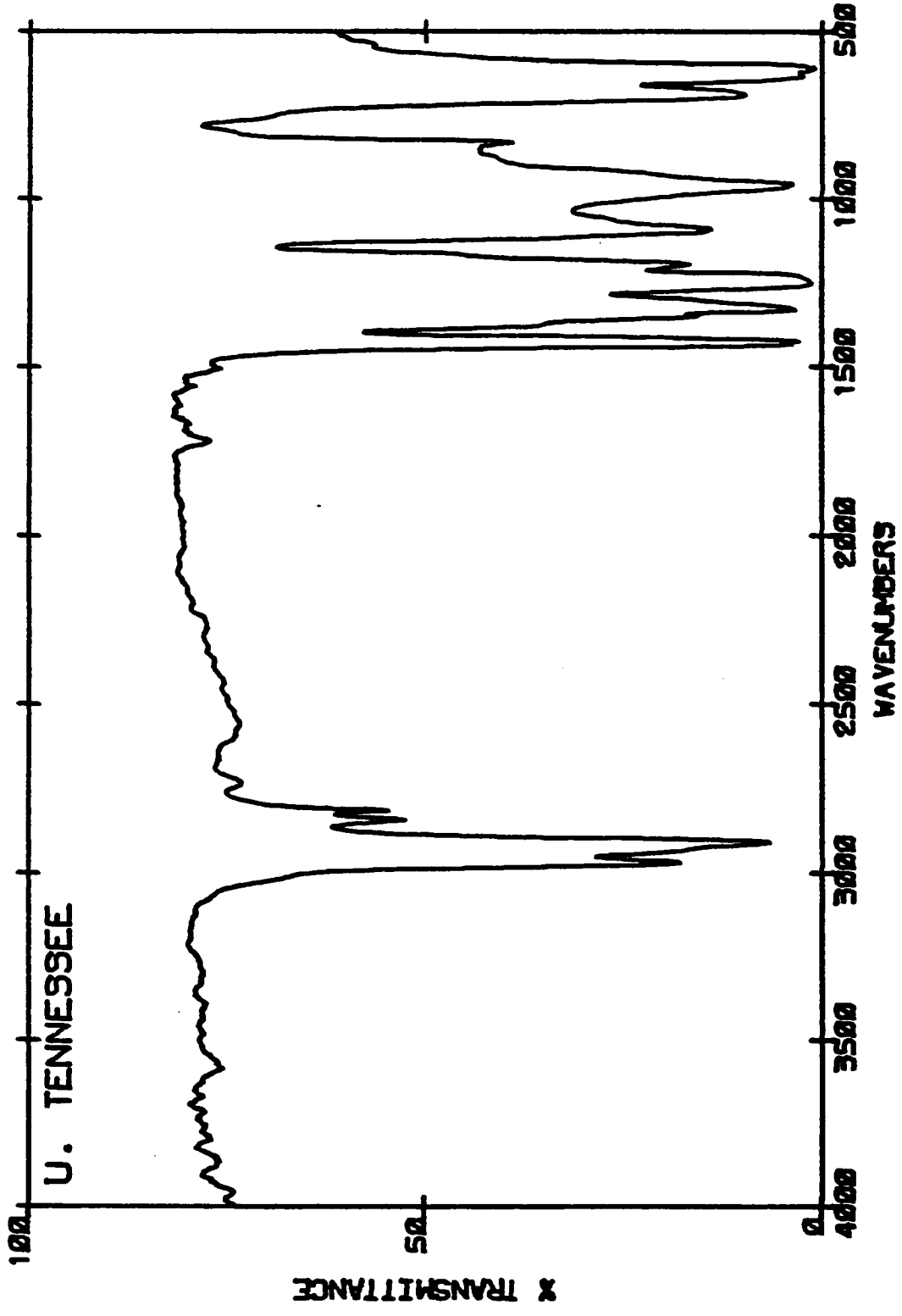


Figure 20. Transmission IR spectrum of modified PVC film taken in vacuum. (Same film as used for spectrum in Figure 17.)

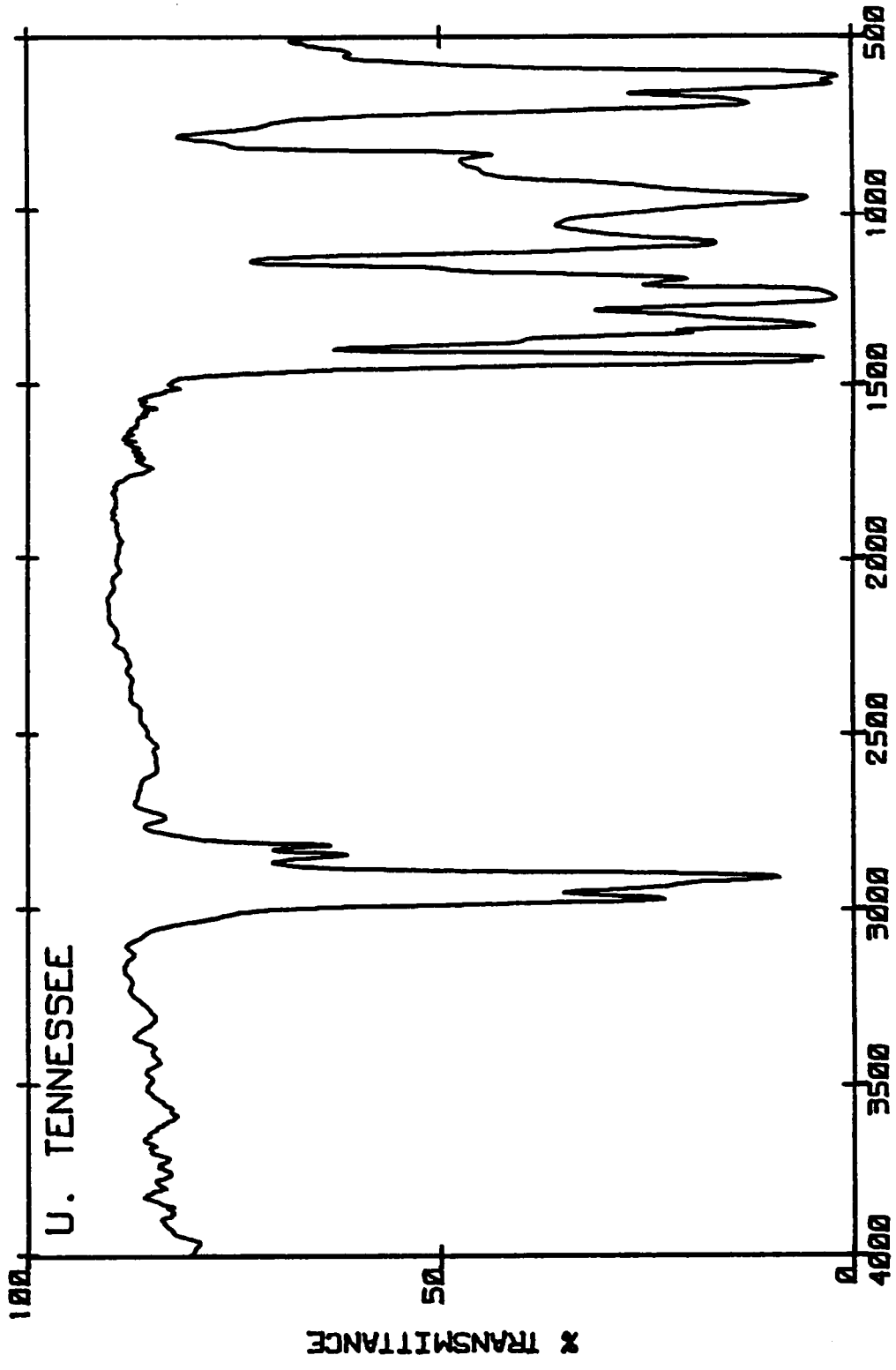


Figure 21. Transmission IR spectrum as modified PVC film taken in vacuum. (Same film as used for spectrum in Figure 18.)

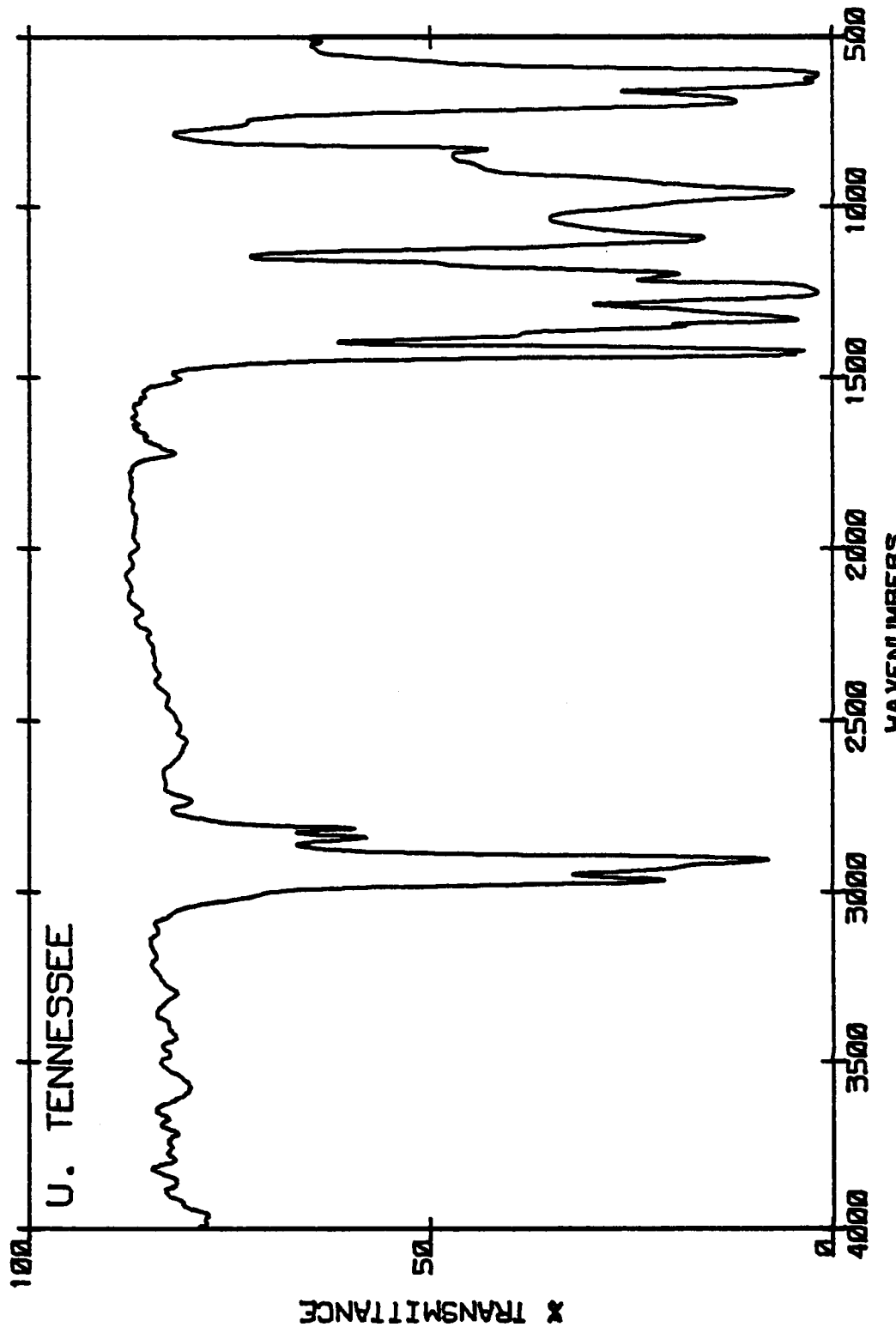


Figure 22. Transmission IR spectrum of modified PVC film taken in vacuum. (Same film as used for spectrum in Figure 19.)

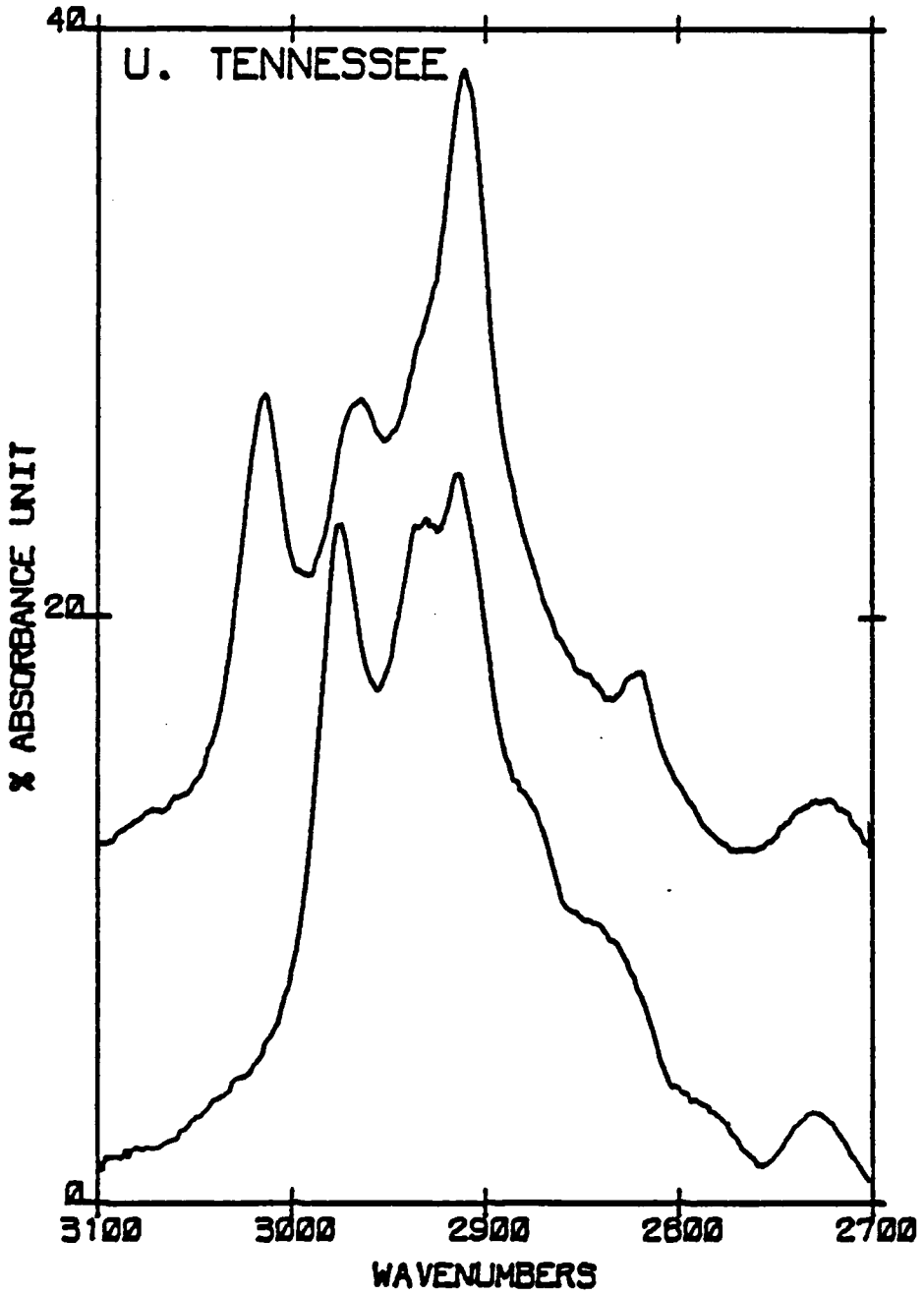
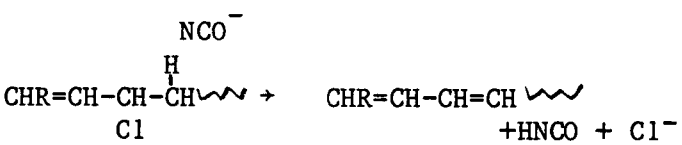


Figure 23. ATR-IR spectra of modified PVC films before chlorination (top plot) and after chlorination (bottom plot) taken at 45 degree angle of incidence (N=20).

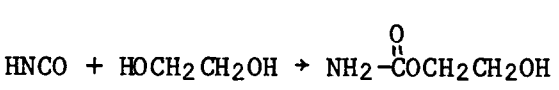
plot in Figure 24, after 6 hr there is a rapid increase of the band at 3016 cm^{-1}, and the increase becomes linear after 9 hr. Note that the slope of this plot after 9 hr is the same as that observed for the top plot in Figure 24, the absorbance of the carbamate groups.

Other evidence for elimination is shown by a band at 990 cm^{-1} in Figure 18, (p 51) for the reacted film for 18 hr at 60° which indicates a trans polyene sequence.[69] This absorption band was not observed on the ATR-IR spectrum of the film reacted at 130° for 15 min, but it was identified in the difference spectrum shown in Figure 15 (p 44). Furthermore, a small band at 3016 cm^{-1} (0.008 absorbance) was observed for this film which indicates less dehydrochlorination of this film's surface compared to the films reacted at 60° due to the shorter reaction time.

Another reaction is undoubtedly the formation of isocyanic acid from the dehydrochlorination reaction:



Since the solvent, ethylene glycol, is present in large excess over potassium cyanate the subsequent reaction is between the isocyanic acid and ethylene glycol to make 2-hydroxyethyl carbamate:



As will be shown later, it is possible for the hydroxyl group to participate in a substitution reaction at the allylic position to give the surface groups:

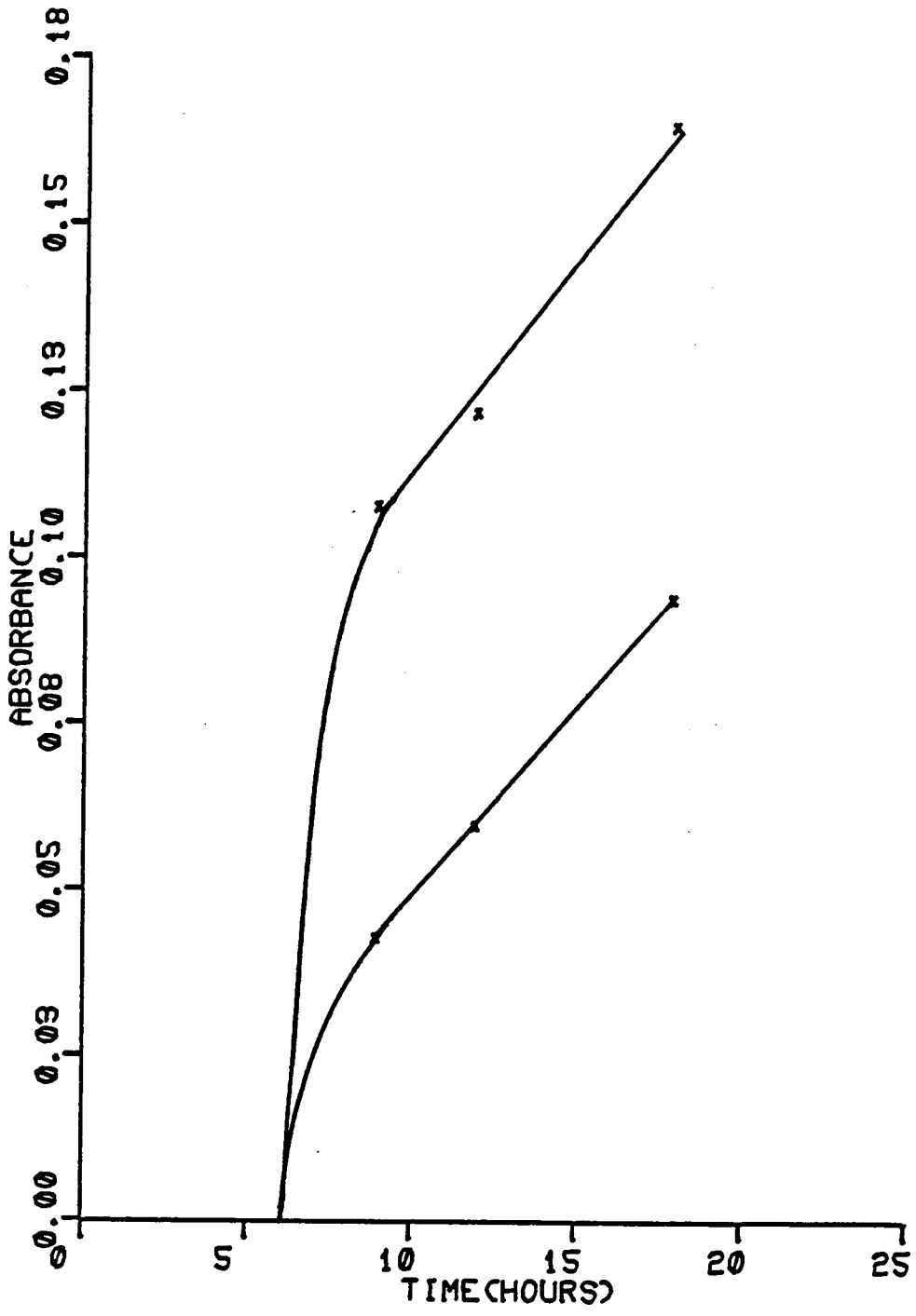
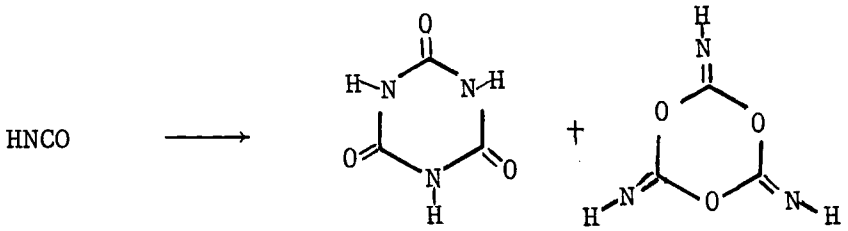


Figure 24. ATR-IR absorbance of the carbamate carbonyl band at 1719 cm^{-1} (top plot) and carbon-hydrogen sp^2-s band at 3016 cm^{-1} (bottom plot) taken as a function of reaction time at 45 degree angle of incidence (N=20). (Reaction Conditions: KNCO, 0.146M (initial concentration); solvent, 80% v:v DMSO-EG; reaction temperature, 60°; reaction times, 6 hr, 9 hr, 12 hr and 18 hr.)

$$PVC\text{-}Cl + HOCH_2CH_2O\overset{O}{\overset{\|}{C}}\text{-}NH_2 \rightarrow PVC\text{-}OCH_2CH_2O\overset{O}{\overset{\|}{C}}\text{-}NH_2$$

However, if similar substitution rate constants are assumed between the active chlorine sites and the hydroxyl group(s) in 2-hydroxyethyl carbamate or ethylene glycol, the larger concentration of ethylene glycol will minimize the above reaction.

Furthermore a host of additional side reactions listed below are possible but are minimized due to the high concentration of ethylene glycol:



$$PVC\text{-}NCO + HNCO \rightarrow PVC\text{-}\overset{H}{\underset{|}{N}}\text{-}NCO$$

$$PVC\text{-}\overset{H}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}NCO + HOCH_2CH_2OH \rightarrow PVC\text{-}\overset{H}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}OCH_2CH_2OH$$

$$PVC\text{-}NCO + NH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2OH \rightarrow PVC\text{-}\overset{H}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}OCH_2CH_2OH$$

$$PVC\text{-}NCO + HOCH_2O\overset{O}{\overset{\|}{C}}NH_2 \rightarrow PVC\text{-}\overset{H}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}OCH_2CH_2O\overset{O}{\overset{\|}{C}}NH_2$$

To determine the depth of the absorbing species for the reactions done at 60°, Blackwell's procedure was tried but gave inconsistent results, perhaps due to a changing concentration of the reference methylene band. For example, $R(45)/R(51.2) = 1.156 \pm 0.034$ at 90% confidence level for the film reacted for 18 hours. As shown in Table II the one angle method gave results which indicated that the depth of

TABLE II

DEPTH ANALYSIS OF THE CARBAMATE GROUP AS A FUNCTION OF REACTION TIME

Reaction Time (Hours)	$\frac{A(ATR)}{A(TRN)}$	t
9.0	16.2 $\pm$ 1.3	$0.44\lambda_1$
12.0	14.3 $\pm$ 2.1	$0.53\lambda_1$
18.0	15.03 $\pm$ .25	$0.50\lambda_1$

a. $\pm$ values are based on three measurements at a 90% confidence limit.

b. Initial concentration of potassium cyanate in 80% v:v dimethyl sulfoxide-ethylene glycol is 0.147M.

c. All above reactions run at 60° $\pm$ 1°.

d. Absolute absorbances were used in the above measurements, and the baseline was drawn from 1800 cm^{-1} to 1650 cm^{-1}.

reaction was on the order of $0.5\lambda_1$. The data suggest that the penetration of the solvent remained relatively constant during the reaction; however, as the reaction proceeded the red reaction mixture became darker in color. Furthermore, addition of the solvent mixture to methanol gave a very small amount of a light brown precipitate powder after about 24 hr.

The above results can be explained as follows. Glassy polymers are known to follow case II diffusion.[70] In case II diffusion the basic parameter is the constant velocity of an advancing front which marks the innermost penetration of the penetrant and is the boundary between the swollen gel and the glassy core of the film. Furthermore, according to Tu and Ouano,[71] for a polymer in a solvent system the gel/solvent interface is characterized by a dissolution of the polymer. As the substitution reactions proceed, polar groups are increasing in concentration at the surface of the polymer which should increase the dissolution rate as a result of polar-polar and hydrogen bonding interactions of the modified polymer's surface with the dimethyl sulfoxide and ethylene glycol solution. However, the velocity of the advancing front of the gel/glass boundary is assumed constant. This means there are two moving boundaries, the gel/solvent interface and the gel/glass interface. Since the depth was smaller than expected for the 18 hr reaction, it indicates that the rate of movement of the gel/solvent interface can have a marked effect on the final measured depth of reaction.

Table III shows the absorbances from internal reflection spectroscopy of the carbonyl band at 1719 cm^{-1} for the above substitution reactions, and the corresponding methylene band at 1424 cm^{-1} in the

TABLE III

INTERNAL REFLECTION ABSORBANCES OF THE CARBONYL BAND AT 1719 cm^{-1} AS A FUNCTION OF REACTION TIME

Reaction Time (Hours)	Absorbance at 1719 cm^{-1}	Absorbance at 1424 cm^{-1}	Apparent Concentration Molarity
9.0	0.108 $\pm$ 0.002	0.880	0.083
12.0	0.122 $\pm$ 0.000	0.828	0.097
18.0	0.165 $\pm$ 0.010	0.833	0.136

a. $\pm$ values are deviations from the mean based on two experiments.

b. Initial concentration of potassium cyanate in 80% v:v dimethyl sulfoxide-ethylene glycol is 0.147M.

c. All above reactions run at 60° $\pm$ 1°.

d. All absorbances were measured at 45 degree angle of incidence, N=20.

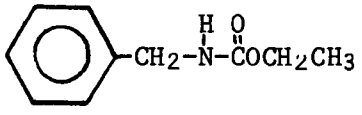
crystalline region of the polymer[51] which was used as a rough measure of film contact. For the reactions carried out at 60°, the general increases in absorbance at 1719 cm^{-1} at longer reaction times shows an increase in the concentration of the carbamate group on the surface of PVC. The top plot in Figure 24 (p 58) show that the increase in absorbance of this band is apparently linear with increasing time after 9 hr.

To determine the concentration of the carbamate groups on the surface of the reacted films at 60°, internal reflection spectroscopy was used. As shown by Equation 25 in Chapter I, an absorbing species on the surface of a polymer can be described by the relationship

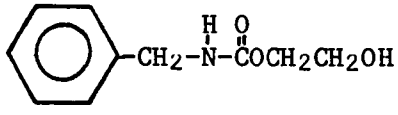
$$A(ATR) = N\varepsilon cd_e/2.303\ [1-e^{-2t/dp}]$$

The basic problem in using this equation is finding the molar absorptivity of the carbamate group.

Two model compounds, ethyl N-benzylcarbamate



and 2-hydroxy ethyl N-benzylcarbamate



were each placed as a physical blend in a PVC matrix by casting films under argon from a solution of tetrahydrofuran, PVC and model compounds. The products, εc, at 1424 cm^{-1} and 1430 cm^{-1} were determined using Beer's Law. The absorbances at 1424 cm^{-1} and 1430 cm^{-1}

were measured using transmission IR spectroscopy. The thickness of the films was determined using the interference fringe method.[72] The film thickness, b, was calculated from the expression

$$b = \frac{N}{2\eta} = \left(\frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1}\right)$$

where N is the number of fringes (peaks or troughs) between two wavelengths, η is the refractive index of the sample, λ_1 is the starting wavelength and λ_2 the finishing wavelength. In this work, η was assumed to be 1.5.[73] A near IR wavelength range was used between 1400 nm $\pm$2 nm and 1700 nm $\pm$2 nm respectively. The εc values at 1424 cm^{-1} and 1430 cm^{-1} were determined to be 217 cm^{-1} $\pm$3 cm^{-1} and 285 cm^{-1} $\pm$ 7 cm^{-1} respectively at a 90% confidence level. A density is necessary to calculate the concentration of the carbamate compounds on PVC. The literature[49] gives a density of 1.37 g/ml for PVC wet with tetrahydrofuran. This density was confirmed with a density gradient column made from potassium carbonate and water. It was used in calculating the volumes of the films which were used to calculate the concentrations of carbamate compounds in PVC.

Figure 25 and Figure 26 are the resulting absorbance versus concentration plots for ethyl N-benzylcarbamate and 2-hydroxyethyl N-benzylcarbamate respectively. These figures suggest that the hydroxy group of the 2-hydroxyethyl N-benzylcarbamate does not markedly affect its linearity for concentrations less than 0.16M. The molar absorptivity was measured at 1719 cm^{-1} and was determined to be 6.0 ($\pm$.2) x 10^5 cm^2/mole for ethyl N-benzylcarbamate and 5.2 ($\pm$.2) x 10^5 cm^2/mole for 2-hydroxyethyl N-benzylcarbamate.

