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A KINETIC STUDY OF THE ANIONIC POLYMERIZATION OF NEOPENTYLETHYLENE OXIDE

BY

ALBERT EDWARD MEISINGER JR.

A DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

DOCTOR OF ENGINEERING SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey

1970

APPROVAL OF DISSERTATION

A KINETIC STUDY OF THE ANIONIC POLYMERIZATION OF NEOPENTYLETHYLENE OXIDE

BY

ALBERT EDWARD MEISINGER JR.

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________ CHAIRMAN

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NEWARK, NEW JERSEY

JUNE, 1970

ABSTRACT

Kinetic data for the anionic polymerization of bulk neopentylethylene oxide were determined. The initiator used for this study was potassium t-butoxide. Polymerization runs were made at temperatures of 39.9, 60.0 and 80.3°C using monomer to initiator ratios of 50/1 and 20/1.

The polymerization reaction was found to follow pseudo first order kinetics up to about 60% polymerization and second order after this. The energy of activation for the propagation reaction was found to be 17.4 ± 1.2 K cal/mole and 18.5 ± 1.5 K cal/mole, respectively, for the pseudo first order and second order portions of the polymerization. The value for the energy of activation should be constant at different degrees of polymerization and these two values are the same within experimental error. The highly negative entropy (-25.9 ± 3.6 cal/mole-deg @ 60.0°C) indicated that the transition state was very sterically hindered which is typical for S_N2 type reactions.

There was evidence that chain transfer was taking place because of the difference in the experimentally determined and calculated number average molecular weights. The rate of chain transfer was found to decrease as the percent polymerization increased. The change in the reaction medium as the polymerization proceeded was thought to cause this change in chain transfer rate. The rate of chain transfer was found to be slower than the rate of polymerization therefore it had a higher energy of activation. The energy of activation for the chain transfer reaction was determined to be 21.5 ± 1.5 K cal/mole at about 75% conversion.

Neopentylethylene oxide was also polymerized using potassium hydroxide, cesium hydroxide, rubidium t-butoxide and zinc chloride as initiators. These runs were made to find out how fast the polymerization would proceed, what type of polymer would be obtained and what the molecular weight of the resulting polymer would be.

Attempts were made to prepare optically active neopentylethylene oxide. Methods that were tried for this preparation were; gas chromatography, distillation, crystallization and stereoselective reactions. However the optically active monomer could not be prepared by any of the methods tried.

Gas chromatographic columns with optically active packing were used to try and separate the enantiomers of neopentylethylene oxide and the enantiomers of the bromohydrin, 4,4-dimethyl-1-bromo-2-pentanol. Gas chromatography was also used to try and separate

the diastereomers that resulted when l-menthoxyacetic acid was reacted with the d,l-bromohydrin. In this reaction and in the following reactions only the purified secondary alcohol bromohydrin was used. Attempts were also made to try and separate these diastereomers by vacuum distillation. Optically active neopentylethylene oxide could then be prepared from the resolved bromohydrin or diastereomers by reacting with potassium hydroxide. Neither the enantiomers or the diastereomers could be resolved by any of the gas chromatograph or distillation methods that were tried.

Stereoselective reactions were also tried with the bromohydrin. The d,l-bromohydrin was reacted with l-menthoxyacetic acid in one attempted separation and with cinchonine in another to try and obtain a partial resolution of the enantiomers. However the unreacted bromohydrin did not show any optical activity in either of these reactions.

Resolution by crystallization was to be tried by reacting the d,l-bromohydrin with phthalic anhydride. The resulting half esters would then be reacted with an alkaloid to form two diastereomers that might be separated by crystallization. However because of difficulty encountered with the reaction of bromohydrin with phthalic anhydride this method was not pursued very thoroughly and the actual crystallization was never tried.

To
Mother and Sally

ACKNOWLEDGEMENTS

The author is grateful to Professor William H. Snyder who suggested the problems contained in this thesis and whose continued encouragement and assistance made this work possible.

In addition the author is indebted to the Department of Health, Education and Welfare for the financial aid received in the form of a National Defense Education Act Fellowship.

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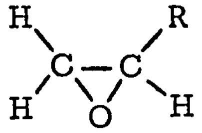
CHAPTER I

INTRODUCTION

Epoxides are cyclic ether compounds containing a three membered ring of one oxygen and two carbon atoms. The simplest epoxide is ethylene oxide. A 1,2-epoxide results when one of the four hydrogen atoms is replaced by any other group, like methyl, t-butyl, phenyl, etc.



These compounds are capable of undergoing stepwise polymerization to polyalkyene oxides, also called polyethers, when reacted with a variety of catalysts. The polymerizations could either be cationic or anionic because of the ease in which the highly strained ring is opened by both acids and bases.

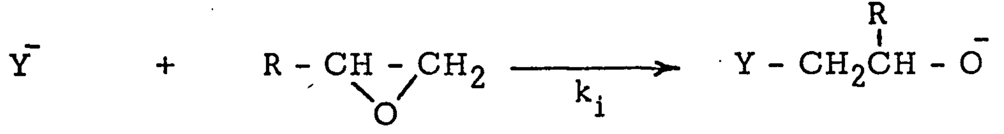
There are several books that review 1,2-epoxides and their resulting polymers, one by Gaylord(1) and another by Furukawa.(2) More recently Gurgiolo(3) has published an excellent review article on work done on the polymerization of epoxides, the properties of the resulting polymers and their applications.

A. Anionic Polymerization

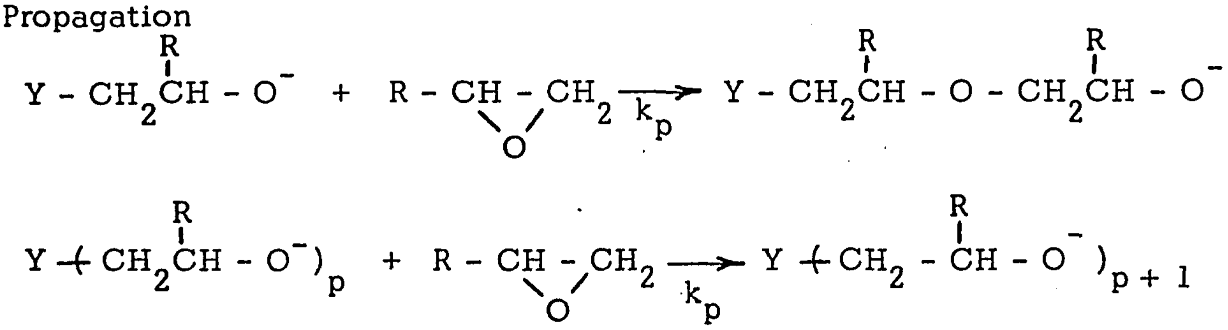
Most of the previous studies on the base-initiated polymerization of epoxides have involved complicating side effects. In some cases the initiator was insoluble in the monomer,(4,5,6) which led to difficulties in interpreting the results. These cases included; St. Pierre and Price,(4) who polymerized propylene oxide with potassium hydroxide, Snyder(5) who polymerized propylene oxide with sodium hydroxide, potassium hydroxide, cesium hydroxide, rubidium hydroxide and other bases, and Steiner, Pelletier and Trucks,(6) who also polymerized propylene oxide with potassium hydroxide. Other studies(7,8,9,10,11,12,13) were carried out in solvents that are known to affect the rate of polymerization. These solvents included alcohols such as methanol, ethanol, propanol and phenol,(7) methanol,(8) 1,2-propanediol,(9) and ethanol, n-butanol and 2-ethylhexanol.(10) Other solvents used in these studies were dimethyl sulfoxide(11,12) and tetrahydrofuran.(13)

To avoid the drawbacks of a non-homogeneous initiator and a solvent that would affect the rate of polymerization Joyce(14) used potassium t-butoxide as the initiator dissolved in the solvent 1,2-dimethoxyethane when he polymerized 1,2-butylene oxide and ethyl glycidyl ether.

The following mechanism has been suggested for the stepwise anionic polymerizations of a 1,2-epoxide(1,2), Initiation

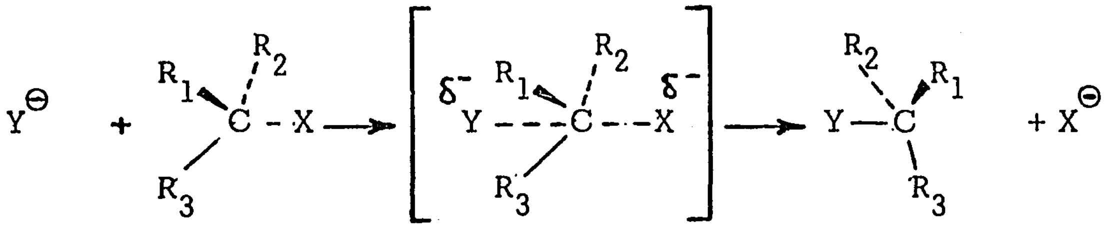


Propagation



There is no termination reaction in this type of polymerization because the polymer chains remain active even after all the monomer has reacted. This can be shown by adding more monomer and seeing that the reaction will continue as before.

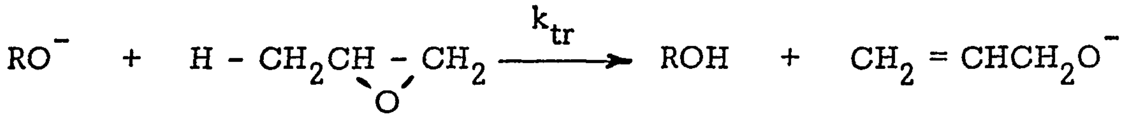
The ring opening reaction has been shown to occur by an S_N2 mechanism.(55) This type of reaction proceeds by the following steps,



Starting Materials Transition State Products

It can be seen that for an S_N2 reaction it is not only necessary that the nucleophile and the substrate come together with the proper energy but also with the proper orientation. Entropy is a measure of the probability of a state. The more probable a state is of existing the higher its entropy. An increase in molecular order is always accompanied by a decrease in entropy. Thus on going from molecules in random positions to the highly ordered S_N2 transition state results in a large decrease in entropy.(53)

While there is actually no termination reaction in anionic polymerization there is a possibility of a chain transfer reaction. With propylene oxide chain transfer has been shown to take place in the following manner(5,6,9,46)



$$\mathrm{RO^-} + \mathrm{H-CH_2\underset{\diagdown O \diagup}{CH-CH_2}} \xrightarrow{k_{tr}} \mathrm{ROH} + \mathrm{CH_2=CHCH_2O^-}$$

The chain transfer reaction does not actually terminate one chain and start another, instead both chains can continue to grow. However because the proton alternates between the two resulting chains only one of these chains can grow at any time.

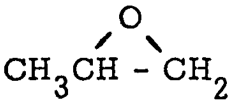
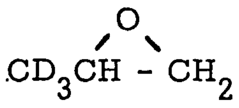
St. Pierre(46) found that when he polymerized propylene oxide with potassium hydroxide the resulting polymer contained vinyl and allyl ether end groups. He determined, by two different methods, that many of the polymer chains were terminated in double bonds. First Infrared studies indicated the presence of these unsaturated end groups and second, a double bond estimation technique was developed to determine the amount of unsaturation. This method consisted of placing a weighed amount of polymer in a flask and adding 10 ml. of chloroform and 10 ml. of glacial acetic acid. After cooling 10 ml. of bromine in glacial acetic acid was added. Then 25 ml. of 10% aqueous potassium iodide was added and then titrated with standard sodium thiosulfate. From this the amount of unsaturation could then be calculated.

Steiner et al(6) used two different methods to show that the transfer reaction does occur by the above reaction. First they tried to copolymerize propylene oxide and trans-2,3-epoxybutane with anhydrous potassium hydroxide. At the end of the reaction the volatiles were collected and found to contain, along with the unreacted trans-2,3-epoxybutane, a small amount of 1-buten-2ol. 1-Buten-2-ol would be the product if trans-2,3-epoxybutane underwent the chain transfer reaction shown above.

Secondary alkoxides have been shown by Gee et al(8) not to add at significant rates to substituted oxirane ring carbon atoms. However the secondary alkoxide can undergo chain transfer and initiate new chains and thus increase the amount of unsaturation in the polymer. Therefore as the results obtained, on the copolymerization of propylene oxide and trans-2,3-epoxybutane, by Steiner et al(6) show, the higher the concentration of secondary alkoxide the greater the unsaturation and the lower the molecular weight.

Banthorpe[(54)] in his discussion of E2(E,elimination; 2,bimolecular) reactions used isotope effects to determine the structure of the transition state in this type of reaction. Some β -deuterated compounds were found to undergo elimination from 3 to 8 times more slowly than the non-deuterated compounds. Because the C-D bond is more difficult to break than the C-H bond these reactions gave direct evidence that the C_{β} - H bond was broken in the rate-determining step of E2 reactions.

The second method that Steiner et al[(6)] used to investigate the chain transfer reaction was based on isotope effects. They polymerized 1,2-epoxypropane-3,3,3-d_3 under the same conditions as propylene oxide using both potassium hydroxide and the potassium salt of the monomethyl ether of dipropylene glycol as initiators. The results of the potassium hydroxide polymerizations are shown below;

	 $CH_3CH - CH_2$	 $CD_3CH - CH_2$
Conversion,%	30	17
Double Bond,mmoles/gm	0.224	0.074
K_H/K_D(corrected)	3.0	

The results show that there is more unsaturation in the propylene oxide polymer than in the 1,2-epoxypropane-3,3,3-d_3 polymer. Because an isotope effect does exist chain transfer probably proceeds by the E2 mechanism shown on page 4.

Snyder(5) did the first work on the comparison of the polymerization of propylene oxide and 1,2-epoxypropane-3,3,3-d_3 with potassium hydroxide catalyst. However his results showed no measurable isotope effect within experimental error on the unsaturation values. Apparently his polymer workup procedure for the deuterated polymer affected the amount of unsaturation in the resulting product yielding faulty data.

There is some discrepancy in the literature as to whether the amount of polymer unsaturation is dependent on the degree of polymerization.

Gee et al(8) concluded that the amount of unsaturation was independent of the degree of polymerization and that unsaturation should only be a function of the polymerization temperature. However they did state the importance of the reaction medium on modifying reaction rates. If this medium effect operated differently on the propagation and transfer reactions the relative rates of the two reactions would change. They felt that their measurements would not be greatly effected by a changing medium since they used a closed reaction system.

Snyder(5) concluded from his polymerization of propylene oxide with potassium hydroxide catalyst that the amount of unsaturation was not dependent on the time of polymerization. He explained his data by saying that the transfer reaction was first-order with respect to polyalkoxide and monomer concentration and overall a second order reaction. The rate of propagation is dependent on these same two variables so the relative rate of the propagation and transfer reaction should stay the same. However when he polymerized propylene oxide with tetramethylammonium and tetramethylarsonium hydroxides it was found that the rate of transfer was reduced relative to the propagation reaction. This was explained by the fact that hydrogen bonding of the polyalkoxide ion with hydroxyl group(s) reduced the chain transfer rate more than the propagation rate.

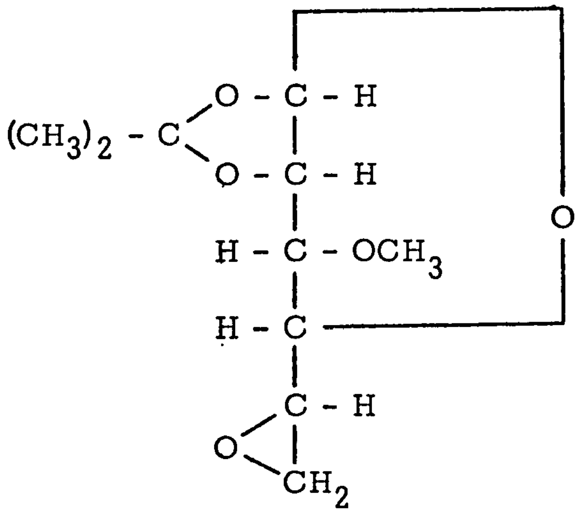
Simons and Verbanc(9) showed that unsaturation was dependent on the degree of polymerization. They wrongly concluded that the reason for this was that the propagation rate was dependent on the concentration of monomer, base and hydroxyl end groups while the rate of chain transfer depended only on the concentration of monomer and base. Thus as the concentration of the hydroxyl end groups and base decreased because of dilution the rate of propagation decreased faster than the rate of chain transfer.

Steiner et al(6) also stated that the relative rates of propagation and chain transfer changed with the degree of polymerization. However unlike Simons and Verbanc(9) they felt that this was probably due to the changing reaction medium.

B. Preparation and Polymerization of Optically Active Monomers

There has not been very much work done on the polymerization of optically active epoxides. Only a few optically active epoxides have been prepared and polymerized.

Nervin, Sarkanen and Schuerch,(16) while investigating possible routes to synthetic polysaccharides, prepared and polymerized 5,6-anhydro-3-O-methyl-1,2-O-isopropylidene-D-glucofuranose. This compound is a substituted ethylene oxide which has the structure shown below,



The compound was prepared by the following steps;

1) 100 gms. of anhydrous copper sulfate, 100 gms. of anhydrous glucose, 2 liters of dry acetone and 15 ml of concentrated sulfuric acid were stirred vigorously for 48 hours to give 1,2,5,6-di-O-isopropylidene-D-glucofuranose.

2) Methylation of this product gave 1,2,5,6-di-O-isopropylidene-3-O-methyl-D-glucofuranose.

3) Partial hydrolysis then gave 1,2-O-isopropylidene-3-O-methyl-D-glucofuranose.

4) Tosylation and reaction with alkali yielded the final product 5,6-anhydro-3-O-methyl-1,2-O-isopropylidene-D-glucofuranose. The resulting epoxide had an optical rotation of $[\alpha]_D^{21} = -62.65^{\circ}$ (2.07M, acetone).

It was found that certain Lewis acid catalysts, such as ferric chloride and zinc chloride, which polymerize simplier epoxides were ineffective with this compound. Also compounds such as sodium naphthalene, n-butyllithium, strontium and barium carbonates and lithium hydroxide did not polymerize the compound at the conditions under which this study was made (25-100°C). However stronger bases such as potassium hydroxide and cesium hydroxide were found to be good catalysts.

All the resulting polymers were white fluffy powders which did not have a true melting point but gradually softened and melted over a wide temperature range. The temperature range over which the polymer melted was not given nor was the optical rotation of the polymer. All the polymers were soluble in benzene, acetone and dioxane but were insoluble in water, methanol and diethyl ether.

The polymerization of l-propylene oxide was first reported by Price and Osgan (17) and later expanded in a more thorough study by these same authors. (18) They compared the polymers obtained when KOH and ferric chloride were used to polymerize racemic propylene oxide and l-propylene oxide at the same conditions. With KOH catalyst, racemic propylene oxide gave liquid polymer of the same molecular weight as the polymer from the optically active monomer. However, the polymer from l-propylene oxide was solid and crystalline with a melting point of 55.5-56.5°C. With the ferric chloride-propylene oxide complex catalyst both monomers gave two types of polymers. The racemic monomer gave a 60% yield of amorphous polymer and a 30% yield of crystalline optically inactive polymer with a melting point of 70-75°C. The optically active monomer gave a 30% yield of optically inactive amorphous polymer and a 20% yield of optically active crystalline polymer with a melting point of 70-75°C.

Some of the methods that have been used for the preparation of optically active propylene oxide are outlined on the following pages.

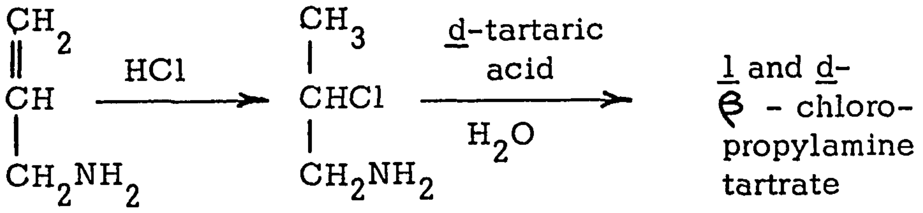
Price and Osgan(18) in preparing optically active propylene oxide first had to prepare optically active propylene glycol. They used the method developed by Levine and Walti (19), which is described below, to prepare optically active propylene glycol. This method involved the microbiological reduction of acetol by the reductase of yeast to l-propylene glycol.

$$CH_3COCH_2OH + 2\,[\,H\,] \xrightarrow[\text{Yeast}]{\text{Reductase of}} CH_3\overset{*}{C}HOHCH_2OH$$

They mixed 1 kg. of sucrose and 9 liters of water with 1 kg. of yeast and 1 liter of water. When this mixture started to evolve gas 100 gms. of acetol was added. After the reaction subsided the mixture was placed in an incubator at 32° for from one to three days. The solution was then filtered and concentrated at less then 40°. The residue was mixed with 400 cc of absolute alcohol and 100 cc of dry ether. The precipitate formed was removed by centrifuging. The supernatant liquid was concentrated under diminished pressure and distilled. The crude product was refractionated and collected at 88-90°/12 mm or 187-189°/760 mm. The final product had a density of 1.04 and a specific rotation of $[\alpha]^{20}_{D} = 15.0^{\circ}$. The yield was 50-60 gms. or 49-58% of the theoretical amount.

Price and Osgan(18) then reacted the l-propylene glycol with dry hydrogen bromide to obtain the l-propylene bromohydrin. The l-propylene bromohydrin was then cyclized to l-propylene oxide by reacting it with concentrated aqueous potassium hydroxide. The oxide had a boiling point of 34.5 - 35°C and an optical rotation of $[\alpha]^{21}_{D} = +15°$ (40% in ether).

