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THE HIGH TEMPERATURE AQUEOUS MODIFICATION OF POLYBUTADIENE AND A STYRENE CROSSLINKED UNSATURATED POLYESTER

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Ronald Reed Campbell

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This dissertation is dedicated to my wife, Yvonne, and to my daughter, Carmen, whose love, understanding, and encouragement helped make this work possible.

ABSTRACT

Polybutadiene and a styrene crosslinked unsaturated polyester were subjected to neutral hydrolytic conditions. This study was carried out in order to determine if neutral hydrolysis is a feasible process for the reclamation of these polymers.

Polybutadiene was subjected to hydrolytic conditions for up to 6 hr and as high at 270°C without weight loss or addition of water to the double bonds. Crosslinking reactions were observed; these were of similar nature to those induced by straight thermal treatment. Although the polybutadiene did not hydrolyze to produce reclaimable material, the resistance to hydrolysis would allow a mixture of polybutadiene and a hydrolyzable polymer to be separated.

Hydrolysis of the styrene crosslinked unsaturated polyester gave a maximum of 60% yield of isophthalic acid. This occurred after hydrolysis for 10 hr at 225°C. A yield of 56% was obtained after 4 hr at 225°C. A copolymer of styrene (used as a diluent and as a crosslinking agent) and fumaric acid (unsaturated diacid in polyester) was also reclaimed. The percent yield of the copolymer greatly increased between 250°C (20%) and 275°C (86%). This increase in yield of copolymer was accompanied by a decrease in the yield of isophthalic acid and propylene glycol (the diol used in the polyester). Neutral hydrolysis appears to be a reasonable process for the reclamation of usable material from the styrene crosslinked unsaturated polyester.

During hydrolysis, especially at the higher temperatures, side reactions of the propylene glycol were observed. Propanal was one of

the products of this side reaction. A study of the high temperature reaction of propanal led to the isolation and characterization of two novel tri-alkyl-substituted cyclopentenones. A mechanism for the formation of 2,4-dimethyl-5-ethyl-2-cyclopentenone and 3,5-dimethyl-2-ethyl-2-cyclopentenone was proposed.

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CHAPTER I

INTRODUCTION

A. General Considerations

Polymeric materials are being used in ever-increasing volume. A study by Stanford Research Institute for the Society of Plastics Industries forecasts that the output of plastics materials will increase at an annual rate of 8.6% between now and the year 2000.[1] Plastics materials will account for 7.2% of the U.S. gross national product in 2000, compared with 1.9% in 1973.

The supply of abundant and relatively inexpensive raw materials and energy has been a key to the past growth of the polymer industry. In 1973, of the 23 million tons of gas and oil consumed by U.S. petrochemical industries, nearly 75% was used in the production of polymers.[2] While the cost of petroleum is increasing, and its long-term availability may be questionable, materials and energy derived from coal may also be used by the polymer industry. Several existing and emerging techniques allow generation of chemical feedstock materials from coal, though partial or complete changeover to coal-derived feedstocks would markedly alter the availability and price structure of certain materials.

The importance of energy considerations is illustrated by the Stanford Research Institute prediction that the energy needed for the polymer industry in the year 2000 will be about nine times that used in 1973.[1] The energy required for production of some polymers and the energy obtainable from the important fuels are listed in Table I.[3]

TABLE I[a]

ENERGY INPUT FOR POLYMERS AND ENERGY OUTPUT FOR FUELS

Polymer	Energy Input (MJ/kg)	Fuel	Energy Output (MJ/kg)
Polyethylene	44.0	Coal	30.0
Styrene butadiene rubber	71.0	Oil (crude)	45.0
Cellulose (crude)	0.3	Gas (methane)	55.5

[a]Source: H. Smith, 7th World Power Conference, Moscow 1968, Paper E 188, 71; European Polym. J., 11, 833 (1975).

Current projections conclude that the oil and gas raw materials base will continue for some years, and that the principal changeover will involve the substitution of coal or coal-derived gases for petroleum-based fuels.[2]

In addition to possible changes in availability and/or sources of raw materials and energy, the treatment of scrap and used polymeric materials is also undergoing change. Direct reuse of "spent" polymeric materials would be most desirable. However, most polymers are dyed, pigmented, coated, crosslinked, partially degraded, or subjected to some other modification or contamination during their initial processing or use cycle. Still, it is sometimes possible to reuse polymers directly, especially if an appropriate less demanding application is available. In certain cases, additives such as chlorinated polyethylene enhance the reprocessability.[4] However, direct reuse of polymeric materials can be accomplished in only a limited number of cases, so scrap and used polymers generally have been discarded.

Disposal techniques for scrap and used polymers include open dumping. In 1972 over 85% of all collected waste was discarded in open dump sites.[5] Open dumping is declining, due to the associated fire and health hazards and the lack of available land.

In so-called sanitary landfills, refuse is compacted, covered with soil, and allowed to settle. Sanitary landfills accounted for 6% of the 12,000 to 14,000 landfills in the United States in 1972.[5] One advantage of the landfill (and open dump) is the lack of any separation step before disposal. Although this method reduces the fire and health problems associated with the open dump, several

disadvantages make it undesirable. A major disadvantage is that the entire material and energy value of the discarded polymeric materials is lost. In addition, the landfill site can have only restricted use after the site is covered.

An important aspect of sanitary landfill technology involves the biodegradability of the buried materials. Biodegradation depends on the susceptibility of the substrate to attack by mircoorganisms such as bacteria, fungi, or enzymes.[6] The very properties that make many polymers valuable, such as impermeability to water, fats, and oils, also cause them to be resistant to microorganism attack.[7] The damage that does occur usually can be traced to low molecular weight components such as textile sizing, lubricant, stabilizer, or plasticizer.[8]

Deliberately biodegradable plastics are of interest to the packaging industry, which uses a large volume of plastics that have a relatively short service life and a high probability of being discarded as litter. Organism-susceptible additives allow initial attack and enhance permeability, thereby facilitating complete physical and chemical breakdown.[9] So modified, a discarded article will disappear faster. This approach does limit the end-use capabilities of the "adulterated" materials, both in terms of applications and of service life. In addition, the complete material and energy value of the polymeric material is wasted.

Another method which is closely related to biodegradation with respect to advantages, disadvantages, and applicability is photodegradation. Polymers may be ultraviolet light sensitive because of their molecular structure or because of additives. Photodegradation occurs

when light is absorbed and a bond is broken to form free radicals. Peroxides and hydroperoxides will form from the radicals in the presence of oxygen. The peroxide and hydroperoxide groups will further decompose to form carbonyl and hydroxyl groups and finally carbon dioxide and water.[10] This reaction greatly reduces the molecular weight of a polymer by breaking the polymer chain backbone. Once this has occurred, the polymer is brittle and will break down by natural forces.

Classically, most research and product development efforts have centered on making polymers resistant to photodegradation. But recently several products have been recognized as useful for deliberate initiation and control of the photodegradation process. These include benzophenones, coal tar, dyes, zinc, and copper oxides.[10] Polymers are also available that will photodegrade without additives. For example, ketone groups, which absorb ultraviolet light but do not absorb visible light, can be placed along a polymer chain. Oxygen is not needed for photodegradation in this case. The degradation time can be varied from a few hours to months by varying the type and concentration of ketone groups.[10]

Since most plastic materials are inherently stable to biological degradation, there has been a considerable amount of research to make the plastics partially photodegrade and then to biodegrade to lower molecular weight material. This is called photobiodegradation. Metal dithiocarbamates are useful additives, helping to reduce a plastic film to a powder after exposure to sunlight.[7] This powder, which contains chemical groups such as carboxyl, carbonyl, and hydroxyl, is hydrophilic. Microorganisms present in soil will then attack the degraded

polymer, as long as oxygen is present. The final products from biodegradation are carbon dioxide and water. The advantages and disadvantages of photodegradation and photobiodegradation are similar to those discussed for biodegradation.

Pyrolysis (non-combustive thermal treatment) of polymeric materials has also been investigated. In many cases, pyrolysis of polymers leads to formation of reclaimable materials--in some instances the reclaimed materials can be used as chemicals and in others as fuels. An example of the former is pyrolysis of poly(methyl methacrylate), which yields methyl methacrylate monomer in yields as high as 90%.[11] The pyrolysis of polyethylene in molten salts at 850°C yields both chemical (ethylene) and fuel (methane) products.[12] The pyrolyses of polystyrene, waste plastics, and scrap tires have been discussed in terms of recovery of reusable chemicals and gaseous or liquid fuels.[13,14] In a few areas, municipal solid wastes are being pyrolyzed, recovering fuel oils and gaseous fuels. The equivalent of two barrels of oil can be produced for each ton of dry waste, and the heat needed for the process is obtained from combustion of the pyrolysis residue.[15] In some cases, however, troublesome products are generated. For example, pyrolysis of poly(vinyl chloride) produces HCl in nearly quantitative amounts, though at least a combustible residue of approximate empirical formula CH is also obtained.[12] Even HCN can be obtained from certain pyrolyses, as will be discussed later.

Thus, the advantages of the pyrolysis approach are that the volumes of waste are markedly decreased, and many times materials useful as chemicals or fuels can be reclaimed. A disadvantage is that generation

of clean products, particularly those for use as chemicals, often requires segregation or sorting of the waste. In certain cases, corrosive or poisonous materials are liberated. Also, large scale pyrolysis equipment is relatively expensive.

Incineration of solid waste can be accomplished without segregation or sorting. Energy in the form of heat can be harnessed directly or used to generate electricity. There appears to be little trouble in the incineration of most large volume polymeric materials. As expected from the preceding discussion, HCl is produced from poly(vinyl chloride). A study of the effects of poly(vinyl chloride) with respect to HCl emission was conducted at the Babylon incinerator in Long Island. With no addition of poly(vinyl chloride) the HCl emission was 511 ppm. When 2% poly(vinyl chloride) was added the HCl emission rose to 1990 ppm, and with 4% poly(vinyl chloride) added the emission rose to 3030 ppm.[16] If the incinerator is properly built and operated, the amount of HCl produced is not harmful to the environment. However, according to Dr. Robert N. Rickles, New York City air resources commissioner in 1971, "there are not well-run incinerators--certainly we don't have any in New York City."[17] The addition of alkalies to the incinerator is a possible solution to the HCl problem. This method works well in laboratory reactors but causes serious problems in commercial facilities, since the alkalies attack the clay bricks used in most incinerators.[18]

Another pollutant produced from the burning of polymers is HCN. Although polyurethanes have received much attention in this area, the amount of HCN produced from polyurethane foam by controlled pyrolysis in air is less than wool and about the same as paper. For example,

polyurethane foam produces 1200 μg HCN/g sample when pyrolyzed in air while paper produces 1100 μg HCN/g sample and wool produces 6500 μg HCN/g sample.[19] The amount of HCN produced by the pyrolysis of nylon and cotton is much less than the amount produced by the pyrolysis of polyurethane foam. It should be pointed out that with polyurethane foam there is a large (approximately 27 fold) increase in the amount of HCN produced after ignition compared to the amount produced prior to ignition.

The major advantages of incineration are the great reduction in volume of waste, the lack of any separation of material, and the recovered energy value in terms of heat or electricity generated if properly performed. A considerably larger investment is required for incineration than for landfill. However, if energy is captured and sold, part of this disadvantage may be offset.[20]

Another, more limited, method for disposal of waste polymeric material is hydrolysis at elevated temperatures. In the past, hydrolysis has generally been considered an undesirable side reaction which decreases the utility of the polymeric product. Thus, much research emphasis has been on increasing the resistance of several polymers to hydrolysis.

Hydrolysis has been used as a method for qualitative and quantitative analysis of polymers, since the structure of a hydrolyzable polymer may be determined by identifying the hydrolysis products. This method of polymer analysis has been reported for polyurethanes[21,22] and for polyesters. The hydrolysis of polyesters will be discussed in a later section.

Hydrolysis may be performed using acidic, basic, or neutral conditions. Several problems are associated with the use of acidic or basic conditions. Strong acids and bases increase the possibility of damage to personnel and equipment. The equipment used in the acidic or basic hydrolysis must be resistant to acidic or basic corrosion. The cost of the acid or base must be considered. Also, the used acid or base must be neutralized, which both increases the cost and forms a generally unwanted salt.

Polymers may be classified into three groups based on their reaction(s) when subjected to hydrolytic conditions. Polymers such as polyethylene, polypropylene, and polystyrene are classified as hydrolytically stable. The second group of polymers includes poly(methyl methacrylate), poly(vinyl acetate), and other polymers with hydrolyzable side groups. These polymers will partially hydrolyze but will not completely degrade to low molecular weight material. The final classification includes polymers such as polyurethanes and polyesters which degrade completely to low molecular weight materials. Reported studies with documented commercial application have centered on polymers in the last classification.

Polyurethane hydrolysis has received much attention from the automobile industry. This interest is due to the large volume of polyurethane foam used in the automobile industry and the large volume of reject material which must be disposed of. Mahoney et al.[23] of the Ford Motor Company recovered 65-85% of the theoretical yield of toluene diamines and 90% yield of liquid poly(propylene oxide) from the hydrolysis of low density polyurethane foam used in molded bucket

seats. The reaction was carried out with superheated water at 200°C for 15 min. The reaction of polyurethane with superheated water is given below. A follow-up study by the U.S. Bureau of Mines in

$$\left| \text{-CNH-R-NHC-O-R'-O-} \right| + H_2O \rightarrow H_2NRNH_2 + CO_2 + HOR'H$$

conjunction with the Ford Motor Company used nonmagnetic reject of automobile shredders as a source of polyurethane scrap.[24] The production of the toluene diamine was greatly decreased, and the production of the polyether was slightly decreased when using this contaminated polyurethane foam.

Campbell and Meluch[25] at General Motors used low-pressure superheated steam to effect hydrolysis of polyurethane foam. The dry superheated steam was from 232-316°C and was at one atmosphere pressure. Because there were no chemicals or liquid water in equilibrium with the vapor, the polyol produced from the hydrolysis of the polyurethane foam was dry and free of most contaminants. The dry polyol could be removed from the reaction chamber and used for the production of more polyurethane. The reclaimed polyols were used in a 5 to 95 ratio with new polyols without processing problems or reduction in the properties of the polyurethane.

A continuous process for the hydrolysis of polyurethanes has been patented by Bayer.[26] A twin screw extruder was used to hydrolyze waste foam in 10-40 min at 30-50 bars in the presence of steam.

Nylon has been hydrolytically degraded to recover ε-caprolactam. One process uses superheated steam,[27] and another process uses a

temperature of 260°C for 4 hr in a sealed tube, the latter producing 79% ε-caprolactam from the original nylon 6.[28]

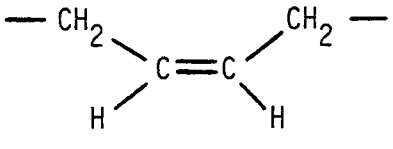
While hydrolysis cannot be a universally applicable disposal-reclamation technique, it does offer major advantages when it is applicable. In addition to reducing waste volume and increasing the manageability of the residual waste products, hydrolysis of many scrap polymers should allow reclamation of chemical materials at an intermediate state of complexity. The chemical intermediates so obtained could be used in place of virgin petrochemical-derived materials for production of polymeric or non-polymeric substances, thereby providing important conservation of both materials and energy.

Ideally, a mixed waste feedstock could be treated in such a disposal-reclamation process, but this could be done best if the high temperature aqueous reactions of a number of individual polymer systems were understood in detail. The two polymer systems of principal interest in this study are often found "naturally segregated" from other materials and are therefore of individual interest; they are not members of the "obviously reclaimable" type so the results are expected to be of interest in both scientific and potentially commercial respects. The polymers are polybutadiene (PBD), which is expected to be little affected by high temperature aqueous conditions, and a styrene cross-linked unsaturated polyester (SXUP), which is expected to be significantly altered by high temperature aqueous conditions. These were studied and will be reported on separately.

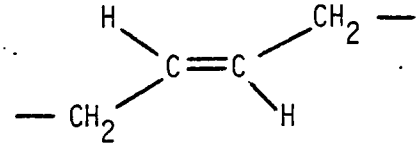
B. Polybutadiene

PBD is widely used as a synthetic rubber. It ranks second only to styrene-butadiene rubber in terms of annual consumption of synthetic rubbers.[29] The projected world consumption of synthetic rubber is 11 million tons by 1985. Approximately 90% of the PBD produced is used in tires, and most of the remaining 10% is used as an additive for rigid plastics.[30]

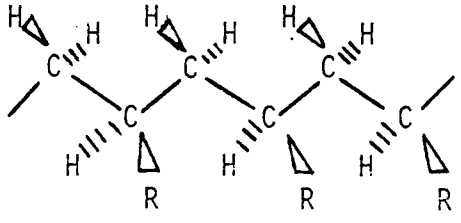
The polymerization of 1,3-butadiene was first reported in 1911.[31] The polymerization of 1,3-butaidene can produce four stereochemically different repeat units: cis-1,4, trans-1,4, syndiotactic-1,2, and isotactic-1,2.



cis-1,4

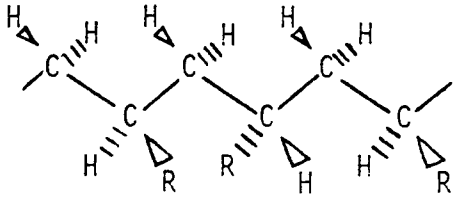


trans-1,4



isotactic-1,2

[R=-CH=CH$_2$]



syndiotactic-1,2

With the proper catalyst and conditions, any one of these stereostructures may be produced with the near exclusion of the others.[32-35] However, most commercially available PBD contains mainly cis-1,4 isomeric units.

Infrared spectroscopy (IR) is the primary method for qualitative and quantitative determination of isomeric units in PBD. IR is also used to determine the occurrence and degree of various structural changes in PBD.

In 1945 Thompson and Torkington[36] used IR to qualitatively study the 1,2 addition in sodium polymerized butadiene. In 1949 Hampton[37] used the following bands for the analysis of PBD: cis-1,4 at 13.8 μ, 1,2 at 10.98 μ, and trans-1,4 at 10.34 μ. Extinction coefficients for each type of unit were also presented. The isomeric composition for a PDB sample could be determined by solving three equations simultaneously. These equations involve the absorption coefficient and intensity of each band.

The microstructure of PBD in copolymers has been studied quantitatively by several workers including Hampton.[37-39] Silas et al.[40] pointed out that the band in PBD due to cis-1,4 at 1.35 varies in position and shape as the amount of cis-1,4 changes. For this reason an empirical function of the area between 12.0 and 15.7 μ, which depends on the intensities of the incident and transmitted radiation at a given wavelength, was used to measure the amount of cis-1,4-PBD.

Haslam et al.[41] point out that if the band at 13.6 μ is used, the laborious method of Silas et al. may be avoided. The following detailed procedure for the calculation for trans-1,4 1,2, and cis-1,4 is from Haslam et al. A sample calculation will be presented using the IR spectrum of the PBD sample shown in Figure 1.

Straight line backgrounds are drawn using X-X' and Y-Y'. The following lines are constructed: ABC at 10.3 μ for trans-1,4, DEF at 11.0 μ for 1,2, GHJ at 13.6 μ for cis-1,4. The corresponding absorbance for each isomer is given as follows:

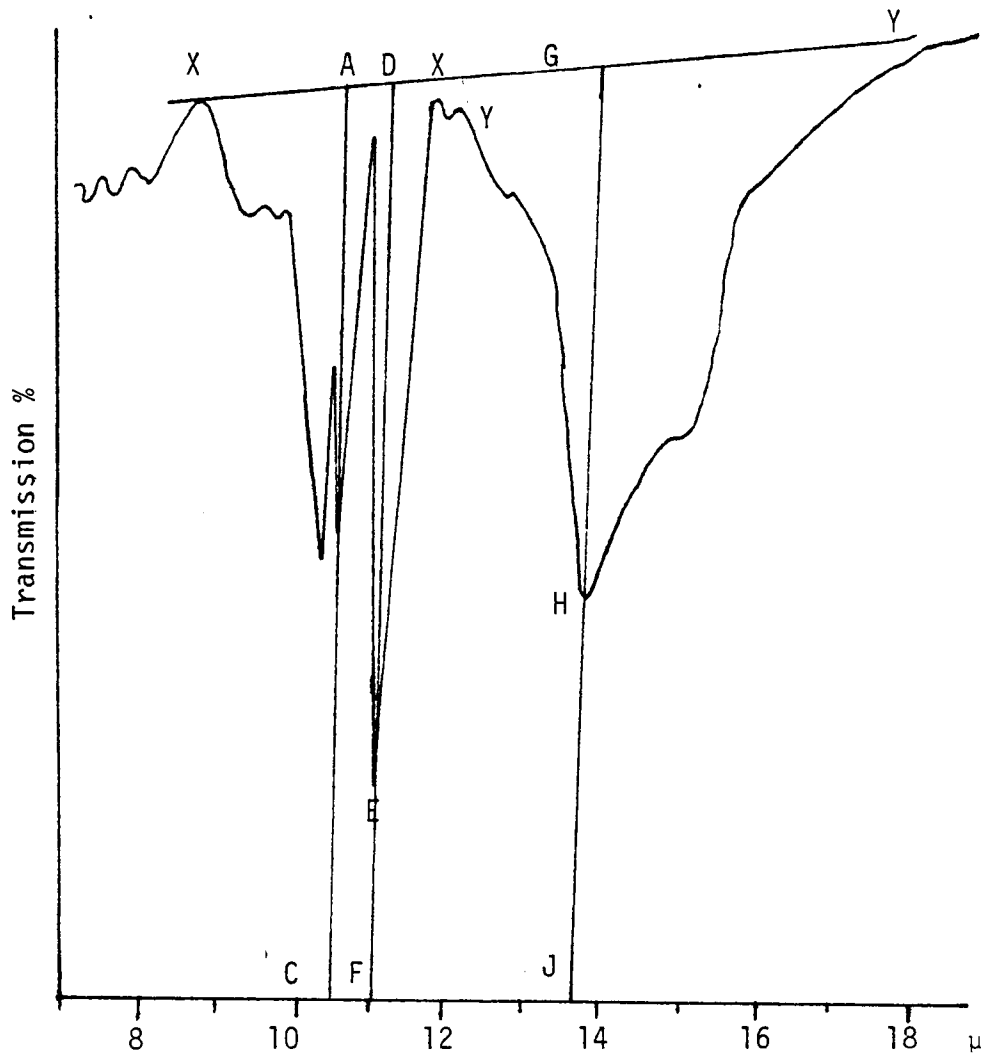


Figure 1. IR bands in PBD due to unsaturation.
trans-1,4-PBD-10.3 μ; 1,2-PBD-11.0 μ; cis-1,4-PBD-13.6 μ.

trans-1,4 Isomer	Absorbance = $\log \frac{AC}{BC} = A_1$
1,2 Isomer	Absorbance = $\log \frac{DF}{EF} = A_2$
cis-1,4 Isomer	Absorbance = $\log \frac{GJ}{HJ} = A_3$

The weight percent of each isomer is then calculated from the absorbance and extinction coefficients for each IR band.

$$\% \text{ trans - 1,4 Isomer} = \frac{A_1/86}{A_1/86+A_2/120+A_3/25} \times 100$$

$$\% \text{ 1,2 Isomer} = \frac{A_2/120}{A_1/86+A_2/100+A_3/25} \times 100$$

$$\% \text{ cis-1,4 Isomer} = \frac{A_3/25}{A_1/86+A_2/120+A_3/25} \times 100$$

Attenuated total reflectance (ATR) has been widely used as a method to study reactions on or near surfaces. ATR is used in conjunction with transmission IR to study the difference between the surface changes and bulk changes of a polymer sample subjected to various reaction conditions.

Nuclear magnetic resonance spectroscopy (NMR) has been used to determine the microstructure of polybutadienes.[42] But solution NMR is of limited use in the study of high temperature PBD reactions due to the insolubility after crosslinking.

PBD will be subjected to high temperatures during this study, so it is important to review prior studies of the thermal reactions of PBD. Although pyrolysis and oxidation to produce low molecular weight material will be mentioned, this review will focus on the reactions

that occur in the nonvolatile portion of the degraded PBD. These reactions include cis-trans isomerization, cyclization, and crosslinking.

The thermal degradation of natural rubber and allied substances was reviewed by Bevilacqua.[43] Polymer degradation in general was reviewed by Grassie in 1972.[44] Grassie points out the lack of research and understanding with respect to the degradation of PBD. The early work on PBD thermal degradation was concerned principally with the volatile products.

Pyrolysis of PBD has been reported by Wall.[45] The pyrolysis of PBD and other diene polymers produces a very low percentage of monomer compared to polystyrene and poly(methyl methacrylate). The percentage monomer produced from pyrolysis of several diene polymers at 400°C is presented in Table II. Braun and Canji[46] studied the pyrolysis of PBD by use of pyrolysis gas chromatography and mass spectroscopy. Over 500 components in the C_1-C_{20} range were detected. The low monomer yield and wide spectrum of volatile products indicated a random type of chain scission.

Microstructural modification of PBD units can be accomplished in several ways. In 1957 Golub[47] reported the first cis-trans isomerization of PBD which was not accompanied by any other structural changes. This was accomplished by means of ultraviolet irradiation in the presence of a suitable sensitizer. This was the first true cis-trans isomerization of a high molecular weight polymer. The sensitizers mentioned include organic bromide, sulfide, disulfide, and mercaptan. Since PBD is transparent at wavelengths above 1900 A, sensitizers are necessary for any reaction to occur. The mechanism proposed for the bromide-sensitized isomerization involves the formation

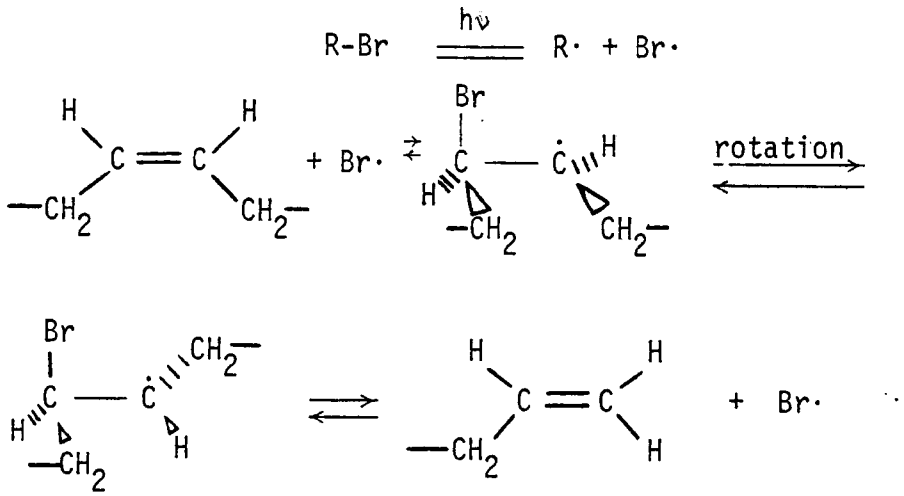
TABLE II[a]

MONOMER YIELDS FROM THE PYROLYSIS OF DIENE POLYMERS AT 400°C

Polymer	Percent, Monomer Yield
Polybutadiene	1
Natural crepe rubber	2
Balata	2
Polyisoprene (synthetic)	5

[a]Source: L. A. Wall, J. Research Nat. Bur. Standards, 41, 315 (1948).

of free bromine atoms from the photolysis of the organic bromide sensitizer. The next step is the addition of the bromine atom to the double bond which results in an organic radical in which rotation is possible. When the bromine atom is released and the double bond reestablished, the predominant geometric isomer formed is the trans which is more thermodynamically stable. This reaction mechanism is shown below.



The initial cis/trans ratio of 57/43 was changed to 90/10 after isomerization with allyl bromide in nitrogen. These ratios were obtained from the IR's of PBD before and after irradiation.

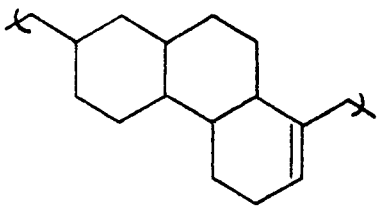
After this report of cis-trans isomerization, several other methods leading to the cis-trans isomerization have been reported by Golub and coworkers. These methods include irradiation in solution in the presence of other free radical initiators,[48] X-ray irradiation in pure benzene solution,[49] and krypton 1236 Å irradiation in the pure solid state where the energy absorbed by the polymer leads to excitation and then to isomerization.[50]

The cyclization of PBD was reported in 1935 by Brizov and Kusov.[51] PBD containing about 40% 1,4 and about 60% 1,2 units was

heated to 230-270°C to obtain 33-67% yield of cyclized product. Natural rubber underwent the same type of cyclization but at a much lower temperature (160°C).

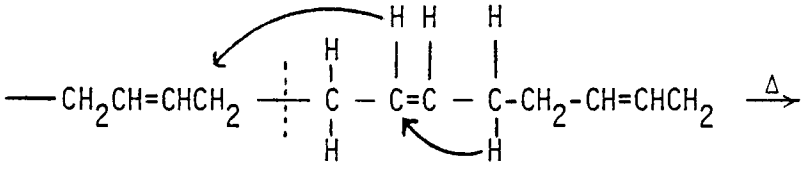
Kossler et al.[52] cyclized a high cis and a high trans PBD at 145°C in a sulfuric acid/p-xylene medium and obtained IR spectra which were identical. The original IR bands indicative of cis and trans were virtually eliminated.

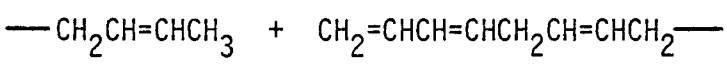
Shelton and Lee[53] cyclized PBD containing 80% 1,4 and 20% 1,2 units by heating a solution of PBD in xylene with concentrated sulfuric acid for 18 hr at 140°C. The resulting cyclized polymer was oxidized. The oxidative degradation products and the unsaturation measurements led to the conclusion that the cyclized PBD had the predominantly tricyclic structure shown below. The overall structure must involve mono and polycyclic groups in addition to uncyclized segments.



The thermally induced reactions of 1,4-PBD have been studied by Golub and Garguilo.[54] The original high cis- or high trans-PBD was pyrolyzed to about 50% weight loss to yield a polymeric residue which was almost completely cyclized. The following structural changes were noted from the IR spectrum of high cis-PBD: (1) a sharp decrease in the 13.6 μ band and the removal of the 6.0 μ band which correspond to the consumption of the cis-CH=CH- units; (2) the appearance of a band at 10.3 μ which is associated with cyclic structures and a small amount

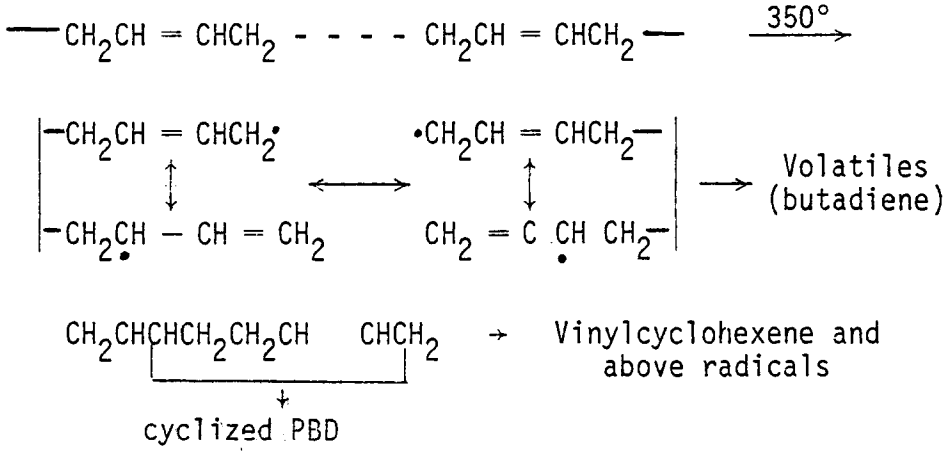
of trans-CH=CH- units, and (3) the appearance of a band at 12.2 μ which is also associated with the cyclized structures. In addition to the above changes, the bands at 7.3 μ (methyl group) and 6.25 μ (conjugated double bonds) provided evidence for the hydrogen transfer reaction shown below.





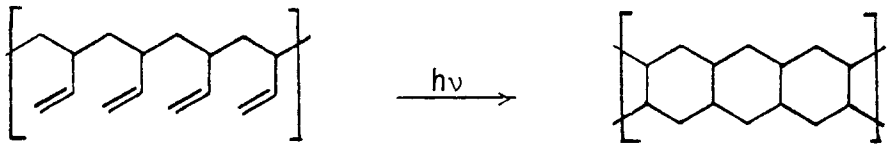
Under the conditions used by Golub and Gargiulo to produce cyclized PBD,[54] IR indication of cis-trans isomerization would not be detected due to the loss of unsaturation in forming cyclic structures. However, when lower temperatures (200-300°C) were used, cis-trans isomerization was detected well below the 350°C at which weight loss began. For example, a cis/trans equilibrium ratio of about 31:69 was approached by thermal isomerization of 1,4-PBD at 260°C.

Golub and Gargiulo's scheme for the thermal cyclization and depolymerization of 1,4-PBD is shown below.[54]

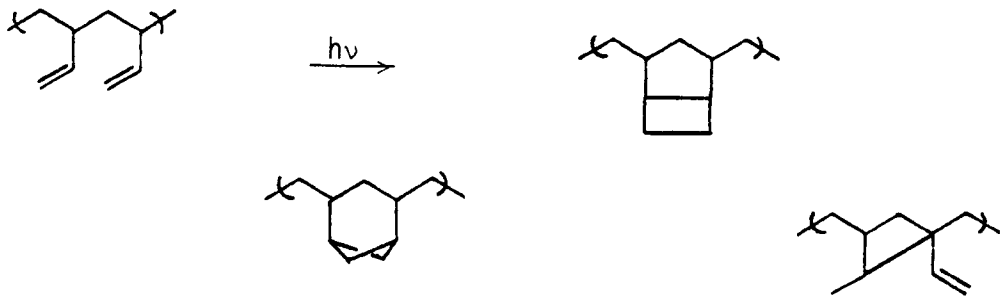


Soon after the above thermal modification work on 1,4-PBD was published, Golub and Sung[55] reported the corresponding research on 1,2-PBD. Pyrolysis of 1,2-PBD until 60% weight loss produced a polymeric residue which was almost completely cyclized. The following structural changes were noted: (1) the disappearance of the IR bands at 11.0, 10.1, 7.1, and 6.1 μ which indicates the loss of the $-CH = CH_2$ units; (2) increased absorption at 6.9 μ which indicates the saturation of these vinyl groups; (3) appearance of a band at 10.35 μ which indicates the formation of cyclized structures and probably of a small amount of trans -CH=CH- units; (4) appearance of a band at 12.2 μ, which was proposed to be due to trisubstituted double bonds in six-membered rings. The 7.3 μ (methyl group) and 6.25 μ (conjugated unsaturation) bands found in the cyclized 1,4-PBD were also present in the cyclized 1,2-PBD. The IR spectrum of the thermally cyclized 1,2-PBD was very similar to the published spectrum of 1,2-PBD that had been cyclized by cationic catalyst.[56]

Golub also studied the photocyclization of 1,2-PBD using 2537 Å radiation.[57] Although the photoinduced cyclization of 1,2-PBD to produce a ladderlike polymer was mentioned as a possibility, all attempts to produce the ladderlike polymer shown below have been unsuccessful.

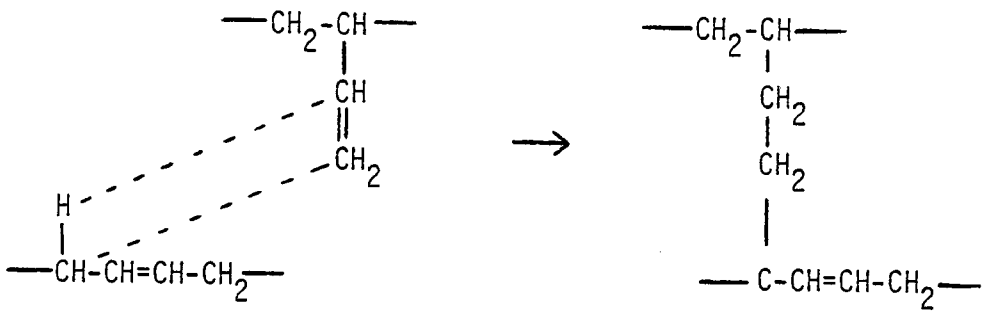


Instead of the regular ladder product, the cyclized structures shown below are obtained. They are presumably formed by cycloaddition of adjacent vinyl groups.



As precedent for the proposed cyclic structures in PBD, model compounds corresponding to the two bicyclic structures shown above were formed from the mercury-photosensitized isomerization of 1,6-heptadiene in vapor phase.[58] Golub points out that this photocyclization of 1,2-PBD cannot be duplicated by any nonphotochemical free radical process.

The thermal reactions of PBD containing 9-14% 1,2 isomeric units were studied by Grassie and Heaney.[59] The PBD became insoluble after 2.5 hr of heating under vacuum at 230°C. When heated to 260°C for 20 hr, this PBD showed a loss of vinyl units but not of cis or trans units. Insolubility and embrittlement occurred under these conditions. The weight loss was less than 1%. The cis and trans structures disappeared only above 350°C, the temperature at which appreciable weight loss began for this PBD. The vinyl loss of a sample of PBD which contained up to 0.15 weight percent of free radical inhibitors was comparable to that observed for the uninhibited PBD. Therefore, the reaction of the pendant vinyl group must occur with low energy of activation and lead to crosslinking. The reaction must not occur by a free radical mechanism. The following reaction has been proposed:[59]



Since much of the PBD in use contains sulfur from a curing process, the reaction of PBD and sulfur is important. Bishop noted that since homolytic scission of the sulfur-sulfur bonds occurs when elemental sulfur or organic polysulfides are heated above 140°C, isomerization could be expected to occur when high cis-PBD is vulcanized.[60] Bishop found a decrease in the cis IR band and an increase in the trans band with no appreciable change in the 1,2 band when PBD was heated to 160°C with an initial sulfur concentration of 1.69 M. Using high sulfur content, the original PBD which contained 94.6% cis could be isomerized to contain a minimum cis content of 36%.

Fujimoto and Wataya studied the structural changes during sulfur or peroxide crosslinking of high cis-PBD.[61] Using a special high temperature ATR device, they found that cis-trans isomerization occurred along with crosslinking. In the peroxide system the cis content decreased more than in the sulfur system, although the increase in trans content was smaller for the peroxide system than for the sulfur system.

Shipman and Golub[62] used the cis polymers of butadiene and butadiene-2,3-d_2 to study the structural changes during vulcanization of the above polymers at 160°C. The use of the deuterated polymer allowed them to distinguish between isomerized, conjugated, and shifted double bonds, as well as cyclic structures. The change of the

cis -CH=CH- (13.6 μ) of PBD and the cis -CD=CD- (15.5 μ) of PBD-2,3-d_2 to the corresponding trans double bonds at 10.4 μ and 14.0 μ was detected by IR spectroscopy. Another change noted in the IR spectrum of PBD-2,3-d_2 was the decrease in the unsaturated C-D band at 4.45 μ and an increase in a band at 4.6 μ corresponding to the formation of saturated C-D bonds. This band did not appear when isomerization was not accompanied by crosslinking. A new band in the IR spectrum of PBD-2,3-d_2 occurring at 10.3 μ was attributed to conjugated trans -CH=CH- units produced by hydrogen abstraction during the formation of cyclic structures. This band was not due to isotopic impurities since it was nearly absent in the spectrum of the unvulcanized polymer. Thus, Shipman and Golub concluded that PBD undergoes isomerization and crosslinking, along with production of saturated ring structures and of conjugated double bonds, when vulcanized at 160°C.

Crosslinking is expected to occur when PBD is subjected to high temperature aqueous conditions. A method for determining the degree of crosslinking in polymer networks based on swelling was reported by Flory and Rehner.[63] The background and results of Flory and Rehner's work was reviewed by Treloar.[64] This work established a relationship between the swelling volume and the concentration of crosslinks. Modifications of the Flory-Rehner equation have been used by several workers to determine the degree of crosslinking of rubber and PBD from swelling data.[65,66]

Since oxygen will be removed from the PBD and water in this study, oxidative degradation will be only briefly discussed. Bevilacqua's[67] study on the thermal oxidation of PBD has shown that

both chain scission and crosslinking occur, with scission slightly exceeding crosslinking. If a polymer system is initially soluble, the solubility will decrease as oxidation proceeds. However, if the polymer is initially insoluble, the solubility will increase during the oxidation process. A limiting solubility, which is related to the ratio of chain scission to crosslinking, is reached during the oxidation process. Bevilacqua discusses these processes using raw cis-PBD and irradiation cured PBD. As the extent of oxidation increased, the fraction soluble in benzene decreased for the originally soluble raw PBD. The irradiation cured PBD, which was initially insoluble, showed an increase in the fraction soluble in benzene. Both curves (originally soluble and originally insoluble) leveled off at about 20% soluble in benzene.

