POLYHYDROXYETHERS SYNTHESIS, ANALYSIS AND CROSSLINKING

by

James Steven Senger

Thesis submitted to the faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Chemistry

APPROVED:

J.E. McGrath, Chairman

G.L. Wilkes

J.G. Mason

April, 1987

Blacksburg, Virginia

POLYHYDROXYETHERS, SYNTHESIS, ANALYSIS, AND CROSSLINKING

James S. Senger

(ABSTRACT)

Epoxy resins are used throughout the commercial field as coatings and adhesives. Commercially, these polymers are generally synthesized via the "Taffy Process" which involves the reaction of $4,4^1$ isopropylidene diphenol (Bis-A) with epichlorohydrin under basic conditions. They may also synthesized from the base catalyzed reaction of diglycidylether of Bis-A and Bis-A, which is referred to as the "Advancement Process". Both processes are complicated by a branching side reaction which consumes epoxy groups and upsets the stiochiometric control and hence influences the materials final molecular weight.

A possible method to eliminate the side reaction and obtain high molecular weight polymers was investigated which involved the use of sterically hindered basic catalysts in a non-polar solvent to promote the reaction between the diglycidylether of Bis-A and Bis-A. Reactions conducted using quaternary ammonium hydroxides in diglyme solutions produced high molecular weight polymers. In contrast, trialkylamine catalyzed systems run under similar conditions only produced polymers of moderate molecular weights at best.

A quantitative ^{1}H-NMR analysis for measuring the degree of branching in polyhydroxyethers has been developed. The ^{1}H-NMR analysis involved the derivatization of the polymers using trichloroacetyl isocyanate. This was performed in order to separate

the methine proton into a branched and non-branched signal. Analysis of both polymers and oligomers synthesized by this method indicate that the degree of branching is less than 10% for all materials. However the low precision of the technique limited the analyiss and the conclusion as to the best reaction conditions required to obtain the lowest amount of branching.

The kinetics of crosslinking oligomeric epoxy resins with multifunctional isocyanates was also studied using fourier transform infrared spectroscopy (FT-IR). The reaction was modeled by using phenyl isocyanate and a low molecular weight epoxy resin synthesized from para t-butyl phenol and diglycidylether of Bis-A. Tin octoate proved to be the most effective catalyst for this reaction.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to Dr. McGrath and thanks to the entire polymer group for their helpful suggestions and overall assistance given to me during the course of this work. Their skill and close cooperation with one another makes it an honor and a pleasure to work amongst them. I would also like to thank Drs. D.K. Mohanty and R. Subramanian for their assistance with various areas of my research. I would especially like to thank Dr. R. Patsiga who with his never ending patience taught this poor engineer how to become a chemist. I would lastly like to thank my parents for their constant encouragement, understanding and love. I could have never come this far without them.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Epoxy resins, also known as polyhydroxyethers, are used in a wide range of fields and applications. These include adhesives, coatings, insulation and composite materials.

Commercially available epoxy resins are generally low molecular weight epoxy terminated materials which are usually cross-linked through the reaction of the epoxy groups with a multifunctional reagent. Alternatively, they can also be crosslinked through their pendant secondary hydroxyl group. These resins have been traditionally synthesized commercially by two different methods known as the Taffy and the Advancement processes.

The Taffy Process involves the reaction of epichlorohydrin with bisphenol A under basic conditions while the Advancement Process utilizes the reaction of the diglycidyl ether of bisphenol A with bisphenol A. Both processes are complicated by a branching side reaction between the pendant hydroxyls and the epoxy groups. This side reaction upsets the stoichiometric ratio between the two monomers resulting in loss of control of the product molecular weight.

The objectives of the research discussed herein were to first synthesize high molecular weight, linear polyhydroxyethers and then secondly, to devise an analysis which would quantitatively measure the amount of branching in the polymers synthesized. Lastly, a preliminary study was made of the kinetics of crosslinking polyhydroxyethers with multifunctional isocyanates. This reaction was modeled by reacting phenyl isocyanate with a linear low molecular weight compound which simulated an epoxy resin.

LITERATURE REVIEW

Epoxy Resin Chemistry

Background

The first patent for epoxy chemistry was awarded to Schlack of I.G. Farben [1] in 1934. At that time though, no commercial applications for the resins had yet been found. It was not till the late 30s and early 40s that Castan [2,3] discovered that epoxy resins could be used in commercial dental products. In 1943, Greenlee [4] received the first patent for the use of epoxy resins as a coating or paint.

With the introduction of epoxy resins as adhesives in 1946, CIBA A.G. of Switzerland demonstrated that the resin was a valuable material for this important market.

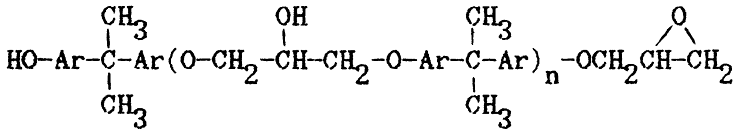
Today, epoxy resins are important materials for a wide range of applications. As adhesives they are used in the construction of cars, buildings, planes, ships and many other areas. One main application is in the replacement of bolts and rivets. Bolts and rivets have been shown to weaken the materials they join causing failures around the fastened regions. They also tend to create a greater likelihood for galvanic corrosion. Suitably applied, epoxy resin adhesives neither corrode or weaken the materials they bond together.

In the coatings field, epoxy resins are widely used in paints and varnishes. They are also used as street coatings, to protect the roads from salt and seepage of water through cracks and in floor tiling in factories and restaurants, due to their chemical resistance.

Epoxy resins are also used as insulation for transformers and other electrical equipment. An important current area is the rapidly growing field of composite mateials.

In almost all applications the resins are crosslinked by a multifunctional reagent which reacts with the epoxy endgroups of the resin. In most cases a low molecular weight resin intermediate is used thus ensuring that the final products will be rigid but unfortunately also brittle.

Higher molecular weight epoxy resins are generally known as polyhydroxyethers. The resins which dominate the commercial market at this time are based on bisphenol A.



$$HO{-}Ar{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}Ar(O{-}CH_2{-}\overset{\overset{OH}{|}}{C}H{-}CH_2{-}O{-}Ar{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}Ar)_n{-}OCH_2\overset{\overset{O}{/\ \backslash}}{CH{-}CH_2}$$

The polyhydroxyethers structures are good adhesives at least partially due to their pendant hydroxyl groups. They are known to have some chemical, impact, and abrasion resistance along with a degree of flexibility. Some representative physical properties of a molded polyhydroxyether are shown in Table 1 [6].

The pendant hydroxyls also makes it possible to derivatize and thus change the material's surface and mechanical properties. Groups such as isocyanates, anhydrides, melamines, etc. will react readily with hydroxyls, thus providing the polyhydroxyethers numerous applications in the coatings field.

TABLE 1

Some Physical Properties of a Thermoplastic,
High Molecular Weight Molded Polyhydroxyether [6]

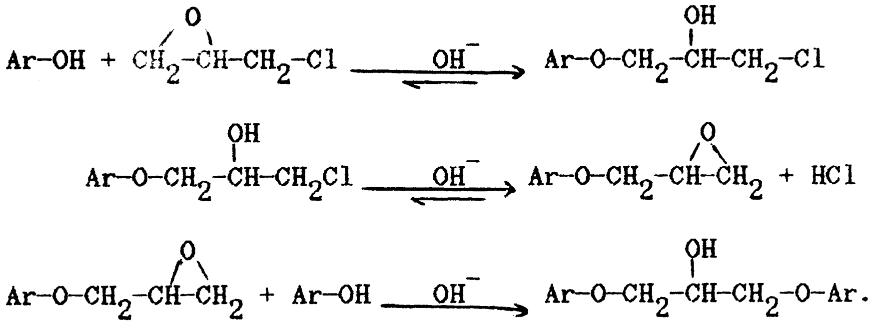
Tensile Strength	9, 500 psi (65.5 MPa)
Elongation	50-100%
Elongation at Yield	3-5%
Flexural Strength	14,000 psi (96.5 MPa)
Flexural Modulus	4.1×10^5 PSI
Specific Gravity	1.182
Heat Distortion	118°F (48°C)

Epichlorohydrin and Bisphenol-A

Polyhydroxyethers based on bisphenol A historically have been made commercially by the Taffy Process. The process involves the reaction of bisphenol A with epichlorohydrin under basic conditions. The process was first described by Castan [2,3]. Later Greenlee [7,10] used this procedure to synthesize high molecular weight polymers.

Mechanism and Kinetics

Several authors [12-16] have proposed the following general mechanism for the reaction between epichlorohydrin and bisphenol A.



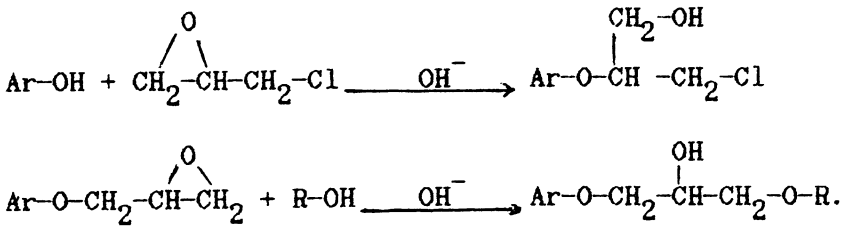
(1)

(2)

(3)

Fisch [13] has reported that step 3 in the reaction is the rate determining step with step 2 occurring at a much greater rate than step 1. Batzer and Zahir [14,15] have confirmed the latter finding.

These authors have also reported two side reactions that can occur in the synthesis of polyhydroxyethers.



(4)

(5)

In the first side reaction, (4), the phenoxide ion could attack the secondary carbon of the epoxy ring instead of the more accessible primary carbon. This reaction has been shown by Brode and Wynstra [17] to occur only to a small extent.

The second more feasible side reaction, (5), involves the attack of a secondary hydroxyl on the epoxy ring creating a branched structure. Batzer and Zahir proposed that the occurrence of this reaction is only possible near the end of the polymerization, when the concentration of free phenol is low and the phenol-alkoxide exchange is thus retarded.

Solvent Effects

In aprotic dipolar solvents, Rokicki and Kuran [18] reported that the rate of reaction is decreased by the addition of phenol to the system. When the reactions were run in a non-polar solvent such as diglyme, the decrease in rate was greatly reduced. They obtained similar results using sterically hindered phenols, and concluded that the changes in the rates were a function of the increasing acidity of the reaction medium.

Interfacial Polymerizations

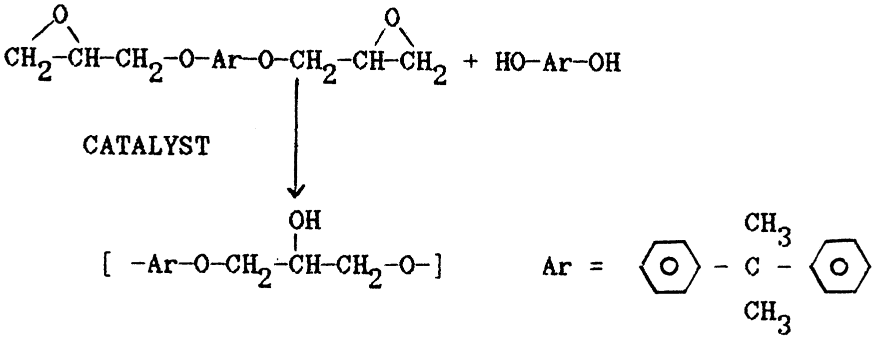
Linear, but only moderate molecular weight polymers have reportedly been obtained in interfacial polymerizations [19-21]. The materials were synthesized in a aqueous alkali-dioxane system using quaternary ammonium salts as the catalyst.

Diglycidyl Ether of Bisphenol A and Bisphenol A

Another process of interest in the synthesis of polyhydroxyethers involves the reaction of the diglycidyl ether of bisphenol A with bisphenol A. When carried out under basic conditions this reaction is termed the Advancement Process.

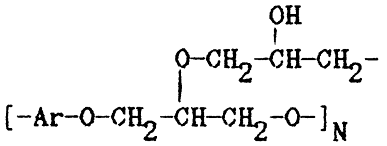
Mechanism and Kinetics

A general reaction scheme for a linear polymerization is shown below.



(6)

A branching side reaction has been reported to occur during the above synthesis by a number of authors [14,22-29]. The resulting branched structure is typically represented as:



$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad \text{OH} \\ \qquad\qquad\qquad\quad \text{O-CH}_2\text{-CH-CH}_2\text{-} \\ [\text{-Ar-O-CH}_2\text{-CH-CH}_2\text{-O-}]_N \end{array}$$

The branching reaction is assumed to be due to either the attack of the pendant alcoholic hydroxyl on an epoxy group or, more likely, the anionic oligomerization of an epoxy group by the alkoxide.

Uncatalyzed Systems

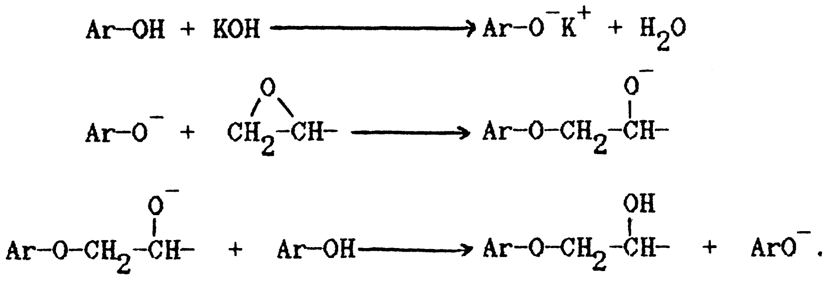
Schechter and Wynstra [25] were perhaps the first to demonstrate the reaction of phenyl glycidyl ether with various alcohols. The order of reactivity of alcohols with epoxy groups can be summarized as, phenol> primary>secondary>tertiary aliphatic hydroxyls. No epoxy-phenol reaction was observed at 100°C. However, when the temperature was raised to 200°C it was found that more of the epoxy had reacted than phenol. This was interpreted as an indication of the proposed branching side reaction. Schecter and Wynstra proposed that the phenol was acting as a catalyst for the reaction between the pendant hydroxyls and the glycidyl ether.

Acid Catalyzed Systems

Schechter and Wynstra [25] reported no reaction between phenol and the phenyl glycidyl ether when stannic chloride (a Lewis acid) was used as a catalyst. However, the same catalyst proved to be effective for the reaction between secondary alcohols and phenyl glycidyl ether at 100°C.

Base Catalyzed Systems

Schechter and Wynstra reported that alkali hydroxides, quaternary ammonium hydroxides, and tertiary amines were all effective catalysts for phenol-phenyl glycidyl ether reactions. All reactions reportedly obeyed first order kinetics and showed no signs of any alcohol-epoxy side reactions. They proposed the following mechanism

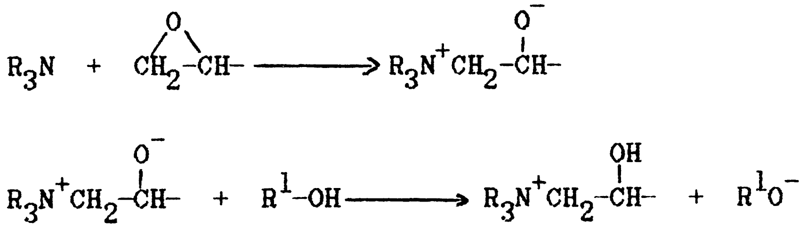


$$\begin{aligned}
&\text{Ar–OH} + \text{KOH} \longrightarrow \text{Ar–O}^{-}\text{K}^{+} + H_2O \qquad (7)\\
&\text{Ar–O}^{-} + \overset{\overset{O}{/\ \backslash}}{CH_2\text{–}CH}\text{–} \longrightarrow \text{Ar–O–}CH_2\text{–}\overset{\overset{O^{-}}{|}}{CH}\text{–}\\
&\text{Ar–O–}CH_2\text{–}\overset{\overset{O^{-}}{|}}{CH}\text{–} + \text{Ar–OH} \longrightarrow \text{Ar–O–}CH_2\text{–}\overset{\overset{OH}{|}}{CH}\text{–} + \text{ArO}^{-}.
\end{aligned}$$

Schechter and Wynstra continued their work with a study of isopropanol-phenyl glycidyl ether reactions. Alkali hydroxides, quaternary ammonium hydroxides, and tertiary amines were once again effective catalysts. In all the catalyzed systems though, it was discovered that over 80% of the isopropanol was left unreacted. The majority of the reaction had involved the anionic polymerization (oligomerization) of epoxy groups.

Tertiary amines catalyzed the reactions in a manner different from either the alkali or the quaternary ammonium hydroxides. The tertiary amine catalyzed reactions obeyed second order kinetics while the other catalysts were observed to be first order. The effectiveness of the amine catalyst was also greatly dependent on the hydroxyl concentration while the others were not.

Two mechanisms were proposed for catalyzed reactions of an alcohol and an epoxy. For the tertiary amine systems:

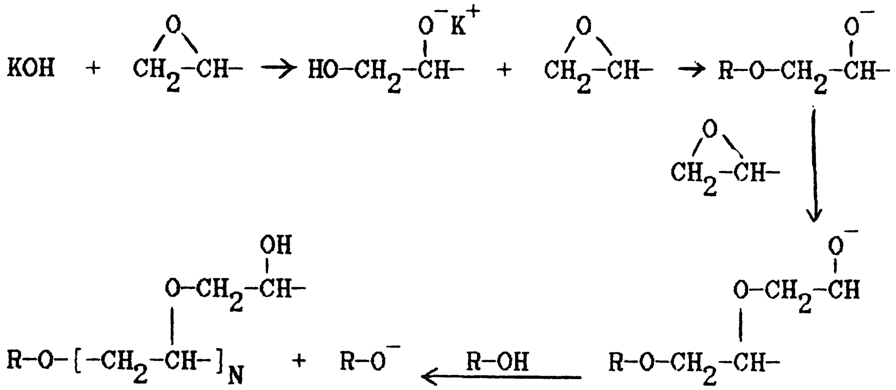


$$R_3N \;+\; \overset{O}{\overbrace{CH_2-CH}}- \longrightarrow R_3N^+CH_2-\overset{O^-}{\overset{|}{C}}H- \qquad (8)$$

$$R_3N^+CH_2-\overset{O^-}{\overset{|}{C}}H- \;+\; R^1-OH \longrightarrow R_3N^+CH_2-\overset{OH}{\overset{|}{C}}H- \;+\; R^1O^- \qquad (9)$$

The amines were reported to not easily polymerize the glycidyl ethers in the absence of an alcohol. The magnitude of the catalyzing affect of the amine was dependent on steric factors and not only on the basicity of the amine.

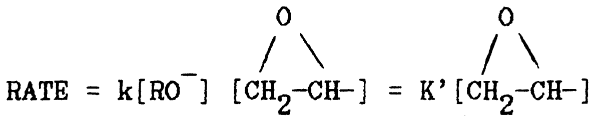
The mechanism for the alkali and quaternary ammonium hydroxides is thus thought to be quite different.



(10)

The catalysts here are basic and/or nucleophilic enough to initiate polymerization of the epoxy groups. A question still remains about the formation of the initial alkoxide unit shown in step 1. Schechter and Wynstra believed it was caused by the attack of the catalyst on the epoxy group. However, the formation could have also been caused by the catalyst-alcohol reaction.