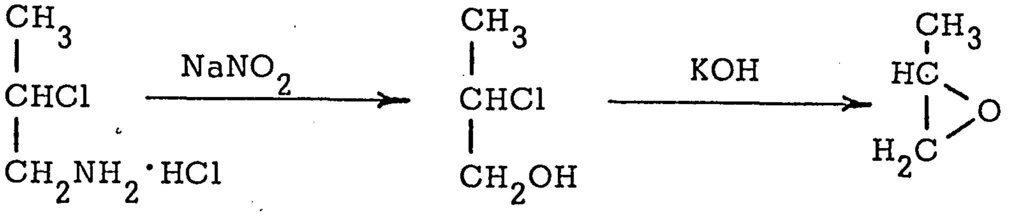
Abderhalden and Eichwald, as reported by Gaylord,$^{(1)}$ prepared the d and l-propylene oxides by the following reaction scheme;



Allylamine

Inactive β - chloro-n-propylamine

The d-isomer separated from solution first and was treated with base to release d-β- chloropropylamine. The epoxide was obtained as follows;



$[\alpha]^{18}_{D} = 12.72°$

From the remaining tartrate solution the l-propylene oxide was prepared in the same manner.

Optically active propylene oxide has also been obtained by asymmetric-induced polymerization. Tsuruta et al (20) resolved racemic propylene oxide by polymerizing the d,l mixture with an optically active catalyst. (+) Borneol/diethylzinc was used to polymerize racemic propylene oxide with the result that the l-propylene oxide was consumed at a faster rate than the d enantiomer. The optical rotation of the unreacted monomer was found to be $[\alpha]_D^{20} = -0.98 \pm 0.05^\circ$, neat, in a 1 dm tube.

It was thought that gas chromatography could be used in the preparation of optically active epoxides. Several references were found which described the gas chromatograph separation of racemic compounds into their optically active enantiomers by using an optically active stationary phase in the column.

Karagounis and Lippold (21) described the partial separation of d,l-sec-butanol, d,l-sec-bromopentane, d,l-ethyl-2-bromopropionate and d,l-ethyl-3-bromobutyrate by this method. The column packing was Al_2O_3 coated with an optically active substance, which was not named. They used columns from 6 to 12 meters long operated at a temperature from 10 to 15°C below the boiling point of the compound being separated. It was found that the separation was sensitive to column temperature, gas flow and the size of the injected sample. Retention times for these separations seemed to be very short, none being over about five minutes.

In a later article by Karagounis and Lemperle (22) the partial separation of other racemic mixtures was obtained using optically active $[Co(en)_3]Cl_3$ as the liquid phase in the column. By selective adsorption of one enantiomer separations of up to 14% were obtainable. The columns were run at from 1 to 60°C below the boiling point of the compound to be separated. Compounds such as d,l-1,2-dichlorohexafluorocyclobutane, d,l-sec-butylmethyl ether and d,l-acetylmethyl carbinol were partially separated.

More recently Gil-Av et al (23) have also resolved enantiomers by gas chromatography. They used capillary columns that were 0.25 mm I.D. and 50 to 100 meters in length. The different columns were estimated to have from 30,000 to 140,000 theoretical plates. The capillaries were coated with N-TFA-L-isoleucine lauryl ester, N-TFA-L-phenylalanine cyclohexyl ester, N-TFA-D-isoleucine lauryl ester and N-isobutyryl-L-phenylalanine cyclohexyl ester (TFA = trifluoroacetyl).

Samples were diluted in etheral solution in the ratio of 1:100 and the total sample size injected into the column ranged from 0.3 to 0.6 μl. Retention times ranged from 25 to 355 minutes. Some of the compounds to be resolved were; N-TFA-(±)-alanine (methyl, ethyl, isopropyl, t-butyl, n-propyl) ester and N-TFA-(±)-α-amino-valeric acid isopropyl esters. It was noticed in these separations that when the column packing was the D phase the L enantiomer emerged first and the D enantiomer emerged first when the L phase was used as the column packing.

Gas chromatography could also be used to separate diastereomers. Diastereomers could be prepared by reacting d and l enantiomers with an optically active substance. The resulting diastereomers would have different physical properties (B.P.,etc.) and thus could be separated by gas chromatography.

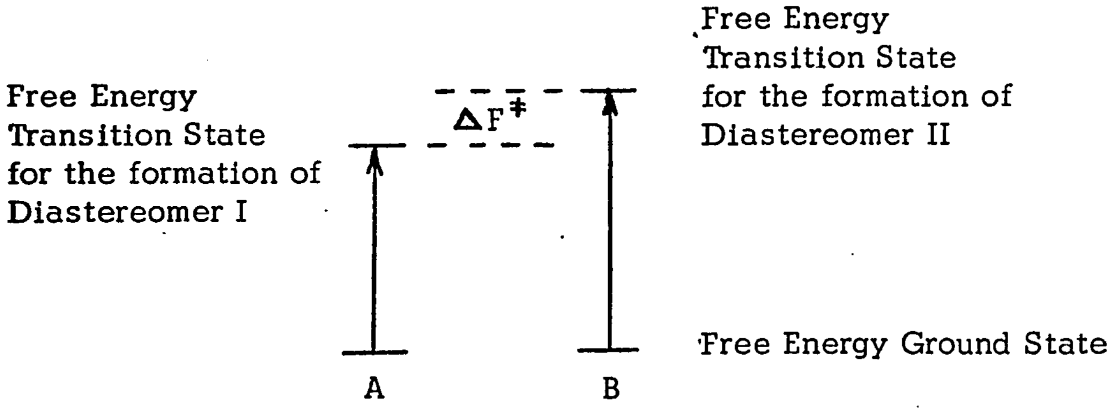
Casanova and Corey(24) completely resolved the diastereomers (M.W.-242) resulting from the reaction of (±) - camphor with optically active 2,3-butanediol. The column used was tricyanoethoxypropane (1/4" x 10', 20% on 80-100 mesh firebrick) operated at 125°C with a helium flow rate of 75 ml/min. The retention times of the two diastereomers were 27 min. and 28 min. 50 sec. Sample sizes of about 10 μl were used in this study. They found with this type of separation that the sample size was limited and that the choice of the liquid phase material was critical.

Stern, Atkinson and Jennings(25) described the separation of meso and racemic 2,3-dichlorobutane (M.W.-127). The difference in boiling points of these compounds was about 3°C. As much as 2 ml of each component (98 to 99.8% pure) was obtained in 4 hours by using a fully automatic preparative scale gas chromatograph. The column was Carbowax 20M (3/8" x 20', 30% substrate on 60-80 mesh firebrick) operated at 125°C and a helium flow rate of 200 ml/min. Sample sizes of up to 300 μl were used in this separation. They also reported that finding the right liquid phase material was critical.

Some work has also been done on the separation of isomers by paper chromatography. Rhuland et al(26) resolved the DD- and LL-isomers of α, ϵ-diaminopimelic acid by means of paper chromatography. This resolution was achieved by three different solvent systems, none of which contained asymmetric components but which were all basic. The system found most satisfactory for this separation was a mixture of methanol (77)-water(20)-pyridine(10).

The optically active monomers could also be prepared by kinetic resolution. This method involves a difference in the rates of reactions of enantiomers with an optically active compound. The free energies of the enantiomers are equal while the free energies are different for the transition states during the formation of the diastereomers. Therefore the energies of activation are different for the two diastereomers and thus one diastereomer is formed faster than the other leaving one unreacted enantiomer in a greater proportion.

A diagram might show this as;

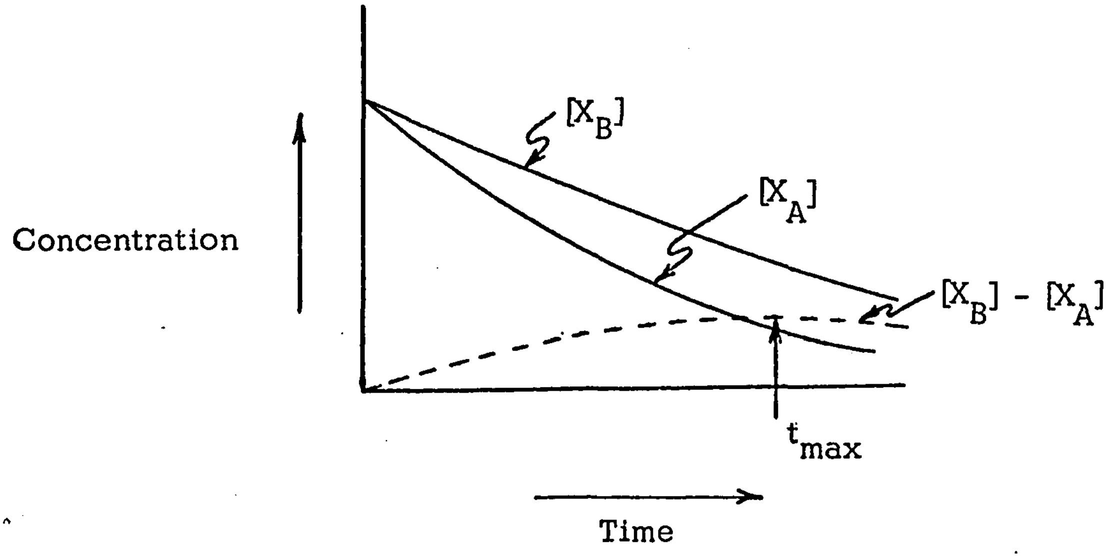


A & B = Enantiomers

where $\Delta F^{\ddagger}$ = Difference in Free Energy of Transition States for formation of Diastereomers.

The phenomenon of one enantiomer being removed or destroyed at a different rate than the other is called stereoselectivity.(27) Reactions in which $\Delta F^{\ddagger} \neq 0$ are stereoselective and the greater the difference in $F^{\ddagger}$ the more one diastereomer will form in preference to the other. On the other hand this difference may be so small that the deviation of the ratio of the products form unity may not be detectable by ordinary means.

Even if there is a large difference in $F^{\ddagger}$ the most that can be hoped for is an enrichment of one of the enantiomers but never a complete separation. The concentration of the two enantiomers and the difference between the two concentrations are shown on the plot below;



Where X_A is the more rapidly reacting enantiomer. This plot is for a first-order reaction where the rate of disappearance of a substance is proportional to the amount of the substance left in solution. As can be seen the difference in concentrations between the two enantiomers becomes a maximum at t_{max}.

C. Scope and Purpose of Present Work

The present work was undertaken to see what effect a bulky side group would have on the rate of polymerization of an epoxide. However, this group was to have no large electron delocalization capabilities, such as would be encountered with styrene oxide. Most of the previous work has been done with epoxides which contained small groups, i.e. hydrogen, methyl, etc. attached to the oxide ring. For this work the monomer chosen was 4,4-dimethylpentane-1,2-epoxide(neopentylethylene oxide) which has the much larger five carbon neopentyl group attached to ethylene oxide.

It was also of interest to try and develop a method for the preparation of optically active epoxides, d or l neopentylethylene oxide specifically. Using enzymes for the preparation of optically active propylene oxide is long and complicated so a new and easier method was sought that could be used for all epoxides.

This thesis will present the preparation of the racemic monomer and the methods attempted to try and prepare the optically active monomer. The kinetics of the anionic polymerization of neopentylethylene oxide using potassium t-butoxide initiator will be presented. In addition to the kinetic study, other initiators were used to polymerize neopentylethylene oxide to find the rate of polymerization and the type of polymer formed. These results are also shown.

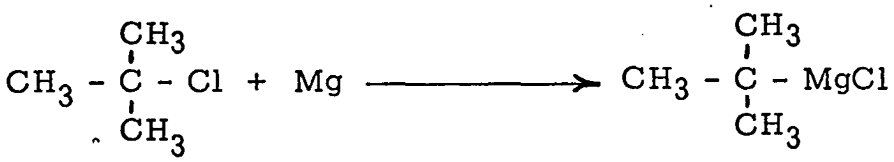
CHAPTER II

EXPERIMENTAL PROCEDURES

A. Preparation of Racemic Monomer

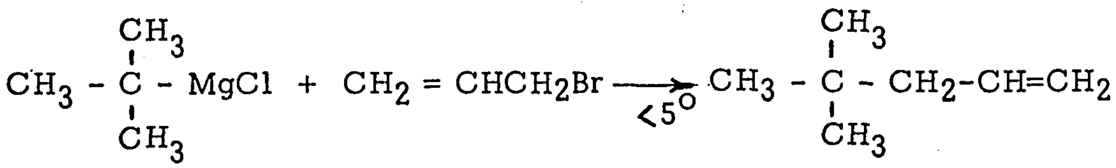
Racemic neopentylethylene oxide was prepared by the following four steps;

1. The reaction of t-butyl chloride with magnesium turnings,



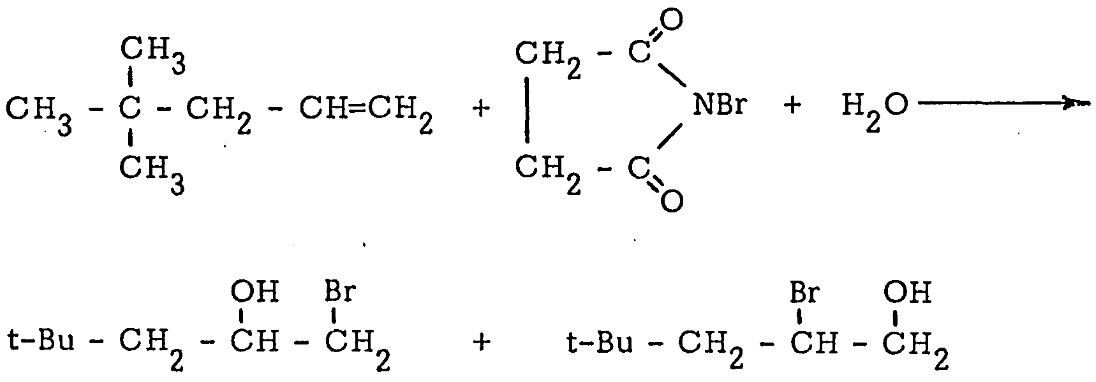
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + Mg \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-MgCl$$

2. The reaction of the t-butylmagnesium chloride with allyl bromide to give 4,4-dimethyl-1-pentene,



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-MgCl + CH_2=CHCH_2Br \xrightarrow[<5^o]{} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH=CH_2$$

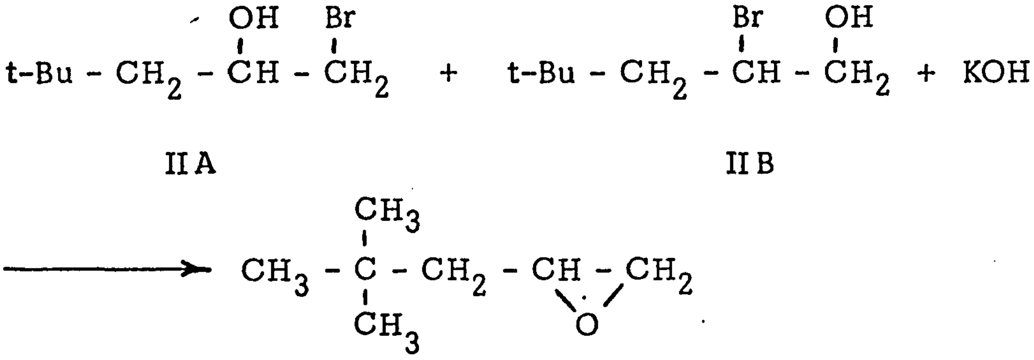
3. The reaction of the olefin with N-bromosuccinimide and water to give the bromohydrin,



$$t\text{-}Bu-CH_2-\overset{OH}{CH}-\overset{Br}{CH_2} \quad + \quad t\text{-}Bu-CH_2-\overset{Br}{CH}-\overset{OH}{CH_2}$$

IIA IIB

4. The reaction of both bromohydrins with KOH to give the racemic monomer,



$$\text{t-Bu}-CH_2-\overset{OH}{\overset{|}{C}H}-\overset{Br}{\overset{|}{C}H_2} \quad + \quad \text{t-Bu}-CH_2-\overset{Br}{\overset{|}{C}H}-\overset{OH}{\overset{|}{C}H_2} \quad + \quad KOH$$

IIA IIB

$$\longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH\overset{O}{-}CH_2$$

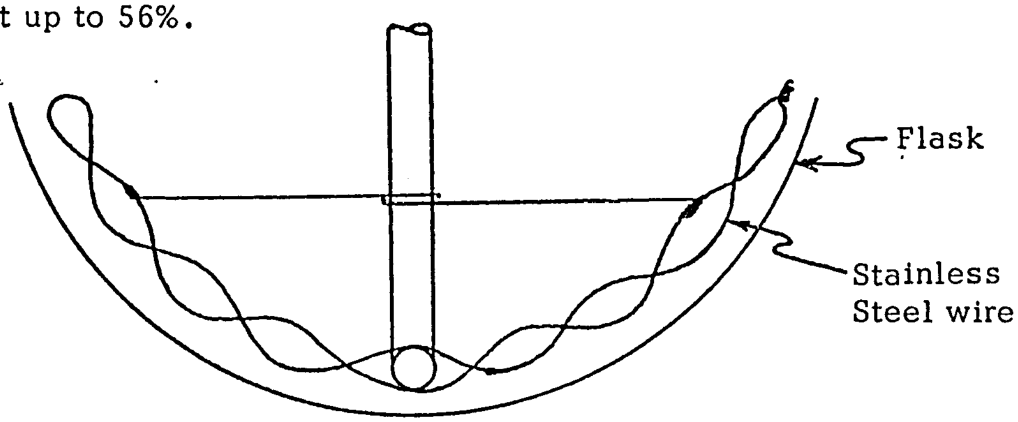
The procedures for these reactions are outlined on the following pages.

Preparation of t-Butylmagnesium Chloride. The t-butylmagnesium chloride was prepared in the manner described by Kharasch and Reinmuth(28) for other similar alkylmagnesium chlorides.

A five liter 3-neck flask equipped with a dropping funnel, stirrer, inlet tube for nitrogen and a reflux condenser was used for this reaction. Magnesium turnings, 195 gms (8 moles) was added to the flask. The system was then heated and swept out with dry nitrogen for about twenty minutes so that any water present would be driven off. The reaction was started by adding 20 ml of t-butyl chloride mixed with 50 ml of anhydrous ether to the magnesium turnings and heating. The rest of the 830 ml (7.5 moles) of t-butyl chloride was mixed with about 2500 ml of ether and slowly added from the dropping funnel at a rate sufficient to maintain refluxing of the ether.

According to Kharasch and Reinmuth the slower the addition of the ether solution the higher the yield of Grignard. When t-butyl chloride is reacted this rate of addition should be exceptionally slow. Dry nitrogen was swept through the system very slowly all during the addition of the chloride which took about 30 hours. The mixture was stirred for an additional ten hours and then allowed to stand another twelve hours. The Grignard was then filtered through cheesecloth to remove the excess magnesium turnings.

Preparation of 4,4-Dimethyl-l-pentene. The olefin, 4,4-dimethyl-l-pentene, was prepared by the method described by Whitmore and Homeyer.(29) For this reaction a five liter 3-neck flask equipped with a Hershberg stirrer, dropping funnel, thermometer and a reflux condenser was used. The Hershberg stirrer (made of heavy stainless steel wire) as shown below, helped increase the yield of olefin because it prevented the unreacted Grignard from caking up on the side of the reaction vessel. When a small stirrer was used for this reaction the yield of olefin was about 35%. However when the Hershberg stirrer was used the yield of olefin went up to 56%.



About 7 moles of t-butylmagnesium chloride was slowly added over a 24 hour period to 6.5 moles of allyl bromide, while keeping the reaction mixture temperature below 5°C by means of an ice-salt mixture.

Purification of Olefin. Allyl bromide and 4,4-dimethyl-1-pentene have close boiling points, 71.3 and 72.5°C respectively. Therefore some other procedure besides just distillation was necessary to purify the olefin. After removing the ether from the products the remaining mixture was reacted at room temperature with powdered KOH for about 48 hours. The mixture was then filtered and distilled through a 12 mm by 90 cm Todd Distillation column packed with glass helices. The fraction taken at exactly 72.5° (atm pressure) gave a positive flame test for halogen, so the mixture was then distilled from powdered KOH in the same column. The mixture was stirred at the same time. Still the fraction at 72.5° showed halogen by the flame test. To remove the last traces of the reactants the olefin was distilled from molten potassium. This time the olefin collected at 72.5° did not contain any trace of halogen and was shown to be greater than 99.8% pure by gas chromatography. The yield of pure olefin based on the allyl bromide used was 56%.

It was found to be best to react the impure product first with KOH and then use the potassium just to remove the last traces of halogen. Otherwise if the potassium is used first a lot of biallyl (B.P. 59.6°C) is formed and this also proved difficult to separate from the olefin by distillation. Care must be taken when distilling from potassium and KOH so as not to remove too much of the liquid from the distilling flask.

Preparation of Neopentylethylene Bromohydrin. The bromohydrin was prepared in the manner described by Guss and Rosenthal.(30) In a 1000 ml creased flask equipped with a stirrer and reflux condenser were mixed 87 ml (0.6 moles) of 4,4-dimethyl-1-pentene, 107 gms. (0.6 moles) N-bromosuccinimide and 400 ml of water. The mixture was stirred at room temperature for 27 hours until all the solid N-bromosuccinimide had disappeared. The layers were then separated and the water layer was extracted with 2 (150 ml) portions of ether. Distillation of the high boiling products at 2 mm. pressure yielded about 75 ml of bromohydrin, (mixture of IIA and IIB, page 21) which was about a 78% yield. The conditions and results for this reaction are shown in Table I, page 64. The specific gravity of the bromohydrin mixture (IIA and IIB) was found to be 1.235 at room temperature.