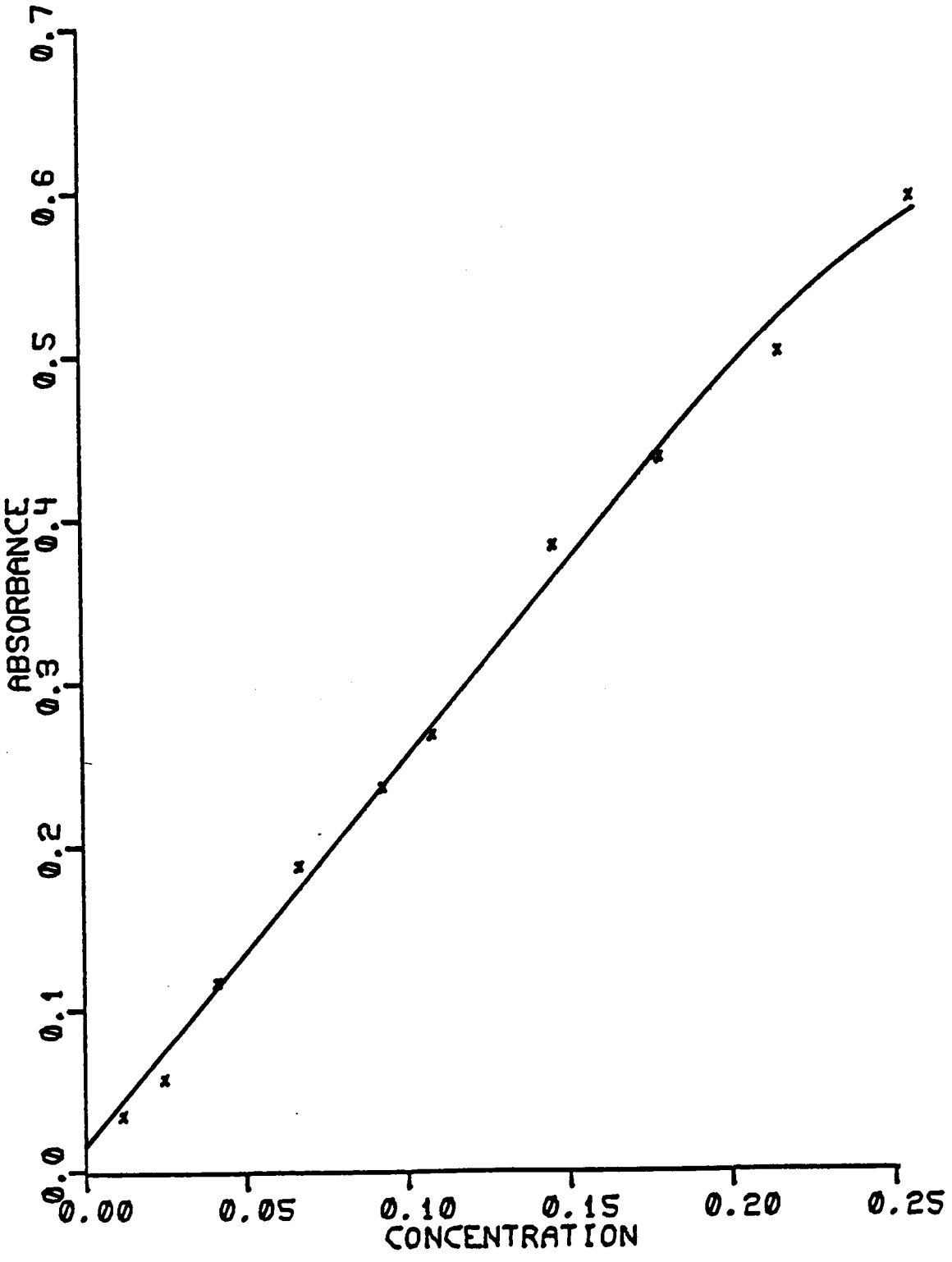


Figure 25. A Beer's Law plot of the transmission IR carbonyl absorbance at 1719 cm^{-1} of ethyl N-benzyl carbamate in PVC.

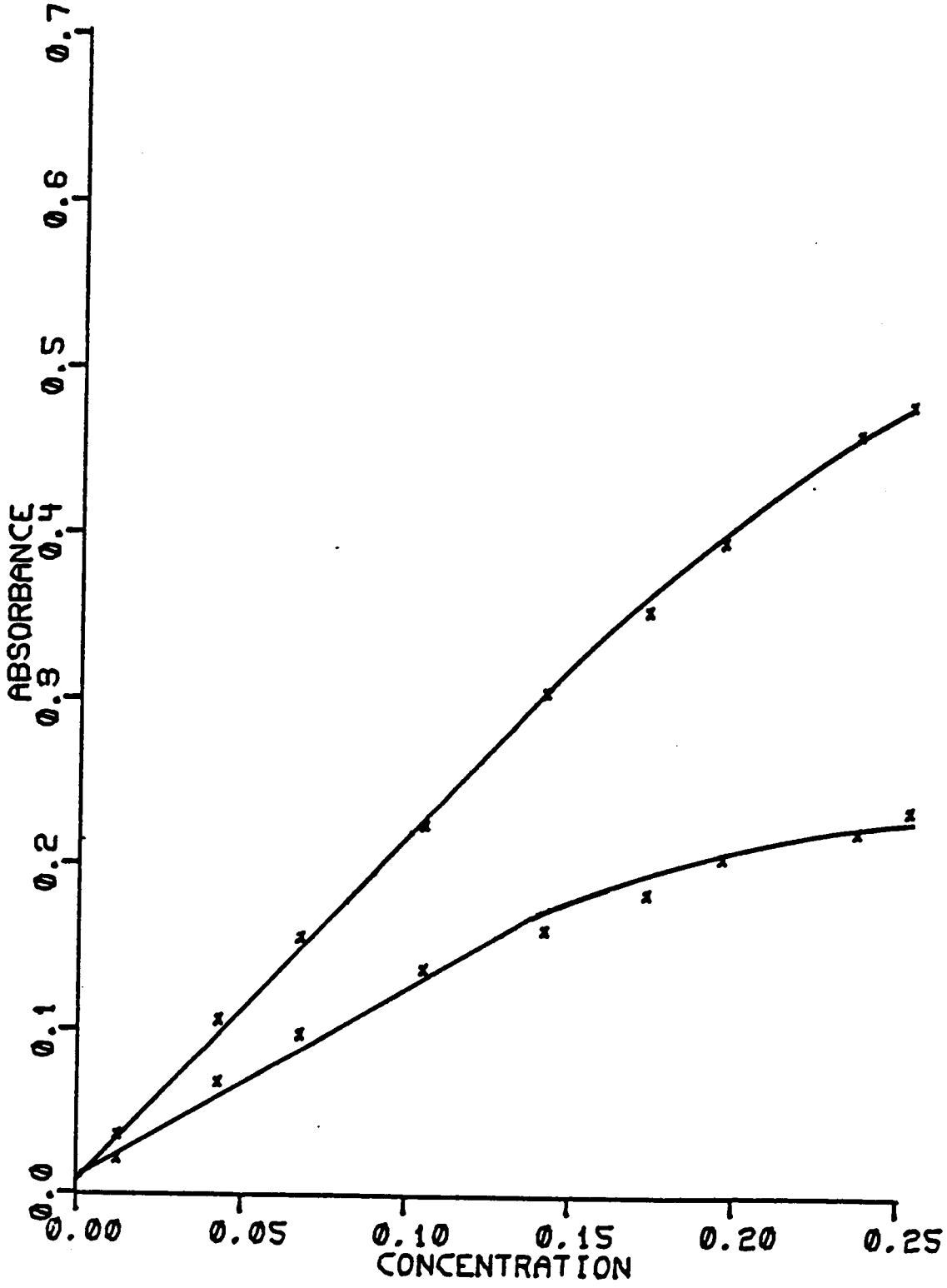


Figure 26. A Beer's Law plot (top plot) of transmission IR carbonyl absorbance at 1720 cm^{-1} of 2-hydroxyethyl N-benzyl carbamate in PVC and an ATR-IR plot (bottom plot) taken at 45° angle of incidence (N=20) of the carbonyl absorption of the same compound.

The bottom plot in Figure 26 is a calibration plot using internal reflection spectroscopy. The band from the methylene group of the crystalline matrix at 1424 cm^{-1} was used as a measure of film contact on the ATR crystal. The absorbance was 0.86 $\pm$ 0.02 at 1424 cm^{-1} at a 90% confidence level based on the nine samples used. From a slope of 1.017, d_e is calculated to be 2.372 x 10^{-4}cm.

To determine the accuracy of the internal reflection plot and to rule out a concentration gradient the approximate relationship

$$\frac{A}{Ar} = \frac{\varepsilon c \lambda}{\varepsilon c_r \lambda_r}$$

was used. A and Ar were measured by internal reflection spectroscopy. The concentration of the carbamate groups were then calculated using the above equation and compared with the known concentrations. The results are shown in Table IV. Note that between the known concentrations 0.0683M and 0.143M, the agreements between calculated and known concentrations are good (error <13%). The data say that no concentration gradient exists or that the method is not sensitive enough to detect it.

Because of the broadening of the carbamate band below 1670 cm^{-1} on the reacted films, perhaps due to side reactions, the empirical ratio method described by Peter, Hayes and Hieftje[74] was used to obtain the absorbance of the absorbing species at 1719 cm^{-1}. The apparent average concentrations shown in Table III (p 62) were obtained using the internal reflection plot in Figure 26 (p 66). The concentration is called average because as shown in Chapter I, this technique cannot tell the difference between a linear decreasing profile or a

TABLE IV

COMPARISONS OF THE KNOWN CONCENTRATIONS AND THE CONCENTRATIONS DETERMINED BY INTERNAL REFLECTION SPECTROSCOPY OF 2-HYDROXYETHYL N-BENZYL CARBAMATE IN POLY(VINYL CHLORIDE)

Known conc. of Carbamate, Molarity	Absorbance ($1720cm^{-1}$) / Absorbance ($1430cm^{-1}$)	Absorbance ($1720cm^{-1}$) / Absorbance ($1424cm^{-1}$)	Conc. of Carbamate by ATR (Reference, $1430cm^{-1}$)	% Error	Conc. of Carbamate by ATR (Reference, $1424cm^{-1}$)	% Error
0.0129	0.0131	0.023	0.016	24	0.015	20
0.0434	0.110	0.0800	0.0552	27.2	0.0530	22.1
0.0683	0.148	0.117	0.0743	9	0.0774	13
0.106	0.207	0.153	0.104	-2	0.101	-5
0.143	0.267	0.203	0.134	-6.3	0.134	-6.3
0.174	0.297	0.219	0.149	-14	0.145	-17
0.197	0.320	0.234	0.161	-18	0.155	-21
0.238	0.386	0.281	0.194	-18	0.186	-22
0.254	0.400	0.286	0.201	-21	0.189	-26

step profile. The concentration is apparent because the absorbance of the reacted film is set equal to the absorbance of the 2-hydroxyethyl-N-benzylcarbamate standard which is uniformly distributed throughout the sample. The reacted films, as shown in Table II (p 60), have depths of reaction which are less than the effective penetration of light. This means that the light beam effectively penetrates deeper into the film than the absorbing species; thus, without taking the depth of reaction into account, the apparent concentration will be lower than the average concentration. Mathematically, this can be shown by rearranging Equation 25 in Chapter I to

$$c_{av} = \frac{A\ 2.303}{N\varepsilon d_e}\left[1-e^{-2t/dp}\right]^{-1}$$

where the terms before the bracket can be replaced by the apparent concentration, c_{ap} to get

$$c_{av} = c_{ap}\left[1-e^{-2t/dp}\right]^{-1}$$

where c_{ap} is obtained from Figure 26. A plot of the apparent concentration of the carbamate groups as a function of time for the reactions done at 60° is shown in Figure 27. The increase in apparent concentration is linear after 9 hr.

A surface density for the carbamate functionality can be found by calculating the average concentration from the depth of reaction in Table II (p 60). For example for the 18 hr reaction, $t = 0.50\lambda_1$, or 1.2×10^{-4} cm, $c_{ap} = 0.136$ M. Substitution into the above equation gives

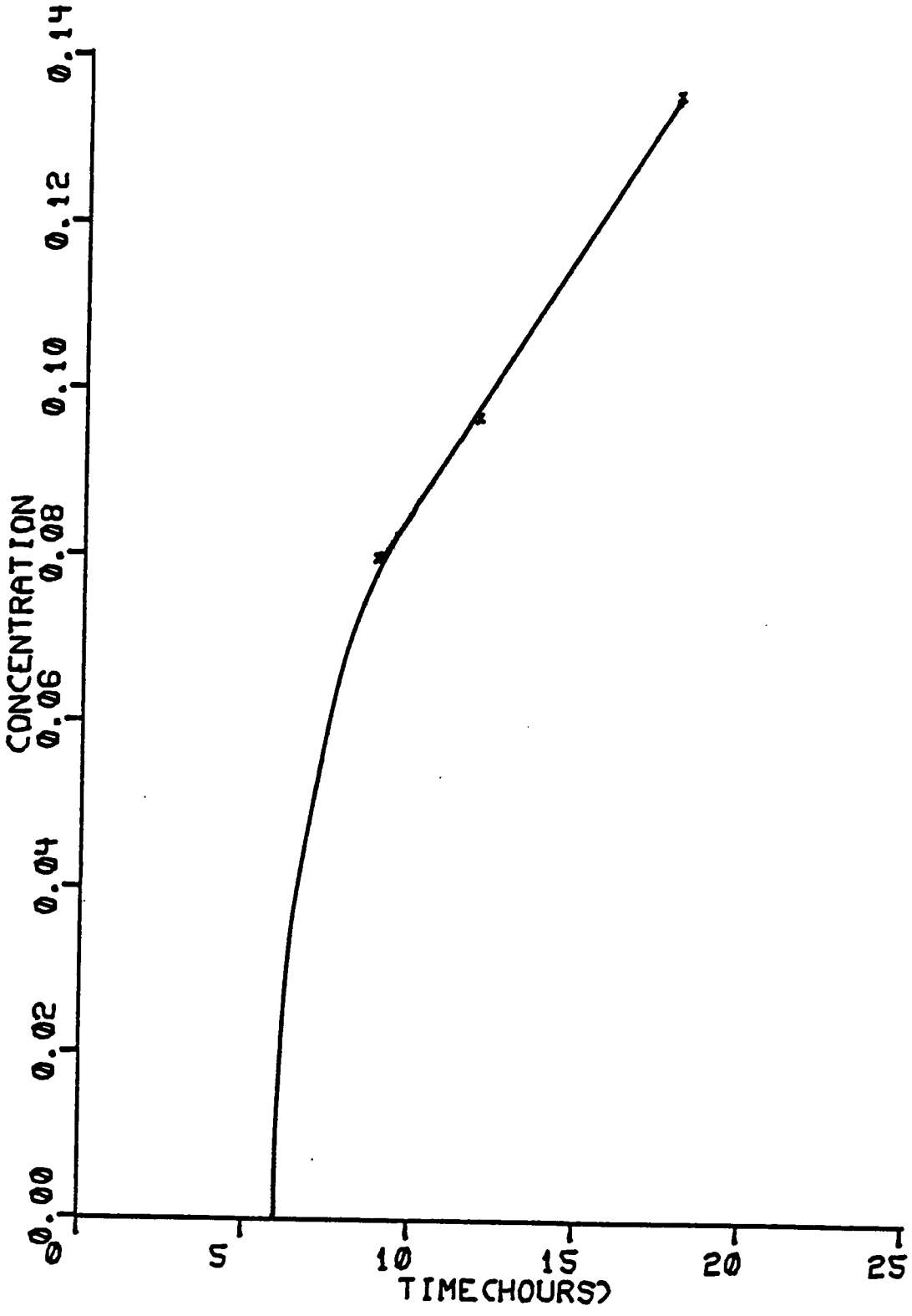


Figure 27. Apparent concentration of the carbamate on the surface of PVC as a function of reaction time.

$$c_{av} = 0.136[1-e^{-2 \times 1.2 \times 10^{-4}/1.16\times10^{-4}}]^{-1}$$

$$c_{av} = 0.16 \text{ M}$$

Using Avagadro's number, the volume per carbamate unit can be calculated to be

$$V_m = 1.0 \times 10^{-20} \text{ cm}^3/\text{unit}$$

From V_m, if one assumes a cubic shape, one can calculate the unit dimension r_m, the length of one side or unit thickness

$$r_m = V_m^{1/3} = 2.2 \times 10^{-7} \text{ cm/unit}$$

Therefore the effective area per carbamate unit, A_m at the surface layer and at each succeeding layer can be calculated

$$\bar{A}_m = r_m^2 = 5.0 \times 10^{-14} \text{cm}^2/\text{unit}$$

The surface density, D_s, is then calculated:

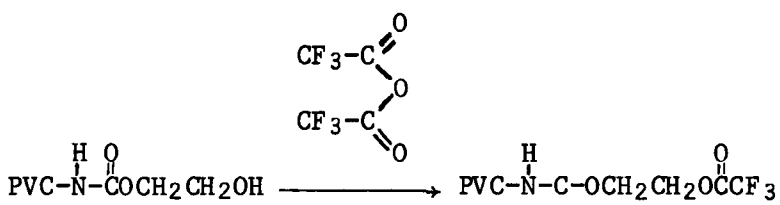
$$D_s = 1/\bar{A}_m = 2.0 \times 10^{13} \text{ units/cm}^2$$

Thus an ideal planar film 1 x 1 cm would expose 2.0×10^{13} carbamate units at the top monolayer and every succeeding monolayer. The above surface density is based on the assumption that the molar absorptivity is 5.2×10^5 cm^2/mole; however, this number was determined from a carbamate compound in the polymer matrix rather than from a carbamate group directly attached to the polymer chain. If the actual molar absorptivity is considered to be between 7.2×10^5 cm^2/mole and 3.2

x 10^5 cm^2/mole then the surface density calculated above should be within a factor of 2 of the absolute value.

An O-H stretch appeared as a broad band from 3800 cm^{-1} to 3200 cm^{-1} in the internal reflection spectrum for reactions done at 130° and 60° respectively, which indicates associated hydroxyl groups via hydrogen bonding. The larger OH stretch for the film reacted for 18 hr at 60° shows a higher concentration of hydroxyl groups. Qualitatively since the concentration of carbamate groups for the films reacted at 130° is higher than the concentration of carbamate groups for all the films reacted at 60°, one would expect to have a higher concentration of hydroxyl groups for the reaction at 130° which should be reflected by a stronger broad absorption from 3800 cm^{-1} to 3200 cm^{-1}.

To verify the above results each film was reacted with trifluoroacetic anhydride[14] in diethyl ether:



After the reaction, each film was extracted with diethyl ether from a bed of calcium hydride in a soxhlet under argon for 18 hr, then vacuum dried at 47° for 24 hr. As shown in Figure 28, the OH band from 3800 cm^{-1} to 3200 cm^{-1} disappeared and (as shown in Figure 29) a second resolved carbonyl band appeared at 1790 cm^{-1} indicating the trifluoroacetate ester. The absorption of the carbamate group moved from 1719 cm^{-1} to 1725 cm^{-1}.

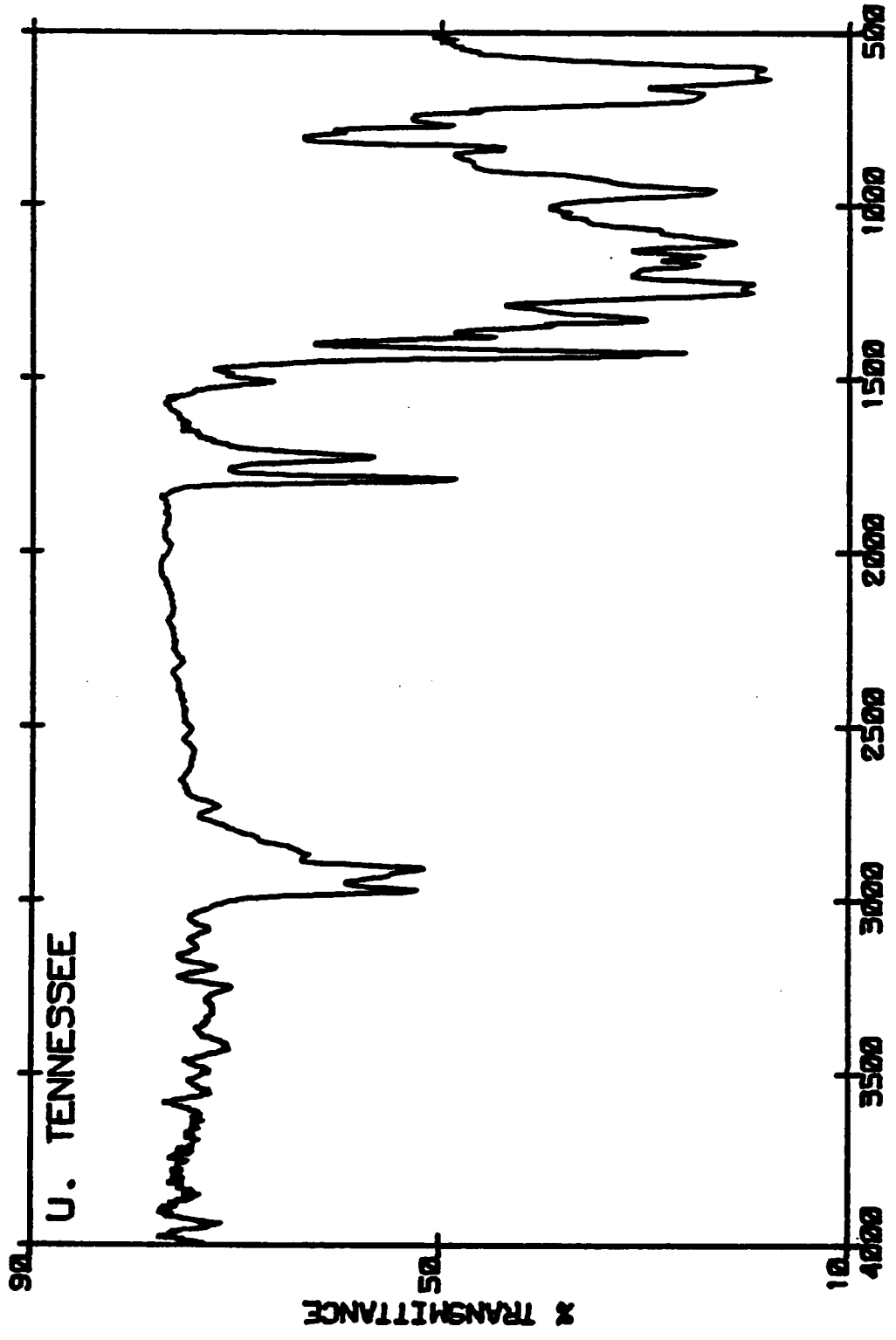


Figure 28. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions: trifluoroacetic anhydride, 1.8 ml (11 mmoles); reaction temperature 23°; reaction, 30 min.)

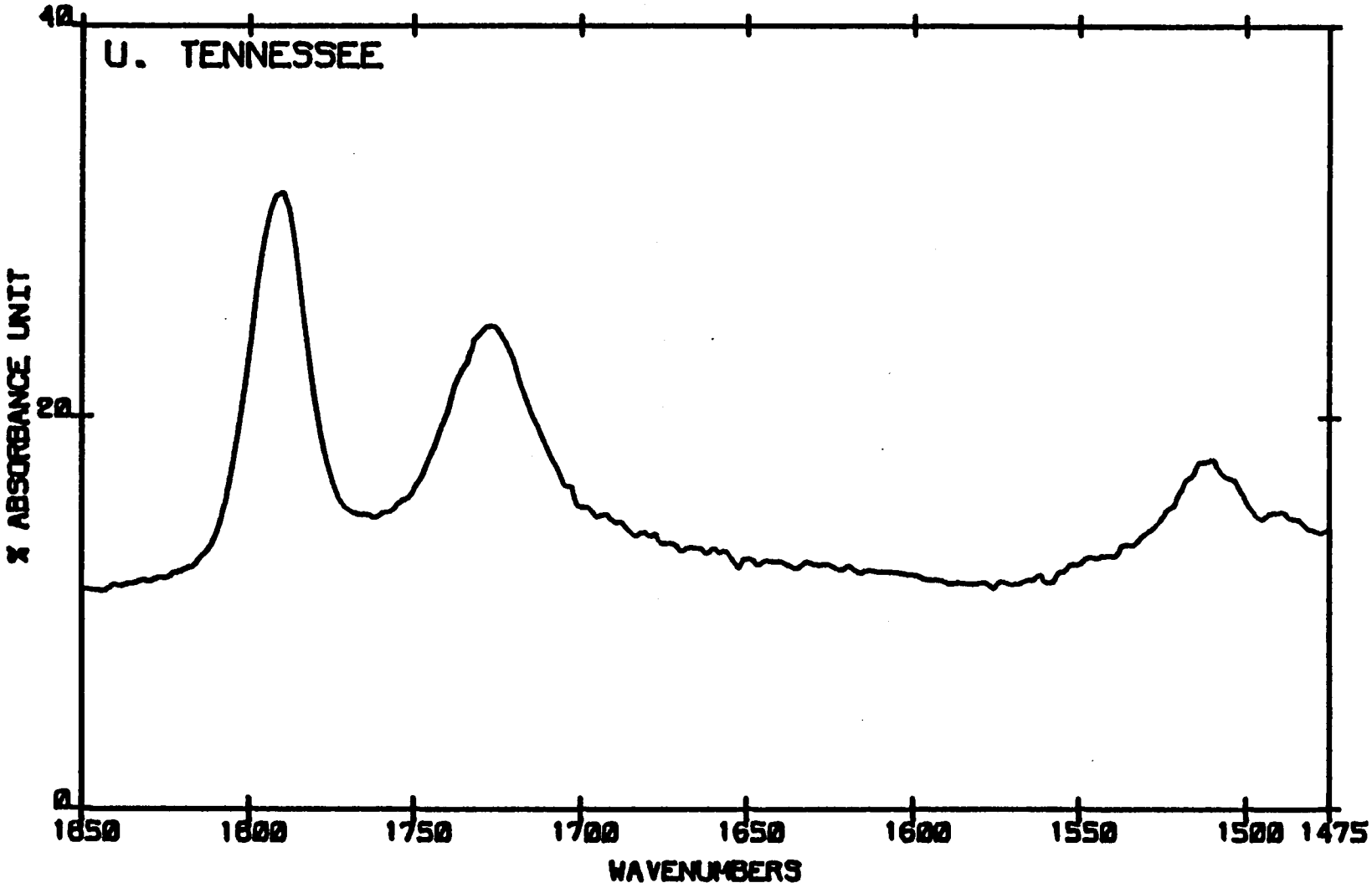
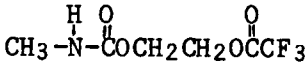


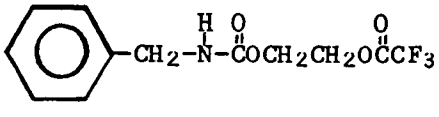
Figure 29. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Closer examination of spectrum shown in Figure 28.)

PVC film that was soaked in 80% v:v DMSO-EG for 18 hr at 60°, then subjected to the same extraction and drying procedure as used for the films reacted with potassium cyanate, produced a normal PVC internal reflection spectrum. Therefore, the OH stretch did not appear to be due to trapped ethylene glycol. This film was then soaked in trifluoroacetic anhydride under the same reaction conditions as the modified PVC film. Again, it was extracted using the same procedure. The internal reflection spectrum indicated no band at 1790 cm^{-1}. This experiment demonstrates that the extracting procedure is sound and that the hydroxyl groups on the surface modified PVC film are chemically bonded to the film. Furthermore, it demonstrates that soaking the film in the solvent mixture does not result in solvolysis of the PVC film with ethylene glycol.

To check the mole ratio of free hydroxyl groups to carbamate groups two model compounds were made, 2-(N-methyl carbamoyloxy)ethyl trifluoroacetate



and 2-(N-benzyl carbamoyloxy)ethyl trifluoroacetate



The molar absorptivity ratio ($\varepsilon_{1790}/\varepsilon_{1725}$) of these compounds was determined via transmission infrared spectroscopy to be 0.85 and 0.83 respectively at 0.1M concentration in a PVC matrix. The A_{1790}/A_{1725} value was found to vary as a function of mirror alignment of the internal reflection apparatus from 0.67 to 0.76. The theoretical A_{1790}/A_{1725} value is 0.80; thus, the mirror alignment

which gave the value 0.76 was used to calculate a $\varepsilon_{1790}/\varepsilon_{1725}$ value of 0.79. This value was used in the analytical calculations. To determine the concentration of the trifluoroacetate groups, the absorbance ratios shown in Table V were measured. For the reaction done at 130°, the absorbance ratio, A_{1790}/A_{1725}, was measured from Figure 29. For the reactions done at 60°, the absorbance of the bands at 1790 cm^{-1} was so large that there was significant overlap of this band with the band at 1725 cm^{-1} which resulted in low ratio values because of an artifically large band at 1725 cm^{-1}. Therefore, the absorbance of the carbamate band at 1719 cm^{-1} was measured before the reaction and the carbonyl of the trifluoroacetate ester at 1790 cm^{-1} after the acetylation reaction. Because of some wrinkling of the films after the acetylation reaction, the carbonyl band at 1790 cm^{-1} was normalized using the methylene band at 1424 cm^{-1}. The absorbance ratios (A_{1790}/A_{1725}) were then used to calculate the apparent concentration of the trifluoroacetate groups. If the trifluoroacetylation reaction is assumed to go to completion then the concentration of the trifluoroacetate group represents the apparent concentration of the hydroxyl groups. The data in Table V show that the apparent concentration ratios of hydroxyl groups to carbamate groups in the reacted films are greater than one. These data support the existence of solvolysis reactions between PVC and the solvent ethylene glycol.

Bentley and Schleyer[75] have shown that tosylate groups in allylic positions under a variety of conditions do solvolyze faster than simple secondary tosylate groups in protic solvents. Furthermore, it is known that isopropyl chloride does not undergo solvolysis at a

TABLE V

COMPARISON OF THE CONCENTRATIONS OF THE CARBAMATE GROUP AND THE TRIFLUOROACETATE ESTER GROUP USING INTERNAL REFLECTION SPECTROSCOPY

Reaction Time (Hours)	Reaction Temperature	Absorbance ($1790cm^{-1}$) / Absorbance ($1719cm^{-1}$)	Concentration ($1790cm^{-1}$) / Concentration ($1725cm^{-1}$)	Concentration of trifluoroacetate group, Molarity
0.25	130°	1.56	2.00	
9.0	60°	5.55	7.02	0.56
12.0	60°	5.90	7.47	0.724
18.0	60°	7.21	9.13	1.24

a. All temperature measurements $\pm$ 1°.

b. Absorbance measurements are not absolute.

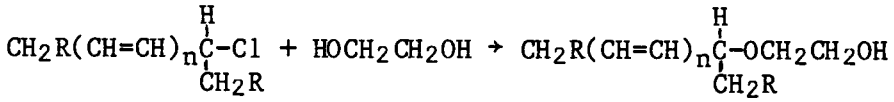
measureable rate in pure ethanol at 44.6° but 3-chloro-1-butene does. Caraculârcu[62] has shown that phenol will solvolyze allylic type chlorine atoms in PVC. Finally, Suzaki[76] obtains solvolytic displacement reactions on PVC in 50 vol % ethanol/water. At 130° after 10 hr he obtains one hydroxyl group and one ether group per 1000 repeat units while measuring a hydrogen chloride loss of 0.80 mg/g PVC/hr. The experimental evidence and the literature support a solvolytic displacement reaction between the allylic type chlorine atoms on PVC film's surface and ethylene glycol:

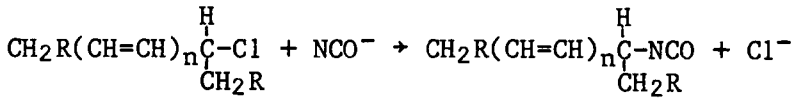
$$\text{CHR=CH-}\underset{\text{Cl}}{\text{CH}}\text{-CH}_2\sim \xrightarrow{\text{HOCH}_2\text{CH}_2\text{OH}} \text{CHR=CH-}\underset{\text{OCH}_2\text{CH}_2\text{OH}}{\text{CH}}\text{-CH}_2\sim$$

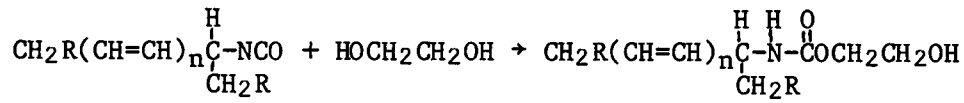
As discussed earlier, hydroxyethyl carbamate is a proposed side product formed in the presence of a large excess of ethylene glycol; as a result, the side reaction below will be minimized

$$\text{CHR=CH-}\underset{\text{Cl}}{\text{CH}}\text{-CH}_2\sim + \text{HOCH}_2\text{CH}_2\text{O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-NH}_2 \rightarrow \text{CHR=CH-}\underset{\text{OCH}_2\text{CH}_2\text{OCNH}_2}{\text{CH}}\text{-CH}_2\sim \overset{\overset{\text{O}}{\|}}{}$$

in favor of the solvolysis reaction between the allylic chloride and ethylene glycol. The data show that the amount of substitution which occurs for the reaction run at 60° is proportional to the amount of elimination. The proposed pathways are shown below:







After the formation of allylic chloride on the surface of PVC, the predominant reactions are simultaneous solvolysis reaction between the allylic chlorides and ethylene glycol, and S_n1 reactions between the allylic chlorides and cyanate anion with subsequent formation of the surface modified 2-hydroxethyl N-PVC carbamate.