The rate for the reactions catalyzed by the alkali and quaternary ammonium hydroxides is given by:



$$\mathrm{RATE} = k[\mathrm{RO}^-]\,[\mathrm{CH_2\text{-}CH\text{-}}] = K'[\mathrm{CH_2\text{-}CH\text{-}}] \qquad (11)$$

This rate equation would appear to be in direct conflict with the branching theory proposed by Batzer, Zahir, and Bantle [14,22,27]. According to their postulation, the branching reaction involves the base catalyzed attack of the pendant alcohols on the epoxy groups. Hence, they concluded that the majority of the side reaction occurs near the end of the polymerizations when the concentration of hydroxyls is highest. Note that the rate equation derived by Schechter and Wynstra has no such dependency on the concentration of the hydroxyls.

Further work on the base catalyzed attack of the hydroxyl on the epoxy ring was performed by Alvey [23]. Alvey studied the selectivity of amines toward the linear polymerization over the branching side reaction in model reaction systems. He was able to demonstrate that the more selective catalysts produce smaller amounts of branching as listed in order of decreasing selectivity in Table 2. He reasoned that if the amine catayst complexes strongly with a secondary hydroxyl, it will have less selectivity. However, if this complexation was prevented, perhaps fewer side reactions would occur. He proposed that if a hydroxyl group was incorporated in the amine structure, as in triethanolamine, it would complex with the nitrogen. This in turn would lower the nitrogen's activity toward complexation with the secondary hydroxyl and hence the catalyst's selectivity would be greater.

The complexing of the hydroxyl may thus be a key feature to the branching reaction. An uncomplexed secondary hydroxyl can not easily attack an epoxy ring, as was noted by Antal, Fuzes, Samay, and Csillac [24]. It is the alkoxide anion formed from the hydroxyl that is the true nucleophile.

Catalyst Concentration Effect

Schechter, et al [26] have reported that excess amounts of base can increase the branching side reaction. Alvey had confirmed this by his observation that the catalyst selectivity increased as catalyst concentration decreased.

TABLE 2

Catalysts for the DGEBA Bis-A Reaction [23]

---

1) Triethanolamine
2) n-Butylamine
3) Di-(3-phenoxy-2 hydroxylpropyl) amine
4) Di-n-butylamine
5) Tri-n-butylamine

Temperature Effect

Zahir and Bantle [27] have reported that the degree of branching increased for polymerizations at 150°C relative to those conducted at 100°C. The catalysts in their systems were quaternary ammonium hydroxides. Alvey has reported though, that less branching is observed in reactions run at 150°C than 100°C for systems using dimethylacetamide as the catalyst.

Higher Molecular Weight Polymerization

To date there has been very little work reported in the open literature using amines or other nitrogen compounds in polymerization reactions. Antal, Fuzes, Samay and Csillac [24] have reported some success using tetramethyl ammonium chloride at 145°C. This catalyst though has a limited lifetime at this temperature. Zahir and Bantle [27] have also reported some success using tetrabutyl ammonium hydroxide but no specifics were provided.

Nuclear Magnetic Resonance Determination of Branching

Nuclear Magnetic Resonance (NMR) had been used successfully in the determination of the degree of branching in polyhydroxyethers. Mak and Rogers [30,31] published the first paper on the analysis of branching using ^{1}H-NMR. Their work applied a technique developed by Goodlett [32] to produce a downfield shift of the carbinol methine proton.

Goodlett produced this shift by adding trichloroacetyl isocyanate to a hydroxyl containing compound. He proposed that the isocyanate reacted with the hydroxyl to form a carbamate linkage which, by its electronegative character, produces the shift.

The peak position of the various protons of a polyhydroxyether both before and after derivatization are given in Table 3. Mak and Rogers used a variety of both commercial and lab synthesized epoxy resins of varing molecular weights. The resins made in their lab were synthesized via the Taffy Process. The epoxy equivalent weights of the samples varied between 548 and 3257.

They calculated the number of branch points in a chain, N, by equation 12.

$$N = n - 6A(n + 1) \tag{12}$$

where A = area of carbinol methine to benzylic methyl

n = the number of repeat units in the resin

The number of repeat units was calculated from the equation

$$n = 2(EEW - 170)/284 \tag{13}$$

where EEW = the epoxy equivalent weight of the resin. They determined the amount of branching to be 10 - 20%.

Batzer and Zahir [22] concluded Mak and Roger's equation for the number of repeat units was based on a simple model which did not take into account a variety of different endgroups which are possible from a polymer synthesized by way of the Taffy Process. They derived a new equation

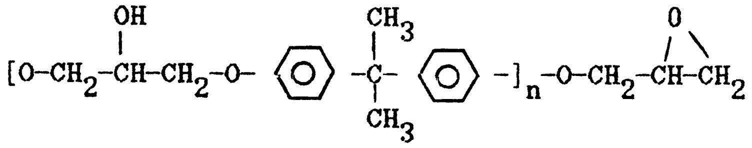
$$F = (N + M)\ Mn/1000 \tag{14}$$

where N + M = number of branches per kilogram of resin.

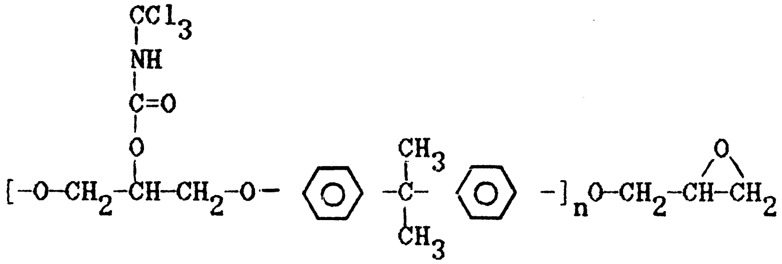
F = number of branch points per number average molecule

TABLE 3

^{1}H-NMR Peak Positions Before and After Derivatization with Trichloroacetylisocyanate [30]



BEFORE



AFTER

PROTON	PEAK POSITION (Before)	PEAK POSITION (After)
BENZYLIC METHYL	1.5 - 1.7 ppm	1.5 - 1.7 ppm
EPOXY METHYLENE	2.6 - 3.0	2.6 - 3.0
CARBINOL HYDROXYL	2.7 - 2.9	8.6 - 8.8
EPOXY METHINE	3.1 - 3.5	3.1 - 3.5
ETHER METHYLENE	4.0 - 4.2	4.2 - 4.4
ETHER METHINE (BRANCHED)	4.2 - 4.4	4.2 - 4.4
ETHER METHINE (UNBRANCHED)	4.2 - 4.4	5.3 - 5.5
BENZYLIC RING	6.7 - 7.1	6.7 - 7.1

Internal Reference: Tetramethylsilane

The number of branches was calculated from NMR integrations using the equation 15.

$$N + M = ((A_{4.0} - 4\,A_{5.5} - A_{2.8})/A_{2.8})\ (2p/5) \qquad (15)$$

where A = intergrated area of the NMR peak after derivation

p = epoxy equivalent per kilogram of resin

The samples they tested were synthesized by the Taffy Process route. The results showed the amount of branching to be between 0.09 and 0.60 per molecule.

Kinetics of Alcohol-Isocyanate Reactions

Background

The reaction of alcohols and isocyanates is used commercially in the production of urethane materials. Wurtz and Hofmann were the first to discover this reaction over 100 years ago. Otto Bayer in 1937, synthesized the first urethane polymer as a competitive material to nylon.

Today segmented copolymers urethane materials are used as fibers, adhesives, and surface coatings. In many of its applications the polyurethane material is used as a foam. Some examples are seat cushions and insulation around pipes.

Reaction Mechanism and Rate

Production of urethanes involves the reaction of isocyanates with alcohols. It is generally believed that the reaction involves an alcohol-isocyanate complex:

$$\text{R-NCO} + \text{R}^1\text{-OH} \longrightarrow \text{COMPLEX} \xrightarrow{\text{R}^1\text{-OH}} \text{R-NHCOOR}^1 \qquad (16)$$

The concept of the alcohol-isocyanate complex has been attributed by several authors [34,35] to Baker and Gaunt [36].

It has been accepted that the rate kinetics roughly follows a second order rate law [34,35,37]. Deviations from the rate law though, have been documented in a number of papers [34,36-41].

Side Reactions

Due to the highly reactive nature of the isocyanate group there exists a series of side reactions that can occur in the synthesis of urethanes:

$$\text{R-NCO} + \text{H}_2\text{O} \longrightarrow \text{R-NHCOOH} \longrightarrow \text{RNH}_2 + \text{CO}_2 \qquad (17)$$

$$\text{R-NH}_2 + \text{R-NCO} \longrightarrow \text{R-NHCONH-R} \qquad \text{urea}$$

$$\text{R-NH}_2 + \text{R}^1\text{-NHCOR}^1 \longrightarrow \text{R}^1\text{-NCOR} \qquad \text{acylurea} \qquad (18)$$

$$\text{R-NCO} + \text{R}^1\text{-NHCONHR}^1 \longrightarrow \text{R}^1\text{-CONHR}^1 \qquad \text{biuret} \qquad (19)$$

$$\text{R-NCO} + \text{R}^1\text{-NCOOR}^1 \longrightarrow \text{R}^1\text{-NCOOR}^1 \qquad \text{allophanate} \qquad (20)$$

These side reactions increase the rate at which isocyanate molecules are consumed [42] and therefore contribute to the reported deviations.

Effect of Alcohol Structure

The rate of the reaction between isocyanates and alcohols is greatly dependent on the structure of the alcohol. In 1949, Baker and Gaunt [36] reported the reactivity of alcohols to phenyl isocyanate decreased as the structure of the alcohol was varied

$$\text{ROH} = \text{MeOH} > \text{EtOH}, \text{PhOH} > \text{PrOH} > \text{BuOH}.$$

Dyer and coworkers [43] reported 1-butanol reacted with phenyl isocyanate three times faster than 2-butanol. Other investigators have reported similar findings [44-46].

Catalysts can effect the extent to which one alcohol dominates over another in reactions with phenyl isocyanate. Rand, Thir, Reegen, and Frisch [39] have shown that the ratio of the rate constants between 1-butanol and 2-butanol increased from 3 for an uncatalyzed system to 12 for a system catalyzed with dibutyltin dilaurate. However Smith [38] using triethylenediamine as a catalyst, reported the ratio of rate constants between 1-butanol and 2-butanol to be 6. The concentration of the catalyst apparently, does not affect this ratio [39].

The proximity of other hydroxyl groups in the molecule also affects the rate of reaction. Rand, et al. [39] reported that using dibutyltin dilaurate as a catalyst, 2,3 butanediol reacted at a greater rate than other secondary alcohols. They proposed that this was due to the hydrogen bonding present between the hydroxyl groups. The hydrogen bonding weakens the hydrogen-oxygen bond enhancing the alcohol reaction with the isocyanate more favored.

Wissman, Rand and Frisch [47] investigated oligomeric polyether diols and other polyols and found that the reaction rates were independent of chain length and steric functionality. Willeboordse [48] came to the same conclusion using different molecular weights of polyethylene glycol.

Smith [38] studied the point of deviation from second order kinetics which occurs in most urethane reactions and found that polyhydroxyl alcohols deviated at a different point in the reaction than the monoalcohol. He also reported that the deviation point occurred at the same time for both primary and secondary alcohols.

Effect of Solvent

The effect of solvent on the rate of the urethane reaction has been reported by a number of authors [34,35,36,43,49,50]. The first attempt to quantify this effect was performed by Ephraim [45] who tried to correlate dieletric constants of solvents with reaction rate. Oberth and Bruenner [34,51] however proposed that it was the hydrogen bonding character of the solvent, not its dielectric constant which produced the changes in reaction rate.

In their work Oberth and Bruenner [34] divided solvents into three categories based on the type of alcoholic complexation they found in their solvent systems. The first category included the solvents which do not complex with alcohols, due to lack of hydrogen bonding character. These solvents included carbon tetrachloride and several alkanes.

In the second group of solvents no complexation of the alcohols occurred. These solvents had enough polar character to break up alcohol-alcohol complexes while at the same time having too little hydrogen bonding character to form an alcohol-solvent complex. Solvents in this group include nitrobenzene and chloroform.

The third class of solvents contained a large degree of hydrogen bonding character and formed complexes with the alcohols. Ethers, ketones, nitriles, and esters are all examples of this group.

Oberth and Bruenner found that it was the first solvent group which gave the greatest rate of reaction while the third group contributed to the slowest reaction rates. The phenyl isocyanate and 1-butanol reacted at a rate 500 times greater in heptane than in dioxane. Rand et al. [39] later found the reaction rate between phenyl isocyanate and various alcohols to be greater in toluene solutions than in cellosolve acetate solutions. Oberth proposed that even though the hydrogen-oxygen bond was weakened in alcohol-solvent complexes, the solvent molecules shielded the hydroxyls from the isocyanate groups.

They proposed a reaction mechanism as follows:

$$(ROH)p + R^1NCO \longrightarrow COMPLEX \longrightarrow R^1NHCOOR + (ROH)p-1 \qquad (21)$$

The rate of reaction was then proposed to be

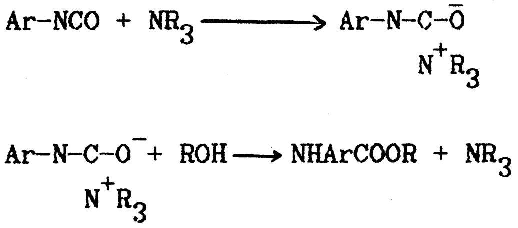
$$d[R^1NHCOOR] = K\ [complex] \qquad (22)$$

According to their model, as the hydrogen bonding character of the solvent increased, the concentration of complexed alcohols decreased, thus decreasing the rate. This agreed with their observation that the rate constant for an assumed second order rate law increased with the dilution of the alcohol in inert solvents, but decreased in all other solvents.

At no time did they detect any shift in the infrared peak of the isocyanate which would indicate any isocyanate-solvent complexation. The hydrogen bonding solvent effect has also been reported [34,38] to be reduced in the presence of an amine or metal catalyst.

Effect of Catalyst

Baker, Gaunt and Holdsworth [36,52] found that basic media promoted the reaction between alcohols and isocyanates. They proposed that a basic catalyst, such as an amine, formed a complex with the isocyanate molecules. This complex increased the partial positive charge on the carbonyl carbon of the isocyanate which promoted an increased reaction rate between the isocyanate and the alcohol.



$$\text{Ar-NCO} + \text{NR}_3 \longrightarrow \text{Ar-N-}\underset{\text{N}^+\text{R}_3}{\text{C}}\text{-}\bar{\text{O}} \qquad (23)$$

$$\text{Ar-N-}\underset{\text{N}^+\text{R}_3}{\text{C}}\text{-O}^- + \text{ROH} \longrightarrow \text{NHArCOOR} + \text{NR}_3$$

This reaction mechanism has been confirmed by other investigators [35,53,54]. The second step has been reported to be rate determining [35].

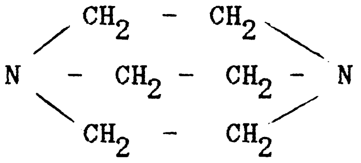
Baker and Gaunt also found by infrared results that an amine catalyst could complex with the hydroxyl of the alcohol. They proposed that this complex would catalyze the urethane reaction in the same manner as free amine molecule. Frakas [35] and Oberth [34] have suggested that an amine-alcohol compelx could react directly with an isocyanate to form an urethane. Schieler [55] proposed that the alcohol-amine complex involved the transfer of a proton. Any type of charge separation though, has been rejected by several other investigators [34,36,56].

The basicity of the amine has been reported [34,36,56] to have no correlation to its catalytic effect. Burkus [56] found that by increasing the size of the alkyl groups on an amine, the rate of the reaction would decrease. He believed that this effect was related to the steric hinderance of the amine.

Other nitrogen containing compounds may also catalyze the urethane reaction. Some of these include urethane itself, along with the products from the side reactions mentioned above, such as allophanates and the trimer of the isocyanate.

These catalysts, which are produced during the urethane reaction, create a positive deviation from second order kinetics [34,36-39]. These deviations are usually only detected toward the end of the reactions. Oberth and Bruenner [34] have proposed that the urethane complexes with alcoholic molecules in much the same manner as a hydrogen bonding solvent would. This they found lowered reaction rates in inert solvents.

Metal catalysts have been shown to be far more effective than nitrogen containing molecules [57-62]. A wide range of organometallic compounds as well as metal salts have been studied. Table 4 lists compounds studied by Anzunio et al. [57] and how they compare to triethylenediamine, DABCO, in catalytic strength. DABCO has long been



an industrial catalyst for urethane reations. Brittain and Gemeinhardt performed a more exhaustive study of various catalysis by measuring the time it took for an urethane gelation to occur. The approximate descending order in catalytic activity in types of compounds is: Bi, Pd, Sn, triethylenediamine, strong bases, Ti, Fe, Sb, U, Cd, Co, Th, Al, Hg, Zn, Ni, trialkylamines, Ce, and Cu.

TABLE 4

Comparison of Catalytic Activity for Urethane Formation of Various Metal Compounds with Triethylenediamine at 100°C [57]

CATALYST	CAT. CONC. (mole/Kg)	k (kg/eq.sec.)
NONE	-	3.7
TRIETHYLENEDIAMINE	1.58×10^{-2}	22.8
$(CH_3COO)_2Hg$	1.58×10^{-3}	163.0
$(CH_3COO)_2Cd\ 2H_2O$	$1.58X10^{-3}$	179.0
$(CH_3COO)_2Cu$	1.58×10^{-4}	353.0
$(CH_3COO)_2Zn\ 2H_2O$	$1.58X10^{-4}$	45.6
$CuSO_4\ 5H_2O$	$1.58X10^{-4}$	172.0

EXPERIMENTAL

Polyhydroxyether Synthesis

Polymerization

Polyhydroxyethers were synthesized in this research via an Advancement Process. The apparatus for solution polymerizations consisted of a 4-neck, 500 ml round bottom flasK fitted with an overhead stirrer, condenser, y-adapter with a thermometer, an argon inlet, and an additional funnel or stopper. Bulk polymerizations used an apparatus shown in Figure 1.

High purity bisphenol A, Bis-A, provided by Dow Chemical, USA, was dried for a period of 12-18 hours in a vacuum oven at room temperature.