Bevilacqua used gas-chromatograph (gc) to determine the low molecular weight oxidation products of PBD.[67] Formic acid is a major low molecular weight product. Acetone and acetaldehyde were also detected. Formic acid formation, which was previously attributed to the oxidation of the pendant vinyl groups, did not appear to be dependent only on pendant vinyl group concentration. Formic acid also seemed to be produced by main-chain scission.

Although the hydration of unsaturated compounds in the presence of a catalyst is a widely used reaction, the uncatalyzed hydration of PBD is not expected to occur under normal conditions. In fact, Maximovich et al.[68] have shown that PBD exhibits very good moisture resistance when subjected to a 24 hr water boil test. If, at higher

temperatures, hydration were to occur to any appreciable extent, the hydroxy groups on the PBD could be used to react with other functional groups. This would be similar to the incorporation of hydroxy terminated PBD into other polymer systems such as polyurethanes.[69]

These background data illustrate that several reactions may occur when PBD is subjected to high temperature aqueous treatment. Cis-trans isomerization should occur at low temperature. Crosslinking, particularly of the 1,2 units, should also occur before high temperature is reached. Cyclization will probably occur as the temperature is increased. Hydration may occur. Oxygen concentration will be so low that oxidation reactions should not occur to any great extent, and closed ampoules will be used so very little volatilization will occur.

C. Styrene-Crosslinked Unsaturated Polyester

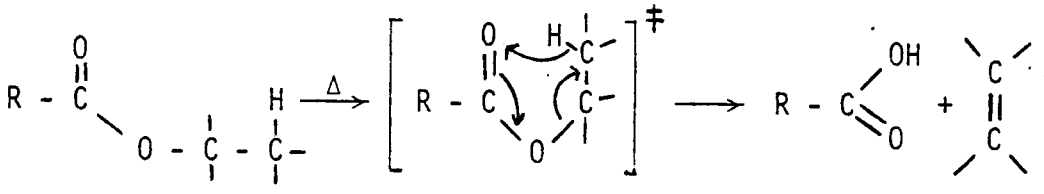
A large number of polymers fall under the general classifications of polyester. Linear polyesters have the general formula

$$\leftarrow C\text{-}R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R'\text{-}O \rightarrow .$$

Lenz discussed five different methods used in the production of polyesters.[70] These methods include direct esterification of a dibasic acid with a glycol, ester interchange, diesterification of an hydride with a glycol, esterification of a dibasic acid with the diester of a glycol, and esterification of a diacid chloride with a glycol. Both linear and crosslinked polyesters are used in high volume applications, including fibers, films, coatings, and plastics. The most widely used polyester is poly(ethylene terephthalate), (PET). This is also the most

widely studied polyester, as will be reflected in the following background discussions. Since the proposed work will involve high temperature hydrolyses, both thermolysis and hydrolysis studies will be reviewed. Other degradation pathways and methodologies, and the analytical techniques used in prior studies, will also be included.

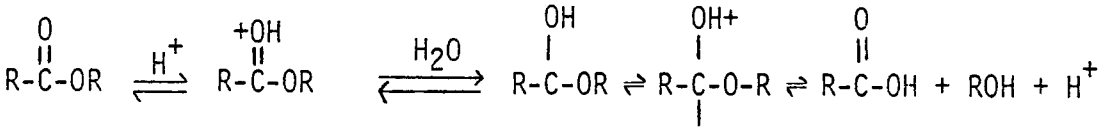
First, the thermal and hydrolytic reactions of small molecule esters will be considered. Ester units exhibit moderate thermal stability, and most low molecular weight esters can be distilled unchanged. At higher temperatures or if physically or chemically entrapped in the thermolysis zone, the ester pyrolysis reaction can occur. As shown in the following equation, this molecular scission reaction forms the carboxylic acid and an alkene.[71] Also evident is



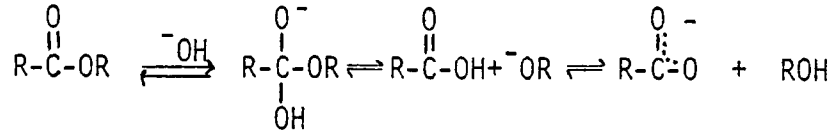
the requirement of a hydrogen atom on the β carbon of the ester group.

The hydrolysis of esters has been classified into eight mechanistic groups by Ingold.[72] The classification depends on whether the hydrolysis occurs with acid or base catalysis, in unimolecular or bimolecular fashion, and by acyl or alkyl cleavage. The two most common mechanisms, in acidic and basic media, proceed through tetrahedral intermediates. Bender studied the acid and base catalyzed

Acid catalyzed



Base Catalyzed



hydrolyses of ^{18}O labeled benzoate esters, and his results are in accord with the tetrahedral intermediate mechanisms shown above.[73]

Thermal and hydrolytic treatments of polymers containing in-chain ester groups cause reactions similar to those observed in low molecular weight esters. In an early study, Pohl showed that many polyesters can degrade at 307°C by the ester pyrolysis pathway, leading to nearly random scission of the polymer chain.[74] Thus PET undergoes random scission in the $\geq$ 300°C range and, as expected from ester pyrolysis reactions, a small amount of diacid but no glycol is recoverable. Marshall and Todd's studies verified the Pohl conclusions and also showed that very rapid hydrolysis occurred if PET was heated to its melting temperature in the presence of a small amount of water.[75] They also showed that the rate of degradation at high temperature was increased as the concentration of added oxygen was increased. Marshall and Tood used viscosity changes (d ln η/dt) for their rate of degradation studies.

McMahon et al. compared the rates of hydrolysis, thermal degradation, and oxidation of thin films at 100°C and 100% relative humidity.[76] Under these conditions the rate of hydrolysis was found to be 1×10^4 times greater than thermal degradation and 5×10^3 times greater than oxidation.

McMahon et al. also studied the effect of acid catalyst on the hydrolysis of PET films. Thin PET films were heated at 130°C for

12-30 hr in neutral water and in an aqueous solution of HCl (1.0×10^{-2} N).[76] There was no difference in the rates of hydrolytic degradation of the two samples based on relative viscosity measurements. It was concluded that PET hydrolysis is not catalyzed by hydrogen ions, in marked contrast to hydrolysis of most simple esters.

The effect of HCl on the rate of hydrolysis was further investigated by Ravens.[77] The rate of hydrolysis of PET appeared to be independent of the concentration of HCl below 3N, in agreement with the results of McMahon et al. But at concentrations greater than 3N the rate of hydrolysis was markedly increased. Ravens offered an explanation for these seemingly contradictory observations. At low HCl concentrations, the aqueous solution is comprised principally of H_2O and dissociated HCl (aquated H^+ and Cl^-). The ionic species do not diffuse effectively into the low dielectric PET, therefore, catalysis is not exhibited. At high HCl concentrations, some HCl molecules exist and these can diffuse into the PET and catalyze hydrolysis. This is consistent with the observations that PET is permeable to ammonia molecules but not to ammonium ions. Further, Ravens and Ward showed that the carboxylic acids formed in the PET by hydrolysis catalyzed further hydrolysis, affording an autocatalytic component to the overall reaction.[78]

Hydrolysis or saponification of polyesters has been used extensively for analysis of diacids and glycols used in polyesters. Methods of polyester analysis have been reviewed by Parker[79] and Jones.[80] The discussion presented here will deal first with analysis of the glycols and then with analysis of the diacids obtained by

saponification of polyesters. The utility of a number of analytical techniques, especially that of gc, will be included.

Several chemical and partition chromatographic techniques have been used for analysis of glycols and mixtures of glycols. Dal Nogare and Safranski[81] used silicone grease as the partition medium, 172°C column temperature, thermal conductivity detector, and a glass column to separate a mixture of glycols. Nadeau and Oaks[82] studied the effects of column polarity on the separation of glycol mixtures and found that polar columns such as Carbowax 750, Carbowax 20M, and tetrahydroxyethylenediamine were more effective than nonpolar columns. They used a column temperature of 105°C. This method could be used to separate glycols in the presence of up to 90% water; the minimum detectable amount of each glycol in a mixture was found to be 0.08% by weight.

Esposito and Swann studied nine different polyols used in polyester manufacture.[83] The polyesters were subjected to aminolysis, forming amides and the polyols. The polyols were converted to their acetates with acetic anhydride, and analyzed by gc. A Carbowax 20M column was used, with the column temperature being programmed from 50 to 225°C at 7.9°C per min.

Trimethylsilyl (TMS) reagents were used by Esposito and Swann[84] to reduce the polarity and increase the vapor pressure of glycols (and polyols) obtained from the polyester resins by aminolysis. The procedure involved adding the TMS reagent to the aminolysis mixture and heating for 30 min at 60°C. This mixture was then injected onto a silicone grease column.

A few methods allow the simultaneous analysis of both glycol and diacid by derivative formation and gc. These will be discussed in the diacid section.

The analysis of diacids used in polyesters developed in a manner similar to that of the glycols. Swann[85] published a graphic representation of a scheme for identification of several common diacids used in polyester production. Insoluble dipotassium salts were separated after the saponification of the polyester resin. The salts were converted to acids by the addition of nitric acid. The acids were then analyzed by their reaction (or lack of reaction) with several standard analytical reagents. This method allowed qualitative separation of maleic and fumaric acids. In one polyester sample that had been prepared with 6-8% maleic anhydride the concentration of fumaric acid was found to be 6.2% with no maleic acid present. This was due to isomerization during polymerization.

The early work on analysis of diacids used in the production of polyesters was discussed by Stafford et al.[86] in 1949. They discussed the increasing problems associated with analysis of the diacids and glycols from polyesters, which was due to the large number of new components used in their production. The method discussed by Stafford et al.[86] for analysis of eight diacids which are commonly used in the polyester industry consisted of the formation of N-benzyl amide derivatives of the diacids and then IR analysis. This method allowed the detection of 1 mole of unsaturated diacid in the presence of 9 moles of saturated diacid. However, this procedure did not allow the differentiation of maleic and fumaric acid due to isomerization during the formation of the derivatives.

Esposito and Swann[87] used programmed temperature gc to separate and identify 19 common mono- and diacids used in polyester production. The procedure involved the lithium methoxide transesterification of the polyester followed by extraction of the methyl esters of the acids and analysis by gc.

Percival used a similar method to analyze the glycols and acids in polyesters.[88] Methanolysis of the polyester was assisted by use of sodium methoxide as a catalyst. The ester linkages were cleaved to produce methyl esters of the diacids and free glycols. The total mixture was analyzed by gc without any preliminary separation steps. The same results were obtained by use of high temperature without the sodium catalyst by Ponder.[89] The above methods were used to detect small amounts of diethylene glycol and dipropylene glycol which had previously been analyzed by chemical methods.[90,91]

Just as the method of methanolysis of polyester developed into a general procedure for the simultaneous analysis of both diacids and glycols, the use of TMS reagents for the analysis of diacids and glycols developed from the original separate determination. Esposito presented a method for the formation of TMS derivatives directly on the gc column.[92] A mixture of glycols or diacids in an aqueous or alcoholic solution was injected and followed immediately by the TMS reagent. The water or alcohol solvent was separated from the rest of the sample during the interval between sample injection and reagent injection, allowing formation of the TMS derivatives on the gc column.

The use of TMS derivatives in the analysis of polyester prepolymers was studied by Atkinson and Calouche.[93] The first step

in the production of PET is the reaction of terephthalic acid with ethylene glycol to form a prepolymeric mixture. This mixture contains the mono and diester of terephthalic acid, diethylene glycol, and higher molecular weight oligomers in additon to the original ethylene glycol and terephthalic acid. This mixture can be analyzed by formation of the TMS derivatives followed by gc analysis. An internal standard was used to construct calibration curves for each sample from which quantitative results were obtained.

The above discussion has dealt with the analysis of the glycol and diacid portion of polyester after the polyester has been degraded. The methods discussed should be applicable to most glycols (or polyols) and diacids used in the production of polyester, even though some methods were discussed in terms of the analysis of PET only. The actual polyester used in this study will be described in the experimental section. It is necessary to point out that the polyester is unsaturated and is crosslinked with styrene by use of a free radical catalyst.

Characterization of such starting materials includes the determination of styrene content. There are several methods used for the determination of solvents (which are subsequently polymerized) in polyester resins. One method involves the spreading of a thin layer (known weight) of the polyester solution on a glass plate and removing the styrene by vacuum and low heat. The difference between original weight and the constant weight after vacuum heating is the weight of styrene.[79] Another method for the analysis of the styrene content is by precipitating the polyester from the solution by adding the solution to a mixture of benzene and petroleum ether. The precipitated polyester

is filtered off, dried, and weighed. The difference between the weight of the polyester and original solution is the weight of the styrene which is soluble in the benzene-petroleum ether mixture.[94]

IR has been used for analysis of polyesters. A brief description of the use of IR for the analysis of polyesters is presented by Haslam et al.[95] and Parker.[96] The assignment of the carboxyl and hydroxyl absorptions of PET has been studied by Patterson and Ward by use of deuterated compounds.[97]

Percival and Stevens used NMR to study 18 different unsaturated polyester formulations.[98] The NMR spectra were obtained either directly from the styrenated polyester or by removing the styrene and using acetone or benzene as a solvent. The NMR spectra were used as a qualitative and semiquantitative method of analysis. The use of NMR was also reviewed by Haslam et al.[99] The use of NMR is very fast compared to the other methods for the analysis of polyester since prior degradation is unnecessary.

Hayes et al. studied the crosslinking reaction of a poly(propylene glycol fumarate) with styrene.[100] From prior copolymerization studies on styrene and fumarate esters, it was predicted that this system would produce a large number of relatively short crosslinks. The styrene content was varied from 20 to 66% by weight of the total resin. A combination of methods was used to study the structure of the final crosslinked product. IR was used to measure the percentage of polyester double bonds consumed. Hydrolysis of the styrene-crosslinked polyester (presumably under strongly basic conditions) yielded fumaric acid, propylene glycol, and a styrene-fumaric

acid copolymer. There was a marked increase in the percent of polyester double bonds reacted (crosslinking) when the styrene content of the resin was increased in the range 30 to 40%. The copolymers obtained from hydrolysis had molecular weights (number average) of about 2500. These data indicated that the average continuous crosslink joined from 6 to 10 polyester chains. It was noted that the number of styrene units per reacted fumarate in the copolymer seemed to be maximum at 35.5% styrene. Only in the products with very high styrene content ($\geq$ 60%) could the presence of homopolymer of styrene be detected; in those cases the crosslinked products were opaque and the polystyrene could be extracted with toluene. No details such as polystyrene weight percent or molecular weight were given.

Funke and Hamann[101] also used hydrolysis of styrenated polyester in a study of the composition of crosslinked polyester. The polyester resins used in their study were produced from maleic anhydride and 1,4-butanediol with or without adipic acid. There was a linear relationship between the amount of styrene in the original polyester and the amount of styrene in the copolymer produced by basic hydrolysis of the cured polyester. The molar yield (moles in hydrolyzed copolymer/-moles in original polyester resin) for the fumaric acid increases up to about 65% as the amount of styrene in the original mixture increased to about 90%. The amount of fumaric acid units in the hydrolyzed copolymer approaches zero at low styrene content. This indicates that the unsaturated acid groups in the polyester do not homopolymerize under the conditions used. The molar yield of styrene was high (ca. 95%)

over a wide range of resins with varying original styrene content. They did not discuss details concerning homopolymerization of styrene.

The reaction of the products of hydrolysis has been neglected in the literature. Since the hydrolysis of a polyester containing propylene glycol and diacid units would produce free acid and propylene glycol, any subsequent reactions of the propylene glycol or acid should be considered. There are several examples of the formation of propanal from the acid catalyzed reaction of propylene glycol.[102-104] Further, the possibility of acid catalyzed aldol condensation would exist if propanal was formed from the propylene glycol.

CHAPTER II

MATERIALS, EQUIPMENT, AND EXPERIMENTAL PROCEDURES

A. Materials

All materials used as received unless otherwise indicated.

Acetone: Fisher, reagent.

Benzene: drum grade.

Benzoic acid: Fisher, reagent.

Benzoyl peroxide: Fisher, reagent (Purified by dissolving in cold chloroform and adding methanol to the point of precipitation. The crystals were separated by filtration and dried.)[105]

Carbon tetrachloride: Fisher, reagent.

Chloroform: Fisher, reagent.

Chromium(III) chloride: Baker, reagent.

Diethylether: Fisher, anhydrous.

Ethanol: drum grade (distilled, boiling range 77-68°C).

Hexanes: drum grade (distilled, boiling range 66-68°C).

Hydrochloric acid: Mallinckrodt, reagent.

Isophthalic acid; Matheson, Coleman, and Bell.

Ligroine: drum grade.

Mercury: Fisher.

Mesitylene: Eastman, red label. (Purified by heating with concentrated sulfuric acid, filtered, saving mesitylenesulfonic acid crystals. The crystals were heated with HCl, and the mixture was steam distilled. The mesitylene was separated from the aqueous layer, dried, and distilled, boiling point 160°C.)[106]

Methanol: Fisher, reagent.

Nitrogen: Selox. (When necessary deoxygenated and dried by passing through an aqueous solution of chromium(III) chloride, zinc amalgamated with mercury, and hydrochloric acid.[107])

Paraffin wax: Fisher.

Phosphorus pentoxide: Fisher, reagent.

Polybutadiene: Phillips, wt 1843 (purified by twice dissolving in hexanes and precipitating in ethanol).

Polyester: Ashland, Aropol 7720 MC.

Potassium bromides: Allied, reagent.

Propanal: Eastman, red label (distilled, boiling range 48-49°C, discarding ca. last third of original propanal).

Propylene glycol: Eastman, red label (distilled, boiling range 188-189°C).

Zinc: Mallinckrodt, mossy reagent.

B. Equipment

Attentuated total reflectance (ATR) attachment:

Wilks Scientific Corporation, Model 9. Equipped with stainless steel solid sample holder and a 45°, 2 mm KRS-5 (Thallium chloride-thallium bromide) reflector plate.

Bombs: Large--used for PBD and polyester studies. American Instrument Company, alloy steel, high pressure vessel, 2.5 in. outer diameter, 1 in. by 10 in. bore. Small--used for propanal study. Same type bomb as above (no name on bomb), 2 in. outer diameter, 5/8 in. by 6 in. bore.

Bomb heaters: Large--American Instrument Company, electric, sealed elements, steel shell about 1/8 in. larger than bomb, bomb slides into shell, temperature measured to nearest 1°C, heater equipped with rocker for agitation. Small--similar in design to large heater (no name on heater), temperature measured to nearest 1°C, equipped with rocker.

Bomb temperature controllers: Large--Versa-Therm Proportional Electronic Temperature Controller, Model 2156-4, equipped with platinum sensor probe. Small--In-house product, similar to large temperature controller.

Calculator: Wang, Model 600, programmable.

^{13}C Nuclear magnetic resonance spectrometer (^{13}C NMR): Nicolet Instrument Corporation, Model 80.

Fourier transform infrared spectrophotometer (FTIR): Digilab, Model 20.

Gas chromatographs: Varian, Model 2700 with thermal conductivity detector and Varian Model A-25 recorder equipped with a disc integrator. All columns used were 5 ft by 0.25 in. stainless steel. The actual column will be described in the section used.

Infrared spectrophotometers: Beckman, Model IR5A. Perkin-Elmer, Model 257.

Mass spectrometer: Perkin-Elmer Hitachi, Model RMU 6E.

Melting point apparatus: Mel-Temp, also Thiele-Dennis melting point apparatus.

Microcaliper: Fisher, with pressure sensitive lock.

Micro-Mill: The Lab Apparatus Company, water cooled grinding chamber.

Proton nuclear magnetic resonance spectrometers: Varian, Models T60 and HA100.

Refractometer: Bausch and Lomb, Abbe type.

Rotary evaporator: Rinco Instrument Company, Inc., Model 1007-4.

Sieves: The Lab Apparatus Company, mesh sizes 20 and 50.

Ultraviolet spectrophotometer: Varian, Cary, Model 17.

Vacuum oven: Precision Scientific Company, Thelco, Model 19.

C. Experimental Procedures for Polybutadiene

1. Original PBD

Several batches of PBD were purified by dissolving 6-10 g of PBD in approximately 800 ml of hexanes. The volume of the solution was reduced to about 300 ml by use of a rotary evaporator. The PBD was precipitated by adding the hexanes solution to about 3:1 of ethanol. The precipitated polymer was dried 4 hr under vacuum. The PBD was again dissolved and precipitated as described above. The final drying was done overnight under vacuum.

Films of the PBD were prepared by pressing the PBD between two aluminum plates covered with aluminum foil. The thickness of each film was determined with a microcaliper. The films prepared by this method were approximately 0.6 mm thick, and too thick for good transmission IR analysis. The films were cut into 40 mm squares. The aluminum foil was removed from one side. The aluminum foil on the other side was used to support the film. The films were wrapped around a KRS-5 crystal so both sides of the crystal were in contact with the film. The original percentage of each isomer was then determined by ATR spectroscopy using the method outlined by Haslam et al.[41]

An alternate method, which produced thinner films and did not use aluminum foil as a support, was used to prepare samples for photo and hydrolytic degradation studies. Glass tubing of outer diameter 0.2 to 0.4 mm was produced by drawing heated capillary tubes. The thin glass tubing was used to make frames of about 1 cm x 1 cm. The glass frames were dipped into a 10% by weight solution of PBD in hexanes. The glass frames were withdrawn from the PBD solution and held horizontally until most of the solvent had evaporated. The PBD solution was flushed with nitrogen, sealed, and stored in a darkened desiccator for future use. The film was then dried for 30 min in a darkened desiccator over paraffin wax. After 30 min drying at atmospheric pressure, the pressure was reduced to 0.05 mm and drying was continued for 4 hr. The films supported by the glass frames were about 10 μm thick,. Each frame was weighed before being dipped into the PBD solution and after drying in order to determine the weight of the PBD film. The films were analyzed for the percentage of each isomer by IR.

2. Photodegradation of PBD Film

When the sample was placed in an undarkened desiccator (either before or after subjection to hydrolytic conditons), the PBD would crosslink after a few weeks. A short study was performed to determine the steps necessary to prevent oxidation and crosslinking of the PBD. Thin films of PBD on glass frames were placed in vials and subjected to various atmospheres, either in the presence or absence of sunlight. IR was used to detect and monitor structural changes in the PBD.

3. Thermal Degradation of PBD

It was necessary to use the thicker films (aluminum foil support) for the dry thermal degradation study since the thinner films (glass frame support) tore upon heating. The PBD film was placed in a 20 cm tube and cooled in a dry ice-acetone bath. A constriction was formed approximately 15 cm from the bottom of the tube. The tube was flushed with nitrogen, cooled, and sealed.

Two asbestos sleeves (1.5 cm wide) were placed around the ampoule to prevent the ampoule from touching the walls of the bomb. The ampoule was placed in the large bomb and partially submerged in water. The water was used to help equalize the inside and outside pressure of the ampoule. The bomb was capped, placed in the preheated heater, and brought to the desired temperature. The time necessary to reach the desired temperature varied from 30 to 60 min. The samples were subjected to the dry thermal degradation conditions for 6 hr at various temperatures. After 6 hr had elapsed, the bomb was removed from the heater and allowed to cool. The ampoule was removed from the bomb and opened. IR was used to detect any changes in the percentages of the isomeric units.

The degree of crosslinking for the samples of PBD which were supported on aluminum foil and subjected to thermal and hydrolytic conditions was monitored by measuring the linear percent swell. There is an inverse relationship between the degree of crosslinking and the linear percent swell. The linear percent swell was determined by measuring the thickness of the sample on the aluminum foil before and after submerging the sample in hexanes for 16 hr. These measurements were made with a pressure lock microcaliper. The difference in thickness

was divided by the original thickness and multiplied by 100 to obtain the linear percent swell.

4. Hydrolytic Degradation of PBD

The thinner films (glass frame support) were used in this study. The PBD film was placed in a 20 cm tube with 10 ml of distilled water. The water and PBD film were cooled in a dry ice-acetone bath and a constriction was formed about 15 cm from the end of the tube. The samples were reflushed with nitrogen, recooled, and sealed. The process used to heat these samples was the same as used in the thermal degradation study.

After subjecting the films to hydrolytic conditions, the films were dried, weighed, and analyzed by IR. The percent of each isomeric unit was obtained from the IR spectrum.

The water used to subject the PBD films to hydrolytic conditions was subjected to gc analysis. The following conditions were used: column = SE-30, column temperature = 95°C, detector temperature = 200°C, injector temperature = 150°C, helium flow rate = 14 ml/min, chart speed - 50 in./hr, attenuation = 32 (set to 4 after water peak had eluted), sample size = 4 ml.

D. Experimental Procedures for Styrene-Crosslinked Unsaturated Polyester

1. Analysis of Original Polyester Solution

Styrene was contained in the original solution and acted both as a diluent and as a crosslinking agent. The amount of styrene was determined by two methods.[108]

A sheet of aluminum foil (approximately 5 $in.^2$) was weighed to the nearest 0.001 g. The polyester solution was poured directly from the original container onto the aluminum foil and weighed. The aluminum foil was folded in half to produce a thin film of polyester solution. The aluminum foil and polyester solution were placed in a vacuum oven. A vacuum was pulled slowly to prevent rapid bubbling of the solution. A vacuum of approximately 0.5 mm was obtained after 30 min. The temperature was slowly increased for 30 min until a temperature of 40°C was obtained. This temperature was maintained for 4 hr. The difference between the original weight and constant weight after vacuum was equated with the weight of styrene in the original solution.

The other method involved the precipitation of the polyester from the styrene-polyester solution. A 250 ml beaker was weighed to the nearest 0.001 g. Approximately 4 g of polyester solution was added to the beaker from the original container and weighed to the nearest 0.001 g. A 50 ml solution of benzene and ligroine (2:3) was added with stirring. The liquid portion was decanted, leaving the precipitated polyester. The precipitated polyester was vacuum dried at 70°C for 3 hr and weighed. The difference between the weight of the original solution and the constant weight after drying was attributed to styrene.

IR spectra were obtained of the original polyester solution and of the polyester after the styrene had been removed. These spectra were useful in comparing IR spectra of the water- and acetone-insoluble portion of the reacted samples. The styrene was removed before the polyester was analyzed by ^1H NMR. The polyester was dissolved in

chloroform-d to obtain a 40% by wt. solution. The ratio of isophthalic acid units and fumaric acid units, and thus the overall composition of the original unsaturated polyester, was determined from the integration of the ^{1}H NMR spectrum in chloroform-d.

2. Preparation of Polyester for Hydrolysis

The polyester was obtained as a styrene solution. The styrene was initiated by benzoyl peroxide and polymerized through the fumaric acid units of the unsaturated polyester to form a rigid crosslinked material. The polyester was crosslinked in the following manner.

Approximately 30 g of the polyester solution was weighed in a 250 ml beaker. Purified benzoyl peroxide was added (0.5% by wt.) and mixed in by hand stirring. The solution was poured into 4 in. test tubes. Nitrogen was bubbled through the solution for 5 min. The test tubes were stored under nitrogen to allow the nitrogen bubbles to rise to the surface.

The test tubes containing the polyester solution were placed in an oil bath maintained at 100°C for 15 min, then removed and allowed to cool to room temperature. The SXUP samples were removed from the test tubes by tweezers, or if necessary by breaking the test tubes.

The SXUP samples were broken and ground in a micromill to increase the surface area. After 10 min of grinding, the SXUP was sieved. The particles with mesh size between 20 and 50 were used for hydrolysis.

Samples of the 20-50 mesh powder (1.000 g) were placed in a 12 mm outer diameter Pyrex glass ampoule with 3 glass beads (5 mm size)

to facilitate mixing. The ampoule contained a constriction approximately 6 cm from the bottom. Deoxygenated distilled water (5.0 ml) was added via a syringe. Nitrogen was used to flush oxygen from the sample and water. The tube containing the water and sample was cooled in a dry ice-acetone bath and sealed.

3. Hydrolysis of Styrene-Crosslinked Unsaturated Polyester

The sealed ampoule was placed inside two asbestos sleeves 1.5 cm wide and placed inside the preheated (ca. 95°C) large bomb. Water was added to the bomb to help equalize the pressures on the inside and outside of the ampoule during heating. The bomb was then capped and placed inside the preheated large heater. The samples were heated at various temperatures for various times, with continuous shaking. After the desired time had elapsed, the bomb was removed from the heater and allowed to cool to room temperature.

4. Separation and Analysis of Products from Hydrolyses

After cooling to room temperature, the ampoules were opened. The products were filtered through a 20-M 15 ml fritted glass filter. The dried and weighed solid portion of the hydrolyzed sample was placed in 200 ml boiling water to dissolve the generated isophthalic aicd (IPA). after stirring the solid portion of the hydrolysis products in boiling water for about 5 min, the solution was filtered hot through a steam jacketed Buchner filter funnel under reduced pressure from a water aspirator. The hot water insoluble portion was placed in 200 ml of boiling water again. The solution was again filtered, and the filtrate added to the above filtrate. The hot water insoluble portion was dried and weighed.

The solution was concentrated from the original 400 ml to approximately 20 ml by use of a rotary evaporator. The generated IPA was allowed to crystallize at room temperature. The crystals were separated by filtration through a 20-F 15 ml fritted glass funnel under reduced pressure. The crystals were dissolved and allowed to recrystallize from water and were subjected to melitng point analysis, IR analysis (10% by weight in KBr on Beckman IR5A), and ^{1}H NMR analysis (10% by weight in dimethylsulfoxide-d_6).

The hot water insoluble portion contained any unhydrolyzed SXUP and the polymer formed from copolymerization of styrene with fumaric acid units in the original polyester. This material was extracted overnight with acetone to remove the styrene-fumaric acid copolymer. Any copolymer not attached to the unhydrolyzed crosslinked polyester was extracted into the acetone while the unhydrolyzed portion remained insoluble. The copolymer was analyzed by IR (film cast on KBr plate) and ^{1}H NMR (acetone-d_6 solvent, 10% by weight solution). The unhydrolyzed crosslinked polyester portion was dried and analyzed by IR (Beckman IR5A) as a 10% solution by weight in KBr.

Propylene glycol (PG) generated during the hydrolysis was in the aqueous phase. The amount of PG in the aqueous phase was determined by analysis. The following conditions were used. Column = Porapac Q, column temperature = 200°C, detector temperature = 250°C, injector temperature = 220°C, helium flow rate = 50 ml/min, chart speed = 0.5 in./min, attenuation = 8, sample size = 4 µl. The calibration curve prepared with known PG under the same conditions is presented in the Appendix.

In certain hydrolyses, a very small amount of a dark brown layer of organic material appeared on the aqueous layer. This organic layer was extracted with diethylether and subjected to gc separation using the following conditions. Column = chromosorb 101, column temperature = 120°C, programmed at 12°C/min to 240°C, detector temperature = 250°C, injector temperature = 250°C, helium flow = 128 ml/min, sample size = 40 µl. Many peaks appeared on the gc trace, indicating that several reactions had occurred. The components present in the greatest amount were isolated by trapping from the gc effluent and were subjected to various analyses, as will be discussed in the next chapter.

5. High Temperature Reactions of Hydrolysis Products

Propanal was identified as one of the products in the oily layer obtained from the above hydrolyses. Since further reactions of propanal under high temperature acidic conditions appeared likely, a series of reactions was carried out using the following procedures. Propanal (distilled) was placed in an Erlenmeyer flask capped with a septum. Nitrogen (passed through an oxygen trap) was bubbled through the propanal for 30 min. Hydrochloric acid (concentrated, 0.02 ml) was pipetted into a 10 mm outer diameter Pyrex ampoule with a constriction about 8 cm from the bottom. A syringe was used to transfer 2.00 ml of the deoxygenated propanal from the Erlyenmeyer flask to the ampoule. The ampoule was flushed with nitrogen, cooled in a dry ice-acetone bath, and sealed.

The reactions were carried out using either the small bomb and heater or, for the low temperature reactions, an oil bath. In both cases, the sample was continuously agitated. The time of reaction

ranged from 2 to 12 hr, in the temperature range from 75 to 175°C. After cooling to room temperature, the ampoules were opened and capped with a septum. The aqueous layer was removed by syringe and weighed.

The organic layer contained several components. Since some of these were not sufficiently volatile to elute from the gc column, several other separation methods were tried. These included thin layer chromatography on silica gel, column chromatography using alumina or silica packing, and distillation (fractionation, vacuum, and spinning band). None of these were completely successful. The method finally settled on was separation of the organic layer into volatile and "nonvolatile" fractions. A vacuum distillation using a modified sublimation-type apparatus was used, with the volatile fraction collected on the dry ice-acetone cooled cold finger.

The volatile portion was then subjected to gc separation, using the following conditions. Column = 10% C-20M, column temperature = 120°C initially, programmed to 220°C at 6°C/min, detector temperature = 250°C, injector temperature = 230°C, helium flow rate = 30 ml/min, chart speed = 0.5 in./min, attenuation = 16, and sample size = 10 μl. The components of interest were trapped by placing a chilled 8 mm glass tube with a constricted end into the exit port of the gc. The trapped liquid was then subjected to the following analyses.

Approximately 5 μl of each sample was subjected to mass spectroscopic analysis under the following conditions: mass range 0 to 600 m/e, sensitivity X10, multiplier voltage 160, ionization potential 20 ev.

IR spectra of the unknown samples were obtained by placing a small amount of the trapped sample between KBr plates. Beckman IR5A was used with a polystyrene film to standardize the instrument.

^{1}H NMR spectra were obtained for both compounds from the T-60 and the HA 100 NMR spectrometers. The conditions used for the T-60 NMR were as follows: 10% solution in chloroform-d, sweep time 250 s, sweep width 500 Hz, filter 1, spinning rate 40 RPS, the radio frequency power 0.05, spectrum amplitude 80, integral amplitude 2, internal standard was TMS. The above conditions were used for the HA 100 NMR of the two compounds, except for the following conditions: radio frequency attenuator 35, spectral amplitude 2500.

Ultraviolet spectroscopy (UV) was also used for the structural elucidation of the unknown compounds. Using molecular weights determined by mass spectral analysis, the unknown samples were dissolved in distilled ethanol to prepare 7.25×10^{-3} M and 7.25×10^{-6} M solutions used for UV analysis. Distilled ethanol was also used in the reference beam during analysis. The λ drive was set at 1 nm/s and the chart scale was 15 nm/in.

Approximately 50 g of each unknown compound was dissolved in 2.0 ml of chloroform-d and analyzed by ^{13}C NMR. The center peak from the chloroform-d solvent was used as an internal standard. The value of the center peak is 76.90 ppm.

The refractometer used to determine the refractive index was calibrated using double distilled water at 20°C. The experimental value was 1.3355 ± 0.0001 for three runs. This was 0.0025 higher than the literature value of 1.3330. Thus, 0.0025 was subtracted from the values obtained for the unknown compounds.

Due to the limited amount of the samples available, the boiling points were determined using the microboiling point technique. A small amount of the sample obtained from gc trapping was placed in the bottom of a Pyrex tube (4 mm outer diameter by 150 mm). A melting point capillary tube was placed (open and down) inside the tube. This was attached to a thermometer and heated in a Thiele-Dennis melting point apparatus. The sample was heated about 6° to 8°C above the point at which bubbles rapidly appeared at the open end of the capillary tube. The sample was then allowed to cool. The temperature at which the bubbles ceased was recorded. The sample was heated slowly until bubbles appeared again. The recorded boiling point range for each of the unknown compounds was an average of three determinations.

The samples were sent to Galbraith Laboratories for carbon and hydrogen analyses. The difference between unity and the total of the carbon and hydrogen was assigned to oxygen.

The organic layer directly from the reaction mixture was further analyzed as follows. The weight and volume of the organic layer of the reaction mixture was determined. Then a 1.0 ml portion of the organic layer was added to a vial that contained 0.100 g of purified mesitylene. The vial was sealed with a rubber septum. The solution containing mesitylene as an internal standard was analyzed by gc using the following conditions: Column 10% FFAP, column temperature = 160°C, detector temperature = 230°C, injector temperature = 200°C (injector port equipped with a glass linear), helium flow rate 50 ml/min, chart speed = 0.5 in./min, attenuation = 256, sample size = 1 μl.

The area of each peak, based on the integrator counts, was measured and an area ratio determined using the ratio of integrator counts for each compound versus the integrator counts for mesitylene. This area ratio was converted to a weight ratio by use of a calibration curve established for each compound (calibration curves are presented in the Appendix).

CHAPTER III

RESULTS AND DISCUSSION

A. Polybutadiene

1. Analysis of the Original Polybutadiene

The original percentages of trans, 1,2, and cis isomeric units were determined by three IR methods. The transmission IR spectrum of an original PBD sample on a glass frame is shown in Figure 2. The percentage of each isomeric unit determined for a PBD sample on a glass frame using the IR5A (Beckman) is shown below.

trans isomeric units = 7%

1,2 isomeric units = 4%

cis isomeric units = 89%

The percentages of the isomeric units was also determined using FTIR. A FTIR spectrum of an original PBD on a glass frame is shown in Figure 3. The percentage of each isomeric unit was:

trans isomeric units = 11%

1,2 isomeric units = 5%

cis isomeric units = 84%

The thicker PBD films, as used for the thermal modification studies, were analyzed using ATR. The ATR spectrum of an original PBD sample is shown in Figure 4. This was obtained on a Perkin Elmer 257 IR spectrophotometer rather than the Beckman IR5A because the intensity of the light on the Beckman IR5A was not great enough to obtain a good

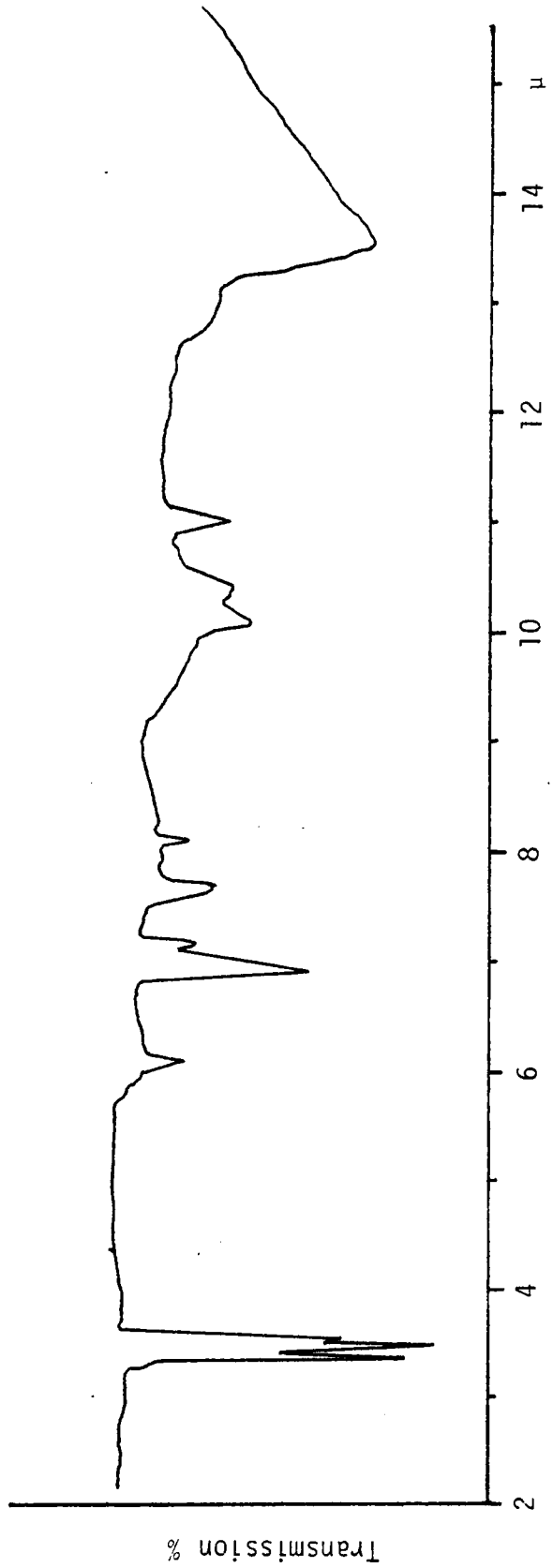


Figure 2. Transmission IR spectrum (Beckman IR5A) of original PBD sample. The PBD film was supported on a glass frame.