In several preliminary runs when impure olefin was used for this reaction up to 65% of the product was 1,2-dibromo - 4,4-dimethylpentane, thus lowering the yield of the desired bromohydrin. The reason for this was not discovered. The dibromide was partially separated from the bromohydrin by using a 20' x 3/8" gas chromatograph column of QF 1 (Fluorosilicone) operated at 140°C. Elemental analyses were run on both samples.

Elemental Analyses: Calculated for $C_7H_{14}Br_2$: C, 32.8%; H, 5.45%; Br, 61.7%. Found; C, 34.02%; H, 5.80%; Br, 59.32%.

Calculated for $C_7H_{15}OBr$: C, 43.3%; H, 7.72%; Br, 40.09%. Found; C, 43.09%; H, 7.69%; Br, 44.5%.

It was found that the bromohydrin was a mixture of the primary and secondary alcohols (IIB and IIA). These were separated by using a 1/4" by 10' gas chromatograph column of 5% Carbowax 1500 on Teflon T-6 run at 160°C. Boiling points were determined by Differential Thermal Analyses and found to be, 90.7 ± 0.5°C at 12.25 mm for the alcohol that had the longer retention time in the gas chromatograph and 81.9 ± 0.5°C at 12.1 mm for the alcohol that had the shorter retention time.

The major component of the bromohydrin mixture was found to be the lower boiling secondary alcohol. This could be separated by distilling in the Todd column. However because the higher boiling compound was only about 15% of the mixture it was purified and collected by gas chromatography using the column mentioned above.

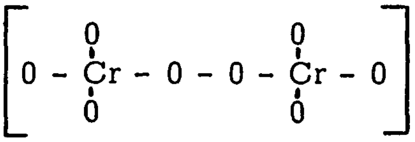
<u>Preparation of Neopentylethylene Oxide.</u> Both bromohydrins (IIA and IIB) could be reacted with KOH to give racemic neopentylethylene oxide. About 2.5 moles(400 ml) of the bromohydrin mixture was added to a 1-liter flask equipped with a reflux condenser, stirrer and dropping funnel.

Potassium hydroxide (2.5 moles, 165 gms., 85% pure) dissolved in 250 ml of water was slowly added to the flask over a five hour period. Stirring was then continued overnight. The organic layer and the water layer were then separated and the water layer extracted with 3 (100 ml) portions of ether. The ether portions were added to the original organic layer. The organic layer was then distilled in the Todd Distillation apparatus and only the fraction showing greater than 99.8% purity by gas chromatography was used in the polymerizations. The yield of neopentylethylene oxide was 84%. The oxide was found to have a specific gravity of 0.814 at 30°C. The boiling point was determined by Differential Thermal Analysis and found to be 124.9 ± 0.2°C at 744.5 mm. This product was previously reported by Hurst and Bruce(31), however they gave the boiling point as 126-128°C at 744 mm for a purity of not less than 99% by vapor phase chromatography.

Elemental Analysis: Calculated for $C_7H_{14}O$: C, 73.64%; H, 12.35%
Found: C, 73.66%; H, 12.09%.

Oxidation of Bromohydrin. To determine whether the bromohydrin obtained in greater proportion was the primary or secondary alcohol, the bromohydrin was oxidized in a manner similar to that described by Shriner and Fuson.(32) This was done to know which alcohol was being used in the reactions for the attempted preparation of optically active neopentylethylene oxide as described in Chapter II, Section D.

In a 100 ml 3-neck flask equipped with a water condenser and stirrer, were mixed 7 gms of sodium dichromate, 15 ml of water and 2 to 3 gms of the bromohydrin obtained in the greater proportion. Slowly added over a 15 minute period was 10 ml of concentrated sulfuric acid. The reaction that followed was very exothermic so no external heating was necessary. After stirring for about one hour the contents of the flask were poured into 250 ml of water. The organic layer was then extracted with 3 (100 ml) portions of ether. The ether layer was then washed with 2 (50 ml) portions of water.

It was noticed that the ether layer was a pale blue color, which may have been due to the formation of a peroxide of chromium such as  $\left[O - \overset{O}{\underset{O}{Cr}} - O - O - \overset{O}{\underset{O}{Cr}} - O \right]$. To remove this the solution was washed with a saturated ferrous sulphate solution. The ether layer was then rewashed with 2 (50 ml) portions of water. This treatment removed the blue color.

The ether was then evaporated and the oxidized bromohydrin was purified and collected by gas chromatography using an Apiezon L on Chromosorb W column operated at 150°C.

Elemental Analysis: Calculated for $C_7H_{13}OBr$: C, 43.55%; H, 6.88%; Br, 41.16%. Found; C, 43.56%; H, 6.79%; Br, 41.41%.

Major Infrared Peaks: 2960 cm^{-1} ($-CH_3$), 1720 cm^{-1} (C=O), 1466 cm^{-1} ($-CH_2-$), 1393 cm^{-1} (t-Bu), 1368 cm^{-1} (t-Bu), 787 cm^{-1} (C-Br).

B. Preparation of Initiators

Preparation of Potassium t-Butoxide. Potassium t-butoxide (t-BuOK) was the initiator used for the kinetic study. It was prepared in a manner similar to that described by Snyder(5), except that a high speed stirrer was not used.

Before the reaction was begun the solvent, 1,2-dimethoxyethane (DME), was distilled from lithium aluminum hydride to remove any water present and the di-t-butyl peroxide was purified by distilling thru the Todd Distillation column at 55° (108 mm). The potassium metal (100 gms, 2.5 moles) was scraped clean under kerosene and then added to the dimethoxyethane (800 ml) in the reaction flask. The system had been flushed out with dry nitrogen and a slow stream of nitrogen was kept flowing through the system all during the reaction. The mixture was heated until the potassium melted and the DME began to reflux; stirring was then begun. The heating mantle was then removed and the pure peroxide added slowly at a rate sufficient to maintain refluxing of the DME.

After 146 gms (1 mole) of peroxide had been added the mixture was heated for an additional half hour to make sure all the peroxide had reacted. The unreacted potassium was allowed to settle out and by means of a nitrogen flushed syringe the liquid was transferred to a nitrogen flushed bottle stoppered with a serum cap. It is very important to follow the proper safety precautions when carrying out this reaction.

Standardization of t-BuOK Solution. A known volume of t-BuOK solution was added, by means of a nitrogen flushed calibrated syringe, to an excess of 0.1 N HCl. The excess acid was then titrated to a phenolphthalein end point with 0.1N NaOH. The initiator was standardized before being used in all polymerization runs. Dimethoxyethane was added to the initiator solution to keep it at constant molarity in case any DME evaporated through the serum cap.

Potassium Hydroxide. Potassium hydroxide (U.S.P. Pellets, approx. 85 wt.%) initiator was prepared by taking the pellets, mixing them with ethyl ether in an explosion proof Waring blender and grinding them to a fine powder. The ether was then evaporated under nitrogen and the powdered KOH stored under nitrogen. When it was used the KOH was transferred in a dry nitrogen filled glove bag so it would not pick up any moisture from the atmosphere.

Cesium Hydroxide. Cesium hydroxide (99.7 wt.% min, City Chemical Corporation) which is also very hygroscopic was stored under dry nitrogen. First the CsOH lumps were dissolved in water and then placed in a Rotovap flask. The flask was heated to 200°C under a high vacuum for about six hours to remove all the water. All work done with CsOH was also done in a dry nitrogen filled glove bag.

Zinc Chloride, Rubidium t-Butoxide and Lithium t-Butoxide. The zinc chloride (Fisher Scientific, Reagent), rubidium t-butoxide (MSA Research Corporation) and lithium t-butoxide (MSA Research Corporation) were used as obtained. Here again all work done with these initiators was done in a dry nitrogen filled glove bag.

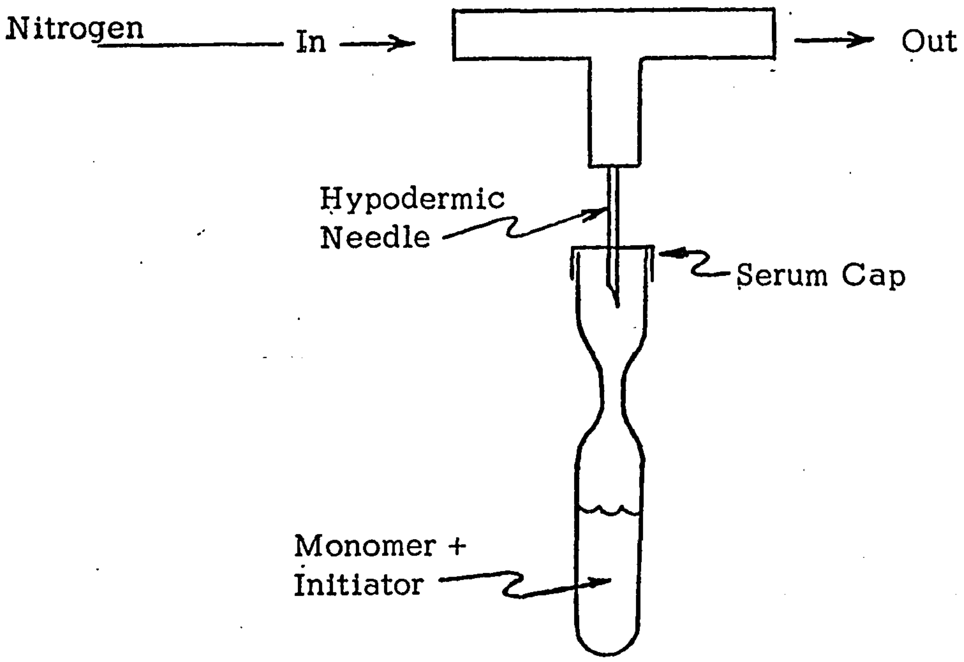
C. Polymerization Procedure for Kinetic Study

The procedure used for making up the individual ampoules for the kinetic study is outlined below;

The desired amount of monomer was injected into a nitrogen flushed tared bottle capped with a serum cap. The bottle was then weighed again. The volume of initiator necessary to give the correct monomer to initiator ratio was then injected into the bottle using a nitrogen flushed calibrated syringe.

Before this was done glass ampoules had been made by necking down pyrex tubes so they could be easily sealed by heating at the neck. The ampoules were flushed with nitrogen and capped with serum caps. From 10 to 15 ampoules were made up for each run.

In a nitrogen filled glove bag the monomer-initiator mixture was transferred to the individual ampoules by means of a syringe. The ampoules were then placed in a dry-ice acetone mixture to cool them so they could be sealed by means of an oxygen-gas torch. To prevent the ampoules from blowing out at soft spots while they were being sealed the setup shown below was used:



A hypodermic needle connected to a glass tee was inserted into the ampoule. Nitrogen was kept flowing through the tee so that expanding gases could escape and air could not get back into the ampoule. The sealed ampoules were then put into a constant temperature bath to react. The ampoules were removed from the bath at specific times so samples could be titrated for unreacted monomer.

Solid Initiator Polymerizations. For the other polymerizations using solid initiators a little different procedure was used. These runs were made at room temperature so screw cap bottles were used. The bottle was first flushed out with nitrogen and then weighed. The initiator was added in a nitrogen filled glove bag and the bottle weighed again. Enough monomer was then added, in the glove bag, to give the desired monomer to initiator ratio. The bottle was weighed again and if the sample was to be shaken it was placed on a Burrell shaker.

Titration of Monomer. All of the kinetic runs were followed by titrating for the amount of unreacted monomer remaining at different time intervals. This was done by the method presented by B. J. Gudzinowicz(33), using dodecanethiol. However it was found that for the titrations the reaction time between the epoxide and the dodecanethiol had to be lengthened from the twenty minutes recommended to one hour because of the slow reactivity of the 4,4-dimethyl-1,2-epoxypentane. When shorter times were used the number of equivalents of epoxide obtained per gram of sample would usually be low. Periods longer than one hour gave the same values that the one hour reaction time gave. The theoretical value for this epoxide is 0.00875 equivalents per gram of sample and the average value obtained by titration was 0.00878 ± 0.0001 equivalents per gram of sample.

Procedure. The sample containing about 2.5 milliequivalents or less of epoxide was weighed in an iodine flask. Forty milliliters of about 0.1 N dodecanethiol in isopropyl alcohol was added. Three milliliters of about 0.9 N KOH in absolute alcohol were added as a catalyst and the mixture stirred for one hour. At the end of the hour ten milliliters of acetic acid and one hundred milliliters of isopropyl alcohol were added. This mixture was then titrated with standard 0.1 N iodine solution to a light yellow end point which remained for thirty seconds. This value of iodine was titer A.

To take into account the effect of air oxidation that occurs during the one hour mixing period forty milliliters of the dodecanethiol solution was mixed with three milliliters of the alcoholic KOH and stirred for one hour. Then ten milliliters of acetic acid and one hundred milliliters of isopropyl alcohol were added and the mixture titrated with the 0.1 N iodine solution. This was titer C. This titration was run at each point along with the A values because its value constantly changed.

Also for each run a mixture of forty milliliters of dodecanethiol solution, ten milliliters of acetic and one hundred milliliters of isopropyl alcohol was titrated with the 0.1 N iodine solution. This was to standardize the dodecanethiol solution. The number of milliliters of iodine solution used here was titer B.

Calculation of the equivalents of epoxide per gram of sample was made as follows;

$$D = B - \frac{A}{B}(B - C)$$

where D is the corrected number of milliliters of 0.1 N iodine solution required for the direct dodecanethiol blanks corrected for air oxidation.

$$\frac{\text{Equivalents epoxide}}{\text{gms sample}} = \frac{(D - A)\ N}{1000 \times \text{gms sample}}$$

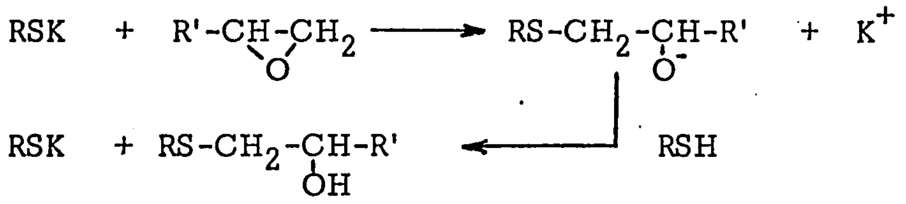
where N = Normality of the iodine solution

The reactions involved in this analysis are;

1. The dodecanethiol with the catalyst,

$$RSH + KOH \longrightarrow RSK + H_2O$$

2. The monomer with the RSK,



$$RSK + R'\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \longrightarrow RS\text{-}CH_2\text{-}\underset{O^-}{CH}\text{-}R' + K^+$$

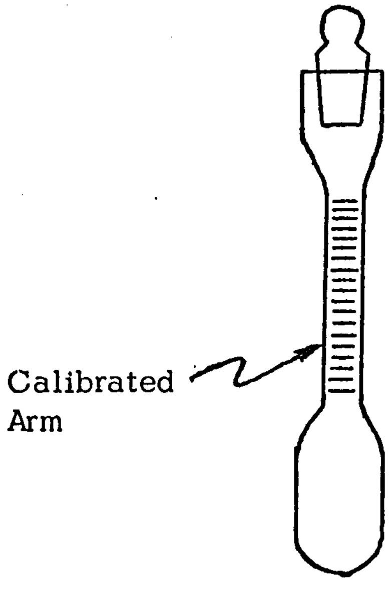
$$RSK + RS\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}R' \longleftarrow RSH$$

The new RSK then reacts with another monomer molecule.

3. The reaction of the iodine solution with the unreacted dodecanethiol,

$$2\,RSH + I_2 \longrightarrow RS\text{-}SR + 2\,HI$$

<u>Density Measurements</u>. Titrations of the samples at various times gave values of the equivalents of unreacted monomer per gram of sample. To put these values into standard units of moles/liter, density was also measured as a function of time. This was done by using a pycnometer as shown below;



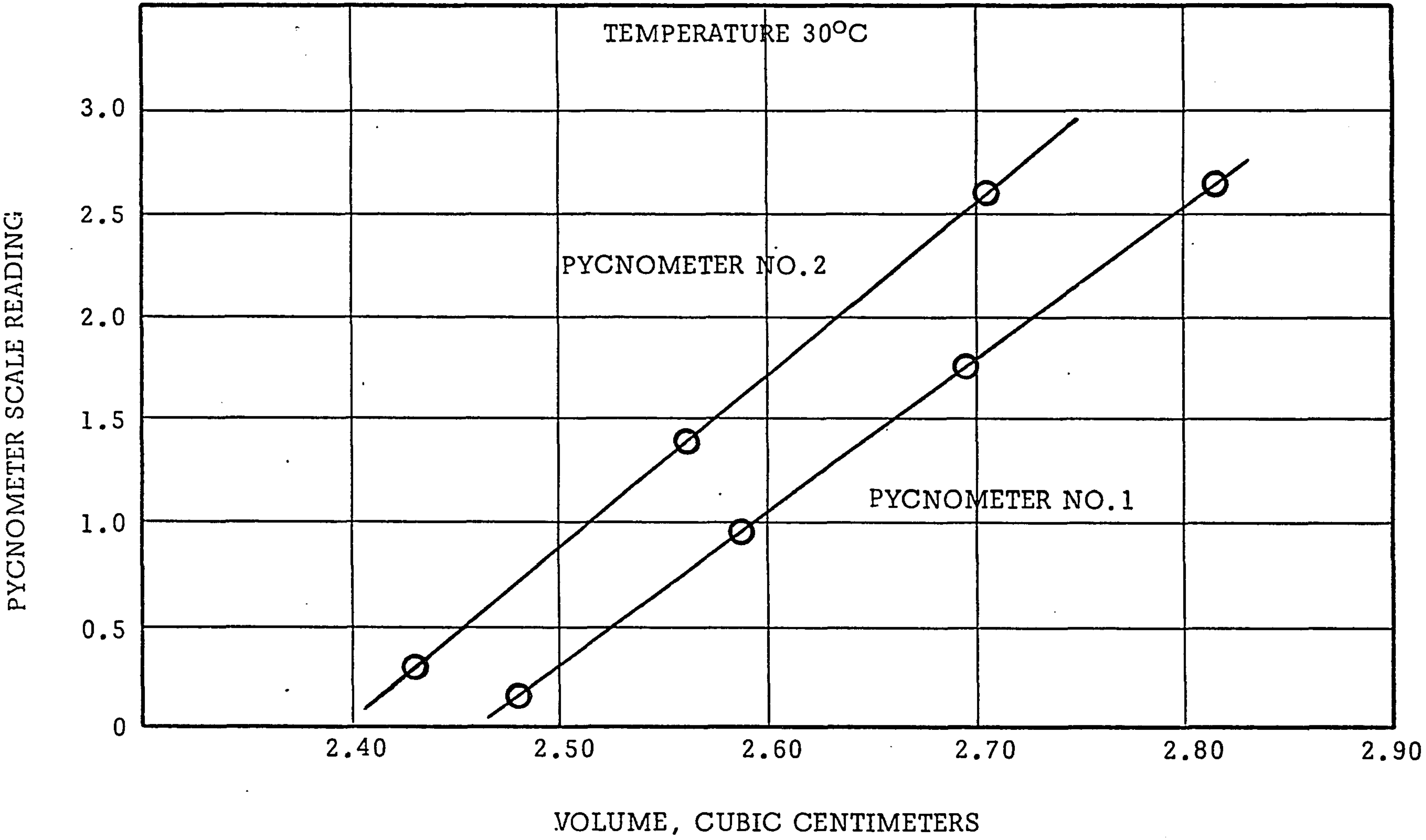
The pycnometer was first flushed out with nitrogen and then weighed. The monomer-initiator mixture was then added to the pycnometer in a nitrogen filled glove bag and the pycnometer was weighed again. In the glove bag stopcock grease was put on the ground glass stopper. Sealing wax was then melted around the stopper seal so that the entire pycnometer could be immersed in the constant temperature bath.

The change in density could be followed by reading the change in height of the liquid in the pycnometer calibrated arm. The calibration curves for the pycnometers used are shown in Fig. I. These volumes which are for 30°C were corrected for the glass expansion for the runs at 40, 60 and 80°C.

The following data were collected for each run;

1. Weight of monomer.
2. Weight, volume and molarity of initiator.
3. Reaction temperature - controlled to ± 0.2°C.
4. Time in hours at the removal of each ampoule.
5. Pycnometer readings converted to densities.
6. Sample weights for titrations - two samples weighed to 0.1 milligram for each ampoule.
7. Titer B, volume of 0.1 N iodine solution required to standardize dodecanethiol solution, once for each run.

FIGURE I PYCNOMETER CALIBRATION CURVES



8. Titer A, volume of 0.1 N iodine solution required to react with dodecanethiol that did not react with the monomer. Duplicate titrations were run for each point.
9. Titer C, volume of 0.1 N iodine solution required to titrate dodecanethiol blanks that are mixed for the same length of time as Titer A. Determined once for each point.

Polymer Workup. All of the workups on the neopentylethylene oxide polymers were done the same way regardless of the initiator used.

When the sample was ready for workup the ampoule or bottle was opened and the contents were diluted with benzene and poured into a separatory funnel. The container was rinsed out several times with benzene to dissolve all the polymer. The solution was then washed twice with 0.1 N hydrochloric acid and then twice with a saturated solution of sodium bicarbonate. Next the benzene solution was washed three or four times with distilled water. To prevent the formation of an emulsion during the water wash, about fifty milliliters of chloroform was added to the benzene solution.

This solution was then put in a tared beaker and air dried until most of the liquid evaporated. The beaker was then placed in a vacuum drying oven at about 40°C for from 12 to 24 hours until constant weight was obtained.