The diglycidyl ether of bisphenol A, DGEBA, was recrystallized from commercially available Dow DER 332. The latter is a vacuum distilled product with an epoxy equivalent weight only slightly higher than DGEBA. A 50/50 mixture of DER 332 in solvent was used for the crystallization. The solvent was a 60/40 mixture of 2-ethyl ethoxyether/methyl isobutyl ketone. The combined DER 332 and solvent mixture was heated slightly to promote solution. The solution was then covered and placed inside a refrigerator at 4°C. After 2-4 days, crystals were formed on the bottom of the beaker. These crystals were crushed with a spatula and blended into the solution. After a period of 4-8 hours a high yield of crystallized product was obtained. The crystals were then filtered, washed with hexane and methanol and

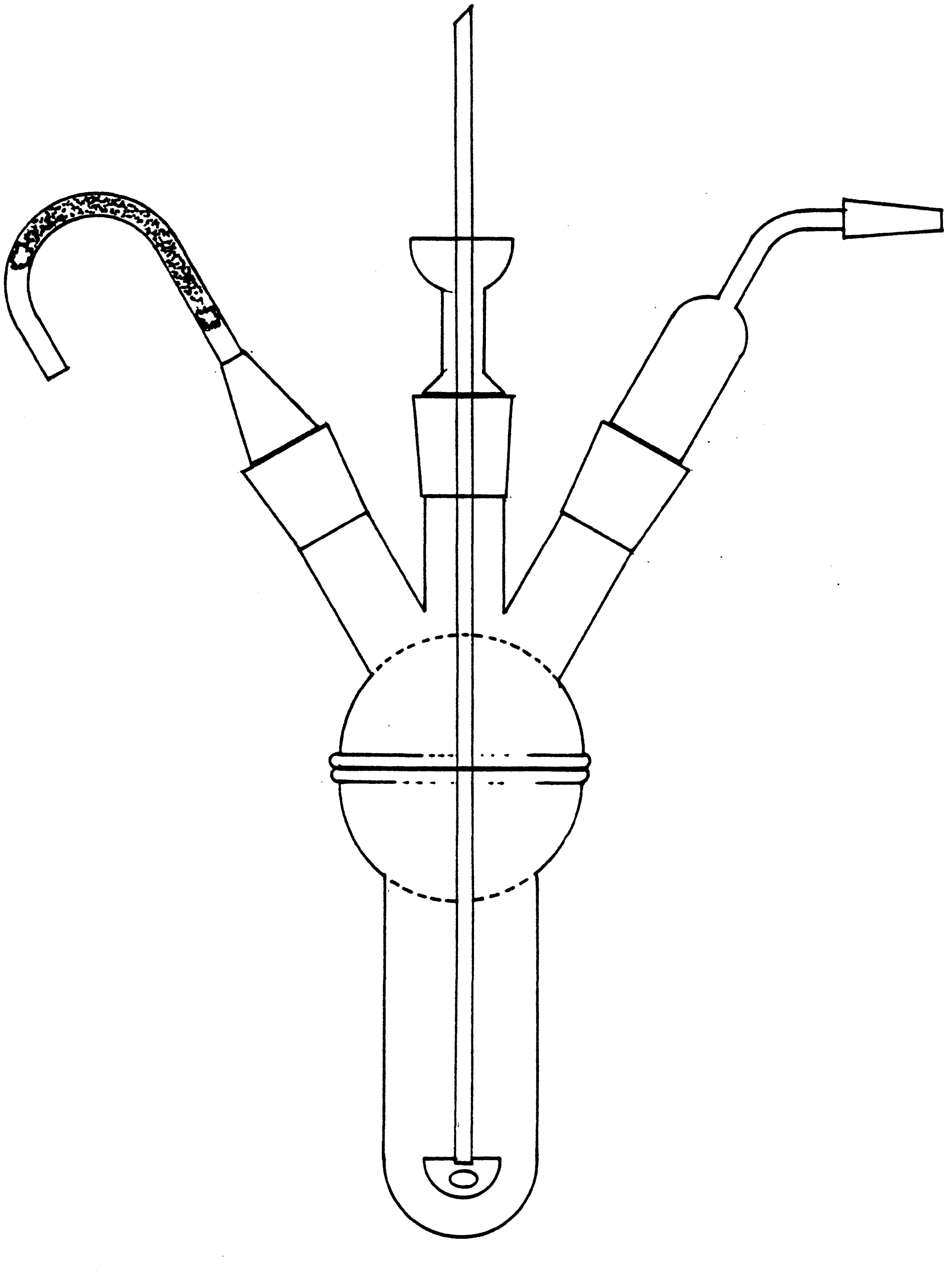


Figure 1: Apparatus for Bulk Polymerizations

transferred to a wide dish and placed in a vacuum oven at room temperature for three days. The crystalline melting point ranged between 41-44°C. If residual 2-ethylethoxy ether could be detected, the crystals were soaked in hexane for 2-3 days and redried.

Two different solvent systems were used in the polymerizations. A dimethylsulfoxide/toluene, (10/90), mixture was used with alkali metal hydroxide catalysts. Diglyme was the solvent of choice with all other catalyst systems. Dimethylsulfoxide was distilled from barium oxide under the reduced pressure of a water aspirator. Toluene and diglyme were distilled from calcium hydride at atmospheric pressure and reduced pressure respectively.

The reaction apparatus was first purged with argon. For the alkali metal hydroxide catalyzed reactions, the catalyst was charged with the Bis-A to the reaction flask. The catalyst concentration was approximately one mole percent based on DGEBA. The reactions were heated to the toluene reflux of about 115°C. The DGEBA was dissolved in toluene and added slowly to the reaction over a periods of 12 to 72 hours. Reaction solutions turned brown upon the first addition of DGEBA to the systems. The reactions were stopped approximately 24 hours after the completed addition of the DGEBA.

For the majority of the rest of the reactions, the DGEBA and the Bis-A were weighed out together in a teflon dish, then transfered to the reaction flask via a funnel. The funnel and the dish were then rinsed thoroughly with the reaction solvent, diglyme. The solution was then heated to the reaction temperature and the catalyst added. The reactions were run over a wide range of times. The reactions were initially clear but turned an opaque white as the reaction proceeded, thus indicating a phase separation.

For several of these reactions the DGEBA was added separately in the manner mentioned above for the alkali metal hydroxide catalyzed systems. At the completion of all the reactions, 100 ml of tetrahydrofuran were added to reduce the solution viscosity. This produced a transparent solution. The polymers were isolated by coagulating in a stirred 20/80 mixture of methanol to water. The polymers were then dried in a vacuum oven at 70°C for 24 hours.

Characterization

Infrared Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) spectra of the polyhydroxyethers were determined using a Nicholet MX-1 FT-IR. Samples were prepared by solution casting a film on a salt plate from a 5% solution in tetrahydrofuran.

Proton Nuclear Magnetic Resonance

Ten weight percent solutions of the polymers in deuterated chloroform were examined by high resolution ambient temperature ^1H NMR, using a Bruker WP-270 SY spectrometer operating at a proton frequency of 270.13 MHz. Typically, 32 transients with a recycle time of 2.5 seconds were accumulated and the resulting free induction decay was fourier transformed. Tetramethylsilane was used as the internal standard.

Carbon Nuclear Magnetic Resonance

Ambient temperature ^{13}C-NMR spectra of the polymers were obtained using a Bruker WP 200 SY spectrometer. The samples were all made up in deuterated chloroform (15% wt./vol.) and TMS was used as the internal reference. Usually 1500 free induction decays (FIDs) with a pulse delay of 4.0 seconds and a flip angle of 40° were accumulated and fourier transformed. A power gated pulse sequence was used to minimize dielectric heating of the samples. The NOE factors were not measured.

Gel Permeation Chromotography

Gel permeation chromotography was performed on a Waters 150-C ALC/GPC. The instrument was equipped with a refractive index detector. The columns were made of microstyragel of pore sizes 500 to 10^6. Elution volumes were calibrated to polystyrene molecular weight standards to calibrate the system. Samples were dissolved to a 0.25% weight by volume concentration in tetrahydrofuran.

Gel Permeation Chromotography-Differential Viscometer

Absolute number and weight average molecular weights were obtained using a combined GPC-differential viscometer apparatus. The apparatus determines the molecular weights by obtaining the hydrodynamic volumes for each particular polymer fraction by way of an universal calibration curve [63]. The hydrodynamic volumes are then multiplied by each fraction's measured intrinsic viscosity to obtain an average intrinsic molecular weight, which is then converted to a number and weight average molecular weight.

The differential viscometer calculates viscosity by measuring the change in pressure in certain flow columns between a pure solvent and a polymer solution using

$$P/P_1 = \eta_{sp}/(2\eta_{sp} + 4) \simeq \eta_{sp}/4 \qquad (24)$$

The differential viscometer used was a Viscotek Corp. model 100. The GPC and its operation conditions are described above.

Intrinsic Viscosity

The intrinsic viscosities of the polyhydroxyethers were measured in tetrahydrofuran at 25°C. Typically 3 flow times were collected for 3 different concentrations using a Cannon 100 viscometer.

Branching Analysis

Vapor Phase Osmometry-Epoxy Titration Analysis

Oligomer Synthesis

Two techniques were attempted to estimate the amount of branching in the polyhydroxyethers. In the first technique, oligomers were synthesized using an excess of DGEBA. The calculated number average molecular weight for the oligomers was 3000. The Carothers equation [64] was used to determine the mole ratio of the reactants.

The oligomers were prepared using the same apparatus used for the high molecular weight polymer synthesis. DGEBA and Bis-A were dried under vacuum for 12 hours. 30.00 grams, 0.088 moles, of DGEBA and

16.64 grams, 0.078 moles, of Bis-A were weighed into a teflon dish and transferred to the reaction flask via a funnel as described earlier. The solvent (diglyme) was added and the solution heated to a predetermined temperature. Once the temperature was obtained the catalyst was added by syringe.

Variables such as the catalyst type and concentration, reaction temperature, and percent solids were examined. The reaction time was held constant at 48 hours. Tetrahydrofuran (100 ml) were added at the end of each reaction to decrease the solution viscosity. The oligomers were coagulated in hexane, redissolved in tetrahydrofuran, filtered and then coagulated again in hexane.

The oligomers in all instances had the consistancy of a viscous glue. The materials were placed in an aluminum foil dish and allowed to air dry for one day. The materials were then placed in an oven under vacuum for an additional two days. The oven temperature varied between 60-80°C. Due to the large amount of solvent that was trapped in the glassy oligomers, at room temperature, the material foamed extensively when vacuum was first applied.

The final appearance of the oligomers depended on the drying temperature of the vacuum oven. At 60°C the final material appeared white and fluffy, but when the drying temperature was about 80°C, the material was a brownish hard solid. This behavior probably brackets the glass transition interval.

Vapor Phase Osmometry

The number average molecular weights of the oligomers were obtained by vapor phase osometry, VPO. The instrument used was a Wescan model

233. HPLC grade tetrahydrofuran was used as the solvent. The instrument was run at a temperature setting of 110, which corresponds to 40°C. For each samples, four different concentrations of the oligomer in the tetrahydrofuran were run along with one of the pure solvent.

For each sample a plot of $\Delta V/C$ vs C was made. ΔV here represents the change in the instrument's reading between the oligomeric sample and the pure solvent. The molecular weight of the samples were then calculated from equation 25.

$$MW = K/Y \tag{25}$$

where MW = the molecular weight of the oligomer

K = solvent constant

Y = the y intercept of the plot $\Delta V/C$ vs C

The constant K was determined from averaging experiments with two standards of known molecular weight. The standards used were sucrose octaacetate and squalane.

Epoxy Endgroup Titration

Titration of the epoxy units at the ends of the oligomeric chains was detemined both potentiometrically and by indicator color change. Approximately 0.06 grams of an oligomer was weighed out and dissolved in a 2/1, acetic acid/cholorobenzene solution. The sample was titrated with a standardized solution of hydrogen bromide, HBr, in acetic acid. A Fisher automatic titrator was used. Crystal violet was used as the color indicator.

Some of the polyhydroxyether oligomers would not dissolve in the acetic acid, chlorobenzene solvent. These samples were dissolved in a 50/50, acetic acid/tetrahydrofuran mixture. Titrations in this case were done manually using just the color change of the indicator to determine the endpoint. The color change observed was dark blue to greenish blue. The slight color change made it difficult to determine the exact endpoint.

Proton Nuclear Magnetic Resonance

The second procedure used to determine branching involved using proton nuclear magnetic resonance to distinguish between branched and nonbranched methine protons occuring along the polymer backbone.

For this procedure, 10% solutions were made of the polymers in deuterated chloroform (Aldrich) to which 1% tetramethylsilane was added as an internal standard. The solution was placed into two separate NMR tubes. To one tube 0.5 ml (800% molar excess) of trichloroacetyl isocyanate were added. A white precipitate often formed which quickly dissolved. The tubes were sealed, shaken and run under the same NMR conditions as those described previously.

Care was taken to use the same vertical scale for both the derivatized and the underivatized samples to ensure high precision possible. A check to insure complete derivatization had occurred was made on every sample by observing the loss of the hydroxyl proton peak at 2.8 ppm. In the epoxy terminated oligomers, however, this was not always possible due to the fact that the epoxy methylene peaks overlaps with the hydroxyl.

The standard deviation for this analysis was obtained using equation 26.

$$s = [\sum^{N}(x_i - x)^2/(N - Y)]^{1/2} \qquad (26)$$

where x_i = value for one data point of a sample

x = average of data for a particule sample

N = total number of analyses

Y = total number of sample sets

Confidence intervals were obtained using equation:

$$\text{confidence interval} = t \cdot s/\sqrt{M} \qquad (27)$$

where t = 1.64 (90% Confidence Limit)

M = number of analyses for one particular sample

Several data points were rejected under the guidelines of the Q Criteria Test [64].

Kinetics of Urethane Crosslinking Reaction

Synthesis of Model Epoxy Resin

A low molecular weight compound which could serve as a model for polyhydroxyethers and epoxy resin was synthesized as a control. Di(4-t-butylphenyl 2-propanol ether) of bisphenol A, EpOH2, was chosen as the model epoxy compound. It was synthesized from DGEBA and para t-butylphenol under basic conditions as described below.

The purification of DGEBA from Dow's DER 332, was discussed above. Para t-butylphenol (Aldrich) was recrystallized from hexane. The crystals were dried in a vacuum oven at 60°C for 12 hours. The melting point of the crystals was approximately 99°C.

The t-butylphenol and sodium hydroxide were weighed directly into the reaction flask. The best results were obtained using three moles of t-butylphenol and 0.02 moles of sodium hydroxide for each mole of DGEBA. The apparatus was assembled as shown in Figure 2. The solvent consisted of a 10/90 dimethylsulfoxide/toluene mixture was added. Both the dimethylsulfoxide (DMSO) and the toluene were distilled from calcium hydride, with DMSO under water aspirator vacuum. The apparatus was purged with argon.

The reactions were run at a 25% solid content and heated to the reflux of the system, (115°C). After 6-8 hours the solutions were observed to have developed a greenish tint.

The DGEBA was dissolved in a minimum amount of toluene and added slowly over a period of a hour from the addition funnel. The solutions turned brownish with the first addition of the DGEBA but slowly turned to a deep reddish brown during the course of the reaction (~ 4-6 hours).

The solutions were purified by first dissolving 150 ml of ethyl ether and extracting twice with equal amounts of water. This procedure was effective in removing DMSO from the solution. The solutions were then washed several times with aqueous sodium hydroxide to remove

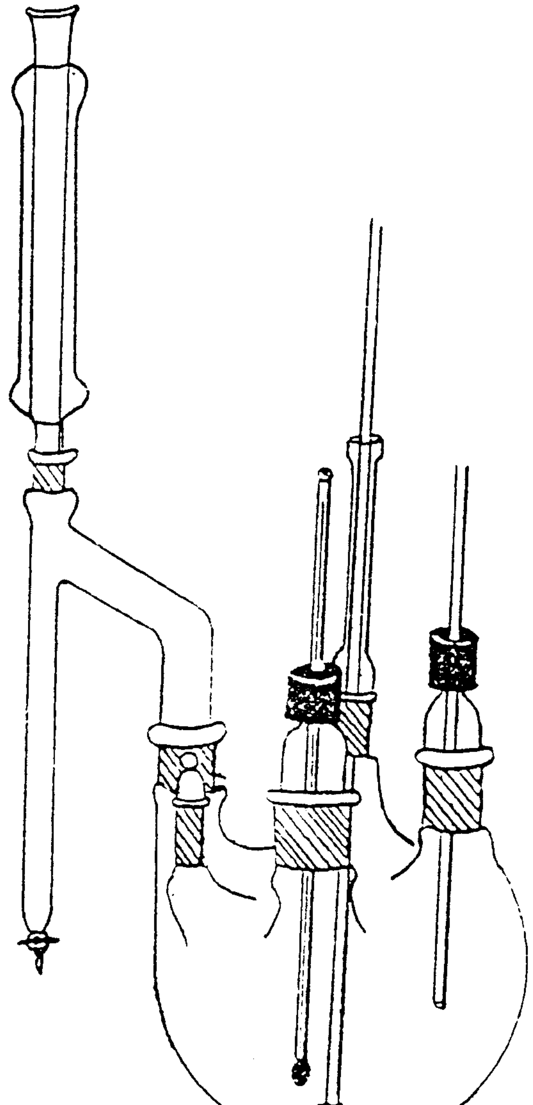


Figure 2: Apparatus for EpOH2 Synthesis

excess t-butylphenol. It was observed that when DMSO was not first extracted by water, the solution temperature increased, causing loss of the ether solvent. The solutions were washed finally with water until a neutral pH was obtained.

The solutions were then transferred into a flask and dried with either sodium or magnesium sulfate. After filtering off the sulfate, the ether was removed by evaporation. The resulting material was a soft, tacky, light brown solid. Several attempts were made to remove the brown color by adding carbon black to a heated solution of the material in ether and then passing it through celite. This tended to lower the final yield without, unfortunately, removing the color.

The crude product was then redissolved in toluene and passed through a four inch silica gel column, 80-200 mesh, followed by removal of the toluene. Methanol and hexane were added to the material during the evaporation to assist in the removal of the toluene. The product was then dried in a vacuum oven at 60°C for 36-72 hours, yielding a brittle semi-solid which softened around 35°C. The recovered yield usually ranged between 60-70%.

Characterization of Model Epoxy Resin

The purity of the product was first compared with t-butylphenol and DGEBA by thin layer chromotography using a mobile phase of 10/90 ethyl acetate/methylene chloride.

Infrared Spectroscopy

Fourier transform infrared spectroscopy was used to check for residual epoxy groups by examining the peak appearing at 917 cm^{-1}. Care was taken to be sure that all ethyl ether was removed from the product since the ether linkage also absorbs at 917 cm^{-1}. The samples were made by dissolving the EpOH2 in ethyl acetate and transferring the solution to a salt plate. The ethyl acetate was subsequently removed by warming the plate with a heat gun.

Proton Nuclear Magnetic Resonance

Proton nuclear magnetic resonance spectra were conducted on the product using a Varian EM-390 NMR. The samples were dissolved in deuterated chloroform. Tetramethysilane was used as the reference.

Secondary Hydroxyl Titration

Titrations were performed on the secondary alcohols of the EpOH2. The EpOH2 was dried in a vacuum oven at 60°C for 12 hours. Approximately one gram of the material was weighed out and transferred to each of three 100 ml round bottom flasks. A solution of 40 ml of pyridine and 2 ml of acetic anhydride was made. The reagents were distilled from calcium hydride at atmospheric pressure and from magnesium respectively.

After flushing the flasks with argon, four milliliters of the solution were added to the EpOH2 along with a stirring bar. The flasks were sealed with a ground glass stopper. The seal between the stopper and the flask was wrapped in teflon tape. The flasks were then lowered into a silicone oil bath set at a temperature of 70°C. A blank of just acetic anhydride and pyridine was also included in the series of experiments.

After the reactions were run for 48 hours, ten drops of freshly boiled distilled water were added to each flask to convert any unreacted anhydride to acetic acid. Several drops of cresol red were added as an indicator. The solutions were titrated with 0.1N alcoholic potassium hydroxide (Fisher) to an endpoint determined by the change in color of the indicator. In some cases the color change was difficult to monitor due to the brown color of the EpOH2 solution.

The molecular weight of the EpOH2 was determined from the titration data using the assumption that only two hydroxyl groups were present per molecule.

To check the accuracy of this procedure, 2-propanol, 3-octanol and para t-butylcyclohexanol were titrated by the above procedure. 2-propanol and 3-octanol were distilled from calcium hydride while the t-butylcyclohexanol was recrystallized from hexane.

Beer's Law Calibration Curves

Infrared spectroscopy was used to study the kinetics of the reaction between phenyl isocyanate and the model epoxy. Two calibration curves were made using Beer's law, relating concentration to absorbance. One curve was for the isocyanate peak appearing at 2260 cm^{-1} and the other for the urethane peak at 1740 cm^{-1}.