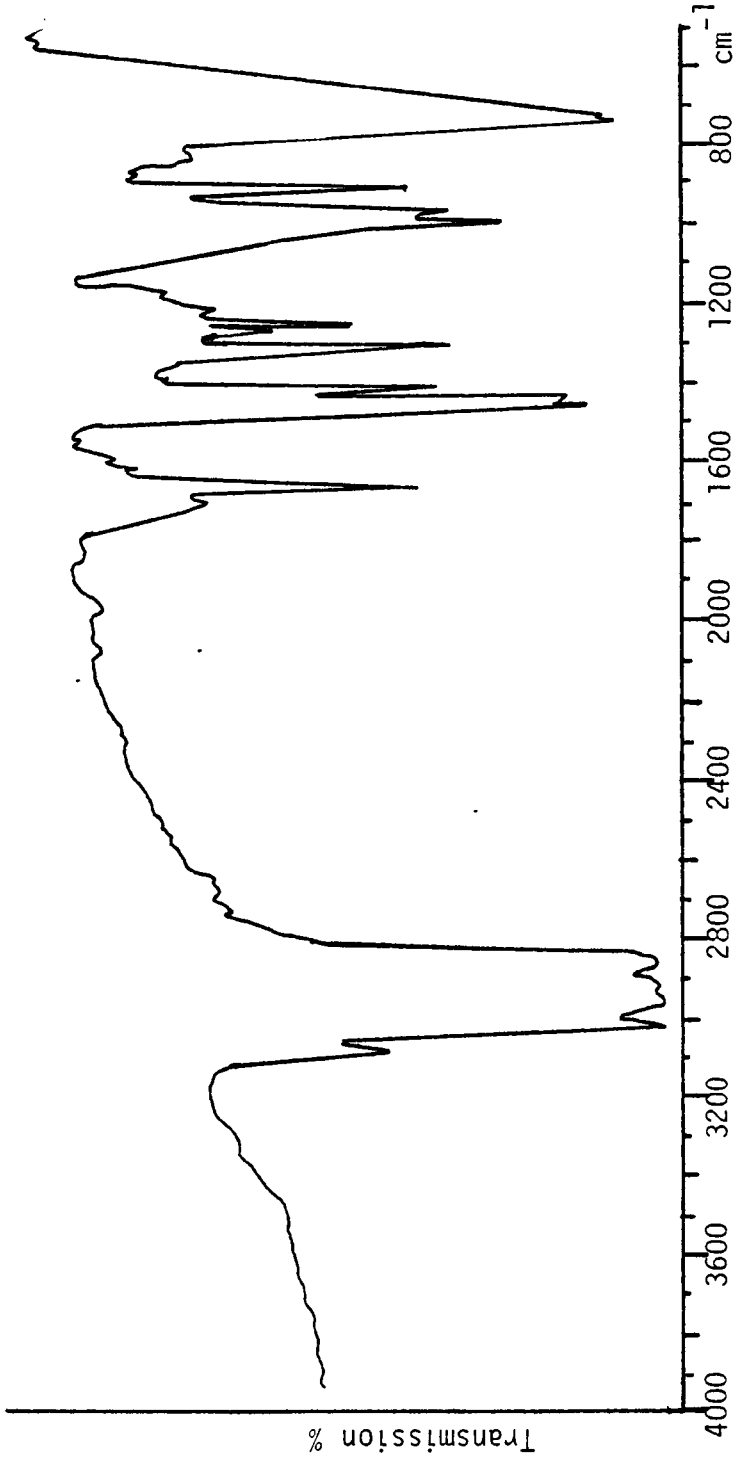


Figure 3. FTIR spectrum of the original PBD sample. The PBD film was supported on a glass frame.

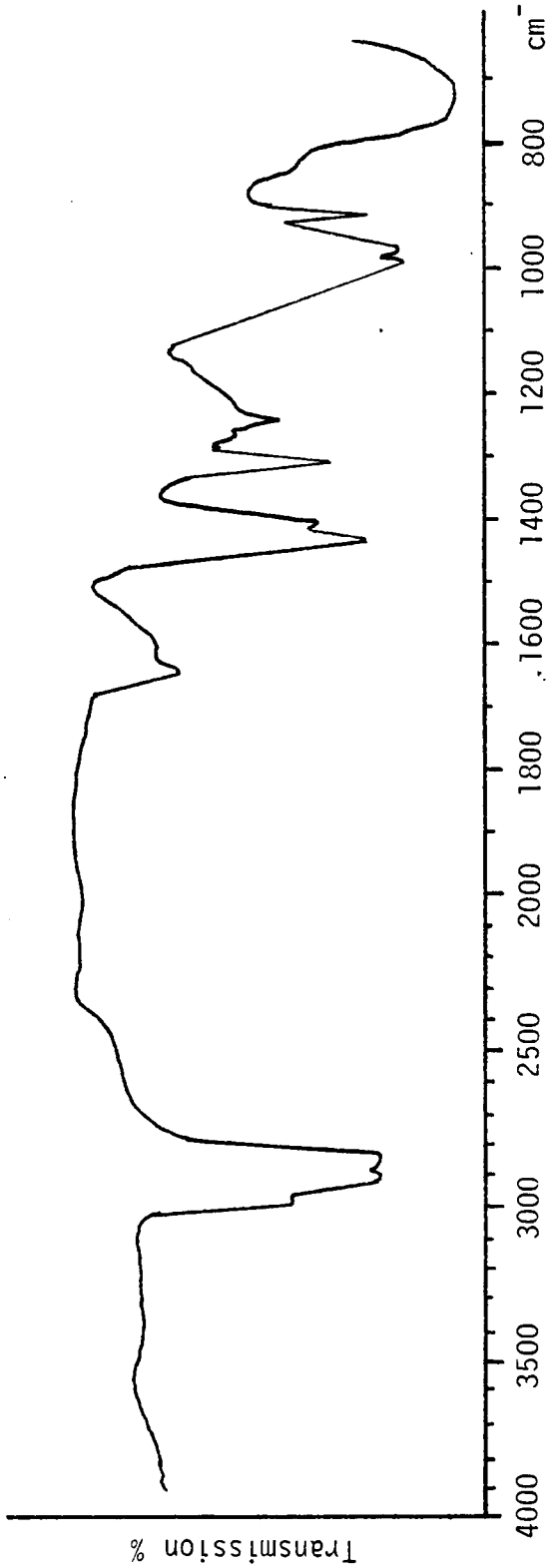


Figure 4. ATR spectrum (Perkin Elmer 257) of the original PBD sample. The PBD film was supported on aluminum foil

ATR SPECTRUM. The Beckman IR5A is linear to μ whereas the Perkin Elmer 257 and FTIR are linear in cm^{-1}. The percentages of each isomeric unti determined using ATR spectroscopy on the thicker PBD films were:

trans isomeric units = 13%

1,2 isomeric units = 5%

cis isomeric units = 83%

Although the reproducibility of a particular method was usually within 1%, these methods should not be used interchangably due to the observed differences in percentages of the isomeric units of the original PBD by the three methods, particularly the ATR. Changes in the spectrum were followed using the same instrument for a given set of experiments, i.e., oxidative degradation was studied using the Beckman IR5A, and thermal vs. hydrolytic conditions was studied using ATR spectroscopy. The percentages of the structural isomers reported in these studies should be used as comparative values to detect change, rather than absolute values.

2. Oxidative Degradation of Polybutadiene

Polybutadiene is known to undergo oxidative degradation, especially in the absence of pigment and/or stabilizer. Therefore, a short series of experiments was carried out to determine the necessary conditions for storage of the purified PBD films.

According to Salimov,[104] appearance of a band at 2.94 μ can be attributed to formation of hydroperoxides and alcohols. The very broad absorption between 7.1 and 13.3 μ and the band between 3.68 and 4.77 μ were assigned to the combination of polymer segments (crosslinking).

Sample A was sealed in air and exposed to sunlight. An IR spectrum of the original PBD sample was recorded. After 3 days of exposure an IR spectrum was again recorded. The sample was exposed to sunlight for the remainder of a week and another IR spectrum was recorded. These three spectra are shown in Figure 5. All spectra in this series started with a baseline on 90% transmission.

After 3 days of exposure to sunlight, sample A developed an absorption band at 2.94 μ. This band, which was not present in the spectrum of the original sample, was about 60% as intense as the major band at 3.4 μ. Appearance of this band was accompanied by a decrease of the baseline in the 7.1 to 13.3 μ region. The band due to the trans unit was no longer distinct. The 1,2 absorption band at 11.0 μ was no longer present. The cis band at 13.6 μ was reduced by approximately 50%.

The spectrum of sample A which was exposed to sunlight for 1 week contained an absorption band at 2.94 μ which was nearly as intense as the 3.4 μ absorption band. There was also a shoulder on the 3.4 μ band, corresponding to the band between 3.68 and 4.77 μ which Salimov attributed to crosslinking. The peak at 5.8 μ was much larger in this spectrum than in the spectrum of the sample taken after 3 days of exposure. Nearly all resemblance in the spectra past 7.0 μ was lost.

Sample B was flushed with nitrogen for 10 min, sealed, and placed in sunlight. The IR spectra of the original sample, and of the sample after 3 days and 1 week of exposure to sunlight, are presented in Figure 6. There was very little difference between the spectra for sample A and sample B. The only significant difference was the intensity of the absorption band at 2.94 μ after 3 days of exposure. This band

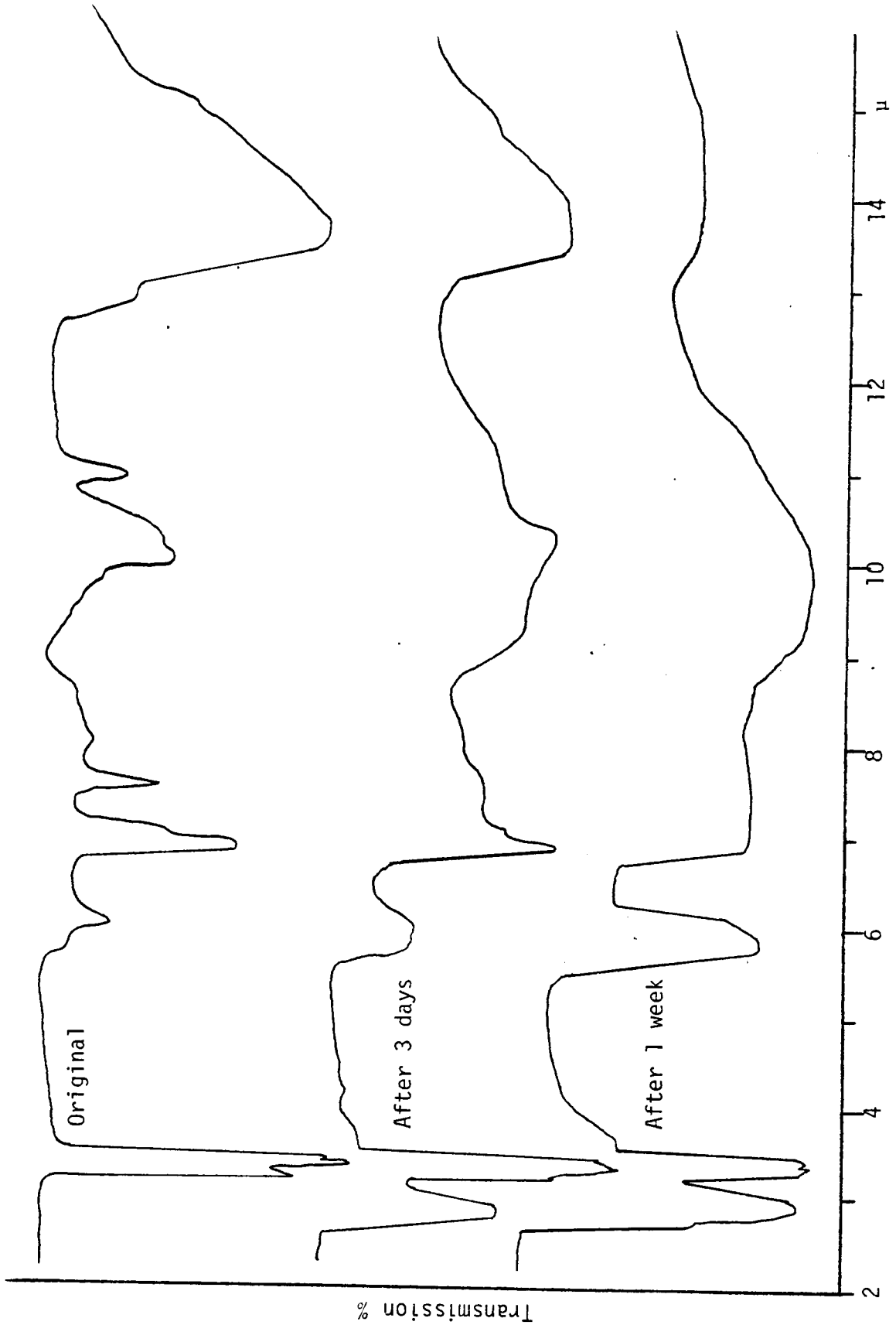


Figure 5. IR spectra of sample A. PBD sample sealed in air and exposed to sunlight.

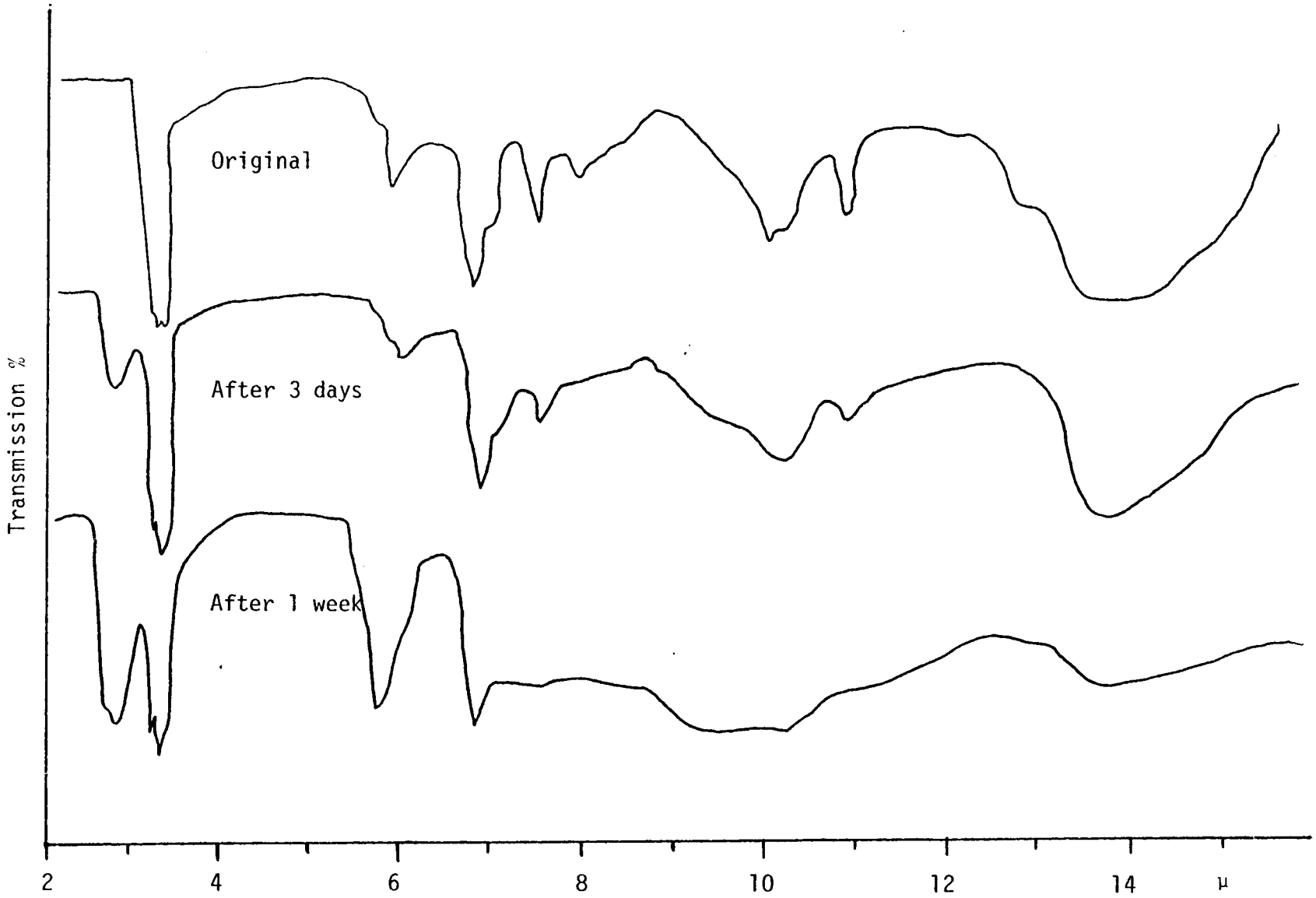


Figure 6. IR spectra of sample B. PBD sample sealed in nitrogen and stored in sunlight.

was about 60% as intense as the 3.4 μ band for sample A; however, it was only about 30% as intense as the 3.4 μ band in sample B. There were no significant differences between the sample stored in air and sunlight and the sample stored in nitrogen and sunlight after 1 week of exposure.

Sample C was flushed with oxygen for 10 min, sealed, and stored in sunlight. The IR spectra of the original sample, and of the sample after 3 days and 1 week exposure are presented in Figure 7.

The absorption band at 2.94 μ was about 60% as intense as the band at 3.4 μ. However, the 3.4 μ band for the sample exposed to sunlight for three days was considerably less intense than the 3.4 μ band in the spectrum for the original sample. The only significant difference between the sample exposed to sunlight for 3 days and the sample exposed to sunlight for 1 week was an increase in the intensity of the band at 5.8 μ for the latter.

Sample D was prepared in the following manner. The PBD film was placed inside a Pyrex tube with a ground glass joint which was connected to a stopcock. The tube was evacuated for 2 min and then filled with nitrogen which was passed through an oxygen trap. This process was repeated twice. The sample was then stored in sunlight. The film was removed after 3 days and after 1 week and analyzed by IR. The IR spectra of the original film, the film after 3 days of exposure, and the film after 1 week exposure are presented in Figure 8. The repeated oxygen-free nitrogen flush greatly reduced the degradation process. The IR spectrum of the sample exposed to sunlight for 3 days was altered only slightly from the IR spectrum of the original film. However, the IR

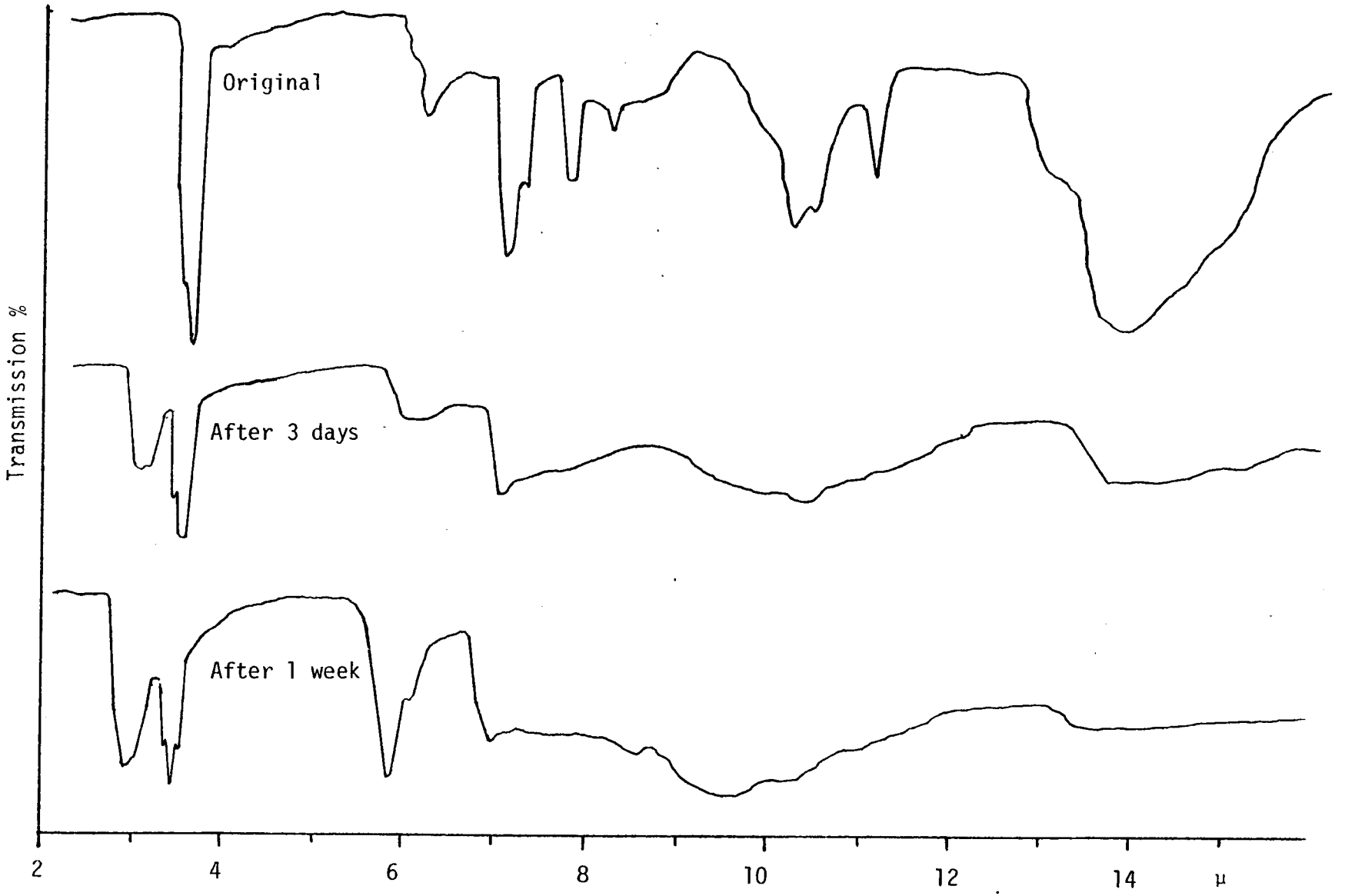


Figure 7. IR spectra of sample C. PBD sample sealed in oxygen and exposed to sunlight.

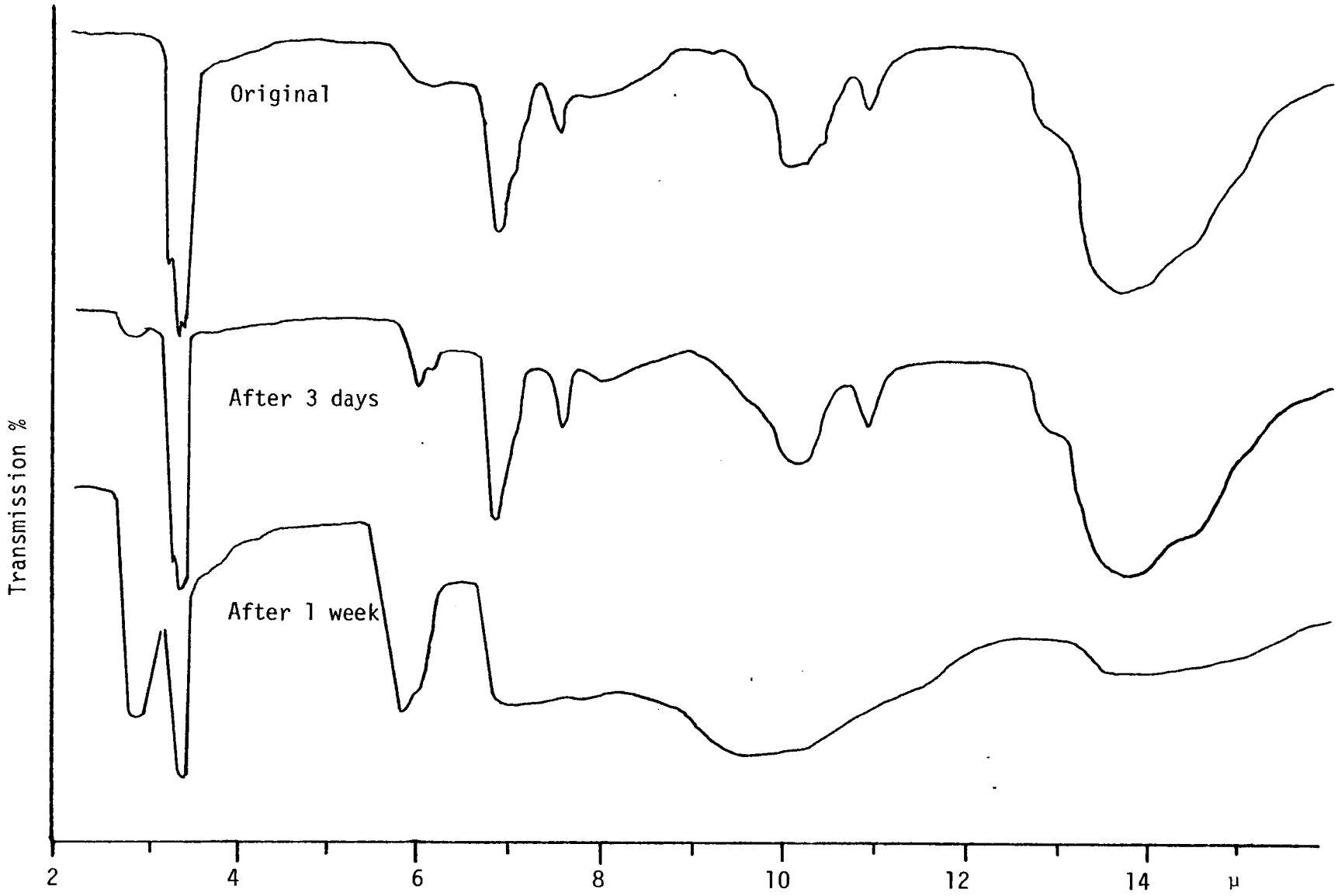


Figure 8. IR spectra of sample D. PBD sample evacuated and flushed with nitrogen three times, sealed under nitrogen, and exposed to sunlight. The nitrogen was passed through an oxygen trap.

spectrum of sample D which was exposed to sunlight for 1 week was greatly altered. There was little difference between the IR spectrum of sample D (evacuated and filled with nitrogen passed through an oxygen trap) and the IR spectrum of sample B (flushed 10 min with nitrogen) after 1 week exposure.

Sample E was placed in a tube similar to the one used in sample D. The sample was evacuated to a pressure of 10^{-6} mm Hg for 24 hr. After 24 hr of evacuating, the tube was filled with oxygen-free nitrogen and exposed to sunlight. The IR spectrum of the original film and the film after 1 week exposure to sunlight are shown in Figure 9. Very little difference in the two spectra were detected. An absorption band at 2.94 μ was not detected, nor was the broad absorption band between 7.1 and 13.3 μ present. The main detectable difference was the development of an absorption band near 5.9 μ.

In addition to the five samples which were exposed to sunlight, two samples were stored in the dark. Sample F was prepared in the same manner as sample B (p. 57) and wrapped in aluminum foil to prevent exposure to sunlight. There was no detectable change in the IR spectra of the film after storage in nitrogen for 3 days or 1 week. These spectra are shown in Figure 10.

Sample G was prepared in the same manner as sample C (p. 60) and wrapped in aluminum foil to prevent exposure to sunlight. There was no detectable change in the IR spectra after the sample was stored for 3 days or 1 week. These results are shown in Figure 11.

Salimov indicated the broad band between 7.1 and 13.3 μ was due to crosslinking.[109] A Soxhlet extractor was used to determine the solubility of samples B (nitrogen and sunlight), C (oxygen and

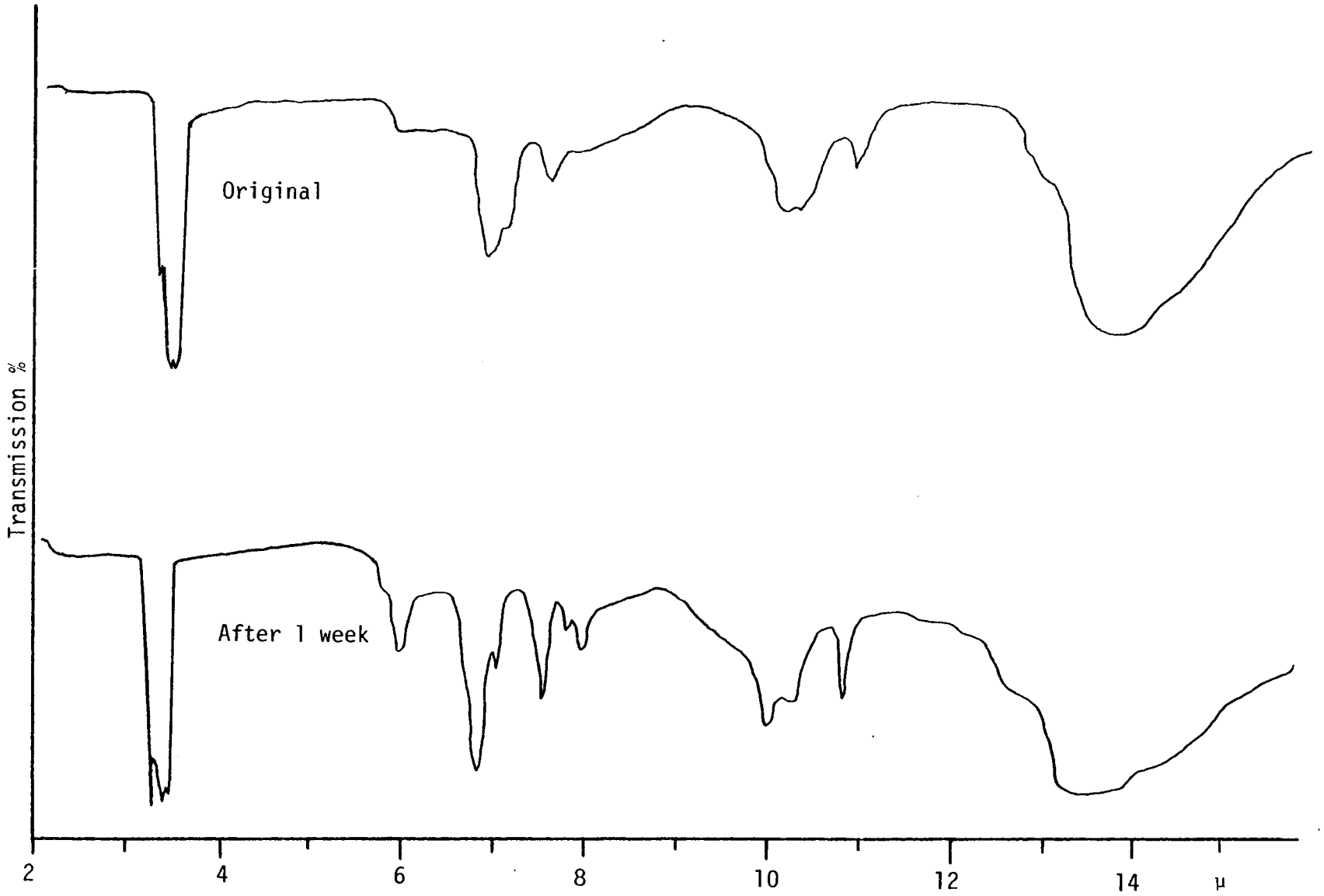


Figure 9. IR spectra of sample E. PBD sample evaucated for 24 hr at 10^{-6} mm Hg pressure, sealed in nitrogen, and stored in sunlight.

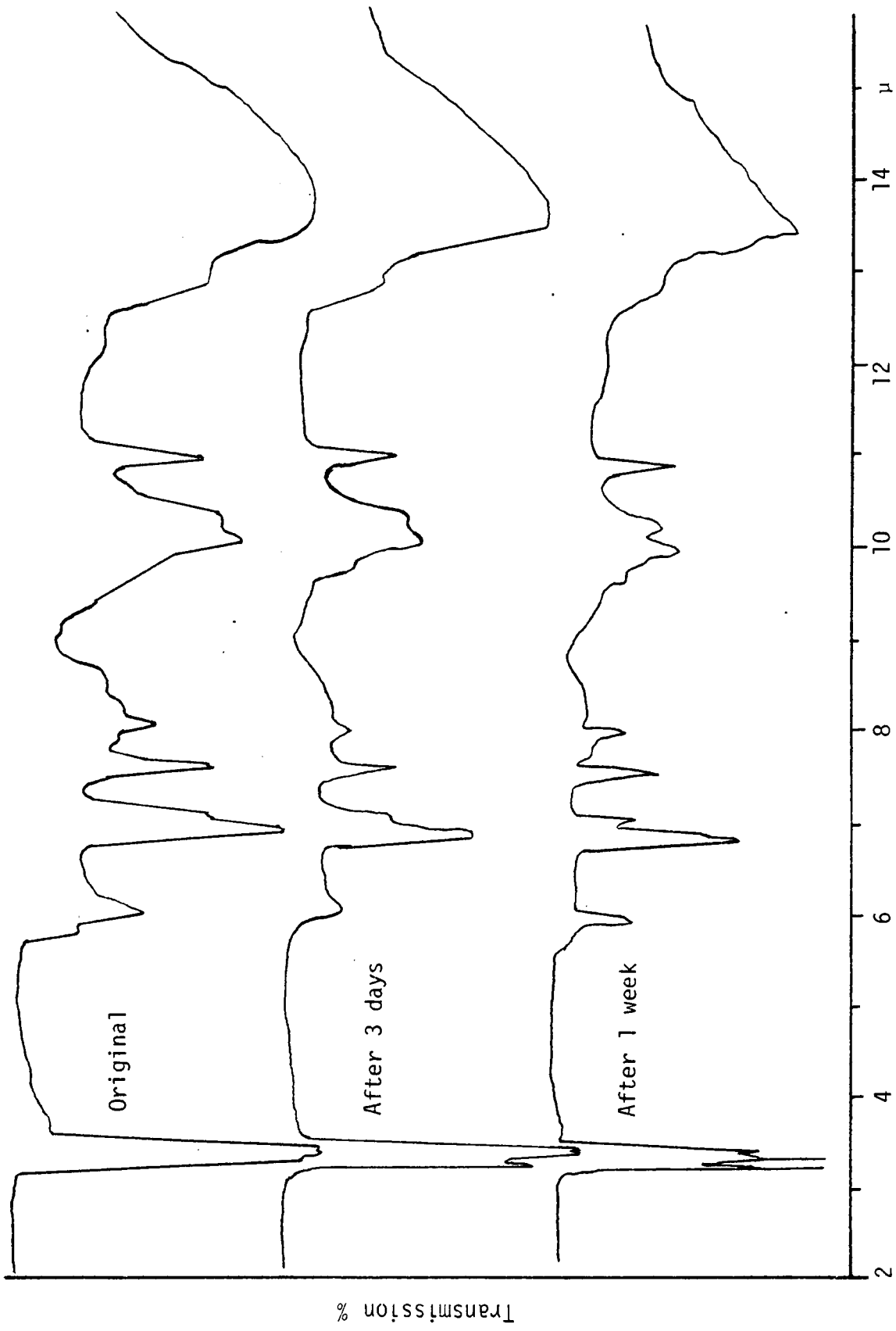


Figure 10. IR spectra of sample F. PBD sealed in nitrogen and stored in the dark.

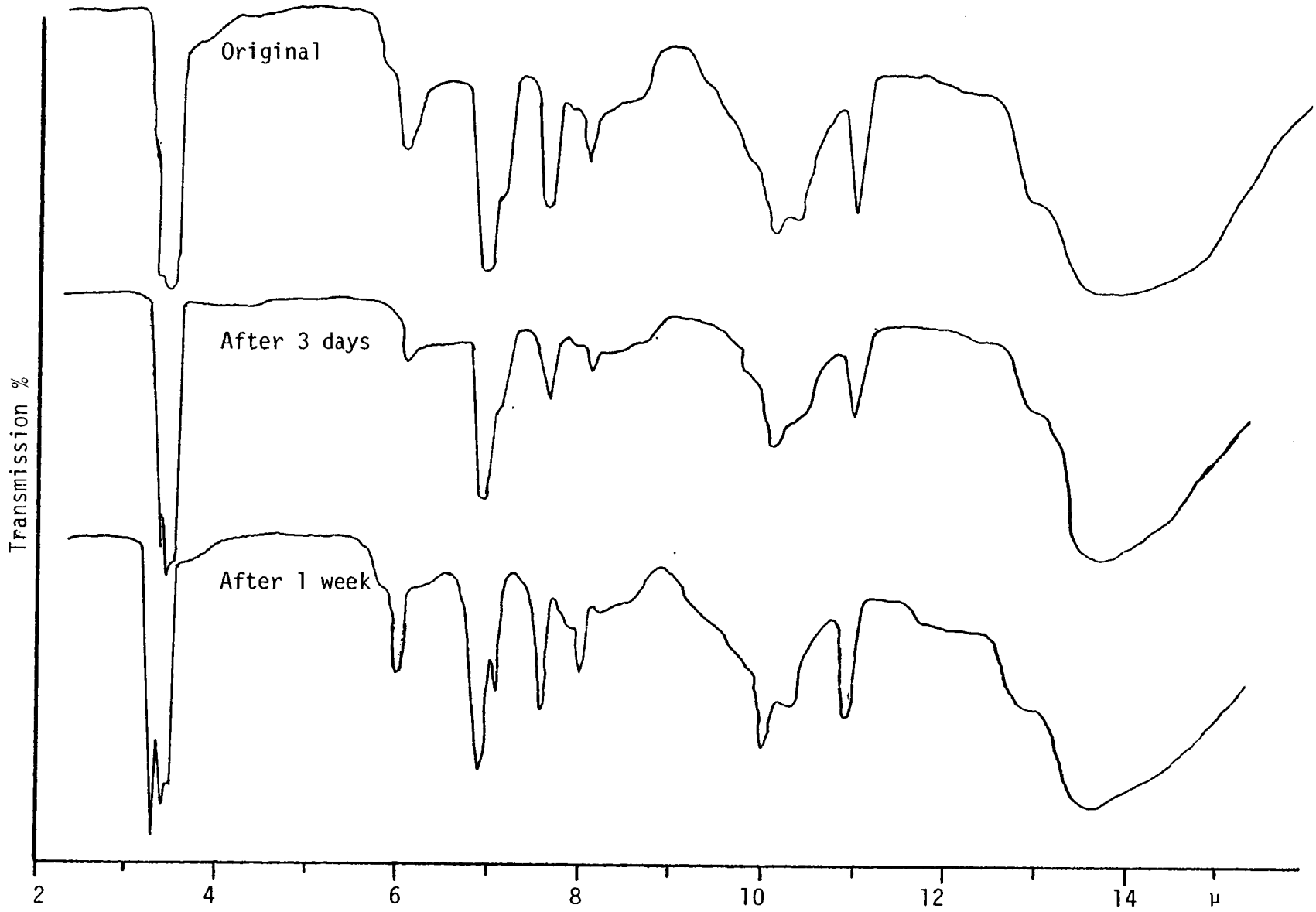


Figure 11. IR spectra of sample G. PBD was sealed in oxygen and stored in the dark.

sunlight), F (nitrogen stored in the dark), and G (oxygen stored in the dark) after storage for 1 week. The samples were extracted with hexanes, dried under vacuum for 24 hr, and weighed. Samples B and C were completely insoluble after 6 hr extraction, while samples F and G were completely soluble after only 3 hr of extraction. Samples B and C showed the broad absorption band between 7.1 and 13.3 μ which Salimov associated with crosslinking. The soluble samples F and G did not develop these wide bands.

The change of weight during the storage process was also studied on these 4 samples. There was approximately 30% weight gain in samples B and C after exposure to sunlight for 1 week. The weight of samples F and G did not change during the storage process. The increase in weight for samples B and C was attributed to the oxygen which reacted with PBD films during exposure to sunlight. The process of flushing the film for 10 min did not significantly reduce the degradation process as shown by the IR spectra and weight increase due to oxidation.

This study indicates that either of two methods may be used to retard the degradation of the unstabilized PBD. The film may either be evaucated for 24 hr and stored in the sunlight, or simply stored in the dark. The latter method was used in this study.

3. Comparison of Polybutadiene Subjected to Hydrolytic Conditions and to Thermal Conditions

The PBD films used in this study were produced by pressing the PBD between aluminum plates. The average thickness of the PBD films used in this study was 0.6 mm. A 40 x 40 mm^2 sheet was used to compare

the reaction of PBD subjected to hydrolytic conditons and thermal conditons. The samples were subjected to hydrolytic or thermal conditions for 6 hr.