In summary, the cyanate anion reacts with PVC film in the presence of ethylene glycol to make the surface modified PVC, 2-hydroxyethyl N-PVC carbamate, and the 2-hydroxyethyl ether. For the reactions carried out at 60°, the ratio of solvolysis to carbamate formation is greater than 7:1 and the depth of reaction about 1 μ. For the 130° reaction the amount of solvolysis is reduced but the depth of reaction is greatly increased. Dehydrochlorination is a competing reaction which gives a polyene system that can undergo addition reactions with chlorine in high yield (>99%) to produce a colorless film.

C. EXPERIMENTAL PROCEDURES

Reaction of PVC with KNCO: A weighed amount of PVC film (two films - each 2.0 x 4.0 cm x 50 μ and weighing about 0.06 g), was placed on a glass screen and held in place by a glass weight. To a 250 ml beaker equipped with a magnetic stirrer, larger stopper, gas inlet and

outlet was added 0.297 g (3.66 mmoles) of potassium cyanate in 25 ml of 80% v:v DMSO-EG. After the potassium cyanate was dissolved, the magnetic stirrer was removed. The gas outlet was then attached to an oil bubbler and the reaction vessel flushed with dried argon gas for 15 min. The flask was lowered into an oil bath and the reaction mixture brought up to reaction temperature (±1°). The film was then lowered with a glass dipper into the reaction medium. After the rection, the reaction vessel was cooled for 5 min and the film was removed. The film was washed once for 5 min then for 15 min in 50 ml of 50% v:v DMSO-methanol. The film was then gradually deswollen by the addition of methanol and extracted in a soxhlet extractor with methanol under argon for 18 hr. After the extraction the film was vacuum dried at 47° for 24 hr.

Trifluoroacetylation: The modified films were placed on a glass screen inside a cylindrical pyrex vessel, 4.5 in x 2 in outer diameter, equipped with a 65/40 ground glass joint. The reaction vessel was evacuated and argon gas introduced into the vessel to bring it to atmospheric pressure. Into the reaction vessel was syringed 50 ml of anhydrous diethyl ether. While the ether was magnetically stirred, 1.8 ml of trifluoroacetic anhydride was syringed into the ether at room temperature and the reaction continued for 30 min. After the reaction, the films were removed, washed in diethyl ether for 5 min, then extracted with diethyl ether from a bed of calcium hydride in a soxhlet extractor under argon for 18 hr. The films were then removed and vacuum dried at 47° for 24 hr.

Ethyl-N-benzylcarbamate: A slurry composed of 12.1 g (150 mmole) of KNCO, 7.8 g (170 mmole) of ethanol, and 80 ml of dimethyl formamide

was heated at 100° in a 250 ml round bottom flask equipped with a condenser and mechanical stirrer. Benzyl chloride (12.7 g, 100 mmole) in 10 ml of dimethyl formamide was added dropwise and the reaction mixture heated an additional 6 hr. The salts were collected by filtration and the liquid residue vacuum distilled at 45° (0.5mm) to remove the solvent. The product was then vacuum distilled at 90° (0.5 mm) and crystallized from petroleum ether (boiling fraction 30-60°) then vacuum dried at 35° for 24 hr. This gave a yield of 56%, IR, Figure 30; NMR, Figure 31, m.p. 40-42°, literature[28], 41.5-42°.

2-Hydroxyethyl N-benzylcarbamate: A slurry composed of 12.1 g (150 mmole) of KNCO, 11.3 ml (200 mmole) of ethylene glycol and 80 ml of dimethyl formamide was heated at 100° in a 250 ml round bottom flask equipped with a condenser and mechanical stirrer. Benzyl chloride (12.7 g, 100 mmole) in 10 ml of dimethyl formamide was added dropwise for 2 hr, then the mixture heated an additional 6 hr. After the reaction the solvent was vacuum distilled. The procedure left an oil and white solid in the reaction flask. The oil was washed from the white solid with diethyl ether and the ether evaporated to give crude 2-hydroxyethyl N-benzylcarbamate, 6.8 g. The crude product was chromatographed on 400 g of alumina (activity IV). The column chromotography was monitored using thin layer chromotography (iodine vapor developer). The chloroform was removed with a rotary evaporator. The product 2-hydroxyethyl N-benzylcarbamate was then crystallized from petroleum ether (boiling fraction 30-60°) to give 4.40 g of product, 22.8% yield, IR, Figure 32; NMR, Figure 33; m.p. 40-42°; literature[77] m.p. 42°.

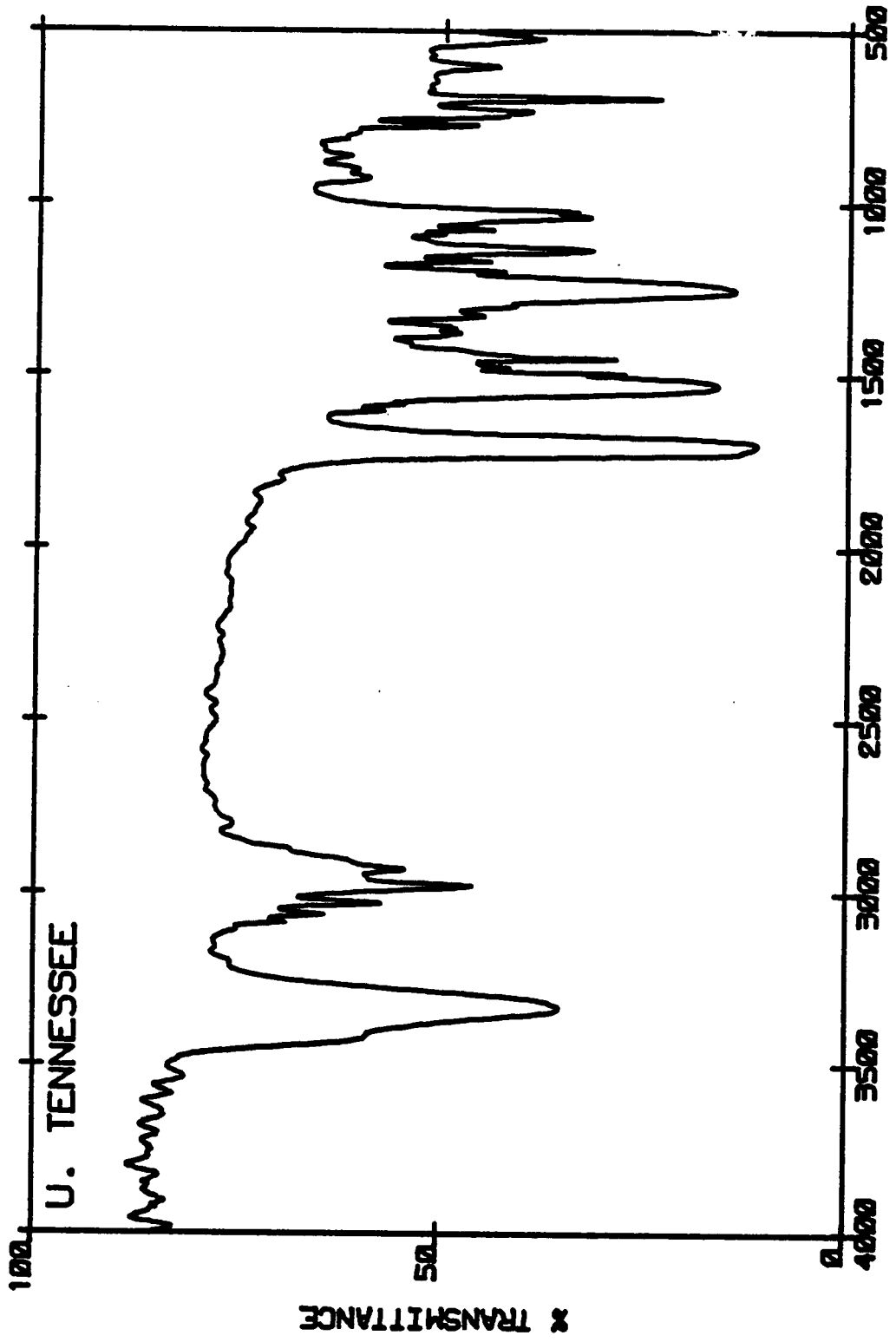


Figure 30. Transmission IR spectrum of ethyl N-benzyl carbamate taken neat in the melt.

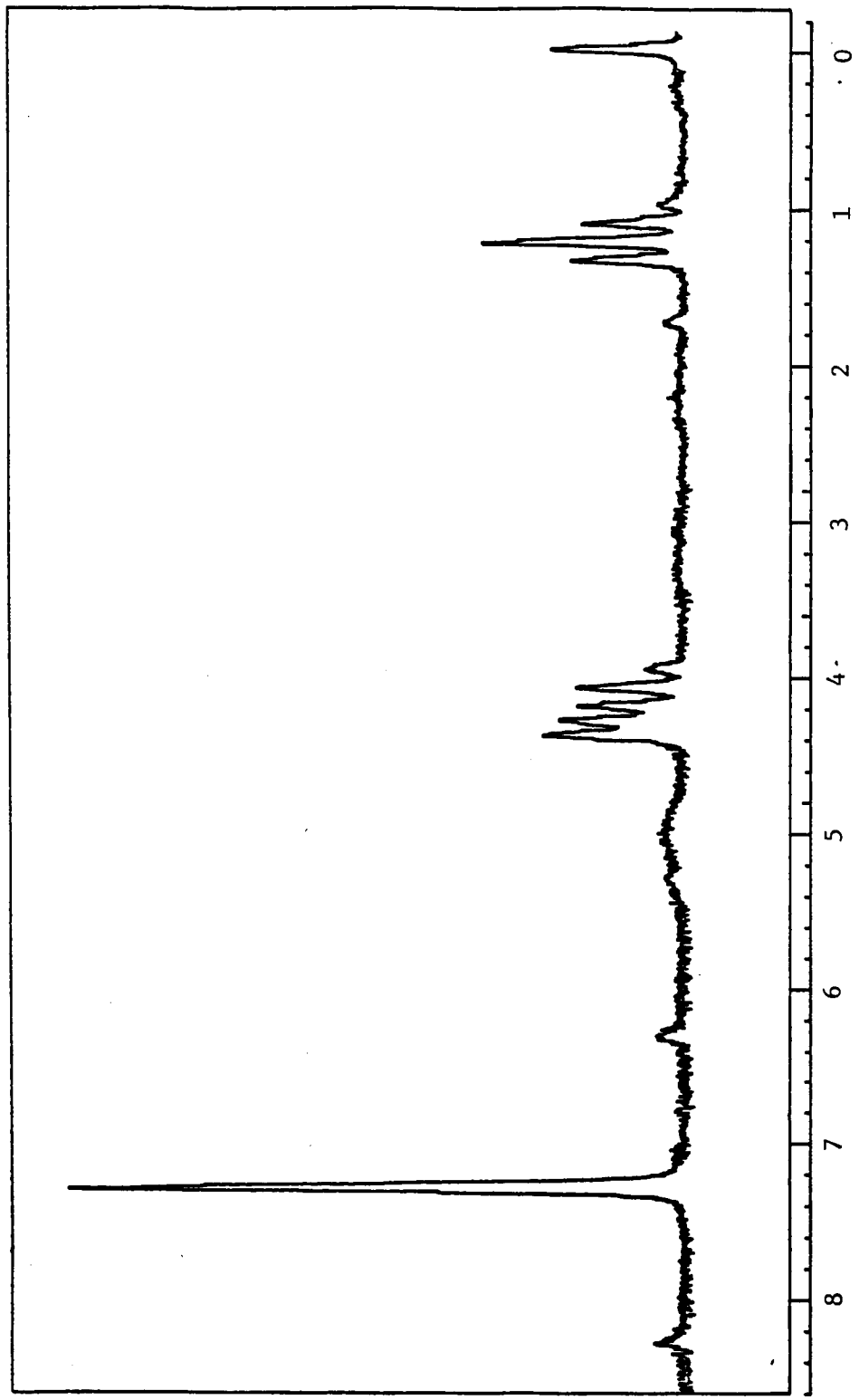


Figure 31. NMR spectrum of ethyl N-benzyl carbamate taken in $CDCl_3$, 1% TMS.

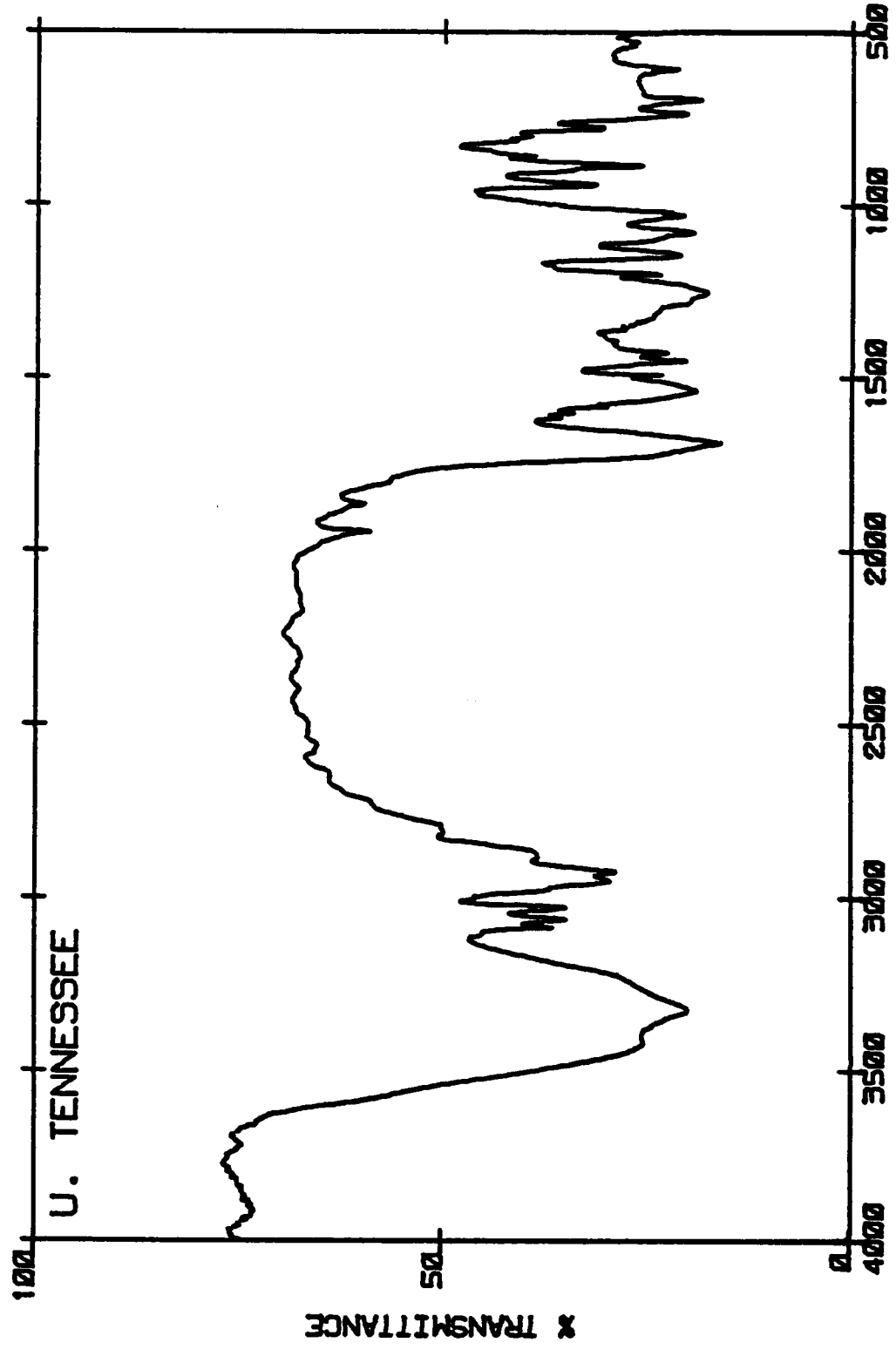


Figure 32. Transmission IR spectrum of 2-hydroxyethyl N-benzyl carbamate taken neat in the melt.

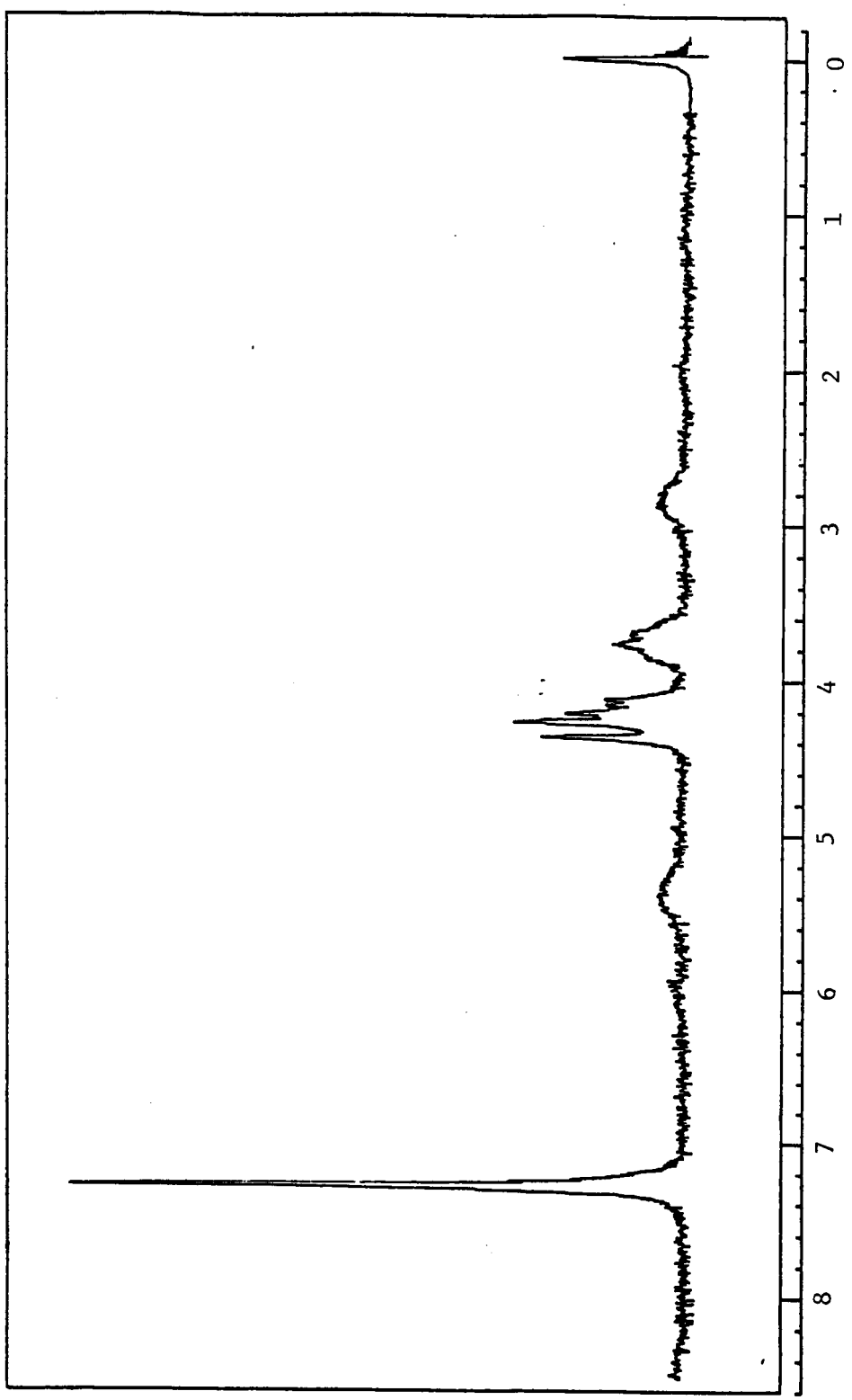


Figure 33. NMR spectrum of 2-hydroxyethyl N-benzyl carbamate taken in $CDCl_3$, 1% TMS.

The white powder in the reaction pot was dissolved in chloroform and the salts again filtered from the chloroform solution. After removing the chloroform with a rotary evaporator, a white powder identified as ethylene bis(N-benzylcarbamate) was then crystallized from petroleum ether (boiling fraction 30-60°), which gave 2.64 g of product, m.p. 138-140°. This powder was then washed 4 times with boiling petroleum ether (30-60°), the solvent decanted and the white residue crystallized from a 1:1 volume of chloroform and acetone to give 1.42 g of the carbamate, NMR, Figure 34; m.p. 152-153.5°; literature,[78] 151-152°; literature,[79] 158-160°.

2-(N-methyl carbamoyloxy)ethyl trifluoroacetate: To a 25 ml round bottom flask fitted with a reflux condenser was added 0.70 g (5.1 mmoles) of sodium trifluoroacetate, 5.6 ml (34 mmoles) of trifluoroacetic anhydride and 1.19 g (10 mmoles) of 2-hydroxyethyl-N-methyl carbamate (IR, Figure 35). The reaction mixture was refluxed for 15 min, and the trifluoroacetic anhydride and trifluoroacetic acid removed by adding 10 ml of dried carbon tetrachloride to the reaction mixture and distilling under reduced pressure at 50° four times. The product was vacuum distilled at 64° (0.5 mm) to get 1.10 g of product, yield 54.2%, IR, Figure 36; NMR, Figure 37; procedure.[80]

2-(N-benzylcarbamoyloxy)ethyl trifluoroacetate: To a 25 ml round bottom flask fitted with a refluxing condenser, magnetic stirrer, was added 0.500 g (2.56 mmole) of 2-hydroxyethyl N-benzyl carbamate, 0.183 g (1.34 mmole) of sodium trifluoroacetate and 2.0 ml (3.55 mmole) of trifluoacetic anhydride. The reaction solution was magnetically stirred for 1 hr under reflux. After the reaction, 20 ml of dry carbon tetrachloride was added to the reaction solution. The salts were

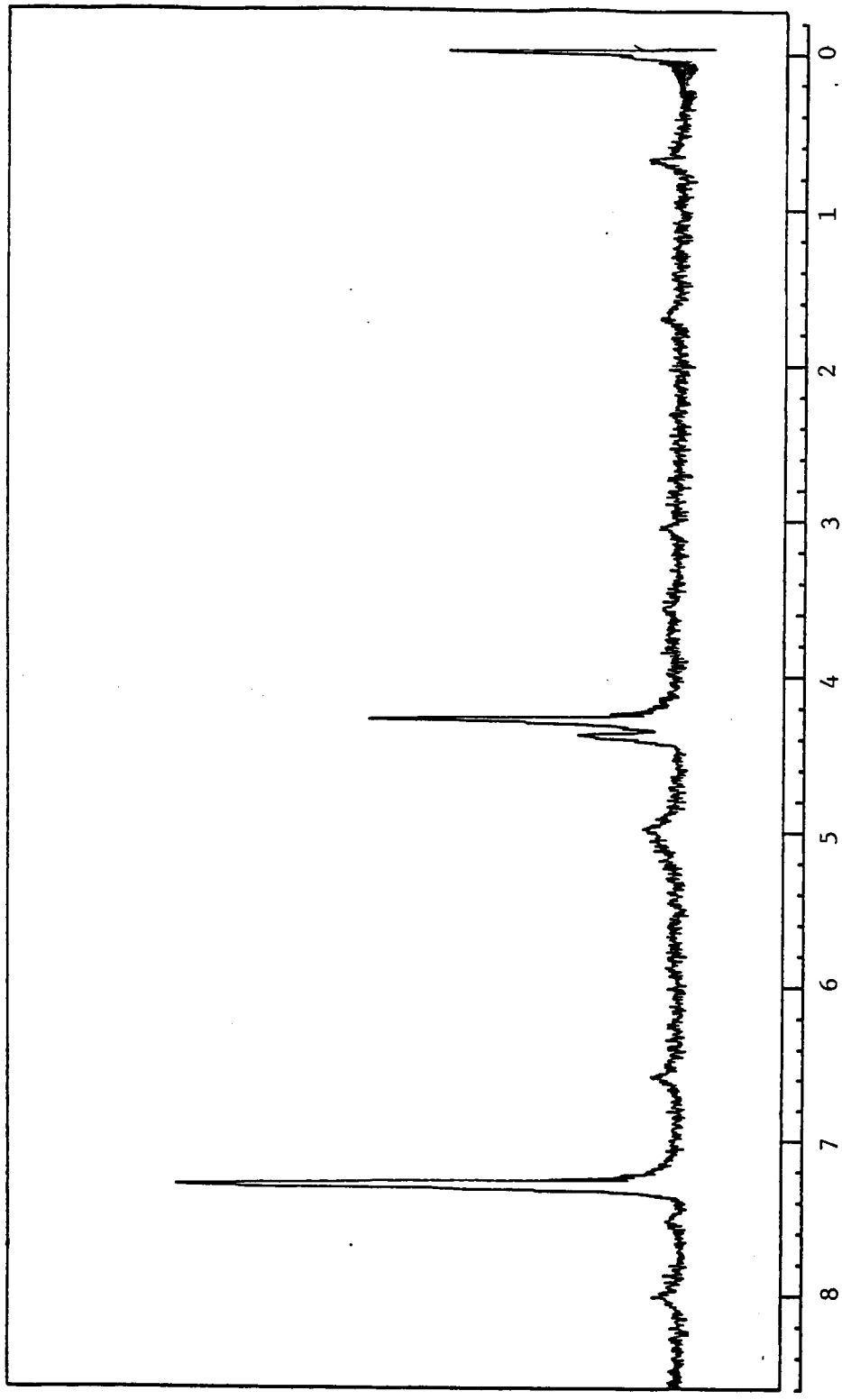


Figure 34. NMR spectrum of ethylene bis(N-phenyl carbamate) taken in $CDCl_3$, 1% TMS.

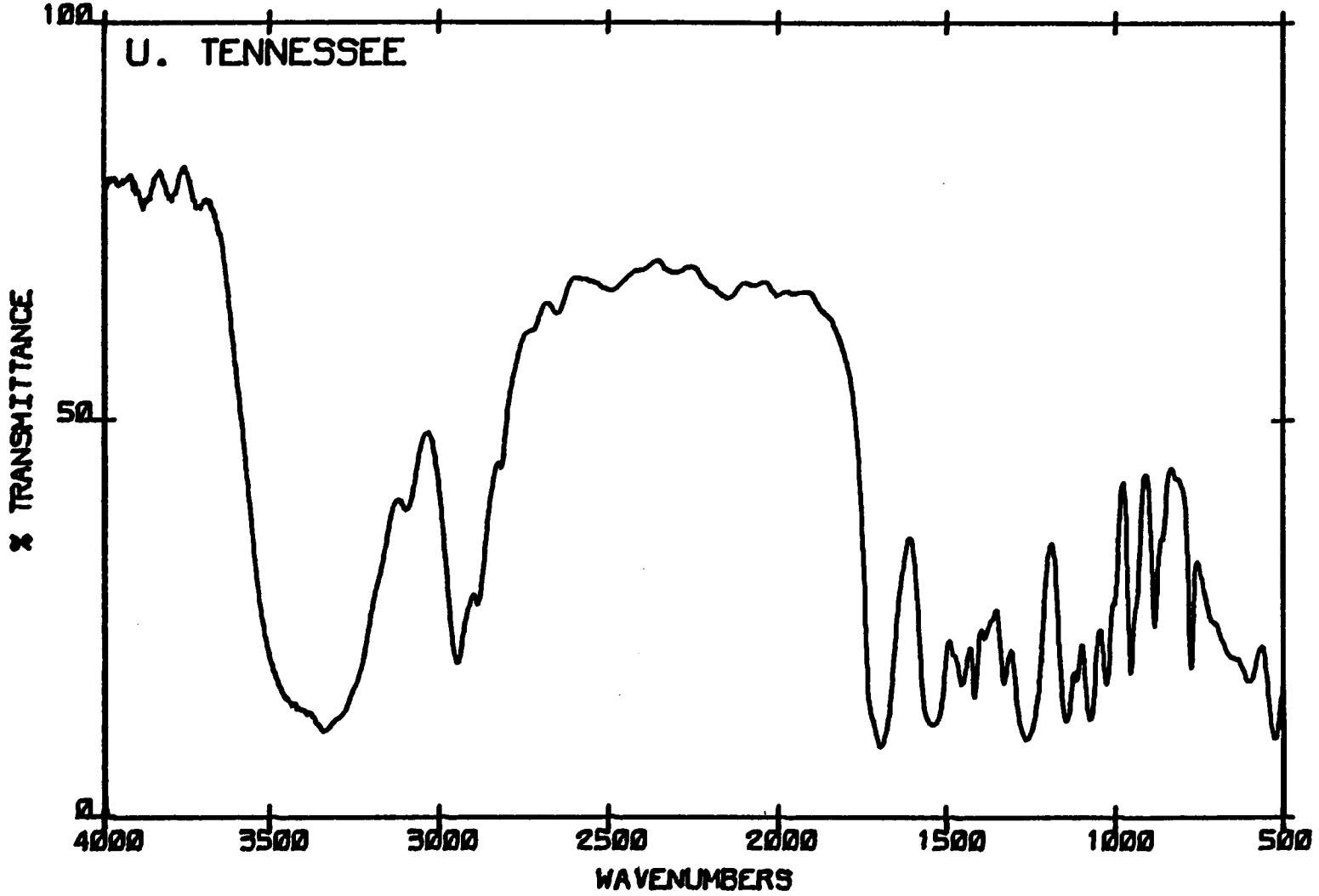


Figure 35. Transmission-IR spectrum of 2-hydroxyethyl N-methyl carbamate taken neat.

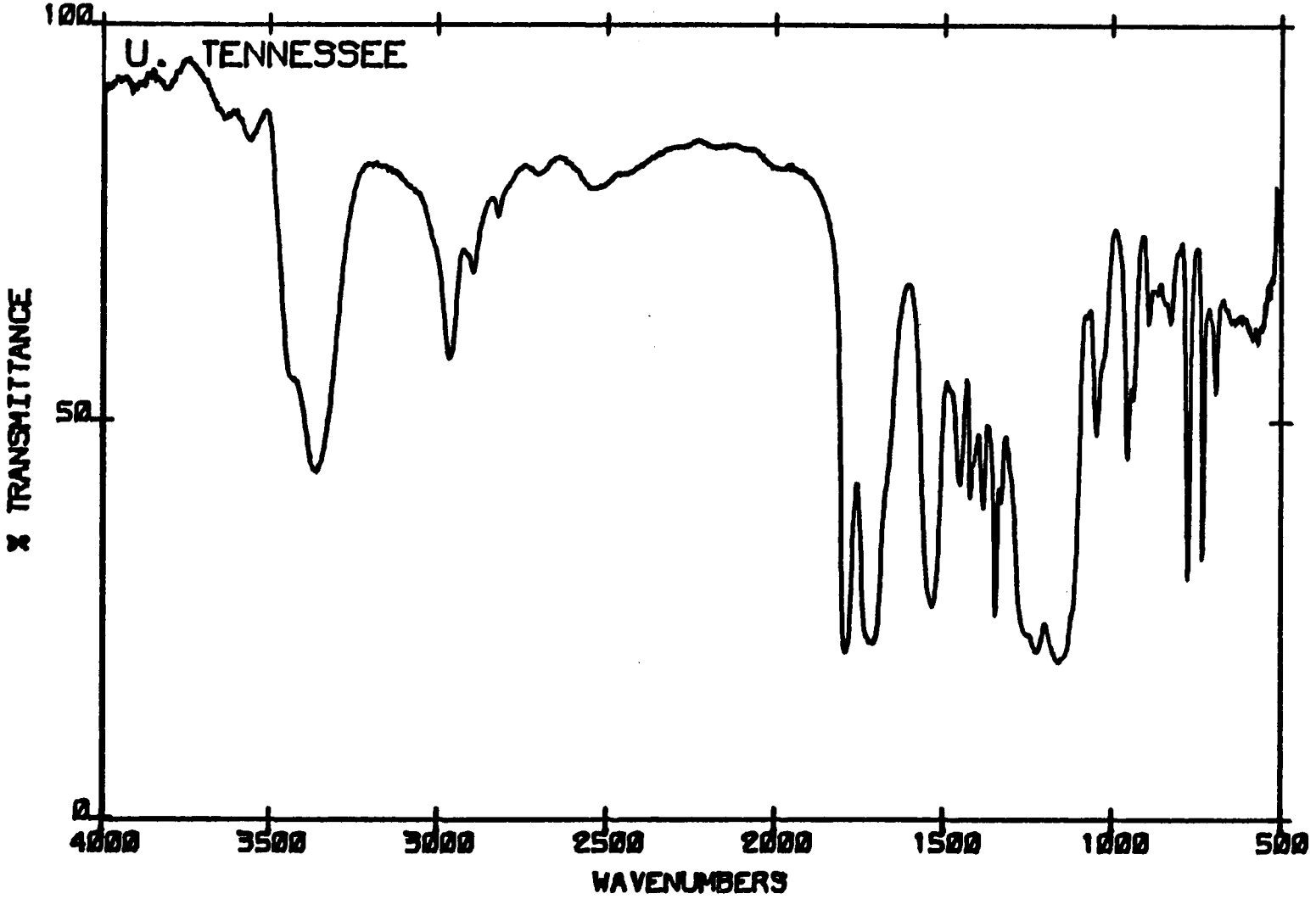


Figure 36. Transmission IR spectrum of 2-(N-methyl carbamoyloxy)ethyl trifluoroacetate taken neat.