Phenyl Isocyanate

The phenyl isocyanate (Aldrich) was distilled at approximately one torr and 55°C. The purity of the isocyanate was checked by a back titration as follows. The isocyanate was reacted with excess dibutylamine over 60-80°C for 15 minutes. The excess unreacted amine was titrated with 0.1N alcoholic hydrogen chloride (Fisher).

The cell used for the IR study was a Wilmad 0.025 mm KBr liquid cell. A series of concentrations of phenyl isocyanate in o-dichlorobenzene were employed. O-dichlorobenzene was chosen as the solvent due to its high boiling temperature, inertness and its complete tramsittance of light in the region of isocyanate absorbtion. The o-dichlorobenzene was distilled from calcium hydride under vacuum. Care was taken to partially fill the volumetric flasks with o-dichlorobenzene before weighing out the phenyl isocyanate. This was done to limit the contact between the moisture in the air and the isocyanate. The spectra were determined and the results plotted according to Beer's law. The resulting line had a 0.995 correlation coeffient.

Urethane Calibration Curve

A calibration curve to relate the urethane absorbance to concentration was also needed to verify the quantitative conversion of the isocyanate to urethane. Any undetected side reaction involving the phenyl isocyanate would of course upset the kinetic results.

The urethane used in plotting the calibration curve was 3-octylphenyl carbamate. This compound was synthesized via the reaction of phenyl isocyanate and 3-octanol at 50°C for one hour using a catalytic amount of dibutyltin dilaurate. Some white precipitate was formed during the reactions, which was possibly an urea. The white material was filtered off and not used further.

Recrystallization of the urethane was attempted in a number of solvents but with no success. The product was passed through silica gel to separate any unreacted alcohol. The product was characterized by ^{1}H-NMR using the EM-390 NMR.

The urethane calibration curve was made in the same manner as the isocyanate curve. The results also gave a correlation coefficient of 0.993.

Kinetic Reaction

The urethane reactions were run in a four neck 250 ml round bottom flask. One neck was connected to a y-shaped adapter with a thermometer and an argon inlet. A condenser, overhead stirring rod and a stopper with a septum were each attached to the remaining necks.

The EpOH2 was first dried by placing it inside a 60°C vacuum oven for a period of 12 hours. For ease of handling the EpOH2 was weighed out while still warm and transferred to the reaction flask. The apparatus described above was assembled and purged with argon. The system was lowered into an oil bath preset at a given temperature. The temperature was held to within ±0.5°C of the set mark. Twenty milliliters of o-dichlorobenzene were added to the flask and allowed to stand for 15 minutes to dissolve the EpOH2. After the epoxy had dissolved stirring was started and the solution was heated to the reaction temperature. Phenyl isocyanate was measured out using a 1 ml syringe which had a precision of ± 0.05 ml.

An initial sample was removed after approximately 30 seconds and injected into the liquid cell. The infrared spectrum regions around 2260 and 1740 cm^{-1} were expanded in order to examine the isocyanate and urethane peaks respectively. The IR plotted out the peak absorbances. The C-H stretch at 2965 cm^{-1} of the methyl units was also expanded to check that path length of the liquid cell remained constant.

Samples were withdrawn at different time intervals depending on the reaction conditions. The reaction temperature was checked at each sample time.

In some cases a catalyst was used. Approximately 0.1 grams of a catalyst was dissolved in 10 ml o-dichlorobenzene and then added to the reaction via a 0.05 ml micro syringe. The catalyst addition came after the isocyanate had been added and a sample had been withdrawn. All reactions, catalyzed and noncatalyzed, were stopped after the reaction of 90% of the isocyanate.

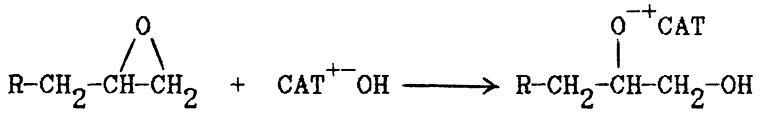
A confidence interval for all the infrared data, in absorbance units, was obtained using equations (26) and (27). Rate constants for the kinetic study were obtained from linear regression of the data plotted in accordance to second order kinectics.

RESULTS AND DISCUSSION

Polyhydroxyether Synthesis

Synthesis

Polyhydroxyethers were synthesized via the advancement process (Figure 3). The reaction is initiated by the abstraction of a proton form Bis-A by a basic catalyst, to form a Bis-A phenate. As discussed earlier, the reaction can also be initiated by the catalyst attacking an epoxy ring, shown below.



$$R\text{-}CH_2\text{-}\overset{O}{\overbrace{CH\text{-}CH_2}} + CAT^{+-}OH \longrightarrow R\text{-}CH_2\text{-}\overset{O^{-+}CAT}{\overset{|}{CH}}\text{-}CH_2\text{-}OH \qquad (28)$$

The latter reaction has been found to occur to only a very small extent as will be discussed later.

The extent to which phenate is formed by the first reaction is dependent on the basicity on the catalyst used. The polymerization proceeds by the reaction of the phenate with the epoxy ring forming a secondary alkoxide. The alkoxide then abstracts a proton from the acidic free phenolic unit to form an alcoholic group pendant to the polymer backbone. The abstraction of the proton also forms a new phenate group which in turn attacks another epoxy. When the reaction is repeated ideally, a linear polymer forms.

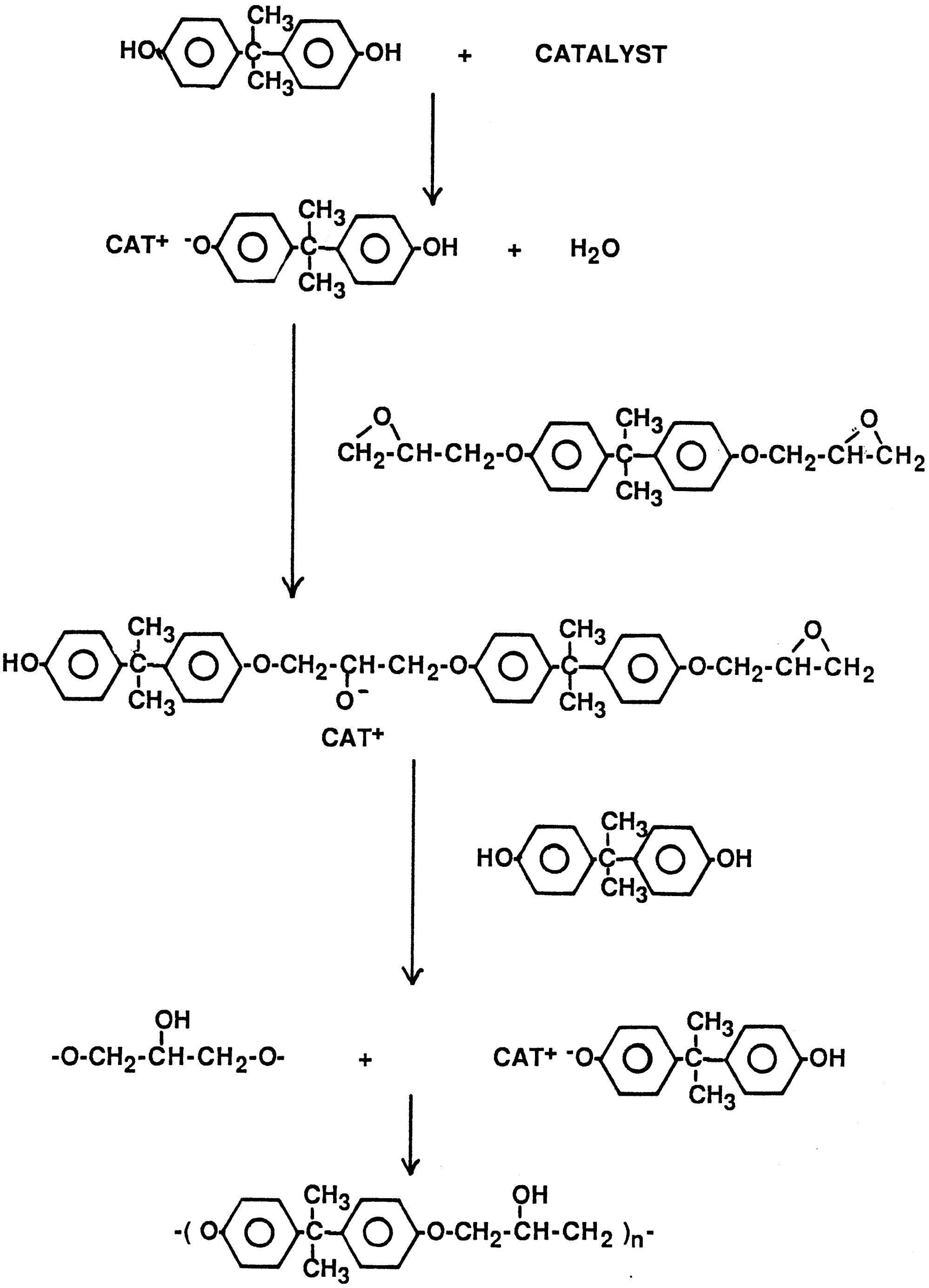


Figure 3: Reaction Mechanism for the Synthesis of Polyhydroxyether

A side reaction (Figure 4) may occur however during the course of the polymerization via the alkoxide formed in Step 3 of Figure 3. The alkoxide formed is a stronger base than a phenate group and therefore can attack an epoxy group thus forming a branched chain pendant to the main polymer backbone. The branched chain can further react to lengthen the chain, form branches off the branched chain, or react with an alkoxide pendant from another polymer chain to form a crosslink.

The branching reaction is generally not desired since it upsets the molar ratio between the two monomers, disrupting control over polymer molecular weight and widening the molecular weight distribution.

The branching reaction can occur at two different steps in the reaction. The first is when the alkoxide is initially formed and has not had time to abstract a proton from a Bis-A molecule. For further reference, this will be labeled as mode 1. Mode 2 branching occurs after the alkoxide has abstracted a proton to form an alcohol. The alcohol under basic conditions can react with an epoxy ring producing a branched chain. The exact mechanism for this reaction has not been clarified in the literature. Undoubtedly though, the basic catalyst must first abstract the proton from the alcohol, in a type of complex.

The second mode may play a major role in branching in the synthesis of low molecular weight epoxy terminated oligomers. During the course of the reaction free phenol from Bis-A prevents the catalyst from abstracting a proton from the alcohol. However, as the reaction nears completion, the concentration of free phenolic groups becomes negligible, while the concentration of alcohol increases. Such stoichiometry allows the catalyst to complex with the alcohol

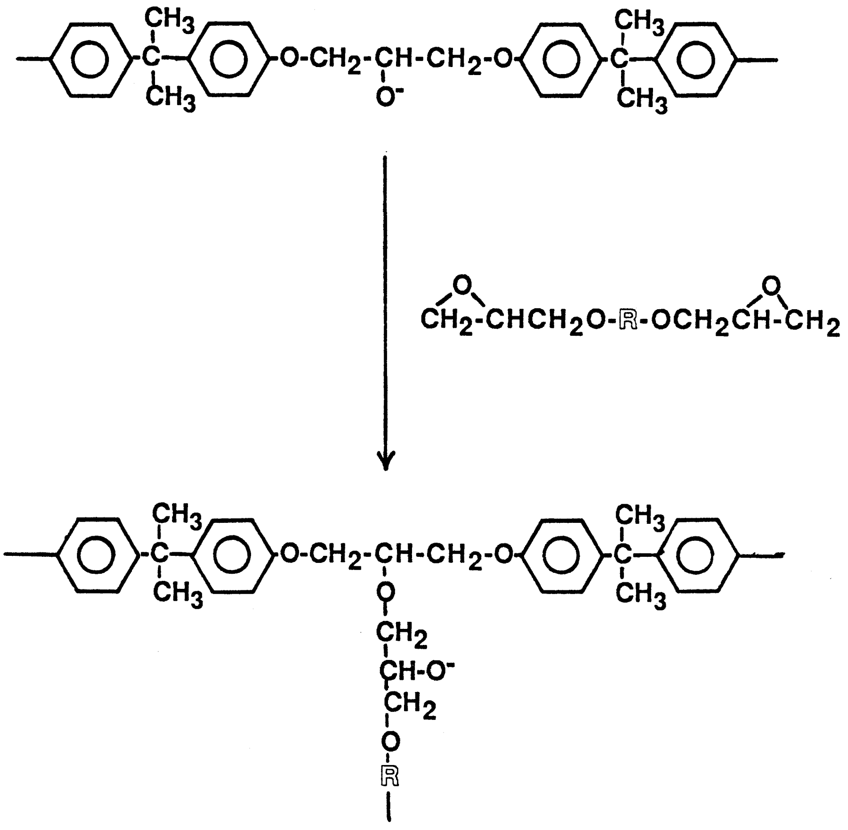


Figure 4: Reaction Mechanism for the Branching Side Reaction in the Synthesis of Polyhydroxyethers

which in turn reacts with an epoxy group which could still be present in significant concentration. The majority of branching would therefore likely come toward the end of the reaction, as has been suggested by others.

This mode of branching could not, however be applied to infinite molecular weight polymerizations (networks) since at the end of the reaction the concentration of epoxy endgroups would be equal to or even less than the concentration of free phenol. Therefore, the probability of mode 2 branching would remain small throughout the reaction.

Alkaline Metal Hydroxide Catalyst

Synthesis of linear high molecular weight polyhydroxyethers was first attempted in this study with the alkaline metal hydroxide catalysts (Table 5). During each reaction the DGEBA was added slowly in order to minimize the concentration of free epoxy groups in hopes of eliminating the first mode of branching. Unfortunately only oligomeric products were obtained.

Quaternary Ammonium Hydroxides

As mentioned previously, quaternary ammonium hydroxides, using diglyme as a solvent, has been used in the formation of polyhydroxyether [27]. The possible success of this catalyst relative to the alkaline metals may be explained as illustrated in Figure 5. Once the alkoxide is formed its reactivity should be greatly dependent on the size and position of the counter cation from the catalyst. A counter

TABLE 5

Alkali Metal Hydroxide Catalysts for Polyhydroxyether Synthesis

CATALYST	SOLVENT	TEMP (C)	RESULTS
LiOH	TOLUENE/2-EEE	115	OLIGOMER
NaOH	TOLUENE/DMSO	115	OLIGOMER
KOH	TOLUENE/DMSO	115	OLIGOMER

DGEBA added to the reactions over a period of 12 hours.

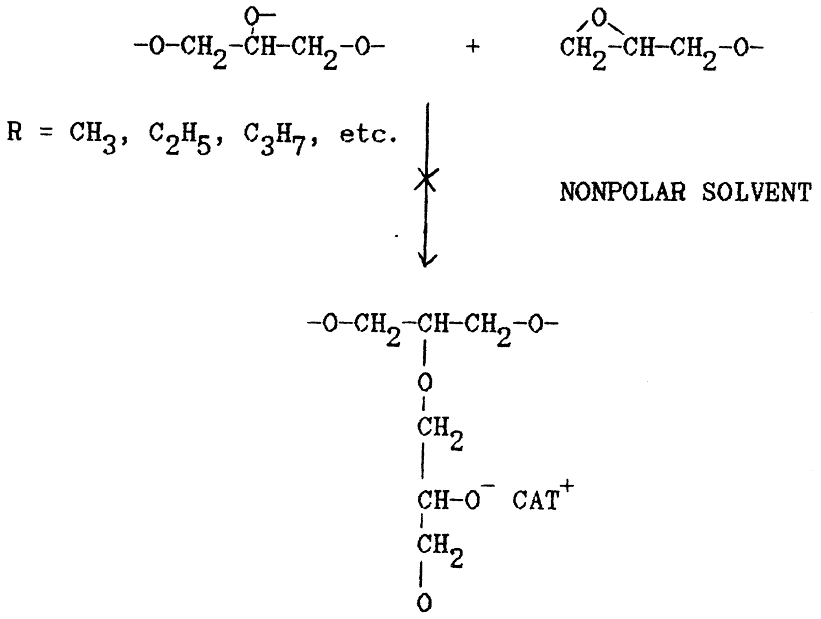


FIGURE 5: Possible Mechanism to Reduce the Branching Side Reaction Using a Hindered Counter Ion Catalyst

ion which has dangling alkyl groups on it, such as a quaternary ammonium hydroxide, could sterically hinder the approach of the epoxy to the alkoxide without preventing the proton transfer necessary to form the alcohol. The relative nonpolarity of the solvent, DMSO to diglyme, would perhaps increase this effect by maintaining a tight ion pair.

Table 6 shows the results of reactions run in diglyme using various quaternary ammonium hydroxides. In several instances high molecular weight materials, $[\eta] > 0.6$, were obtained. A problem in reproducibility of several of the experiments was observed which was believed due to the high viscosity of the solutions, preventing reproducible agitation. Running reactions with additional solvent, monomer/solvent < 0.25, however, failed to product high molecular weight material under the conditions studied.

The lack of reproducible stirring makes the task of comparing the effectiveness of the catalyst difficult. The problem of comparison is compounded by the fact that as the viscosities increased, the reactions proceeded under diffusion control, minimizing the differences due to kinetic effects.