Determination of Molecular Weight. The number average molecular weights were determined by means of a Thomas Isothermal Molecular Weight Apparatus. The basic principle of this method is that a drop of solvent and solute will absorb molecules of solvent from a solvent vapor atmosphere in direct proportion to the solute molal concentration. This phenomenon is exothermic causing a rise in the temperature of the drop relative to the temperature of the solvent.

In the apparatus are two thermistors which are first balanced in a Wheatstone bridge by putting a drop of pure solvent on each thermistor. Then a solution of known concentration is placed on one thermistor and the resulting temperature difference is measured by rebalancing the bridge with a potentiometer. These readings are then used to calculate a molecular weight for each concentration. By plotting 1/M.W. vs. Molality and extrapolating to zero concentration the number average molecular weight can be obtained. A sample calculation is shown in Appendix B.

The conditions used for operating the apparatus were:

Bath Temperature: 45°C

Solvent: Benzene

Bridge Current: 20 ma

Sensitivity: maximum

Time for drops to come to equilibrium: 1 1/2 minutes

Cell constant: Determined to be 22,000

Infrared Absorption Spectra. Most of the infrared spectra were run on a Beckman IR-8 Infrared Spectrophotometer fitted with sodium chloride optics. Occasionally spectra were run on a Perkin-Elmer Model 137 Spectrophotometer. The band at 6.238 microns from a piece of polystyrene film was used to calibrate the instruments for each spectrum run.

For infrareds in the region of 400 to 800 cm^{-1} a Perkin-Elmer Infracord was used fitted with KBr cells or discs. Some of the infrareds obtained during the course of this work are shown in Appendix C. The wavelenghts of the Infracord were calibrated with tribromomethane.

Gas Chromatography. All the gas chromatographic work, both analytical and preparative, was done on an Aerograph A-700 Autoprep Unit using helium as the carrier gas.

Boiling Points. Boiling points were determined for the author by Dr. Herbert Kemme. A DuPont 900 Differential Thermal Analyzer was used for these determinations.

N.M.R.Spectra. All the N.M.R.spectra were run on a Varian A 60 Spectrometer. The compounds were run in CCl_4 solutions using tetramethylsilane as an internal standard. Spectra of the monomer and several polymers are shown in Appendix C.

D. Methods Attempted for the Preparation of Optically Active Neopentylethylene Oxide

To obtain the optically active epoxide attempts were made to resolve the enantiomers of both the bromohydrin and the epoxide. The various methods that were tried to make this separation are described in the following sections.

Preparation of Diastereomers. By reacting the bromohydrin enantiomers with an optically active acid two diastereomers would result. These diastereomers would have different physical properties and therefore might be separated by distillation or gas chromatography.

The bromohydrin when prepared was a mixture of the primary and secondary alcohols. The pure lower boiling secondary alcohol was obtained by distillation in a spinning band column. Only the pure secondary alcohol was used in the preparation of the diastereomers. If the primary alcohol had not been removed two sets of diastereomers would have resulted and thus complicated the separation. l-Menthoxyacetic acid was used to react with the bromohydrin because there is only one reactive group on this acid.

The optical rotation for l-menthoxyacetic acid was given by Frankland and O'Sullivan (34) as $[\alpha]_D^{20} = -92.93^\circ$ for a 4.218 gm/100 cc solution. The optical rotation of the acid used in these experiments was $[\alpha]_D^{20} = -88.3^\circ$ for a 4.25 gm/100 cc solution. Methanol was used as the solvent for both of these solutions.

The reaction between the l-menthoxyacetic acid and the bromohydrin was carried out in a three neck creased flask equipped with a stirrer, Dean-Stark trap, condenser and thermometer. This was done so that the benzene-water azeotrope could be boiled off and collected in the Dean-Stark trap. In the Dean-Stark trap the water and benzene would form two immiscible layers with the water settling to the bottom. By measuring the amount of water formed the percent conversion to product could be calculated. The water was removed from the reaction vessel to drive the reaction to completion.

Mixed in the flask were 37 ml (0.234 moles) bromohydrin, 50 gms (0.234 moles) l-menthoxyacetic acid and 100 ml of benzene. About 0.5 gms p-toluenesulfonic acid was used as the catalyst. The flask was heated at about 90°C (refluxing) for 30 hours until about 3.5 ml (0.194 moles) of water were collected in the trap.

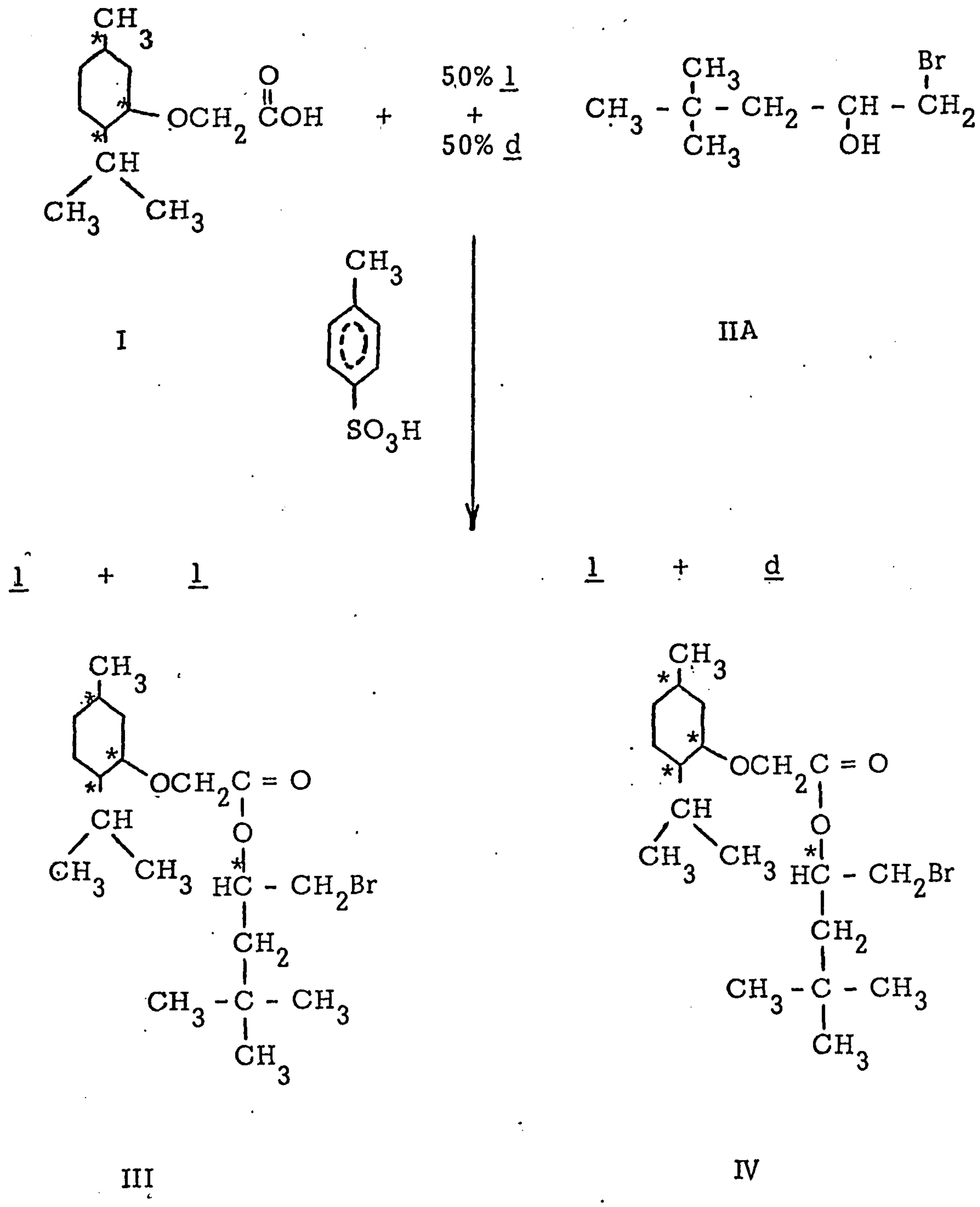
The products were washed twice with sodium bicarbonate solution then three times with distilled water and then dried over calcium chloride. The diastereomers were partially purified by distillation in a semimicro-distillation apparatus at about 170°C and 2 mm Hg. The density of the diastereomers was 1.11 gm/ml and the optical rotation was measured as, $[\alpha]_D^{20} = -52.8^\circ$, neat in a 1 dm. tube.

The reaction proceeded, as shown on the following page, to give the two diastereomers.

Attempted Resolution of Diastereomers by Distillation and Gas Chromatography. The diastereomers were distilled in both a Todd distillation apparatus and a spinning band column. The Todd column had about 60 theoretical plates while the spinning band column about 120 theoretical plates. The lowest pressure that could be obtained in this equipment was 0.5 mm Hg.

The main effort to separate the diastereomers was made by means of gas chromatography. The following columns and conditions were used in the attempted separation. For all the columns used the injector temperature was kept above 225°C and the detector temperature was about 250°C. Sample sizes injected into the various columns were kept between 1 and 10 µl.

1.



I

IIA

III

IV

1. 20% SE-30 (Silicone gum rubber) on 45/60 Chromosorb W, 10 ft. preparative column

Conditions:

Column Temperature	Flow Rate
300°C	150 cc/min
250	200
Programmed from 120 to 300	200

Results: At 250°C one ester peak came out after a retention time of 10 minutes.

2. 20% SF-96 (Silicone fluid) on 60/80 Chromosorb W, 5 ft. analytical column

Conditions:

Column Temperature	Flow Rate
195 to 220°C	200 cc/min

Results: Esters came out as one peak after a retention time of 10 minutes.

3. 20% Apiezon L on 60/80 Chromosorb W, 10 ft. analytical column

Conditions:

Column Temperature	Flow Rate
225°C	100 cc/min
250	100

Results: After retention times of about 50 minutes only one very broad peak was obtained in each case.

4. 20% Carbowax 20M on Chromosorb P, 10 ft. analytical column

Conditions:	Column Temperature	Flow Rate
	$220^{\circ}C$	200 cc/min

Results: Ran for times as long as 70 minutes after injecting esters but did not get any peaks on recorder.

5. 5% Carbowax 1500 on Teflon T-6, 10 ft. analytical column

Conditions:	Column Temperature	Flow Rate
	$135^{\circ}C$	200 cc/min

Results: Ran for times as long as 60 minutes but no ester peak came out.

6. 10% Carbowax 4000 & TPA(Terephthalic acid) on Fluoropak, 10 ft. analytical column

Conditions:	Column Temperature	Flow Rate
	$160^{\circ}C$	200 cc/min

Results: Esters did not come out of column even after running for 60 minutes.

7. 20% QF-1 (Fluorosilicone) on 60/80 Chromosorb W, 10 ft. analytical column

Conditions:	Column Temperature	Flow Rate
	$225^{\circ}C$	100 cc/min
	210	50
	175	150

Results: At the two higher temperatures some sort of reaction may have occurred on the column because four sharp peaks were obtained. While at 175°C only one peak was obtained after a retention time of 30 minutes.

8. 20% QF-1 (Fluorosilicone) on 30/60 Chromosorb P, 5 ft. analytical column

Conditions:

Column Temperature	Flow Rate	Retention Time
230°C	35 cc/min	8 min
225	50	-
225	110	-
215	200	16
200	200	29

Results: At the highest temperature tried, the chromatogram showed one long peak with a slight dip in the middle, which may have been a partial separation of the two diastereomers. However when the other conditions, giving longer retention times, were tried only one broad peak was obtained.

9. 20% Silicone 550 on 60/80 Chromosorb W, 10 ft. analytical column

Conditions:

Column Temperature	Flow Rate
220°C	100 cc/min
250	150.

Results: At 220°C nothing came out after running for 1 1/2 hours.

At 250°C one peak came out after a retention time of 18 minutes.

10. 20% DEGS (Diethyleneglycol succinate) on 60/80 Chromosorb W, 10 ft. analytical column

Conditions:	<u>Column Temperature</u>	<u>Flow Rate</u>
	190°C	250 cc/min

Results: Ran for 90 minutes but the esters did not come through the column.

11. 20% STAP (All purpose Steroids) on 60/80 Chromosorb W, 10 ft. analytical column

Conditions:	<u>Column Temperature</u>	<u>Flow Rate</u>
	250°C	200 cc/min

Results: Ran for 90 minutes but the esters did not come through the column.

12. 20% NPGS (Neopentyl glycol succinate) on 60/80 Chromosorb W, 10 ft. analytical column

Conditions:	<u>Column Temperature</u>	<u>Flow Rate</u>
	230°C	250 cc/min

Results: Ran for 150 minutes but the esters did not come through the column.

13. 20% XE-60 (Cyano silicone gum) on 60/80 Chromosorb W, 10 ft. analytical column

Conditions:	Column Temperature	Flow Rate
	235°C	90 cc/min

Results: After a 10 minute retention time one sharp peak was obtained.

Preparation of Gas Chromatograph Columns With Optically Active Substrate. The columns with optically active substrate were usually prepared in a manner similar to that used in the preparation of the α-D-glucose pentaacetate column. For a 20 weight percent column 4.2 gms of α-D-glucose pentaacetate was mixed with 16.8 gms of Chromosorb W and 100 ml of benzene. These were mixed in a Rotovap flask and then the benzene was removed under vacuum at about 50°C. The dried mixture was then put into a 10' by 1/4" gas chromatograph column. This was done by adding the mixture to one end of the column while shaking the column and pulling a slight vacuum at the other end. A small piece of glass wool was placed at both ends of the column so that the solid material would not fall out. The column was then attached in the gas chromatograph and allowed to purge overnight. The purge temperature was about 10°C above the highest operating temperature.

Columns Used for Attempted Separation. The following columns were prepared and used to try and separate the enantiomers of the oxide or the bromohydrin or both.

1. 20% D-(+)-Galactose on Chromosorb W, 10 ft. analytical column. Melting point - 167-169°C

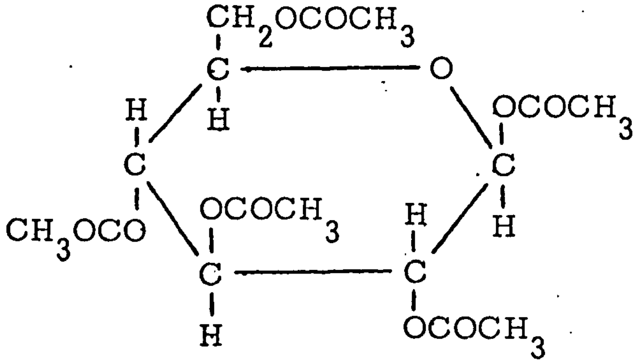
   Conditions: For the attempted separation of d and l bromohydrin

   Injector Temperature-175°C   Detector Temperature-200°C

Column Temperature	Flow Rate
150°C	10 cc/min
170°C	10

   Results: After retention times for the bromohydrin of 10 and 6 minutes respectively one sharp peak was obtained at both the above conditions.

2. 20% α-D-Glucose Pentaacetate on Chromosorb W, 10 ft. analytical column. Melting point - 109-111°C



Condition: For the attempted separation of d and l bromohydrin

Injector Temperature-175°C Detector Temperature-200°C

Column Temperature	Flow Rate
150°C	10 cc/min

Results: After a retention time of 54 minutes only one broad peak was obtained.

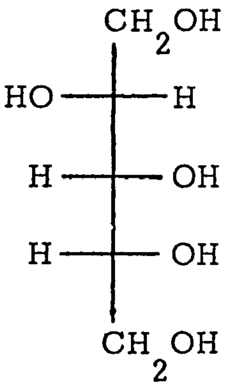
Conditions: For the attempted separation of d and l oxide

Injector Temperature-135°C Detector Temperature-175°C

Column Temperature	Flow Rate
100°C	20 cc/min
125	5

Results: At 100°C after a retention time of 7 minutes one peak was obtained and at 125°C one peak was obtained after a retention time of 40 minutes.

3. 20% L-(-)-Arabitol on Chromosorb W, 10 ft. analytical column.
Melting point - 98-101°C



L-(-)-Arabitol

Conditions: For the attempted separation of d and l oxide

Injector Temperature-130°C Detector Temperature-175°C

Column Temperature	Flow Rate
115°C	10 cc/min
90	20

Results: At both temperatures one peak was obtained after retention times of 10 and 5 minutes respectively.

Conditions: For the attempted separation of d and l bromohydrin

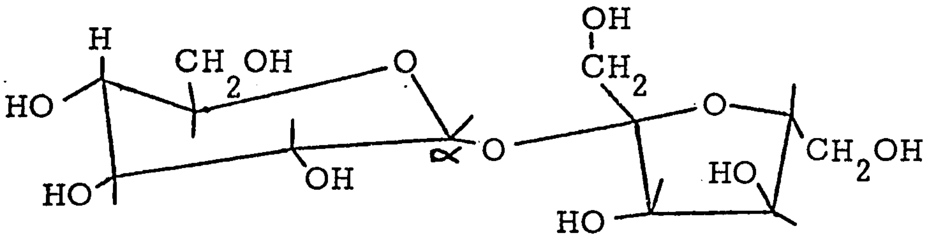
Injector Temperature-170°C Detector Temperature-200°C

Column Temperature	Flow Rate
130°C	10 cc/min
145	10
153	10
160	10

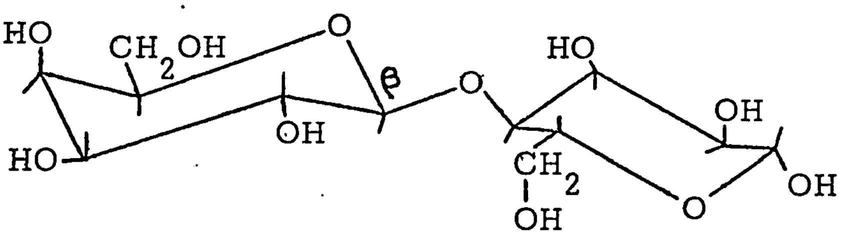
Results: Retention times ranged from 4 minutes to 9 minutes. At the lowest temperature two peaks were obtained, however as the temperature was raised the relative sizes of the two peaks changed with one peak growing larger while the other got smaller. Finally at 160°C only one peak was obtained, this was collected and run on the infrared. The IR showed the collected sample to be a mixture of bromohydrin, epoxide and also showing up was a strong C=O peak similar to that obtained when the bromohydrin was oxidized as described on page 27. This would seem to indicate that some sort of reaction was occurring between the bromohydrin and the L-(-)-arabitol.

4. 20% Nujol - 40% Sucrose - 40% Lactose, 10 ft. analytical column.

Sucrose,



Lactose,



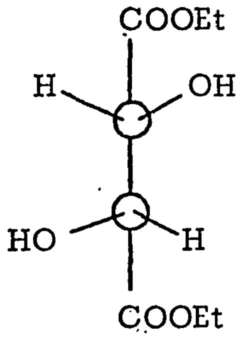
Conditions: For the attempted separation of d and l oxide

Injector Temperature-130°C Detector Temperature-175°C

Column Temperature	Flow Rate
115°C	100 cc/min

Results: After a retention time of 1/2 hour one long peak was obtained with no apparent separation.

5. 20%(+) Diethyl-D-Tartrate on Chromosorb W, 10 ft. analytical column, Boiling point - 152-155°C/12 mm



This column had to be prepared in a different way because diethyl-D-tartrate was a liquid at room temperature. The coiled column was first straightened out and then filled with chromosorb W. The liquid tartrate was poured into the vertical column and allowed to slowly flow down and coat the chromosorb. The column was then recoiled and purged overnight on the gas chromatograph. This column was found to be good only up to a temperature of 105°C.

Conditions: For the attempted separation of d and l oxide

Injector Temperature-130°C   Detector Temperature-175°C

Column Temperature	Flow Rate
70°C	120 cc/min
88	100
100	120

Results: After retention times of 22, 18 and 9 minutes respectively for the increasing temperature of 70, 88 and 100°C only one peak was obtained in all three cases.

Conditions: For the attempted separation of d and l bromohydrin

Injector Temperature-170°C Detector Temperature-200°C

Column Temperature	Flow Rate
100°C	120 cc/min

Results: Ran at these conditions for over two hours but nothing came out of the column.

Attempted Resolutions by Differences in Reaction Rates. Diastereomers have different heats of formation(27), therefore it was thought that the enantiomers could be partially separated because they would react at different rates with an optically active substance. Two different procedures were tried, one by reacting the bromohydrin with an unequal number of moles of l-menthoxyacetic acid and the other by reacting the bromohydrin with an alkaloid.

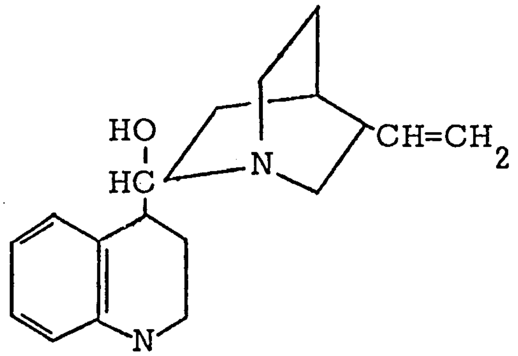
Reaction of Bromohydrin with l-Menthoxyacetic Acid. For the reaction of the bromohydrin with l-menthoxyacetic acid the same procedure as described on page 44 was used except that an unequal number of moles of reactants was used. Mixed in 100 ml of benzene were 0.1 moles (21.5 gms) of l-menthoxyacetic acid, 0.154 moles (30 gms) of bromohydrin and 0.5 gms of p-toluenesulfonic acid.