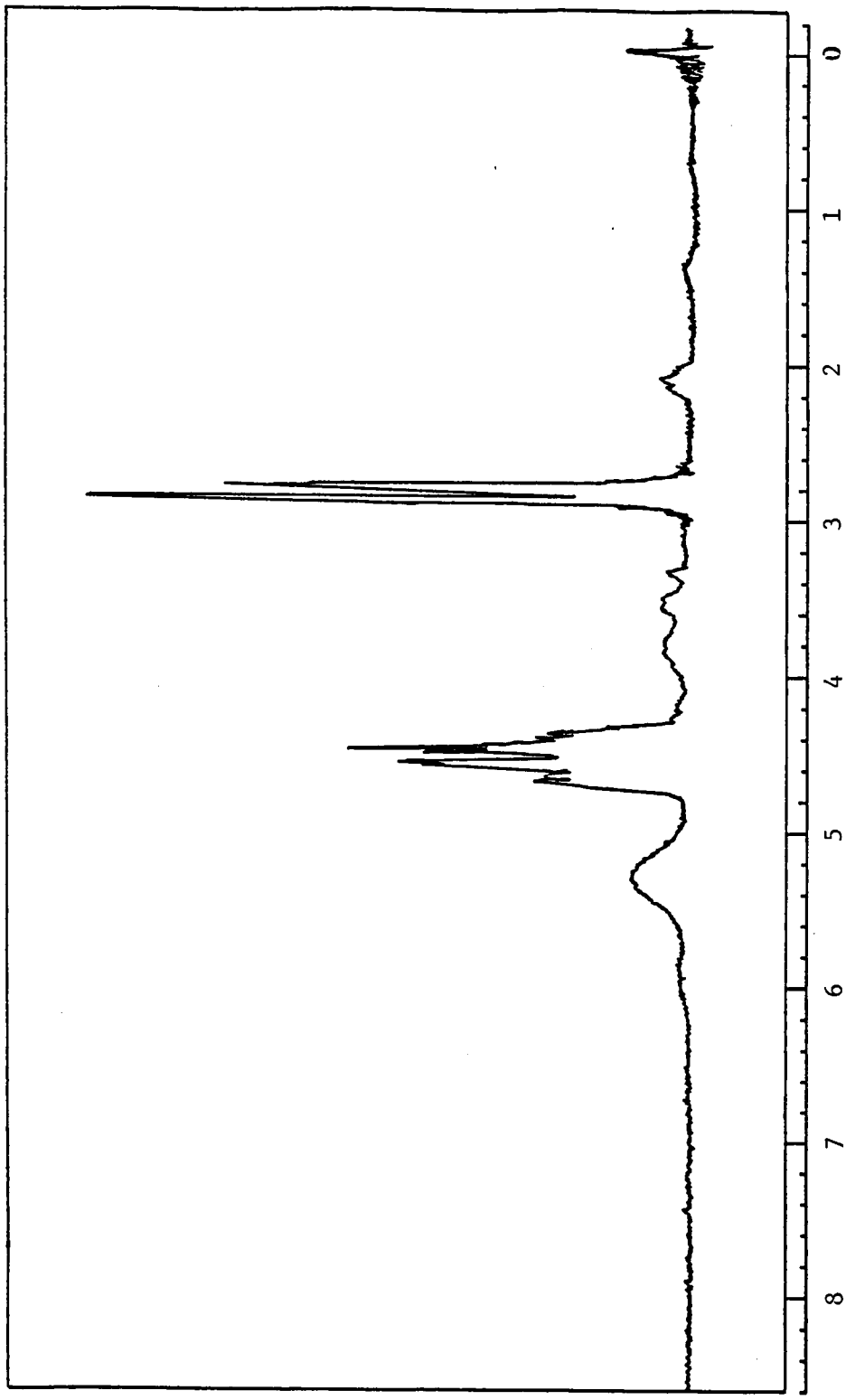


Figure 37. NMR spectrum of 2-(N-methyl carbamoyloxy)ethyl trifluoroacetate taken in $CDCl_3$, 1% TMS.

filtered from the reaction solution and the carbon tetrachloride, trifluoroacetic acid, and trifluoroacetic anhydride were removed from the carbamate under vacuum (0.1 mm) at 25°. Carbon tetrachloride (200 ml) was added and the procedure repeated again. After about a week, starting material was filtered from the clear liquid to give 0.62 g of product, yield 84%; IR, Figure 38; NMR, Figure 39; procedure,[80] m.p. 11-12°.

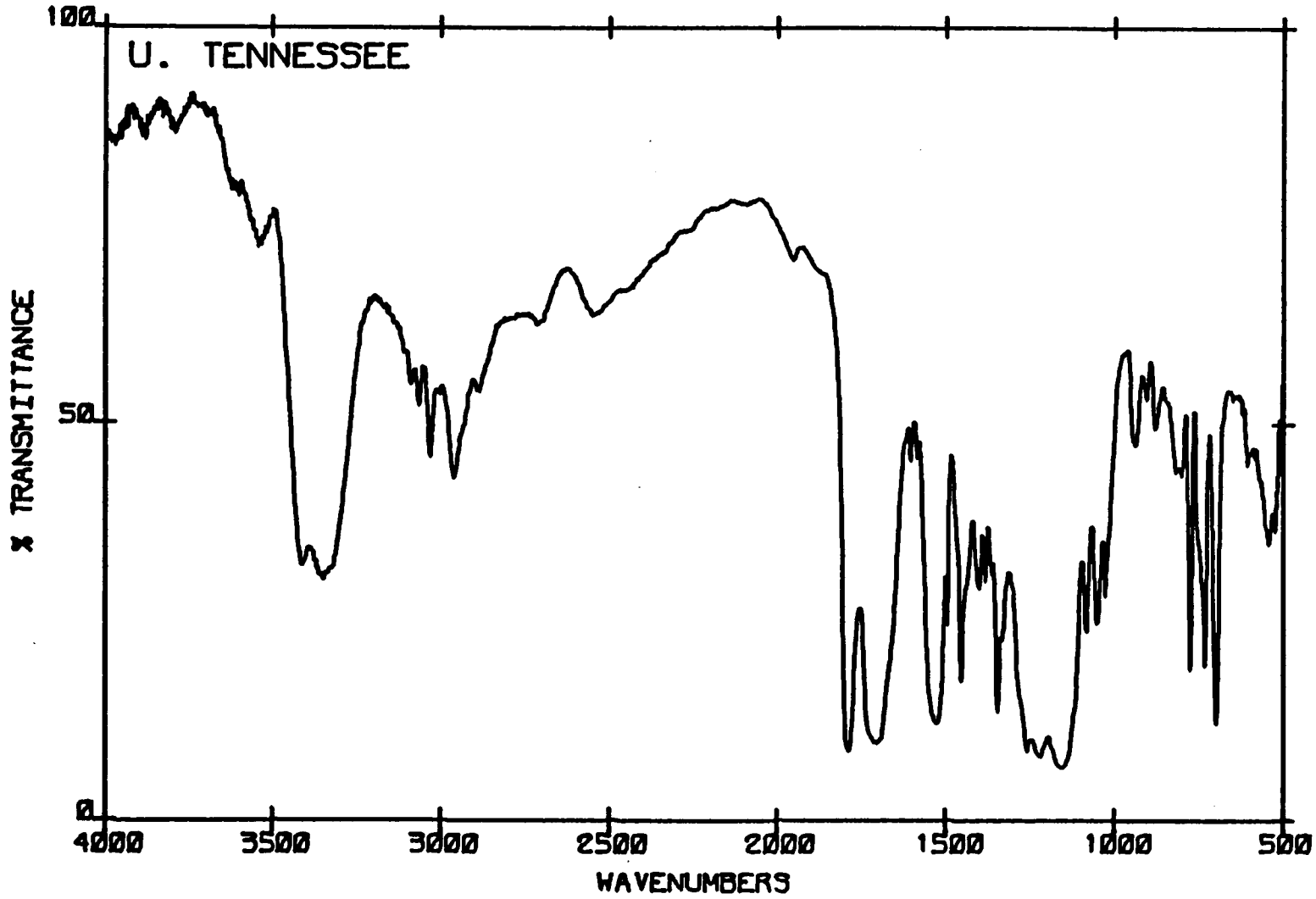


Figure 38. Transmission IR spectrum of 2-(N-benzyl carbamoyloxy)ethyl trifluoroacetate taken neat.

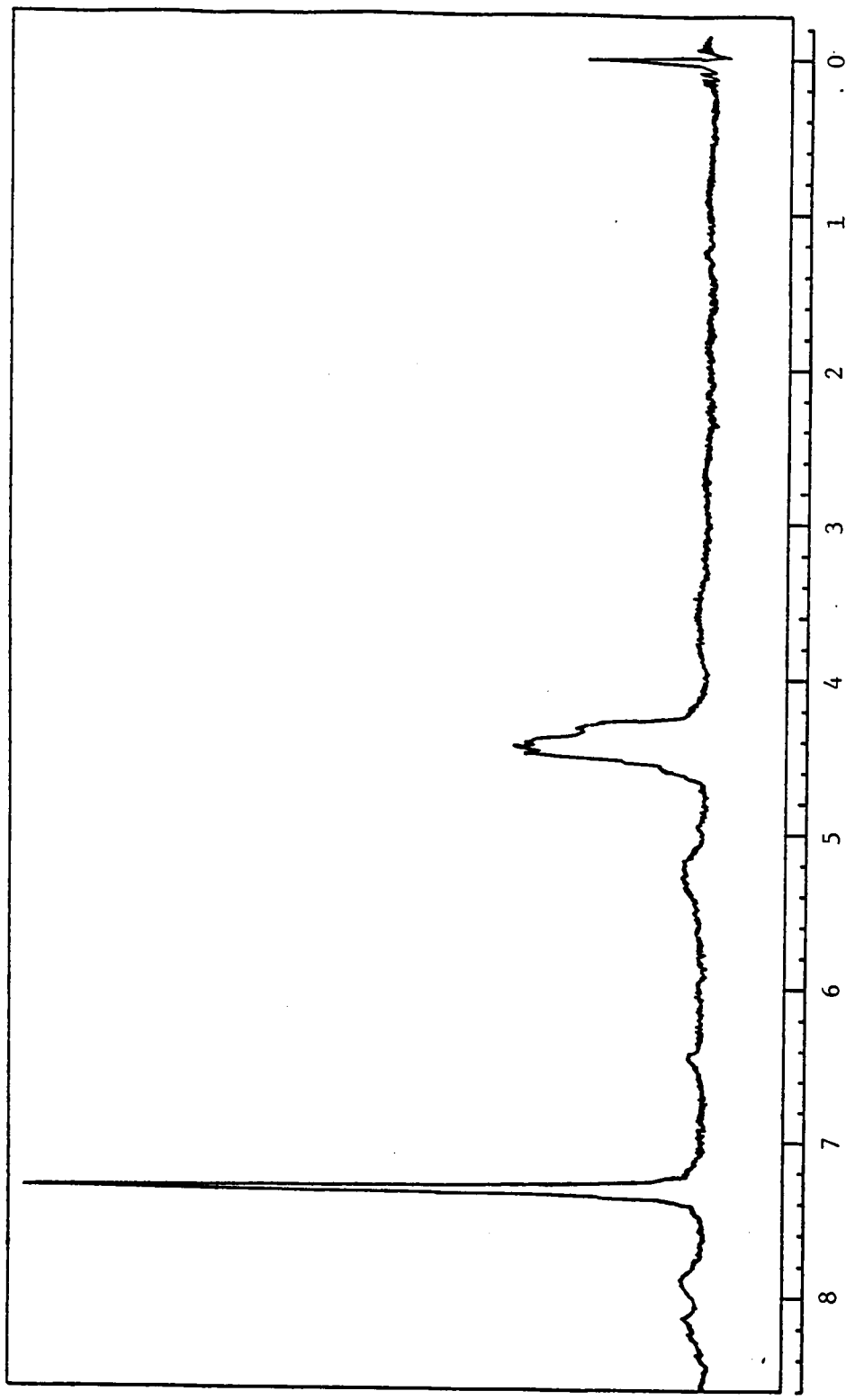


Figure 39. NMR spectrum of 2-(N-benzyl carbamoyloxy)ethyl trifluoroacetate taken in $CDCl_3$, 1% TMS.

CHAPTER IV

INCORPORATION OF ISOCYANATE GROUPS ON THE SURFACE OF POLY(VINYL CHLORIDE) BY ELIMINATION-ADDITION REACTION SEQUENCE

A. INTRODUCTION AND BACKGROUND

As shown in Chapter II, incorporation of isolated isocyanate groups directly on PVC's surface is not possible due to the polymerization of the isocyanate groups which is initiated by the cyanate anion. Chapter III shows that the isocyanate groups can be trapped as their carbamate derivatives by reaction with ethylene glycol. Solvolysis and elimination were competing reactions. This chapter will show that the elimination of HCl from PVC can be used to advantage by using addition reactions across the polyene system to incorporate isolated isocyanate groups on the surface of PVC.

B. RESULTS AND DISCUSSION

The dehydrochlorination of PVC's surface was accomplished using the strong base, sodium methoxide (25% by weight of sodium methoxide in methanol) in dimethyl sulfoxide. It is well known that dimethyl sulfoxide increases the basicity of bases resulting in faster elimination reactions.[81,82,83,84,85,86] The methanol was necessary to prevent dissolution of the polymer in dimethyl sulfoxide. For PVC films exposed to a solution consisting of 50% by volume of dimethyl sulfoxide, the reaction proceeded smoothly at 23°. Figure 40 shows the ATR-IR absorbance of the carbon hydrogen sp^2-s stretch at 3015 cm^{-1} as a function of time. After 30 min, the amount of elimination is directly proportional to time.

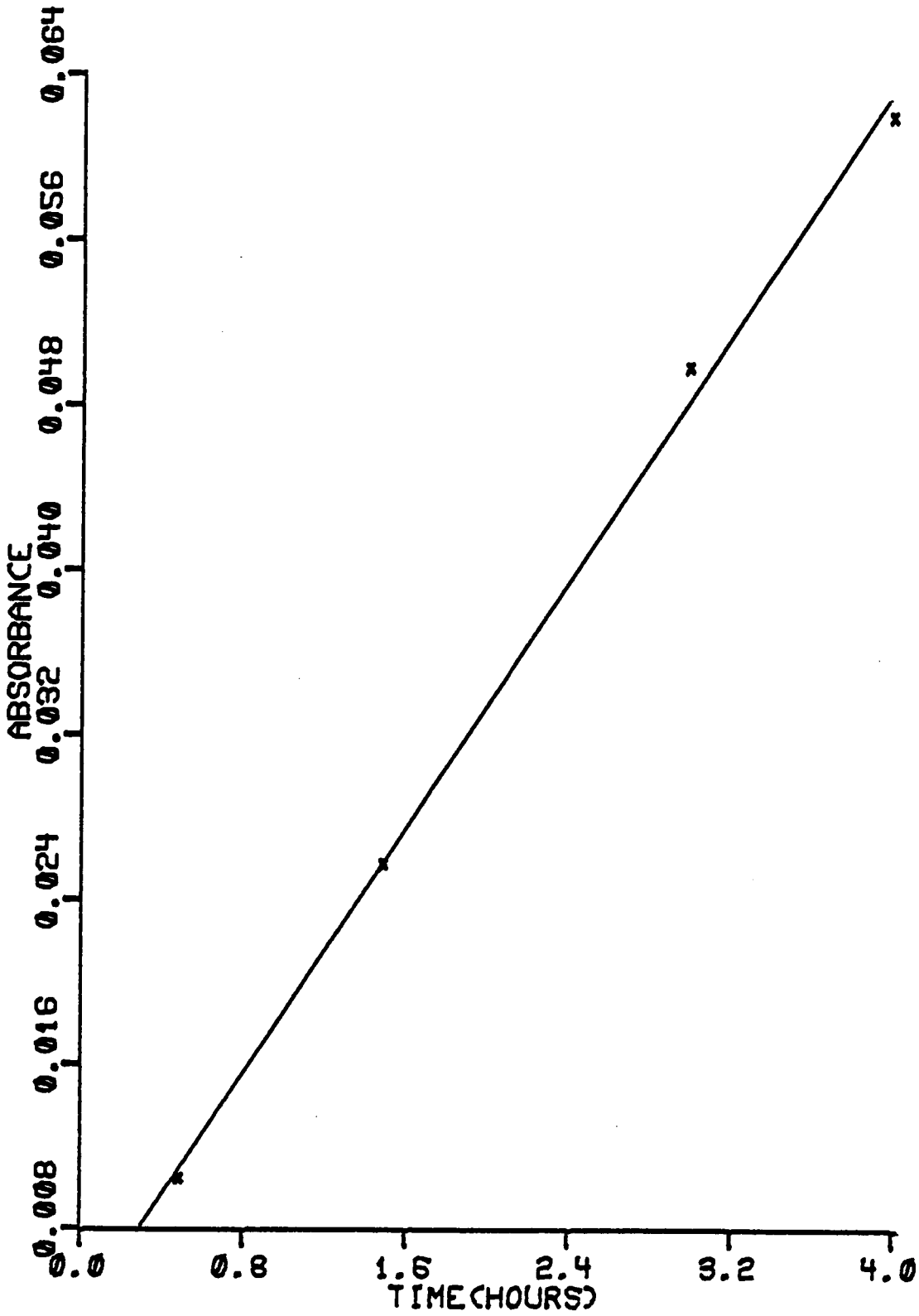


Figure 40. ATR-IR absorbances of the sp^2-s carbon-hydrogen bands at 3015 cm^{-1} taken as a function of reaction time at 45 degree angle of incidence (N=20).

Each eliminated PVC film in Figure 40 (p 95) was microtomed on its edge in epoxy, then photographed at 1000x. The depth of elimination was then calculated by projecting its image via a slide on a white screen and measuring the depth of the colored polyene system into the bulk of the film. From the known thicknesses of the films obtained from near infrared fringe measurement, the depth of reaction was calculated. Figure 41 shows the depth so determined as a function of reaction time. Note that at 5 hr, the depth of elimination is less than in the preceeding films. All films previous to the 5 hr reaction had no measurable weight loss and their reaction medium was clear after the reaction. The film reacted for 5 hr had a measurable weight loss, and the reaction medium had a slight brown color; thus, the surface of this film was beginning to dissolve away.

Figure 42 shows the ATR-IR of modified PVC film after 30 min of reaction time in the basic methanol solution. The presence of a band at 1672 cm^{-1} and a broad band between 1650 cm^{-1} and 1470 cm^{-1} indicates conjugated double bonds of various lengths. Figure 43 shows the difference spectrum of the modified PVC film minus the unreacted PVC film. Note absorptions at 1008 cm^{-1} and 1135 cm^{-1} which indicate a trans conjugated double bond[69] system and methyl ether linkages,[87] respectively. The methyl ether linkage results either from substitution of methoxide ion during the elimination, or from a solvolysis reaction between the allylic chlorides and methanol during the extraction of the film after the elimination reaction. A band characteristic of an α-chlorine atom in an olefin but of unknown origin is present at 1250 cm^{-1}.[88]

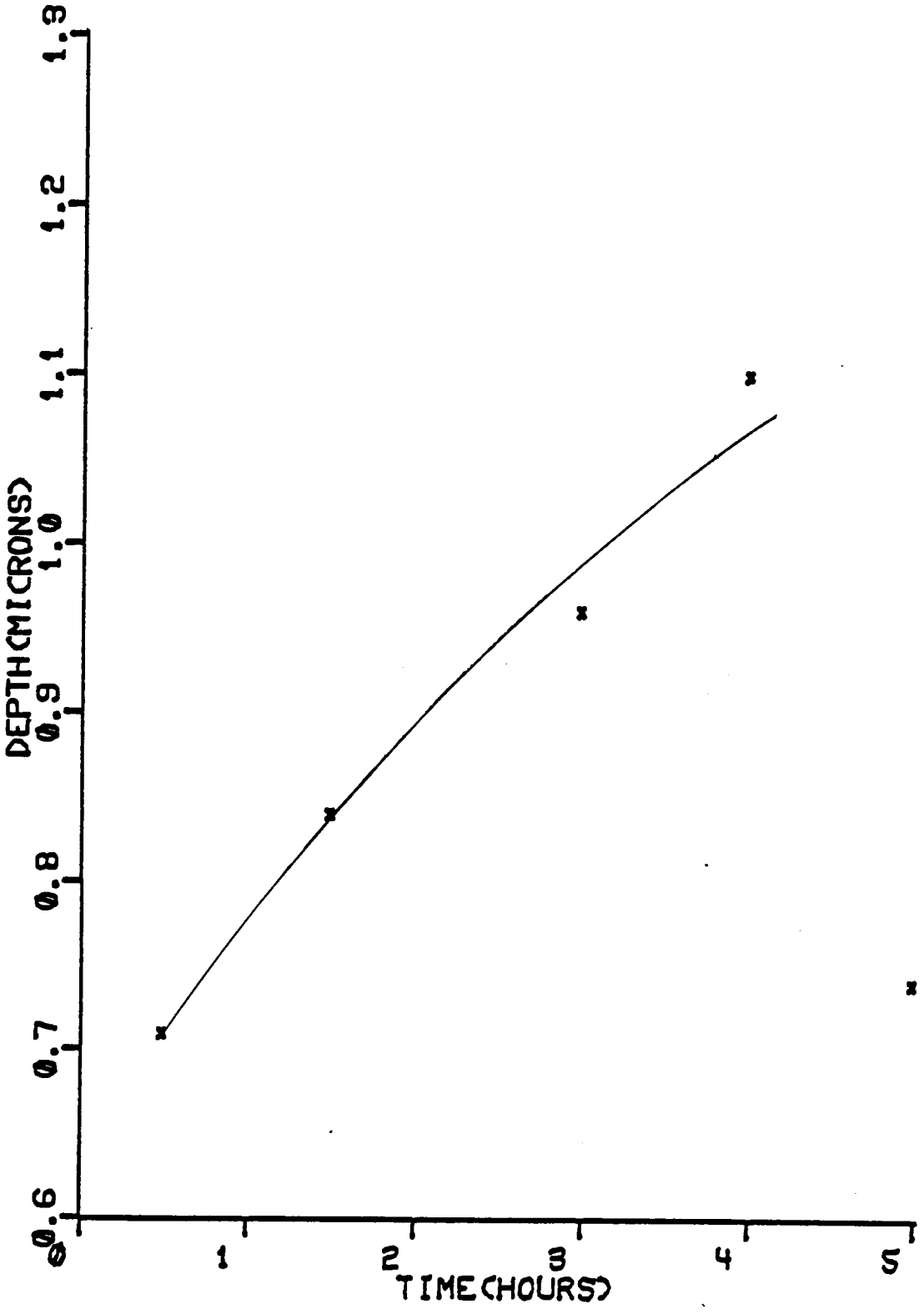


Figure 41. Depth of elimination of HCl from PVC's surface as a function of reaction time.

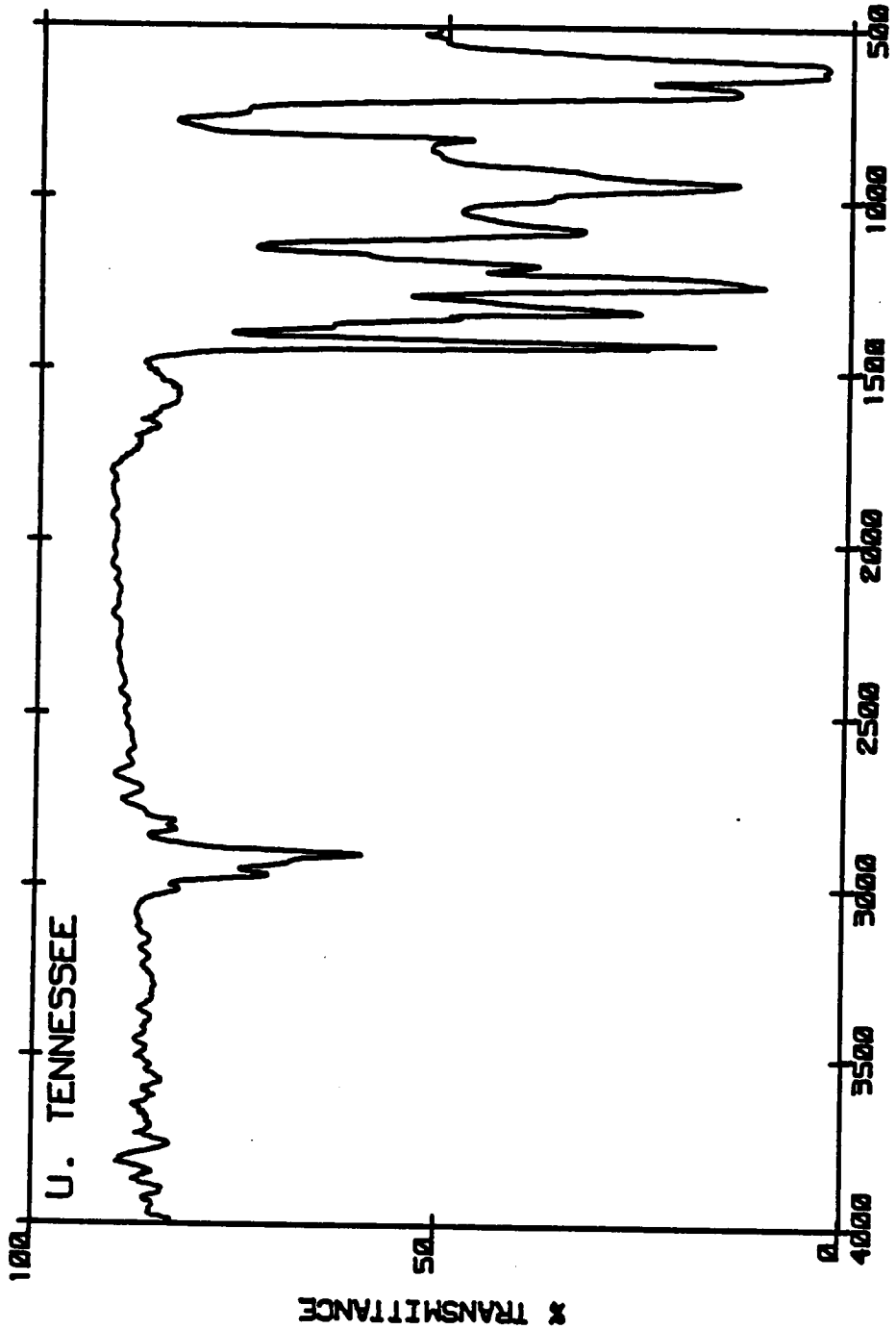


Figure 42. ATR-IR spectrum of surface dehydrochlorinated PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions: sodium methoxide, 25% by weight in methanol; solvent; 50% v:v DMSO-basic methanol solution; reaction temperature, 23°; reaction time, 30 min.)

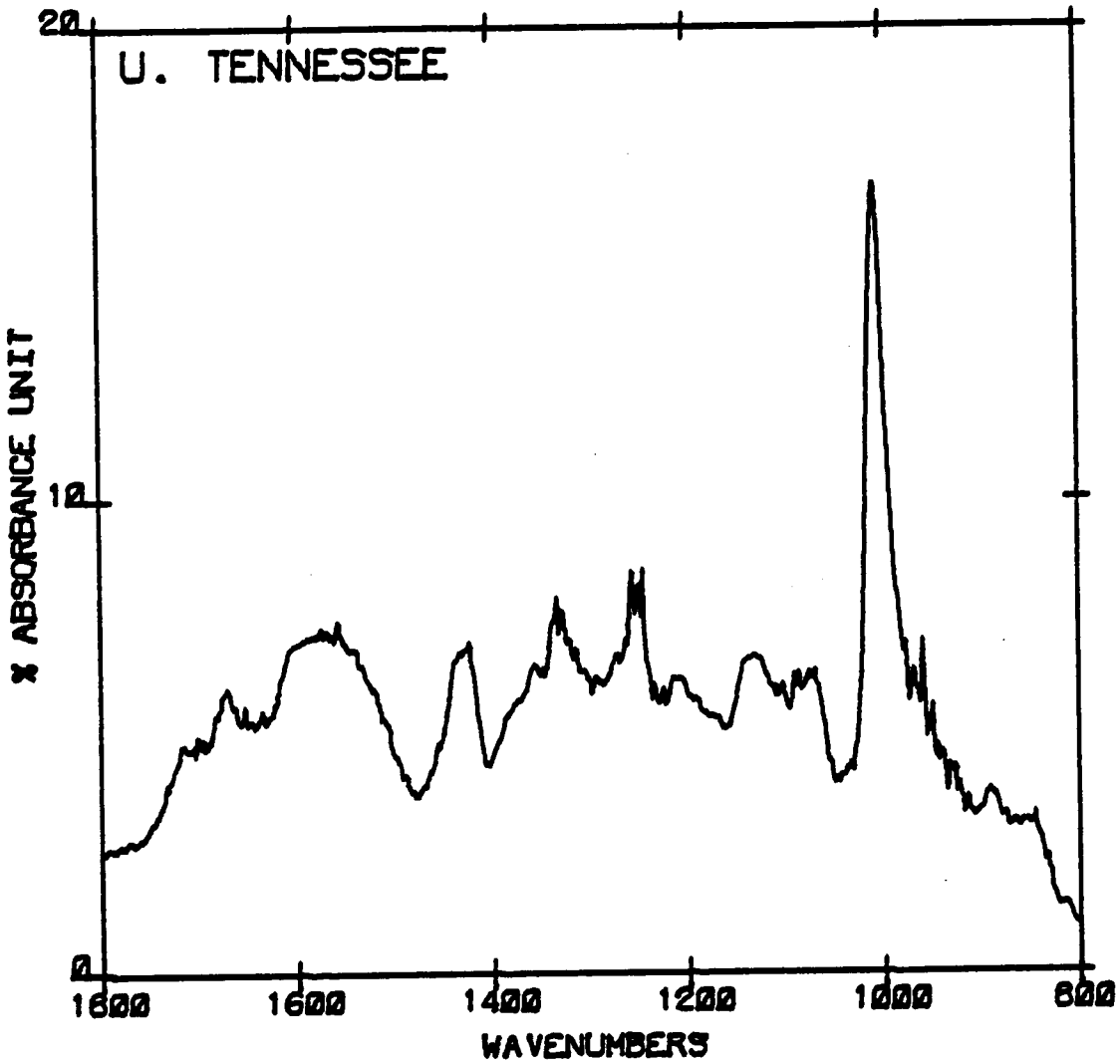


Figure 43. ATR-IR difference spectrum of modified PVC minus PVC.