A kinetic plot of a reaction run using tetrabutylammonium hydroxide (Figure 6) shows a upturn in the molecular weight after 15 hours. After the upturn, it appears the number average molecular weight, Mn, levels off while the weight average molecular weight, Mw, continues to increase. Whether this is an indication of mode 2 branching, is still uncertain. Another interesting effect is the decline in Mn and Mw between the fourth and fifth data points. After the fourth sample was

TABLE 6

Tetraalkyl Ammonium Hydroxide Catalysts for the Synthesis of Polyhydroxyethers

CATALYST	% SOLIDS	TEMP (°C)	TIME (HRS)	$[\eta]$THF 25°C	Mn (10^{-3})	Mw/Mn
TMAH	50	100	45	0.56	27	3.2
	50	100	30	0.56	-	-
	80	110	16	0.45	21	3.3
TEAH	50	100	56	0.38	14	3.6
	50	100	48	0.22	-	-
	75	130	2	1.30	65	3.0
TPAH	50	100	24	0.40	24	2.5
	50	100	56	-	2	4.0
	70	100	24	0.31	22	2.0
	80	125	2	0.50	24	2.8
TBAH	15	100	36	0.19	7	2.0
	25	100	48	NO POLYMERIZATION		
	35	110	30	0.92	80	2.7
	50	100	16	0.26	16	3.0
	60	105	42	0.86	50	2.7
	60	100	40	0.40	19	2.1
	75	120	5	0.45	27	3.0
	80	100	0.5	1.07	28	6.1

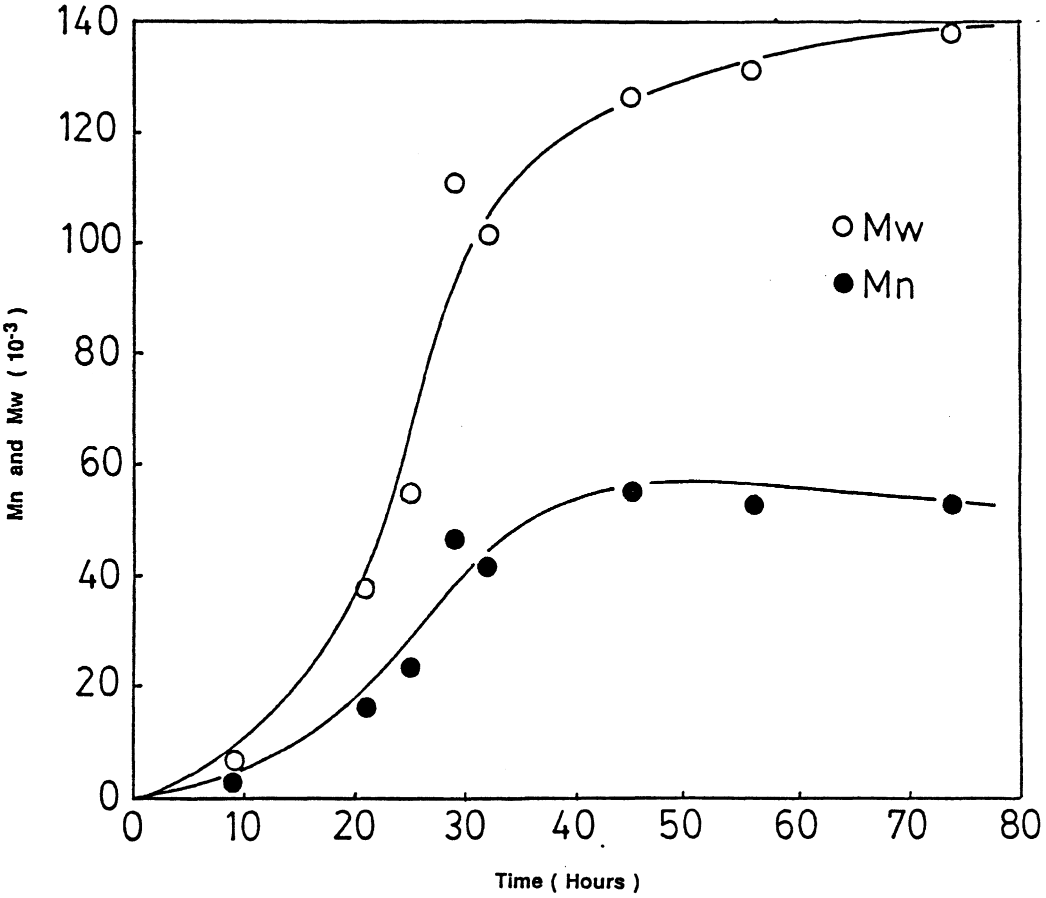


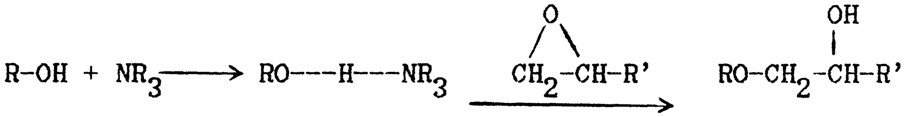
Figure 6: Mn and Mw versus Time for a Polyhydroxyether Synthesis using TBAH at 100 °C

taken, an additional 20 ml of diglyme was added to reduce the solution's viscosity. Whether this effect is real or if it is, what is the reason behind it, is also not understood.

Although the catalysts used were obtained in solutions of either methanol or water. No significant differences were observed between the two different catalyst solvents.

Trialkylamines

Trialkylamine catalysts are of interest in the study of the second mode of branching. Amines have been shown in the literature to be unable to abstract a proton from an alcohol. Therefore if branching occurred through mode 2, it would do so through some sort of a non-ionic alcohol-amine complex.



$$\text{R-OH} + \text{NR}_3 \longrightarrow \text{RO---H---NR}_3 \xrightarrow{\overset{\text{O}}{\text{CH}_2\text{-CH}}\text{-R'}} \text{RO-CH}_2\text{-}\overset{\text{OH}}{\text{CH}}\text{-R'} \qquad (29)$$

Lower molecular weights were obtained using trialkylamine catalysts (Table 7) as compared to quaternary ammonium hydroxides catalysts. This would be expected since the basicity of the amines is less than that of the ammonium hydroxides. With the decrease in basicity one could postulate that a smaller concentration of phenate would be formed, causing the rate of reaction to be much slower.

From the data in Table 7 it is seen that the triheptyl and tridodecylamine systems, while having the greater Mn (based on polystyrene), also had narrower distributions. This may be due to

TABLE 7

Trialkylamine Catalysts for the Synthesis of Polyhydroxyethers

CATALYST	% SOLIDS	TEMP (C)	TIME (HRS)	[η]THF 25°C	Mn (10^{-3})	Mw/Mn
TRIPROPYLAMINE	60	105	56	0.32	7.8	3.2
TRIBUTYLAMINE	50	100	56	0.26	8.7	3.4
TRIHEPTYLAMINE	50	100	68	0.35	12.3	3.1
TRIDODECYLAMINE	50	100	72	0.32	11.2	2.6

these amines having a greater basicity while at the same creating more steric hinderance to branching than the tripropyl and tributylamines. The experimental error in the numbers stated in the table are not known however, thus leaving a question concerning the validity of the trend.

Temperature Effects on Polymerizations

Next, the effect of temperature was studied (Table 8). For quaternary ammonium hydroxide catalyzed systems, higher molecular weight materials were obtained at 100°C than at 130°C. Adding the DGEBA slowly at 130°C in hopes of reducing mode 1 branching made little difference in the final molecular weights.

It would be expected that as temperature is raised, the degree of branching would increase. This is due to the assumption that the linaer polymerization reaction must have a lower activation energy compared to the branching reactions, since it is the linear reaction which dominates. Therefore as the temperature is increased, the percentage of epoxy groups forming branches should increase.

The additional branching should cause a larger distribution of molecular weights and assuming no crosslinking, a smaller Mn. Even though a smaller Mn is observed, no increase in distribution is observed.

For reactions run using trialkylamines, no measurable different was observed for the reactions run at 100°C and 130°C.

TABLE 8

Effect of Temperature on the Synthesis of Polyhydroxyethers

CATALYST	% SOLIDS	TEMP (°C)	TIME (HRS)	[η]THF 25°C	Mn (10^{-3})	Mw/Mn
TBAH	50	105	42	0.86	50	2.7
TBAH	50	130	50	0.40	22	2.5
TBAH	50	130	50	0.40	24	2.4
TRIBUTYLAMINE	50	100	56	0.26	9	3.4
TRIBUTYLAMINE	50	130	70	0.02	6	2.5
TRIBUTYLAMINE	80	130	5	0.22	9	3.4

DGEBA slowly added to the reaction over a period of 18 hours

Catalyst Concentration Effect on Polymerizations

Table 9 shows the effect of catalyst concentration on polymerization reactions. It would be expected that a decrease in catalyst concentration would cause a decrease in the reaction rate and therefore a lower molecular weight polymers for reactions run for about the same amount of time. Results do show a decrease in molecular weight was associated with a decrease in catalyst concentration. Starred reactions indicate where only half the catalyst was charged at the start of the reaction; this does not appear to play a factor.

The degree of branching would be expected to remain constant, assuming only mode 1 branching occurred.

$$R_L = k_L \, [\,RO^-] \, [BIS\text{-}A] \tag{30}$$

$$R_B = k_B \, [RO^-] \, [DGEBA] \tag{31}$$

In the polymerization reaction run, the concentration of Bis-A and DGEBA were equal. So from equations (30) and (31) it can be seen that with an increase in catalyst concentration, the concentration of alkoxide would increase but the ratios of R_L to R_B would remain the same.

Miscellaneous Catalysts

Table 10 includes a series of miscellaneous catalysts and combination of catalysts used. Of the catalysts shown, triphenylphoshine gave the best results. D. Lunsford [21] also showed

TABLE 9

Effect of Catalyst Concentration on the Synthesis of Polyhydroxyethers

CATALYST	CAT CONC.	% SOLID	TEMP (°C)	TIME (HRS)	$[\eta]$ THF 25°C	Mn (10^{-3})	Mw/Mn
TBAH	0.007*	55	105	42	0.86	50	2.7
TBAH	0.004	50	100	48	0.70	45	2.4
TBAH	0.004*	50	100	96	0.72	46	2.7
TBAH	0.002	60	100	56	0.40	19	2.2

*Half of the catalyst added initially, the other half after 12-18 hours.

that triphenylphosphine was an effective catalyst, obtaining an intrinsic viscosity of 0.70 dl/gm.

The combination of tetrabutylammonium hydroxide and tributylamine was used to check the possible partial degradation of tetrabutylammonium hydroxide to tributylamine by the Hoffmann process.

$$R_4N^{+-}OH \longrightarrow R_3N + \text{Alkene} + H_2O \qquad (32)$$

The results obtained however, did not show it to be a superior catalyst system.

TABLE 10

Miscellaneous Catalysts for the Synthesis of Polyhydroxyethers

CATALYSTS	% SOLIDS	TEMP (°C)	TIME (HRS)	$[\eta]$THF 25°C	Mn (10^{-3})	Mw/Mn
TRIPHENYLPHOSPHINE	50	105	68	0.35	13	2.3
2,4,6 TRIMETHYLPYRIDINE	50	100	48	0.19	6	3.8
DIETHANOLBUTYLAMINE	50	100	53	NO POLYMERIZATION		
DIBUTYLAMINE	50	105	72	0.12	5	2.4
TETRAMETHYL AMMONIUM IODIDE	25	100	36	NO POLYMERIZATION		
TBAH & TRIBUTYLAMINE	60	100	48	0.46	27	2.4

Branching Determination

Titration and VPO Analysis

Due to the negative effects of branching mentioned earlier, an attempt was made to create a procedure whereby the degree of branching could be determined in the polyhydroxyethers synthesized. The optimum conditions to limit branching could then be determined.

Two procedures were explored for this analysis. The first involved the synthesis of epoxy terminated oligomers which could be titrated to determine moles of epoxy per gram of sample, while also having their number average molecular weights determined by vapor phase osmometry. The oligomers were synthesized following the same reaction mechanism, as the polymers mentioned earlier (Figure 3).

Equation (33) was used to calculate the number of branches on an average chain.

$$B = (N)(V)/(W/M) - 2 \tag{33}$$

where B = the number of branches

N = the normality of the titrate

V = the volume of the titrate

W = the weight of the sample

M = number average molecular weight of the oligomer

The subtraction of two in the equation was needed since the oligomers were epoxy terminated, so even a linear chain would have two epoxy groups.

The results from this procedure using potentiometric titrations are shown in Table 11. The negative results obtained would tend to indicate a number of chains were capped with phenolic groups instead of epoxy. This would imply that a large amount of branching occurred, lowering the concentration of excess epoxy and allowing phenolic groups to remain unreacted. The possibility of this occurring was rejected however since such a large amount of branching would almost certainly cause the reaction to gel and no such gel was observed. It is believed that the negative results are due to a flaw in the technique itself.

The HBr titration of epoxy groups, while effective for monomers, does not seem to be quantitative for oligomeric materials. A nonquantitative reaction between the epoxy endgroups and the HBr would cause the calculated moles of epoxy per gram of sample to be lower than its actual value and therefore lower the calculated number of branches. A possible superior technique which was not attempted due to time restrictions, would be to perchloric acid as a titrant [66].

Negative results were also obtained for titrations done manually, shown by *, using THF/acetic acid as the solvent and crystal violet as a color indicator. The color change associated with the titration endpoint using this indicator was only a change in the shade of blue which made the probability for error a concern.

Non reproducible results were also a problem using the VPO. Molecular weights obtained using THF as the solvent were as much as

TABLE 11

Branching Determination of Polyhydroxyether Oligomers Using Epoxy Titration and Vapor Phase Osmometry

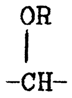
Sample	Moles Epoxy Per Gram of Sample	Mn (VPO)	Number of Branches
3/65	6.3×10^{-4}	1700	-0.9
3/65*	5.4×10^{-4}	1700	-1.1
3/67	6.2×10^{-4}	2400	-0.5
3/70	6.7×10^{-4}	2100	-0.6
3/71	1.1×10^{-3}	1800	-0.1
3/79*	4.1×10^{-4}	2700	-0.9

twice the value as the results using methylethyl ketone. Unfortunately due to time restrictions, these variations were not explored further and the entire technique was dropped.

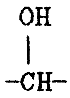
^{1}H-NMR Analysis

The second procedure explored to determine branching involved the use of nuclear magnetic resonance. The focus of attention centered around the differences between the methine carbon and proton of a branched linkage compared to a nonbranched linkage.

(branched)



$\overset{\overset{\text{OR}}{|}}{\text{-CH-}}$



$\overset{\overset{\text{OH}}{|}}{\text{-CH-}}$

(nonbranched)

The carbon 13 NMR (Figure 7) shows no separation of the two carbon peaks. The same is true for the methine protons using ^{1}H-NMR (Figure 8).

In order to separate the proton peaks, derivatization of the nonbranched hydroxyl group was made using trichloroacetyl isocyanate (Figure 9). The isocyanate reacts almost instantly with the hydroxyl to form a carbamate but cannot break the ether linkage of the branched structure. The electronegative character of the carbamate group, shifts the nonbranched methine proton downfield away from the branched methine (Figure 10 and Table 3).

The branched methine unfortunately is overlapped by the shift of the nonbranched methylene peak and therefore cannot be used to determine amount of branching directly. The relative amount of