The changes were determined using an ATR attachment on the Perkin Elmer 257 IR spectrophotometer. The percentages of the trans, 1,2, and cis isomeric units were determined using the method described in Haslam et al.[41]

The percentages of the trans and cis isomeric units for PBD samples which have been subjected to either hydrolytic or thermal conditions are shown in Figure 12. There appears to be little cis/-trans isomerization occurring below 200°C. Above 200°C the percentage of trans (and the decrease in the percentage of cis) increased more rapidly for the PBD samples subjected to hydrolytic conditions than the PBD samples subjected to thermal conditions. The percentage of the 1,2 isomeric unit remained near 3%.

The difference in cis/trans ratio for the PBD samples subjected to hydrolytic and thermal conditions is shown in Figure 13. At low temperatures the cis/trans ratios for the thermal samples were lower than the cis/trans ratios for samples subjected to hydrolytic conditions. At higher temperatures the PBD samples subjected to hydrolytic conditions produced more cis-trans isomerization (resulting in a lower cis-trans ratio) than the sample subjected to thermal conditions.

The linear per cent swell was also measured for the two methods of degradations. The linear per cent swell was used as a comparative method for the degree of crosslinking, assuming the linear percent swell is inversely proportional to the crosslink density. The linear per cent swell for the smaple used in this study are shown in Figure 14. The samples which

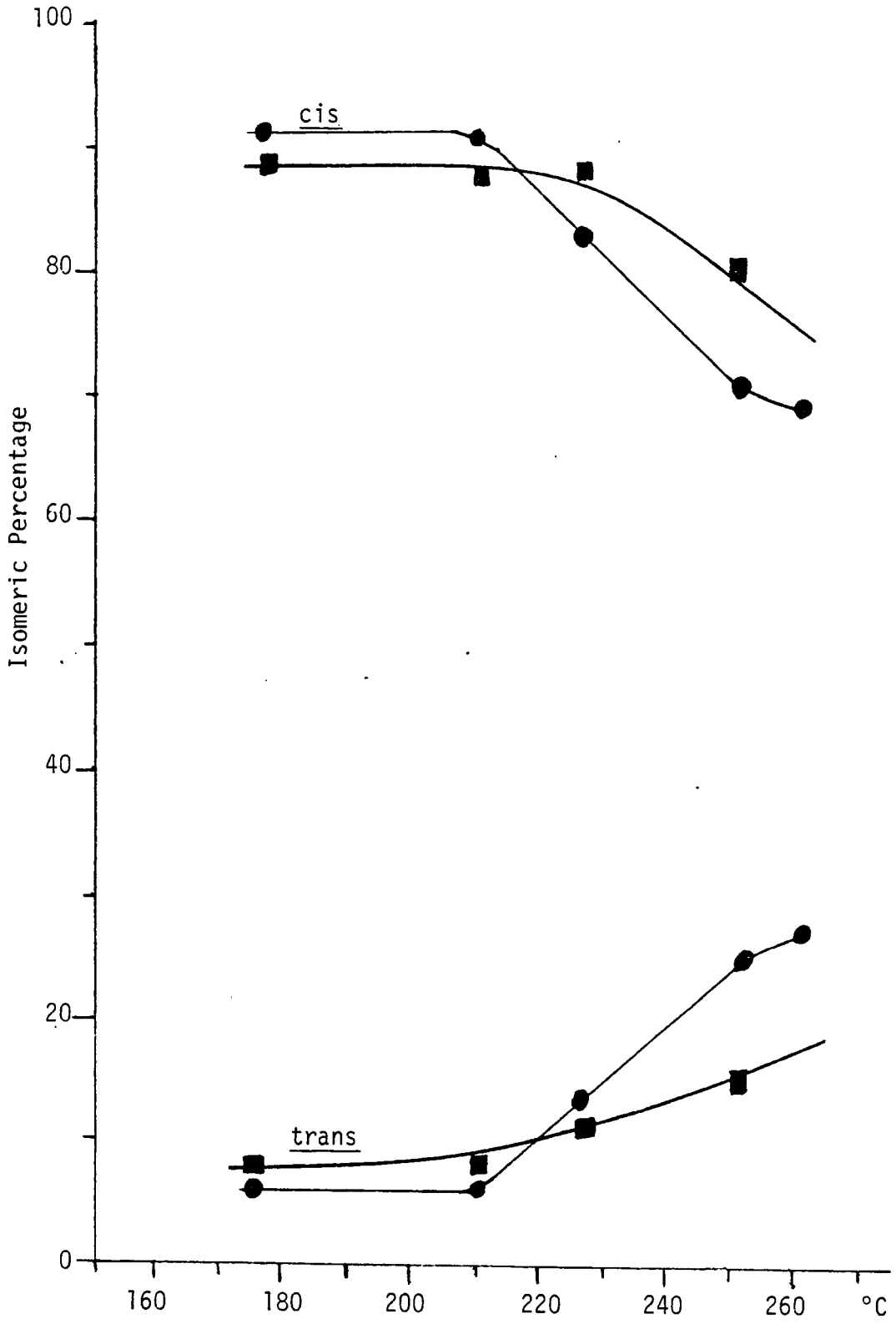


Figure 12. Percentage of cis and trans isomeric units after subjecting PBD film to hydrolytic (●) and thermal (■) conditions for 6 hr.

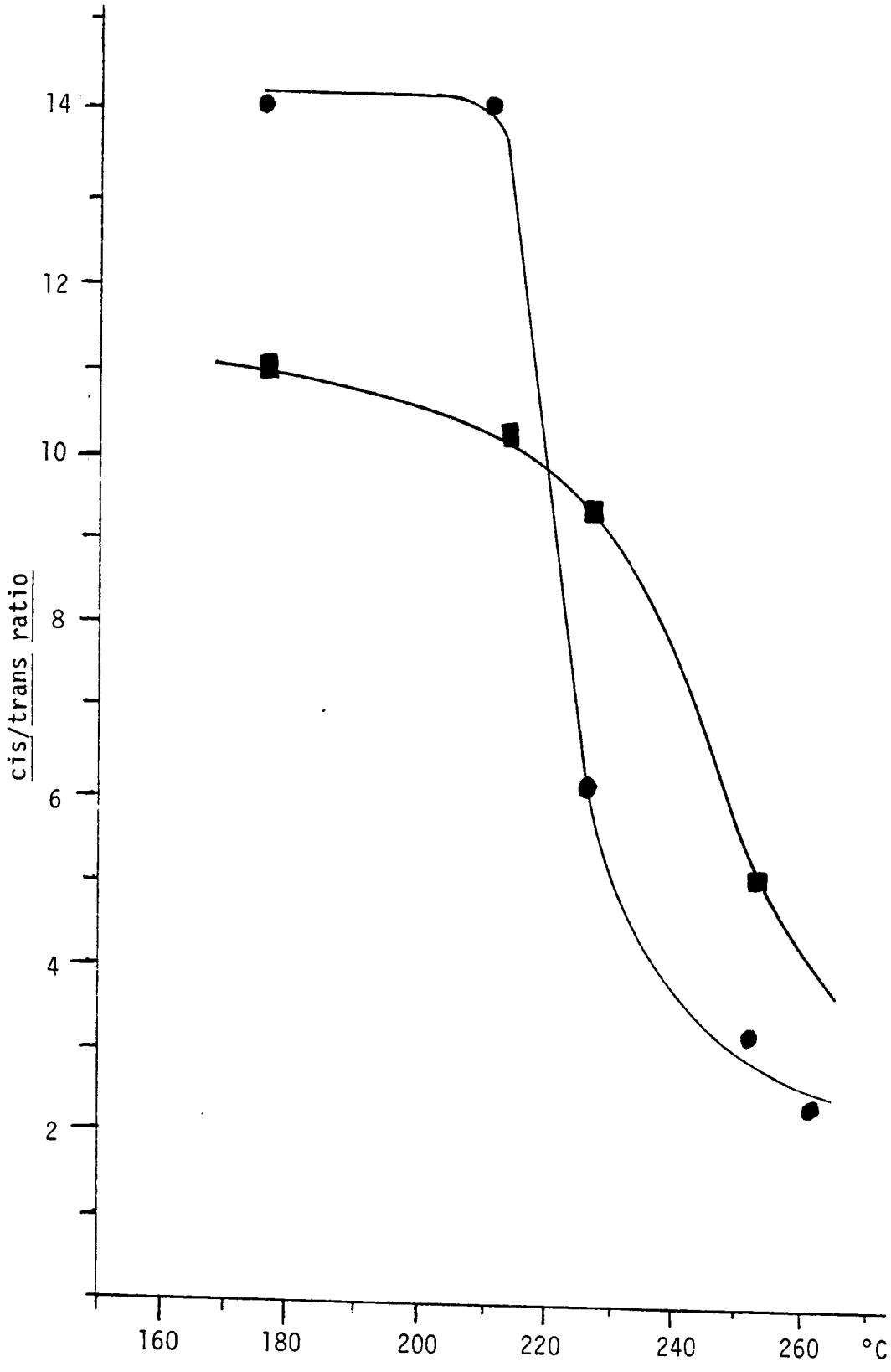


Figure 13. cis/trans ratio of PBD samples subjected to hydrolytic (●) and thermal (■) conditions for 6 hr.

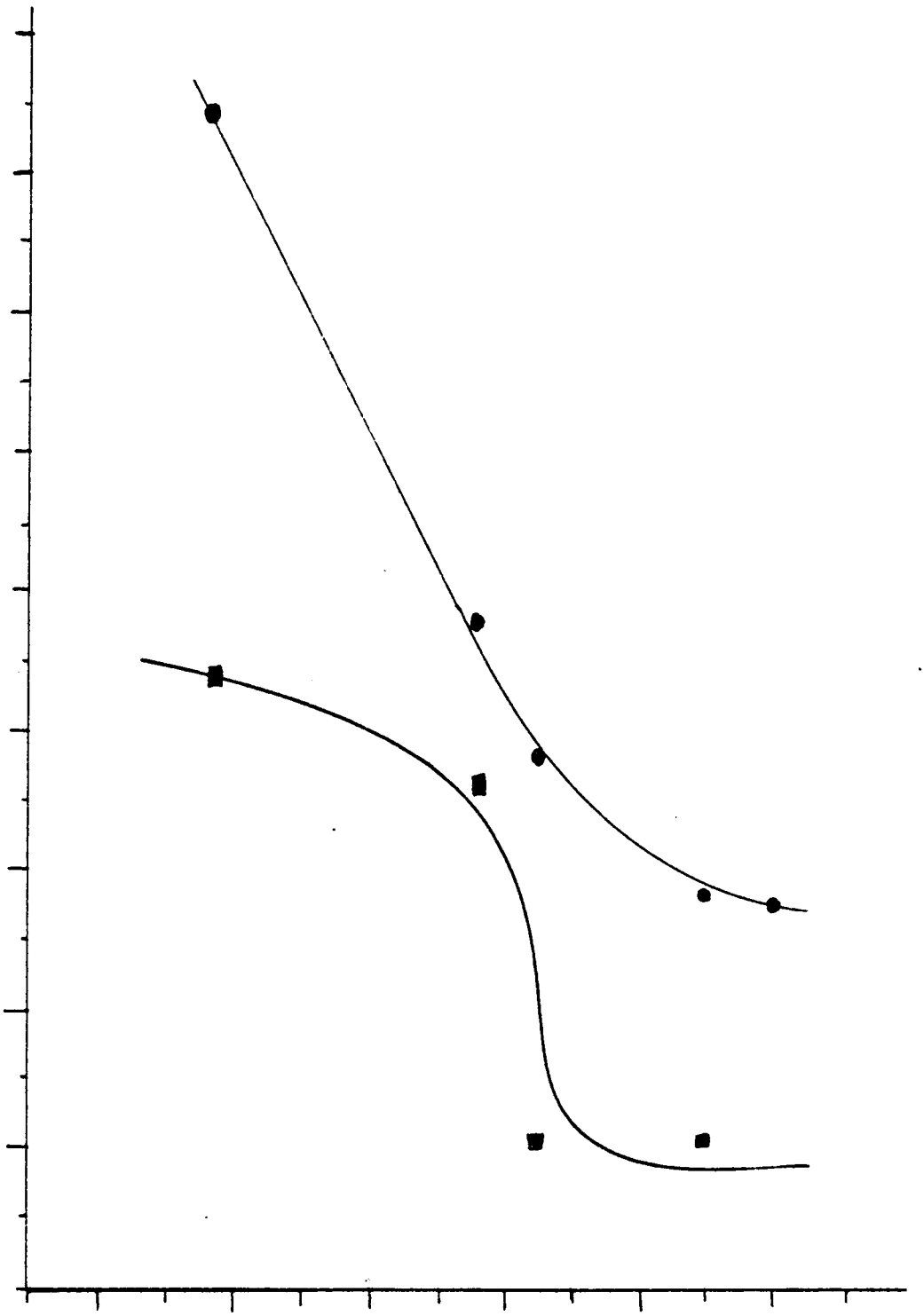


Figure 14. Linear percent swell of PBD sample subjected to hydrolytic (●) and thermal (■) conditions for 6 hr.

were subjected to thermal conditions apparently cross linked more than samples subjected to hydrolytic conditions for the same time and at the same temperature. Figures 13 and 14 indicate that at the same temperature and reaction time, cis-trans isomerization was more predominant for the PBD which was subjected to hydrolytic conditions than the PBD subjected to thermal conditions. The crosslinking (which is inversely related to the linear per cent swell) was more predominant for the PBD samples which were subjected to the thermal conditions compared to hydrolytic conditions. The linear per cent swell reached a minimum value (indicating a higher degree of crosslinking) for the samples subjected to thermal conditions compared with samples subjected to hydrolytic conditions. The presence of water increased the cis-trans isomerization reaction and decreased the crosslinking reaction.

4. Polybutadiene Subjected to High Temperature Aqueous Conditions

The PBD samples used in this study were supported on glass frames. After drying, the PBD samples were placed in a glass tube containing 10 ml of distilled water. The glass tube was cooled in a dry ice-acetone bath to prevent over heating, a constriction was formed, the water was flushed with nitrogen for at least 10 min, and the ampoule was placed in the dry ice-acetone bath and sealed.

Figure 15 shows the cis/trans ratio of PBD samples subjected to hydrolytic conditions at 120 and 140°C with times varied. The appreciable variation in cis/trans ratio appeared to be random. This variation was primarily due to the nonuniform thickness of the film. The values used in Figure 15 were the average of two determinations.

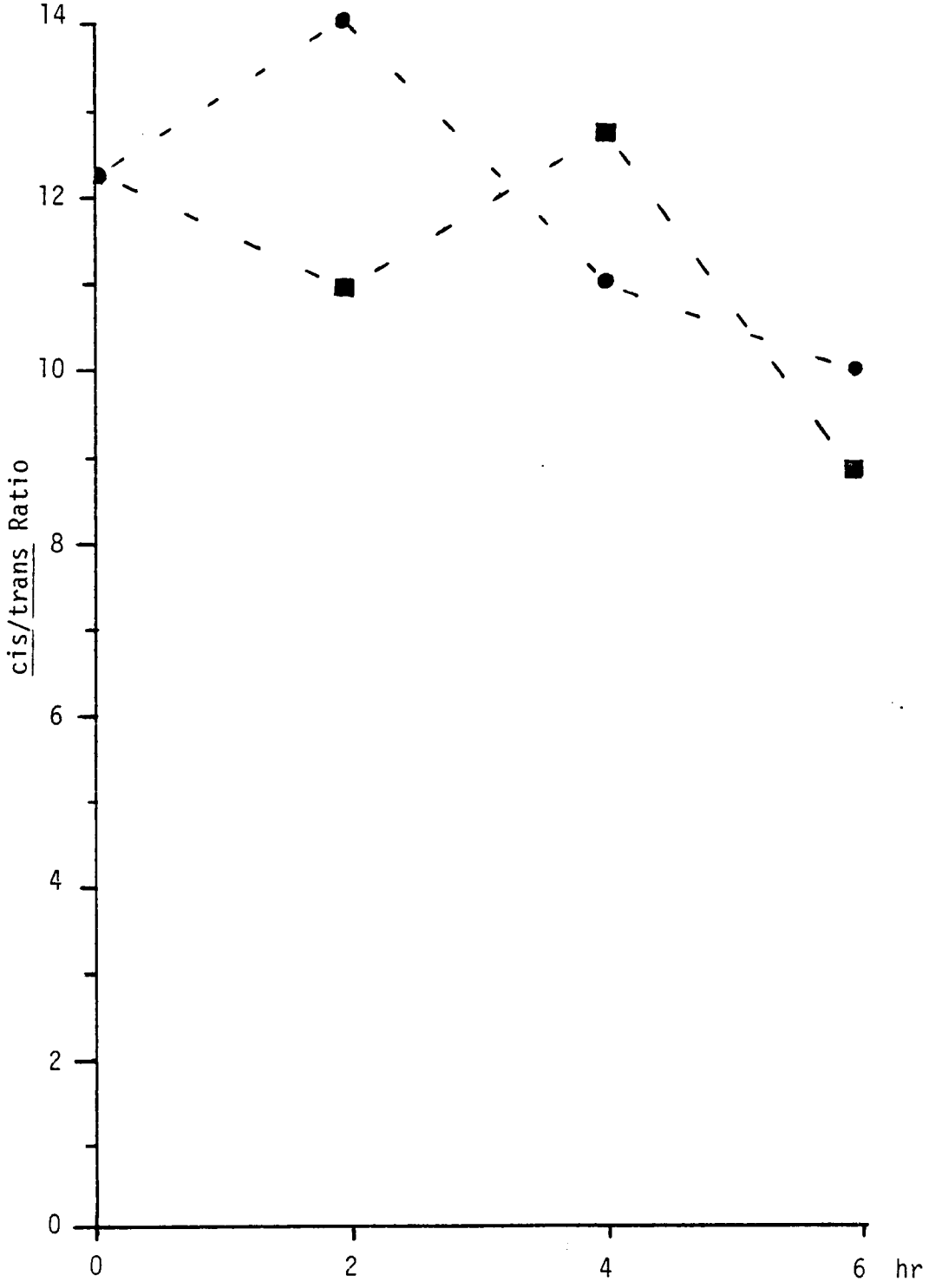


Figure 15. Cis/trans Ratio of PBD subjected to hydrolytic conditions at (●) 120 and (■) 140 °C as a function of time.

Figure 16 shows the change of the cis/trans ratio of PBD samples subjected to hydrolytic conditions as a function of temperature. The PBD samples were subjected to hydrolytic conditions for 6 hr. The cis/trans ratio decreased from an original value of 12.3 to 3.0 at 175°C. The cis/trans ratio was decreased even more when the experiment was conducted at 270°C. The final cis/trans ratio was 1.1 at 270°C.

The cis/trans ratio was also determined using FTIR. Although the values determined by transmission IR and FTIR differed considerably, the same decrease in the cis/trans ratio was noted. The minimum cis/trans ratio determined by FTIR was 1.4 after subjecting the PBD to hydrolytic conditions for 6 hr at 270°C.

Figure 17 shows the IR spectra of the original PBD, a PBD sample subjected to hydrolytic conditions for 6 hr at 150°C, and a PBD sample subjected to hydrolytic conditions for 6 hr at 250°C. In addition to the change in the cis/trans ratio, several changes were noted in these spectra. There was a decrease in the absorption band at 6.0 μ. A decrease in this band and the 13.6 μ band was attributed to the consumption of cis units by Golub and Gargiulo, based on their data from thermal degradation studies of 1,4-PBD.[54] The formation of methyl groups (7.3 μ), conjugated unsaturation (6.25 μ), and cyclized structures (12.2 μ) noted in Golub and Gargiulo's work was not noted in this study when high cis-PBD was subjected to hydrolytic conditions.

There was a decrease or elimination of the bands at 11.0, 10.1, 7.1 and 6.1 μ which Golub and Sung[55] attributed to the loss of $-CH=CH_2$ units. Their assignments were based on a pyrolysis study of 1,2-PBD. Golub and Sung also noted an increased absorption at 6.9 μ which was

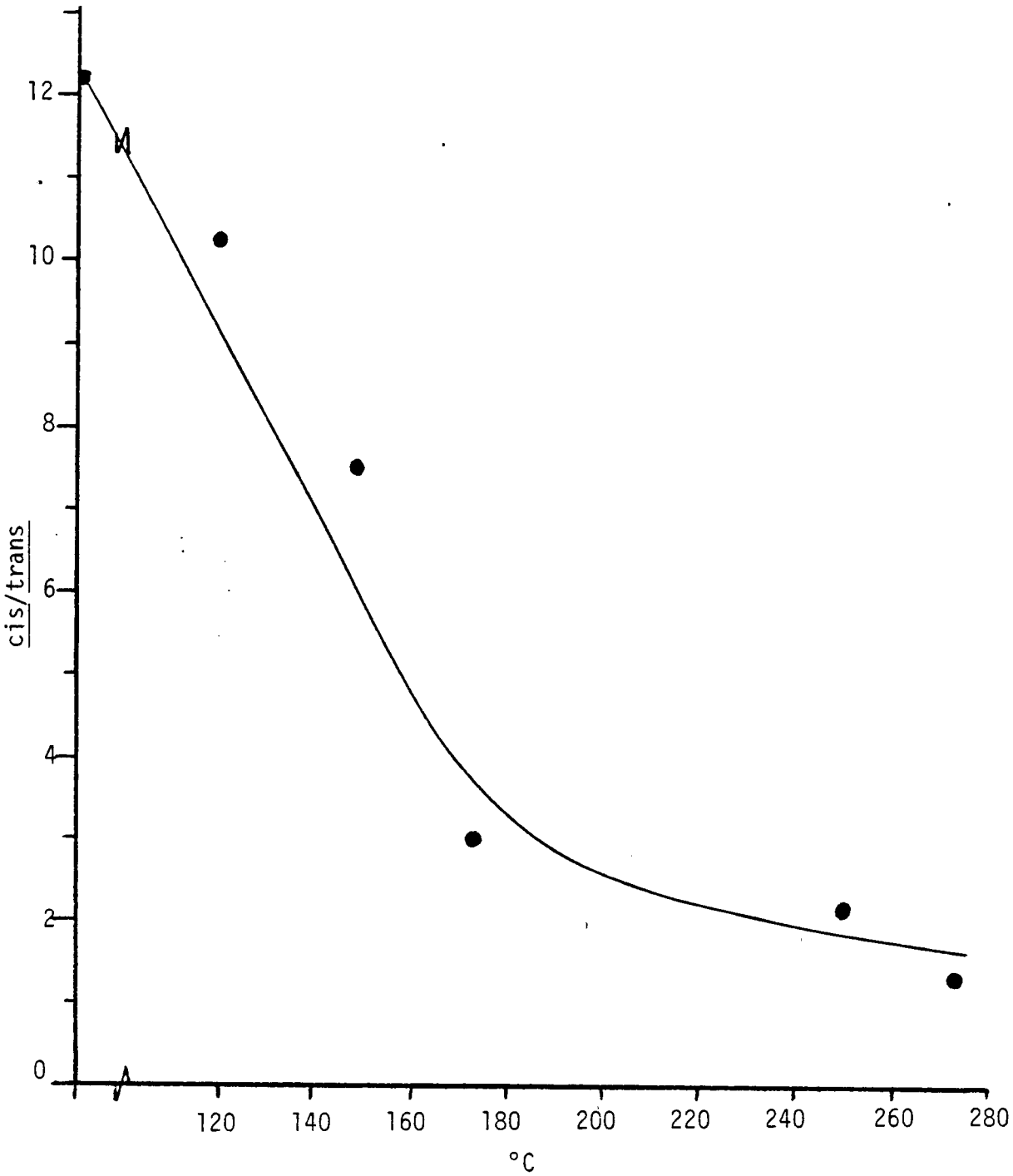


Figure 16. Cis/trans ratio of PBD subjected to hydrolytic conditions for 6 hr as a function of temperature.

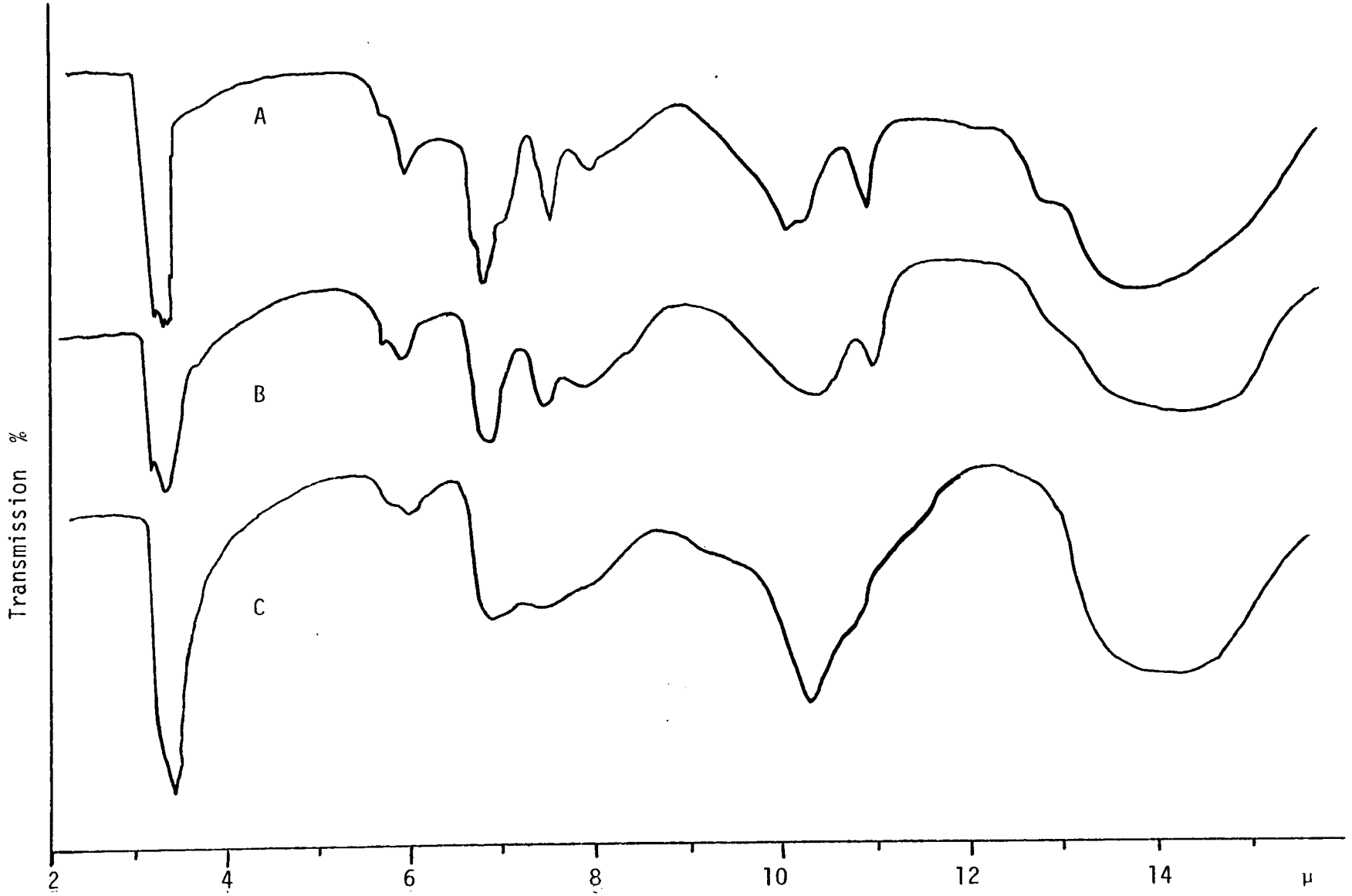


Figure 17. IR spectra of PBD. A, original PBD; B, after subjecting PBD film to hydrolytic conditions for 6 hr at 150°C; and C, after subjecting PBD film to hydrolytic conditions for 6 hr at 250°C.

attributed to the saturation of these vinyl groups. Due to the broadness of the absorption band in this area, it is difficult to detect any absorption changes in this portion of the IR spectrum of PBD subjected to hydrolytic conditions at 250°C.

There was a random appearance of absorption bands at 2.9 and 5.9 μ in the IR spectrum of PBD subjected to hydrolytic conditions. This band appeared in some of the samples subjected to hydrolytic conditions at 120°C for 2 hr and in some of the samples subjected to hydrolytic conditions for longer times and higher temperatures. Figure 18 contains the IR spectrum of a normal run and the IR spectrum in which oxidation occurred. In addition to the absorption bands at 2.9 and 5.9 μ there was a decrease in the transmission past 7 μ. Apparently, there was a small amount of oxygen which was not removed by bubbling nitrogen through the water containing the PBD sample. The presence of oxygen greatly decreased the cis/trans ratio. The cis/trans ratio was about 50% less for the samples which contained oxygen. The samples in which oxidation occurred were not used in the cis/trans ratio versus temperature discussion.

5. Conclusion

It was noted in this study that purified PBD readily undergoes oxidation during storage at room temperature when exposed to sunlight. A difference was noted between the cis/trans ratio of samples subjected to thermal conditions and hydrolytic conditions. The cis/trans ratio of samples subjected to hydrolytic conditions decreased faster than those subjected to only thermal conditions. The crosslinking of PBD appeared to be retarded by the presence of water.

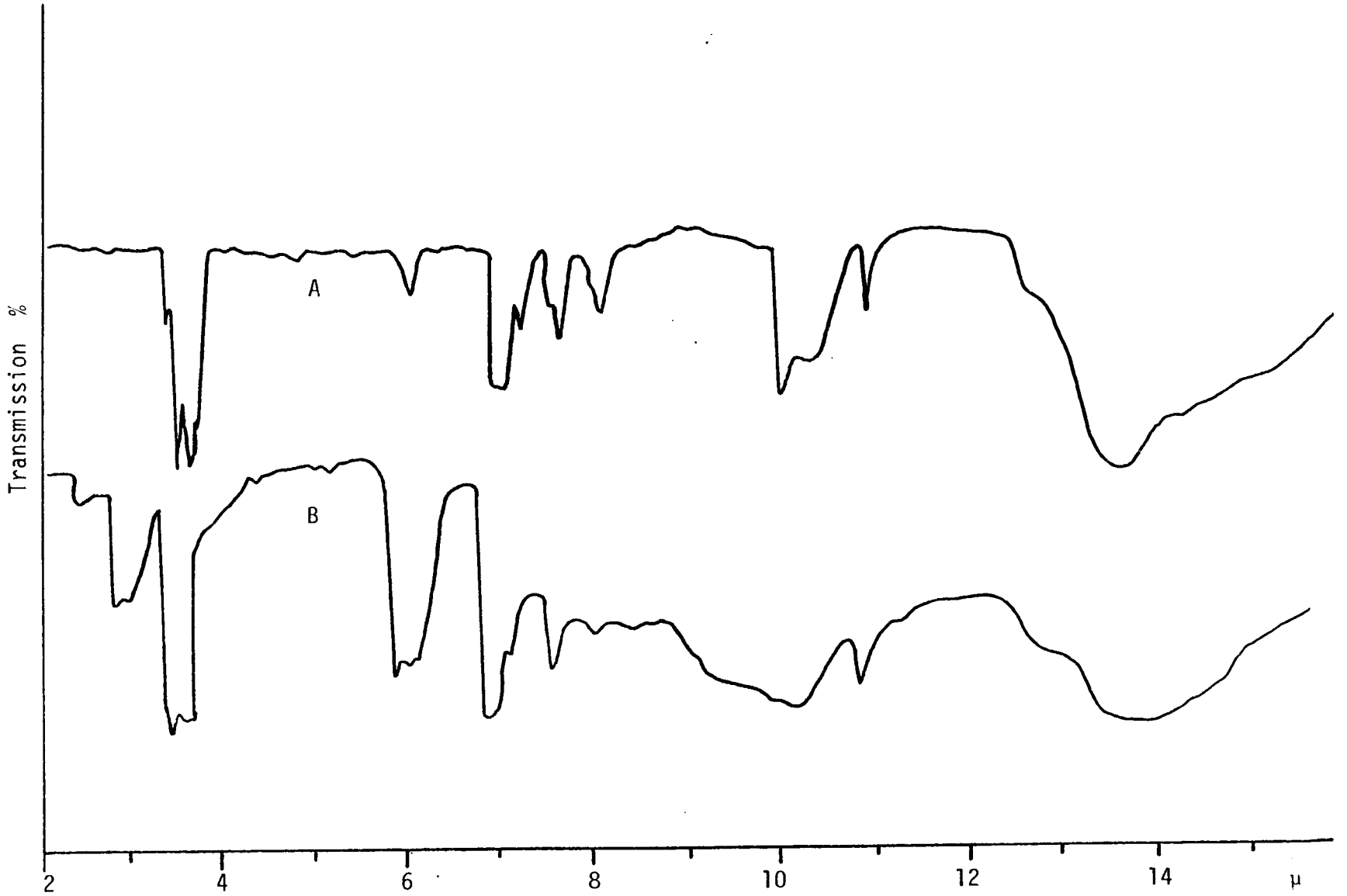


Figure 18. IR spectra of PBD subjected to hydrolytic conditions at 140°C for 6 hr. A shows no evidence of oxidation, B shows absorption bands at 2.9 and 5.9 μ indicative of oxidation.

There were several problems associated with the hydrolytic modification of PBD. The oxygen could be removed by evacuating for a long period of time. This was not pursued since the removal of all oxygen entrapped in polymeric scrap would be difficult for a large scale system. The large difference in the three methods used to determine the percentage of each isomeric unit prevented a detailed discussion of the absolute value of the cis and trans content. The randomness of the cis/trans ratio at lower temperatures indicated the large variance in the method used for determining the cis/trans ratio. The remaining discussion was limited to general trends displayed by the cis/trans ratio when the PBD was subjected to increasing temperatures.

There was no indication of the formation of cyclic structures in the samples subjected to hydrolytic conditions. No evidence of the formation of conjugated double bonds or methyl groups was noted in the IR spectrum of the samples subjected to hydrolytic conditions.

There was no indication of true hydrolysis of the double bonds of PBD to form alcohol functional groups. No weight loss was noted for the samples subjected to hydrolytic conditions. Also, there were no by-products detected in the water of hydrolysis based on gc analysis.

This indicates that PBD would not interfere with the hydrolysis and separation of hydrolyzed products from such polymers as nylon and polyurethane. This statement does not consider the effect of the acidity or basicity of the hydrolyzed products. Therefore, a mixture of PBD and a hydrolyzable polymer may be separated. The unhydrolyzed

PBD could be separated out with the insoluble fraction and incinerated to reclaim the fuel value of the PBD.

B. Styrene Crosslinked Unsaturated Polyester

1. Composition of the Original Polyester Solution

The percentage of styrene contained in the original polyester solution was determined by two methods. The film method involved spreading a known amount of polyester solution on a piece of aluminum foil and removing the volatile styrene portion under vacuum. The reduction in weight was attributed to the loss of the sytrene. The percentage styrene was also determined using a polyester precipitation method. The original polyester solution was mixed with a benzene-ligroine solution. The unsaturated polyester precipitated, while the styrene remained in solution. The difference in weight between the original polyester solution and the precipitated, dried polyester was ascribed to loss of styrene. The results of these determinations are presented in Table III.

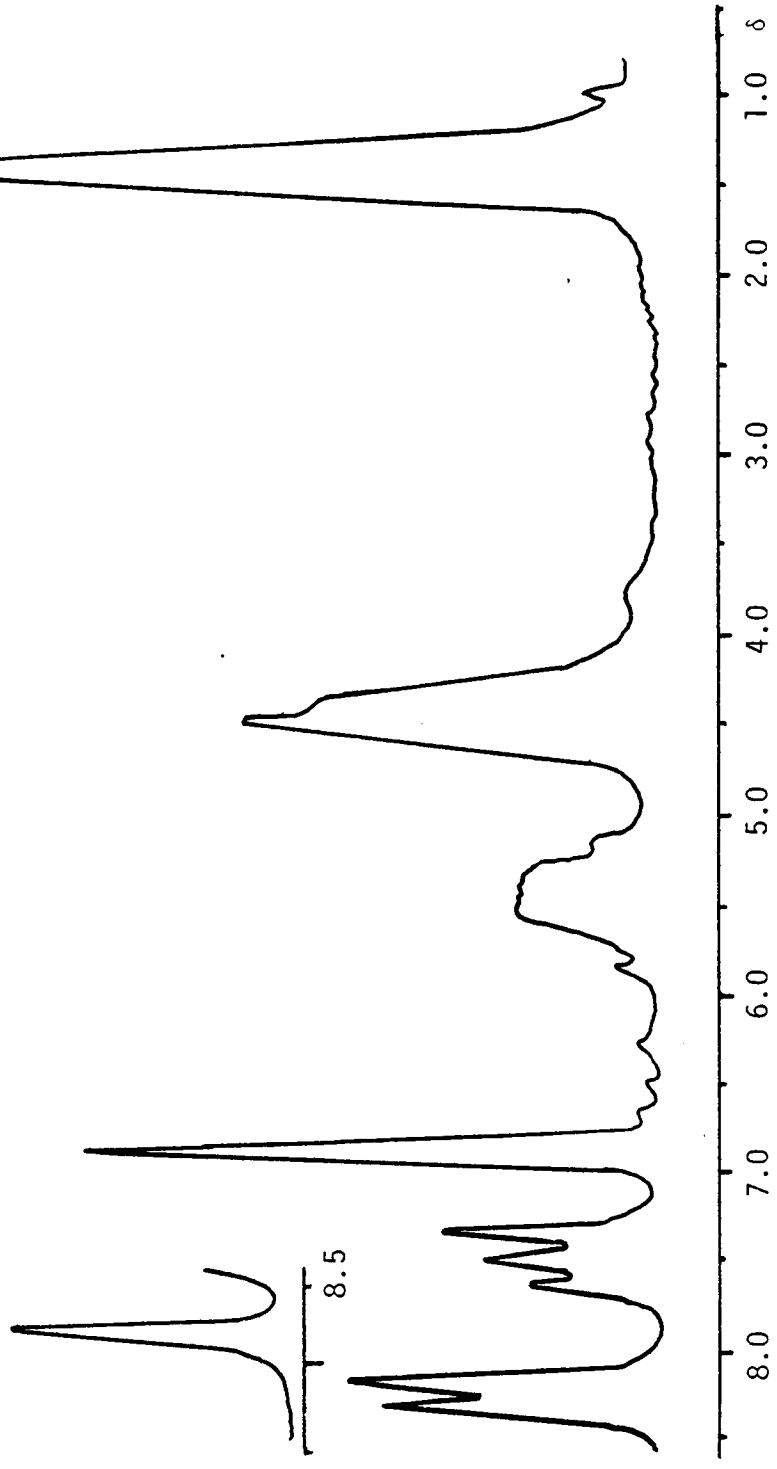
The film method would be expected to give low results for per cent styrene, since a small amount of styrene would remain trapped in the polyester matrix. The precipitation method would most likely give high values for per cent styrene, since some low molecular weight polyester would not precipitate. Therefore, the average of the per cent styrene values (33.8%) was used in subsequent calculations.

The ^{1}H NMR spectrum of the isolated polyester was used to determine the relative amounts of the two diacids used in its preparation. In Figure 19 is shown the ^{1}H NMR spectrum of a 10% solution of

TABLE III

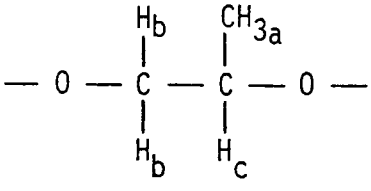
PERCENT STYRENE IN ORIGINAL POLYESTER SOLUTION

	Wt. original polyester solution, g	Wt. after drying, g	Wt. isolated polyester, g	Wt. loss g	Wt. loss %
Film method	3.338	2.256	--	1.082	32.4
	7.965	5.322	--	2.643	33.2
Precipitation	5.489	--	3.536	1.953	35.6
	6.218	--	4.104	2.114	34.0

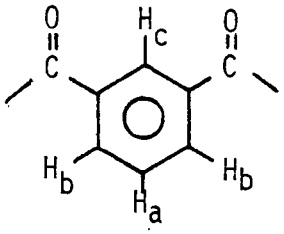


Fiugre 19. ^{1}H NMR of original polyester in CCl_3-d (styrene removed).

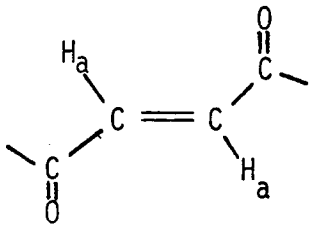
the isolated polyester in chloroform-d, obtained on the T-60 NMR. The δ values (relative to tetramethylsilane internal standard) are presented in Table IV. The following notation will be used in designating the ^1H NMR peaks at the various units of the polyester chain.