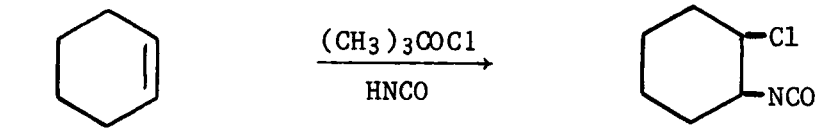
To obtain the most surface-like reaction, the PVC film that had been reacted with sodium methoxide for 30 min was used. To incorporate the isocyanate group across the double bonds, isocyanic acid was considered; for example, vinyl butyl ether adds the isocyanic acid to give the isocyanate in 90% yield:[89]

$$CH_3(CH_2)_3\text{-}O\text{-}CH{=}CH_2 \xrightarrow{HNCO,H^+} CH_3(CH_2)_3\text{-}O\text{-}\underset{\displaystyle NCO}{\underset{|}{CH}}\text{-}CH_3$$

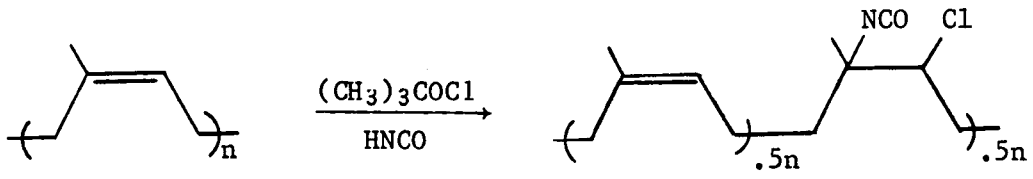
However, isobutylene adds isocyanic acid to form the t-butyl isocyanate in only 10% yield:[90]

$$CH_2{=}C(CH_3)_2 \xrightarrow{HNCO,H^+} CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}(CH_3)\text{-}NCO$$

Harper, Laurel, and Thomas[91] have shown that cyclohexene adds isocyanic acid across its double bond in the presence of t-butyl hypochlorite to form the 2-chlorocyclohexyl isocyanate in 80% yield:



Harper, Laurel and Daniels[92] have shown that a solution of cis-isoprene in chloroform will undergo the above reaction to form the modified polymer:



In this thesis work, the above reaction was used on dehydrochlorinated PVC. The slow addition (in the dark) of t-butyl

hypochlorite in chloroform to a solution of 2M-4M isocyanic acid in chloroform at 0° containing the eliminated film resulted in the placement of isocyanate groups on the surface of PVC. Figures 44 and 45 show the resulting ATR-IR and transmission IR spectra of the colorless film after the reaction. The band at 2258 cm^{-1} indicates the isocyanate functionality.[93] Furthermore, no band was detected at 3015 cm^{-1} which is characteristic of a carbon-hydrogen sp^2-s stretch.[68] This observation indicated that the addition occurred in high yield (>99%). Note the band at 755 cm^{-1} which indicates residual chloroform.[94] If isocyanic acid was used without t-butyl hypochlorite, no reaction was detectable by ATR.

Vacuum drying the film at 47° to remove residual solvent often proved difficult but was possible if exposure time of the film to the reaction solvent was minimal and if washing of the films after the reaction was done with cold solvent (0°). Trapped chloroform could be removed by vacuum drying the film at 80° for at least 12 hr. Extracting the films for 20 hr using a soxhlet extractor under argon with diethyl ether from a bed of calcium hydride also resulted in the removal of chloroform, but this procedure also led to 44% reduction in the absorbance of the isocyanate band and a corresponding increase in intensity and broadening of a carbonyl band.

The addition reaction was tried in a 30% v:v diethyl ether-chloroform solution at 0°. The ether was added to control solubility of the PVC film and to stabilize the isocyanic acid against trimerization; however, after the reaction the film had an unexpected layer of white powder on it which began forming on addition of the t-butyl

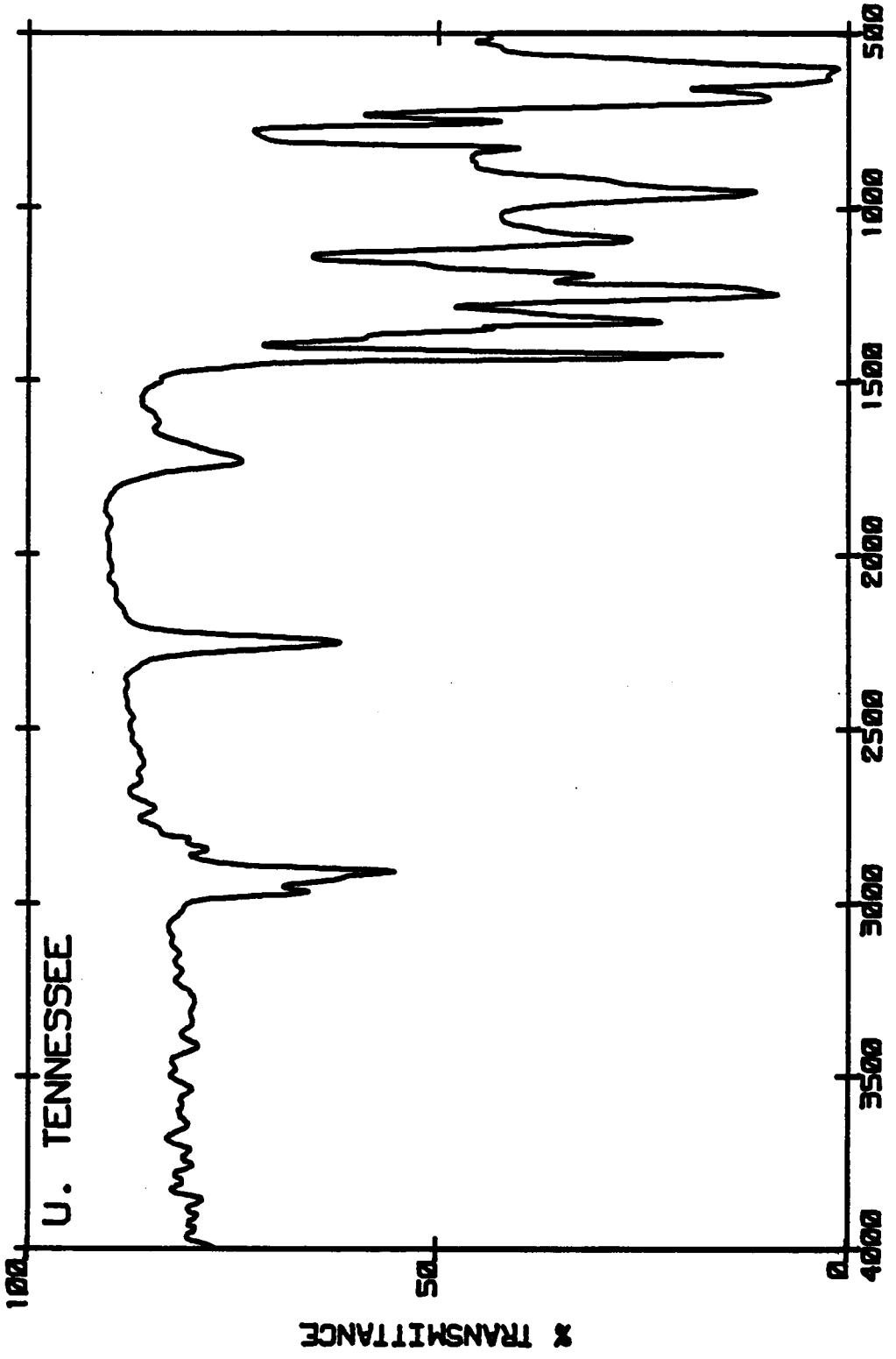


Figure 44. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions: HNCO, 1.9M (initial concentration); t-butyl hypochlorite, 21 mmoles; solvent, chloroform; reaction temperature, 0°; reaction time, 1 hr.)

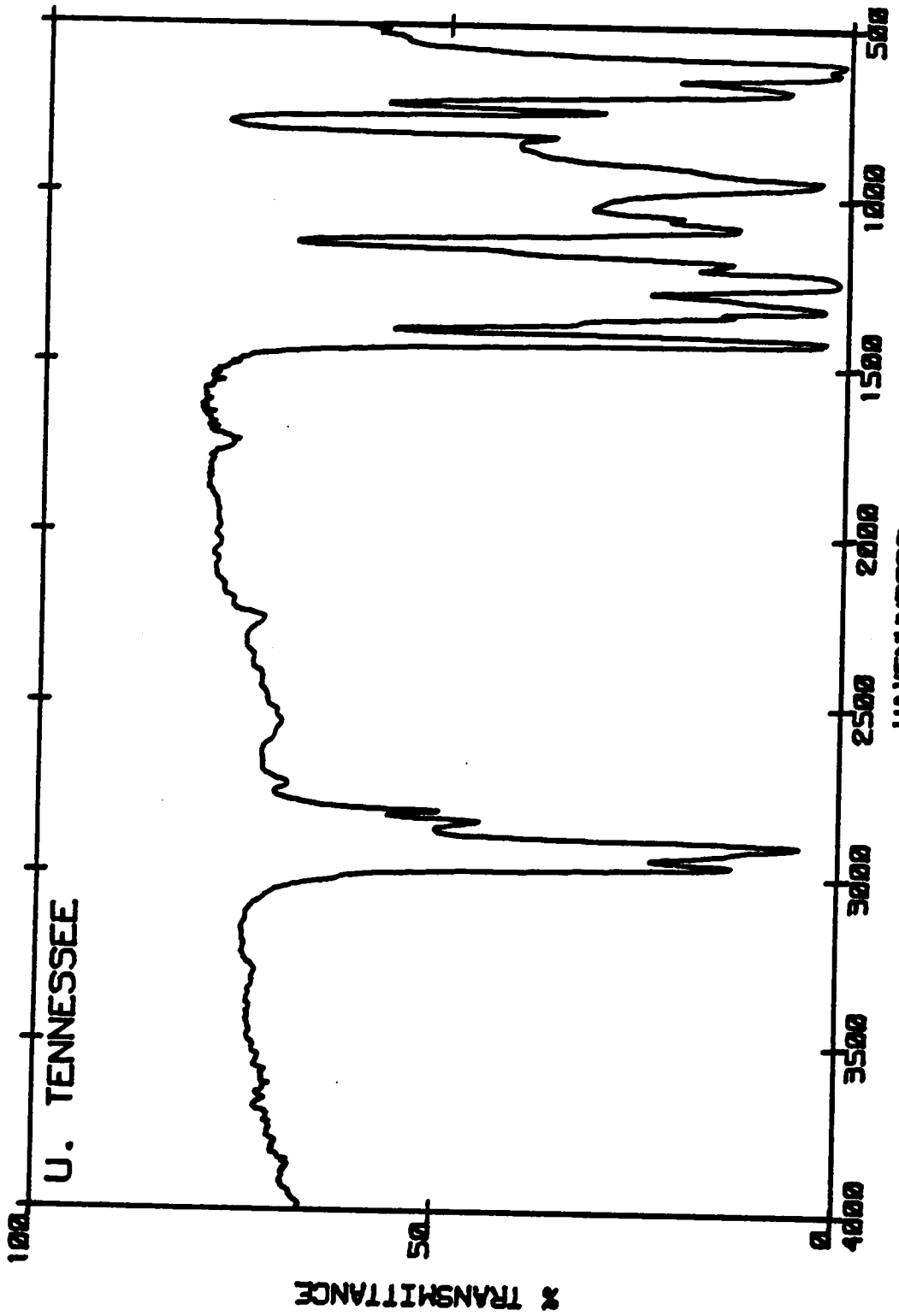


Figure 45. Transmission IR spectrum of modified film taken in vacuum. (Same film as used for spectrum in Figure 43.)

hypochlorite to the reaction medium. After this reaction had been conducted, prior work[95] was discovered that shows that t-butyl hypochlorite reacts with diethyl ether to form 1-chloroethyl ether. The proposed mechanism is free radical in nature:

$$(CH_3)_3COCl \longrightarrow (CH_3)_3CO\cdot + Cl\cdot$$

$$(CH_3)_3CO\cdot + CH_3CH_2OCH_2CH_3 \longrightarrow (CH_3)_3COH + CH_3\dot{C}HOCH_2CH_3$$

$$CH_3\dot{C}HOCH_2CH_3 + (CH_3)_3COCl \longrightarrow CH_3CHClOCH_2CH_3$$

Apparently, the decomposition of the isocyanic acid was initiated by free radicals in the reaction mechanism as a result of the radical reaction between diethyl ether and t-butyl hypochlorite. Transmission IR spectroscopy did reveal a very small isocyanate absorption; however, this solvent system was discarded due to the above side reactions.

Figure 46 shows a proposed mechanism for the isocyanic acid addition to a double bond in the presence of t-butyl hypochlorite using chloroform as the solvent. The t-butyl hypochlorite acts as an electrophile to open up a double bond. The t-butoxide ion is produced in solution with excess isocyanic acid. The second reaction shows the rapid acid/base reaction that occurs. This reaction lies far to the right since the cyanate anion is a much weaker base than the t-butoxide ion. As shown in the third reaction, the nucleophilic cyanate anion rapidly combines with the carbocation to produce the isocyanate group. The success of this addition depends on the rapid addition of the cyanate anion and the very slow addition, if any, of the t-butoxide. The addition of the t-butoxide is slow due to two factors: (1) its low concentration and (2) its size. The resulting t-butyl alcohol formed

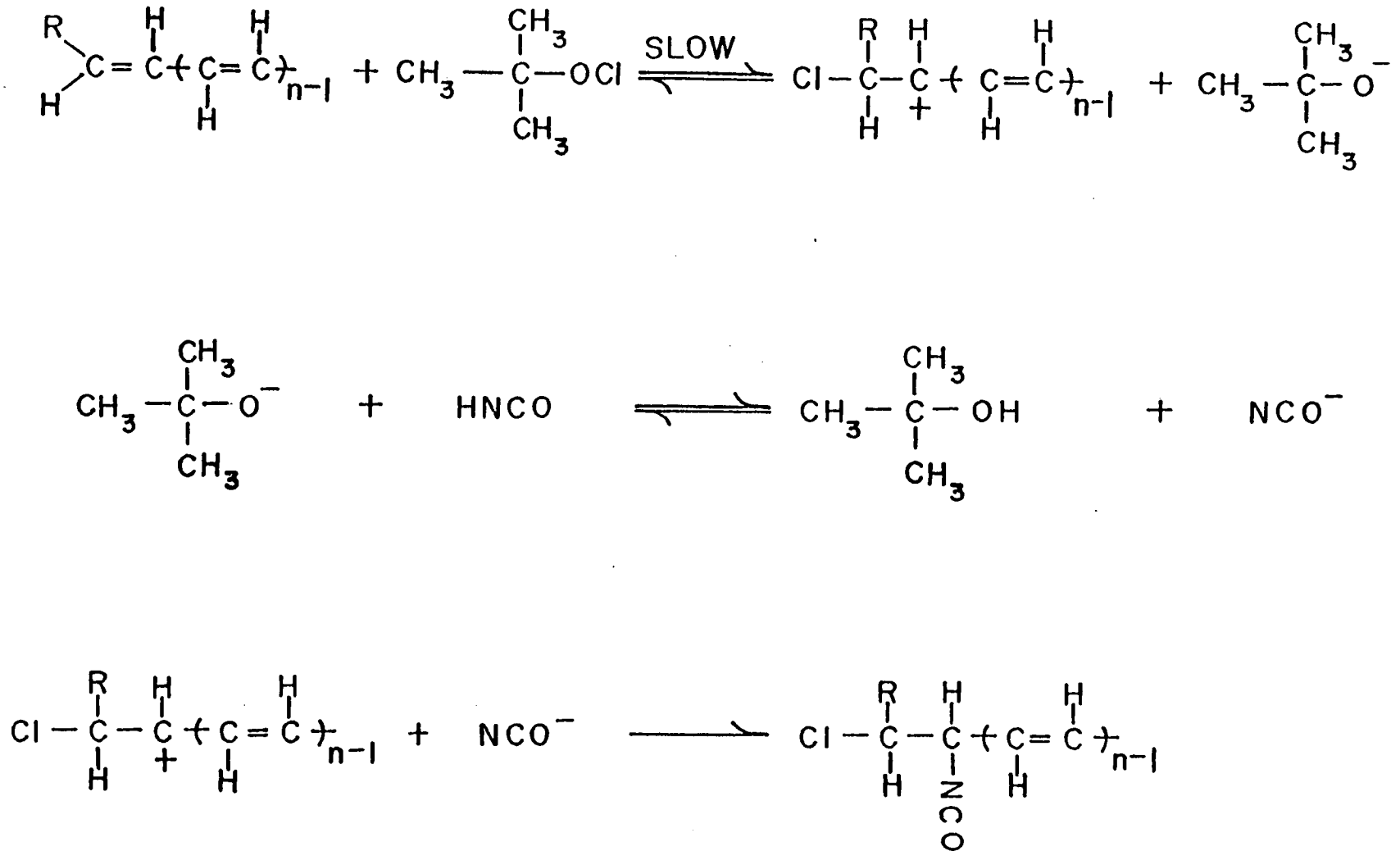
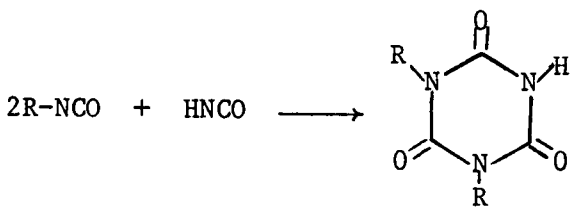


Figure 46. A proposed mechanistic pathway for the addition reaction using t-butyl hypochlorite isocyanic acid as reactants to incorporate the isocyanate group.

in the second reaction is bulky and should not be a competitive nucleophile in reactions with the carbocation.

The second step in Figure 46 shows that the acid/base reaction between the t-butoxide and isocyanic acid produces the cyanate anion. The broad carbonyl band at about 1730 cm^{-1} in Figure 47 may result from the polymerization of isocyanate groups which is initiated by the low concentration of cyanate anions. There is also the possibility that a trimerization reaction may result from the isocyanate groups and isocyanic acid



The isocyanate group undergoes a host of reactions. One important reaction, which is rapid at room temperature, is the reaction of the isocyanate group with n-butyl amine to form the urea. Biologically, this is an important reaction since the hydrolysis of ureas in aqueous solution is very slow and, in general, occurs with a measurable rate only at about 100°.[96] Figure 48 shows the resulting urea absorption[97] at 1670 cm^{-1} after reaction of the surface isocyanate with n-butyl amine. There was no indication of the isocyanate group after the reaction.

Another reaction is that of isocyanates with water to form ureas and amines. Figure 49 shows the resulting ATR-IR spectrum after reacting the surface isocyanate with water for 6 hr. A broad carbonyl band from a urea appears at 1675 cm^{-1} and a N-H bend is visible at 1508 cm^{-1}. As shown in Figure 50, although the isocyanate group is

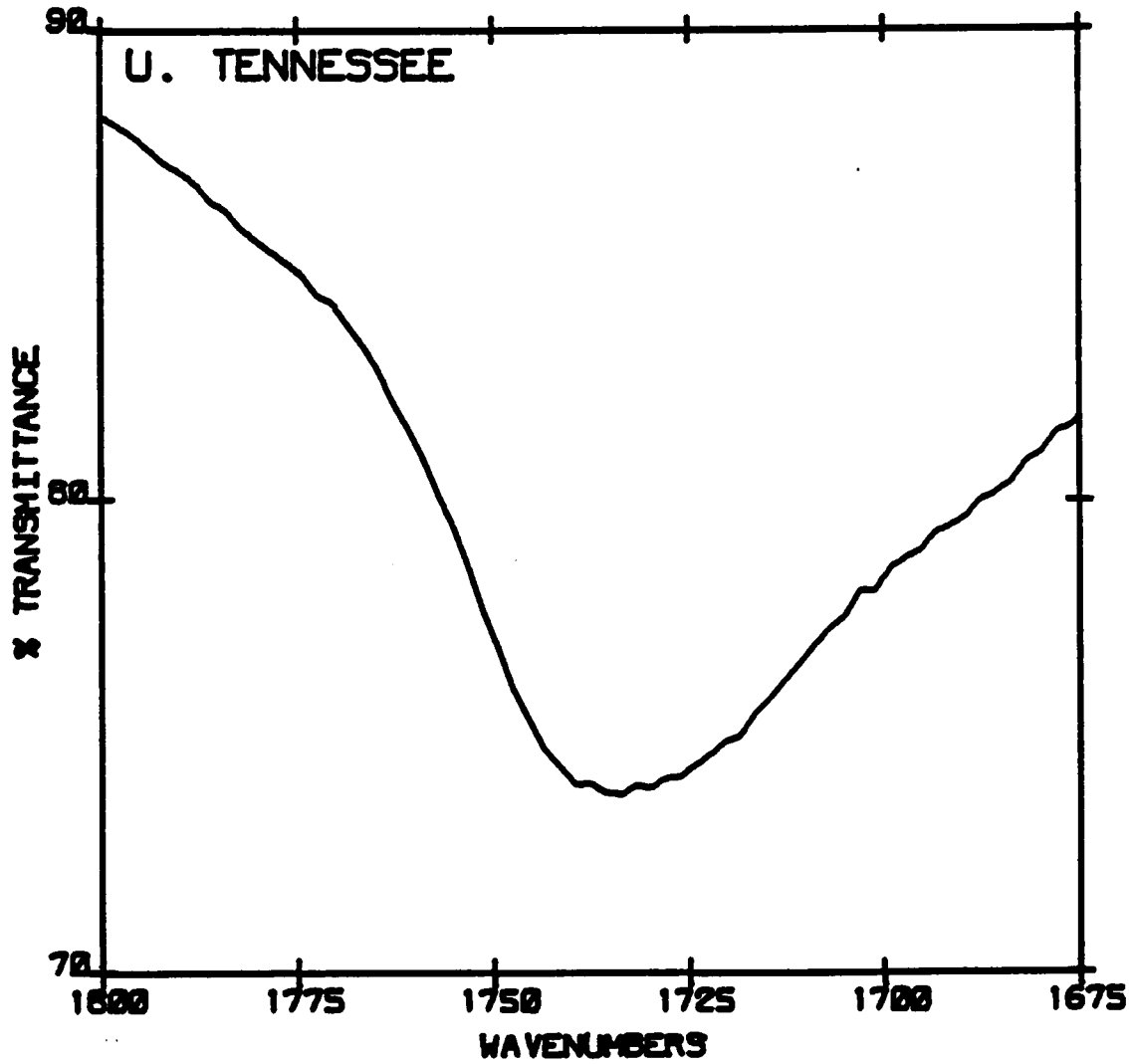


Figure 47. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Closer examination of part of spectrum shown in Figure 43.)

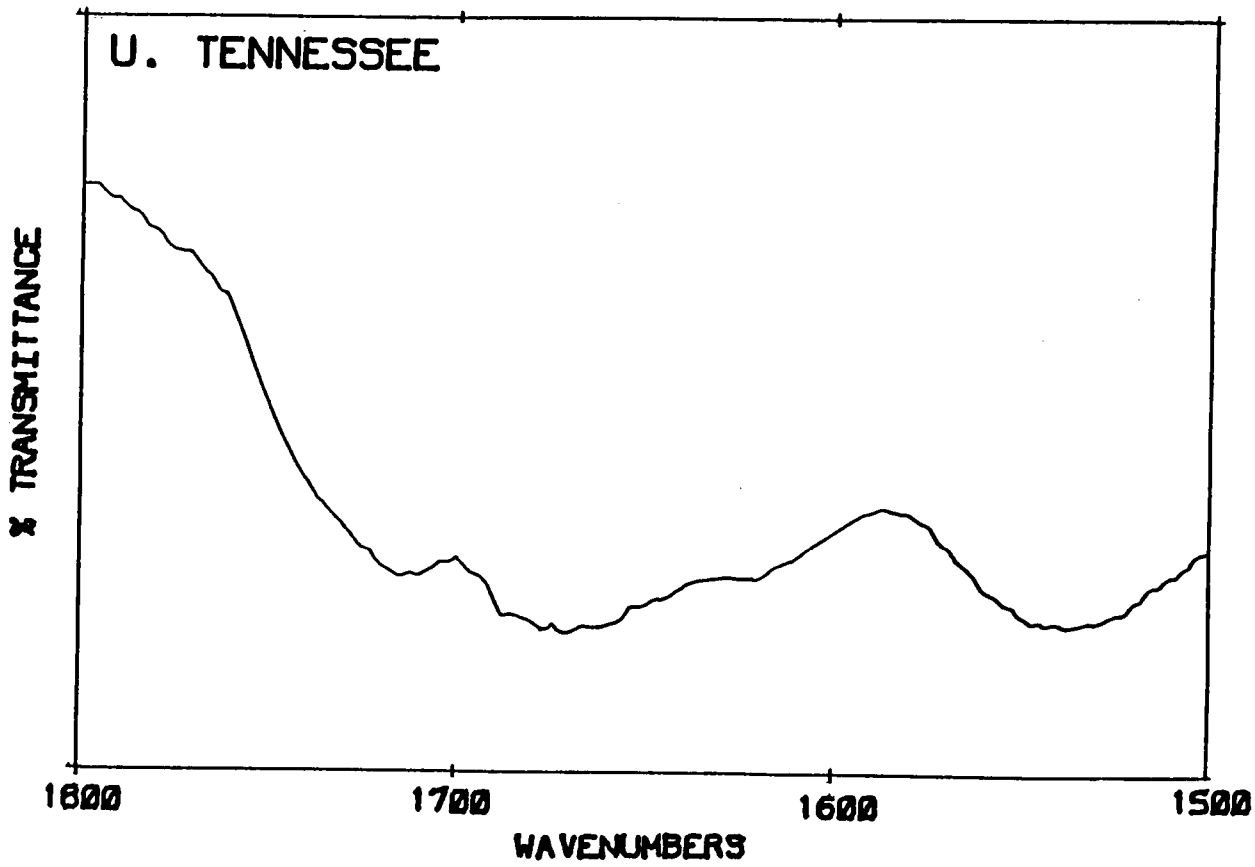


Figure 48. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Reaction Conditions: modified film, PVC-NCO; 1-butyl amine, 1.0 ml (10 mmoles); solvent, ether; reaction temperature 23°; reaction time, 2 hr.)

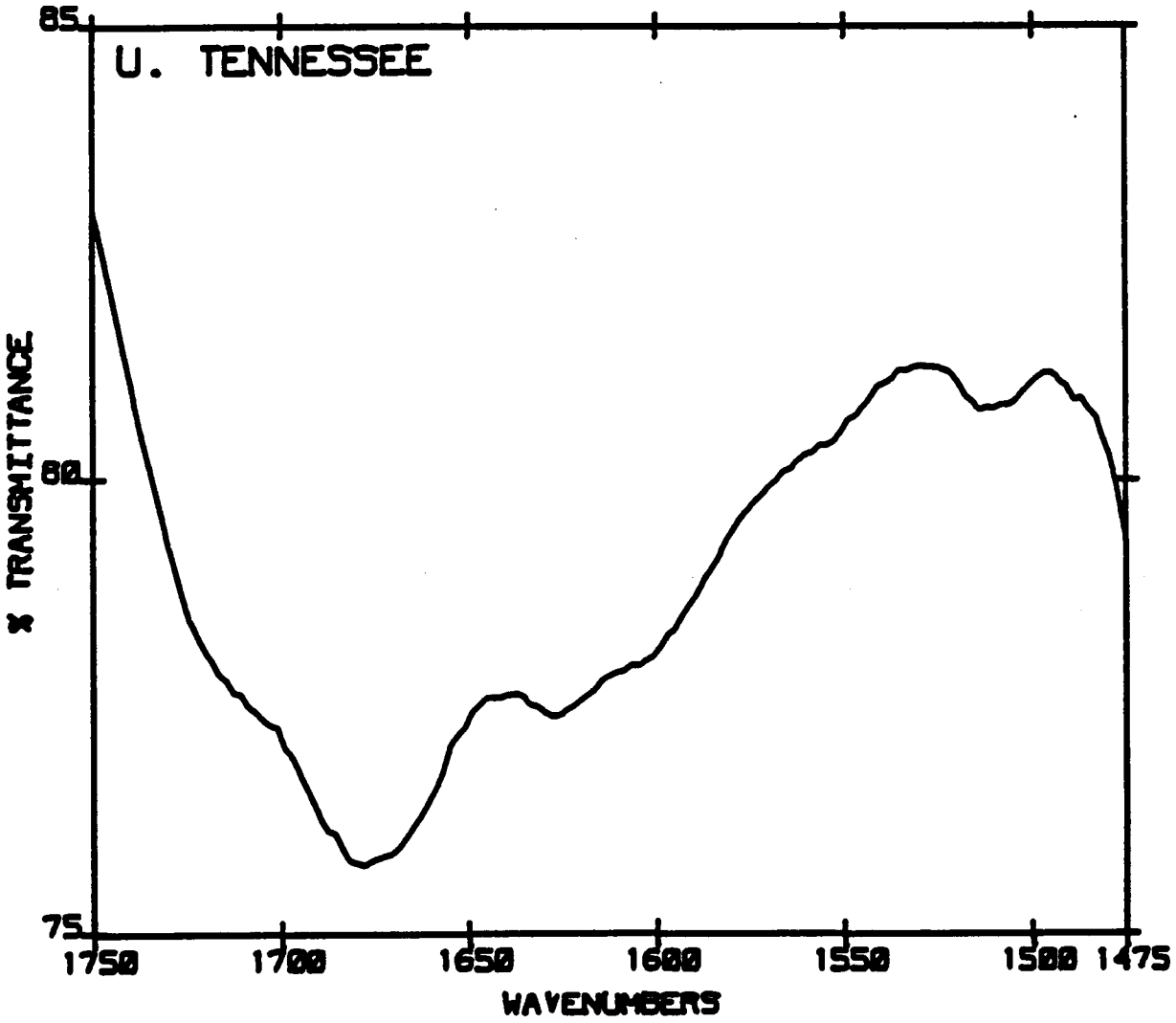


Figure 49. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20) after its reaction with water. (Reaction Conditions: reaction temperature, 60°; reaction time, 6 hr.)