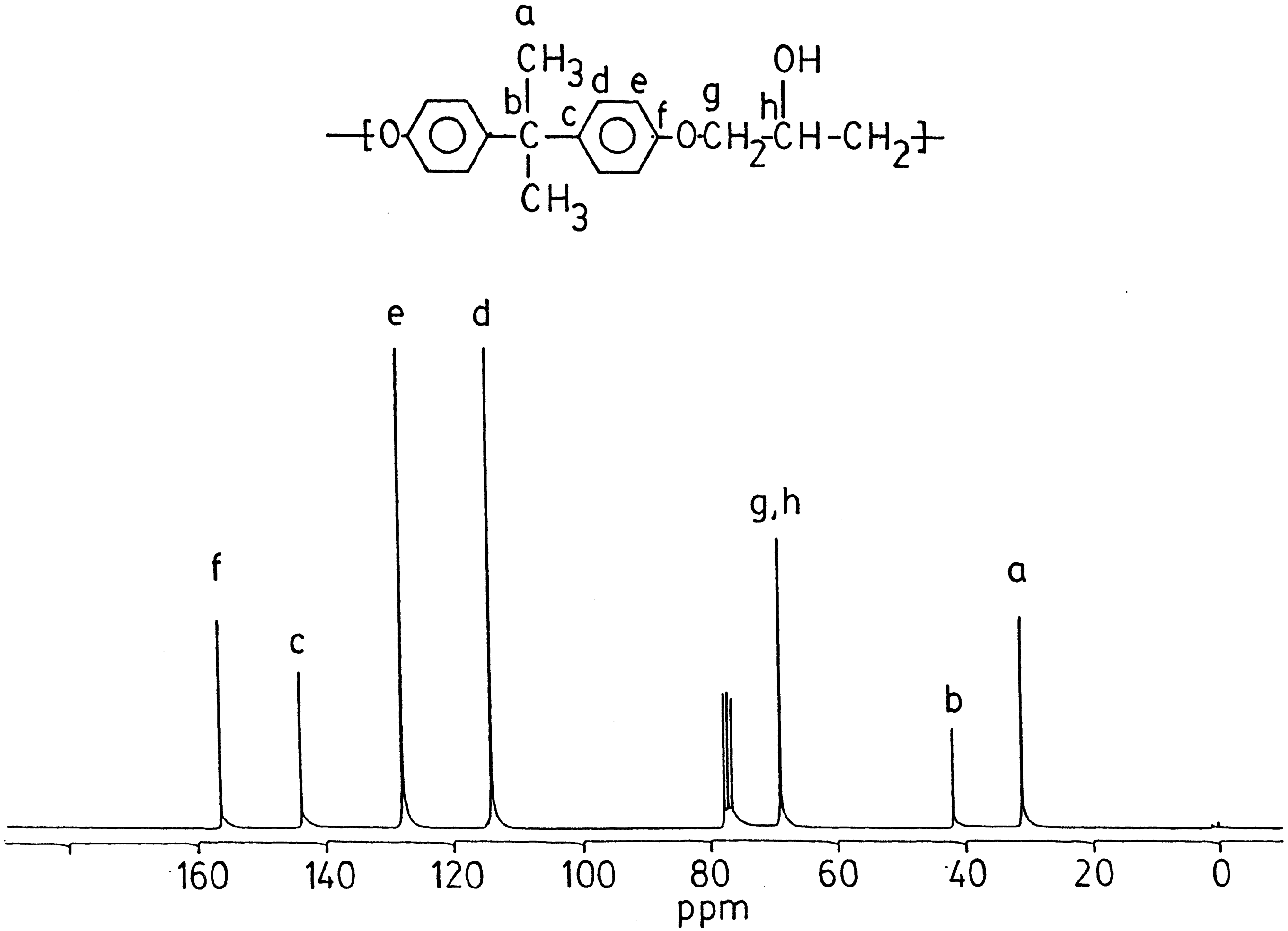


Figure 7: ^{13}C-NMR Spectrum of a Polyhydroxyether

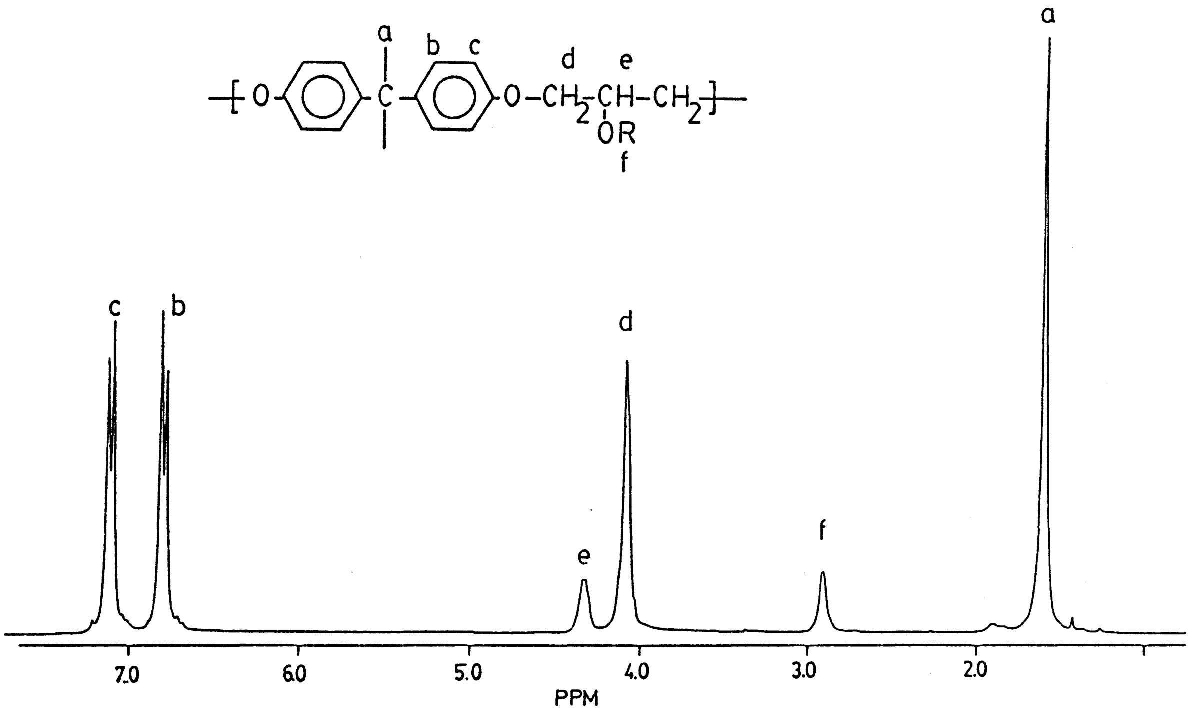


Figure 8: ¹H-NMR Spectrum of a Polyhydroxyether

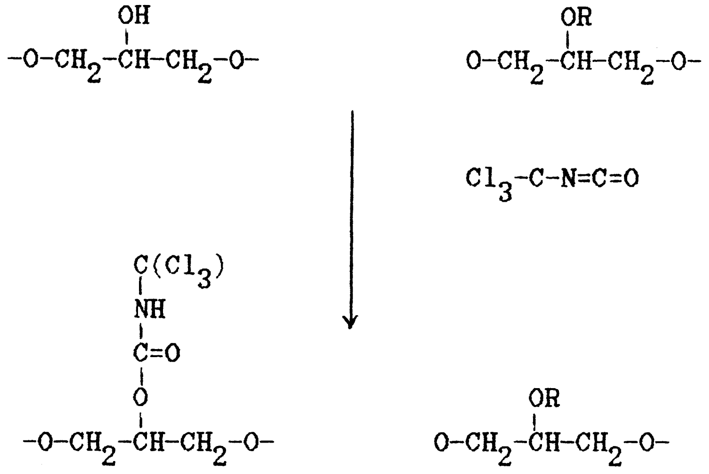


Figure 9. Derivatization of a Polyhydroxyether with Trichloroacetyl Isocyanate

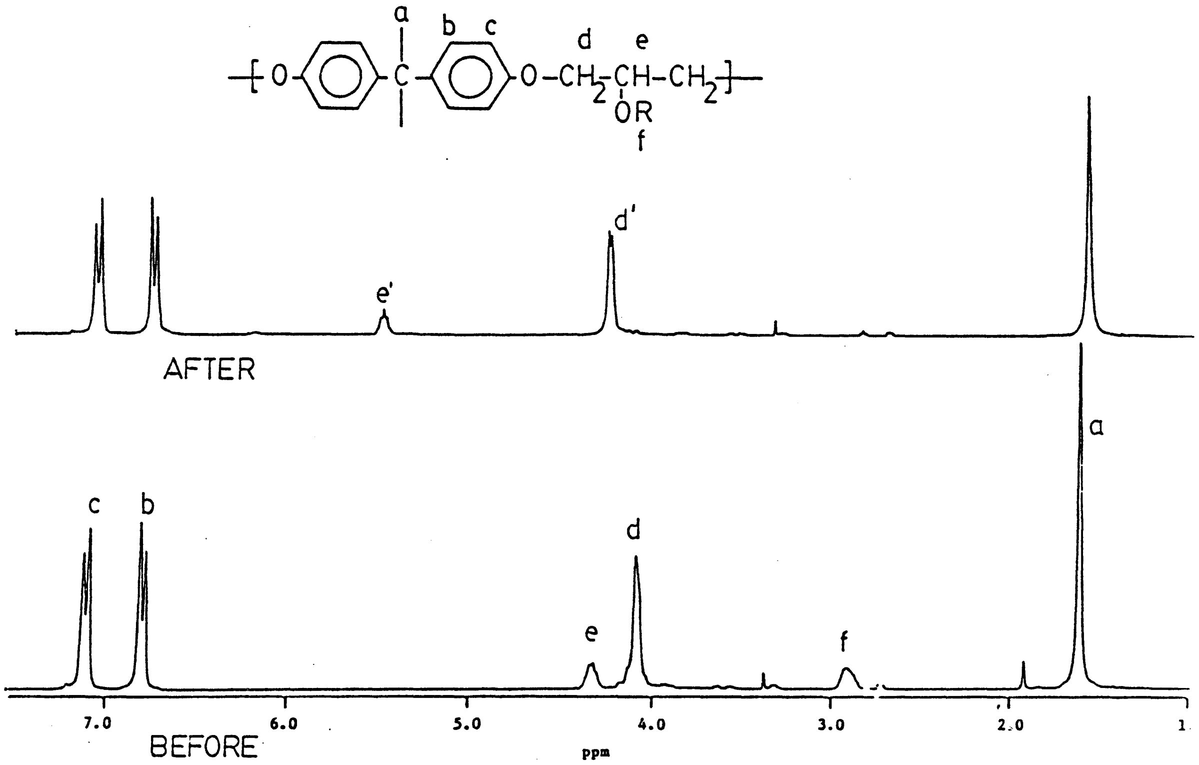


Figure 10: H-NMR of a Polyhydroxyether Before and After Derivatization with Trichloroacetyl Isocyanate

branching can however be determined indirectly by calculating the decrease in the area of the nonbranched methine peak relative to the aromatic peaks (Equation 34).

$$\% \text{ Branching} = ((A^{o}_{CH}/A^{o}_{Ar}) - (A^{o}_{CH}/A^{o}_{Ar}))/(A^{o}_{CH}/A^{o}_{Ar}) \qquad (34)$$

The previously described ^{1}H-NMR method used by Zahir and coworkers was not repeated here due to the probable decrease in precision incorporated in his analysis. The probable decrease in precision was directly due to their inability to separate methine and methylene proton peaks using a 100MHz NMR. This forced them to derive an equation which incorporated the integrated peak areas of a large number of the proton signals found in a polyhydroxyether to determine the degree of branching, equation (15). One would expect precision to decrease with the increase in the number of peaks areas measured. To further decrease the precision, the samples had to be titrated to obtain an epoxy equivalent weight.

Results using the ^{1}H-NMR analysis for both polymers and oligomers synthesized under varying conditions are shown in Tables 12-15. As mentioned earlier, it had been hoped that through this analysis procedure optimum conditions could be found to minimize branching, unfortunately as seen from the large confidence intervals, no trend can be distinguished. It is interesting to note however that only one sample gave a possible result of greater than 10% branching after taking into account the error interval.

TABLE 12

^{1}H-NMR Branching Analysis Results for Polyhydroxyethers Synthesized with Varying Monomer Concentrations

Catalyst	Solids Conc.	$[\eta]^{THF}_{25C}$	Mn (10^{-3})	Branch %	Number Analyses
OLIGOMERS					
Tributylamine	40	0.18	6.5	6.0 ± 3.1	(2)
	60	0.28	7.2	2.1 ± 2.6	(3)
	80	0.30	8.0	5.4 ± 3.1	(2)
POLYMERS					
TBAH	35	0.92	79.6	3.5 ± 3.1	(2)
	55	0.86	50.0	2.9 ± 3.1	(2)
	80	1.07	27.8	4.4 ± 3.1	(2)

TABLE 13

^{1}H-NMR Branching Analysis Results for Polyhydroxyethers Synthesized With Various Trialkylamine Catalysts

Catalyst	$[\eta]_{25C}^{THF}$	Mn (10^{-3})	Branch %	Number Analyses
OLIGOMERS				
Tripropylamine	0.20	6.4	2.8 ± 1.8	(6)
Tributylamine	0.20	6.5	3.6 ± 3.1	(2)
	0.28	7.2	2.1 ± 2.6	(3)
	0.17	6.5	3.9 ± 2.6	(3)
	0.19	6.1	1.0 ± 2.6	(3)
	0.22	6.4	3.0 ± 2.2	(4)
Tripentylamine	0.30	8.4	2.2 ± 3.1	(2)
Trihexylamine	0.22	5.6	3.0 ± 3.1	(2)
Triheptylamine	0.27	5.8	2.3 ± 2.0	(5)
POLYMERS				
Tripropylamine	0.21	7.8	3.0 ± 2.2	(4)
Tributylamine	0.46	-	5.1 ± 4.4	(1)
Triheptylamine	0.35	12.3	2.5 ± 3.1	(2)
Tridodecylamine	0.32	11.2	-0.3 ± 3.1	(2)

TABLE 14

^{1}H-NMR Branching Analysis Results for Polyhydroxyethers Synthesized at Various Temperatures

Catalyst	Temp. (°C)	$[\eta]_{25C}^{THF}$	Mn (10^{-3})	Branch %	Number Analyses
OLIGOMERS					
Tributylamine	100	0.28	7.2	2.1 ± 2.6	(3)
	125	0.19	5.9	8.3 ± 3.1	(2)
	137	0.20	4.8	0.4 ± 3.1	(2)
POLYMERS					
Tributylamine	100	0.26	-	5.1 ± 4.4	(1)
	130	0.20	5.9	4.0 ± 3.1	(2)
TBAH	100	0.86	50	2.9 ± 3.1	(2)
	130	0.40	19	3.5 ± 3.1	(2)

TABLE 15

^{1}H-NMR Branching Analysis Results for Polyhydroxyethers Synthesized with Various Catalyst Concentrations

Catalyst	Cat. Ratio	$[\eta]^{THF}_{25C}$	Mn (10^{-3})	Branch %	Number Analyses
OLIGOMERS					
Tributylamine	0.004	0.28	7.2	2.1 ± 2.6	(3)
	0.010	0.25	10.4	4.7 ± 3.1	(2)
	0.016	0.27	7.9	3.7 ± 3.1	(2)
POLYMERS					
TBAH	0.007*	0.86	50.0	2.9 ± 3.1	(2)
	0.004*	0.92	79.6	3.5 ± 3.1	(2)
	0.004	0.43	24.5	5.0 ± 4.4	(1)
	0.002	0.40	19.1	5.5 ± 3.1	(2)

* Half of the catalyst added initially, the other half after 12-18 hours

** Cat. Ratio references to moles of catalyst per mole of DGEBA

The standard deviation of 2.7 which was obtained after running over 80 analyses on 33 different samples, was equal for both polymers and oligomers alike. This would make it necessary to run 20 analyses on any one sample to obtain a plus or minus error interval of one percent branching. It should be noted that 5 samples in particular gave highly non reproducible results and increased the standard derivation from 1.80 to 2.71. No reason could be found to drop the data however, so they were included.

Several possible explanations for the large standard derivation was checked in hopes of increasing precision. The first was the possible nonquantitative reaction between the isocyanate and the hydroxyls. As mentioned previously, the epoxy methylene proton peak made it impossible to determine if 100% of the hydroxyls had reacted in the oligomers since both the hydroxyl and the epoxy have similar peak positions. In the polymers however, the concentration of epoxy groups was small enough that its peaks did not appear on the ^{1}H-NMR spectrum. In these samples the hydroxyl peak always completely disappeared with the addition of the isocyanate. Therefore, it was concluded that nonquantitative derivatization was not a factor in the large standard of derivation.

Next the possibility that the isocyanate was reacting with some other functional group, which created a proton signal corresponding to the nonbranched methine, was examined. The first possibility was the reaction of the isocyanate with an epoxy group which is a known reaction in the production of oxazolidones [67]. The NMR however, detected no peak around 5.4 ppm when trichloroacetyl isocyanate was added to a solution of DGEBA in d-chloroform inside a NMR tube.

The second possible side reaction was between the isocyanate and a primary alcohol. The alcohol could be formed from the reaction of a hydroxyl containing catalyst with an epoxy, equation (28). Reacting 2,3 propanediol with the isocyanate showed the creation of a proton signal at 5.1 ppm but not at 5.4 ppm. This proved that neither of these reactions in any way affected the results. It should be noted that the proton peak at 5.1 ppm was not seen in any other spectrum of polyhydroxyether. It was felt that this indicated little or no reaction between the basic catalyst and the epoxy groups took place during the synthesis of polyhydroxyethers.

A second possible way of calculating branching existed by ratioing the methylene proton signal at 4.0 ppm both before and after derivatization. This can be done since the nonbranched methylene peak is shifted downfield 0.2-0.3 ppm by the carbamate group leaving the branched methylene at 4.0 ppm. Unfortunately the presence of the branched peak could not be detected. It was felt that the accuracy of this method would be in doubt anyway due to the possible presence of proton signals from residual THF and diglyme existing around 4.0 ppm.

To check the reproducibility of the experiments run, 5 different batches of oligomers synthesized under the same conditions were made and their results included in Table 14. All the results were within the experimental error of the analysis.

Crosslinking Kinetics

A preliminary study was made into the kinetics of crosslinking epoxy resins with multifunctional isocyanates. The research set out to model the crosslinking reaction by studying the reaction kinetics of phenyl isocyanate with a low molecular weight linear epoxy resin.

Phenyl isocyanate was chosen due to the favorable commercial properties associated with aromatic urethane linkages. A linear low molecular weight epoxy resin was used in order to avoid the possible complications due to branched chains found in higher molecular weight resins.

Synthesis of EpOH2

The epoxy resin was synthesized following the reaction mechanism shown in Figure 11. The reaction is initiated by the formation of the phenate of para t-butylphenol by the basic catalyst, sodium hydroxide. The by-product, water, was azeotroped off by the solvent toluene. With the addition of DGEBA, the phenate attacks the epoxy group forming the secondary alkoxide. A proton transfer takes place between excess t-butylphenol and the alkoxide to reform a phenate and create a secondary alcohol. The final product, EpOH2, is shown.

The fourier transform infrared and ^{1}H-NMR spectrums of the purified EpOH2 molecule are shown in Figures 12 and 13, respectively.

In order to determine the exact molecular weight per hydroxyl, a titration procedure for secondary alcohols was devised. The results from several secondary alcohols and from several batches of EpOH2 is shown in Table 16. The reaction times of 48 hours was required to