The mixture was heated gently for about 170 hours. To remove the water formed the mixture was heated up to reflux several times during the reaction. A total of 1.6 ml (0.089 moles) of water was collected in the Dean-Stark trap. The bromohydrin that did not react was collected by distillation.

In a one decimeter long polarimeter tube the pure unreacted bromohydrin did not show any optical rotation. The bromohydrin was converted to the epoxide by the usual reaction with KOH, but the epoxide did not show any optical rotation either.

Reaction of Bromohydrin with an Alkaloid. For this reaction as in the previous one only the secondary alcohol of the bromohydrin mixture was used. The secondary alcohol was separated from the primary alcohol by means of a spinning band distillation column. For this reaction the alkaloid cinchonine was used. Cinchonine has the following structure;

(+)



Mixed in a 150 ml, 3 neck, flask equipped with stirrer and reflux condenser were 15 ml (0.947 moles) of bromohydrin and 16.8 gms (0.6 moles) of cinchonine. These were stirred at room temperature for 65 hours.

The resulting pasty mixture was diluted in ether and filtered. The liquid layer was distilled and 8 ml (0.0505 moles) of unreacted bromohydrin was recovered. Again in the one decimeter polarimeter tube the unreacted bromohydrin showed no optical rotation.

Attempted Resolution by Crystallization. Crystallization was tried in an attempt to resolve the enantiomers. This was done by mixing 0.2 moles of bromohydrin (secondary alcohol) with 0.2 moles (29.6 gms) of phthalic anhydride in 25 gms of dry pyridine. The mixture was heated on a water bath for 1.5 hours, then cooled and mixed with 400 ml of acetone.

After evaporation of most of the acetone, two immiscible layers were obtained. Infrared spectra run on the lower layer showed ester and acid bands but no pyridine bands. Some of this mixture was reacted with KOH. An IR of the resulting mixture showed no epoxide bands, however absorption in the double bond region was found.

To prevent any reactions that might occur with pyridine, the bromohydrin was reacted with phthalic anhydride in ether with a few drops of concentrated H_2SO_4 as catalyst. After refluxing for six hours the mixture was cooled and mixed with acetone. Solid was precipitated by adding ice and water. The solid was separated by filtering and then air dried. The melting point of this solid was found to be 130-31°C, the same as pure phthalic anhydride.

The same reaction was tried using benzene as the solvent and 10 ml of concentrated H_2SO_4 as catalyst. However upon heating, the mixture turned deep purple indicating decomposition of the bromohydrin.

The reaction between the bromohydrin and phthalic anhydride should have given the enantiomeric half esters. These half esters could then have been reacted with an alkaloid to form two diastereomers. The diastereomers might have then been separated by crystallization. However during the present work this method was never carried far enough to actually try the resolution by crystallization.

CHAPTER III

RESULTS AND DISCUSSION

A. Preparation of Racemic Neopentylethylene Oxide.

The reactions involved in the four step synthesis of neopentylethylene oxide are shown on pages 21 and 22. A table of the physical properties of 4,4-dimethyl-1-pentene and neopentylethylene oxide is given in Appendix A.

During the preparation of the olefin two main problems had to be solved. These were, inadequate stirring of the reaction mixture and the removal of unreacted t-butyl chloride and allyl bromide from the olefin.

Because the reaction for preparing the olefin was run at less than 5°C the unreacted Grignard tended to solidify and build up on the sides of the flask. However by using a Hershberg stirrer the Grignard was scraped off the flask and kept mixed with the allyl bromide. When the Hershberg stirrer was used the yield of olefin went up about 20% over runs with smaller stirrers.

It was found that impurities in the olefin interfered with its subsequent reaction with N-bromosuccinimide (NBS). When impure olefin was used the reaction was very exothermic and all the solid NBS disappeared in about 1 1/2 hours. Analysis showed the reaction product to be 66% bromohydrin and 34% dibromide. The reason for the formation of the dibromide was not determined. To prevent the formation of the dibromide, which could not be used in the preparation of the oxide, great care was taken to purify the olefin. The procedure described in the experimental section removed the last traces of halide but much olefin was lost as distillation holdup. The best yield obtained following these procedures was 56% based on the allyl bromide.

Whitmore and Homeyer(29) purified the olefin by making the dibromide, purifying this by distillation and then converting back to the olefin by reacting with zinc dust in 95% alcohol. Their overall yield of halogen free olefin was about 66% based on the allyl bromide.

It is interesting to note here that when Millikin, Wakenen and Gerry(35) prepared 4,4-dimethyl-1-pentene by adding the allyl bromide to the Grignard instead of the reverse, a yield of only 5% was obtained. During the present work this method was also tried but a yield of 33% (greater than 98% pure olefin) was obtained.

Botteron and Shulman(36) prepared 4,4-dimethyl-1-pentene by the same method as Whitmore and Homeyer.(29) However they used allyl chloride instead of allyl bromide. Their yield of olefin was only 38%.

The reaction of the olefin with NBS and water yielded a mixture of bromohydrins as shown on page 21. Some of the results from this reaction are shown in Table 1, page 64.

It was found that the 4,4-dimethylpentene bromohydrin was actually a mixture of the primary and secondary alcohols. This mixture could be used for the preparation of racemic neopentylethylene oxide because ring closure of both bromohydrins would yield the same epoxide. However when the bromohydrin was used in reactions to make the optically active epoxide it was of interest to know which alcohol was obtained in greater proportion. Also each alcohol would yield two diastereomers when reacted with _l_-menthoxyactic acid. This would result in a mixture of two sets of diastereomers which would considerably complicate the attempted resolution procedures. Therefore it was necessary to purify the predominate lower boiling alcohol by distilling through a spinning band column.

To try and identify which alcohol was obtained in greater proportion, the bromohydrins were separated by gas chromatography and their infrared spectra run. To help differentiate the primary and secondary alcohols of the 4,4-dimethylpentene bromohydrin the bromohydrins of propene were also separated by gas chromatography and their infrared spectra run.

TABLE 1

YIELDS OF BROMOHYDRIN

N-Bromo succinimide Moles	Olefin Moles	Water ml	Reaction Time, Hrs.	Yield BH
0.7	0.7	400	40	77.7[a]
2.75	2.75	1000	40	85[a]
2.75	2.75	1000	85[b]	83.5[c]
1.0	1.0	500	84[b]	75[c]
0.6	0.6	400	27[d]	78.5[c]
0.345	0.345	300	72[b,d]	80[c]

a. Bromohydrin 95% pure
b. Reaction cooled to about 15°C
c. Bromohydrin 98% pure
d. Stirred in creased Morton flask at high speed

For the propene bromohydrins it was known which fraction was the primary alcohol and which was the secondary alcohol. The major peaks of all four spectra are listed in Table 2, page 66.

In the 3600 cm^{-1} region the primary alcohols both showed a weak peak at 3650 cm^{-1} and a much stronger peak at 3603 cm^{-1} for the 4,4-dimethylpentene bromohydrin and at 3597 cm^{-1} for the propene bromohydrin. In this region both secondary alcohols showed one strong peak. However the peak at 3650 cm^{-1} was only a shoulder in the major peak.

According to Zeiss and Tsutsui(37) saturated secondary aliphatic alcohols probably absorb in the 1125-1085 cm^{-1} range. However, the only common absorption for the secondary alcohols was at 1136 cm^{-1} for the propene bromohydrin and at 1147 cm^{-1} for the 4,4-dimethylpentene bromohydrin. These are a little high and may not be due to the alcohol group. For straight chain primary alcohols the range of 1085-1050 cm^{-1} was given for the C-O stretching. As can be seen from the table both primary alcohols absorb at 1055 cm^{-1}.

Nakanishi(38) has stated that secondary alcohols have an out-of-plane bending vibration at about 650 cm^{-1}. Both the secondary alcohol of the propene bromohydrin and the 4,4-dimethylpentene bromohydrin have

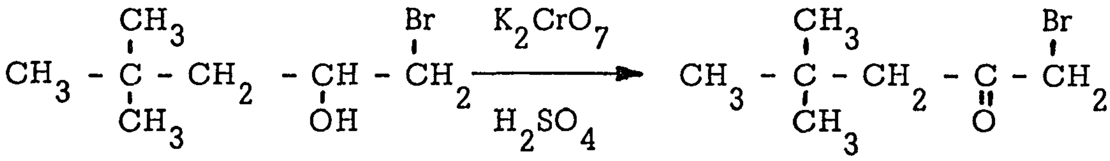
TABLE 2

MAJOR INFRARED BANDS OF BROMOHYDRINS

$CH_3\text{-}\underset{OH}{CH}\text{-}\underset{Br}{CH_2}$	$CH_3\text{-}\underset{Br}{CH}\text{-}\underset{OH}{CH_2}$	$t\text{-}Bu\text{-}CH_2\underset{Br}{CH}\text{-}\underset{OH}{CH_2}$	$t\text{-}Bu\text{-}CH_2\underset{OH}{CH}\text{-}\underset{Br}{CH_2}$
3650 cm^{-1}(Sh)	3650 cm^{-1}(Sh)	3650 cm^{-1}(Sh)	3650 cm^{-1}(Sh)
3610 (S)	3597 (S)	3603 (M)	3603 (M)
3448 (S)	3484 (S)		
2985 (S)	2985 (S)	2967 (S)	2967 (S)
2941 (M)	2941 (S)		
2915 (M)		2915 (W)	2915 (Sh)
	2870 (S)	2882 (W)	2882 (M)
1453 (M)	1451 (S)	1473 (S)	1473 (M)
1425 (S)			1425 (M)
	1391 (S)	1385 (M)	
1379 (S)	1376 (Sh)	1370 (S)	1366 (S)
1344 (M)	1351 (W)		
1325 (W)			1314 (M)
1258 (S)	1241 (S)	1245 (Sh)	1248 (S)
1222 (S)	1229 (Sh)	1225 (S)	1224 (Sh)
		1200 (Sh)	
1183 (W)	1171 (M)		
1136 (S)			1147 (W)
1110 (S)	1112 (W)		
	1099 (W)		
1075 (W)	1086 (W)	1076 (S)	1088 (M)
	1056 (S)	1055 (S)	
1049 (W)			
1031 (S)	1024 (S)	1026 (M)	1021 (M)
936 (S)	913 (M)		
676 (M)			676 (W)
661 (S)			
	639 (M)		642 (M)

bands at 675 cm^{-1}. However, this absorption could have been due to the C-Br linkage, but neither of the primary alcohols showed absorption in this region so the C-Br may absorb at a lower frequency.

Because comparison by infrared was not good enough to positively identify the bromohydrin obtained in greater proportion as the secondary alcohol, this bromohydrin was purified and oxidized by the method described on page 27. An infrared spectrum of the oxidized bromohydrin showed a major peak at 1727 cm^{-1} which is in the region for an α-halogen-substituted ketone. Also the absence of the two bands near 2700 cm^{-1} usually present in aldehydes helps confirm the belief that the compound was a ketone. The compound also had a highly pungent odor which is usually associated with α-bromo ketones. Under these conditions the primary alcohol would have been oxidized to the acid giving a strong I.R. band at 1200-1300 cm^{-1}. However no acid bands were found in the spectrum.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{OH}{CH}-\overset{Br}{CH_2}\xrightarrow[H_2SO_4]{K_2CrO_7}CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{O}{\overset{\|}{C}}-\overset{Br}{CH_2}$$

Secondary Alcohol

α-Bromo Ketone
1-bromo-4,4-dimethylpentan-2-one

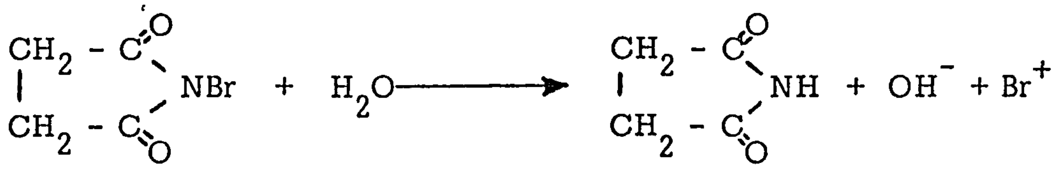
Also the initial compound had the lower boiling point of the two bromohydrins. For alcohol isomers a secondary alcohol usually has a lower boiling point than a primary alcohol. For these reasons it was concluded that the initial compound was the secondary alcohol.

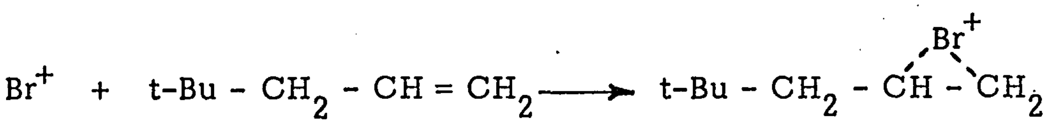
This compound has been prepared previously by Asinger and Gentz.(39) They treated 2,2-dimethylpentan-4-one with dioxane dibromide to give a mixture of the isomeric bromine derivatives, 3-bromo-2,2-dimethylpentan-4-one and the compound obtained in this study, 1-bromo-4,4-dimethylpentan-2-one. The α-bromo ketone was reported to have a boiling point of 72-73°C at 11 mm. Hg and a refractive index of $n_D^{20}=1.4627$.

There appears to be a relationship between the reaction temperature and the amount of minor product (primary alcohol) formed. However, no careful study to determine the effect of temperature was made. In the reactions run at room temperature there was about 14% of the primary alcohol formed while for the reactions run at 15°C there was only 7.7% primary alcohol formed.

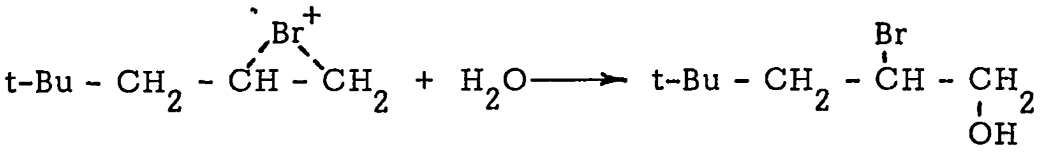
The reaction of olefin, N-bromosuccinimide and water probably occurs by the following steps;

(a)

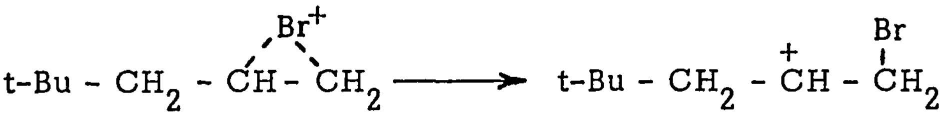


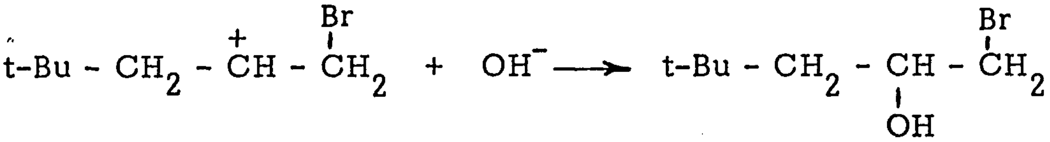
(b) 

The primary alcohol is the minor product.

(c) 

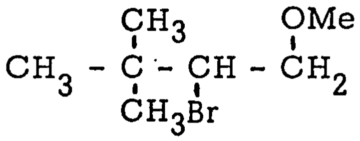
The secondary alcohol is the major product.

(d) 

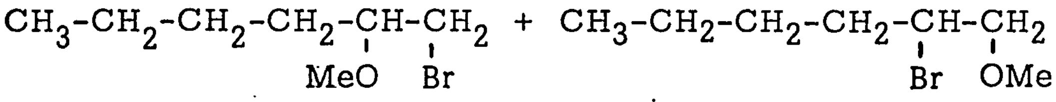
(e) 

$$\text{t-Bu} - CH_2 - \overset{+}{C}H - \overset{Br}{C}H_2 + OH^- \longrightarrow \text{t-Bu} - CH_2 - \underset{OH}{CH} - \overset{Br}{C}H_2$$

This type of reaction mechanism was suggested by Gould(40) for the reaction of HOCl with olefins and would seem to apply to this reaction. The presence of the secondary carbonium ion would account for the major product being the secondary alcohol. The primary alcohol could come from the H_2O attacking the primary position on the cyclic bromonium ion.

Puterbaugh and Newman(41) reacted several olefins with bromine in methanol. Their results are interesting when compared to the results obtained from the preparation of the bromohydrin used in this study. When they used t-butylethylene a mixture of roughly equal amounts of the 1,2-dibromo compound and  $CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - \underset{Br}{CH} - \overset{OMe}{CH_2}$ was obtained.

When 1-hexene was used the product consisted of 31% of the dibromo compound and 59% of a mixture of the methoxybromo compounds. The methoxybromo compounds were obtained in the following proportions;

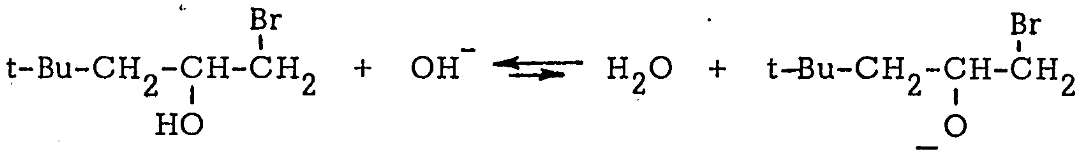


$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{MeO}{CH}\text{-}\underset{Br}{CH_2} + CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{Br}{CH}\text{-}\underset{OMe}{CH_2}$$

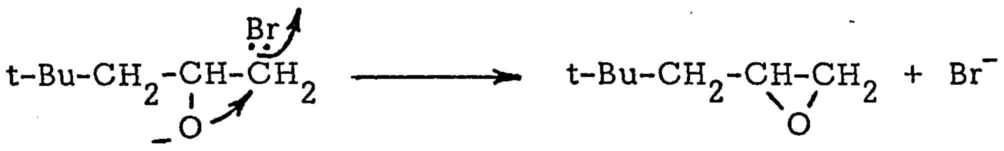
80% 20%

These results seem to indicate that the reaction medium could influence the equilibrium position between the carbonium ion and the cyclic bromonium ion. This would then effect the relative amounts of the primary and secondary bromo compounds formed. Also steric effects would seem to play a very important role in these reactions.

The reaction of a base with a bromohydrin to produce an epoxide is an adaptation of the Williamson synthesis. However, in this case a cyclic ether is produced because both the alcohol and the halide are on the same molecule. The reaction proceeds by the following mechanism as suggested in Gould;(40)

(1) 

$$t\text{-Bu-}CH_2\text{-}\underset{HO}{CH}\text{-}\overset{Br}{CH_2} + OH^- \rightleftharpoons H_2O + t\text{-Bu-}CH_2\text{-}\underset{{}^{-}O}{CH}\text{-}\overset{Br}{CH_2}$$

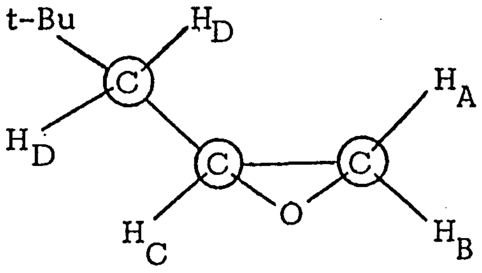
(2) 

$$\text{t-Bu-CH}_2\text{-}\underset{{}^{-}\text{O}}{\text{CH}}\text{-}\overset{\text{Br}}{\text{CH}_2} \longrightarrow \text{t-Bu-CH}_2\text{-}\underbrace{\text{CH-CH}_2}_{\text{O}} + \text{Br}^-$$

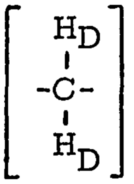
The mixture of primary and secondary alcohols can be used in this reaction because both produce the same epoxide. The yield of greater than 99.8% pure monomer from this reaction was 84%.

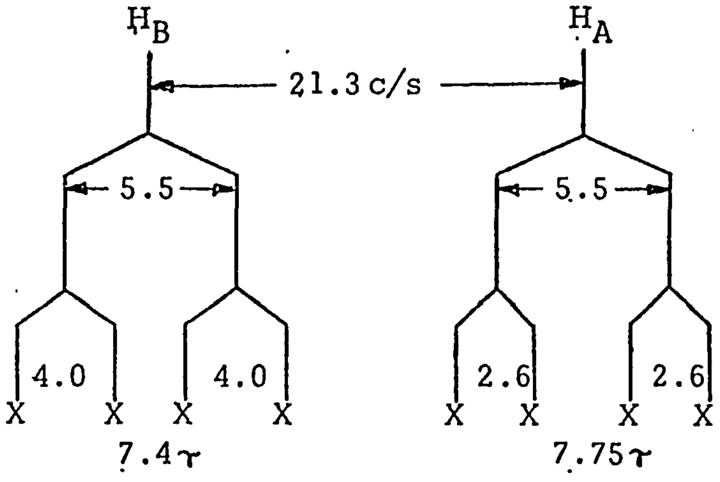
The infrared spectrum of neopentylethylene oxide is shown in Appendix C, Figure X. The infrared bands useful in identification are (in cm^{-1}) at 3050 (terminal epoxy), 3000 (-CH_2 in terminal epoxy), 2967 (methyl asymmetric stretching), 2880 (methyl symmetric stretching), 1475-1471 doublet (hydrogen bending vibrations), 1395 and 1368 (t-butyl bending vibrations) 1250 and 1203 (t-butyl skeletal vibrations), 1264 (epoxy ring breathing vibration, C-C, C-O and C-O bonds all stretching in phase), 956 (epoxy ring stretching vibrations), 901 (t-butyl group) and 847 (epoxy ring stretching vibration). Most of the infrared peaks in this spectrum and of the other spectra in this thesis were interpreted with the aid of Bellamy.(42)

The nuclear magnetic resonance spectrum of neopentylethylene oxide is shown in Appendix C, Figure XI.