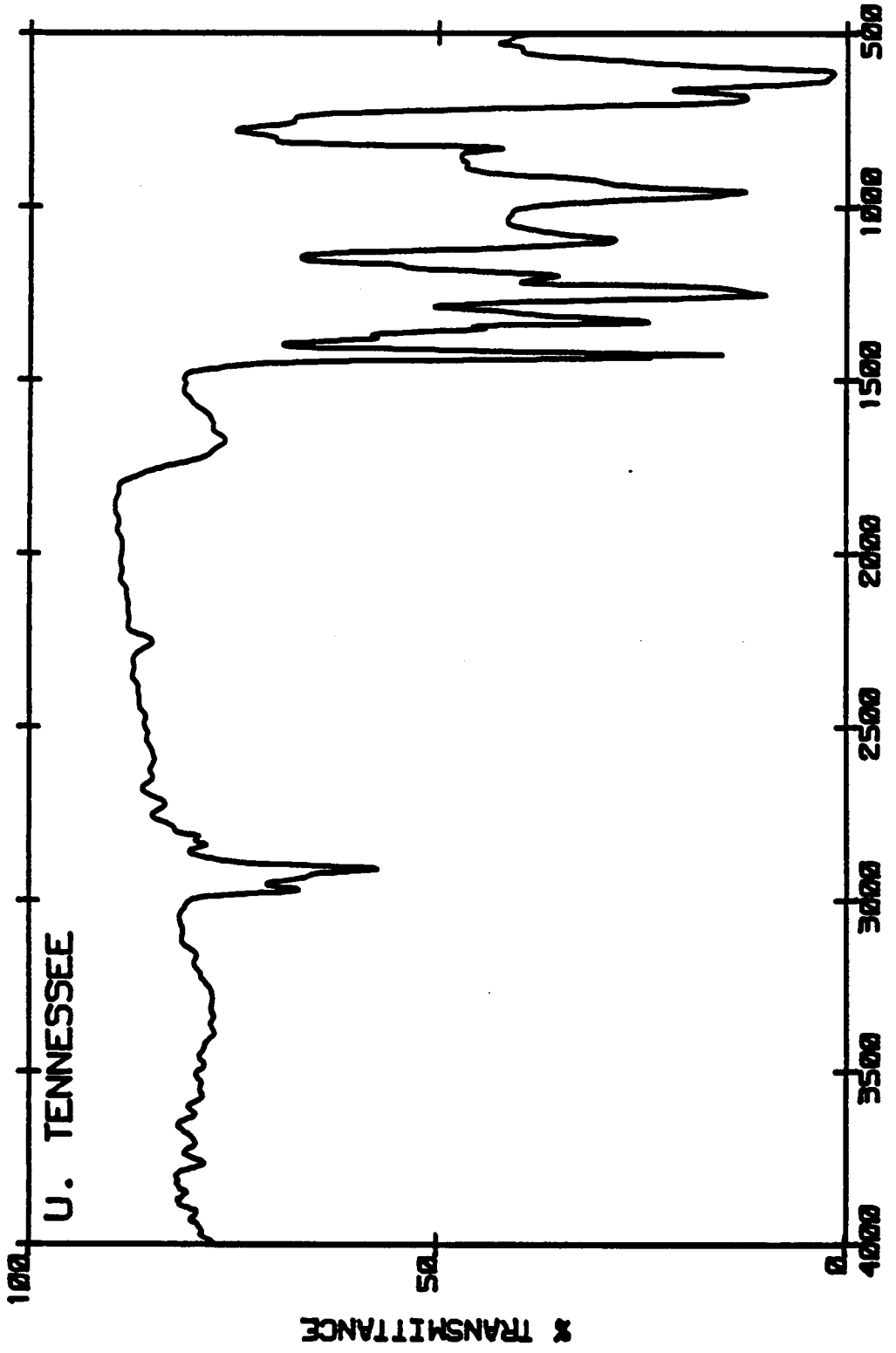
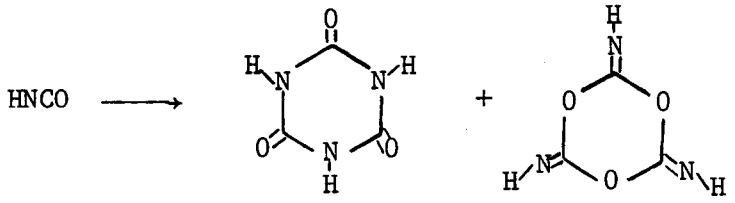


Figure 50. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20). (Complete spectrum of film shown in Figure 49.)

very reactive towards water not all the isocyanate groups reacted. Apparently, these groups are too deep in the polymer for them to react with water.

The isocyanic acid was generated by the thermal decomposition of isocyanic acid at temperatures between 600° and 800°.[98] Pure isocyanic acid decomposes violently above -10° to isocyanuric acid and cyamelide[99] unless it is first diluted with an appropriate solvent in which case it is stable up to 5° in dilute solution.



It was found that isocyanic acid could safely be stored at -77° for at least a month with no noticeable decomposition. Above 5° in chloroform, it decomposed slowly. It is important to prevent the formation of cyamelide since it is almost insoluble in water and organic solvent;[100] thus, if cyamelide is trapped in the film, it cannot be removed by extraction.

To determine the concentration of isocyanate groups on the surface of the modified PVC film, the molar absorptivity of the isocyanate group in a PVC matrix was determined using transmission IR spectroscopy. n-Octadecyl isocyanate (IR spectrum Figure 51) was used as the model compound and was placed as a physical blend in a PVC matrix by casting films under dried argon from a solution of tetrahydrofuran, PVC and n-octadecyl isocyanate. After measuring the absorbance of the crystalline methylene band at 1424 cm^{-1}, the product, εc, which was found in Chapter III to be equal to 285 cm^{-1}

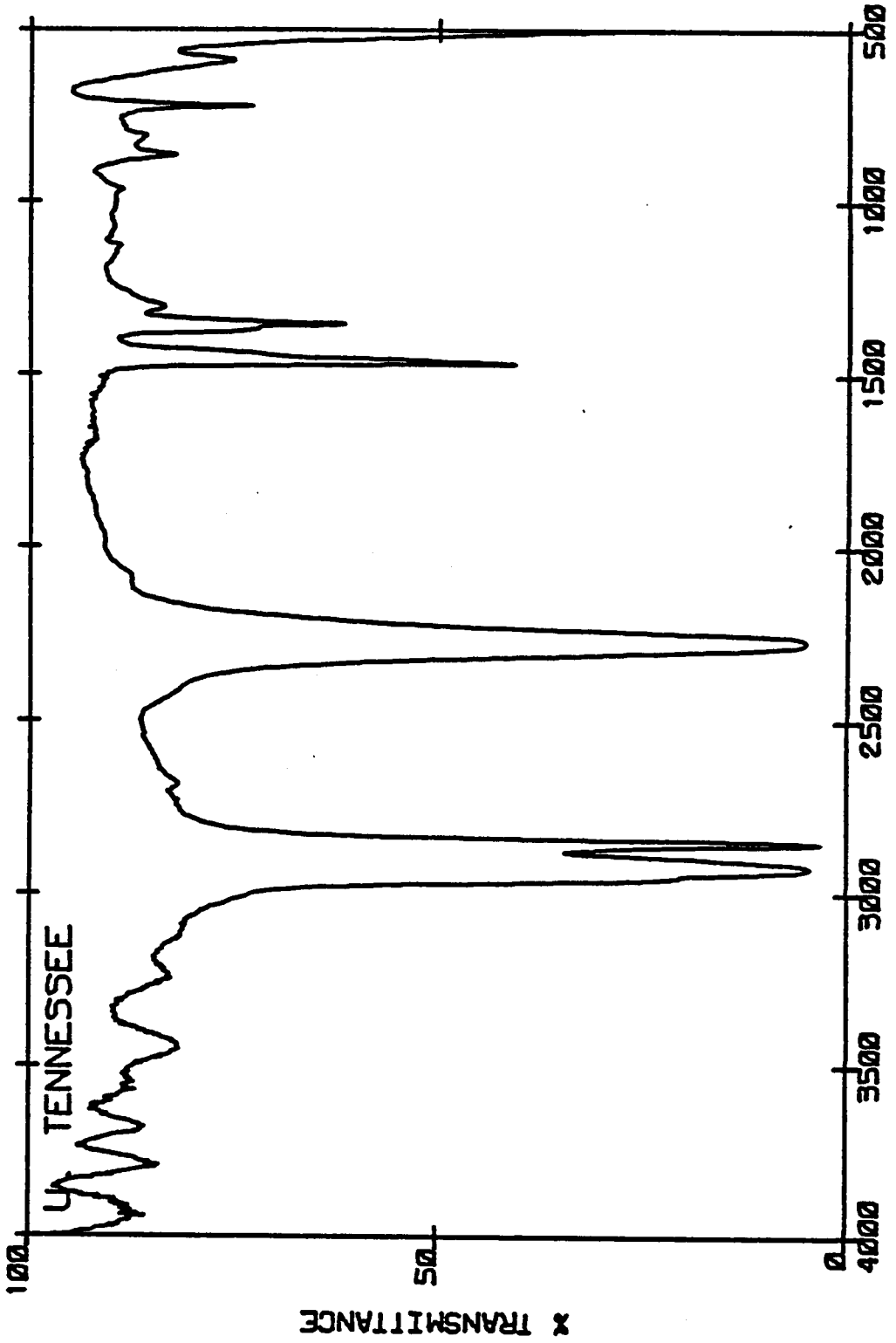


Figure 51. Transmission IR spectrum of 1-octadecyl isocyanate taken neat.

$\pm$ 7 cm^{-1} at a 90% confidence level, was used to calculate the film's thickness using Beer's Law. To calculate the concentration of n-octadecyl isocyanate in PVC film wet with tetrahydrofuran, a density of 1.37 g/ml was assumed.

Figure 52 is the resulting Beer's Law plot for n-octadecyl isocyanate. From the slope a molar absorptivity of 7.2($\pm$0.2) x 10^5 cm^2/mole is calculated. The top plot in Figure 53 shows the absorbance versus concentration plot using internal reflection spectroscopy. The dotted line in Figure 53 is a theoretical plot using Equation 20 in Chapter I using the known concentrations of the model compound in PVC matrix. The larger than expected absorbance in the experimental internal reflection plot can be explained as follows: a migration of the model compound to the surface (a phase separation) occurs because of the incompatibility of this particular compound with PVC. The molecular interactions (Van der Waals, polar) between the model compound and the polymer chains are not strong enough to prevent phase separation. As the concentration of the model compound increases in the PVC, Figure 53 shows that the phase separation is dampened. This is a result of an increasing concentration gradient as the concentration of the model compound builds up on the surface of the polymer which results in a driving force for diffusion of the model compound back into the bulk of the polymer (Fick's Law).[101]

The one angle method was used to calculate the depth of the isocyanate groups. To use Equation 28 in Chapter II the effective thickness must be known. Since d_e is linear with wavelength, an effective thickness of 1.807 x 10^{-4} cm at 2258 cm^{-1} is calculated from

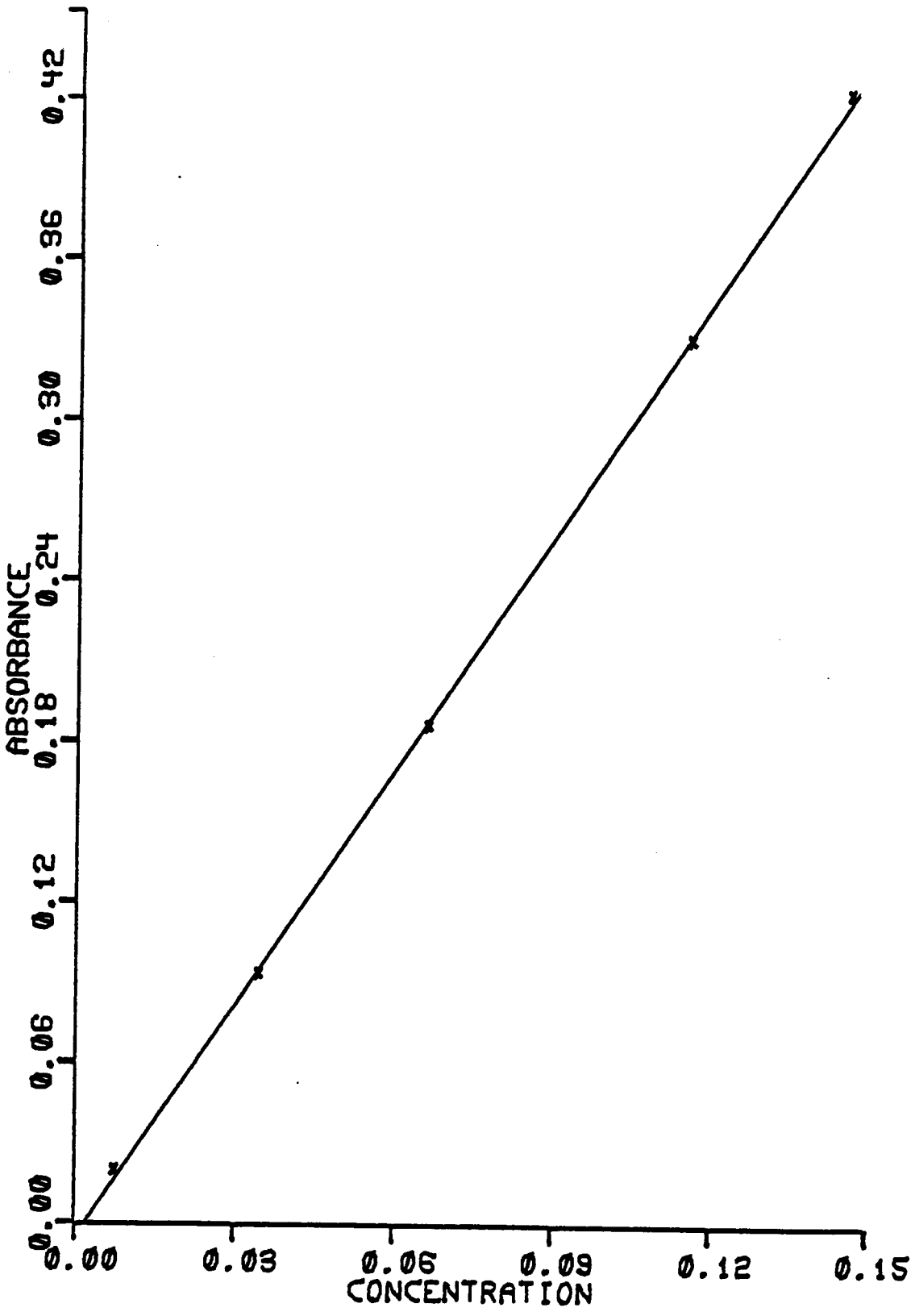


Figure 52. A Beer's Law plot of the transmission IR isocyanate absorbance at 2272 cm^{-1} of n-octadecyl isocyanate in PVC.

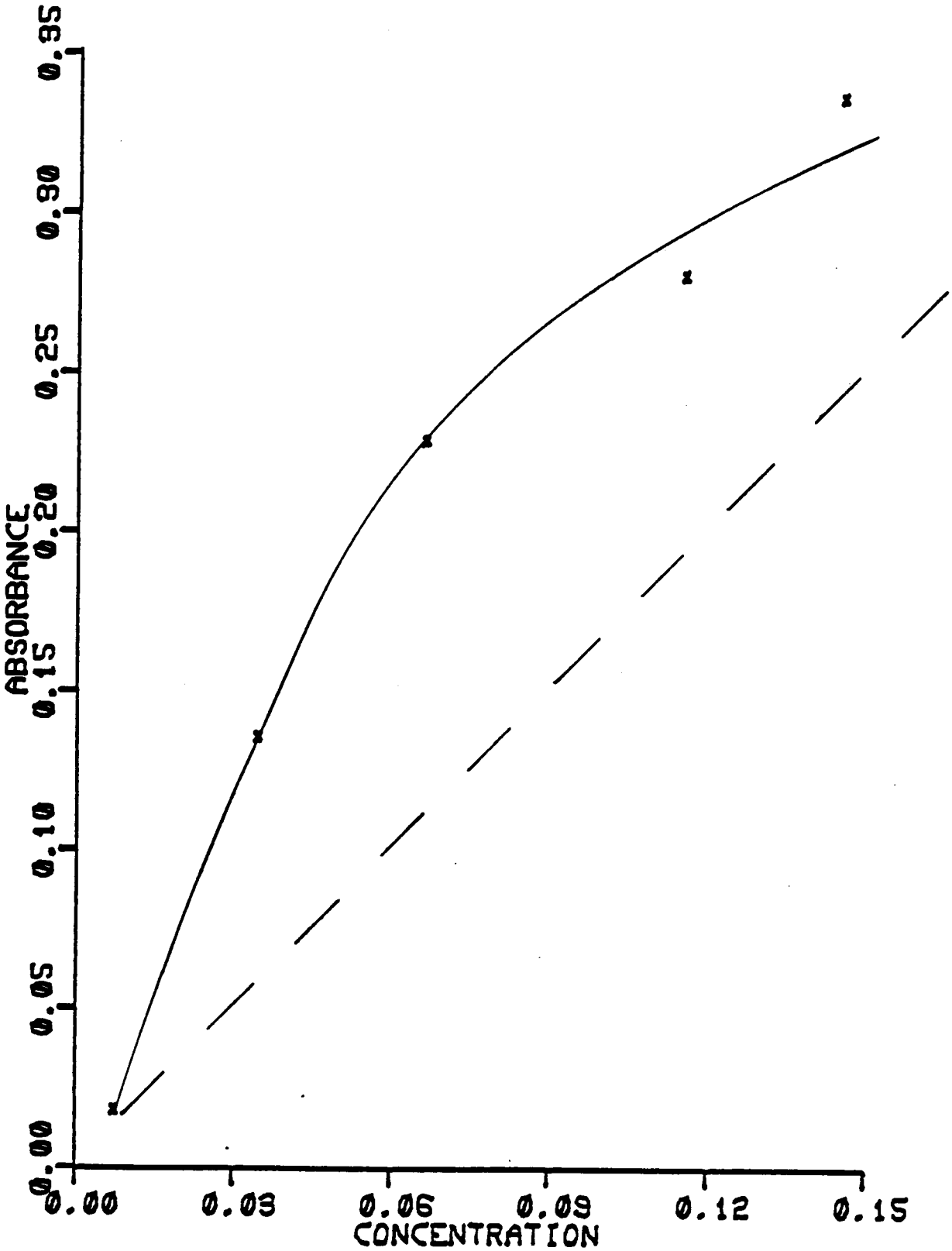


Figure 53. ATR-IR absorbances of n-octadecyl in PVC isocyanate taken at 45 degree angle of incidence (N=20) (top plot) and the ATR-IR absorbances of n-octadecyl isocyanate calculated from Equation 20 (bottom plot) using the known concentrations of n-octadecyl isocyanate.

the effective thickness given in Chapter III at 1720 cm^{-1}. For two films, each 2.0 cm x 4.3 cm, an ATR absorbance of 0.180 $\pm$ 0.037 at 90% confidence level was determined based on three random film contacts. Using transmission IR spectroscopy, two films were placed back-to-back and an absorbance of 0.0083 calculated for one surface of a film containing isocyanates. The above absorbance gave an A(ATR)/A(TRN) value of 21.7. Figure 54 was then plotted from the equation:

$$\frac{A(ATR)}{A(TRN)} = \frac{1.687 \times 10^{-3}}{t} \left[1-e^{-2.259 \times 10^{4}t}\right]$$

Using Figure 54 a depth of reaction of $0.3\lambda_1$, or 5.5×10^{-5} cm was determined. This value is less than the measured depth of elimination of $7.\overset{2}{\cancel{4}} \times 10^{-\overset{5}{\cancel{4}}}$ cm. This discrepancy might result from the fact that a step profile function is used, and/or from the possibility that some dissolution of the polymer's surface occurred during the addition reaction.

Corrected 1/14/84 JWT

After determining the depth of the isocyanate groups the apparent concentration of these absorbing species was calculated. Equation 18

$$A = N\varepsilon c_{ap} d_e / 2.303$$

gave upon substitution of the proper values

$$c_{ap} = \frac{0.180 \times 2.303 \times 10^{3} cm^{3} l}{21.5 \times 7.2 \times 10^{5} cm^{2}/mole \times 1.807 \times 10^{-4} cm}$$

or

$$c_{ap} = 0.15 \text{ M}$$

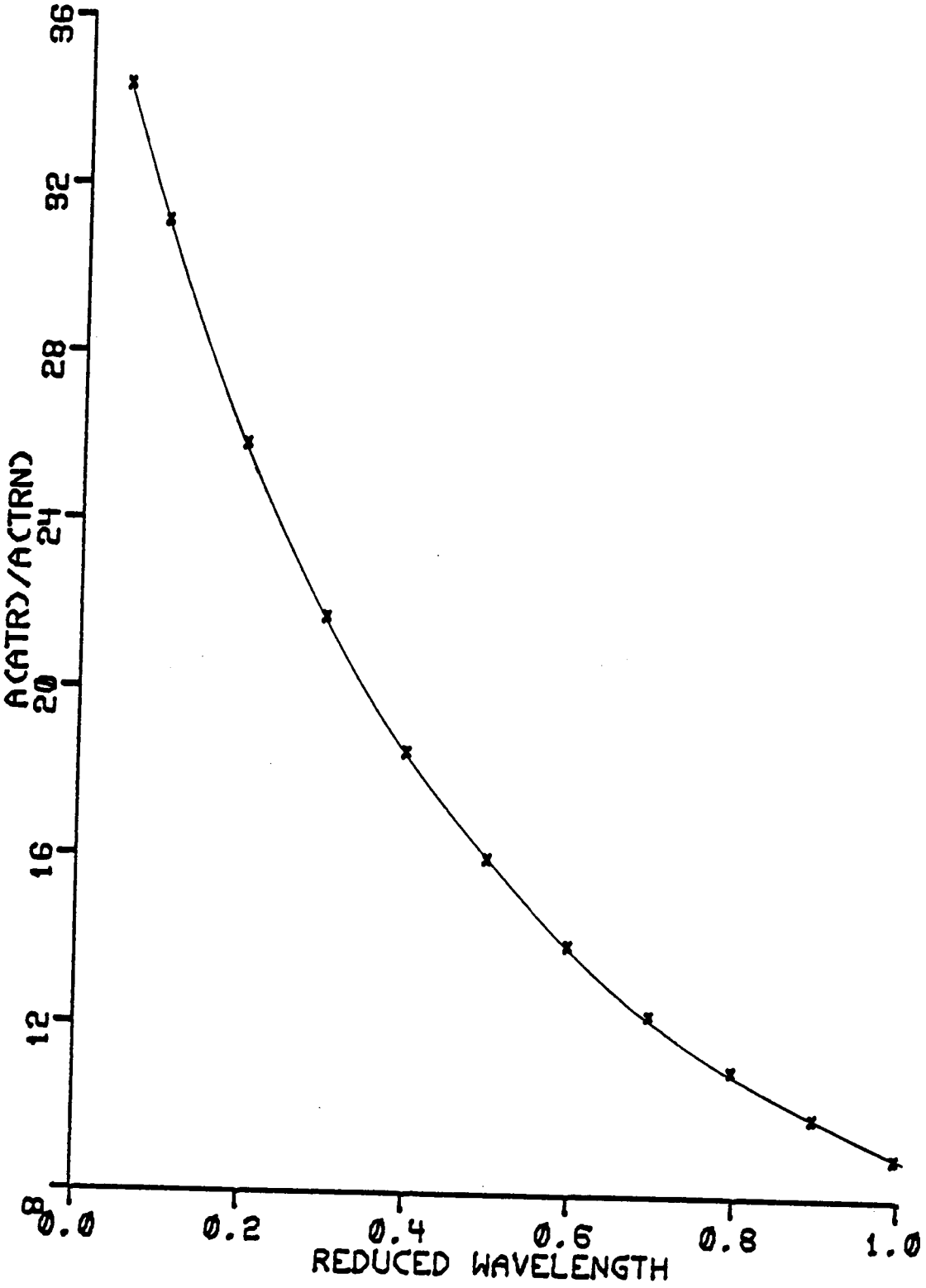


Figure 54. A one angle depth analysis curve for the isocyanate band at 2258 cm^{-1}.

The apparent concentration was then calculated using Equation 20 in Chapter I:

$$\frac{A}{A_r} = \frac{\varepsilon\ c\ \lambda}{\varepsilon_r c_r \lambda_r}$$

using the methylene absorption at 1424 cm^{-1} as the reference band. The answer obtained in this equation will depend on changes in crystallinity which would affect the crystalline band at 1424 cm^{-1}, the decrease in concentration of methylene groups from the initial elimination reaction, and mirror alignment but not film contact. Rearrangement of the above equation gives

$$c_{ap} = \frac{A\varepsilon_r c_r \lambda_r}{A_r \varepsilon \lambda}$$

Substitution of the proper values then gives

$$c_{ap} = \frac{.185}{.88} \times \frac{285\ cm^{-1} \times 7.02 \times 10^{-4} cm \times 10^3 cm^3/l}{7.2 \times 10^{-5} cm^2/mole \times 4.43 \times 10^{-4} cm}$$

or

$$c_{ap} = 0.13\ M$$

The agreement between the apparent average concentrations using Equation 20 and Equation 18 is good. As shown in Chapter III

$$c_{av} = c_{ap}\left[1-e^{-2t/dp}\right]^{-1}$$

thus for an apparent concentration of 0.15 M we have

$$c_{av} = 0.15\ [1\text{-}e^{-2x5.5\ x\ 10^{-5}/8.854\ x\ 10^{-4}}]\text{-}1$$

$$c_{av} = 0.15\ M/.711$$

$$c_{av} = 0.21\ M$$

Once the average concentration is determined it can be checked using Beer's Law: thus

$$c_{av} = \frac{A}{\varepsilon t}$$

where A is the transmission absorbance for one surface. Substitution of the proper values gives

$$c_{av} = \frac{.0083\ x\ 10^3 cm^3/l}{7.2\ x\ 10^5 cm^2/mole\ x\ 5.5\ x\ 10^{-5} cm}$$

$$c_{av} = 0.21\ M$$

This value was then used to get a surface density of 2.5×10^{13} units/cm^2.

A second method for incorporation of the isocyanate group utilized the pseudo-halogen, chloroisocyanate. Hassner *et al.*[102] have added iodoisocyanates across double bonds. Their iodoisocyanate was generated *in situ* by the addition of silver cyanate to an ether solution of iodine. In 1967, Hassner[103] pointed out that the elements of chloroisocyanate could be added across double bonds of olefins by exposing the olefin to an excess of trichlorocyanurate in the presence of isocyanic acid. Apparently, Hassner and his coworkers were not aware that in 1966, Naubaur and Gottardi[104] had generated

chloroisocyanate by the thermal decomposition of trichlorocyanurate at 310°-320°, < 1 torr. Its reaction with olefins was not studied; however, it was shown that reaction with ethanol was almost quantitative:

$$Cl\text{-}NCO + 2CH_3CH_2OH \longrightarrow NH_2COOCH_2CH_3 + CH_3CH_2OCl$$

Hocking, Williams and Gerry[105] have shown that the chloroisocyanate molecule is planar and give the structure as follows: r(Cl-N)=1.705 ±0.005A°; r(N-C)=1.226 ±0.005A°; r(C-O)=1.162 ±0.005A°; (Cl-N-C)=118 50' ±30'; (N-C-O)=170 52' ±30', with Cl and O trans.

The addition of chloroisocyanate was accomplished in two ways. In one, a measured amount of chloroisocyanate was condensed onto frozen chloroform containing the dehydrochlorinated film. The vessel was then put under a dried argon atmosphere and the reaction vessel allowed to warm up to 0°. The colorless film was then removed and vacuum dried for 24 hr at 25°, and 90 hr at 47°. The ATR-IR spectrum in Figure 55 shows an isocyanate band at 2258 cm^{-1} and a carbonyl band at 1725 cm^{-1}. The concentration of isocyanate groups was 17% of that obtained by the addition of the isocyanate using t-butyl hypochlorite and isocyanic acid. The carbon hydrogen sp^2-s stretch present in the spectrum before the reaction was absent after the reaction. The reaction solution contained no evidence of any precipitate after the reaction. In the second procedure, a solution of chloroisocyanate in argon gas was bubbled into a 50% v:v chloroform-carbon tetrachloride solution at 0° in the dark which contained the dehydrochlorinated PVC. The film turned colorless almost instantaneously upon the addition of

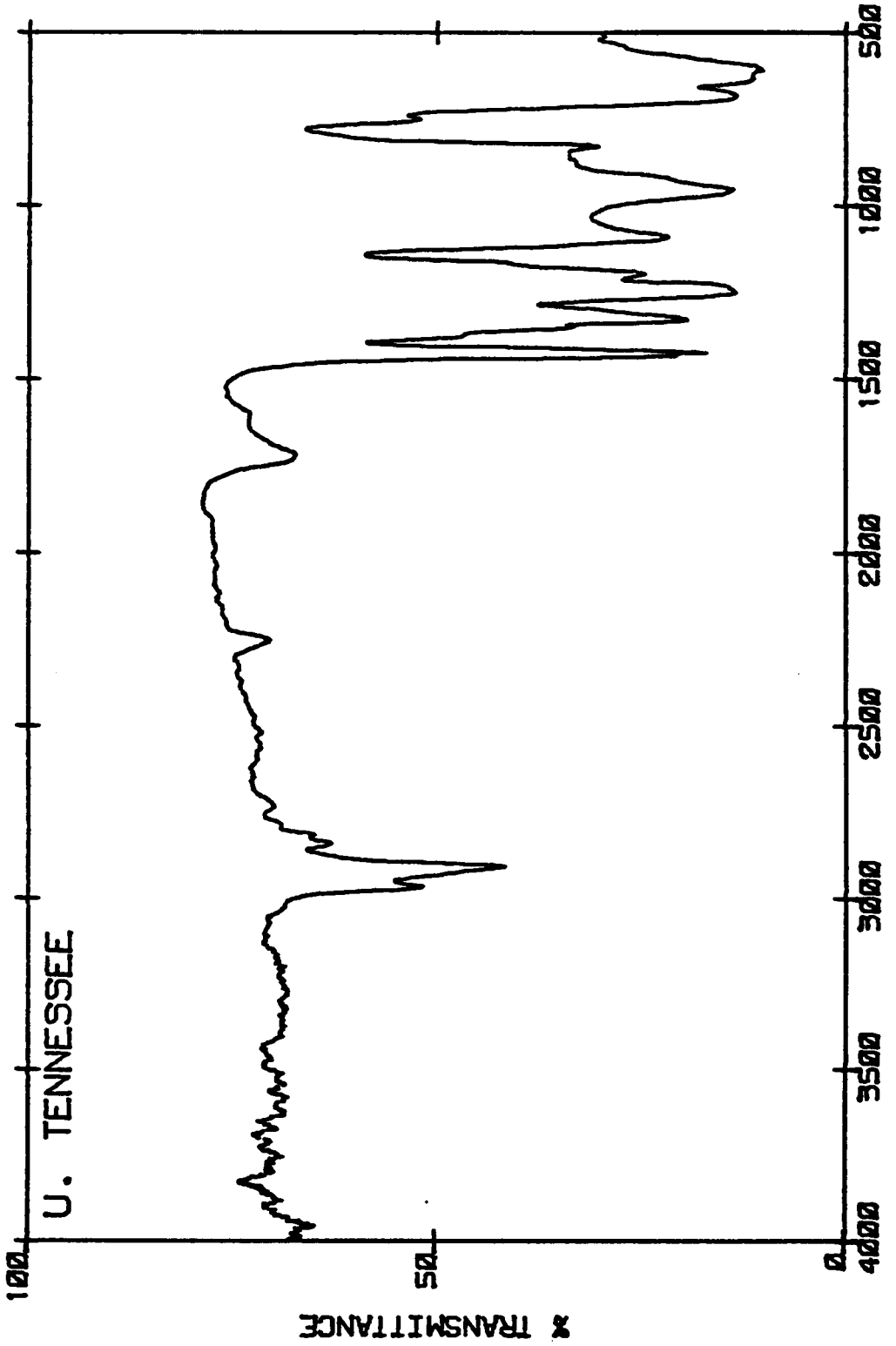


Figure 55. ATR-IR spectrum of modified PVC film taken at 45 degree angle of incidence (N=20).

chloroisocyanate. The ATR-IR again revealed an isocyanate and carbonyl band. There was no noticeable increase in the absorbance of isocyanate groups compared to the first method.

The proposed mechanism of the chloroisocyanate addition can be rationalized by analogy with proposed mechanisms for bromine and chlorine additions. The reaction of these halogens with olefins is thought to proceed by electrophilic attack of the halogen on the double bond.[106] The reaction is accelerated by electron donating substituents in the olefins and by use of polar solvents.[107] Furthermore, for conjugated dienes, there are 1,2 and 1,4 additions with the 1,4 product often being the product of highest yield; however, chlorination of a cyclic diene often gives the 1,2 syn addition as the major product.[108] In conjugated systems syn attack is possible because after electrophilic attack of the halogen at one of the double bonds, there is a dispersal of positive charge in the allylic system:

corrected 1/14/84 SWT

$$C_1=C_2-C_3=C_4 \xrightarrow{X_2} C_1-C_2-C_3-C_4 \quad (X^- \text{ and } X^- \text{ shown})$$

The dispersal of this charge results in a weakened bond between the halogen and C_2. This allows the possibility of front-side attack by the halogen anion resulting in the formation of a syn 1,2 product.[108] In the long conjugated system in dehydrochlorinated PVC, this means the carbocation is most likely free and not bonded to the halogen.