Propylene glycol (PG) unit



Isophthalic acid (IPA) unit



Fumaric acid (FA) unit

The integration of the IPA and FA peaks was used to calculate the relative amount of each diacid used to produce the original unsaturated polyester. Each IPA unit contains 4 protons, and each FA unit contains 2 protons. The relative area due to the IPA unit (the peaks at 8.7, 8.2, and 7.4 δ was 61, and that was due to the FA unit (6.8 δ) was 20. So the ratio of IPA to FA is 61/4:20/2 or 15.2:10.0. This corresponds to mole ratio of 0.60 IPA to 0.40 FA. Thus the average repeat unit (aru) of the original polyester used in this study had three IPA units for every 2 FA units. This aru is shown below.

-PG-IPA-PG-FA-PG-IPA-PG-FA-PG-IPA-

The molecular weight of the aru (931 g/m) and the percentage of styrene were used to calculate the theoretical yield of PG, IPA, and

TABLE IV

^1H NMR PEAK ASSIGNMENTS OF THE ORIGINAL POLYESTER

δ value	Assignment
8.7	IPAc
8.2	IPAb
7.4	IPAa
6.8	FAa
5.3	PGc
4.4	PGb
1.3	PGa

copolymer (styrene-FA-styrene) produced from the hydrolysis of SXUP samples. A 1.00 g sample of the original polyester solution (before crosslinking) contained 0.338 g styrene and 0.662 g polyester. The number of moles of aru in 1.00 g of the original polyester solution is calculated below.

$$\frac{0.662 \text{ g polyester}}{931 \text{ g polyester/m aru}} = 0.711 \times 10^{-3} \text{ m aru}$$

$$0.711 \times 10^{-3} \text{ m aru} \xrightarrow{\text{hydrolyzed}} \begin{cases} 2.13 \times 10^{-3} \text{ m (0.354 g) IPA} \\ 1.42 \times 10^{-3} \text{ m (0.165 g) FA} \\ 3.56 \times 10^{-3} \text{ m (0.271 g) PG} \end{cases}$$

Thus the complete hydrolysis of 1.00 g of SXUP should produce 0.354 g IPA, 0.271 g PG, and 0.503 g of copolymer containing FA and styrene.

2. Hydrolysis of SXUP

Following the procedures related in Chapter II, samples of SXUP were prepared, ground, and sieved. Samples were hydrolyzed at several temperatures and for various times, in each case using 1.000 g SXUP and 5.0 ml water in a sealed glass tube. The most useful data are those derived from hydrolyses at 225°C for 2, 4, 6, 8, 10, and 12 hr and those run for 6 hr at 200, 225, 250, and 275°C. In all cases, except the 275°C hydrolysis that will be discussed later, the post-hydrolysis samples consisted only of a solid precipitate and a homogeneous aqueous phase.

The phases were separated by use of a 20-M 15 ml fritted glass filter. The solid portion was washed with about 5 ml of distilled water. The filtrate and wash water were combined. The analysis of the aqueous portion will be discussed after the analysis of the solid portion.

The solid portion from the above filtration was dried and weighed. This solid portion was composed of IPA and copolymer produced by the hydrolysis reaction, in addition to any unhydrolyzed SXUP material. The IPA was separated from the copolymer and unhydrolyzed SXUP by dissolving the IPA in 200 ml of boiling water. The boiling water solution was filtered hot. The above process was repeated for the insoluble portion. (The solubility of IPA in boiling water is 0.21 g/100 ml.[110] Therefore, the theoretically available IPA would be soluble in 170 ml of boiling water.) The above filtrates were combined, rotoevaporated, and the IPA was allowed to crystallize. The solubility of IPA at room temperature is 0.012 g/100 ml.[110] The crystals were separated by filtrated under reduced pressure, dried, and weighed.

The melting point of the reclaimed IPA was about 5°C lower than the value for pure IPA. The reclaimed IPA was dissolved in hot water and allowed to recrystallize before the IPA was analyzed by IR, ^{1}H NMR and the melting point redetermined. There was good correlation of the recovered IPA and the pure IPA based on the above tests. The melting point of the reclaimed IPA was 343°C and the melting point of pure IPA was 345°C.

The reaction products of 1.00 g of SXUP hydrolyzed at 225°C for various times are shown in Table V. Figure 20 shows the percent yield of reclaimed IPA from these hydrolyses. The yield of reclaimed IPA reached a value of 56% after hydrolysis for 4 hr. An increase in the time did not greatly increase the percent yield. The percent yield was 60.6% after 10 hr of hydrolysis.

TABLE V

RECLAIMED IPA FROM THE HYDROLYSIS OF SXUP AT 225°C

Reaction time, hr	Solid after hydrolysis, g	Hot water insoluble, g	Reclaimed IPA, g	% Yield
2	0.873	0.621	0.147	42
4	0.876	0.574	0.199	56
6	0.870	0.575	0.204	58
8	0.887	0.547	0.210	60
10	0.818	0.517	0.214	61
12	0.800	0.472	0.211	60

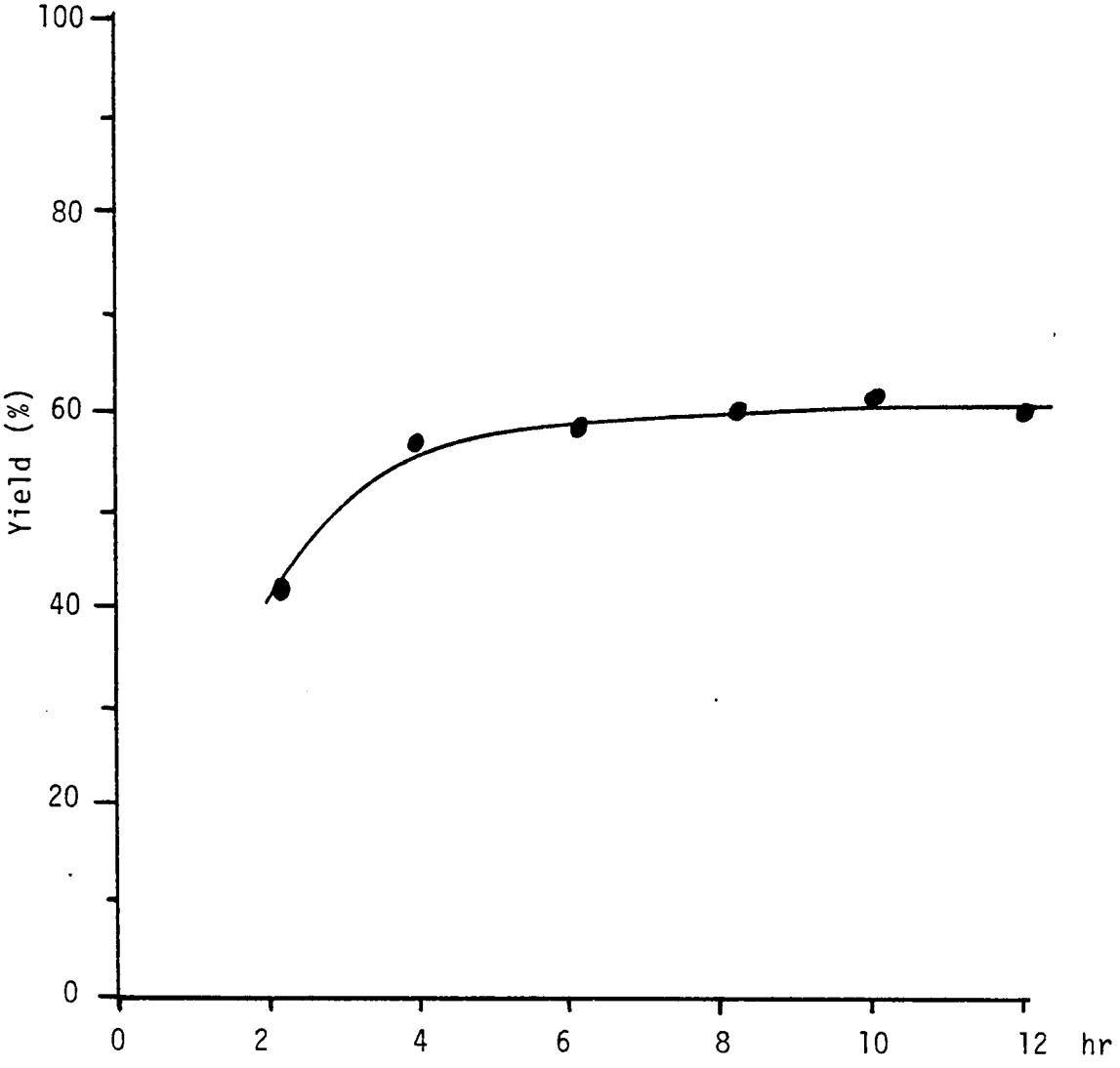


Figure 20. Yield of reclaimed IPA from the hydrolysis of SXUP at 225°C.

The hydrolysis experiment at 225°C for 4 hr was repeated to determine the reproducibility of the percent yield of the reclaimed IPA. The value of the percent yield for the repeated experiment was 54. This differs by 2% from the original determination of 56%. The major sources of this error were probably due to loss during the washing and transferring of solid material, filtration, and weighing.

The reaction products of 1.000 g SXUP hydrolyzed for 6 hr at various temperatures are shown in Table VI. Figure 21 shows the yield of reclaimed IPA from the hydrolysis of SXUP for 6 hr as a function of temperature. The yield of reclaimed IPA increased up to a temperature of 225°C. The yield at this temperature was 58%. An increase in the temperature above 225°C produced a rapid decrease in the yield of reclaimed IPA. This decrease in the yield of reclaimed IPA may be due to further reactions of the IPA at the higher temperatures.

A similar trend was noted by Valle[111] during a hydrolytic degradation study of poly(1,4-cyclohexylenedimethylene isophthalate teraphthalate). A maximum in the amount of diacid formed was reached between 225 and 250°C and decreased at higher temperatures.

One possible explanation for the decrease in the amount of diacid in this study and in Valle's study is the decarboxylation of the diacids at temperatures above 250°C. The applicability of this hypothesis to the current work is partially supported by the presence of a small amount of bubbles when the high temperature samples were opened in this study.

The decarboxylation of aromatic acids has been discussed by March.[112] Although most decarboxylation reactions are carried out in the presence of a catalyst (Cu, CuO, etc.),[113,114] some acids

TABLE VI

RECLAIMED IPA AFTER 6 HR HYDROLYSIS OF SXUP

Temperature	Solid after hydrolysis, g	Hot water insoluble, g	Reclaimed IPA, g	% Yield
200°C	0.895	0.708	0.102	29
225°C	0.870	0.575	0.204	58
250°C	0.887	0.542	0.166	47
275°C	0.743	0.508	0.508	16

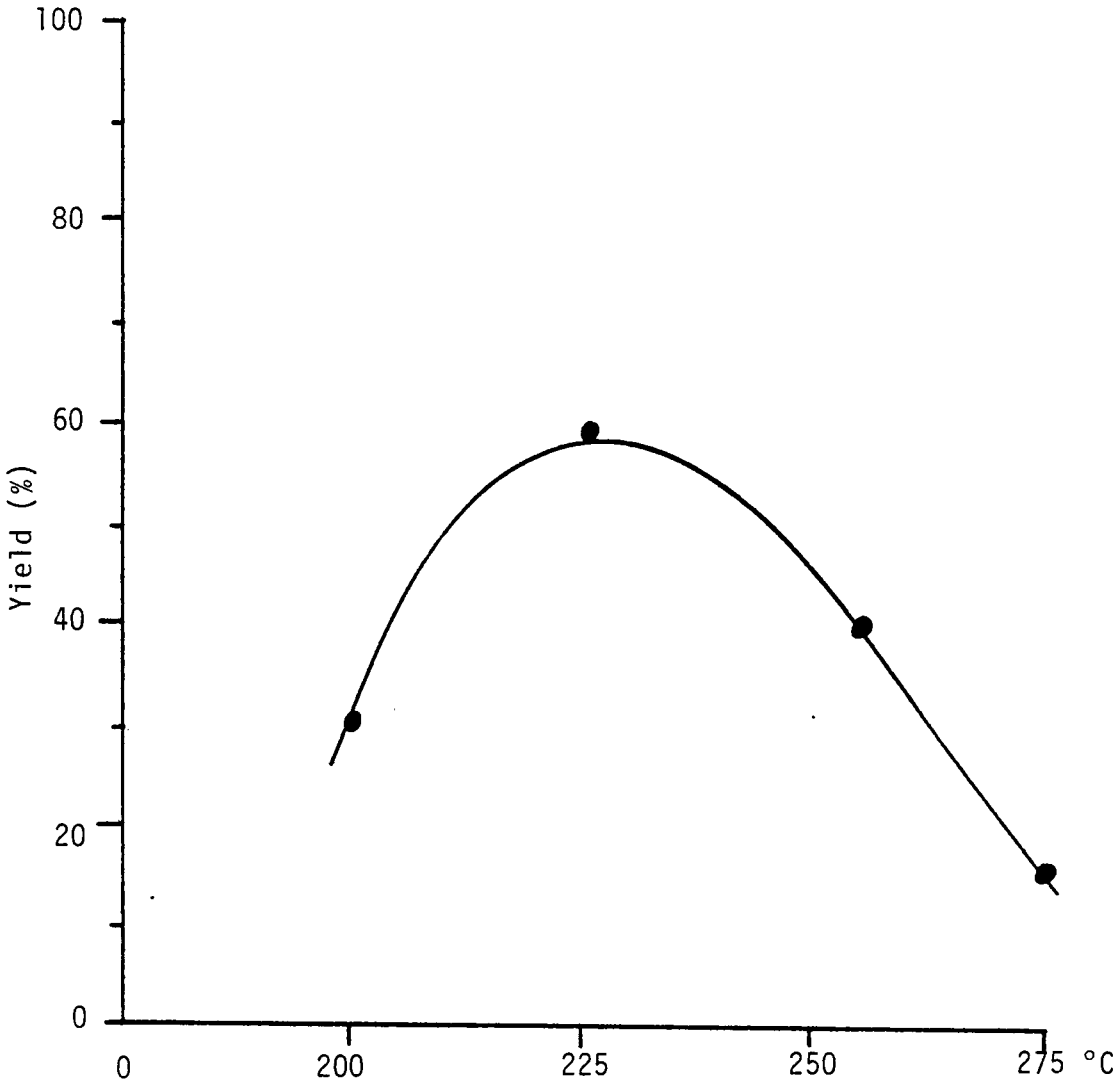


Figure 21. Yield of reclaimed IPA from the hydrolysis of SXUP for 6 hr.

decarboxylate without the addition of a catalyst. For example, 1,3-dihydroxy-2-naphthoic acid will decarboxylate when placed in boiling water for 2 hr to form 1,3-naphthalenediol.[115]

Gomory et al. observed the decarboxylation of the thermoxidative degradation products of poly(ethylene phthalate) above 300°C to a minor degree.[116] The high temperature necessary for the decarboxylation of phthalic acid was attributed to the formation of phthalic anhydride.

The monodecarboxylation product of IPA is benzoic acid (BA). If decarboxylation did occur, the BA would be partially soluble in the water of hydrolysis. The solubility of BA in water (0.34 g/100 ml)[10] is 28 times that of IPA at 25°C.

The presence of BA was checked by evaporating the water of hydrolysis of the SXUP sample hydrolyzed at 275°C for 6 hr to near dryness. This was done after the sample had been analyzed for PG by gc. The residue was extracted with diethylether and analyzed by IR (Figure 22). The IR spectrum was compared with the IR spectrum of pure BA and IPA. Although the IR spectra of BA and IPA are very similar, absorption bands at 9.3, 9.8, 10.0, and 13.7 μ indicate the presence of a small amount of BA. No separation or quantitative analysis of this small amount of residue was undertaken.

The hot water portion was extracted with acetone. The acetone insoluble portion (unhydrolyzed SXUP) was dried and weighed. The loss in weight was due to the copolymer. Figure 23 shows an IR spectrum of the copolymer obtained by casting a film from the acetone solution onto a KBr plate. The ^{1}H NMR spectrum of the copolymer is shown in Figure 24.

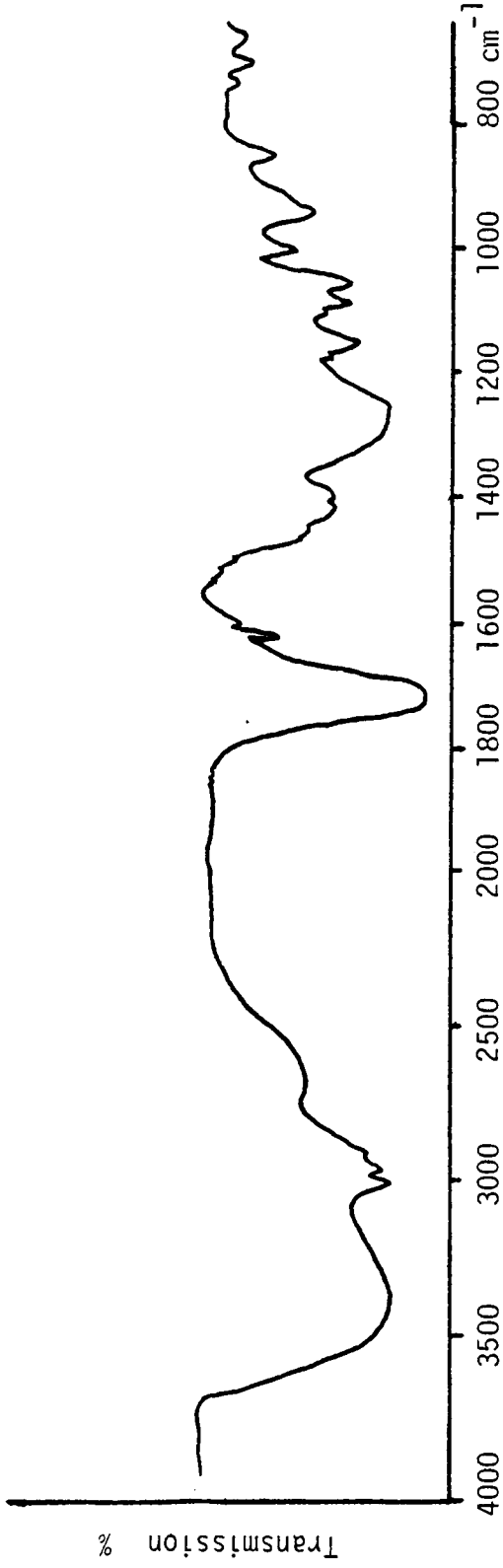


Figure 22. IR spectrum of the diethylether soluble portion of the aqueous layer of SXUP hydrolysis.

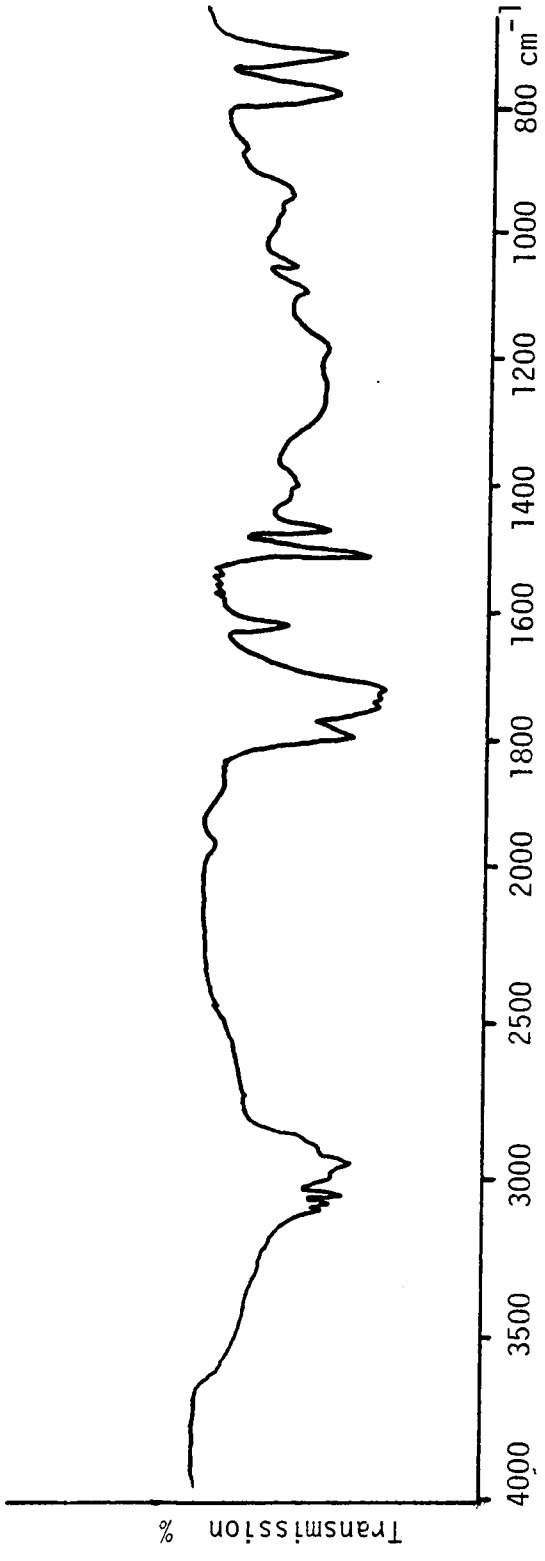


Figure 23. IR spectrum of copolymer from the hydrolysis of SXUP.

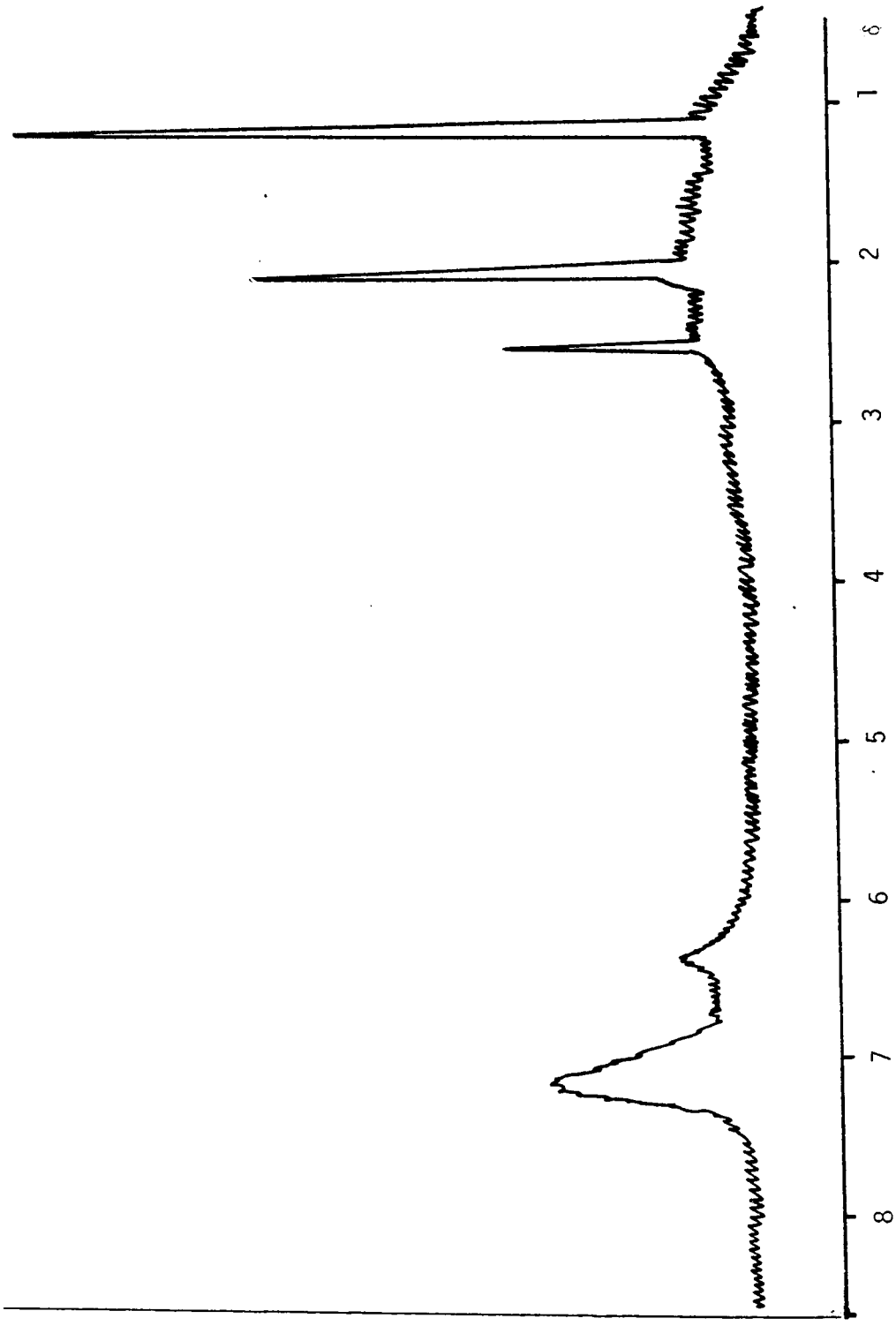


Figure 24. ^{1}H NMR spectrum of copolymer obtained from the hydrolysis of SXUP.

The IR spectrum of the insoluble portion (Figure 25) was compared with an IR spectrum of the SXUP sample before hydrolysis (Figure 26). Based on this comparison, the acetone insoluble portion was determined to be unhydrolyzed SXUP. These spectra were obtained from a 10% solution in KBr.

Quantitative data on the copolymer and unhydrolyzed portion for the hydrolysis at 225°C are presented in Table VII. Figure 27 shows the yield of copolymer (based on 0.503 g theoretical yield of copolymer from the complete hydrolysis of 1.000 g of SXUP). The yield increases nearly linearly with time. The weight of unhydrolyzed SXUP as a function of time at 225°C is shown in Figure 28. There is a linear decrease in the weight of unhydrolyzed SXUP as the time increases.

The quantitative data on the copolymer and unhydrolyzed SXUP from the 6 hr hydrolysis are presented in Table VIII. The percent yield of copolymer as a function of temperature is shown in Figure 29. Increasing the temperature from 200 to 250°C did not greatly increase the yield of copolymer; however, there was a large increase in the amount of copolymer produced by increasing the temperature from 250° to 275°C. This resulted in an increase from 20 to 86% yield.

The concurrent decrease in the g of unhydrolyzed SXUP as a function of temperature is shown in Figure 30. There was a sharp decrease in the amount of unhydrolyzed SXUP at 250°C.

The aqueous layer (containing the wash water) was subjected to gc analysis using the conditions stated in Chapter II. The retention times for water and PG under the conditions used were 0.8 and 4.8 min, respectively. When the aqueous samples were subjected to gc analysis, no peak

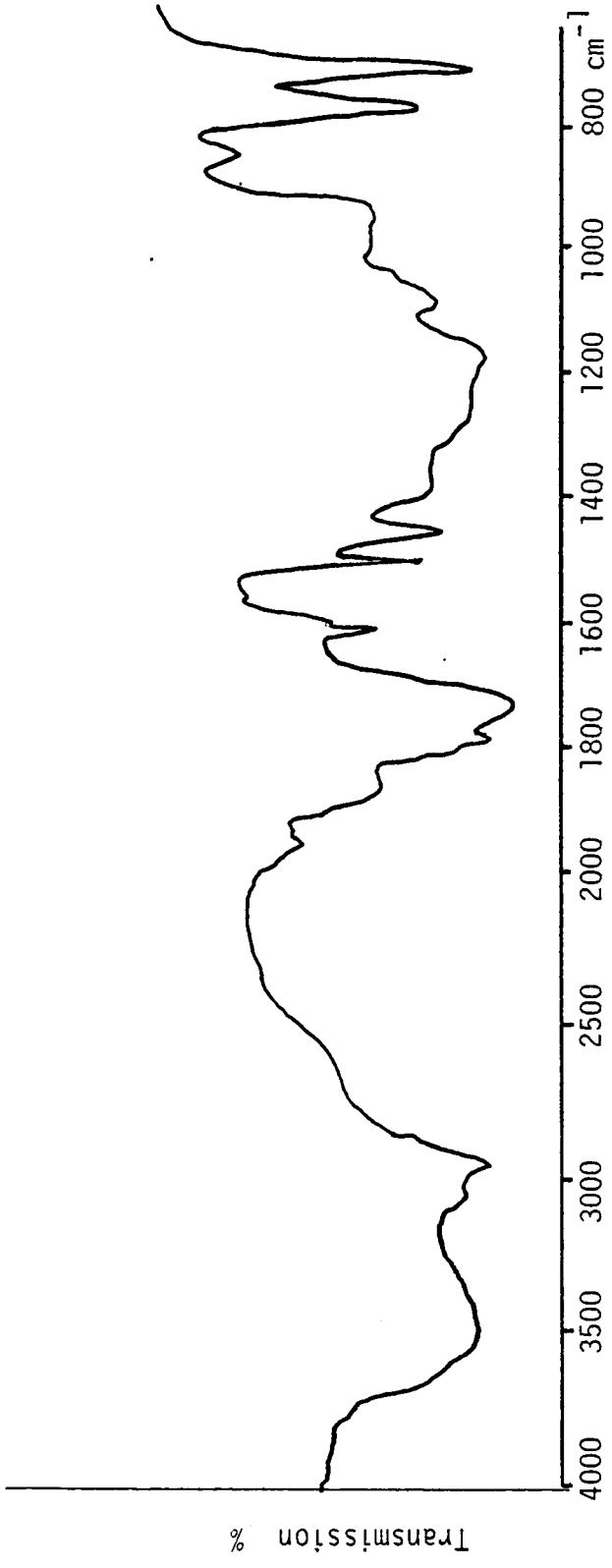


Figure 25. IR spectrum of unhydrolyzed portion of SXUP subjected to hydrolysis for 6 hr at 225°C.

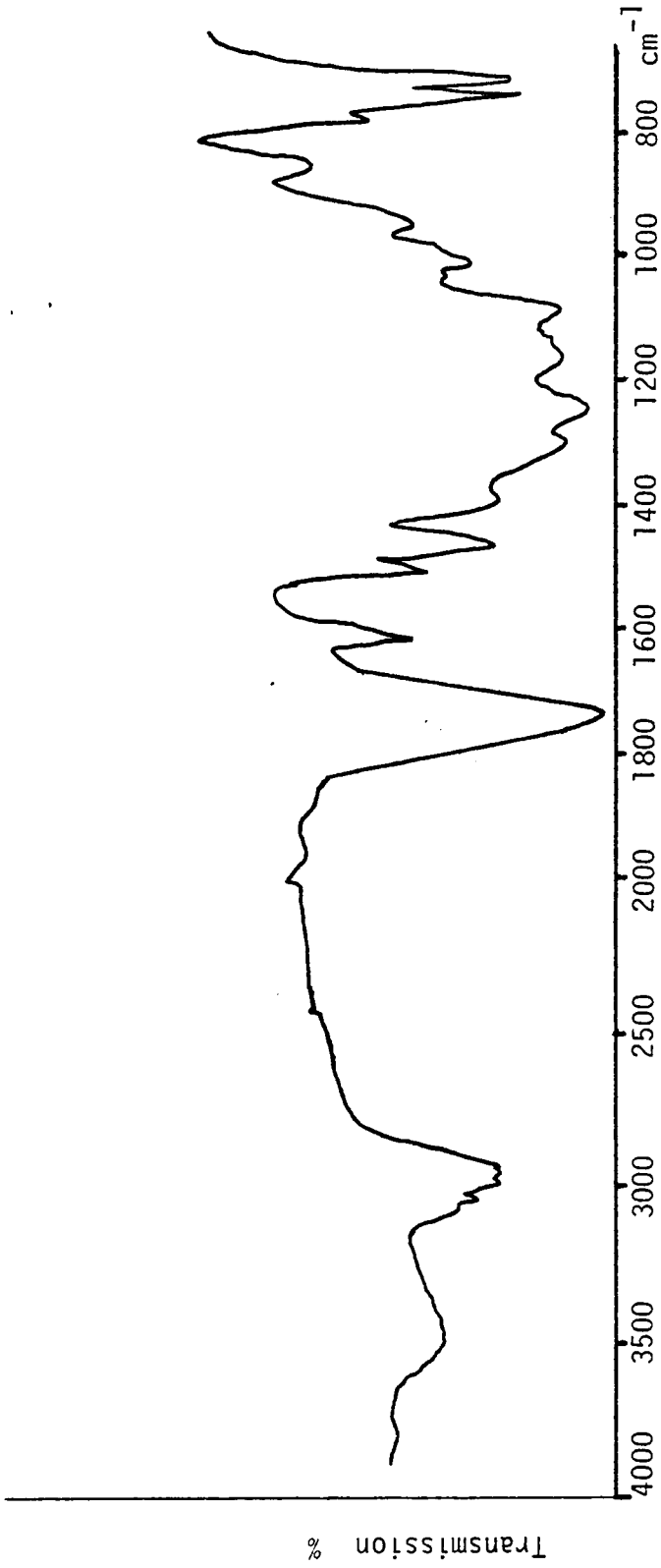


Figure 26. IR spectrum of SXUP before hydrolysis.

TABLE VII

HOT WATER INSOLUBLE PORTION OF SXUP HYDROLYZED AT 225°C

Time, hr	Hot water insoluble portion, g	Acetone soluble (copolymer), g	% yield	Acetone insoluble (unhydrolyzed SXUP), g
2	0.621	0.048	10	0.573
4	0.574	0.082	16	0.492
6	0.575	0.084	17	0.491
8	0.547	0.112	22	0.435
10	0.517	0.071	14	0.446
12	0.472	0.166	33	0.306

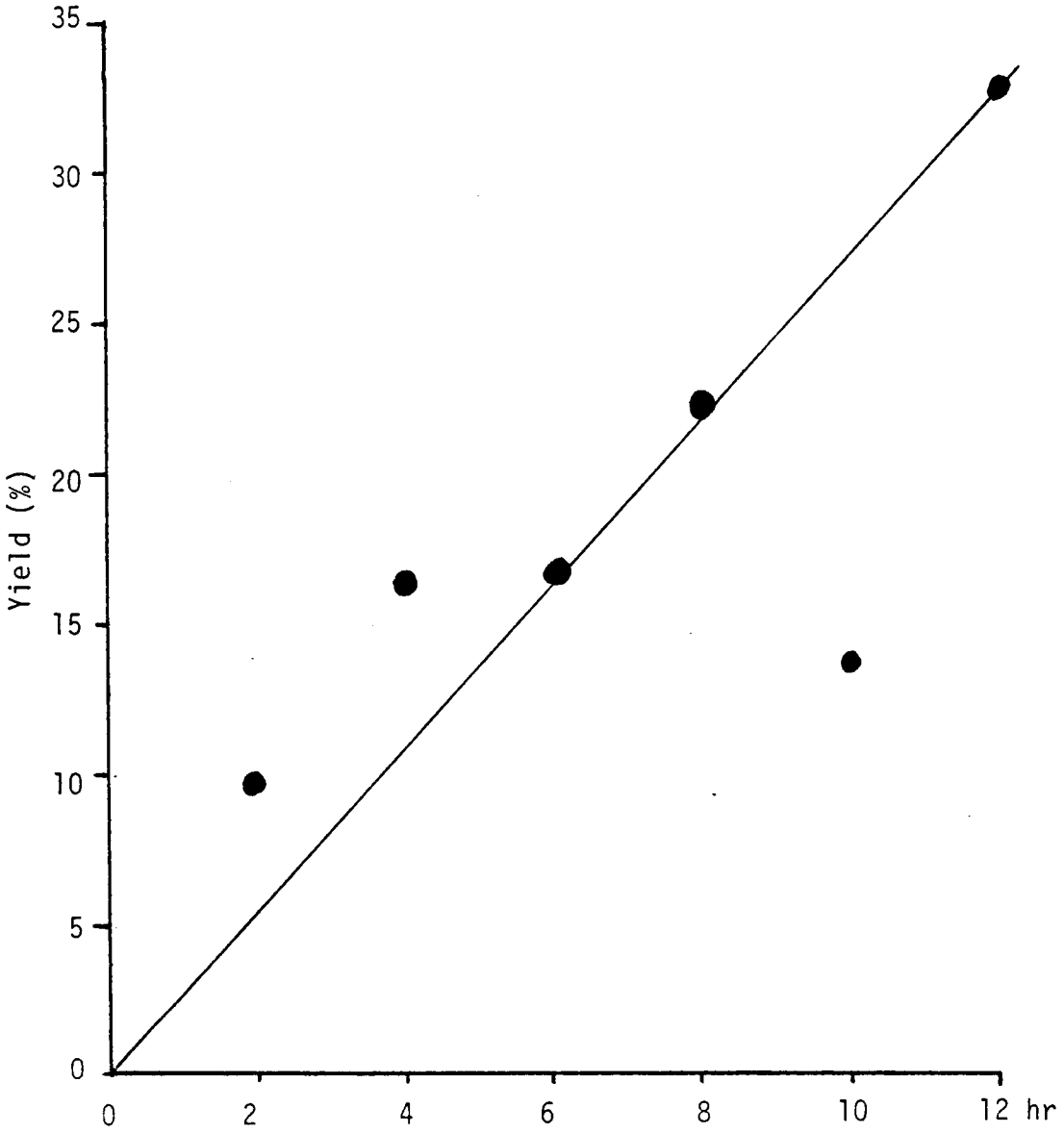


Figure 27. Yield of copolymer as a function of time for the hydrolysis of SXUP at 225°C.

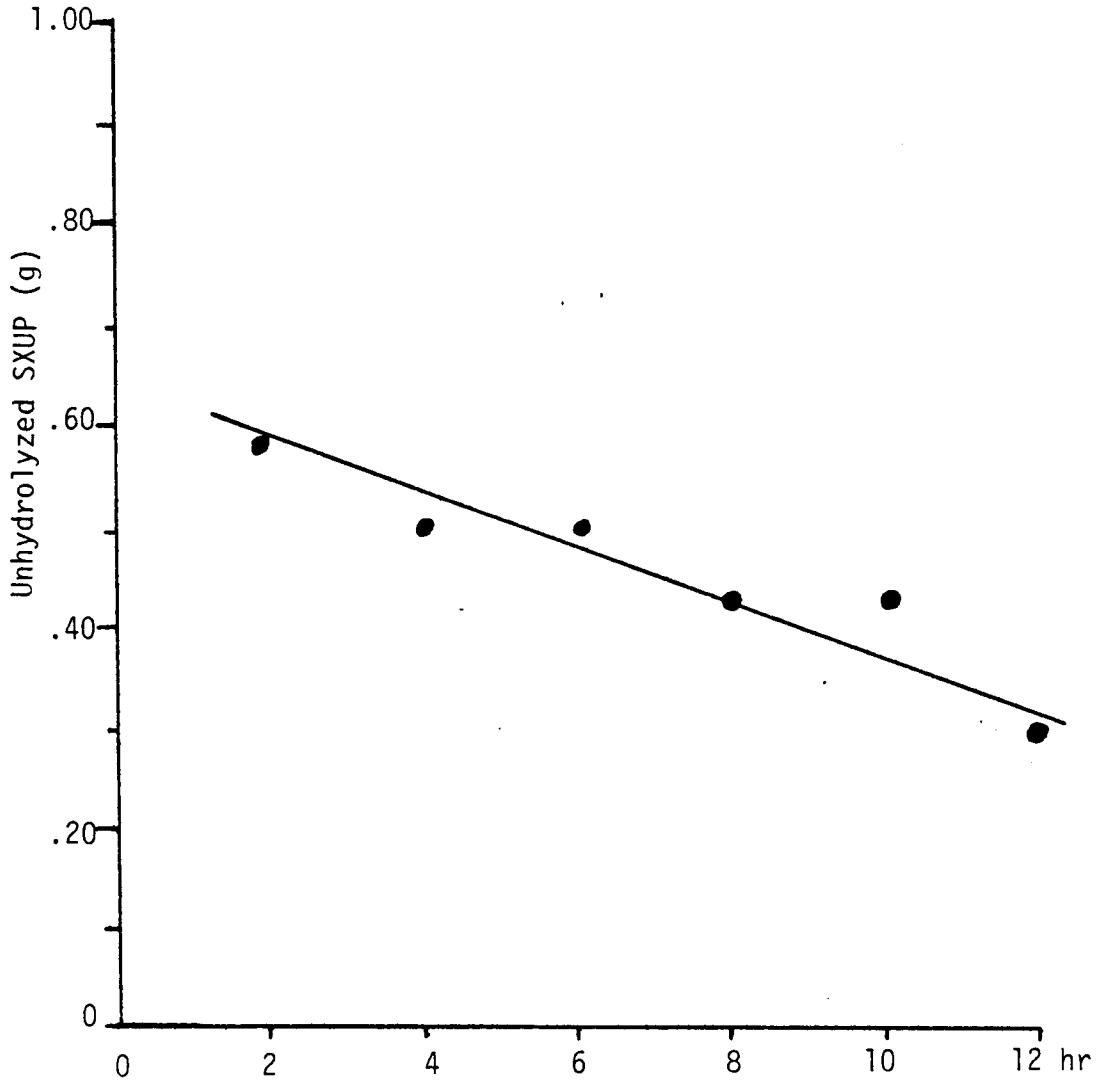


Figure 28. Unhydrolyzed SXUP as a function of time subjected to hydrolysis at 225°C.