The integration line of the spectrum gives the correct ratios of hydrogens for the structure shown on the previous page, that is 9:2:1:2.

The three methyl groups absorb as a singlet at 9.01τ. The saturated methylene group  $\left[\begin{array}{c} H_D \\ | \\ -C- \\ | \\ H_D \end{array}\right]$ absorbs at 8.63τ and is split into a doublet by the methine hydrogen (H_C). The coupling constant for this group is; J = 5.5 c/s. The methylene hydrogens H_A and H_B appear in the region of about 7.75 τ and 7.4 τ respectively. H_A and H_B split each other and are then split again by the methine hydrogen as follows so that an octet is obtained. Each X represents a peak on the spectrum with the center of each quartet being separated by 21.3 cycles/second.



H_A and H_B split each other by J=5.5 c/s and are then split by the methine hydrogen (H_C) giving values of $J_{\underline{(cis)}}$ = 4.0 c/s and $J_{\underline{(trans)}}$ = 2.6 c/s.

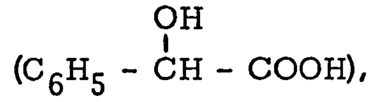
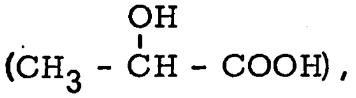
Based on the spectrum of a single compound it is impossible to assign definitely the *cis* and *trans* J values. However, in the spectrum of ethylene oxide all the protons fall at 7.45 τ and as can be seen from the sketch of NPEO on the previous page, the hydrogen that lies in an enviroment closest to that of the ethylene oxide protons is H_B and it therefore should have a similar tau value, which is chosen to be 7.4 τ. Also, in work done by Williamson et al (43) on some monosubstituted epoxides, it was reported that the proton *cis* to the substituted group always had the highest tau value and that J_{cis} was always greater than J_{trans}. By assigning H_A the higher tau value, J_{cis} comes out greater than J_{trans} for neopentylethylene oxide.

The methine hydrogen peak is split into a complex multiplet, by the four methylene hydrogens adjacent to it, at about 7.2 τ. Similar τ and J values for neopentylethylene oxide were obtained by Price and Carmelite (11) and Allen et al. (44)

B. Attempted Preparation of Optically Active Monomer

Attempted Separation of Diastereomers by Distillation. The diastereomers, from the reaction of the racemic bromohydrin with l-menthoxyacetic acid, were distilled in a Todd Distillation column at 0.5 mm and about 150°C. Eight fractions of the distillate were taken and infrared spectra were run on all the fractions and the pot residue. The only difference in the nine spectra was the disappearance of a band at 966 cm^{-1} from the first to the fifth fraction. The reason for this was not determined. Differential Thermal Analysis of fractions II and VIII showed that there was a slight difference in boiling point and also that both fractions were extremely impure. These two fractions were tested for unsaturation with bromine in CCl_4. Disappearance of the red color indicated the presence of a double bond formed by decomposition of the diastereomers on heating.

The attempted distillation of the diastereomers probably did not work because the molecular weights (391) of the compounds were too high. If another optically active acid is tried it should have as low a molecular weight as possible. Or l-menthoxyacetic acid could be tried with propylene bromohydrin where the molecular weights of the esters would be 335 compared to the 391 for the neopentylethylene bromohydrin esters. These lower molecular weight esters could possibly be separated by distillation.

Unfortunately, a lot of lower molecular weight optically active acids have two reactive groups, for instance; d-mandelic acid  $(C_6H_5 - \overset{OH}{\overset{|}{C}}H - COOH)$, molecular weight, 152.1 or lactic acid  $(CH_3 - \overset{OH}{\overset{|}{C}}H - COOH)$, molecular weight, 90.1. These could be tried but under conditions where the acids are least likely to react with themselves, i.e. when the acid is fairly dilute and the bromohydrin concentrated. Also the distillation might succeed if lower pressures could be obtained. This would mean a lower pot temperature so the compounds would be less likely to decompose.

Attempted Separation of Diastereomers by Gas Chromatography. The high molecular weight of the diastereomers may have also been the reason why the attempted separations by gas chromatography failed. Wilkens Instrument, makers of the Autoprep 700 Gas Chromatograph unit used in this work, also felt that the molecular weight of the esters was too high. They stated that compounds with molecular weights of about 400 and above are not suited to gas chromatographic analysis.(45)

The high molecular weight of the esters was probably the reason that they did not pass through the following columns; 20% Carbowax 20 M on Chromosorb P, 5% Carbowax 1500 on Teflon T-6, 10% Carbowax

4000 & TPA on Fluoropak, 20% D EGS on 60/80 Chromosorb W, 20% STAP on 60/80 Chromosorb W, 20% NPGS on 60/80 Chromosorb W. In most of these cases the column was at its maximum operating temperature which was probably still too low to allow the esters to pass through the column in a reasonable length of time.

However, there were columns where the esters did pass through (20% SE-30 on 45/60 Chromosorb W, 20% SF-96 on 60/80 Chromosorb W, 20% Apiezon L on 60/80 Chromosorb W, 20% Silicone 550 on 60/80 Chromosorb W, 20% E-60 on 60/80 Chromosorb W) but emerged as one peak with no apparent separation even with retention times of up to fifty minutes. This probably indicates that the difference in physical properties (i.e. the rate of adsorption and desorption on the column material) of the two diastereomers are very slight, making the separation very difficult.

One column that was tried (20 QF-1 on 30/60 Chromosorb P) appeared to give a partial separation at the highest temperature. However at lower temperatures only one broad peak was obtained. This column was only a 5 ft. analytical one so it was thought that a 20 ft. preparative column might give a better separation at the higher temperatures. However, only one peak was obtained when the new 20 ft. preparative column was tried.

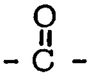
Sample size was a very important factor in these attempted separations of the diastereomers. Sample sizes used in this work ranged from 1 to 10 µl. Even if samples of this size showed a partial or total separation of the two peaks, once the sample size is increased so that enough sample can be collected for further reaction, the separation may become totally inadequate. Columns with larger diameters would have to be used for these larger sample sizes or else much longer retention times would have to be used in the smaller columns. However, longer retention times might make the separation as impractical as the small sample size.

With the present work the largest handicap was probably the molecular weight of the diastereomers. If the compounds were low enough in molecular weight so that they could have been vaporized without decomposing the method might have succeeded.

Attempted Separation of Enantiomers by Gas Chromatography. For resolution of enantiomers by gas chromatography there has to be some kind of association between the optically active column material and the solute passing through the column. The optically active solvent and the two enantiomers would form diastereomeric like compounds (that is, they would be joined by hydrogen bonding instead of covalent bonds). These two diastereomeric like compounds would then have different energies of formation. This would cause the partition coefficients, and thus the retention times, to be different for the two enantiomers.

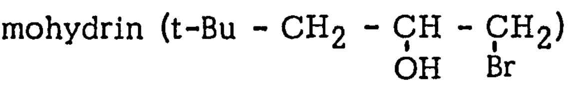
For separating enantiomers, the optically active packing in the column should be a liquid at the operating temperature. Therefore, the compounds used had melting points that were below the boiling points of either the oxide or the bromohydrin. If the oxide was to be separated, the melting point of the column material should lie between 90 and 120°C. For separation of the bromohydrin enantiomers the melting point should be around 150-160°C. However, resolution of both the oxide and bromohydrin was tried on most of the columns that were made.

For the attempted separation of the enantiomers of neopentylethylene oxide the following columns were tried; 20% nujol - 40% sucrose - 40% lactose, 20% α-D-glucose pentaacetate on Chromosorb W, 20%L-(-)-arabitol on Chromosorb W, and 20% diethyl-D-tartrate on Chromosorb W. None of these columns gave any separation of the neopentylethylene oxide enantiomers.

For the attempted separation of the bromohydrin enantiomers columns made of; 20% D-(+)-galactose on Chromosorb W, 20% α-D-glucose pentaacetate on Chromosorb W, 20% L-(-)-arabitol on Chromosorb W, and 20% diethyl-D-tartrate on Chromosorb W, were tried. All but two of these columns gave single peaks after retention times ranging from six to fifty-four minutes. The maximum operating temperature for the 20% diethyl-D-tartrate column was 100°C. As a result of the low operating temperature the injected sample remained in the column even after operating for two hours. With the L-(-)-arabitol column there may have been a reaction between the bromohydrin and the arabitol because an infrared spectrum of a collected sample showed a strong  $-\overset{O}{\overset{\|}{C}}-$ band.

From the above results it appears that separation of enantiomers by gas chromatography is very difficult. Having the right optically active column material is critical for the separation of enantiomers. Finding the right material seems to be a matter of trial and error at present. Sample size is also very important in this type of separation. Again the smaller samples are easier to separate and thus collecting large enough samples to do further work with may make this method impractical.

Attempted Resolution by Difference in Reaction Rates

1. Reaction of Bromohydrin with l-Menthoxyacetic Acid. The reaction between bromohydrin  $(t\text{-}Bu - CH_2 - \underset{OH}{CH} - \underset{Br}{CH_2})$ and l-menthoxyacetic acid was carried out with an excess of bromohydrin. The bromohydrin enantiomer reacting with the lower energy of activation would be consumed

the fastest. Therefore the unreacted bromohydrin would no longer be racemic but would have an excess of one enantiomer and thus be optically active. In this way a partial separation of the enantiomers could be obtained.

However, when the unreacted bromohydrin was purified and collected no optical activity could be measured. This was probably because the difference in the energies of activation of the d and l bromohydrin reacting with l-menthoxyacetic acid was too small to cause any noticeable difference in the rates of the two reactions.

2. Reaction of Bromohydrin with Cinchonine. This reaction is similar to the ring closure of the bromohydrin with potassium hydroxide. However here the base, cinchonine, is optically active and therefore will react at different rates with the d and l bromohydrin enantiomers. This would cause the resulting NPEO to be optically active. However the unreacted bromohydrin did not show any optical activity. This was probably because the difference in reaction rates was too small to have one NPEO enantiomer formed noticeably faster.

Attempted Resolution by Crystallization. It was thought that by reacting racemic 1-bromo-4,4-dimethyl-2-pentanol with phthalic anhydride to form the acid esters and then reacting the acid esters with an optically active base would yield two diastereomers that could be separated by crystallization. The two diastereomers could then be converted to the optically active epoxide by reacting with KOH.

When the reaction of the bromohydrin with phthalic anhydride was run in pyridine it was found that after reacting the products with KOH, to convert back to the bromohydrin, double bond bands appeared in the I.R. spectrum of the products. Double bonds may have resulted from pyridine reacting with the $-CH_2-Br$ end group. Reaction with KOH then caused elimination of the bromine to form the double band.

When the solvent was changed to ether the reflux temperature may have been too low for any reaction to take place. When benzene was used as the solvent probably too much H_2SO_4 catalyst was used causing the decomposition of the bromohydrin.

This method of separation was not pursued any further after these three trials.

C. Polymerization of Neopentylethylene Oxide Using Various Initiators

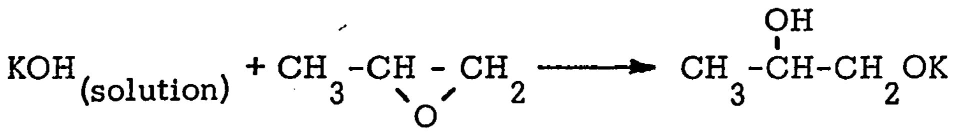
Discussed in this section are the results of some non-homogeneous polymerizations that were made using the following initiators; potassium hydroxide, cesium hydroxide, rubidium t-butoxide (t-BuORb), lithium t-butoxide (t-BuOLi) and zinc chloride ($ZnCl_2$). The results from these runs are listed in Table 3, page 84.

Some homogeneous polymerizations using a solution of potassium t-butoxide dissolved in dimethoxyethane as initiator were also run. This was additional data to that obtained in the kinetic study. The results from these runs are listed in Table 5, page 93.

Potassium Hydroxide Initiated Polymerizations. The results of the potassium hydroxide (KOH) initiated polymerizations are shown in Table 3, page 84. The powdered potassium hydroxide used in these runs was 85 weight percent pure, the rest being water. This is equivalent to 55 mole percent of the KOH existing as the monohydrate. The monohydrate has been shown to be a noninitiator.(46)

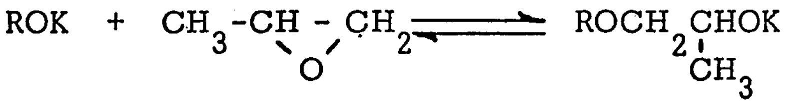
In the reaction sequence proposed by Snyder(5) and Steiner et al(6) for KOH initiated polymerization, water is produced in one of the reactions. This water then combines with more KOH to make the noninitiating monohydrate as shown below;

$$\mathrm{KOH_{(solid)}} \rightleftharpoons \mathrm{KOH_{(solution)}} \qquad (1)$$



$$\mathrm{KOH_{(solution)}} + \mathrm{CH_3{-}\underset{\diagdown O \diagup}{CH{-}CH_2}} \longrightarrow \mathrm{CH_3{-}\overset{OH}{\overset{|}{C}H}{-}CH_2OK} \qquad (2)$$

$$\mathrm{ROK} + \mathrm{CH_3{-}\underset{\diagdown O \diagup}{CH{-}CH_2}} \longrightarrow \mathrm{ROH} + \mathrm{CH_2{=}CH{-}CH_2OK} \qquad (3)$$



$$\mathrm{ROK} + \mathrm{CH_3{-}\underset{\diagdown O \diagup}{CH{-}CH_2}} \rightleftharpoons \mathrm{ROCH_2\underset{\underset{CH_3}{|}}{C}HOK} \qquad (4)$$

$$\mathrm{ROH} + \mathrm{KOH_{(solution)}} \rightleftharpoons \mathrm{ROK} + \mathrm{H_2O} \qquad (5)$$

$$\mathrm{H_2O} + \mathrm{KOH_{(solid)}} \rightleftharpoons \mathrm{KOH \cdot H_2O_{(solid)}} \qquad (6)$$

where R may be any of the possible organic moieties. These reactions show how KOH goes into solution to react homogeneously with the oxide and also how the non-initiating monohydrate is produced. If the product of reaction (2) reacts with $\mathrm{KOH_{(solution)}}$ as shown in reaction (5) an anion capable of propagating at both ends will be produced. This will result in higher molecular weights than if propagation occurred only at a single end of each anion.

From the results in Table 3, page 84, it can be seen that the KOH initiated polymerizations produced very high molecular weight polymers. However the limited amount of data would make it very difficult to explain the differences in the results of these polymerizations.

TABLE 3

POLYMERIZATIONS OF NEOPENTYLETHYLENE OXIDE BY INITIATORS OTHER THAN t-BuOK

Run No.	Initiator	Weight Percent Initiator	Moles Monomer / Initiator	Reaction Temperature	Reaction Time, Hrs.	Percent Conversion	Number Average M.W.
3A	KOH	29.2	2.35/1	Room Temperature	7000	44.6	5800 ± 250
3B	KOH	28.1	2.48/1	Room Temperature	7000	42.0	3200 ± 150
3C	KOH	18.9	4.16/1	40°C	144	11.5	N.M.
3E	KOH	9.6	9.16/1	Room Temperature	1850	39.5	6700 ± 800
5A	CsOH	11.0	10.6/1	Room Temperature	5500	29.6	2900 ± 100
6	$ZnCl_2$	10.0	10.5/1	Room Temperature	5100	56.5	410 ± 20
8	t-BuORb	12.2	10/1	Room Temperature	160	89.5	830 ± 50
10	t-BuOLi	6.4	10/1	Room Temperature	5000	<0.5	-

All runs except 3A were shaken

The elemental analysis of the polymers obtained from runs 3A and 3B are given in Table 6, page 96. Comparing these two it is found that there is more oxygen in polymer 3A than in 3B. However, polymer 3A has a higher molecular weight and should contain less -OH end groups and therefore should have a lower percentage of oxygen than polymer 3B. No explanation can be given for this except that either there were impurities in the polymers when the elemental analysis were made or the molecular weights were inaccurate. Also air oxidation might have accounted for more oxygen in polymer 3A.

The neopentylethylene oxide slowly turned light yellow after it was mixed with the potassium hydroxide. The color remained all through the reaction but slowly disappeared during the polymer workup when the benzene solution of the reaction mixture was added to dilute HCl. The polymer produced using KOH initiator was partially cloudy in appearance and very tacky.

According to Snyder(47), poly (propylene oxide) made with KOH initiator showed signs of decomposition upon standing in the air for a few months. However KOH initiated poly (neopentylethylene oxide) made in the present study showed no noticeable decomposition after standing in air for over a year.

Infrared spectra of these polymers were run and the spectrum for run 3B is shown in Appendix C, Figure XII. The two major bands due to the C-O-C linkages fall at 1125 cm^{-1}, which is an asymmetric stretching vibration, and at 1075 cm^{-1}, which is the symmetric stretching vibration. There was also weak absorption at 3500 and 3600 cm^{-1} due to the small amount of -OH end groups.

Nuclear magnetic resonance spectra of the worked up polymer of runs 3A and 3B were made, with the major peaks of these runs being listed in Table 4, page 87. The ratios of the number of protons on each kind of group are also listed in this table. The N.M.R. spectrum (CCl_4 solution) for the polymer obtained in run 3B is shown in Appendix C, Figure XIII. As was noted by Allen et al(44) for poly (propylene oxide) and poly (t-butylethylene oxide) the absorption of the protons that were in the epoxide ring moved downfield to a lower tau value and they also collapsed to a strong single peak. Thus all the peaks obtained at 7.2 τ, 7.4 τ, and 7.75 τ for the methine and methylene hydrogen on the ring of neopentylethylene oxide collapsed to a strong single peak at 6.62 τ for poly (neopentylethylene oxide). This lowering of the tau values of the ring protons is thought to be caused primarily by the loss of ring strain when the ring is opened during polymerization. Also the methylene protons of the neopentyl group went from a doublet at 8.63 τ to a single broad peak at 8.65 τ. The

TABLE 4

NUCLEAR MAGNETIC RESONANCE SPECTRA OF POLYMERS

Run No. & Initiator	$\overline{\text{Mn}}$	Wt.% Polymer in CCl_4		Major Tau Values and Proton Ratio by Integration: Methyl	CH_3-(C)$_3$-Cl	t-BuO-	CH_2(Sat)	HO-	(CH_2-CH-O-)
Run 3A	5800	10	τ Value	9.07 τ	-	-	8.65 τ	-	6.64 τ
KOH			Proton Ratio	8.7			2.0		3.04
Run 3A	5800	40	τ Value	9.07 τ	-	-	8.65 τ	-	6.62 τ
KOH			Proton Ratio	8.84			2.0		2.82
Run 3B	3200	10	τ Value	9.06 τ	-	-	8.66 τ	-	6.62 τ
KOH			Proton Ratio	9.0			2.0		3.0
Run 5A	2900	10	τ Value	9.07 τ	-	-	8.68 τ	-	6.62 τ
CsOH			Proton Ratio	9.06			2.0		2.84
Run 6	410	10	τ Value	9.05 τ	9.02 τ	-	8.64 τ	7.33 τ	6.57 τ
$ZnCl_2$			Proton Ratio	9.0			2.05	0.261	2.91
Run 13	950	16.8	τ Value	9.05 τ	-	8.82 τ	8.66 τ	-	6.59 τ
KO-t-Bu			Proton Ratio	9.1		1.2	2.0		2.98

peak for the methyl groups stayed as a singlet at 9.06τ.

Cesium Hydroxide Initiated Polymerizations. The results from run 5A using cesium hydroxide (CsOH) as the initiator are shown in Table 3, page 84.

The amount of water remaining in the CsOH after drying at 200°C and a pressure of less than 2 mm of Hg. was not known. Therefore the amount of CsOH existing as the monohydrate could not be calculated. The monohydrate of CsOH would probably also be a non-initiator similar to the KOH monohydrate. For calculation purposes it was assumed that all the water had been removed by drying and that all the CsOH acted as initiator. The ratio of monomer to initiator was then calculated to be 10.6 to 1.

Snyder (5) found that the rate of polymerization increased as the size of the cation from the hydroxide initiator increased. Therefore going from KOH to CsOH to RbOH increased the rate of polymerization. This was explained by the fact that the larger cation would spread the electrostatic charge over a larger volume and thus decrease the attraction to the given anion. This would affect the rate because the propagation reaction is actually a combination of two reactions, with an equilibrium existing between the two propagating end groups. This is shown below as,

$$\sim\!\sim M^-, A^+ \rightleftharpoons \sim\!\sim M^- + A^+ \qquad K_{diss}$$

where: $\sim\!\sim M^-$ is the growing polymer chain of monomer M.

A^+ is the cation of the hydroxide initiator.

K_{diss} is the dissociation constant of the two ions.

Both the ion pair, $\sim\!\sim M^-, A^+$ and the free ion M^- are capable of propagating, as shown in the following equations;

$$\sim\!\sim M^-, A^+ + M \xrightarrow{k_p^{\pm}} \sim\!\sim M\text{-}M^-, A^+$$

$$\sim\!\sim M^- + M \xrightarrow{k_p^{-}} \sim\!\sim M\text{-}M^-$$

where: $k_p^{\pm}$ is the propagation rate constant of the ion pair.