As the conjugated system becomes longer, the mechanistic picture becomes more conjecture but again reasonable assumptions can be made

from known systems. For example, the reaction of 1,3,5-hexatriene with bromine gives 5,6-dibromo-1,3-hexadiene and 1,6-dibromo-2,4-hexadiene but not 3,6-dibromo-1,4-hexadiene:[109]

$$Br_2 + CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH{=}CH{-}\underset{Br}{CH}{-}\underset{Br}{CH_2}$$

$$+$$

$$\underset{Br}{CH_2}{-}CH{=}CH{-}CH{=}CH{-}\underset{Br}{CH_2}$$

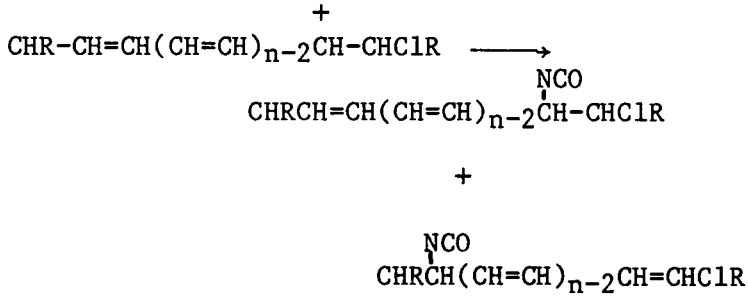
Formation of 3,6-dibromo-1,4-hexadiene would result in destruction of the conjugated double bond system; apparently, this disruption of the conjugated system does not occur. Therefore, the addition then for a conjugated system with n double bonds, is 1,2 or 1,n.

In the proposed mechanism for the addition of chloroisocyanate in the polyene system of eliminated PVC, a positive chlorine species approaches the end of the conjugated system and in the first step forms a σ-bond:

$$\delta^+Cl\text{—}\overset{\delta^-}{NCO} \qquad\qquad NCO^-$$

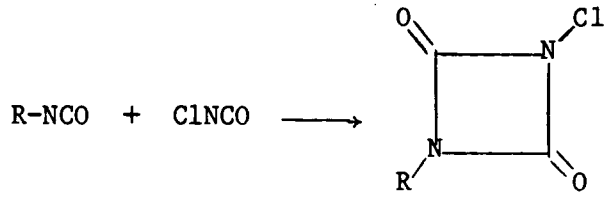
$$CHR(CH{=}CH)_{n-1}CH{=}CHR \longrightarrow CHR(CH{=}CH)_{n-1}\overset{+}{C}H{-}\underset{Cl}{CHR}$$

The positive charge is stabilized by resonance. In this mechanism the chlorine species may not be an actual positive ion but may be the end of a dipole or induced dipole. The second step involves the combination of the cyanate anion with the stabilized carbocation. The attack will occur such as not to break up the conjugated system:



The process continues until complete addition occurs.

The appearance of the carbonyl band in the ATR-IR after the addition means that the above mechanistic picture is oversimplified. After or during the addition reaction free isocyanate anion may be attacking the cyanate groups. As described in Chapter II, this attack results in polymerization of these groups. Other carbonyl products may result from the reaction of chloroisocyanate molecules with isocyanate groups:



Although the simplified mechanistic picture above is ionic, it is also possible that radicals are generated from the chloroisocyanate and could be involved in the overall scheme, producing either the isocyanate groups or the unwanted carbonyl band.

One observation: a mixture of chloroisocyanate in tetrahydrofuran ignited when warmed slowly up to room temperature, an indication of a rapid radical mechanism; thus, it is possible that radicals are in the mixture.

In conclusion, PVC can be eliminated efficiently with base to produce a polyene system. Placement of isocyanate groups is possible

by addition reactions using either t-butyl hypochlorite and isocyanic acid or chloroisocyanate. The addition reaction occurs in high yield, producing isocyanate and carbonyl groups. The addition reactions using t-butyl hypochlorite and isocyanic acid produced isocyanate groups in the highest yield; surface density, 2.5×10^{13} isocyanate groups/cm^2.

C. PROCEDURES

Reaction of PVC film with sodium methoxide: A weighed amount of PVC film (±0.0003g) ~6 cm in diameter and 50 μ thick, was placed on a glass screen and held in place by a glass weight. To a 250 ml beaker equipped with a magnetic stirrer, large stopper protected with aluminum foil, gas inlet and outlet was pipetted 25.0 ml of basic methanol solution (25% by weight sodium methoxide in methanol) and 25.0 ml of anhydrous dimethyl sulfoxide. The solution was magnetically stirred for 5 min and the magnetic stirrer removed. The gas outlet was attached to an oil bubbler, and the reaction vessel purged with dry argon gas. The PVC film was then lowered with a glass dipper into the reaction medium and the reaction allowed to proceed for the allotted time at 23°. After the reaction, the film was washed twice in 100 ml of methanol, first for 5 min, then for 15 min. The film was then extracted in a soxhlet extractor with methanol under argon for 18 hr. After the extraction, the film was dried at 47° to constant weight (±0.0003g).

Generation of isocyanic acid: About 100 g of cyanuric acid was placed inside a 1000 ml round bottom flask fitted with a distillation

head and empty condenser. To the end of the condenser was attached a filter made from a 100 ml two neck round bottom flask filled with glass wool. The filter was attached with a gas outlet which was connected to a trap made from a 50 ml graduated cylinder fitted with a 24/40 joint and an outlet attached to a calcium chloride drying tube. The 1000 ml round bottom flask was heated with a Fischer burner to 600-680°. About 20 ml of liquid isocyanic acid could be collected in the trap at -77° before the subliming cyanuric acid clogged the filter. The isocyanic acid was then vacuum distilled onto P_2O_5 and stored under vacuum at -77° for at least 24 hr before use.

Addition reaction using t-butyl hypochlorite and isocyanic acid: The dehydrochlorinated PVC films (two films - each 2.0 cm x 4.3 cm x 50 μ and weighing about 0.06 g) were placed on a glass screen inside a cylindrical pyrex vessel, 4.5 in x 2 in outer diameter, equipped with a magnetic stirrer and 65/40 ground glass joint. The 65/40 ground glass joint was fitted with a 24/40 ground glass joint adapter. The reaction flask was evacuated and argon gas introduced into the reaction vessel to bring it to atmospheric pressure (The exposure time of the films to the air was < 3 min). The films were then frozen with liquid nitrogen and 50 ml of anhydrous chloroform slowly dripped into the reaction vessel by a pressure-equalizing dropping funnel. The reaction vessel was again evacuated and 3.5 to 4.5 ml of anhydrous isocyanic acid vacuum distilled at -20° into the reaction vessel. The reaction vessel was then brought back to atmospheric pressure with argon gas, and the reaction vessel brought up to 0°. Into a pressure-equalizing funnel was then syringed 20 ml of anhydrous chloroform and 2.5 ml of t-butyl

hypochlorite. The t-butyl hypochlorite solution was dropped slowly (about 1 hr) in the dark into the magnetically stirred isocyanic acid solution. After the addition was complete, the reaction vessel was cooled to -23°, and the colorless films were removed and immediately placed in cold anhydrous chloroform (0°) for 15 min. The washing procedure was repeated, and the films were immediately placed in a vacuum and dried (first for 24 hr at 23°, then until constant weight at 47°; ~24 hr). If necessary, the films were dried at 80° to remove residual chloroform.

Generation of chloroisocyanate: To a pyrex pyrolysis tube, 48 cm in length and 2.5 cm in diameter, sealed at one end and equipped with 1 24/40 ground glass joint, was added 10 g of trichloroisocyanurate. The pyrolysis tube was then placed under vacuum (<1 Torr) and heated in two sections. The first section, 30 cm in length, used to decompose the trichloroisocyanurate, was heated from 310° to 320°. The trichloroisocyanurate was then sublimed by slowly raising the temperature of the second section, 10 cm in length, to 150°. The chloroisocyanurate was trapped with liquid nitrogen over a 5 hr to 7 hr period and stored under vacuum at -77° until used.

Addition reaction using chloroisocyanate: The dehydrochlorinated PVC films (two films-each 2.0 cm x 4.3 cm x 50 μ and weighing about 0.06 g) were placed on a glass screen inside a cylinderical pyrex vessel, 4.5 in x 2 in, equipped with a magnetic stirrer and 65/40 ground glass joint. The 65/40 ground glass joint was fitted with a 24/40 ground glass joint adapter. The reaction flask was evacuated and argon gas introduced into the reaction vessel to bring it to atmospheric

pressure. The films were then frozen with liquid nitrogen and 50 ml of anhydrous chloroform slowly dripped into the reaction vessel from a pressure-equalizing dropping funnel. The reaction vessel was evacuated and 3.9 x 16^{-3} mole of chloroisocyanate distilled onto the solid chloroform. The reaction vessel was allowed to warm up to 0° in the dark (about 1 hr). After the addition, the reaction vessel was cooled to -23°, and the films were removed and immediately placed in cold anhydrous chloroform (0°) for 15 min. The washing procedure was repeated, and the films immediately placed in a vacuum and dried first for 24 hr at 23° then until constant weight at 47°.

Addition reaction using chloroisocyanate: The dehydrochlorinated PVC films (each 2.0 cm x 4.3 cm x 50 μ and weighing about 0.06 g) were placed on a glass screen inside a cylindrical pyrex vessel, 4.5 in x 2 in equipped with a magnetic stirrer and 65/40 ground glass joint. The 65/40 ground glass joint was fitted with a 24/40 ground glass joint adapter. The reaction flask was evacuated and argon gas introduced into the reaction vessel. To the reaction vessel was added a 50% v:v chloroform-carbon tetrachloride at 0°.

A 0.26 l manifold at 23° was pressurized to 275 Torr with chloroisocyanate. The gas was brought to atmospheric pressure with argon, then isocyanic acid bubbled with a stream of argon into the reaction solution containing the film for 1.5 hr. After the reaction, argon was bubbled through the reaction solution for 30 min. The films were washed in a solution of 50% v:v chloroform-carbon tetrachloride at 0° for 30 min, then vacuum dried at 47° for 32 hr and at 80° for 14 hr.

Reaction of the isocyanate modified PVC films with n-butyl amine: The modified PVC films (two films-each 2.0 cm x 4.3 cm x 50 μ) were placed in a 250 ml round bottom flask equipped with a 65/40 ground glass joint, gas inlet and outlet. The reaction flask was purged with argon and 50 ml of diethyl ether distilled from calcium hydride directly into the flask. Into the flask was syringed 0.50 ml (0.005 moles) of n-butyl amine and the reaction allowed to proceed for 2 hr at 23°. The films were removed, washed with diethyl ether, then vacuum dried at 80° for 6 hr.

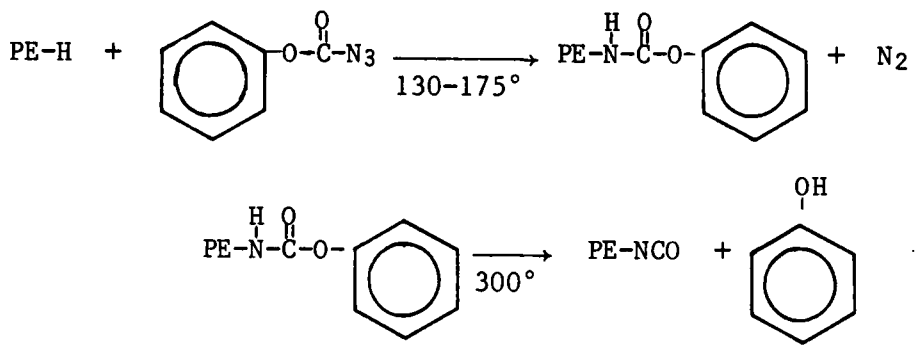
Reaction of the isocyanate modified PVC films with water: The modified PVC films (two films-each 2.0 cm x 4.3 cm x 50 μ) were placed into a 250 ml beaker containing 100 ml of water at 60° and the reaction allowed to proceed for 6 hr. The films were then removed, washed in diethyl ether for 15 min, then vacuum dried at 47° for 24 hr.

CHAPTER V

INCORPORATION OF THE ISOCYANATE GROUP ON THE SURFACE OF HIGH DENSITY POLYETHYLENE BY ELIMINATION/ADDITION SEQUENCES

A. INTRODUCTION AND BACKGROUND

This chapter will show two methods for incorporation of the isocyanate group on the surface of HDPE. Gallucci incorporated the isocyanate group on low-density polyethylene (LDPE) by thermally decomposing a carbamate intermediate.[110] Azidoformates were used to incorporate the desired carbamate on LDPE in the melt. An example of this sequence is shown below:



The high heat necessary to obtain the isocyanate group generated a yellow polymer, undoubtedly a result of polyene formation.

Rasmussen, Stedronsky and Whitesides[14] generated isocyanates on the surface of PE through a series of steps shown below:

$$PE\text{-}H \xrightarrow[70\%\ HNO_3]{CrO_3/H_2SO_4} PE\text{-}CO_2H$$

$$PE\text{-}CO_2H \xrightarrow{CH_2N_2} PE\text{-}CO_2CH_3$$

$$PE\text{-}CO_2CH_3 + NH_2NH_2 \longrightarrow PE\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{N}}\text{-}NH_2$$

$$PE\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{N}}\text{-}NH_2 \xrightarrow[\text{warming}]{HNO_2} PE\text{-}NCO + PE\text{-}\overset{O}{\overset{\|}{C}}\text{-}N_3$$

In both of the above approaches either high temperature or a long series of steps was necessary to incorporate the isocyanate group. This work was designed to incorporate the isocyanate group on the surface of HDPE at a lower temperature and with a minimum number of steps. The approach taken was incorporation of the isocyanate on the surface of ClHDPE by substitution or by elimination/addition reactions.

B. RESULTS AND DISCUSSION

HDPE film, after being extracted with pentane for 24 hr and dried to constant weight, was placed inside a photolysis cell and irradiated in the presence of chlorine gas (380 Torr). After the reaction, the photolysis cell was evacuated, then the ClHDPE was removed, extracted with pentane for 24 hr, and vacuum dried to constant weight. Irradiating the HDPE film (0.38 μ thick) for 1.0 hr produced a film containing 3.0 % chlorine by weight. Figures 56 and 57 show the ATR-IR spectra of the film before and after chlorination. After the chlorination reaction, new absorptions shown in Figure 58 appeared at 668 cm^{-1} and 612 cm^{-1}. These bands have been assigned by Quenum, Berticut, and Vallet[111] as the carbon chlorine stretch mode of (CHCl) unit in a PVC syndiotactic sequence for the band at 612 cm^{-1}, and the (CHCl) unit surrounded by PE units for the band at 668 cm^{-1}.

Comparison of the ATR-IR spectrum (Figure 58) and the transmission-IR spectrum (Figure 59) shows that the chlorination

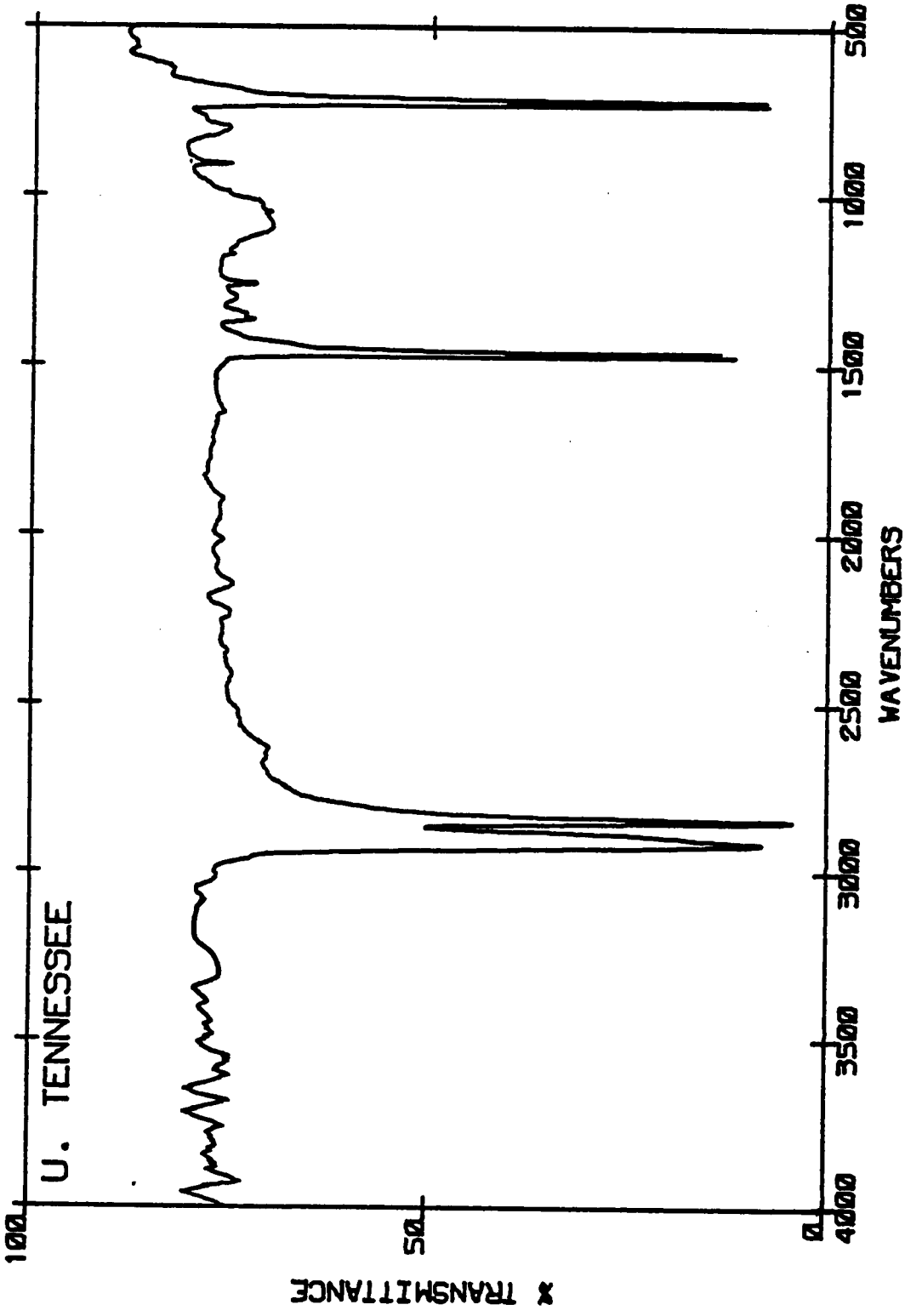


Figure 56. ATR-IR spectrum of HDPE taken at 45 degree angle of incidence (N=22.5).

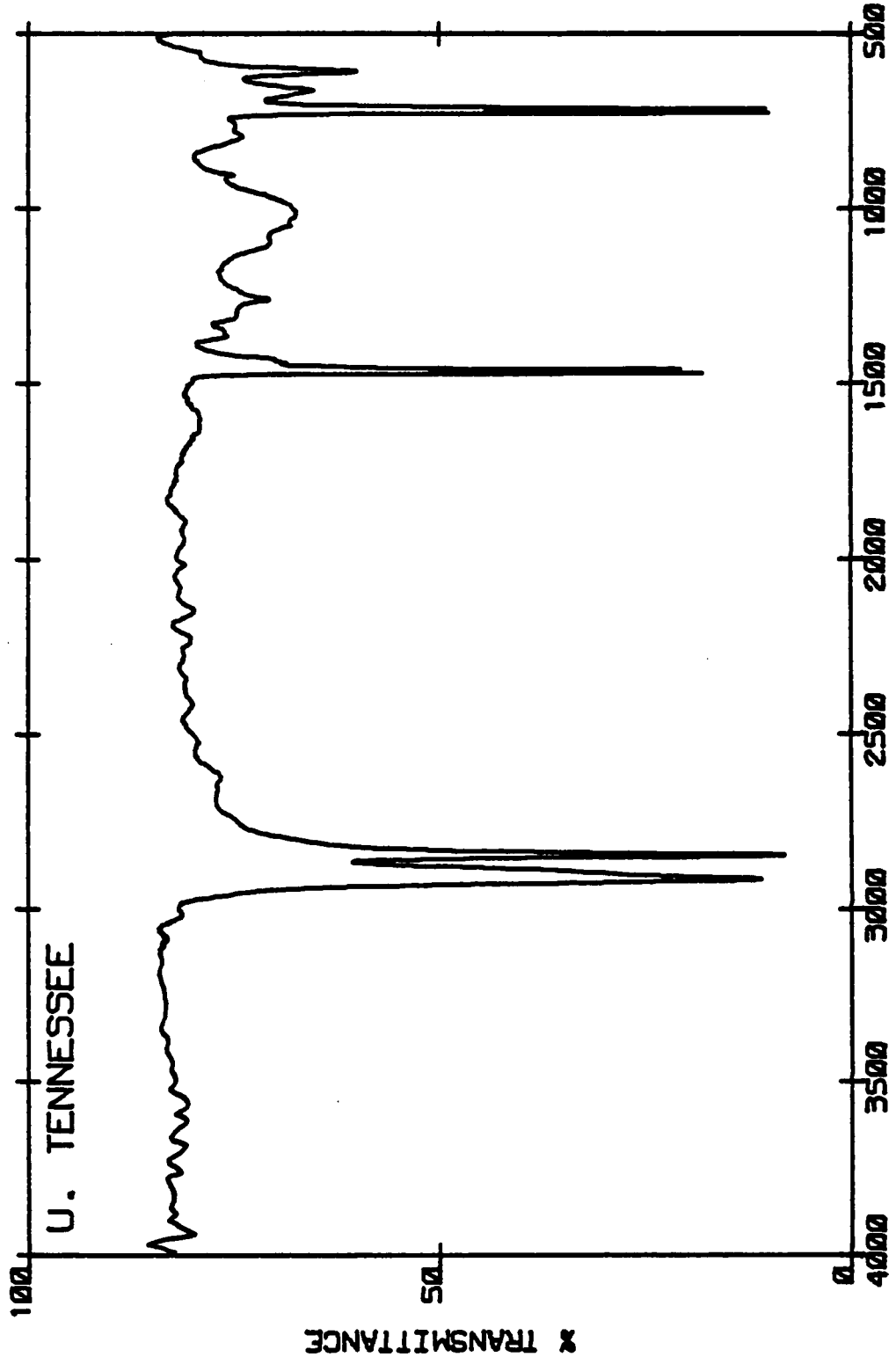


Figure 57. ATR-IR spectrum of C1HDPE taken at 45 degree angle of incidence (N=22.5).

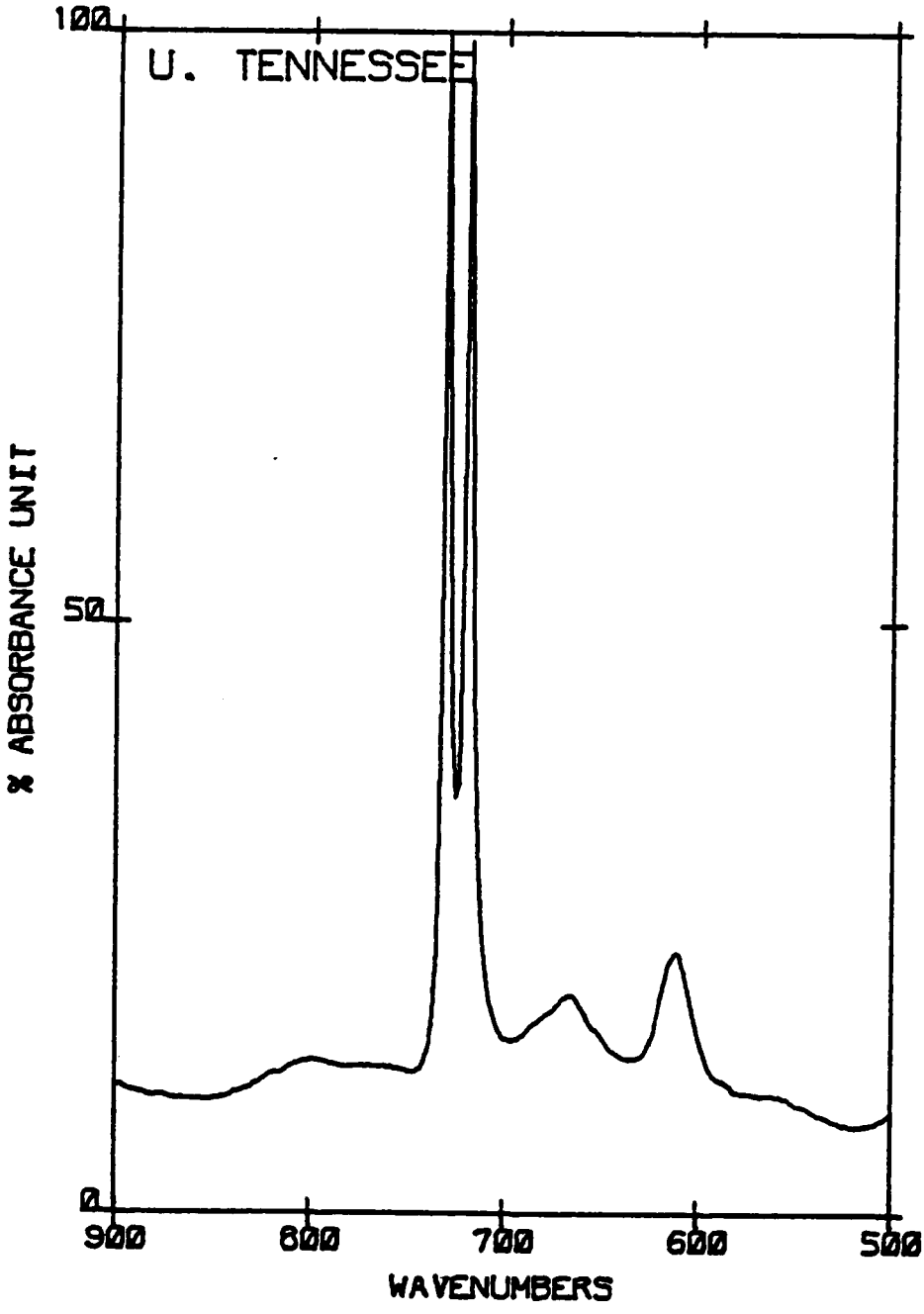


Figure 58. ATR-IR spectrum of ClHDPE taken at 45 degree angle of incidence (N=22.5). (Closer examination of film used in Figure 57.)

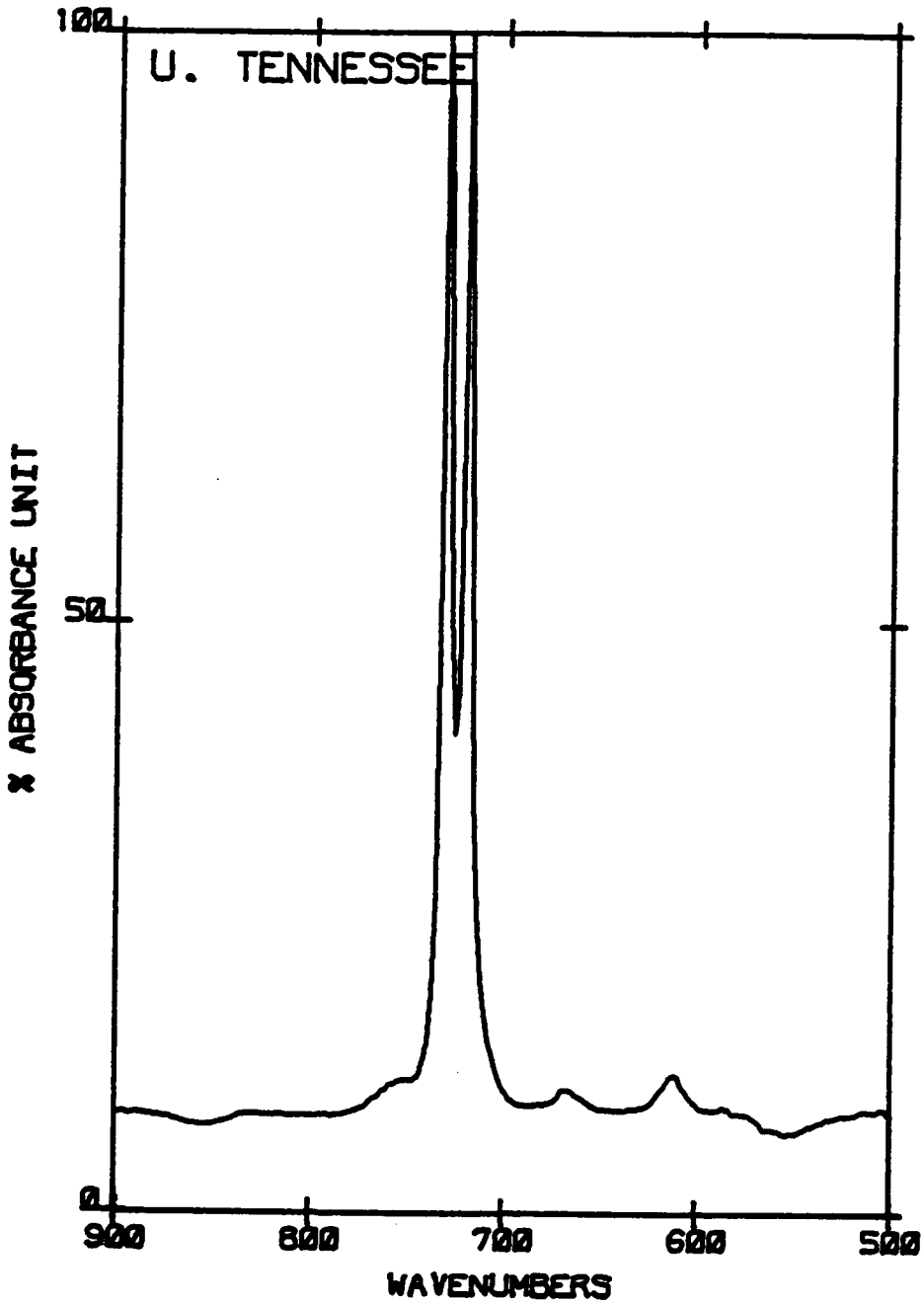


Figure 59. Transmission IR spectrum of ClHDPE taken in vacuum. (Same film as used for spectra in Figures 57 and 58.)

reaction occurred predominately on the surface. Presumably, the mechanism of chlorination is conventional free radical:[112]

$$Cl_2 \xrightarrow{h\nu} 2\ Cl^{\bullet}$$

$$Cl^{\bullet} + (CH_2) \longrightarrow (\dot{C}H) + HCl$$

$$(\dot{C}H) + Cl_2 \longrightarrow (CHCl) + Cl\bullet$$

$$(\dot{C}H) + Cl\bullet \longrightarrow (CHCl)$$

At a low degree of chlorination the monochloro methylene unit is formed,[113] but at higher degrees of chlorination (about 20% by weight) gem-dichlorinated units began to appear. Chlorination occurs in the amorphous region of the polymer and at the surface of crystallites.[114]

Substitution reactions were attempted on ClHDPE with a 0.065 M 18-crown-6 ether solution saturated with potassium cyanate. No isocyanate or carbonyl groups were detected by ATR-IR after 1, 2, 4 or 7 hr of reaction time; however, the reaction produced slightly yellow films after 2 hr. The substitution reaction was tried at 18-crown-6 ether concentration of 1.0×10^{-4}M, 1.0×10^{-3}M, and 1.0×10^{-2}M using toluene as the solvent at 23° at reaction times of 8, 24 and 48 hr at each 18-crown-6 ether concentration. Again, no substitution product was detected by ATR-IR. Increasing the 18-crown-6 ether concentration to 0.095 M and increasing the temperature to 84° again gave no substitution after 9 hr of reaction.