TABLE VIII

HOT WATER INSOLUBLE PORTION OF SXUP HYDROLYZED FOR 6 HR

Temperature °C	Hot water insoluble portion, g	Acetone soluble (copolymer) g	% Yield	Acetone insoluble (unhydrolyzed SXUP), g
200	0.708	0.051	10	0.656
225	0.575	0.084	17	0.491
250	0.542	0.102	20	0.440
275	0.508	0.432	86	0.076

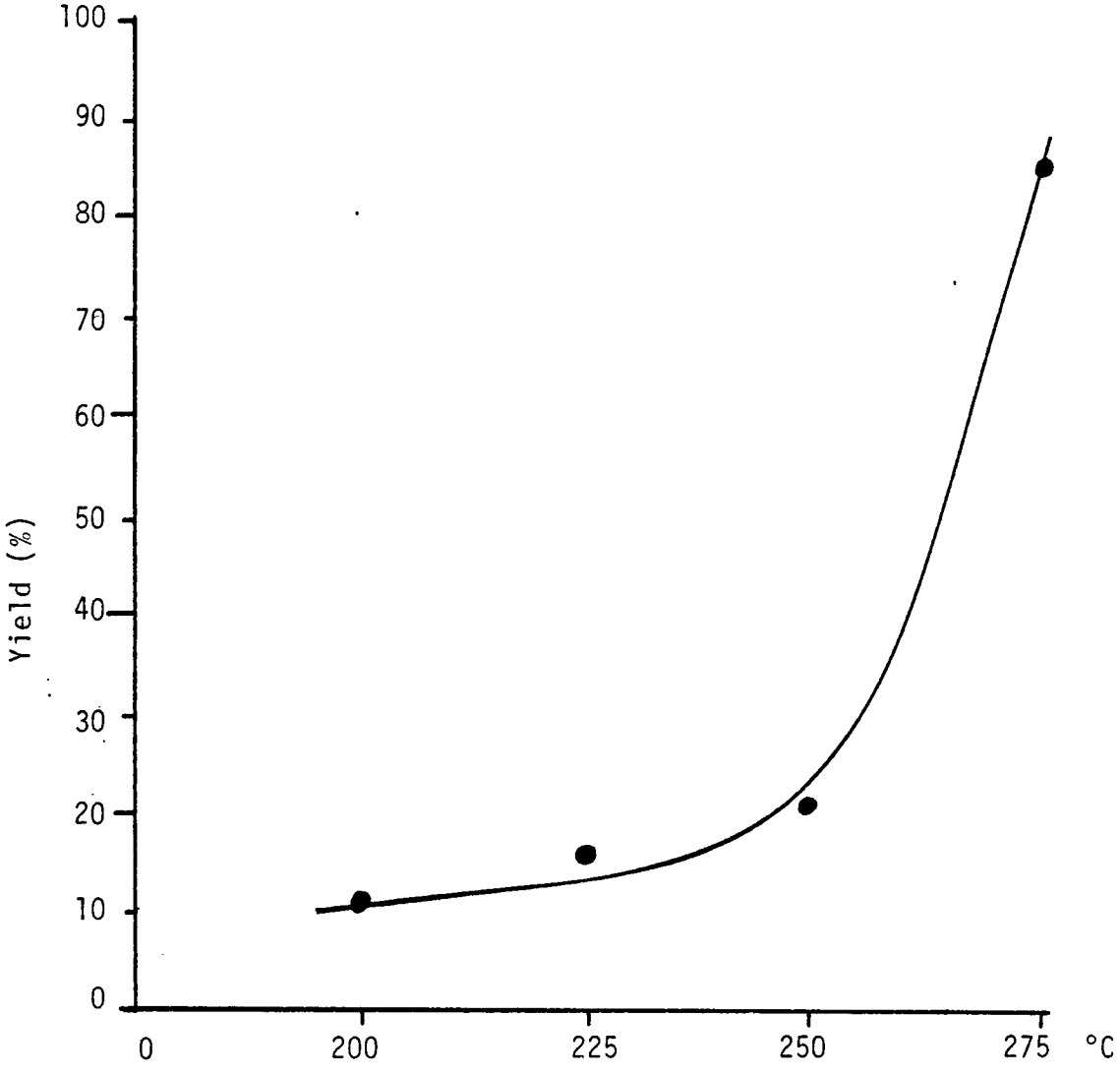


Figure 29. Yield of copolymer from the hydrolysis of SXUP for 6 hr as a function of temperature.

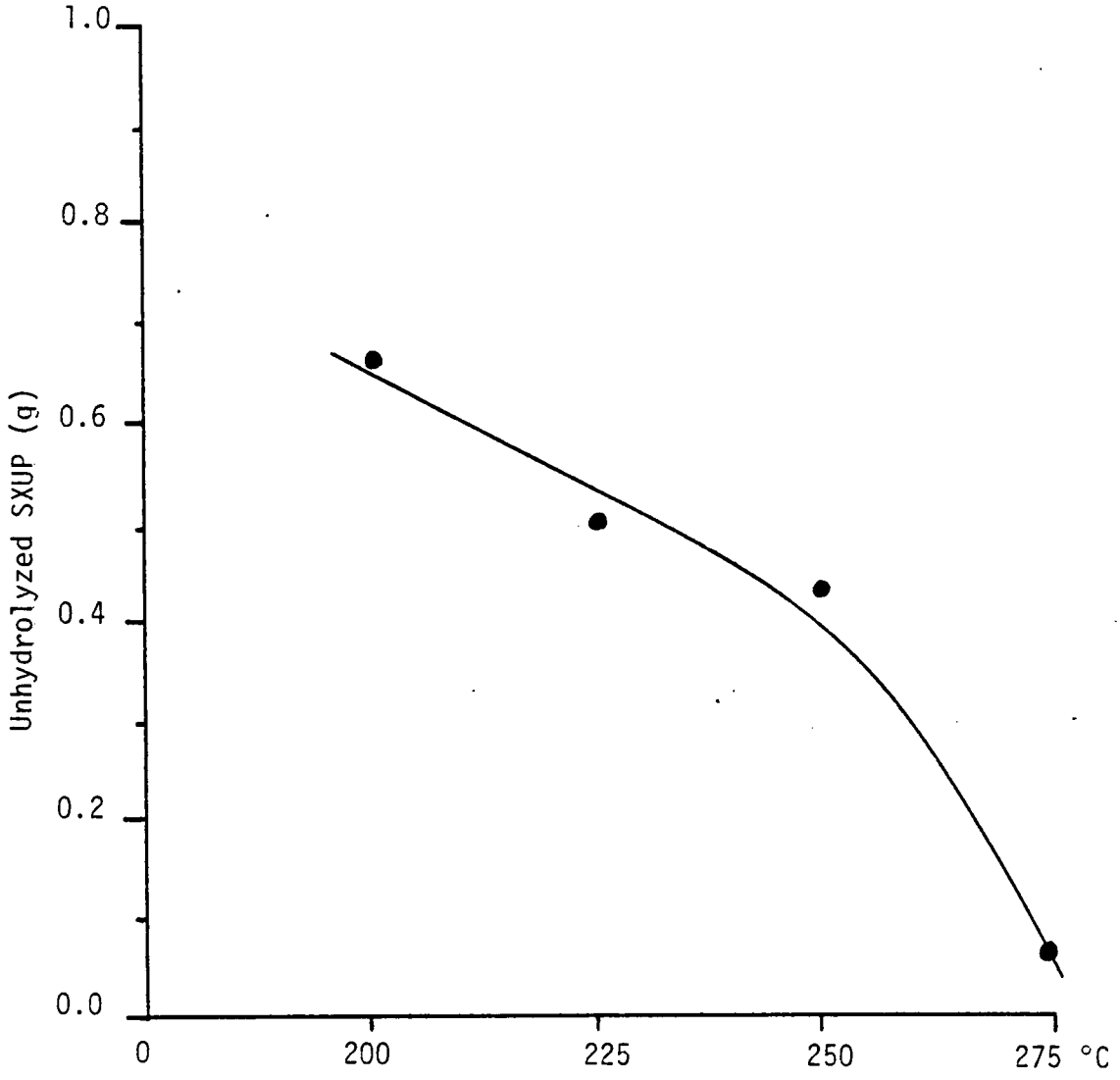


Figure 30. Weight of unhydrolyzed SXUP as a function of temperature. One g of SXUP was subjected to hydrolytic conditions for 6 hr.

appeared for PG. The aqueous layer was stored over phosphorus pentoxide until the volume was reduced to approximately 2 ml. The volume was measured and reanalyzed by gc.

The data for the analysis of PG from the hydrolysis of SXUP at 225°C are presented in Table IX. The volume percent of PG in the PG-water solution was obtained from the integration of each PG peak and the calibration curve (see Appendix). The percent yield was based on the theoretically available amount of PG (0.271 g) which could be produced from complete hydrolysis of 1.000 g of SXUP. Figure 31 shows the percent yield of PG as a function of time from the hydrolysis of SXUP at 225°C. There was a general increase in the percent yield of PG produced as a function of time at 225°C. However, there appeared to be little increase in the percent yield of PG as the time was increased past 8 hr. The maximum percent yield of PG was 40 at 10 hr.

The effect of increasing the temperature of hydrolysis produced the anomalous results shown in Table X and Figure 32. There was a general decrease in percent yield of PG as the temperature increased. There was no PG detected at 275°C. This can be explained by reaction of the PG to form by-products. This hypothesis was supported by the presence of an oil that appeared either as a separate layer or as a covering on the solid portion of the samples which were hydrolyzed at 250° and 275°C.

The oily layer was extracted from the ampoule with diethylether. An attempt was made to analyze this oil. In view of the small amount of the oil (ca. 5 µl) formed in the reaction tube, the principal intent of the analysis was to determine the functional groups present and

TABLE IX

PG FROM THE HYDROLYSIS OF SXUP AT 225°C WITH TIME VARIED

Time hr	Volume of PG-water solution, ml	PG in solution (volume %)	PG, g	% Yield
2	4.28	1.20	0.053	13
4	1.48	4.78	0.073	27
6	3.10	1.64	0.053	19
8	1.06	9.50	0.104	38
10	2.45	4.29	0.109	40
12	3.33	3.11	0.107	40

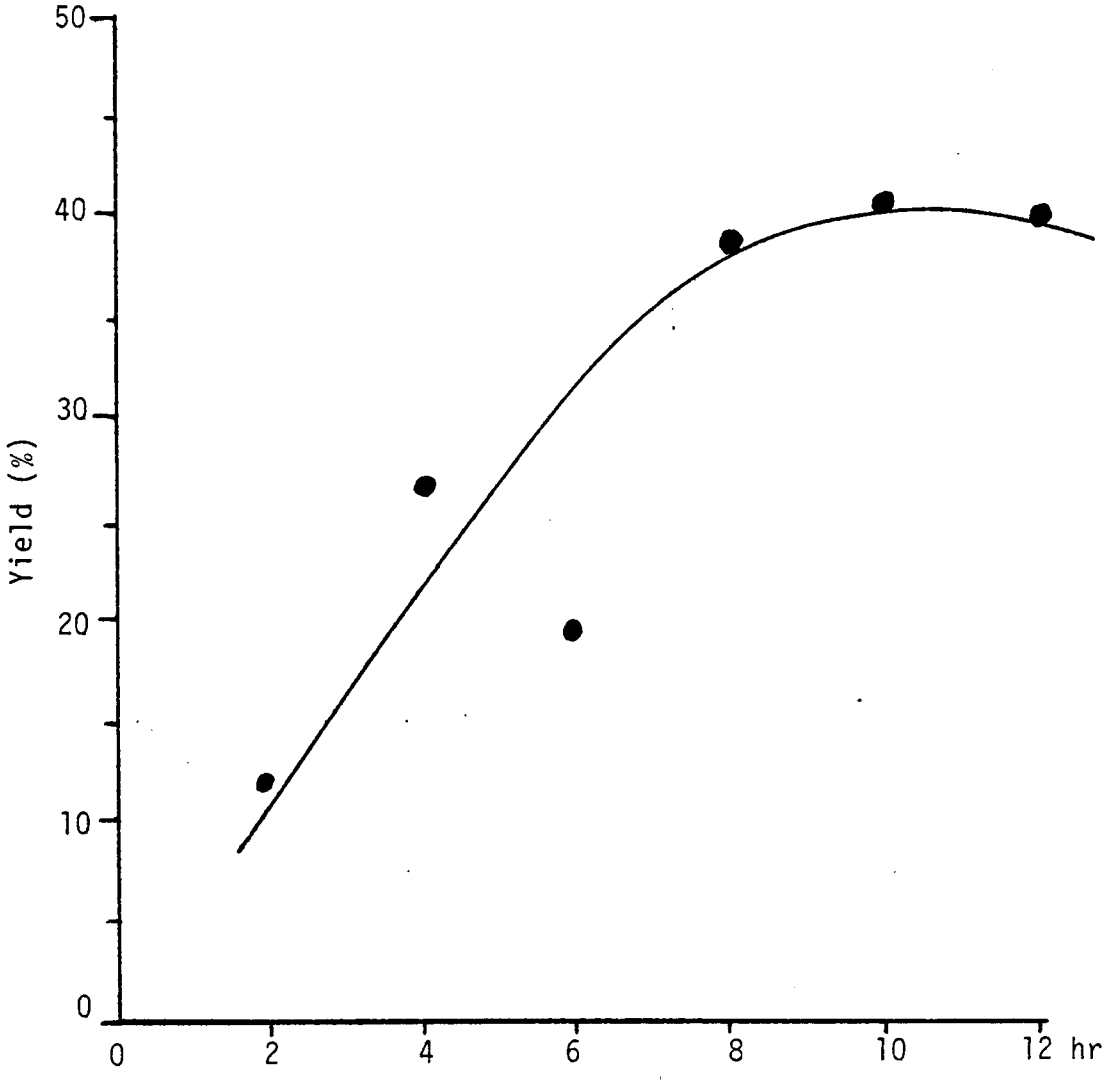


Figure 31. Yield of PG from the hydrolysis of SXUP at 225°C with time varied.

TABLE X

PG FROM THE HYDROLYSIS OF SXUP FOR 6 HR AT VARIOUS TEMPERATURES

Temperature °C	Volume of PG-water solution, ml	Pg in solution (volume %)	Pg, g	% Theoretical yield
200	1.15	4.74	0.056	20.8
225	3.10	1.64	0.053	19.4
250	3.21	0.53	0.019	6.5
275	1.12	--	--	--

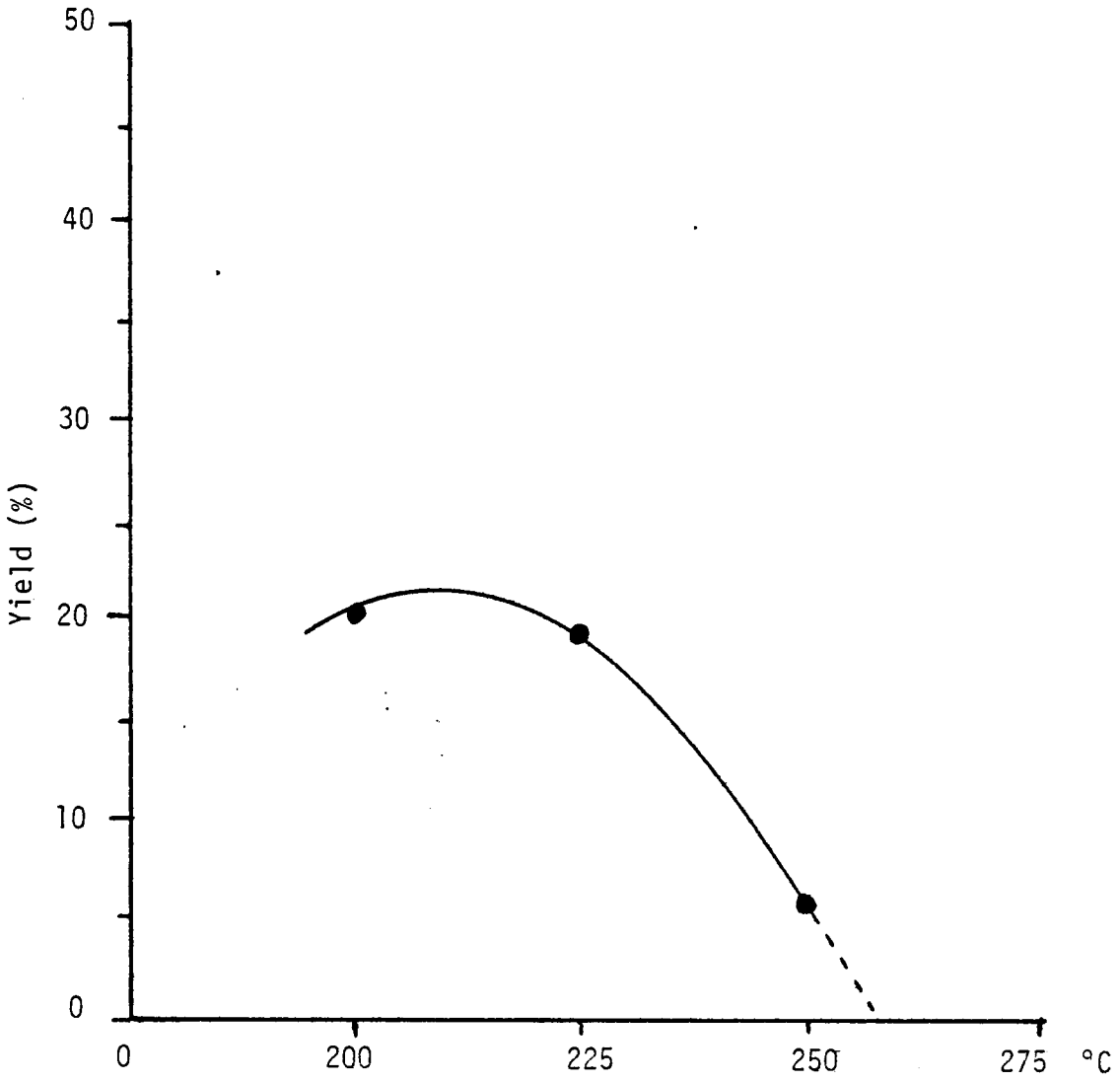


Figure 32. Percent yield of PG produced from the hydrolysis of SXUP for 6 hr as a function of temperature.

thereby the origin of the compounds. IR bands due to OH, C=O, and nonconjugated C=C were exhibited by the oil. Thus, the most likely source of the oil was PG and the products formed by further acid catalyzed reactions of PG.

The diethylether solution of the oil was subjected to gc analysis. The conditions used were described in Chapter II. The chromatogram contained about 20 peaks with intensities varying between full scale and less than 1% of full scale. The retention time of the peaks varied from 0.75 min to over 30 min. However, most of the peaks with retention times larger than 12 min were very small and not well resolved. All the large peaks occurred at low retention times. Attention was focused on the peaks with retention times of 0.75 min, 1.6 min, 4.2 min, 7.2 min, 8.4 min, 10.0 min, and 12.1 min.

The peak with a retention time of 0.75 min was assigned to water based on a match of retention time with distilled water. No further analysis was performed for this peak.

The compound giving the peak with retention time of 1.6 min was trapped from the gc in an evacuated flask and subjected to mass spectral analysis. There was good agreement between this mass spectrum and the mass spectrum of diethylether. The retention time of this peak was also equal to the retention time of diethylether. Thus, this peak was assigned to diethylether.

The compound giving a peak with retention time of 4.2 min was also trapped in an evacuated flask and subjected to mass spectral analysis. There was a good match between this mass spectrum and the mass spectrum of propanal, with two exceptions. First, there was a peak present at m/e = 40 in this mass spectrum which was not present in the reference

mass spectrum. Also, the peak at m/e = 44 was larger in this spectrum than in the reference spectrum. These may be due to a small amount of contamination from other compounds on the column. There was a match of retention time with that of distilled propanal. Thus, the peak with a retention time of 4.2 min was assigned to propanal.

The peak with a retention time of 7.2 min appeared to be a single peak under the conditions initially used. The intensity of this peak was very small. A mass spectrum was obtained. The major m/e values were 28, 29, 32, 40, 44. The highest m/e value was a small peak at 69. Although this gc peak at 7.2 min did appear to be a single peak under the conditions initially used, upon changing the flow rate the peak began to separate into 2 peaks. Due to the very low intensity of this peak and the presence of more than one compound with similar retention time, this peak was not assigned.

The remaining peaks were due to less volatile compounds and these compounds could be trapped in a cooled tube rather than in an evacuated flask. The peak with a retention time of 8.4 min was assigned to PG. This assignment was based on the retention time of pure PG, IR, and mass spectral analysis of the trapped sample. There was good agreement for the retention times and IR spectra of the pure PG and the trapped sample. Although the mass spectrum of this trapped sample contained all of the m/e values for pure PG, the mass spectrum also contained m/e values as high as 160.

The samples with retention times of 10.0 and 12.1 min were trapped and analyzed by mass spectroscopy. There was very little difference in the mass spectra of these two samples. Both mass spectra contained small

peaks with m/e values up to 160. Apparently the trapped samples were being contaminated from higher molecular weight material eluting slowly from the gc column.

The first samples (low retention time) which were trapped in the vapor state did not show this contamination. Since the first samples were transferred to the mass spectrometer in the vapor phase, any nonvolatile material apparently remained on the walls of the sample flask.

3. Acid Catalyzed Reactions of Propanal

The presence of propanal in the oily layer of the hydrolyzed SXUP indicated that some of the products resulted from the high temperature reaction of the PG. Several examples of the catalyzed reaction of PG to form propanal were found in the literature. Propanal was the major product when PG was catalyzed by H_3PO_4 on celite.[117,118] However, a catalyst such as Al_2O_3 produced acetone.[118] The catalytic transformation of PG on $Cu \cdot Al_2O_3 \cdot SiO_2$ at 250°C produced propanal, acetone, propylene oxide, methylglyoxal, 2,3-pentanedione, propionic acid, pyruvic acid, water, as well as unidentified residue and gas.[119] The amount of propanal decreased as the temperature increased. The amount of water and residue increased as the temperature increased.

The high temperature acidic conditions under which the propanal was formed are conducive to further reactions such as aldol condensation. Since the aldol condensation product of propanal is also an aldehyde, trimers and possibly tetramers of propanal may also be formed. A study was undertaken to determine the products from the high temperature acid catalyzed reaction of propanal.

HCl was used as the acid to eliminate any possible products due to the reaction of IPA. The temperature needed to obtain the oily layer was also reduced by using the stronger acid. (Distilled propanal, 5.0 ml, and 0.2 ml of concentrated HCl was placed in an ampoule, cooled, and sealed.) After heating for 4 hr at 110°C, the ampoule contained about 90% oily layer and about 10% aqueous layer. The oily organic layer was pipetted from the aqueous layer and subjected to gc. analysis. The gc conditions were described in Chapter II.

The gc contained peaks with retention times of 0.6 min, 1.5 min, 5.8 min, 11.7 min, 12.7 min, and 17.7 min in addition to several small peaks with retention times larger than 17 min. A gc trace is presented in Figure 33. The peaks with retention times of 0.6 and 1.5 min were assigned to water and propanal, respectively. The component with a retention time of 3.5 min was trapped and analyzed by mass spectroscopy, IR, and ^{1}H NMR. The peak was assigned to propionic acid. Retention time of pure propionic acid was also used in confirming this assignment. The propionic acid was produced from the oxidation of propanal. The oxygen was removed by bubbling nitrogen through the propanal and HCl before reacting in the remaining experiments. This process removed the gc peak at 3.5 min.

The component with a retention time of 5.8 min was trapped and analyzed. This peak was assigned to 2-methyl-2-pentenal (2M2P) by comparison of the mass, IR, and ^{1}H NMR spectra of the trapped sample with those of pure 2M2P. The gc retention time was also used in the assignment. The 2M2P was formed from the propanal by an aldol condensation-dehydration reaction. The following mechanism is proposed.

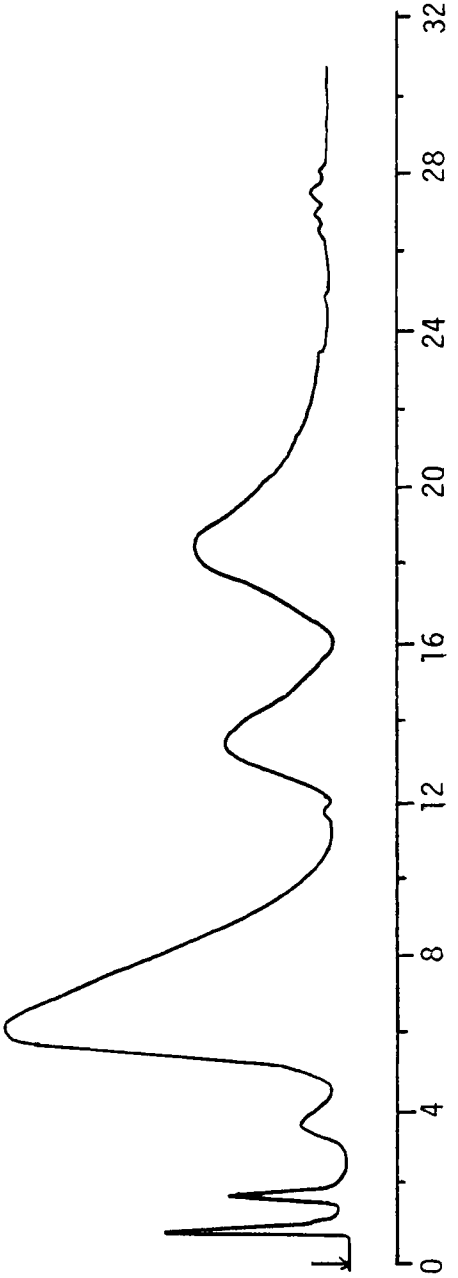
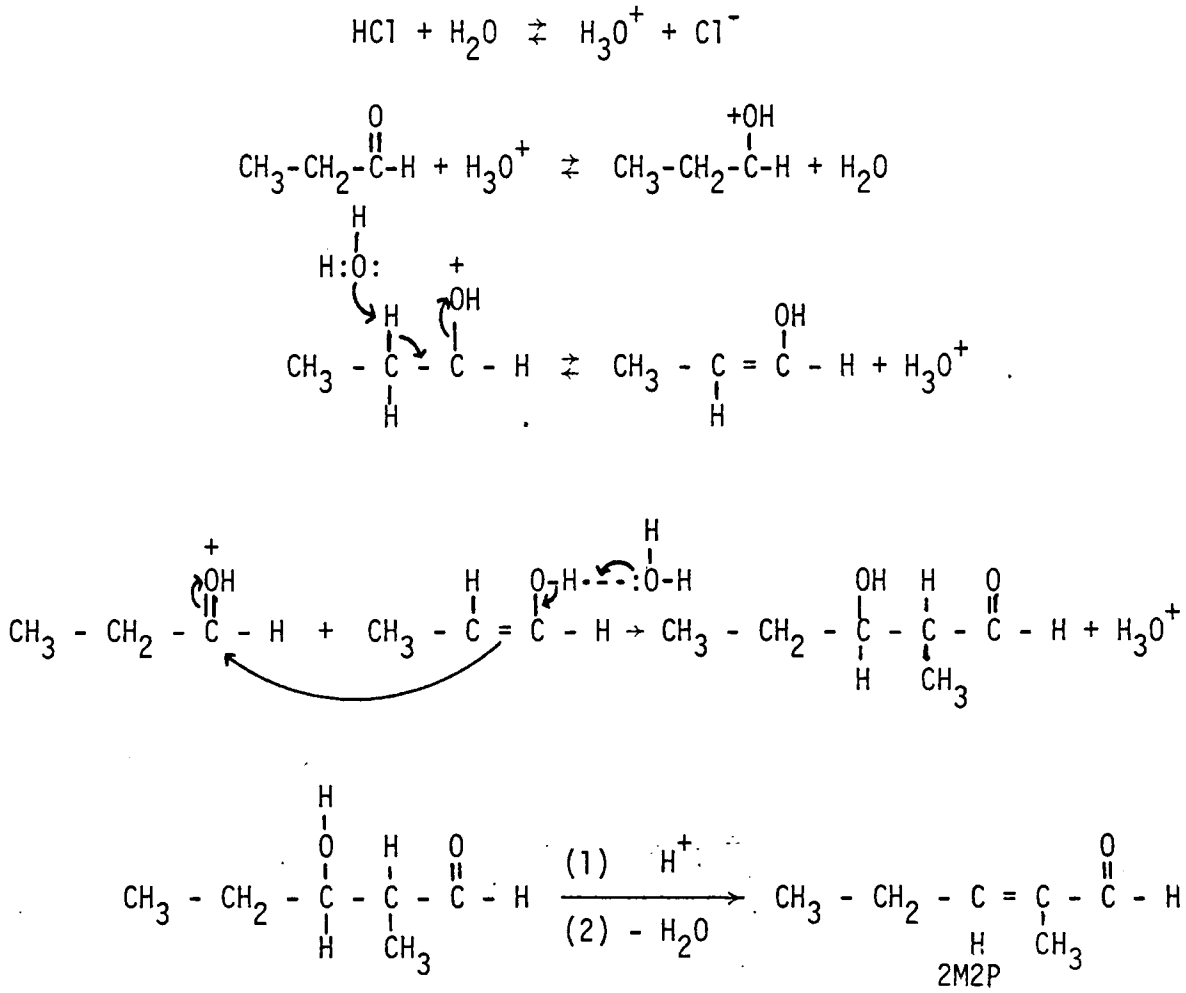
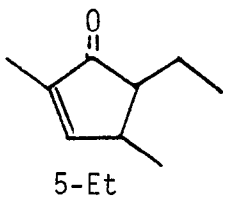


Figure 33. A gc trace of the reaction products of propanal and HCl.



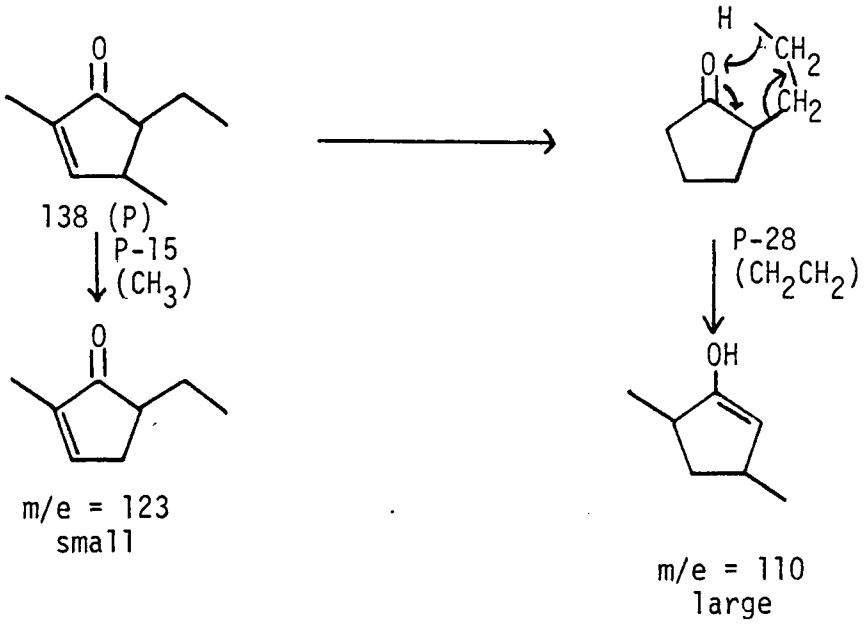
The peak with a retention time of 11.7 min was very small (less than 1% of full scale on the recorder). Analysis of this component was not undertaken due to its low concentration.

The peak with a retention time of 12.7 min was assigned to 2,4-dimethyl-5-ethyl-cyclopent-2-enone (5-Et). The structure of 5-Et is shown below. This assignment was based on several analyses. These include mass spectral, IR, ^{1}H NMR, ^{13}C NMR, ultraviolet spectroscopy (UV), and elemental analysis. The boiling point and refractive index were also measured.



5-Et

The data from the mass spectrum of 5-Et are presented below. The m/e value is followed by the relative peak height. Major peak 110 (100), parent peak 138 (50), 109 (12), 95 (12), 58 (12), 43 (12), 123 (11). The first portion of the fragmentation pattern is presented below. The proposed fragmentation pattern involves a McLafferty



rearrangement to produce a P-28 peak at 110 which was the major peak. The remaining m/e values may be explained by loss of common fragments (CH_3, C_2H_2, C_2H_3O, etc.).

The IR spectrum of 5-Et is shown in Figure 34. The spectrum contains absorption bands at the following μ values: 3.39 S, 3.50 M, 5.83 S, 6.10 M, 6.87 M, 7.25 M, 7.43 M, 7.58 M, 9.76 W, 9.62 W, 10.15 W, and 11.36 W. (S, M, and W designate strong, medium, and weak, respectively.) The band at 5.83 μ (1715 cm^{-1}) was assigned to the C=O stretching. This assignment is in good agreement with the assignment by Jones[120] for the C=O stretching of an α-β unsaturated 5-member cyclic

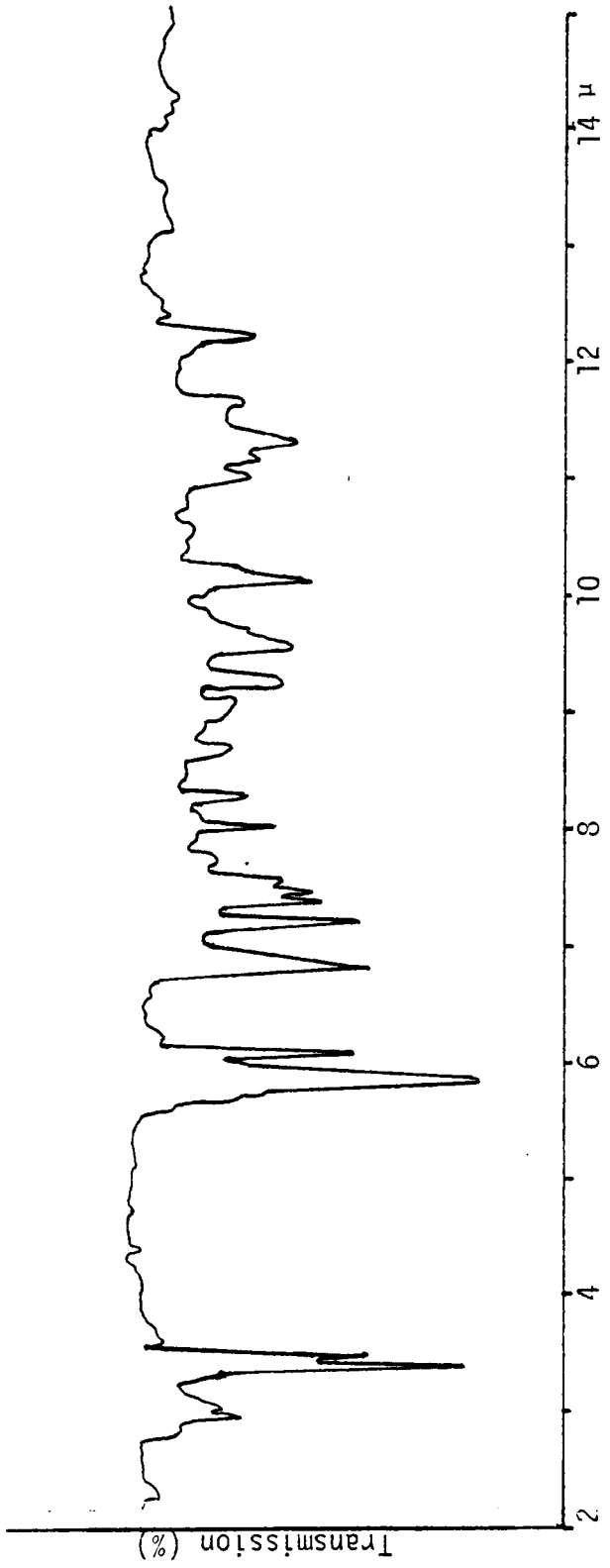
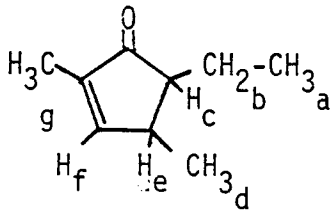


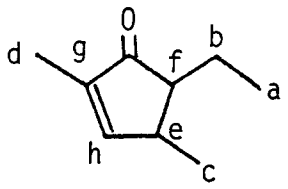
Figure 24. IR spectrum of 5-Et.

ketone. The band at 6.10 μ (1645 cm^{-1}) was assigned to C=C stretching. The remaining bands may be assigned to C-H stretching, C-H bending, C-C stretching, and C-H rocking.

The 100 MHz ^{1}H NMR spectrum of 5-Et is shown in Figure 35. The information obtained from this spectrum and peak assignments are presented in Table XI. The structure of 5-Et with the corresponding proton designation is shown below.



The ^{13}C NMR spectrum of 5-Et is shown in Figure 36. The assignments obtained from the ^{13}C NMR spectrum of 5-Et are presented in Table XII. The structure of 5-Et with the corresponding carbon atom designation is presented below.



The values for λ_{max} and molar absorptivity (ε) for the $\pi \rightarrow \pi^*$ transition and the $n \rightarrow \pi^*$ transition were obtained from the UV spectra of 5-Et. Ethanol (distilled-95%) was used as the solvent. The $\pi \rightarrow \pi^*$ was obtained from a 7.25×10^{-5} M solution. λ_{max} was 228 nm and ε was 1.21×10^{4}. The λ_{max} value for the $n \rightarrow \pi^*$ transition was determined

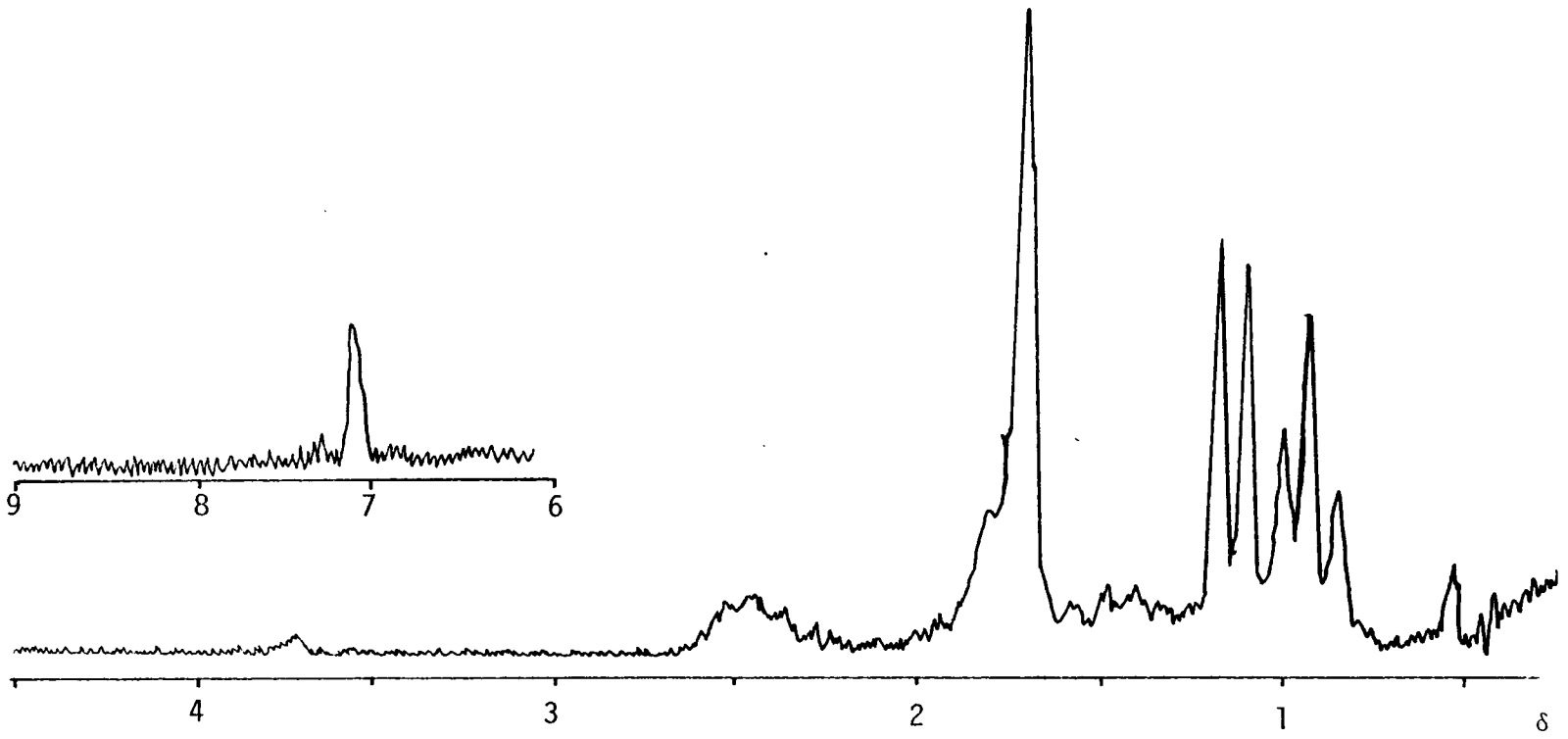


Figure 35. ^{1}H NMR (100 MHz) spectrum of 5-Et.