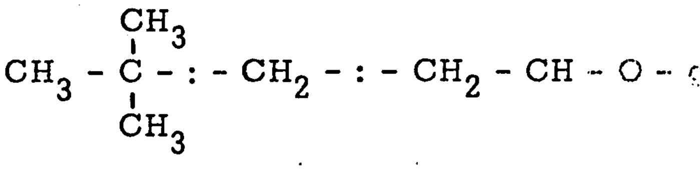
k_p^{-} is the propagation rate constant of the free ion.

It has been shown by Szwarc et al (48 ,49) that k_p^{-} is greater than $k_p^{\pm}$. Therefore if the cesium ion is held less tightly to the anion than the potassium ion more of the free anion should exist. This would then make the propagation reaction go faster. However as can be seen in Table 3, page 84, the CsOH initiated polymerization, run 5A, gave a lower percent conversion than the KOH initiated polymerization, run 3B, under similar conditions. This may indicate that the CsOH was still a little wet and therefore some of it existed as the non-initiating monohydrate, thus slowing the rate of polymerization.

It is interesting to compare the colors of two CsOH initiated polymerizations. With the present work the mixture of NPEO and CsOH was a pale yellow color; however, Snyder(5) reported that the mixture of propylene oxide and CsOH was brown.

The infrared spectrum of run 5A, (not shown) the CsOH initiated polymer, is interesting in that it differs slightly from the spectrum of run 3B, the KOH initiated polymer. While runs 5A and 3B are about the same molecular weight the KOH initiated polymer shows very weak O-H stretching in the 3400 to 3200 cm^{-1} range while the CsOH initiated polymer shows a very broad and fairly strong absorption in this range. The difference in the concentration of -OH end groups due to the small difference in molecular weight should not have made this big a difference in the amount of absorption in this range. This strong absorption by the CsOH initiated polymer could not be accounted for.

The major peaks appearing in the N.M.R. spectrum for this polymer are listed in Table 4, page 87. The relative number of protons on each kind of group obtained from the integration curve of the spectrum is very close to the exact 9: 2: 3 ratio that should be obtained for the



$$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - : - CH_2 - : - CH_2 - CH - O -$$

groups. The actual values obtained were 9.06 : 2: 2.84.

<u>Rubidium t-Butoxide and Lithium t-Butoxide Initiators.</u> With t-butoxide initiators cation size should have the same effect as it does with the hydroxide initiators. As the size of the cation is increased, the rate of polymerization should increase. This is confirmed in the present work because when going from Li to K to Rb cation the polymerization rate increased. The lithium t-butoxide (t-BuOLi) proved such a poor initiator that even after 5000 hours at room temperature less than 0.5% polymerization took place.

Comparing the polymerization rates using potassium t-butoxide (t-BuOK) and rubidium t-butoxide (t-BuORb) initiators under the same conditions showed that the t-BuORb run was only 2.8 times as fast as the t-BuOK run. This difference is very small when compared to some results obtained by Snyder.(5) He obtained a rate difference of over 300 when going from sodium methoxide to potassium methoxide in the polymerization of propylene oxide. Probably the main reason that the difference in rates was so small was that the t-BuOK was already in solution (in DME) while the t-BuORb was added to the NPEO as a solid but slowly went into solution. This may have considerably slowed the initiation reaction for the t-BuORb and thus decreased the difference in rates.

The mixture of t-BuORb and NPEO was a pale yellow color while the mixture of t-BuOLi and NPEO turned a pale brown. The resulting polymer from the t-BuORb was a clear very viscous fluid. The t-BuORb polymer should have had a molecular weight of about 1100 at 90% polymerization. However, the molecular weight was only 830 ± 50 indicating that chain transfer was taking place. Chain transfer is discussed in Chapter III, Section E.

Potassium t-Butoxide Initiator. Some additional polymerizations were made with t-BuOK which were not part of the kinetic study. The results from these runs are shown in Table 5, page 93.

The mixture of t-BuOK and NPEO was always yellow in color, while the final polymers were all clear. At low molecular weights the polymer was very viscous but became tacky at high molecular weights.

TABLE 5

ADDITIONAL POLYMERIZATIONS OF NEOPENTYLETHYLENE OXIDE WITH t-BuOK INITIATOR

Run No.	Weight Percent t-BuOK	Moles Monomer / t-BuOK	Reaction Temperature	Reaction Time, Hrs.	Percent Yield	$\overline{Mn}$(Obs)	$\overline{Mn}$(Calc)
17	16.9	20/1	9°C	2500	65.5	1600 ± 100	1574
13	24.25	9.6/1	Room Temperature	700	97.7	950 ± 50	1150
14	7.7	50/1	40°C	382	80.2	3400 ± 200	4675
4	13.25	20/1	40°C	220	96.1	-	-

From the number average molecular weight values listed in Table 5, page 93, it can be seen that as the temperature is raised there is an increase in the difference in the observed $\bar{M}n$ and the calculated $\bar{M}n$. At 9°C (run 17) the two molecular weights are the same within experimental error. At room temperature (run 13) there is a slight difference, while at 40°C (run 14) this difference becomes very large. From these values it can be seen that a side reaction (chain transfer) is taking place and that this reaction has a greater energy of activation than the propagation reaction. Therefore, as the temperature is increased a greater proportion of the chain transfer reactions to propagation reactions takes place. This will be discussed further in Chapter III, Section E.

Infrared spectra of poly (NPEO) showed the usual bands for C-H stretching and bending. There is also a doublet for the t-butyl group at 1395 and 1363 cm^{-1}. At 1125 and 1075 cm^{-1} there is the strong absorption from the C-O-C bonds. The bands at 3450 and 3600 cm^{-1} for the O-H end groups were also present. A typical I.R. spectrum for a t-BuOK initiated polymer (run 13) is shown in Appendix C, Figure XVI. The N.M.R. spectrum for run 13 is also shown in Appendix C, Figure XVII. This spectrum is the same as the one obtained from the KOH initiated polymer except for a weak singlet appearing at 8.82 τ.

This peak is therefore probably due to the t-butoxy end groups. It can be seen from Table 4, page 87, that the ratio of areas for the 9.06 τ (t-butyl) peak to the 8.82 τ (t-butoxy) peak of 7.6 to 1 is very close to the calculated degree of polymerization of 8.2.

The t-BuOK initiated polymers showed strong absorption at 1730 cm^{-1} in the infrared spectra after standing in the air for several months. There was also a very noticeable change in the odor of the polymer. However, as noted before, the KOH initiated polymer had no odor or I.R. band at 1730 cm^{-1} even after standing in air for over a year. This may have been due to the fact that the t-BuOK polymers were lower molecular weight and therefore more easily air oxidized or the t-BuOK solution may have contained an impurity that made the polymer more prone to air oxidation.

Zinc Chloride Initiator. All the previous runs discussed were made with anionic initiators, however, with dry granular zinc chloride ($ZnCl_2$) initiator the polymerization was cationic. The results from run 6 where $ZnCl_2$ was used as the initiator are shown in Table 3, page 84. An elemental analysis of the polymer is shown in Table 6, page 96. Infrared and N.M.R. spectra of the polymer are shown in Appendix C.

TABLE 6

ELEMENTAL ANALYSIS OF POLYMERS

Run No.	Initiator	%Carbon	%Hydrogen	%Oxygen[1]	%Chlorine
3A	KOH	71.72	12.26	16.02	None
3B	KOH	73.59	12.29	14.12	None
6	$ZnCl_2$	67.78	11.50	13.44	7.28
23[2]	t-BuOK	70.81	11.77	17.42	None
23[3]	t-BuOK	71.56	11.99	16.45	None

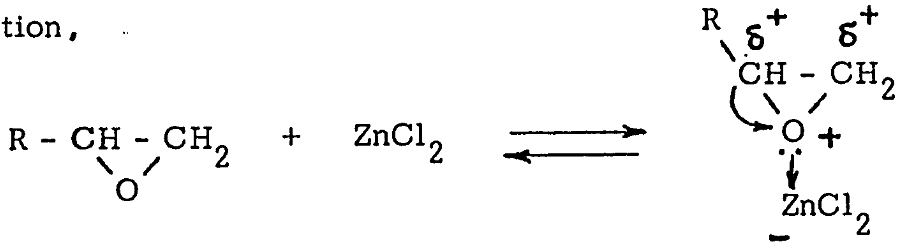
1. By difference
2. Reaction time 16 hours
3. Reaction time 75 hours

Addition of the $ZnCl_2$ to the NPEO (run 6) resulted in an exothermic reaction with the mixture becoming very warm. Some solid settled to the bottom of the bottle. However, with shaking, all the solid disappeared during the first twelve hours of the reaction. Despite the fact that the reaction mixture was shaken at room temperature for 5100 hours only 56.5% of the monomer reacted.

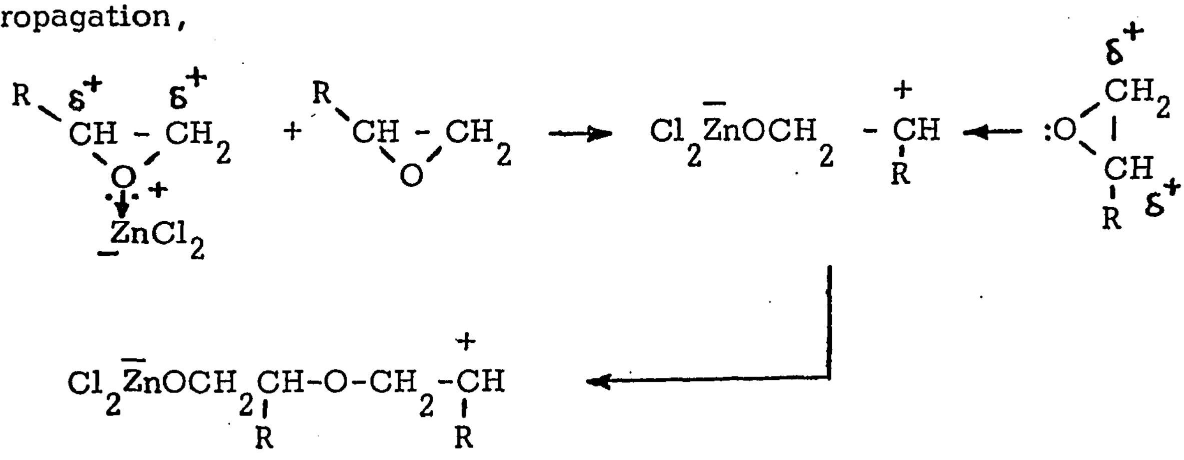
The resulting polymer was a clear viscous oil with a number average molecular weight of 410 ± 20. The elemental analysis of the polymer showed that it contained 7.28 weight percent chlorine. From this weight percent and the total weight of recovered polymer it was calculated that 75% of the total chlorine in the initial amount of $ZnCl_2$ was contained in the polymer. For the weight percent chlorine obtained in the polymer one chlorine atom per polymer chain would give a molecular weight of 487 which is close to the 410 ± 20 actually found.

The cationic polymerization may have proceeded by the following steps;

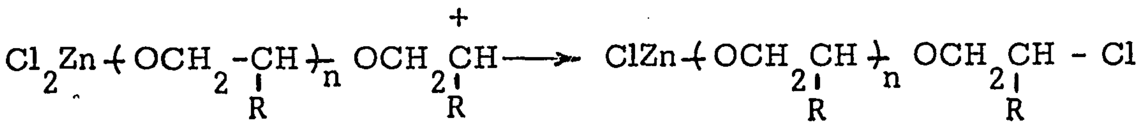
Initiation,



Propagation,

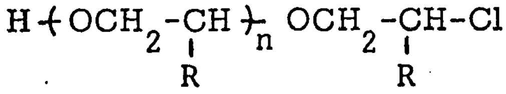


Termination may occur by the following mechanism,



$$Cl_2Zn\left(OCH_2-\underset{R}{CH}\right)_n OCH_2\overset{+}{\underset{R}{CH}} \longrightarrow ClZn\left(OCH_2\underset{R}{CH}\right)_n OCH_2\underset{R}{CH}-Cl$$

When the polymer was worked up the ZnCl at the end of the polymer would be replaced by a hydrogen to give the final polymer,



$$H\left(OCH_2-\underset{R}{CH}\right)_n OCH_2-\underset{R}{CH}-Cl$$

This mechanism explains some of the data obtained in this polymerization but does not explain all of it. Cationic polymerizations with metal halide catalysts are complex reactions and no definite conclusions could be drawn about the mechanism because of the small amount of work done with $ZnCl_2$ initiator.

The infrared spectrum (Fig.XVI) of this polymer is similar to that of the anionic initiated polymers. There is a strong broad O-H absorption at about 3400 cm^{-1} which is expected because of the high concentration of -OH end groups for this low a molecular weight. The N.M.R. spectrum of the polymer is very interesting. The proton ratios for the various groups are listed in Table 4, page 87. The three main groups again give the correct proton ratio of 9 : 2.05 : 2.91. However for this polymer all the t-butyl groups do not appear at the same tau value. This is because the t-butyl groups are not all in the same environment. The t-butyl groups closest to the end chlorine atom fall at a lower tau value than the other t-butyl groups. The reason that the two peaks are unequal would result from the fact that only one t-butyl group would be affected by the chlorine atom. The spectrum also contains a singlet at 7.33 τ. This peak has a proton ratio to the total t-butyl peak of 1 to 35, indicating that there are four t-butyl groups to one of these groups. This peak is therefore probably due to the -OH end groups.

D. Kinetic Study

The polymerizations for the kinetic study were run at three different temperatures and two initiator concentrations. The initiator used in these polymerizations was potassium t-butoxide. Temperatures of 39.9, 60.0 and 80.3°C were used while the monomer to initiator ratios were 50/1 and 20/1.

The potassium t-butoxide concentration was kept constant at 1.89 molar in dimethoxyethane for runs at 50/1 and 1.94 molar for runs at 20/1. This was done so that one set of densities could be used for any duplicate runs made at these same conditions. Figure II, page 101, shows how the density of the reaction mixture increased as the amount of monomer decreased. Because such a large weight percentage of monomer was used, about 83% for runs at 20/1 and about 92.2% for runs at 50/1, there was a very large change in the density. For runs at 20/1 the average density change was about 11% while for runs at 50/1 there was an average change of 13.2%. The percentage change in density was calculated by extrapolation to 100% conversion of monomer to polymer. For a run made at a monomer to initiator ratio of 5/1 where the weight percent of monomer was 67.2 the percent change in density dropped to 8.6. This decrease in change of density is to be expected as the amount of solvent increases. The results from the

EQUIVALENTS MONOMER/GM SAMPLE vs DENSITY
RUN 20

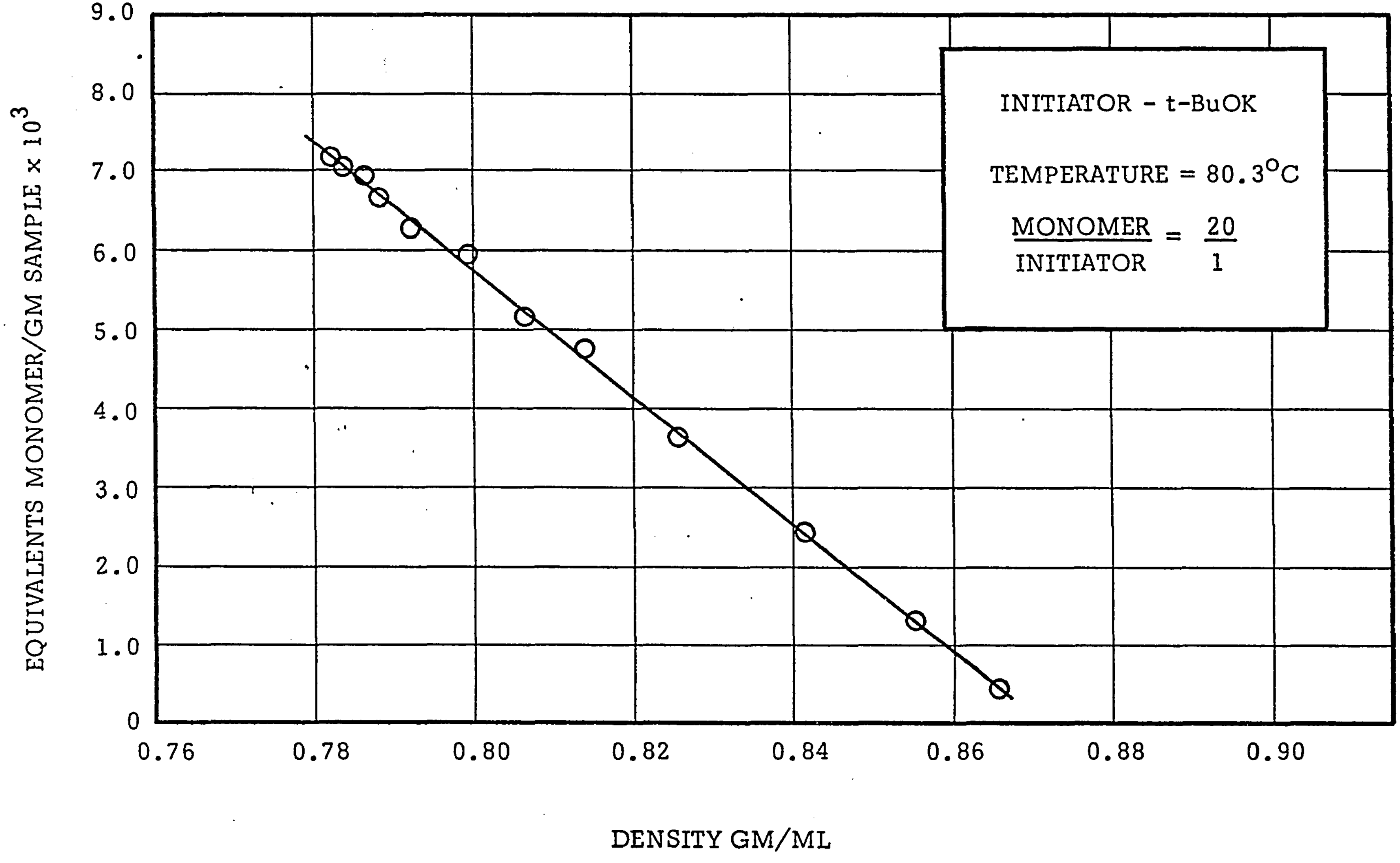


FIGURE II

density readings and the monomer titrations for the kinetic study runs are shown in Tables 18 to 25 which are tabulated in Appendix A.

The propagation reactions shown on page 3 can be written as,

$$P_x + M \longrightarrow P_{x+1}$$

where; P_x is the polymer anion x units long.

M is the monomer.

The above reaction should therefore be first order with respect to monomer concentration and first order with respect to polymer anion concentration and overall a second order reaction.

To write this as a kinetic expression several assumptions have to be made. The first is that all the polymer anions, no matter what the degree of polymerization, react at the same rate. After a degree of polymerization of 2 or 3 this is a good assumption as has been discussed in Flory.(50) The second assumption is that every initiator ion starts a polymer chain. For the strong base used in this study this is also a good assumption.

The rate of polymerization can then be written as,

$$\text{rate} = k_2\,[\text{Polymer Anions}]\;[\text{Monomer}] \qquad (1)$$

where; k_2 is the second order rate constant, liters/mole-sec.

[Polymer Anions] is the concentration of polymer anions, moles/liter.

[Monomer] is the concentration of monomer, moles/liter.