A possible substituted product was obtained by reacting the ClHDPE film with potassium cyanate in 80% v:v dimethyl formamide-ethylene glycol by using n-butyl ammonium bromide as a phase transfer agent. As shown in Figure 60, a carbonyl band appeared at 1725 cm^{-1}. The expected band due to N-H bend in the suspected carbamate group was not detected; perhaps its absence was due to the broad nature of the band from about 1680 cm^{-1} to 1550 cm^{-1} which indicated elimination. Furthermore, a white powder was visible in the yellow film; this powder could not be removed by washing in water, methanol, or dimethyl sulfoxide, or by extracting the film in a soxhlet extractor for 18 hr with chloroform. This film was not studied further because obtaining carbamate groups in high yield appeared difficult due to the elimination. Furthermore, the trapped salts in the film complicated the analysis making it difficult to determine the contribution of these salts to its infrared spectrum.

The second approach involved elimination of hydrogen chloride from ClHDPE followed by addition of the isocyanate group across the double bond. The ClHDPE was reacted with a 83% v:v dimethyl sulfoxide-basic methanol solution (25% by weight of sodium methoxide in methanol) at 60° for 30 min. This reaction produced a brown film within minutes. As shown in Figure 61 elimination was indicated by a small broad band between 1700 cm^{-1} and 1600 cm^{-1}, an indication of a polyene system. The addition reaction was accomplished as in Chapter IV: first, the addition of the isocyanate group across the double bond using isocyanic acid in cold chloroform and t-butyl hypochlorite. The reaction produced an isocyanate band on ClHDPE at 2260 cm^{-1} shown by the ATR-IR in Figure 62. As in Chapter IV, a carbonyl peak appeared at

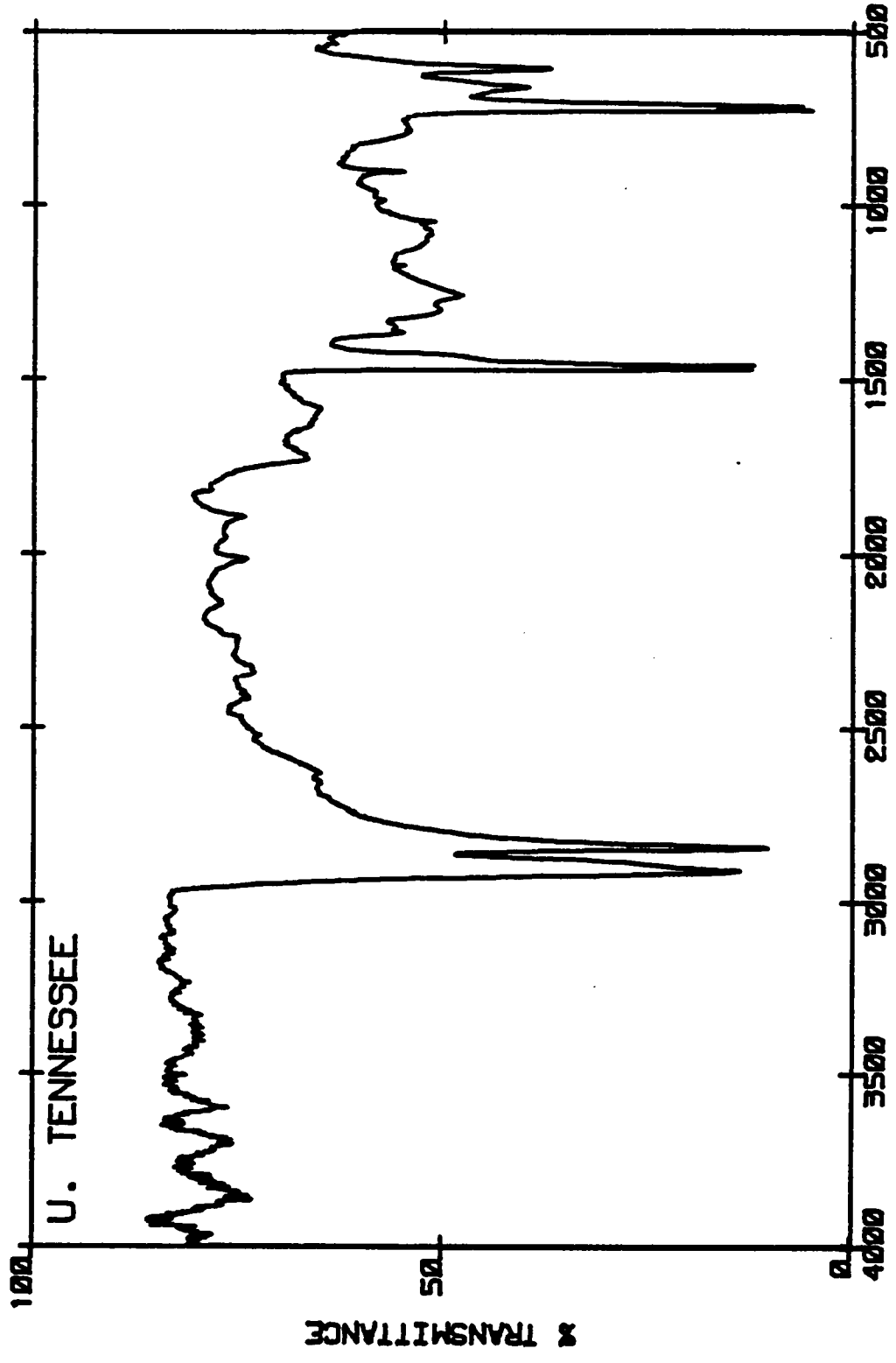


Figure 60. ATR-IR spectrum of modified C1HDPE taken at 45 degree angle of incidence (N=22.5).

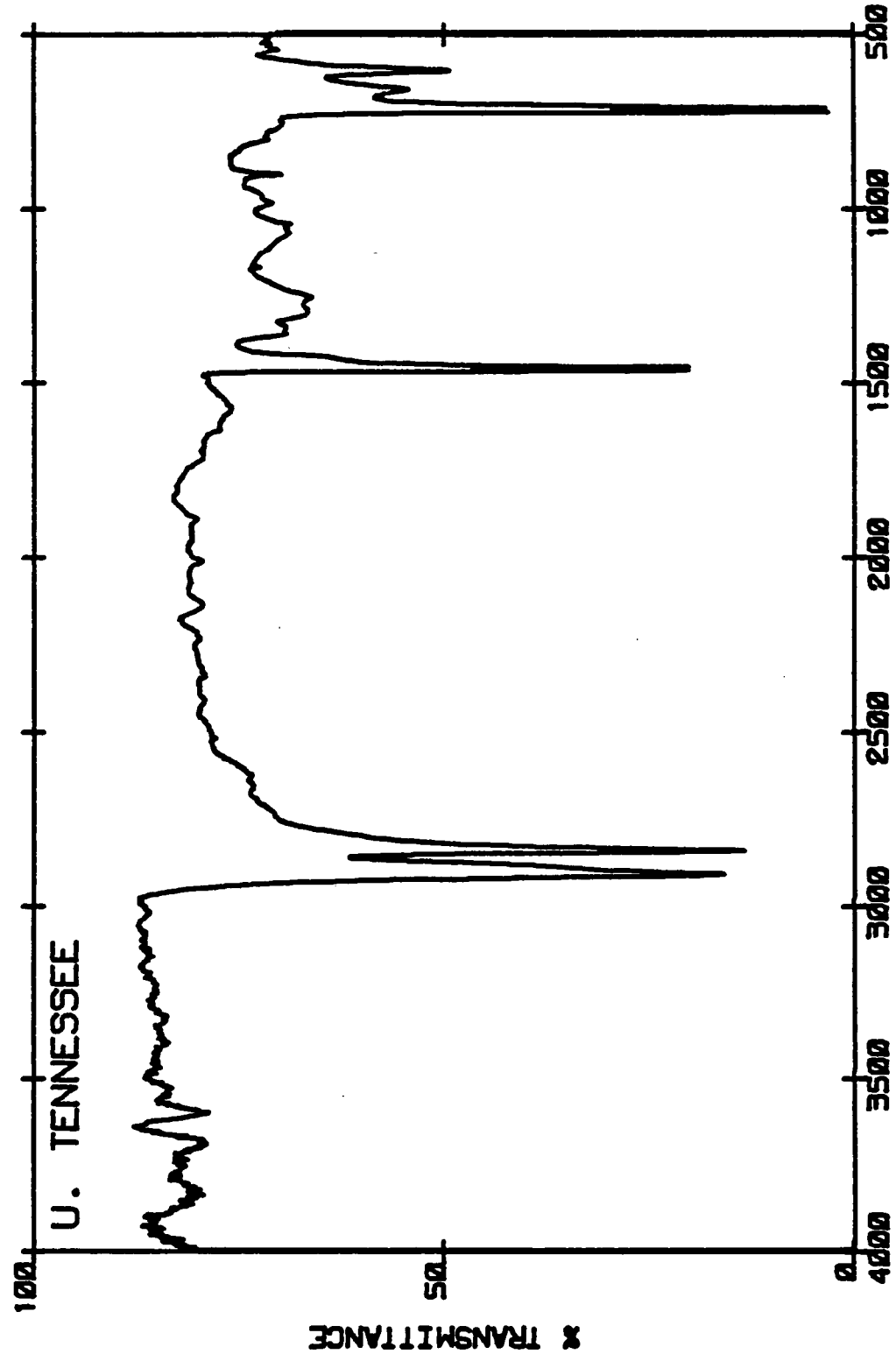


Figure 61. ATR-IR spectrum of surface dehydrochlorinated ClHDPE taken at 45 degree angle of incidence (N=22.5).

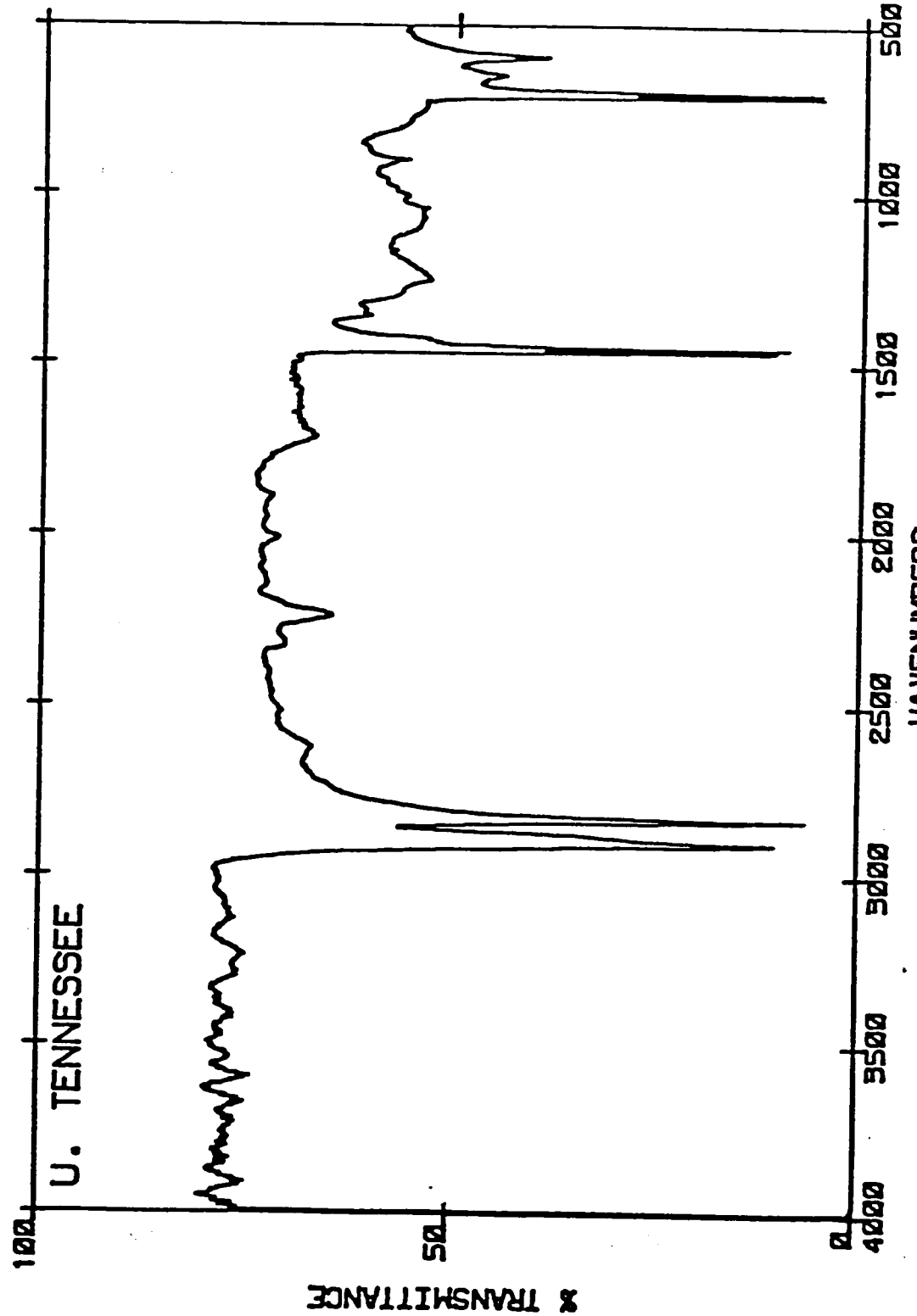


Figure 62. ATR-IR spectrum of modified ClHDPE (using t-butyl hypochlorite and isocyanic acid as reactants) taken at 45 degree angle of incidence ($\overline{N}$=22.5).

1725 cm^{-1}. Secondly, addition of the pseudohalogen, chloroisocyanate, across the double bonds again produced an isocyanate band at 2260 cm^{-1} and a carbonyl band at 1725 cm^{-1}, as shown in Figure 63. No weight gain was detected in either case (± 0.0003 g). The proposed mechanistic pathways are shown in Chapter IV.

To determine an approximate apparent average concentration of isocyanate groups on the modified surface of HDPE, the molar absorptivity of the isocyanate group was obtained using n-octadecyl isocyanate as a standard. Measured amounts of HDPE (0.37792g ± 0.00003g) and n-octadecyl isocyanate (0.01110g ± 0.0003g) were dissolved in 23 ml of hot o-xylene. A film was cast from the hot o-xylene solution (110°) onto a sodium chloride plates. The film was then cooled and dried in an argon atmosphere. The average thickness of the film 1.77 (± 0.06) x 10^{-3}cm was obtained from the absorbance of the unsaturated band at 910 cm^{-1} using an εc value of 4.61 (± 0.16) cm^{-1}. The εc value was obtained from a film of known thickness 3.8 (± 0.1) x 10^{-3} cm. A density of 0.96 (± 0.02) g/ml (est.) was used for the cast film to calculate the volume of the film. From the measured absorbance of 0.0180 (± 0.0007) for the isocyanate groups using transmission infrared spectroscopy a molar absorptivity of 1.1 (± .2) x 10^5 cm^2/mole was obtained.

The t-butyl hypochlorite/isocyanic acid addition reaction gave an isocyanate ATR-IR absorbance of 0.0586 (± 0.0007) for an N value of 22.5. An apparent average concentration of isocyanate of 0.29M was calculated using Equations 18 or 20, respectively, where the reference band was the crystalline methylene group at 1462 cm^{-1} in

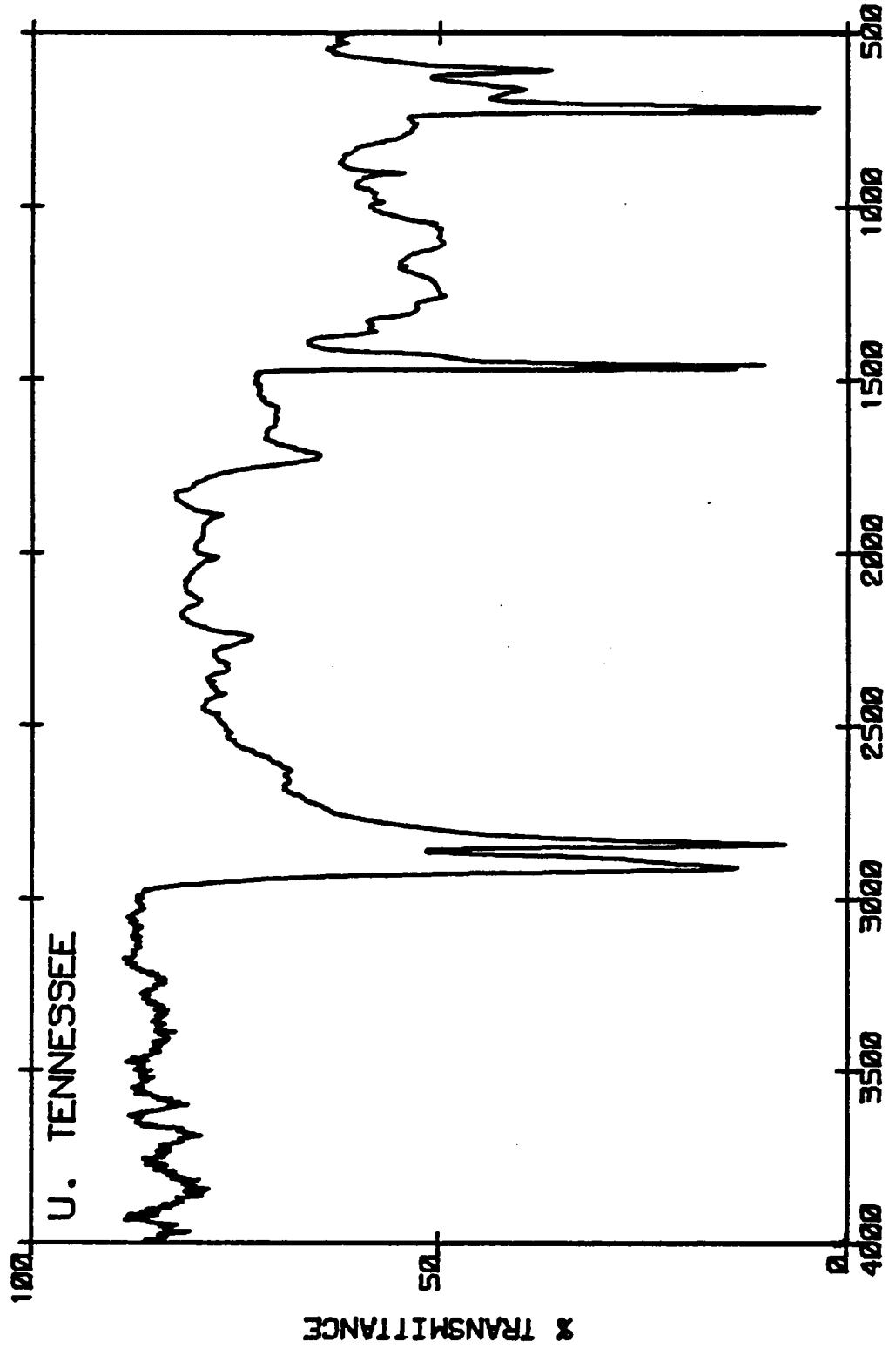


Figure 63. ATR-IR spectrum of modified ClHDPE (using chloroisocyanate as the reactant) taken at 45 degree angle of incidence (N=22.5).

Equation 20. The above apparent average concentration of 0.29M gives a minimum surface density of $3.1(\pm 0.2) \times 10^{13}$ units/cm^2. A useful absorbance for the isocyanate band could not be obtained using transmission infrared spectroscopy; thus, the depth of reaction was not obtained. The chloroisocyanate addition reaction gave an apparent average isocyanate concentration that was about 74% of the t-butyl hypochlorite/isocyanic acid addition reaction.

C. EXPERIMENTAL PROCEDURES

Film preparation: The HDPE film (20.0 cm x 4.0 cm x 38μ) was extracted with pentane for 24 hr, then vacuum dried at 47° to constant weight (± 0.0003 g).

Chlorination of HDPE: HDPE film (20.0 cm x 4.0 cm x 38μ) was placed in the center of a cylindrical photolysis cell to insure equal amounts of chlorine and equal radiation on both sides. The photolysis cell was constructed of Pyrex, 13 mm outer diameter and 60 cm in length. One end of the tube was sealed, and the other end was equipped with a standard taper 24/40 outer ground glass joint. The photolysis tube top consisted of a standard taper 24/40 inner ground glass joint connected to a 4 mm oblique-bore high vacuum stop cock. The cell was evacuated to 10^{-5} mm, and chlorine distilled into the cell to 380 Torr. The filled photolysis cell was then irradiated in a Rayonet photoreactor for 1 hr. After the reaction, the residue gases were evacuated, the ClHDPE removed, extracted with pentane, and vacuum dried at 47° to constant weight.

Elimination of ClHDPE: To a 100 ml three necked round bottom flask equipped with a gas inlet and outlet and magnetic stirrer was

added a 75 ml portion of dimethyl sulfoxide and 15 ml of 25% by weight of sodium methoxide in methanol. The total content was warmed to 60° and the flask flushed with argon gas for 15 min. While flushing the flask with argon gas, ClHDPE film (4.0 cm x 20.0 cm x 38μ, about 0.29 g) was placed in the reaction medium and an argon atmosphere maintained. After 30 min the brown film was removed and extracted with methanol in a soxhlet extractor under argon for 18 hr. The film was then vacuum dried at 23° to constant weight (±0.0003 g).

Addition reaction using t-butyl hypochlorite and isocyanic acid: The dehydrochlorinated ClHDPE films (two films - each 2.0 cm x 4.5 cm x 38μ, about 0.066 g) were placed on a glass screen inside a cylindrical pyrex vessel, 4.5 in x 2 in outer diameter, equipped with a magnetic stirrer and 65/40 ground glass joint. The 65/40 ground glass joint was fitted with a 24/40 ground glass joint adapter. The reaction flask was evacuated and argon gas introduced into the reaction vessel to bring it to atmospheric pressure. (The exposure time of the films to the air was < 3 min). The films were then frozen with liquid nitrogen and 50 ml of anhydrous chloroform slowly dripped into the reaction vessel by a pressure-equalizing dropping funnel. The reaction vessel was again evacuated and 3.5 ml (0.093 moles) of anhydrous isocyanic acid vacuum distilled at -20° into the reaction vessel. The reaction vessel was then brought back to atmospheric pressure with argon gas, and the reaction vessel brought up to 5°. Into a pressure-equalizing dropping funnel was then syringed 20.0 ml of anhydrous chloroform and 2.5 ml (0.021 moles) of t-butyl hypochlorite solution. This solution was dropped slowly (about 1 hr) in the dark into the magnetically stirred

isocyanic acid solution. After the addition was complete, the reaction vessel was cooled to -23°, the yellow films removed and immediately placed in cold anhydrous chloroform (0°) for 15 min. The washing procedure was repeated, and the films immediately placed in a vacuum and dried at 23° for 24 hr then vacuum dried at 47° to constant weight.

Addition reaction using chloroisocyanate: The dehydrochlorinated ClHDPE films (two films-each 2.0 cm x 4.5 cm x 38μ, about 0.066 g) were placed inside a modified graduated cylinder equipped with a 24/40 ground glass joint. The reaction vessel was evacuated, then brought back to atmospheric pressure with argon. To the reaction vessel was added 24 ml of anhydrous carbon tetrachloride. The carbon tetrachloride and films were frozen (-196°) and the reaction vessel evacuated. Into the reaction vessel was distilled 0.80 ml of ClNCO. The reaction vessel was then brought to atmospheric pressure and the reaction contents warmed to 0°. After 3.5 hr at 0°, the films were vacuum dried for 16 hr at 23°. The films were then extracted with anhydrous tetrahydrofuran (from a blue solution of tetrahydrofuran, benzophenone, and sodium) for 21 hr in a soxhlet extractor under argon then vacuum dried at 23° to constant weight.

CHAPTER VI

GENERAL CONCLUSIONS

This work allows the following conclusions to be drawn. Isolation of the isocyanate group on the surface of PVC via a substitution reaction is not possible due to the effective competition of elimination reactions, and to attack of the cyanate anion on any newly attached isocyanate groups. These reactions lead to polyene structures or to the proposed nylon-1 type structure, respectively. Substitution for chlorine on PVC's surface with the cyanate anion in the presence of ethylene glycol results in the formation of the carbamate group by trapping the transient isocyanate group before the initiation of subsequent reactions by the cyanate anion. Unsaturation sites in PVC are initiation sites for the propagation of double bonds to form a conjugated polyene system. Random elimination and elimination initiated at allylic sites by the cyanate anion result in the formation of allylic chlorides which undergo solvolysis with the solvent ethylene glycol to form hydroxyethyl ether groups on PVC's surface. Attempted substitution reactions on ClHDPE using potassium cyanate and 18-crown-6 as the phase transfer agent produced colored films with no infrared spectroscopic evidence of substituted products.

The ease of elimination of PVC's surface can be used to advantage by using addition reactions across the polyene system. Isocyanic acid in the presence of t-butyl hypochlorite adds isocyanate groups to double bond sites in the polyene system. The presence of a carbonyl group after the reaction results either from a polymerization of the

isocyanate groups initiated by cyanate anions present in low concentration from the weak isocyanic acid or by a trimerization type reaction from the isocyanate groups and isocyanic acid. The pseudohalogen, chloroisocyanate, was added across the double bonds of the polyene system. The isocyanate absorption and a carbonyl absorption appeared in the ATR-IR spectrum. The presence of the carbonyl group resulted from reactions between the cyanate anion and isocyanate groups, between the chloroisocyanate molecule and isocyanate groups forming a trimer product, or via radical initiated reaction on the isocyanate group produced by the cleavage of the chloroisocyanate molecule. The incorporation of isocyanate groups on the surface of ClHDPE was also accomplished by the previously described elimination/addition reactions.

A new method for determining the depth of an absorbing species in a polymer matrix was developed. By measuring the absorbance of an absorbing species in a polymer matrix by transmission infrared spectroscopy and by internal reflection spectroscopy (at one angle), a depth of the absorbing species was calculated. If a reference band is not available, the method allowed an approximate depth to be calculated, if d_e, the effective thickness, is known. If the polarization of light is unknown, d_e can be determined from a calibration plot. All depths derived by this method assumes a step profile. The method is limited by the ability of the infrared instrument to measure the small absorbance of an absorbing species in transmission infrared spectroscopy, and the assurance of film contact if a reference band is not available.

CHAPTER VII

EXPERIMENTAL SUPPLIES AND EQUIPMENT

A. MATERIALS

All materials were Reagent Grade and used as received unless otherwise specified.

Alumni: Fisher, Neutral, 20-80 mesh, Brockman Activity 1.

Argon: Selox, passed through anhydrous calcium chloride column.[115]

Benzophenone: Eastman.

Benzylchloride: Fisher, dried over 4A° molecular sieves.

2-Bromooctane: Matheson, vacuum distilled 68-70° at 10 mm.

1-Butyl amine: Fisher.

Calcium Chloride: Fisher, Anhydrous, 4-20 mesh.

Calcium hydride: Fisher (Purified).

Carbon tetrachloride: Fisher, stored over 4A molecular sieves.[115]

Chlorine: Matheson, fractionally distilled three times.

Chloroform: Fisher, passed thru a column of alumina (Activity 1) prior to use.[116]

Chloroform-d: Aldrich.

18-Crown-6-ether: Aldrich.

Cyclohexane: Fisher, stored over 4A° molecular sieves for one week prior to use.[115]

Cyanuric acid: Eastman (Practical).

Dimethyl sulfoxide: Fisher, stirred over calcium hydride for 3

d, vacuum distilled through an 18-cm vigreux column at 47°, and stored over 4A° molecular sieves.[117]

Ethanol: Aaper Alcohol and Chemical Company, distilled from magnesium and stored over 3A° molecular sieves.[118]

Ethyl ether: Fisher, Anhydrous.

Ethylene glycol: Fisher, dried over sodium sulfate for 1 week, vacuum distilled through a 30 cm vigreux column at 110 then stored over 3A° molecular sieves.[119]

2-Hydroxyethyl carbamate: donated by Hani Farah.[120]

Magnesium metal: Mallinckrodt.

Methanol: Fisher.

Molecular Sieves: Fisher.

N,N-dimethyl formamide: Fisher, dried over calcium hydride for 24 hr, vacuum distilled then stored over 3A° molecular sieves.[118]

O-xylene: Eastman.

Pentane: Eastman.

Petroleum ether: Fisher, boiling fraction 30-60°.

Polyethylene, high density: Film of 0.038 mm thickness specially prepared by Phillips Petroleum Company from marlex 6006 linear polyethylene with a molecular weight distribution. The density was previously determined to be 0.955 gcm^{-3} which yield a calculated crystallinity of 71%.[12]

Poly(vinyl chloride): Pliovic Type Bk75, Prepared by Goodyear by bulk polymerization using a peroxycarbonate initiator, dilute viscosity experiments gave a $[\eta] = 0.74$. The density of poly(vinyl chloride) films after casting from tetrahydrofuran under argon, vacuum

drying for 90 hr at 47°, 6 hr at 80°, extracting with methanol for 18 hr, vacuum drying for 24 hr at 47°, 6 hr at 80° was determined to be 1.3970 g cm^{-3}, which yielded a calculated crystallinity of 12% based on a crystalline density of 1.49 g cm^{-3}.

Potassium carbonate: Fisher.

Potassium cyanate: Fisher, vacuum dried at 55° for 24 hr prior to use.

Sodium metal: Fisher.

Sodium sulfate: Fisher, Anhydrous.

Sodium methoxide 25% in methanol: Matheson.

t-Butyl hypochlorite: Baker.

Tetrahydrofuran: Fisher, distilled from a blue solution containing sodium metal and benzophenone under argon.[122]

Toluene: Fisher, stored over 4A° molecular sieves.[115,123]

Trichloroisocyanuric acid: Eastman (Practical).

Trifluoroacetic acid sodium salt: Aldrich.

Trifluoroacetic anhydride: Aldrich.

B. INSTRUMENTATION

The near infrared fringe measurements were accomplished with a Carey 17 Spectrophotometer (Applied Physics Corporation). Infrared Spectra were accomplished with a Fourier Transform Infrared Spectrometer FTS-20 (Digilab, Inc.). All ATR spectra were accomplished using a Model 9 Wilks single beam multiple internal reflection attachment under vacuum. Proton nuclear magnetic resonance spectra were accomplished with a T60 spectrometer. A TI-59 Texas Instrument calculator was used to perform linear regression analyses. Density measurements were

accomplished on a density gradient column employing potassium carbonate and water. Viscosities were determined with a Ubbelohde viscometer. Melting points (uncorrected) were determined on a Thomas Hoover Unimelt Apparatus. Films were microtomed on an Americal Optical Microtome, model 820.

C. EQUIPMENT

Chlorination reactions were performed in a Rayonet Type RS Preparative Photochemical Reactor (South New England Ultraviolet Company) equipped with four 12.5 RUL 3500A° lamps. The reactor had a fan incorporated in the bottom to assist cooling during irradiation. Samples were heated under vacuum with a Thelco Model 19 vacuum oven. The vacuum system used was constructed of glass and was equipped with a Welch Duo-Seal vacuum pump, a two-stage mercury diffusion pump (H. S. Martin Co.), a McLeod gauge capable of reading to 10^{-5}mm Hg (Consolidated Vacuum Corporation), a mercury manometer, a Bourdon vacuum gauge (Fisher) which was calibrated with a mercury manometer. Analytical weight measurements ($\pm$ 0.0003 g) were done using a Mettler (HSO) analytical balance.

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LIST OF REFERENCES

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VITA

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