TABLE XI

PEAK ASSIGNMENTS FOR ^{1}H NMR SPECTRUM OF 5-Et

Peak Assignment	δ Value ppm	Number of Peaks	Integration Value	Number of Protons
a	0.93	3	23	3
c	2.45	6	9	1
d	1.15	2	20	3
f	7.08	2	7	1
*b, e, g	1.3 - 1.9	25 (Theoretical)		

*δ values and integration assignments not possible in the area between 1.3-1.9 due to the large number of peaks in this region.

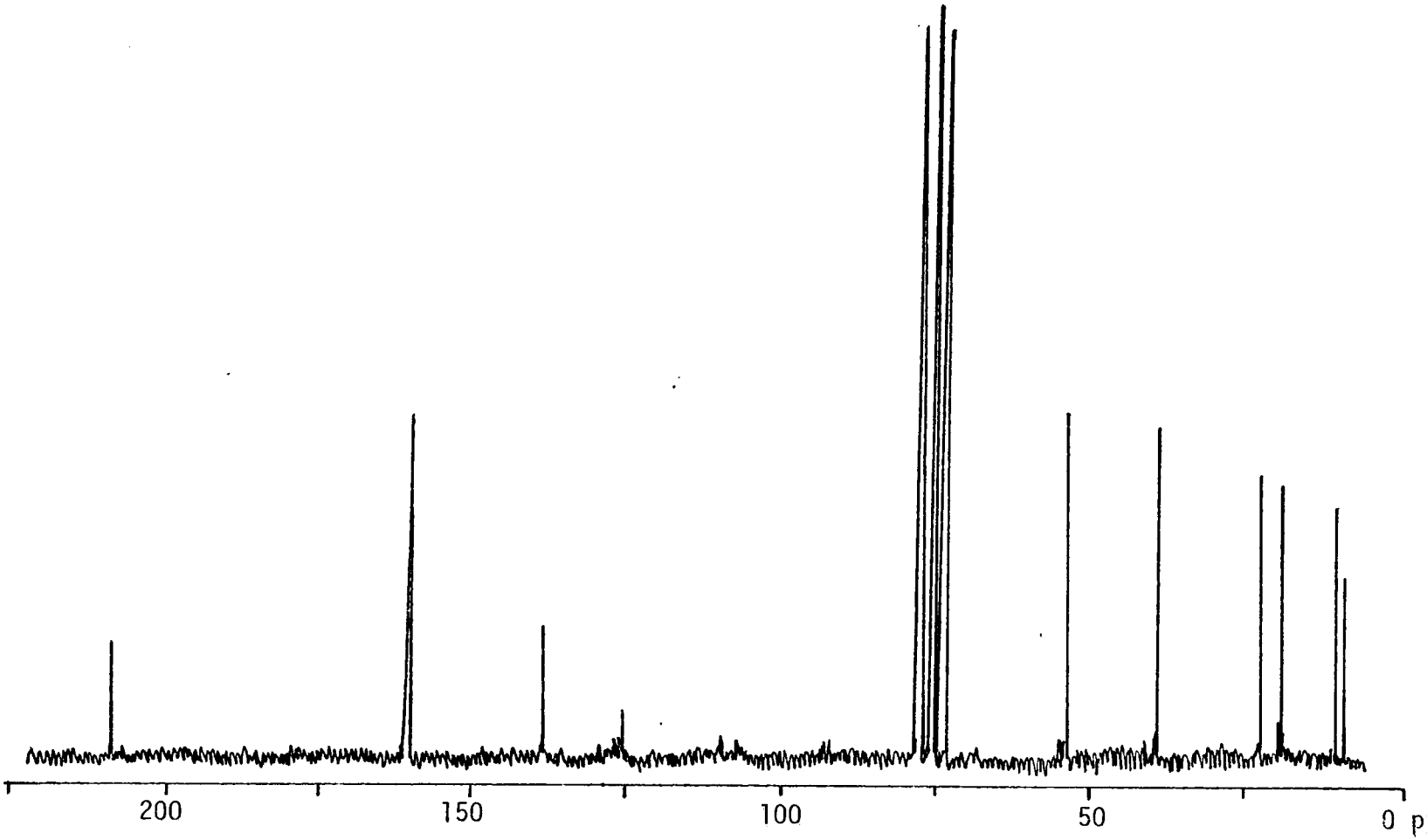


Figure 36. ^{13}C NMR spectrum of 5-Et.

TABLE XII

PEAK ASSIGNMENTS FOR ^{13}C NMR SPECTRUM OF 5-Et

Peak Assignment	ppm*
a	9.8
b	11.5
c	19.9
d	23.5
e	39.8
f	55.1
g	140.0
h	161.8
i	211.6

*ppm using CCl_3D as an internal standard. The center peak of CCl_3D has a value of 76.90 ppm.

from a 7.25 x 10^{-3} M solution. The λ_{max} value was 312 nm and ε was 45.5. The UV spectrum of 5-Et showing the λ_{max} values for the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ is presented in Figure 37.

The Woodward rules were used to calculate a λ_{max} for the $\pi \rightarrow \pi^*$ transition.[121] The experimental value of 228 nm for λ_{max} for the

202 nm for base value for 5-member cyclic α,β unsaturated ketone
+12 nm for β substituent to form ring
+10 nm for α substituent (methyl group)
224 nm

$\pi \rightarrow \pi^*$ is in reasonable agreement with the calculated value of 224 nm.

The percentage carbon and hydrogen in 5-Et was determined by elemental analysis. The percentage oxygen was determined by the difference between unity and the total of carbon and hydrogen. The theoretical and experimental percentages of carbon, hydrogen, and oxygen are shown below. Also, the percent error is reported for each element.

	carbon	hydrogen	oxygen
Theoretical	78.20	10.23	11.57
Experimental	78.28	10.25	11.47
Percent error	0.1	0.20	0.86

Additional data obtained for 5-Et were the boiling point (193 $\pm$ 1°C for three determinations by the microboiling point technique) and the refractive index (n_d^{20} = 1.4622 $\pm$ 0.0001 for three determinations).

The gc peak with a retention time of 17.7 min was assigned to 3,5-dimethyl-2-ethylcyclopent-2-enone (2-Et). The structure for 2-Et is shown below. The assignment was based on the following analyses: mass spectral, IR, ^{1}H NMR, ^{13}C NMR, UV, and elemental analysis. The boiling point and refractive index were also measured.

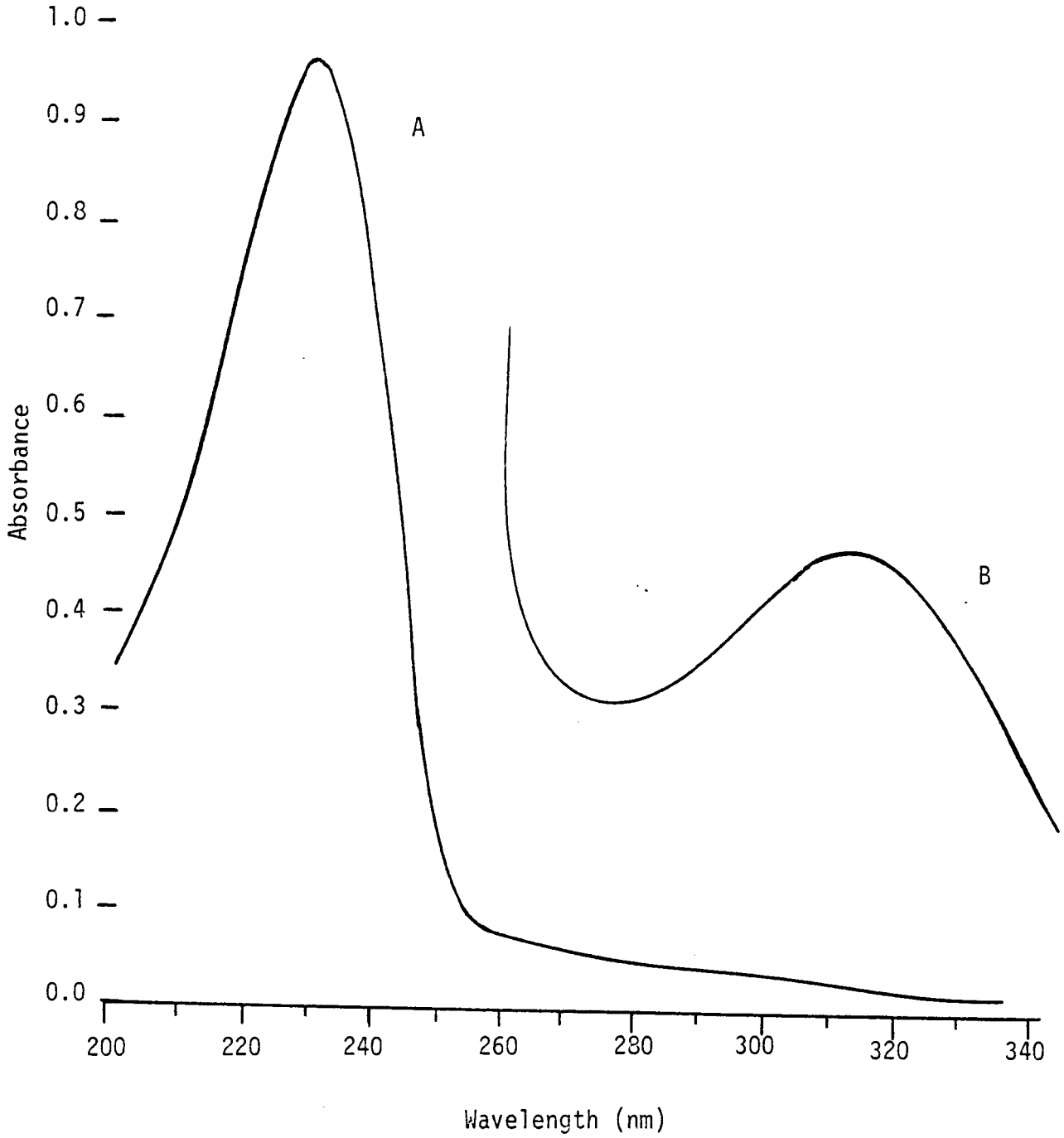
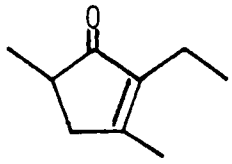
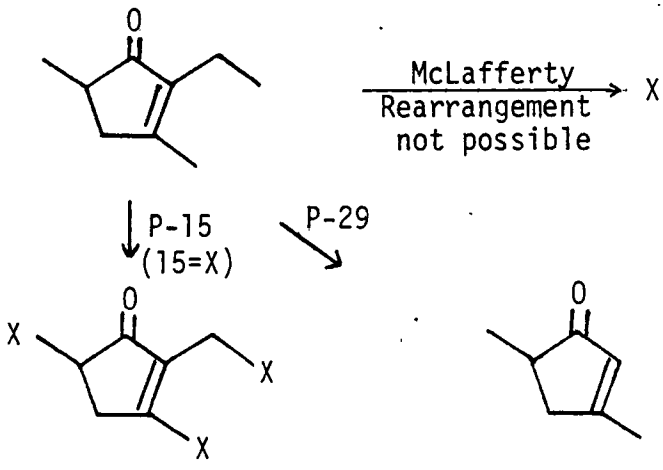


Figure 37. UV spectra of 5-Et. Spectrum A is $\pi \rightarrow \pi^*$ transition, conc. = 7.25×10^{-5} M. Spectrum B is $n \rightarrow \pi^*$ transition, conc. = 7.25×10^{-3} M.



2-Et

The data from the mass spectrum of 2-Et are presented below. The m/e value is followed by the relative peak height. Major peak 123 (100), parent peak 138 (76), 95 (60), 109 (32), 110 (24), 67 (24), 82 (18). This fragmentation pattern shows the major peak at a m/e value of P-15. This compound cannot undergo a McLafferty rearrangement which would explain the difference in the initial portion of the fragmentation patterns of 2-Et and 5-Et. The initial portion of the fragmentation pattern is shown below.



The IR spectrum of 2-Et is shown in Figure 38. The spectrum contains absorption bands at the following μ values: 3.39 S, 3.45 M, 5.84 S, 6.06 M, 6.90 M, 6.94 M, 7.19 M, 7.41 M, 7.61 W, and 7.91 W. The important absorption bands in this spectrum are the 5.84 μ (1712 cm^{-1}) band assigned to the O=O group and the 6.06 μ (1650 cm^{-1})

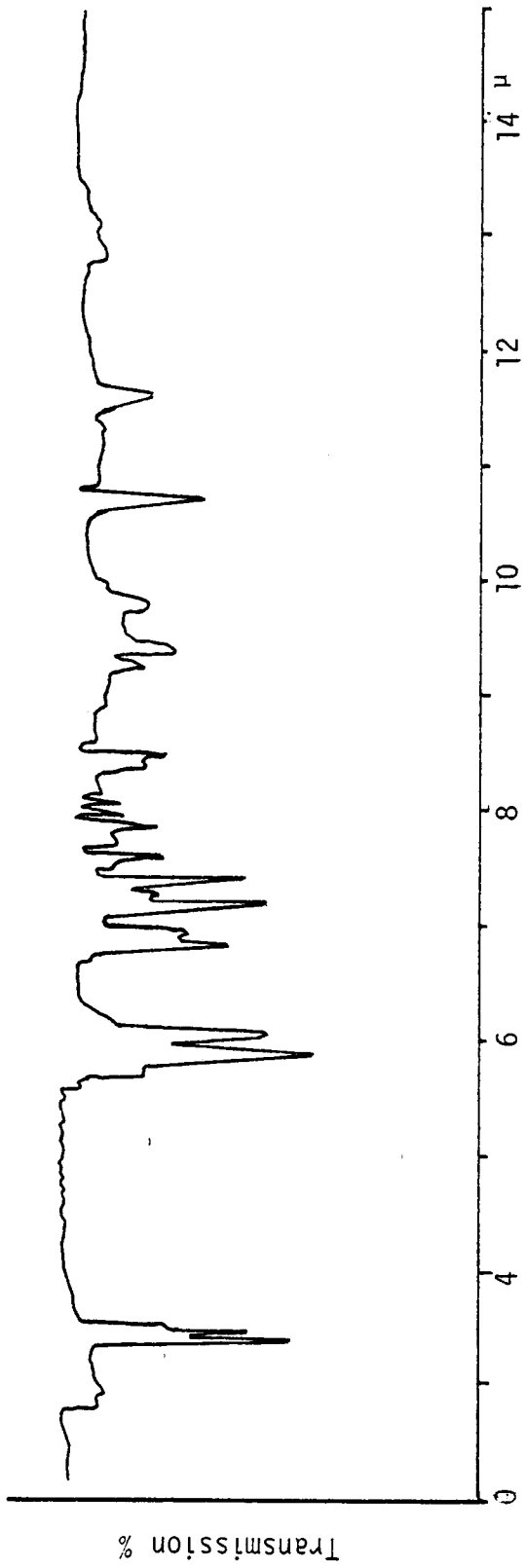
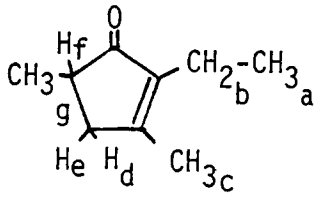


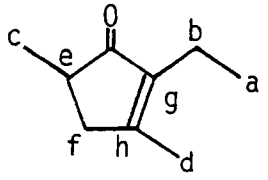
Figure 38. IR spectrum of 2-Et.

band assigned to the C=C group. These bands are very close to the absorption bands for these groups found in the IR spectrum of 5-Et. The remaining bands may be assigned to C-H stretching, C-H bending, C-C stretching, and C-H rocking.

The 100 MHz ^{1}H NMR spectrum of 2-Et is shown in Figure 39. The information obtained from this spectrum and the peak assignments are presented in Table XIII. The structure of 2-Et with the corresponding proton designation is shown below.



The ^{13}C NMR spectrum for 2-Et is shown in Figure 40. The assignments obtained from the ^{13}C NMR spectrum of 2-Et are presented in Table XIV. The structure of 2-Et with the corresponding carbon atom designation is presented below.



The values for λ_{max} and ε for the $\pi \rightarrow \pi^*$ transition and the $n \rightarrow \pi^*$ transition were obtained from the UV spectra of 2-Et. Ethanol (distilled-95%) was used as the solvent. The λ_{max} and ε values for the $\pi \rightarrow \pi^*$ transition were obtained from a 7.25×10^{-5} M solution. λ_{max} was 235 nm and ε was 1.79×10^{4}. The λ_{max} and ε values for the

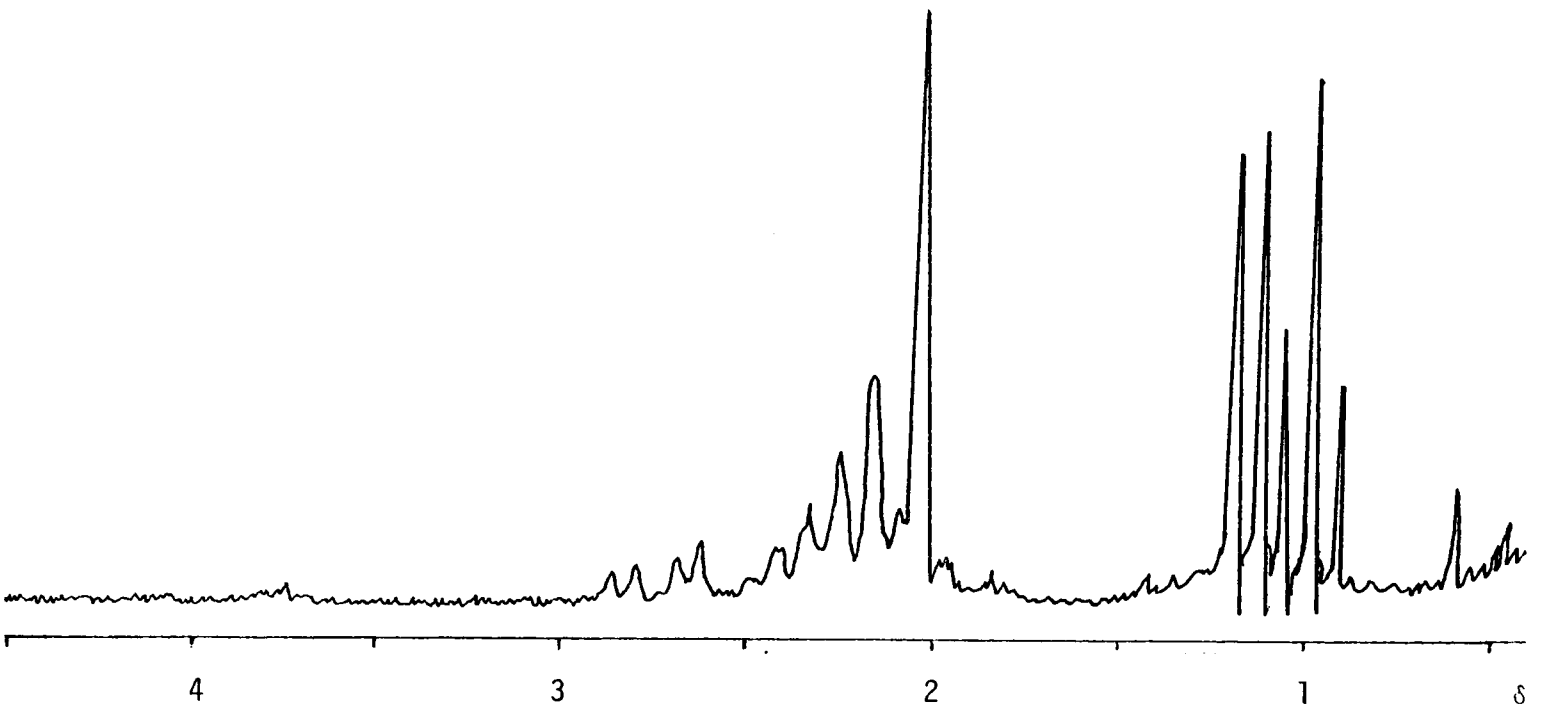


Figure 39. ^{1}H NMR (100 MHz) spectrum of 2-Et.

TABLE XIII

PEAK ASSIGNMENTS OF ^{1}H NMR SPECTRUM OF 2-Et

Peak Assignment	Value	Number of Peaks	Integration Value	Number of Protons
a	0.97	3	30	3
c	2.03	1	29	3
g	1.16	2	30	3
*b, d, e, and f	2.05-2.90	10	53	5

*δ values and integration assignments are not possible in the area between 1.3-1.9 due to the large number of peaks in this region.

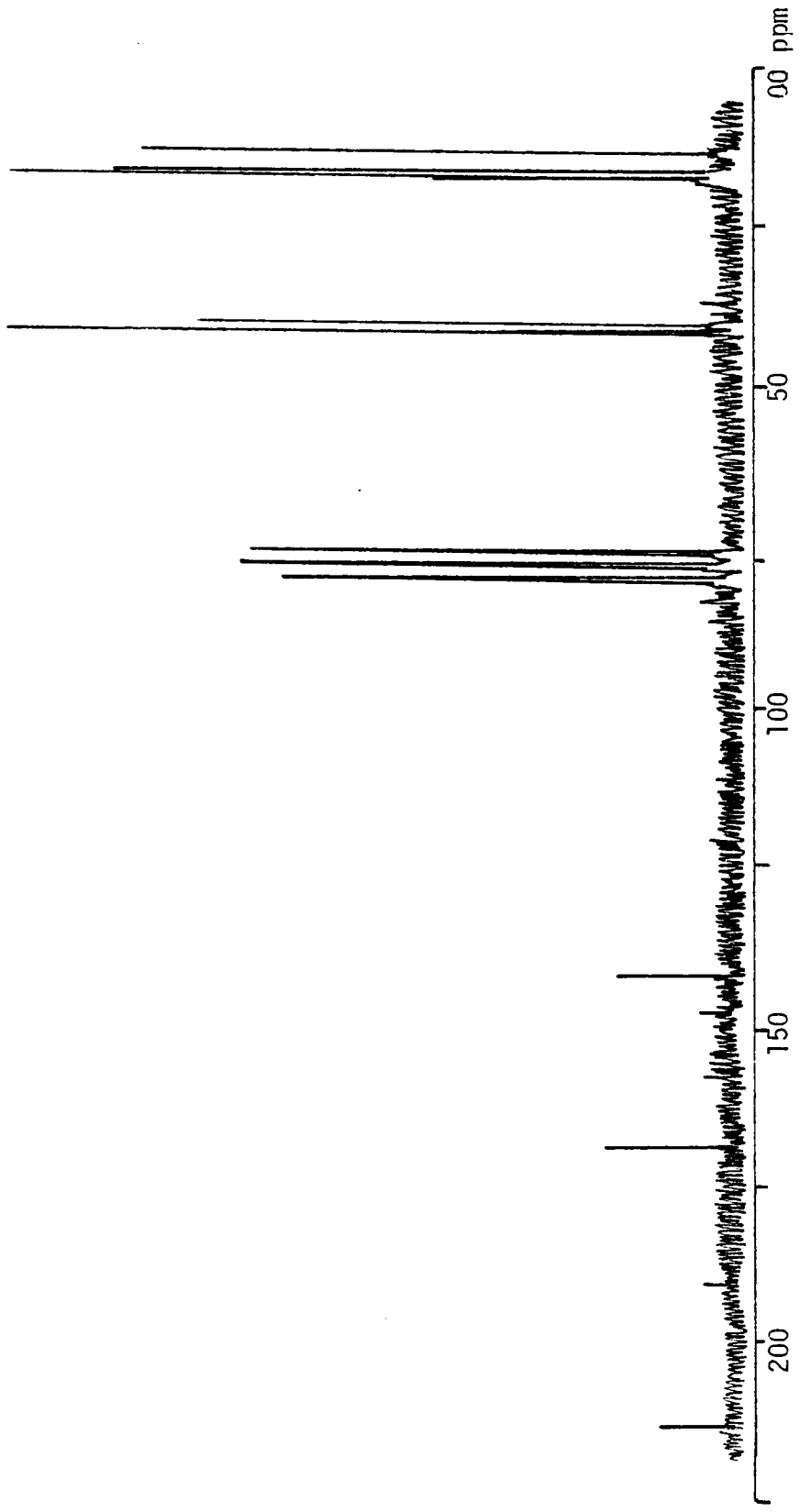


Figure 40. ^{13}C NMR spectrum of 2-Et.

TABLE XIV

PEAK ASSIGNMENTS FOR THE ^{13}C NMR SPECTRUM OF 2-Et

Peak Assignment	ppm*
a	12.8
b	16.1
c	16.4
d	16.7
e	39.4
f	40.5
g	140.6
h	167.4
i	211.7

*ppm using CCl_3D as an internal standard. The center peak of CCl_3D has a value of 76.90 ppm.

$n \rightarrow \pi^*$ transition was obtained from a 7.25×10^{-3} M solution. λ_{max} was 305 nm and ε was 70. The UV spectrum of 2-Et showing the λ_{max} values for the $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ transition for 2-Et is shown in Figure 41.

The experimental value of 235 nm for λ_{max} for the $\pi \rightarrow \pi^*$ transition agrees well with the calculated value of 236 nm using the Woodward rules.[121]

202 nm for 5-membered cyclic α,β unsaturated ketone

+12 nm for β substitutuent to form ring

+10 nm for ethyl group on α position

+12 nm for methyl group on β position

236 nm (calculated λ_{max} for $\pi \rightarrow \pi^*$ transition)

The percentage of carbon and hydrogen in 2-Et was determined by elemental analysis. The percentage oxygen was determined as the difference between unity and the total of carbon and hydrogen. The theoretical and experimental percentages of carbon, hydrogen, and oxygen are shown below. Also, the percentage error is reported for each element. Additional data obtained for 2-Et were the boiling point

	carbon	hydrogen	oxygen
Theoretical	78.20	10.23	11.57
Experimental	78.33	10.16	11.51
Percent error	0.17	0.68	0.52

(202 $\pm$ 1°C) for three determinations using the microboiling point technique) and the refractive index (n_D^{20} = 1.4740 $\pm$ 0.0001 for three determinations).

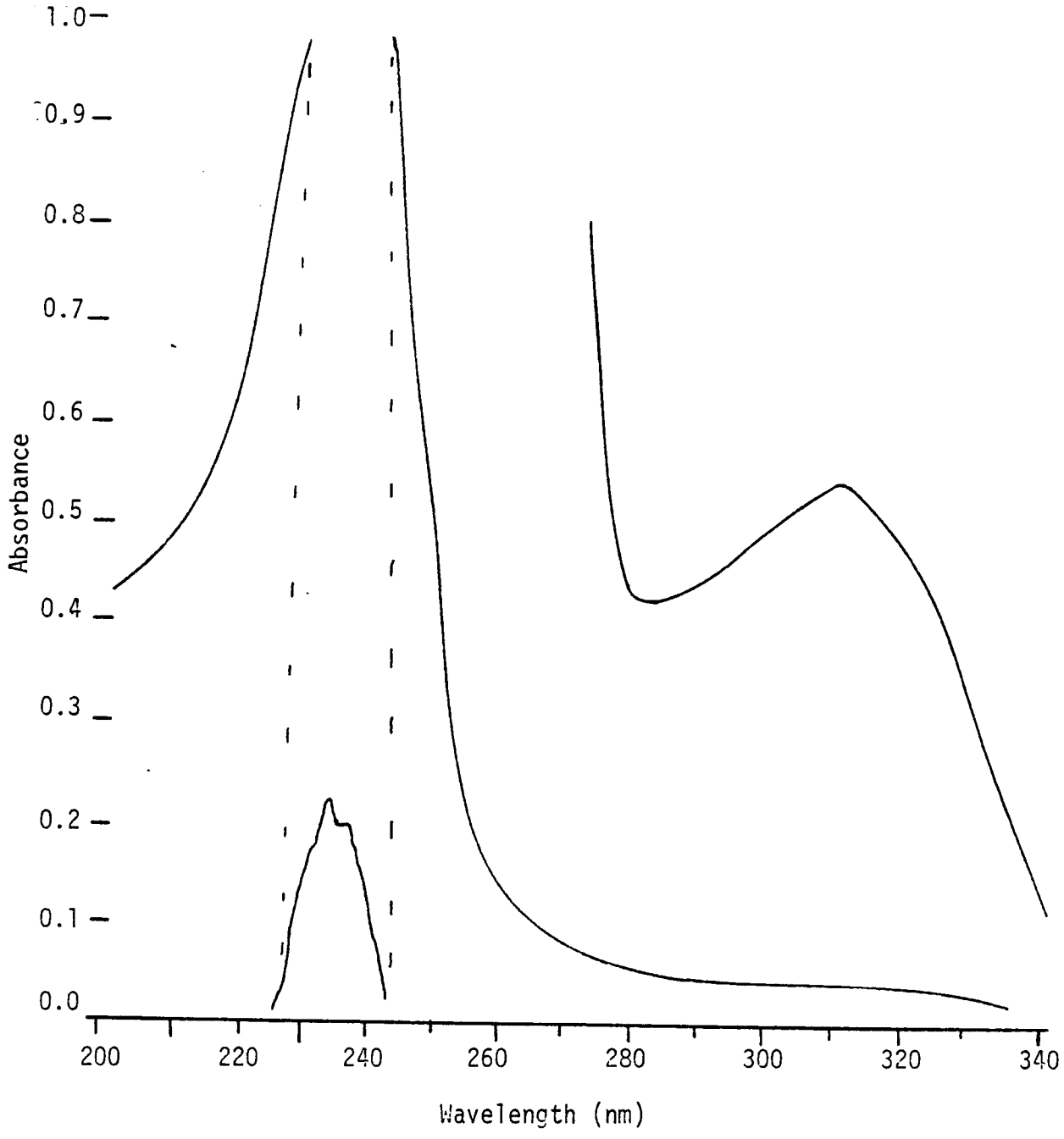


Figure 41. UV spectra of 2-Et. Spectrum A is $\pi \rightarrow \pi^*$ transition, conc. = 7.25×10^{-5} M. Spectrum B is $n \rightarrow \pi^*$, conc. = 7.35×10^{-3} M.

After the elucidation of the structures of the two compounds was completed, a literature search was undertaken to find reference to these compounds. This search found several substituted cyclopentenones; however, reference to the cyclopentenones analyzed in this study was not found. A brief discussion will be presented here for the background related to the formation of 5-Et and 2-Et.

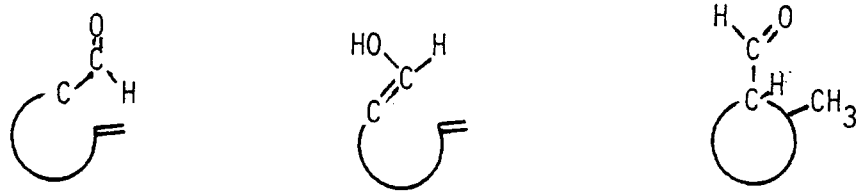
The molecular formulae of 5-Et and 2-Et ($C_9H_{14}O$) indicate that the compounds were probably formed from trimers of propanal. The trimeric form of propanal produced by aldol condensation and dehydration of 2M2P and propanal is shown below.

$$CH_3 - CH_2 - CH = \overset{\overset{CH_3}{|}}{C} - CH = \overset{\overset{CH_3}{|}}{C} - \overset{\overset{O}{\|}}{C} - H$$

The acid catalyzed aldol reaction is well known. The fate of a dehydrated trimeric aldol product depends, of course, on the relative reactivity of the molecule and on the relative stabilities of the products that might be formed from it. For example, the acid catalyzed reaction of the dehydro aldol trimer of acetone leads to mesitylene.[122] The compounds of interest here, specifically the dehydro aldol derivative of propanal and the cyclic compounds presumably derived from it, have apparently not been studied. The possibilities of, and references to, acid catalyzed cyclization of unsaturated aldehydes were of primary interest.

The cyclization of unsaturated aldehydes using heat and/or an acid catalyst has recently been reviewed by Conia and LePerchec.[123] Unsaturated aldehydes and ketones were reported to undergo a cyclization reaction when heated to high temperatures (ca. 300°C). The cyclization reaction involved the interaction of an enol intermediate

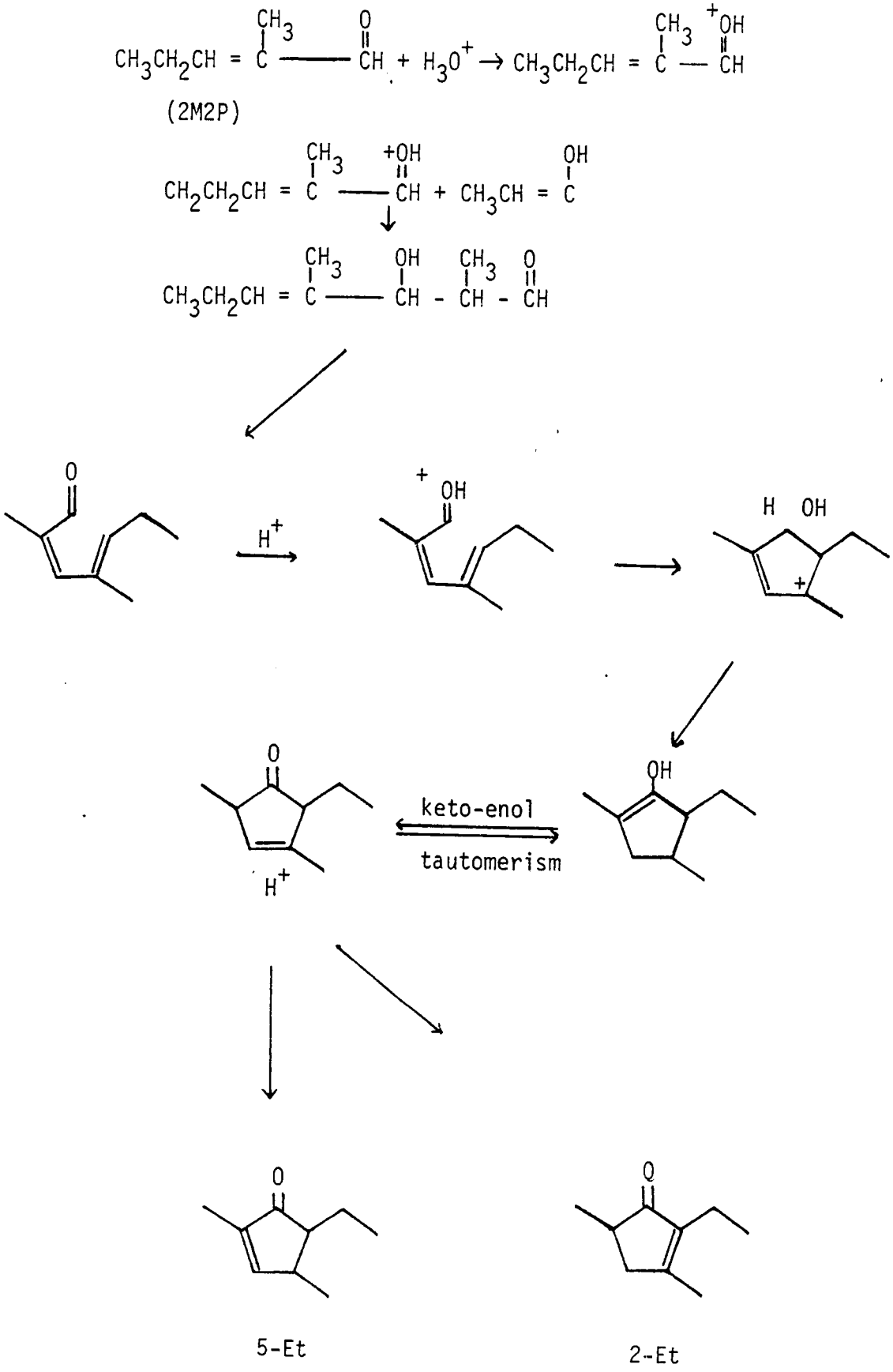
with a C = C group. This reaction produces cyclic compounds with retention of the aldehyde group.



In 1969 Saikachi and Ogawa reported the first acid catalyzed formation of a substituted cyclopent-2-enone from a substituted pentadienal.[123] In a following publication, a mechanism for the cyclization was proposed.[124] Curiously, the proposed mechanism involved the initial formation of an acylium ion by loss of hydride from the aldehyde group in their acidic medium. The next step was the rearrangement of the acylium medium. The next step was the rearrangement of the acylium ion to a ketene intermediate which formed a bicyclo[2.1.0] pentanone derivative. Acid cleavage of the cyclopropane ring then converted the bicyclo[2.1.0]-pentanone derivative into the cyclopent-2-enone derivative. The above mechanism was reported to occur when a substituted pentadienal was heated for 2 hr at 100°C in dilute hydrochloric acid.

The mechanism proposed in this study for the formation of 5-Et and 2-Et involved a substituted dienal cyclizing to form a substituted cyclopentenone similar to that reported by Saikachi and Ogawa.[124] The proposed mechanism in the current study does not involve the loss of hydride from the aldehyde group in an acid medium, a ketene intermediate, or a bicyclo derivative.

The proposed mechanism for the formation of 5-Et and 2-Et from propanal is shown below. The formation of 2M2P was shown on page 116 and will not be duplicated.


(2M2P)
keto-enol
tautomerism
5-Et
2-Et

The relative amounts of 5-Et and 2-Et should be determined by their relative thermodynamic stability. The quantitative determination of 5-Et and 2-Et produced from the HCl catalyzed reaction of propanal was performed by use of gc. Samples containing 2 ml of propanal, which had been deoxygenated by nitrogen bubbling, was reacted with 0.10 ml of concentrated HCl. The reaction was conducted at various temperatures in the 75° to 175°C range, and the time of reaction was varied from 2 to 10 hr. The amount of propanal, 2M2P, 5-Et, and 2-Et after 6 hr reaction of propanal and HCl (temperature varied) as determined by gc using mesitylene as the internal standard is reported in Table XV.

The percent yield of 5-Et and 2-Et are plotted as a function of temperature in Figure 42. The percent yield of 5-Et was greater than the percent yield of 2-Et at low temperatures. An increase in temperature produced more of the thermodynamically favored product, 2-Et, with a concurrent decrease in the amount of 5-Et. There was very little 5-Et detected above 150°C. The maximum yield of 5-Et (10.8 percent) was obtained at 100°C. The maximum yield of 2-Et (21.7 percent) was obtained at 150°C.

The mechanism as proposed on page 137 for the formation of 5-Et and 2-Et could not be used to explain a higher yield of 5-Et at lower temperatures. The effect of time and acid concentration on the relative amounts of 5-Et and 2-Et will be discussed before refinements to the mechanism presented.