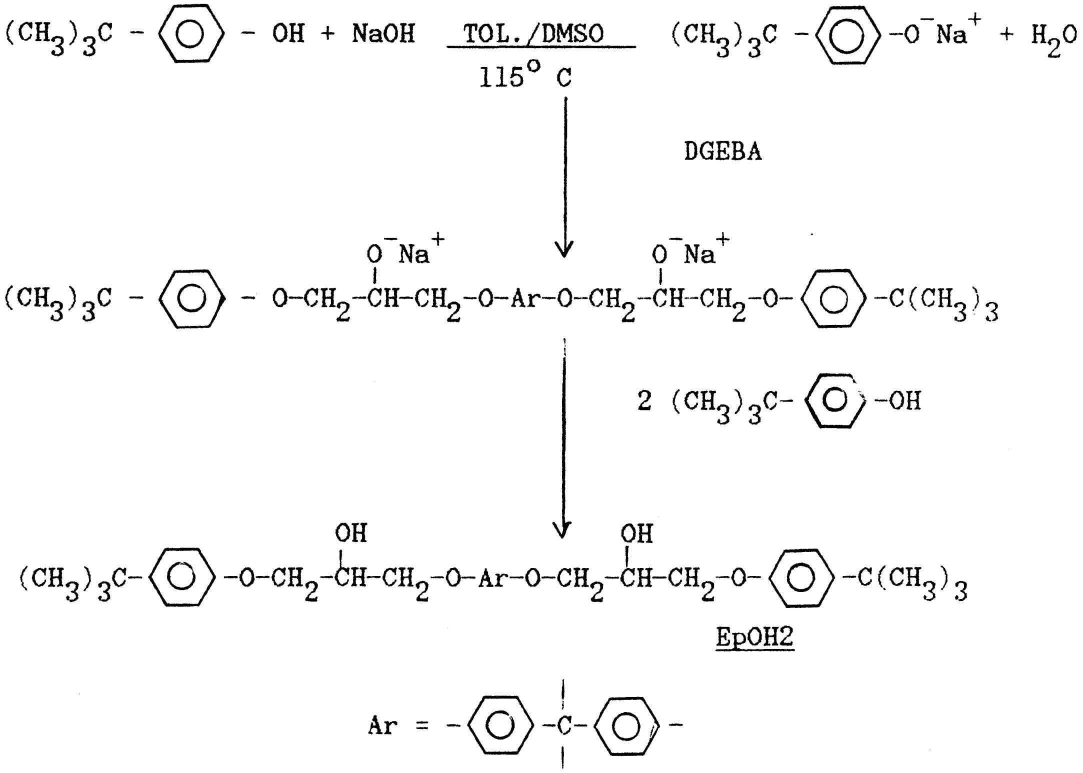


Figure 11: Reaction Mechanism for the Synthesis of EpOH2

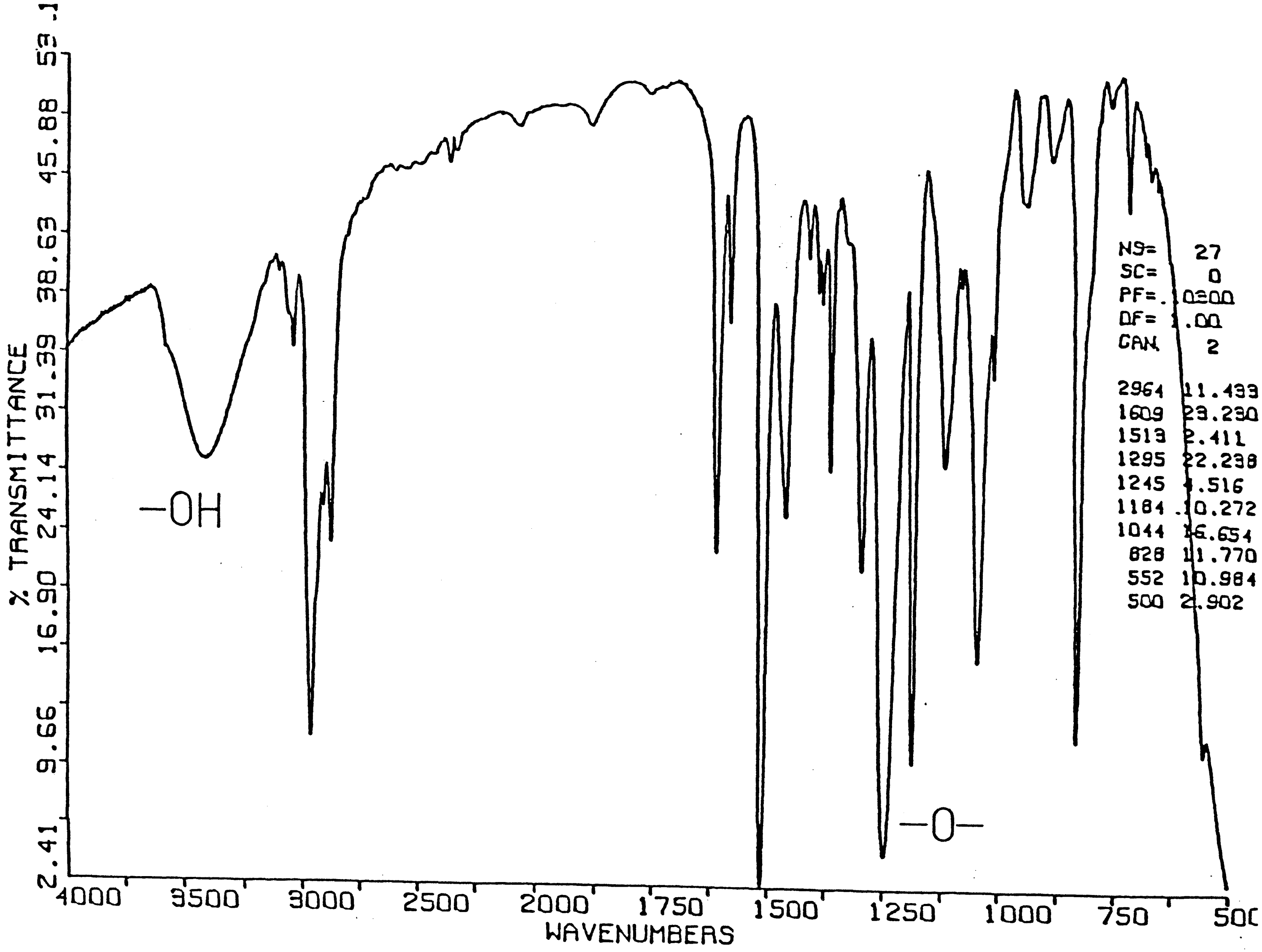


Figure 12: FT-IR of Purified EpOH2

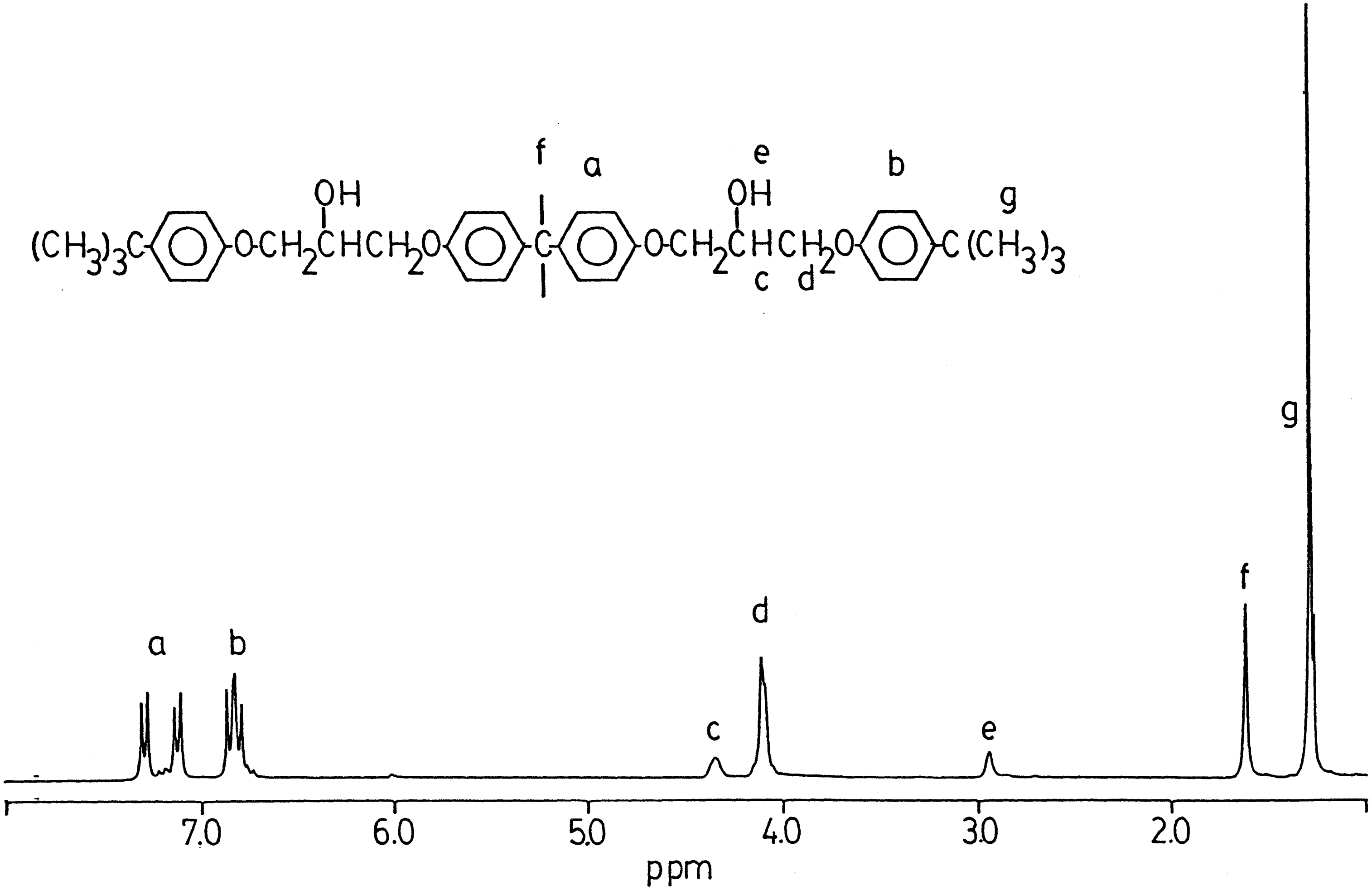


Figure 13: ^{1}H-NMR of Purified EpOH2

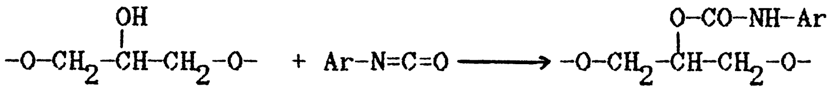
TABLE 16

Secondary Hydroxyl Titration Results for Various Alcohols

Alcohol	Actual Mn	Titrated Mn
Isopropanol	59	65
3-Octanol	130	137
Cyclo p-tert-Butylhexanol	156	166
EpOH2 (Batch 1)	640	630
(Batch 2)		627

ensure complete derivatization. It has been suggested that phthalic anhydride may be a superior derivatizing agent due to its faster rate of reaction. However, no reactions were run with this compound however.

In reaction between phenyl isocyanate and EpOH2 the hydroxyl adds to the isocyanate carbon,

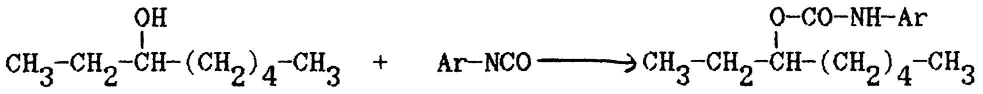


$$\text{-O-CH}_2\text{-}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{-CH}_2\text{-O-} + \text{Ar-N=C=O} \longrightarrow \text{-O-CH}_2\text{-}\overset{\text{O-CO-NH-Ar}}{\overset{|}{\text{CH}}}\text{-CH}_2\text{-O-} \qquad (35)$$

The hydroxyl proton then bonds with the nitrogen to form the product.

The rate of reaction between phenyl isocyanate and the hydroxyls of EpOH2 was studied by infrared spectroscopy. In order to study the changes in concentration versus time, a Beer's Law calibration curve for the isocyanate group, 2260 cm^{-1}, was constructed using a liquid cell (Figure 14).

Due to the highly reactive nature of phenyl isocyanate, an estimate on the yield of the urethane product was needed in order to ensure no side reactions had taken place. To obtain this estimate a calibration curve of a model urethane was made. The urethane was synthesized from 3-octanol and phenyl isocyanate.



$$\text{CH}_3\text{-CH}_2\text{-}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{-(CH}_2)_4\text{-CH}_3 + \text{Ar-NCO} \longrightarrow \text{CH}_3\text{-CH}_2\text{-}\overset{\text{O-CO-NH-Ar}}{\overset{|}{\text{CH}}}\text{-(CH}_2)_4\text{-CH}_3 \qquad (36)$$

The ^1H-NMR and calibration curve for the urethane group, 1740 cm^{-1}, are shown in Figures 15 and 16, respectively.

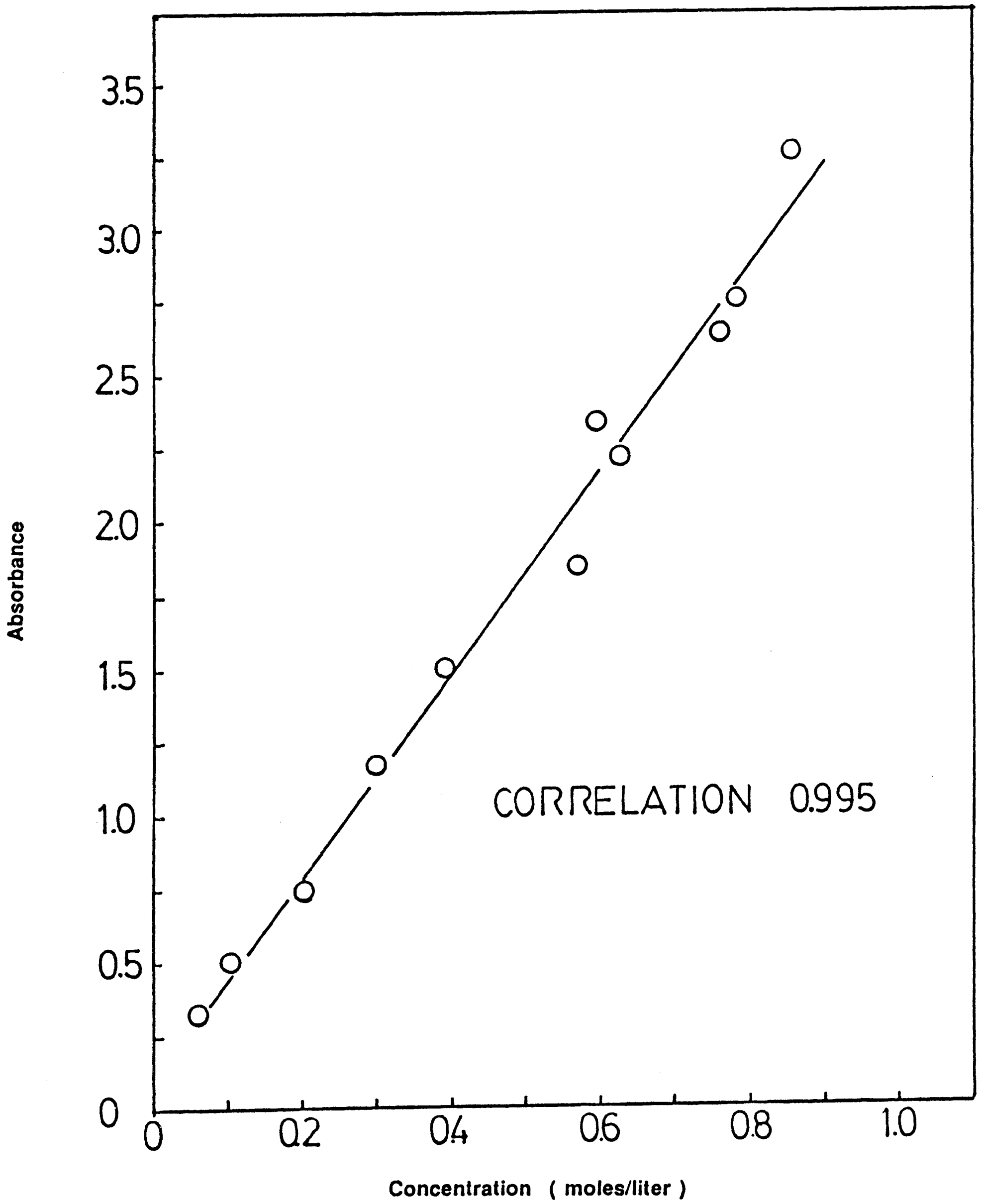


Figure 14: Isocyanate FT-IR Calibration Curve

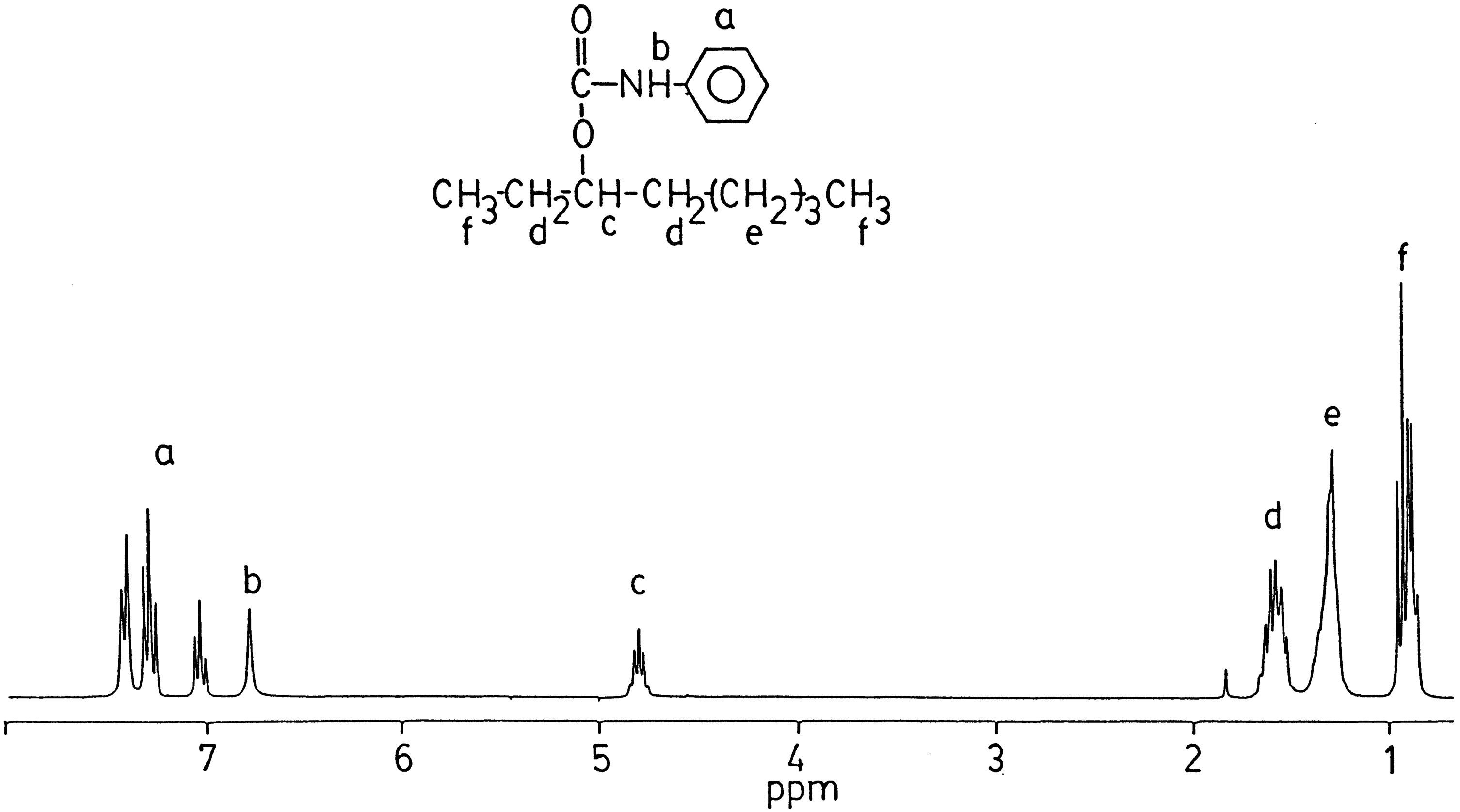


Figure 15: ^{1}H-NMR of 3-Octylphenyl Carbamate

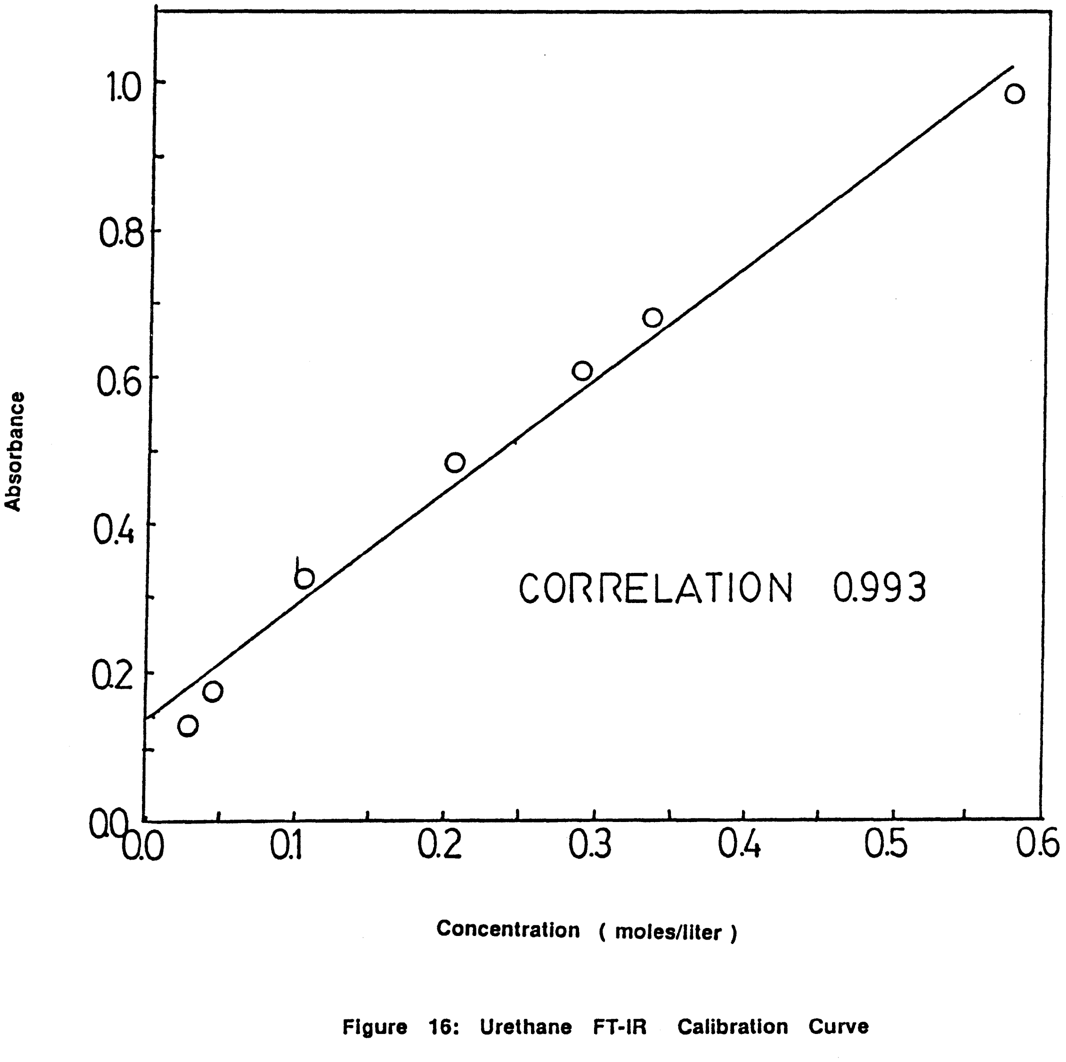


Figure 16: Urethane FT-IR Calibration Curve

Uncatalyzed reaction results were plotted with respect to a number of rate laws. A typical infrared spectra midway through a reaction is shown in Figure 17. Second order kinetics provided the highest correlations coefficients for a linear plot. Figure 18 shows the plots of the reactions for various temperatures. Table 17 gives the rate constants and estimated energy of activation for the reaction. All rate constants taken were for the initial rates.

It should be noted that the final urethane concentration was greater than 90% of the isocyanate concentration decrease, for both catalyzed and uncatalyzed reactions. This was felt to indicate that little or no side reactions had taken place. Also in the infrared spectra, no indication of allophanate group formation was observed.

Plots and rate constants for catalyzed reactions are shown in Figure 19 and Table 18, respectively. The catalyst which promoted the greatest activity was in Tin Octoate. Metal salts such as mercuric acetate which have been reported to be excellent catalysts, were not used due to their insolubility in o-dichlorobenzene.