The amount of propanal, 2M2P, 5-Et and 2-Et as determined by gc using mesitylene as the internal standard is reported in Table XVI

TABLE XV

REACTION PRODUCTS FROM HEATING PROPANAL AND HCl FOR 6 HR AT VARIOUS TEMPERATURES

Temperature, °C	Water, g	Organic, g	Propanal		2M2P		5-Et		2-Et	
			g	%	g	%	g	%	g	%
75	0.207	1.25	0.167	10.4	0.973	71.6	0.060	4.7	0.023	1.7
100	0.230	1.28	0.068	4.2	0.938	69.0	0.139	10.8	0.063	4.9
125	0.321	1.27	0.016	1.0	0.768	56.5	0.110	8.6	0.226	17.6
150	0.370	1.18	0.010	0.5	0.324	23.9	0.004	0.4	0.278	21.7
175	0.430	1.11	0.010	0.5	0.027	2.0	0.000	0.0	0.237	18.5

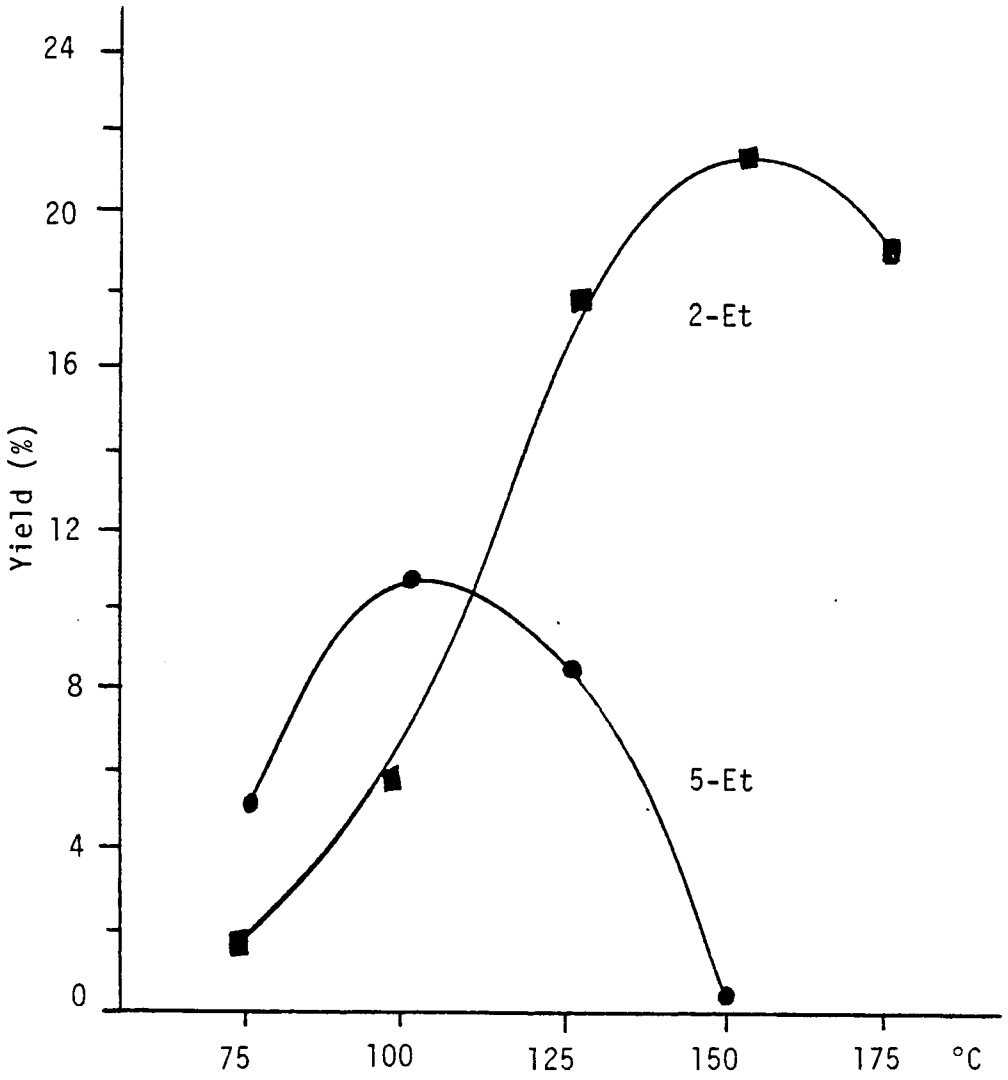


Figure 42. Yield of trisubstituted cyclopentenones from propanal reacted for 6 hr as a function of temperature. HCl concentration = 5.0% by volume.

TABLE XVI

REACTION PRODUCTS FROM HEATING OF PROPANAL AND HCl AT 100°C FOR VARIOUS TIMES

Reaction time, hr	Water, g	Organic, g	Propanal		2M2P		5-Et		2-Et	
			g	%	g	%	g	%	g	%
2	0.260	1.197	0.155	9.6	0.875	64.3	0.115	8.9	0.036	2.5
4	0.269	1.273	0.081	5.0	0.867	64.0	0.126	9.8	0.044	3.4
6	0.289	1.272	0.058	3.6	0.997	73.4	0.155	12.1	0.069	5.4
8	0.289	1.268	0.038	2.4	0.868	62.9	0.161	12.6	0.081	6.3
10	0.292	1.253	0.029	1.8	0.696	51.2	0.147	11.5	0.077	6.0

for the reaction at 100°C with the time varied. The percent yields of 5-Et and 2-Et are shown as a function of time in Figure 43. At 100°C the amount of 5-Et was consistently greater than the amount of 2-Et. The percent yield of 5-Et and 2-Et reached a maximum at 8 hr and began to decline slightly.

Table XVII shows the yields of cyclopentenones produced from propanal at 125°C as a function of acid concentration.

Figure 44 shows a series of plots of the percent yields of 5-Et and 2-Et as a function of acid concentration. The percent concentrated HCl was varied from 1.0 to 10.0 percent by volume and the time was varied from 2 to 10 hr. At low acid concentration (1.0% HCl) the formation of 5-Et was favored. There was near equimolar amounts of 5-Et and 2-Et produced at 5.0% HCl. However, the formation of 2-Et appears to be much more favored at 10.0% HCl. The runs at 10.0% HCl produced 2-Et with the near exclusion of 5-Et.

The above information indicates that the formation of 5-Et is favored over the formation of 2-Et using either a low reaction temperature (below about 110°C) or low concentration of HCl (below 5.0% by volume). This could not be explained using the mechanism proposed on page137 and the associated thermodynamic arguments. If all of 5-Et and 2-Et was produced from the keto-enol tautomerization as indicated by the reaction proposed on page 137, then the formation of 2-Et would be favored at any temperature or acid concentration. Steric factors and the stability of the carbonium ion both favor the formation of 2-Et over 5-Et using the mechanism proposed on page 137 and given again in more detail below.

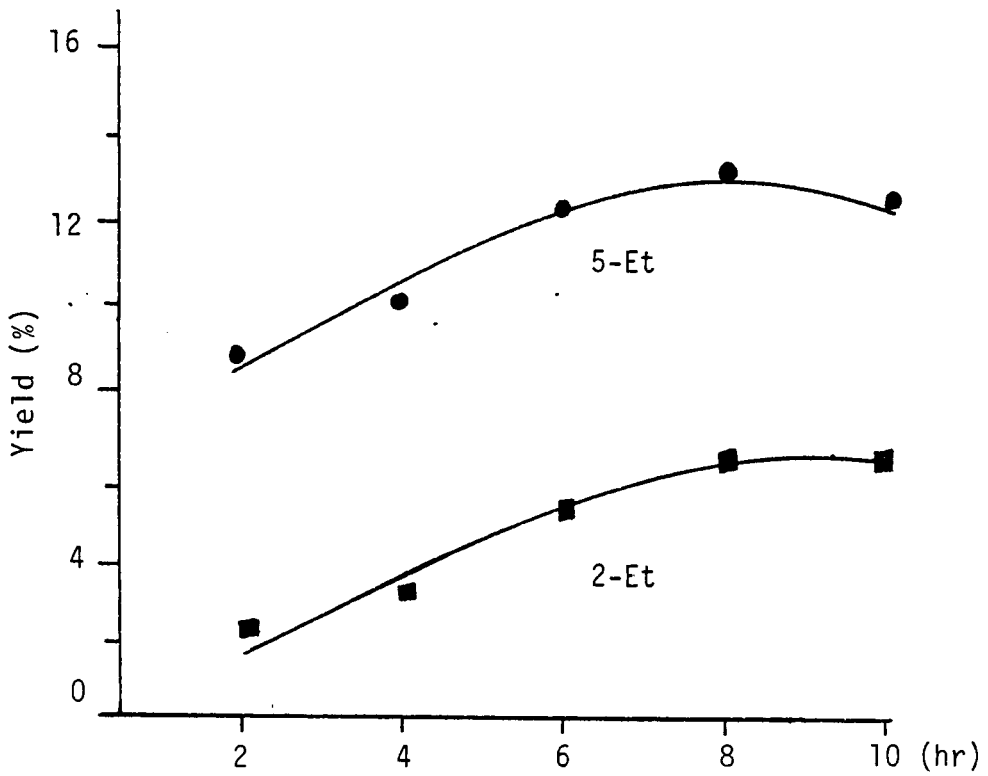


Figure 43. Yield of trisubstituted cyclopentenones from propanal at 100°C as a function of time. HCl concentration = 5.0% by volume.

TABLE XVII

YIELD OF CYCLOPENTENONES FROM PROPANAL AT 125°C
AS A FUNCTION OF ACID CONCENTRATION

Reaction time, hr	1.0% HCl % yield		5.0% HCl % yield		10.0% HCl % yield	
	5-Et	2-Et	5-Et	2-Et	5-Et	2-Et
2	4.4	1.3	9.3	6.3	0.5	17.4
4	8.8	3.8	9.6	8.9	0.1	18.1
6	11.3	4.9	8.4	6.7	0.2	22.2
8	8.9	6.7	12.7	15.2	0.1	18.9
10	9.6	5.9	7.8	8.6	0.1	17.3

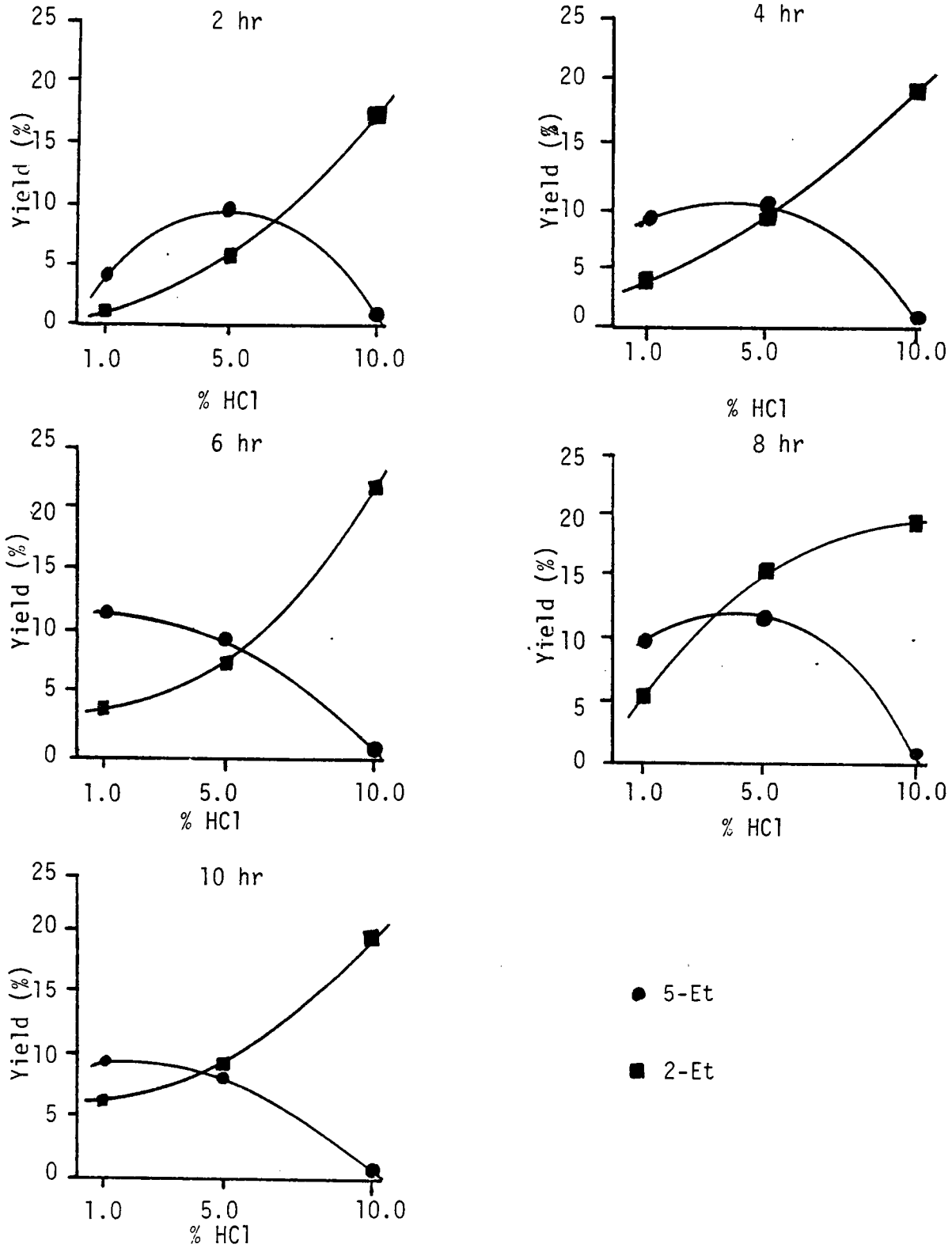
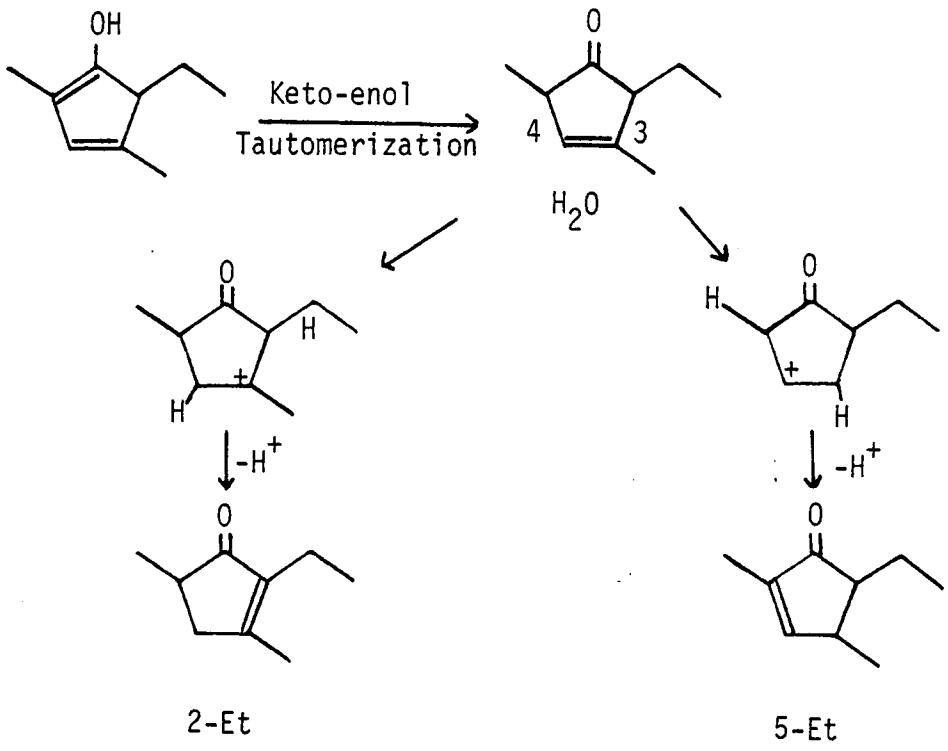
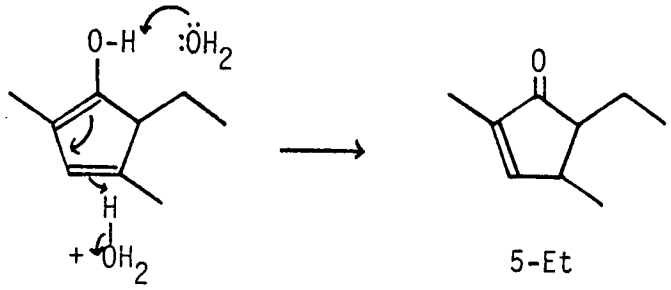


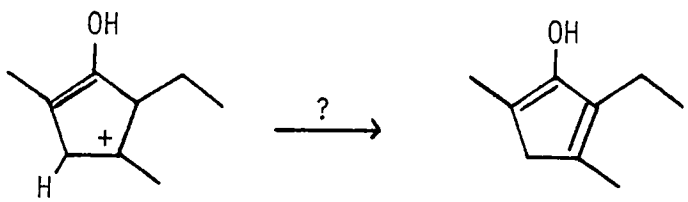
Figure 44. Yield of trisubstituted cyclopentenones from propanal as a function of acid concentration at various times. Temperature of reaction = 125°C.



An additional pathway is proposed for formation of 5-Et. Before the substituted cyclopentadienol undergoes keto-enol tautomerization, it may be protonated at carbon 4, allowing ready rearrangement to 5-Et.



Protonation at carbon 3 of the substituted cyclopentadienol would lead to the structure shown below,



which could form 2-Et by keto-enol tautomerization. Apparently, the formation of 5-Et by the above mechanism is a lower energy process than the several step process which involves keto-enol tautomerization. At high temperatures or high acid concentrations, the preference for the pathway leading to 5-Et is lost. The formation of the thermodynamically more favored 2-Et is found under conditions of high temperature or high acid concentration.

The inability to find reference to these trisubstituted cyclopentenones was initially surprising. However, there are several explanations for these trisubstituted cyclopentenones not being reported in the literature. The aldol condensation-dehydration product of propanal (2M2P) is not widely used, and when produced, is normally produced by a base catalyzed reaction.

If 2M2P was produced by an acid catalyzed reaction of propanal, the 2M2P would be distilled and the "high boiling fraction" would be discarded. The only product found in this study for the reaction of propanal and HCl under reflux conditions (bp propanal = 48°C) was 2M2P. This indicates the need for higher temperatures (and possibly higher pressures) than normally used in organic reactions.

A mechanism for this type of ring closure has only recently been reported,[124] and its validity appears questionable. The above reasons justify not finding these new compounds and indicate the need for future work in this area. The work needed in this area include a detailed mechanistic study, maximizing the yield by use of different catalysts and pressures, the applicability of this type of reaction for different aldehydes, the use of this reaction in synthetic organic

areas of interest include maximizing the yield by use of different catalysts and pressures, the applicability of this type of reaction for different aldehydes, the use of this reaction in synthetic organic chemistry, and the use of the products from this reaction.

4. Summary of SXUP Hydrolysis Studies

The percent yield of IPA reclaimed from the hydrolysis of SXUP was 56.2 after 4 hr of hydrolysis at 225°C. The maximum yield of over 60 percent was reached at 10 hr. After recrystallizing the reclaimed IPA from water, the IR, ^{1}H NMR, and melting point indicated the reclaimed IPA was quite pure.

It is important to stress the simplicity of the separation scheme for the reclaimed IPA. The process did not require expensive solvents, complicated equipment, or much time. Hot water was used as the solvent for the IPA, and a filter was used to separate the dissolved IPA from the copolymer and any unhydrolyzed SXUP. This ease of separation, short process time, and simplicity of equipment may allow this process to be used by the manufacturer, fabricator, and user of large amounts of crosslinked polyesters.

The percent of copolymer reclaimed from the hydrolyzed SXUP increased with either increased time or temperature. The percent yield was 32.9 for the hydrolysis of SXUP at 225°C for 12 hr. There was a large increase in the yield of copolymer when the temperature was increased from 250 to 275°C. The percent yield increased from 20.4 to 85.9. However, this increase in the yield of copolymer was concomitant with a decrease in the yield of IPA and PG. Therefore, the optimum

hydrolysis temperature and time would be dictated by the relative prices of the reclaimable IPA, PG, and copolymer.

The composition and physical properties of the reclaimed copolymer depends on the percent styrene in the original polyester solution. This value varied widely. The copolymer could be used to provide functional sites along the polystyrene backbone. The acid groups provide a reaction site for a large number of chemical modifications of the copolymer. The modified copolymer may then be used as a composite material or perhaps blended with polystyrene.

The PG reclaimed from the hydrolysis was difficult to measure due to the low concentration of the PG in the water of hydrolysis. The 5.0 ml of water used was 40 times the amount needed to completely hydrolyze the SXUP. The amount of water may be reduced to produce a PG-water solution which may be separated or used as produced.

The maximum percent yield for PG was 40.2 obtained from the hydrolysis at 225°C for 10 hr. The yield of PG decreased as the temperature was increased to 250°C. PG was not detected by gc when the reaction temperature was increased to 275°C.

The decrease in yield of PG with increasing temperature led to a study of the high temperature reaction of propanal which was found in the reaction products of PG under acidic conditions. Two trialkyl-substituted cyclopentenones were isolated and identified. The yield of 5-Et and 2-Et was dependent on the time of reaction, temperature, and acid concentration. The maximum yield for 5-Et was 12.6 at 100°C for 8 hr. The maximum yield of 2-Et was 21.7 percent at 150°C for 6 hr. These maxima were from reactions using 5.0 percent by volume of HCl as

the catalyst. Decreasing the amount of HCl favored the production of 5-Et, while increasing the amount of HCl greatly decreased the production of 5-Et.

A mechanism was proposed to explain the production of these cyclopentenones. This mechanism was modified to explain the larger amount of 5-Et at lower temperatures or lower concentration of HCl.

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APPENDIX

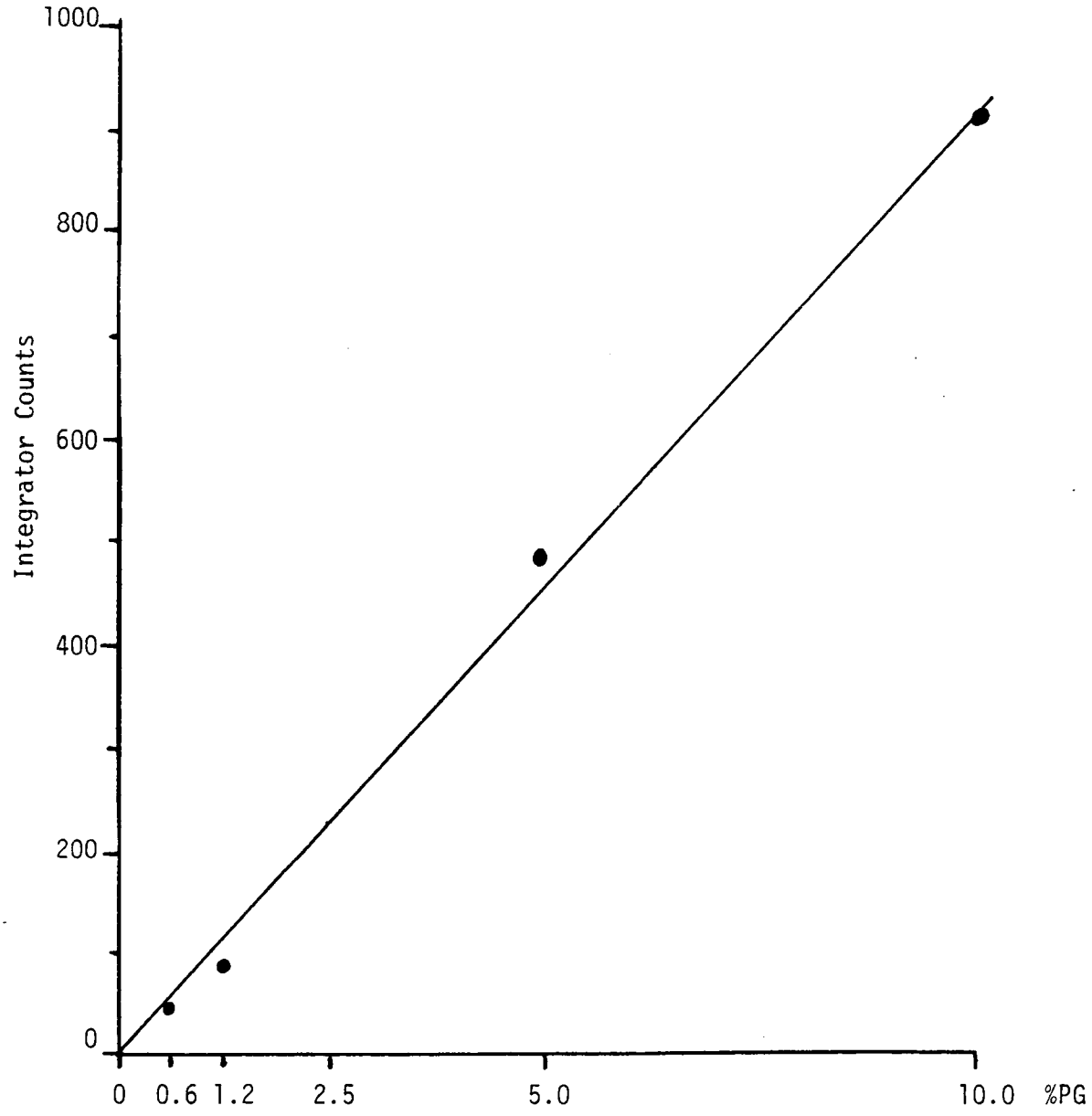

Figure 45. Calibration curve from gc for volume percent of Pg in water versus integration counts. A least squares program yielded an A value of 0.129 and a B value of 0.010 for the equation Y = AX + B.

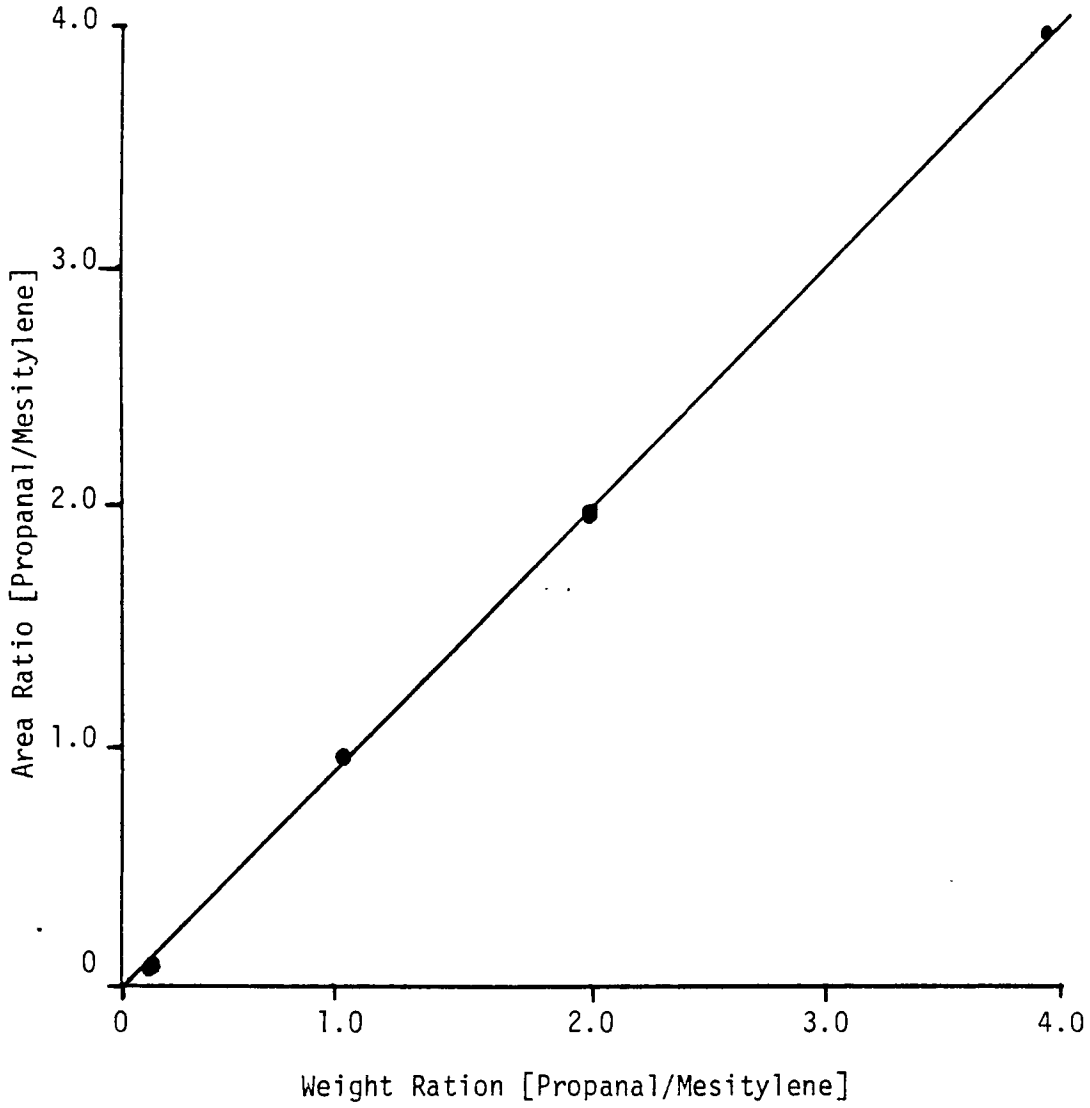

Figure 46. Calibration curve from gc for weight ratio of propanal/mesitylene versus area ratio of propanal/mesitylene. The area ratio was determined from the integrator counts fpr the peaks. A least squares program yielded an A value of 0.036 and a B value of 1.001 for the equation Y = AX + B.

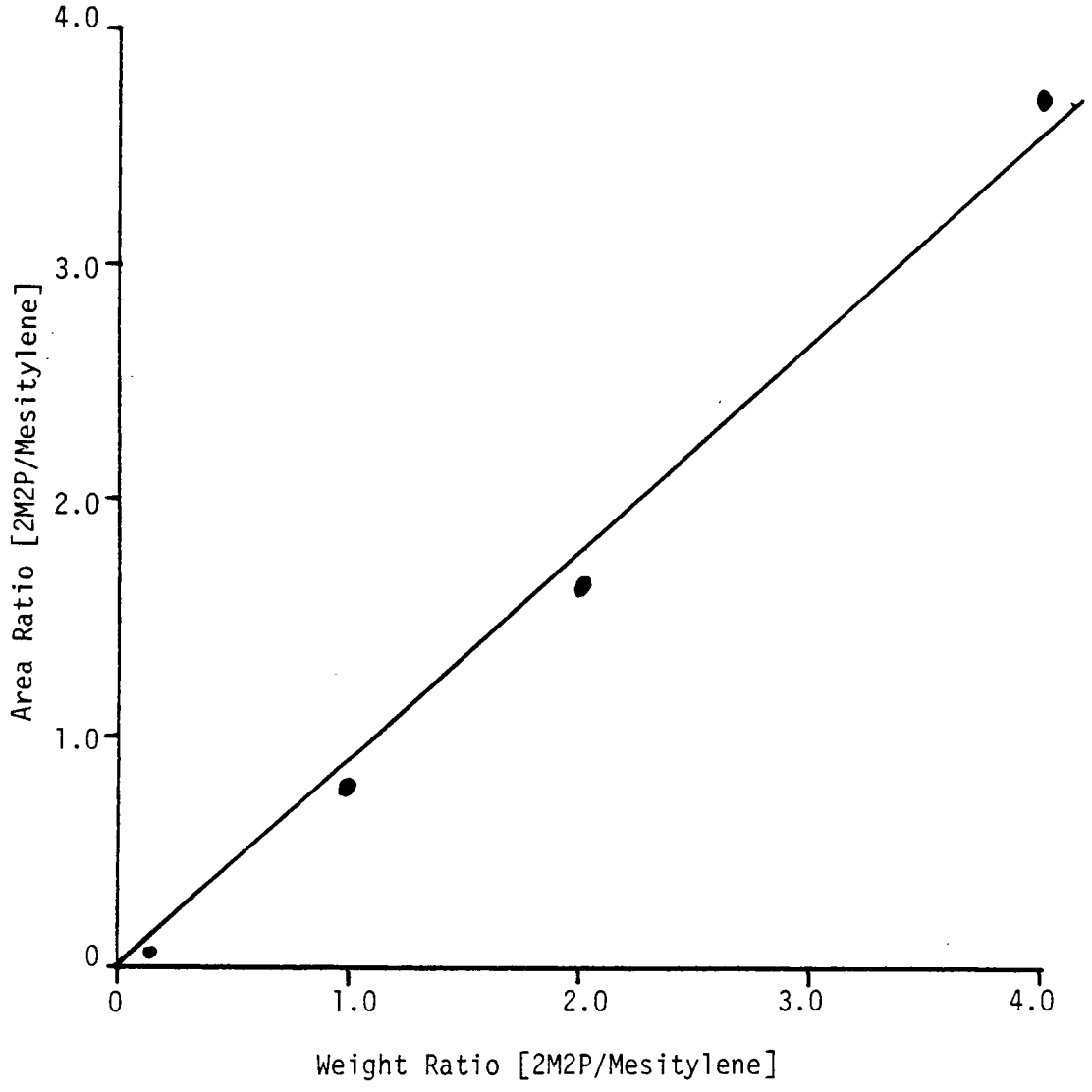

Figure 47. Calibration curve from gc for weight ratio of 2M2P/mesitylene versus area ratio of 2M2P/mesitylene. The area ratio was determined from the integration counts for the peaks. A least squares yielded an A value of 0.096 and B value of 1.081 for the equation Y = AX + B.

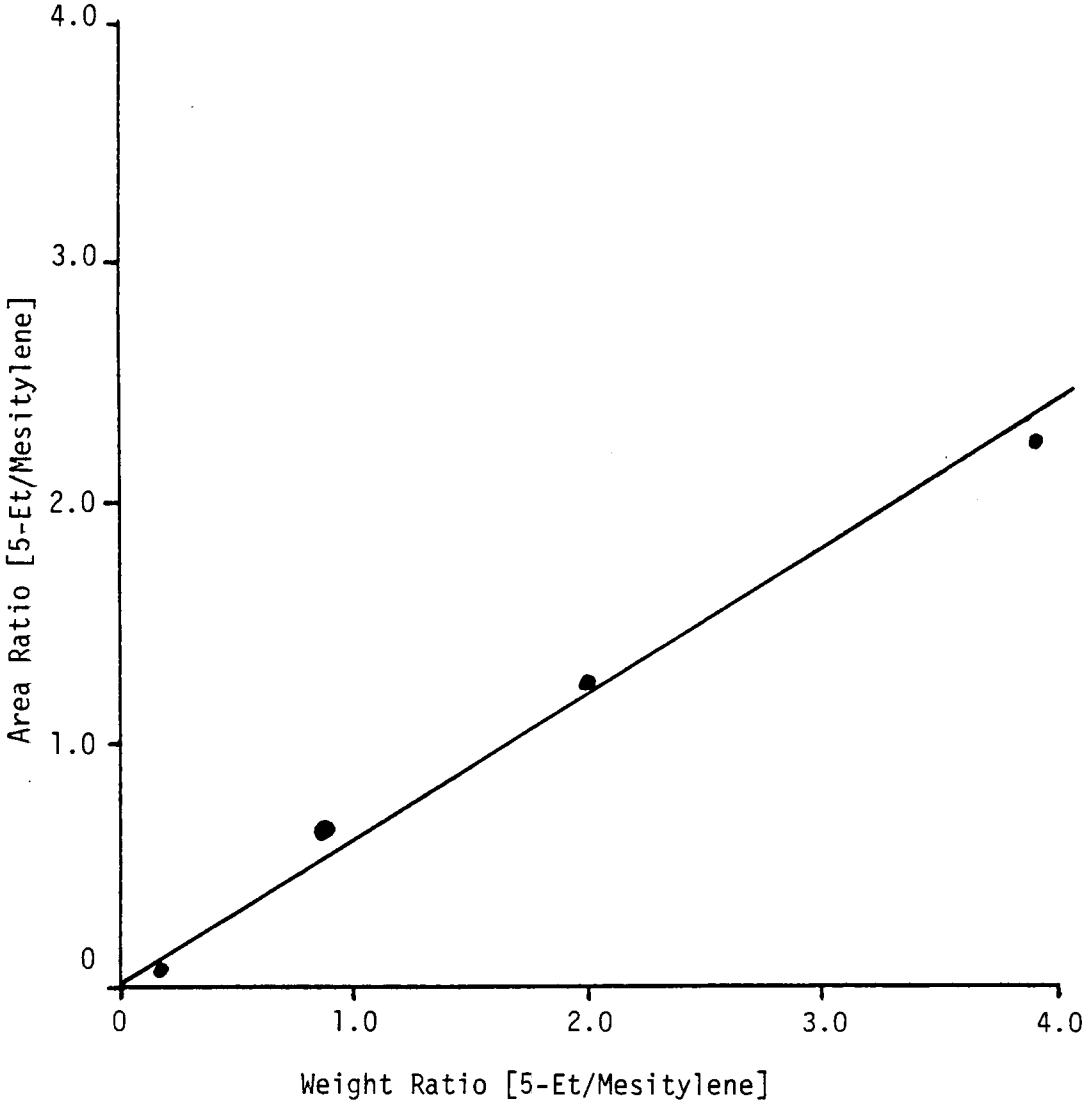

Figure 48. Calibration curve from gc for weight ratio of 5-Et/mesitylene versus area ratio of 5-Et/mesitylene. The area ratio was determined from the integrator counts from the peaks. A least squares program yielded an A value of 0.093 and a B value of 1.765 for the equation Y = AX + B.

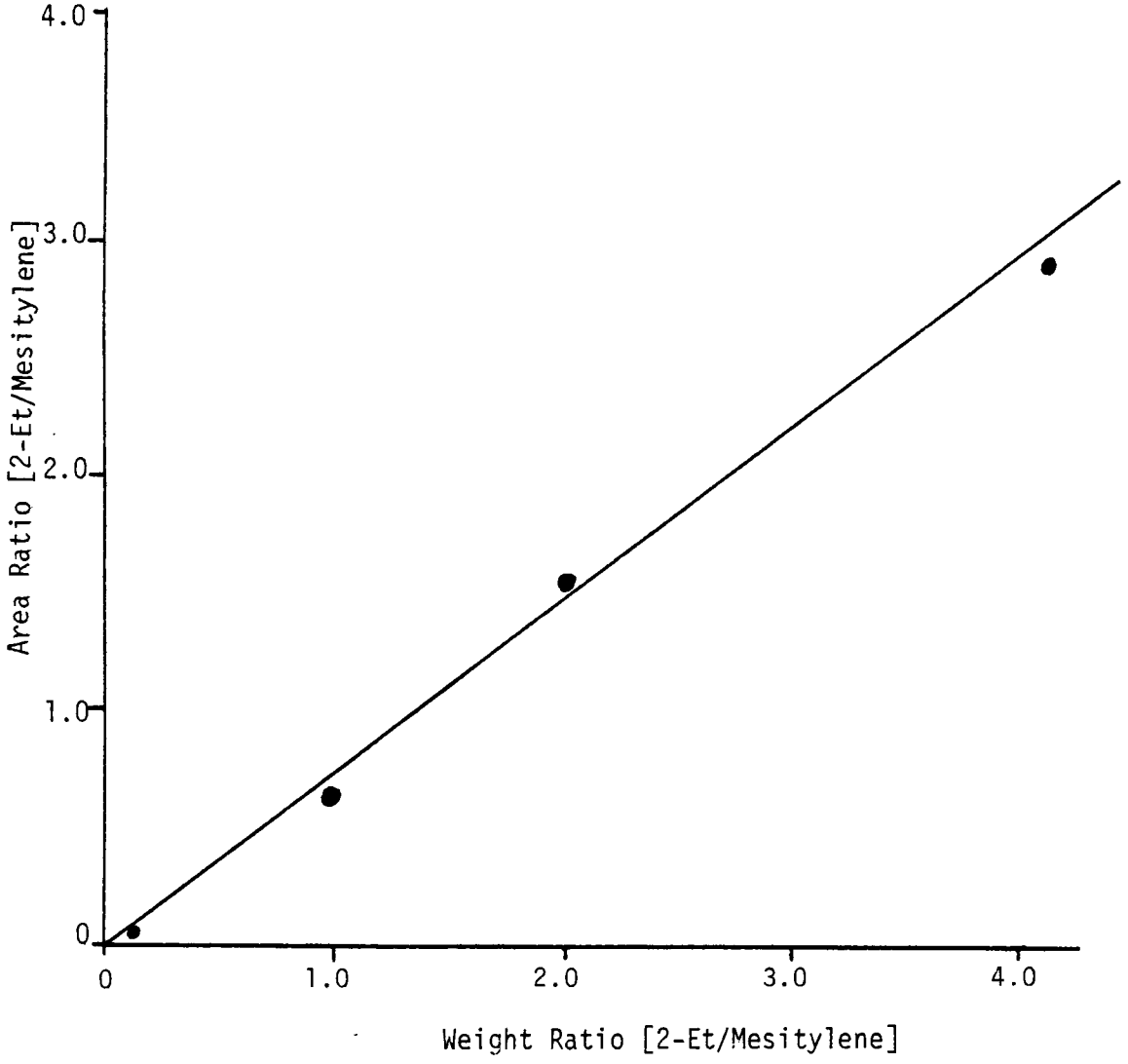

Figure 49. Calibration curve from gc for weight ratio of 2-Et/mesitylene versus area ratio of 2-Et/mesitylene. The area ratio was determined from the integrator counts for the peaks. A least squares program yielded an A value of 0.010 and a B value of 1.457 for the equation Y = AX + B.

VITA

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The author is a member of the American Chemical Society and the American Chemical Society Polymer Division, Inc. In June 1970, he married Yvonne Pinkston, and he is the father of a daughter born in November 1971.