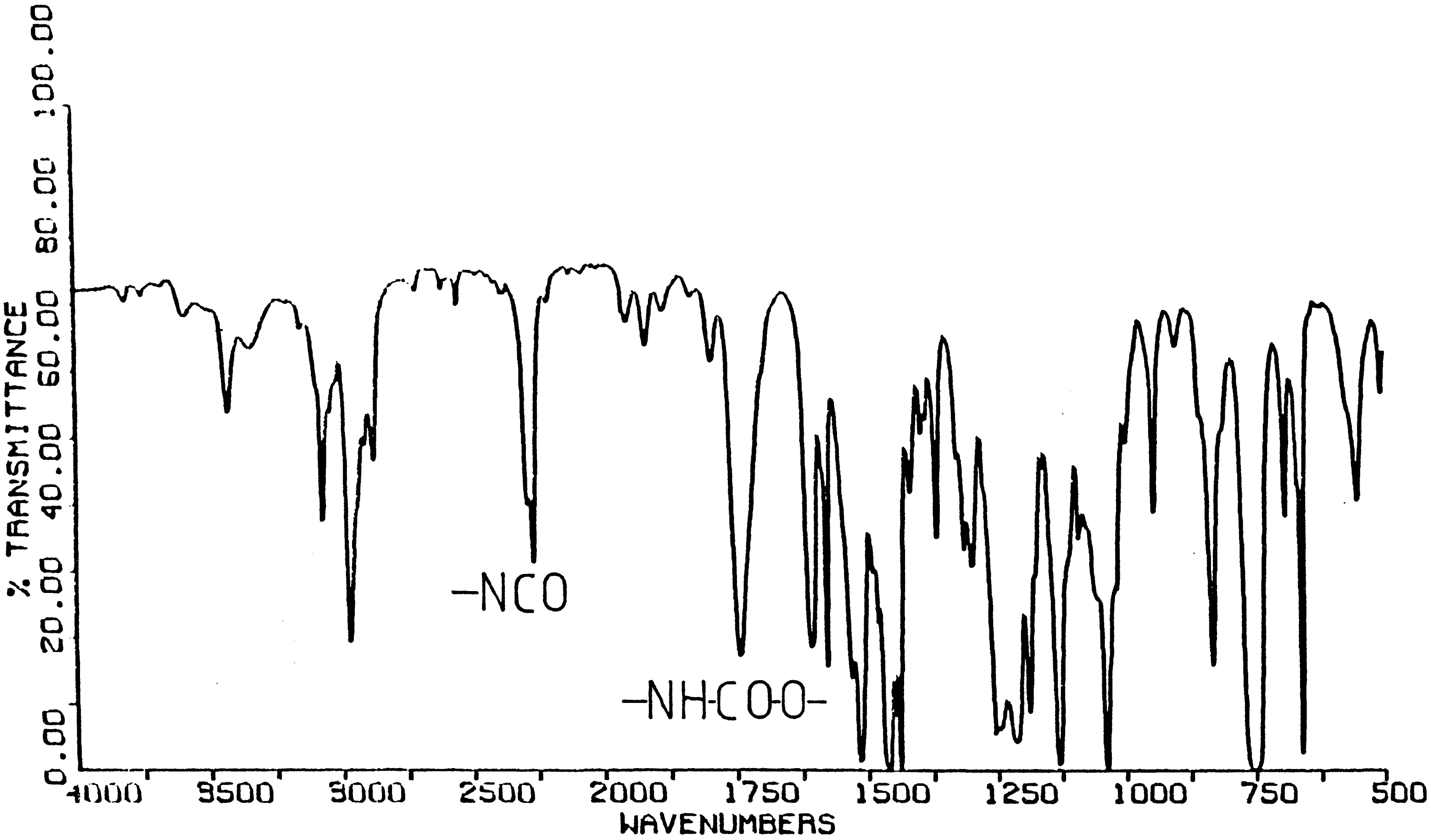


Figure 17: FT-IR Spectrum of a Typical Kinetic Reaction

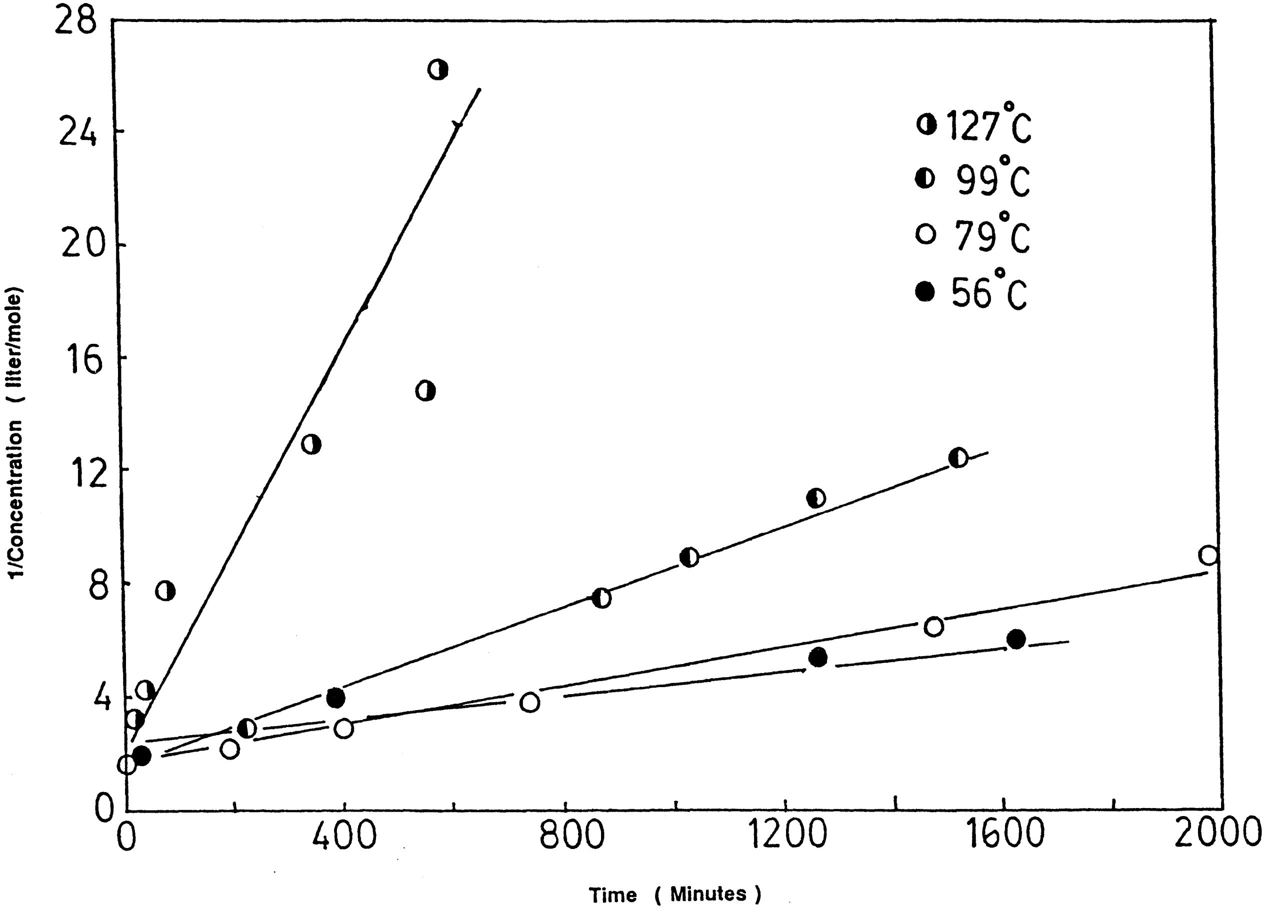


Figure 18: Uncatalyzed Urethane Kinetic Reactions Run at Various Temperatures

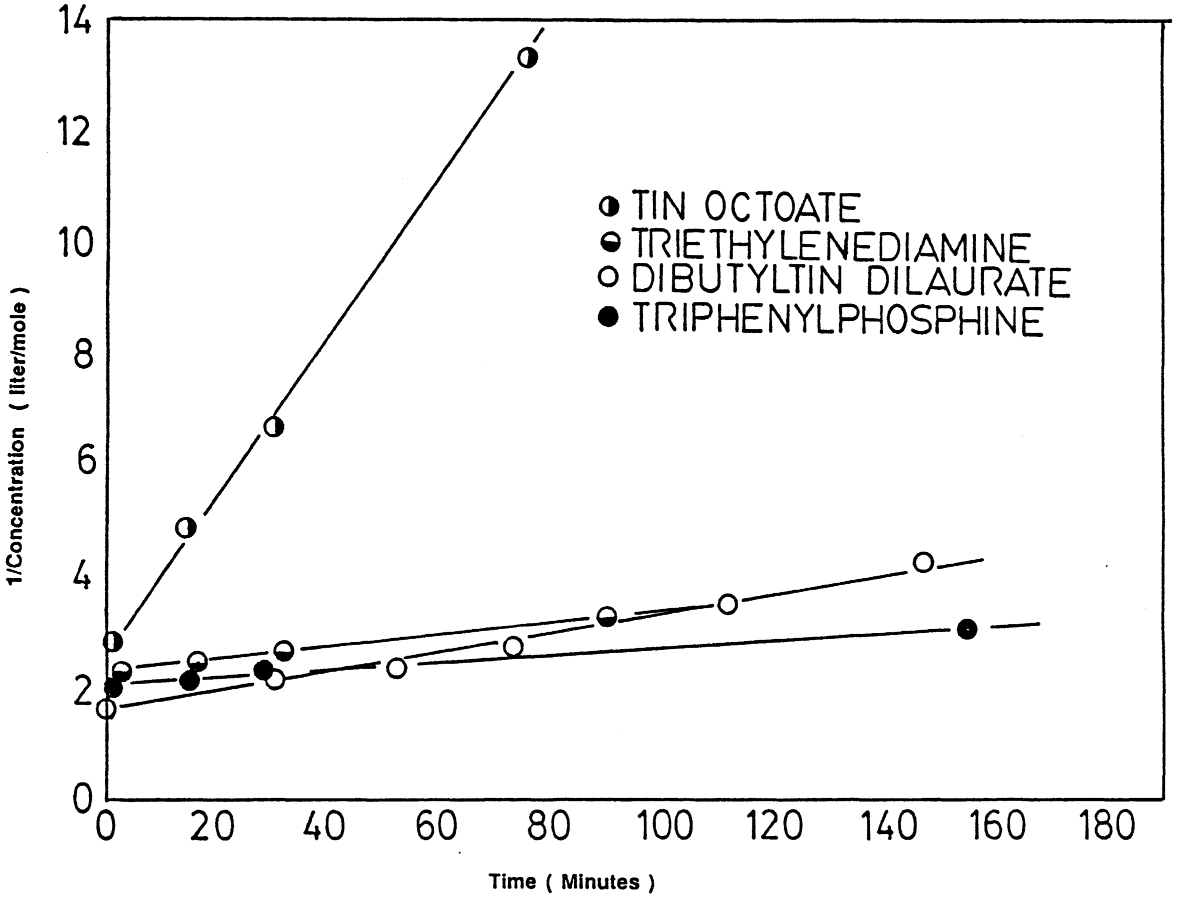


Figure 19: Urethane Kinetic Reactions Run with Various Catalysts

TABLE 17

Rate Constants for Uncatalyzed Urethane Reactions at Various Temperatures

Temperature (°C)	k (l/mol.min.)
56	0.0032
79.5	0.0052
80.5	0.0052
99	0.0088
127	0.0621

Activation Energy (o-Dichlorobenzene): 46 KJ/mole

TABLE 18

Rate Constants for Catalyzed Urethane Reactions

Catalyst	Temp. (°C)	Cat.* Conc.	k (l/mol.min.)
Tin Octoate	61	9.2	0.126
Triethylene Diamine	61	9.3	0.038
Dibutyltin Dilaurate	62	7.4	0.017
Triphenylphosphine	61	9.2	0.0076
Uncatalyzed	56	-	0.0032

* 10^{-6} moles catalyst per mole of isocyanate

CONCLUSIONS

The research which has been presented in this thesis has addressed the subjects of synthesis, analysis and crosslinking of polyhydroxyethers. High molecular weight materials have been prepared using quaternary ammonium hydroxides catalysts in diglyme solutions. Reproducibility of results was often difficult to obtain however due to the high viscosity of the reaction solutions which prevented adequate agitation. Trialkylamine catalyzed systems by contrast failed to produce high molecular weight material.

A technique to quantitatively measure the degree of branching in the polymers synthesized was developed using ^{1}H-NMR. All materials tested (except for one) showed less than 10% branching even after taking into account the possible error of the technique. The relatively low precision of the technique along with the close proximity of the results thus prevents the detailed comparison of the influence of various reaction conditions on the quantitative amount of branching. Another technique to determine branching, which involved the titration of epoxy terminated oligomers along with the determination of their number average molecular weights by vapor phase osmometry, failed to produce realistic results.

In the kinetic study of crosslinking resins with isocyanates, a linear low molecular weight resin was synthesized from para t-butylphenol and diglycidyl ether of bisphenol A using sodium hydroxide as the catalyst and toluene-dimethylsulfoxide as the solvent system. An approximate activation energy was given for the reaction of the resin with phenyl isocyanate in o-dichlorobenzene. Tin octoate proved to be the most effective catalyst for the reaction of those studied.

REFERENCES

1. Schlack, P., (I.G. Farben), German Patent 676, 117, 1934.

2. Castan, P., (De Trey Freres), British Patent 518, 057, 1938.

3. Castan, P., (I.G. Farben), British Patent 579, 698, 1943.

4. Greenlee, S.O., (Devoe and Raynolds), United States Patent 2,503,726, 1943.

5. Potter, W.G., Epoxide Resins, Springer-Verlag Inc., New York, 1970.

6. Dauksys, R., SPE Journal, 27, 59-64, 1971.

7. Greenlee, S.O., (Devoe and Raynolds), United States Patent 2,582,985, 1952.

8. Greenlee, S.O., (Devoe and Raynolds), United States Patent, 2,615,0007, 1952.

9. Greenlee, S.O., (Devoe and Raynolds), United States Patent 2,615,008, 1952.

10. Greenlee, S.O., (Devoe and Raynolds), United States Patent, 2,694,694, 1952.

11. Greenlee, S.O., (Devoe and Raynolds), United States Patent, 2,698,315, 1954.

12. Aleman, J.V., J. Polym. Sci. A-1, 9, 3509, 1971.

13. Fisch, W., Chimia, 16, 66, 1962.

14. Batzer, H., S. Zahir, J. Appl. Polym. Sci., 19, 585, 1975.

15. Batzer, H., S.A. Zahir, J.Appl. Polym. Sci., 21, 1843, 1977.

16. Enikopyan, N.S., M.A. Markevitch, L.S. Sakhonenko, S.Z. Rogouina, V.G. Oshmyan, J.Polym. Sci. Polym. Chem. Ed., 20(5), 1231, 1982.

17. Brode, G.L., J. Wynstra, J. Polym. Sci., A-1, 4, 1045, 1966.

18. Rokicki, G., W. Kuran, Polymer, 21, 1069, 1980.

19. Lunsford, D., A.K. Banthia, J.E. McGrath, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 22(1), 194, 1981.

20. Banthia, A.K., D. Lunsford, D.C. Webster, J.E. McGrath, J. Macromol. Sci-Chem., A15(5), 943, 1981.

21. D.J. Lunsford, M.S. Thesis, Virginia Polytechnic Institute and State University, 1981.

22. Batzer, H., S. Zahir, J. Appl. Polym. Sci., 19, 601, 1975.

23. Alvey, F.B., J. Appl. Polym. Sci., 13, 1173, 1969.

24. Antal, I., L.Fuzes, G. Samay, L. Csillac, J.Appl. Polym. Sci., 26, 2783, 1981.

25. Shechter, L., J. Wynstra, Ind. Eng. Chem., 48, 86, 1956.

26. Shechter, L., J. Wynstra, R.P. Kurkjy, Ind. Eng. Chem., 48, 94, 1956.

27. Zahir, S.A., S. Bantle, R.S. Bauer, ed., ACS Symposium Series 221 (Epoxy Resin Chem. 2) 245-261.

28. Bantle, S., W. Burchard, Polymer, 27, 728, 1986.

29. Celanese Specialty Resins, Inc. (USA), Res. Discl., 264, 174, 1986.

30. Mak, H.D., M.G. Rogers, Anal. Chem., 44(4), 837, 1972.

31. Rogers, M.G., J. Appl. Polym. Sci., 16, 1953, 1972.

32. Goddlett, V.W., Anal.. Chem., 37(3), 432, 1965.

33. Hepburn, C., Polyurethane Elastomers, Applied Science Publishers, 1-4, 1982.

34. Oberth, A., R. Bruenner, J. Phys. Chem., 72(3), 84, 1968.

35. Farkas, A., P.F. Strohm, Ind. Eng. Chem. Fundam., 4(1), 32, 1965.

36. Baker, J., J. Gaunt, J. Org. Chem., 9, 1947.

37. Anzunic, G., A. Pirro, O. Rossi, L. Polo Friz, J. Polym. Sci.: Polym. Chem. Ed., 13, 1657, 1975.

38. Smith, H.A., J. Polym. Sci.: Part A-1, 6(5), 1299, 1968.

39. Rand, I., B. Thir, S. Reegen, K. Frisch, J. Appl. Polym. Sci., 9, 1787, 1965.

40. Sugawara, K., S. Hayashida, H. Miyazaki, K. Hara, Proc. SPI. Annu. Tech./Mark. Conf., 28, 6, 1984.

41. Kastelic, C.A., A. Sebenik, I. Vixovisek, Hem. Ind., 38(12), 249, 1984.

42. Frisch, K., S. Reegen, B. Thir, J. Polym. Sci.: Part C, 16, 2191, 1967.

43. Dyer, F., A. Talyor, S.J. Mason, J. Samson, J. Am. Chem. Soc., 71, 4106, 1949.

44. Baker, J., M.M. Davies, J. Gaunt, J. Chem. Soc., 24, 1949.

45. Ephraim, S., A.E. Woodward, R.B. Mesrobian, J. Am. Chem. Soc., 80, 1326, 1958.

46. Davis, T.L., J.M. Farnum, J. Am. Chem. Soc., 56, 883, 1934.

47. Wissman, H., L. Rand, K. Frisch, J. Appl. Polym. Sci., 8, 2971, 1964.

48. Willeboordse, F., J. Phys. Chem., 74(3), 601, 1970.

49. Sato, M., J. Am. Chem. Soc., 82, 3893, 1960.

50. Sato, M., J. Org. Chem., 27, 819, 1962.

51. Oberth, A., R. Bruenner, Ing. Eng. Chem. Fundam., 8(3), 383, 1969.

52. Baker, J., J. Holdsworth, J. Org. Chem., 713, 1947.

53. Britain, J.W., P.G. Gemeinhardt, J.Appl. Polym. Sci., 4(41), 207, 1960.

54. (Union Carbide Corp.), Jpn. Kokai Tokkyo Koho Jp 57/87, 414, 1982.

55. Schieler, L., Jet Propulstion Laboratory, California Institute of Technology, Tech. Rpt., 32, (July 1, 1961).

56. Burkus, J., J. Org. Chem., 26, 779, 1961.

57. Anzuino, G., A. Pirro, O. Rossi, L. Polo Friz, J. Polym. Sci. Polym. Chem. Ed., 13, 1667, 1975.

58. Yilgor, I., J.E. McGrath, J. Appl. Polym. Sci., 30, 1733, 1985.

59. Teyssie, P., R. Jerome, Ba Gia Huynh, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.), 21(2), 307, 1980.

60. Olczyk, W., H. Szpakowska, Chem. Stosow, 26, 333, 1982.

61. Abbate, F., H. Ulrich, J. Appl. Polym. Sci., 13(9), 1929, 1969.

62. Gia, H.B., R. Jerome, F.E. Bailey, ed., ACS Symposium Series 212 (Initiation of Polymerization), 1983.

63. Haney, M.A., J. Appl. Polym. Sci., 30, 3023, 1985.

64. Odian, G., Principles of Polymerization, John Wiley & Sons, 55, 1970.

65. Skoog, D.A., D.M. West, Analytical Chemistry, Saunders College, 72, 1979.

66. Kerker, R., M. Stori, Chimia, 33, 84, 1979.

67. Patsiga, R.A., J.S. Senger, I. Yilgor, J.E. McGrath, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.), 26(1), 244, 1985.

The vita has been removed from the scanned document