However, the concentration of polymer anions was not measured but was assumed to be equal to the initiator concentration. Equation 1 can then be written as,

$$\text{rate} = k_2\,[\text{Initiator}]\,[\text{Monomer}] \tag{2}$$

At a given initiator concentration a plot of monomer concentration versus time gave a straight line from about 15% to 60% conversion. Figure III, page 104, shows a typical plot of monomer concentration versus time. Therefore for a given initiator concentration the polymerization follows pseudo zero order kinetics and the above equation can be written as,

$$\text{rate} = k_o = \frac{\Delta\ \text{Monomer Concentration}}{\Delta\ \text{Time}} \tag{3}$$

where k_o is the pseudo zero order rate constant, moles/liter-sec. The reaction follows pseudo zero order kinetics because after the initiation reaction, when all the initiator ions have reacted with monomer molecules, the concentration of polymer anions is practically constant. Also because the polymerizations were run at such high

MONOMER CONCENTRATION vs TIME

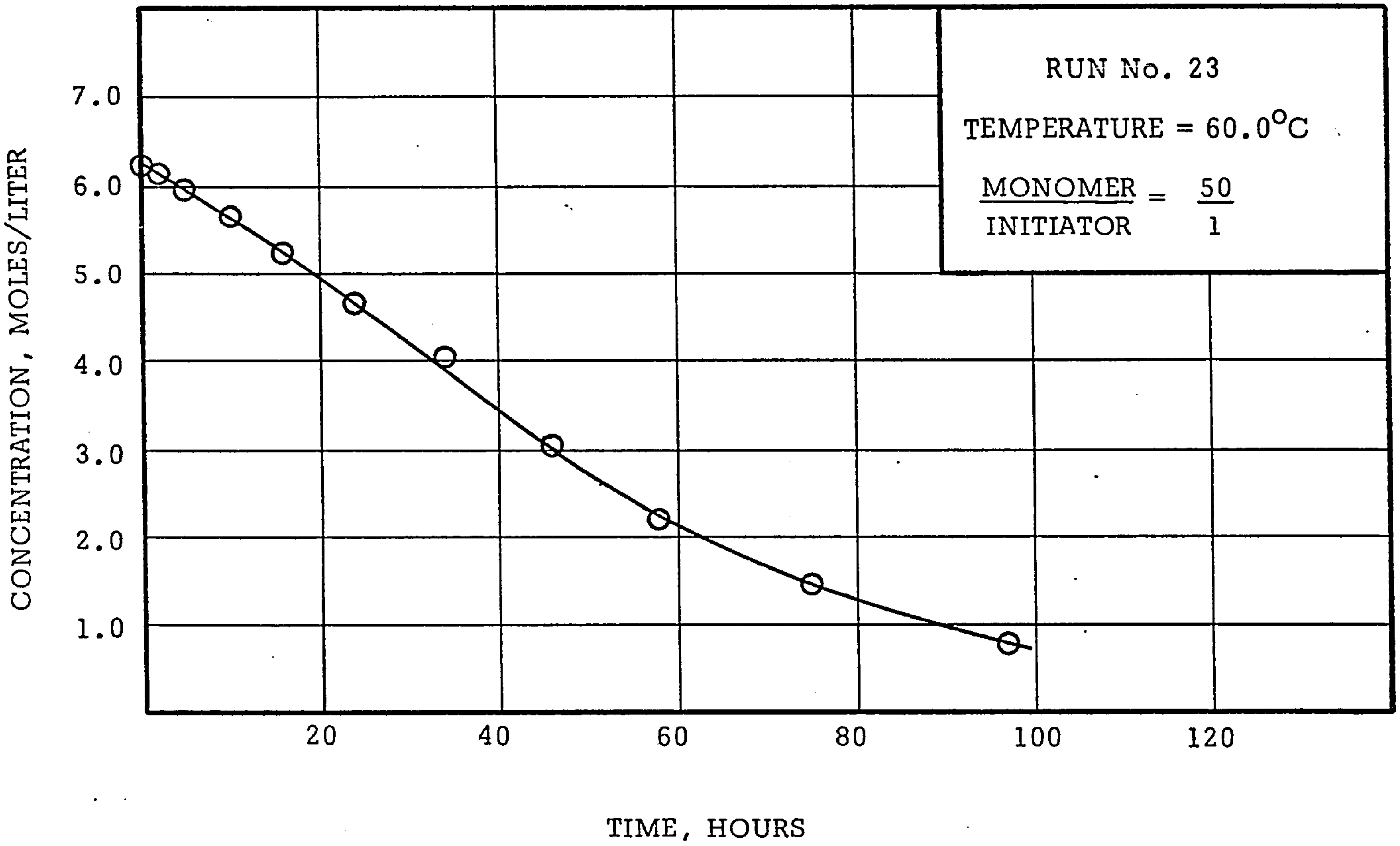


FIGURE III

monomer concentrations this concentration could also be assumed constant. For the sake of clarity these constants (k_o), along with their experimental errors, are listed in Table 7, page 106 and are called the slope of monomer concentration versus time. A computer program using the method of least squares was used to determine the most accurate slope of the points that fell between about 15% and 60% conversion. This program also calculated the standard deviation in the slope of these points.

When the different initiator concentrations are taken in account Equation 3 is written as,

$$\text{rate} = k_1\,[\text{Initiator}] \qquad (4)$$

where k_1 is the pseudo first order rate constant, 1/sec.

The pseudo first order rate constants are obtained by setting Equations 3 and 4 equal to each other and solving for k_1.

$$\text{rate} = k_1\,[\text{Initiator}] = k_o \qquad (5)$$

$$k_1 = \frac{k_o}{[\text{Initiator}]} \qquad (6)$$

The pseudo first order rate constants are listed in Table 9, page 111 for the three different temperatures that the polymerization was run at.

After about 60% conversion the plot of monomer concentration versus time becomes curved. If, however, log monomer concentration is plotted against time the latter portion of the curve then becomes a

TABLE 7

SLOPE OF MONOMER CONCENTRATION vs TIME

EARLY STAGES OF POLYMERIZATION

Run No.	Temperature °C	t-BuOK Concentration Moles/Liter	Mole Ratio Monomer/Initiator	Slope $\frac{\text{Moles}}{\text{Liter-Sec.}} \times 10^{+5}$
14	39.9	0.1317	50/1	0.34 ± 0.01
18	39.9	0.2974	20/1	1.08 ± 0.02
23	60.0	0.1280	50/1	1.99 ± 0.02
22	60.0	0.2897	20/1	5.06 ± 0.35
15	80.3	0.1256	50/1	8.3 ± 0.20
19	80.3	0.2840	20/1	22.6 ± 0.3
20	80.3	0.2850	20/1	20.5 ± 0.2

straight line. The slopes of these curves are listed in Table 8, page 108. These curves show that the polymerization rate is now dependent upon monomer concentration. Figure IV, page 109, of log monomer concentration versus time for run 18 shows that the polymerization follows pseudo first order kinetics at high conversions. The second order rate constants were then calculated by dividing the slope of each curve by the initiator concentration used for that run. The second order rate constants are listed in Table 10, page 112, for the three different polymerization temperatures.

To obtain the energy of activation for the polymerization reaction an Arrhenius type equation was used. This is shown below for the second order rate constants.

$$k_{prop} = A_p e^{-E_p/RT}$$

where; k_{prop} = Propagation Rate Constant, liter/mole-sec.
A_p = Collision Frequency Factor, liter/mole-sec.
E_p = Energy of Activation of the propagation reaction, cal/mole.
R = Gas Constant = 1.987 cal/mole - ^{o}K.
T = Absolute Temperature, ^{o}K.

This calculation was carried through for both orders of reaction by making a plot of log rate constant versus the reciprocal of absolute temperature. This is shown in Figure V, page 110, for the pseudo

TABLE 8

SLOPE OF LOG MONOMER CONCENTRATION vs TIME

LATTER STAGES OF POLYMERIZATION

Run No.	Temperature °C	t-BuOK Concentration Moles/Liter	Mole Ratio Monomer/Initiator	Slope $(1/\text{Sec.}) \times 10^{+6}$
14	39.9	0.1317	50/1	1.10 ± 0.05
18	39.9	0.2974	20/1	3.5 ± 0.1
23	60.0	0.1280	50/1	7.4 ± 0.3
22	60.0	0.2897	20/1	17.9 ± 0.8
15	80.3	0.1256	50/1	33.5 ± 1.0
19	80.3	0.284	20/1	87.5 ± 3.0

FIGURE IV

LOG CONCENTRATION vs TIME

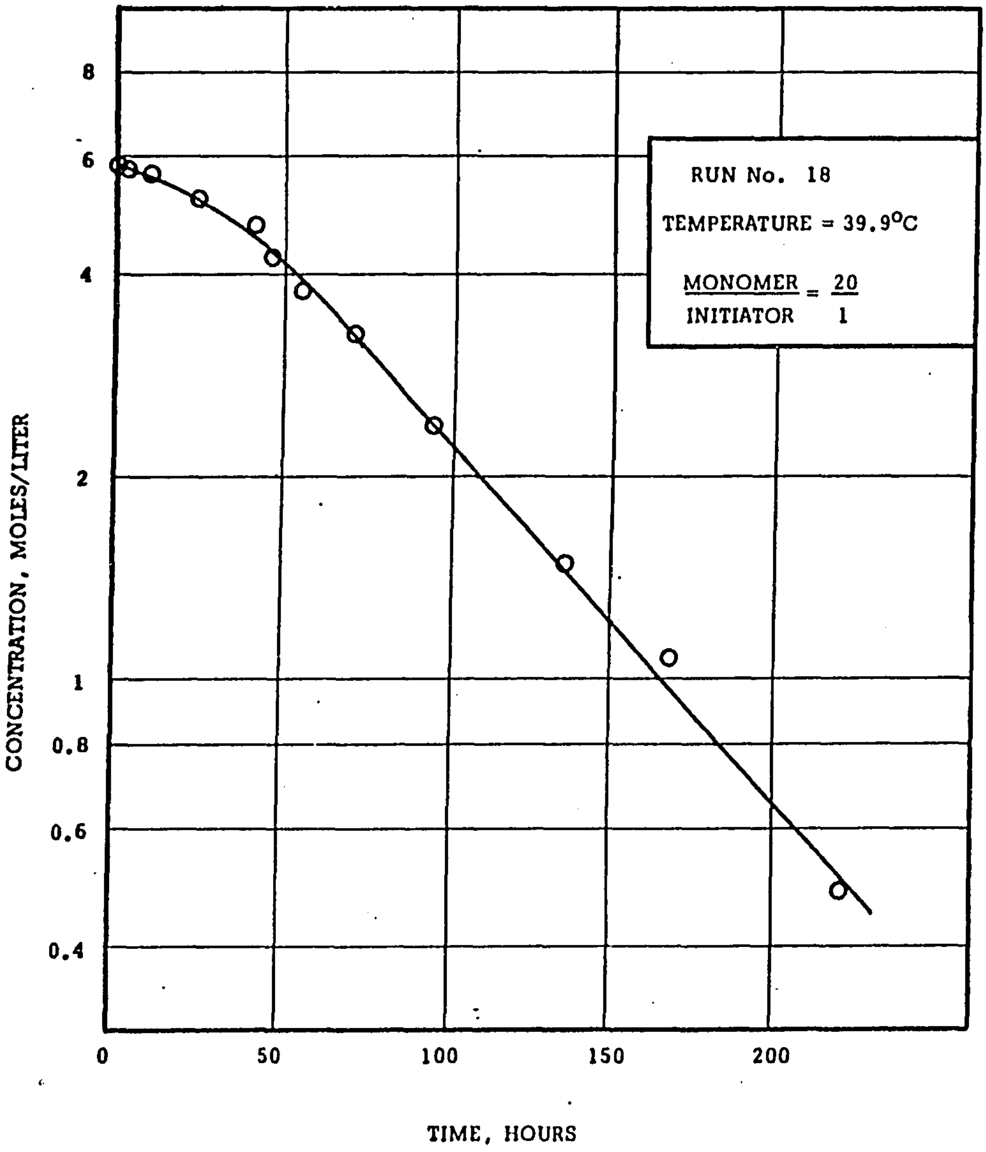


FIGURE V

PSEUDO FIRST ORDER RATE CONSTANTS vs RECIPROCAL TEMPERATURE

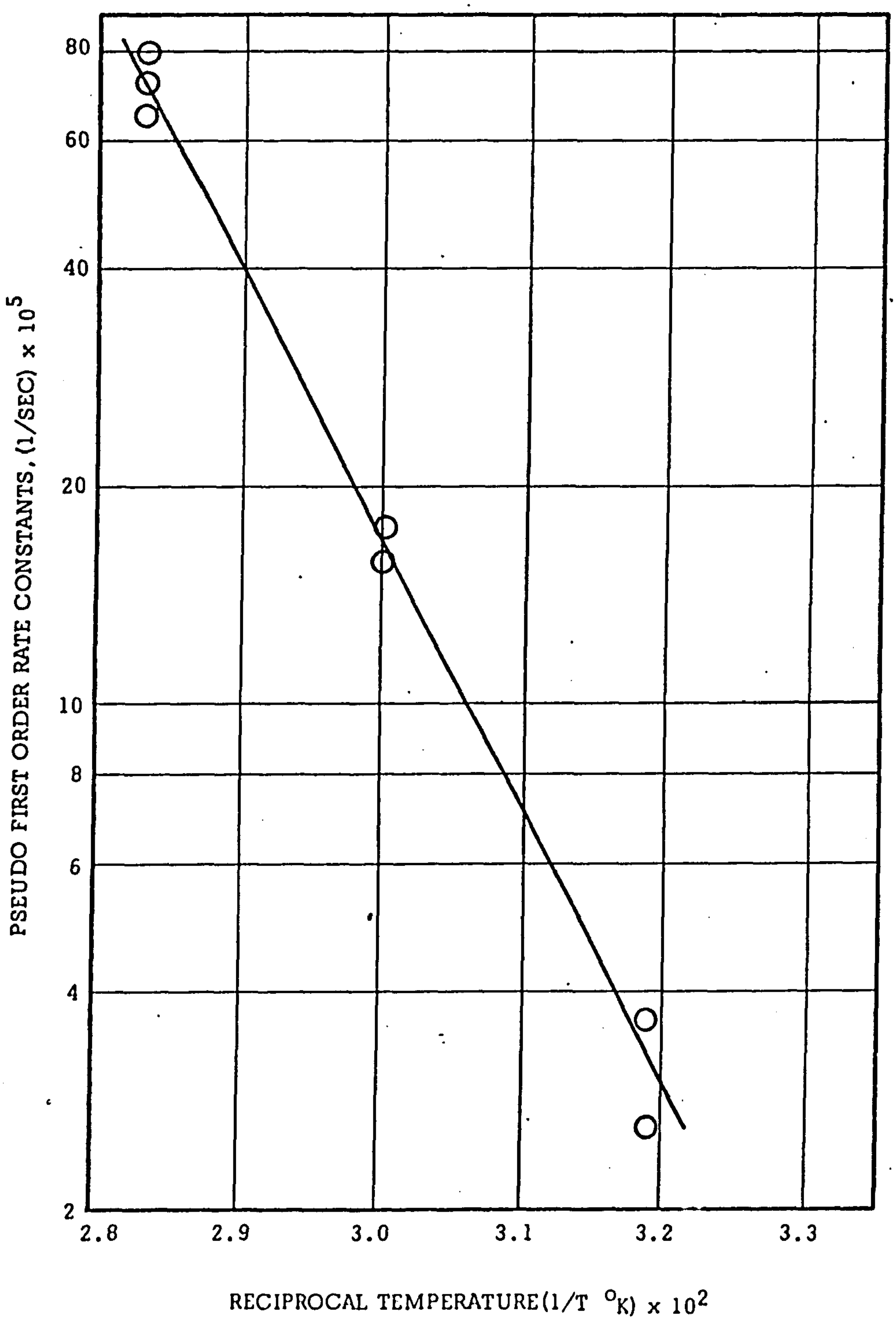


TABLE 9

PSEUDO FIRST ORDER RATE CONSTANTS

Temperature °C	Rate Constant, k_1 $\frac{1}{\text{Sec}} \times 10^{+5}$
39.9	2.55 ± 0.08
	3.64 ± 0.07
60.0	15.6 ± 0.2
	17.5 ± 1.2
80.3	65.0 ± 1.6
	79.5 ± 1.1
	72.0 ± 0.7

TABLE 10

SECOND ORDER RATE CONSTANTS

Temperature °C	Rate Constant, k_2 $\frac{\text{Liter}}{\text{Mole-Sec}} \times 10^{+6}$
39.9	8.4 ± 0.4
	11.8 ± 0.4
60.0	57.8 ± 2.3
	61.7 ± 2.8
80.3	266 ± 8
	308 ± 11

first order propagation reaction was found to be 17,400 ± 1,200 cal/mole, while for the second order portion the value was 18,500 ± 1,500 cal/mole. These two values agree within experimental error as they should.

The following equation was used to calculate the entropy of activation.

$$k_{prop} = (KT/h)\, e^{\Delta S^{\ddagger}/R} \cdot e^{-\Delta H^{\ddagger}/RT}$$

where; k_{prop} = Propagation Rate Constant
$\Delta H^{\ddagger}$ = Heat of Activation = Ep - RT
R = Gas Constant, 1.987 cal/mole - ^{o}K
T = Absolute Temperature, ^{o}K
K = 1.300×10^{-16} erg/^{o}K
h = 6.624×10^{-27} erg-sec
$\Delta S^{\ddagger}$ = Entropy of Activation

The heat of activation was calculated at each of the three reaction temperatures using the energy of activation found for both the pseudo first order and the second order portions of the polymerization. Using these values of the heat of activation the entropy of activation was also calculated at each temperature for the pseudo first order and the second order portions of the polymerization. The heats of activation are listed in Table 11, page 114, and the entropies of activation are listed in Table 12, page 115. The highly negative entropy values are very typical of S_N2 type reactions.

TABLE 11

HEAT OF ACTIVATION

Temperature °C	Heat of Activation($\Delta H^{\ddagger}$) Pseudo First Order Cal./Mole	Second Order Cal./Mole
39.9	16,800 ± 1,200	17,900 ± 1,500
60.0	16,700 ± 1,200	17,800 ± 1,500
80.3	16,700 ± 1,200	17,800 ± 1,500

TABLE 12

ENTROPY OF ACTIVATION

Temperature °C	Entropy of Activation ($\Delta S^{\ddagger}$) Pseudo First Order Cal./Mole-°K	 Second Order Cal./Mole-°K
39.9	-25.6 ± 3.8	-24.3 ± 4.8
60.0	-25.9 ± 3.6	-24.7 ± 4.5
80.3	-25.9 ± 3.4	-24.6 ± 4.3

To check the reproducibility of the kinetic runs two polymerizations (runs 19 and 20, shown in Figure VI, page 117) were run under exactly the same conditions. The two polymerization rate constants were found to agree within 10 percent. These runs were made at 80°C so it was felt that they would give the poorest reproducibility because any difference would be magnified by the high temperature. The runs made at lower temperatures would probably show better agreement.

During the propagation reaction of an unsymmetrical epoxide it would be possible for the epoxide ring to be attacked at the primary or secondary carbon atom. For correct analysis of the kinetic results this ratio of attacks should be known. Gee et al(51) showed, by gas chromatographic analysis of the products, that when propylene oxide was reacted with sodium methoxide 97% of the secondary alcohol and 3% of the primary alcohol was obtained. This showed that attack at the primary carbon was about 32 times as great as attack at the secondary carbon. With 1,2-butylene oxide only attack at the primary carbon took place. For the present work with NPEO it was felt that attack would also occur almost exclusively at the primary carbon atom.

From the plot of monomer concentration versus time for run 23, Figure III, page 104, it can be seen that there is a slight downward

REPRODUCIBILITY OF EQUIVALENTS OF MONOMER vs TIME

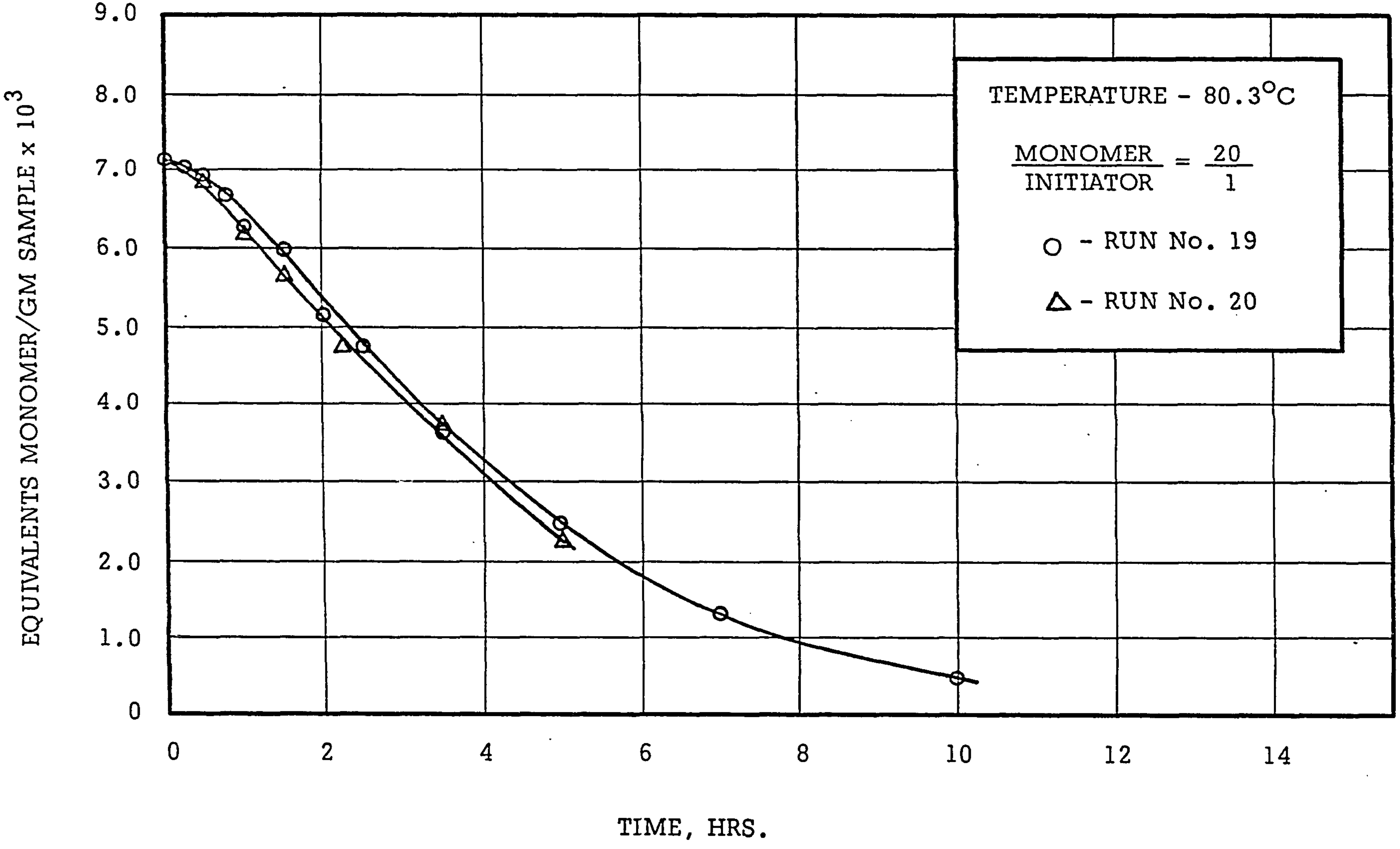


FIGURE VI

curve at the beginning of the reaction leveling off to a straight line relationship. This would indicate a slow initiation reaction followed by a faster propagation reaction. Gee et al(8) reported just the opposite result when they polymerized propylene oxide with sodium methoxide. They found a rapid initiation reaction followed by a slower propagation. However, it was noticed in the present study that a small amount of solid precipitated when the initiator was added to the monomer, but became soluble after about 5 to 10% conversion of monomer. This solid may have affected the initiation reaction so no definite conclusions could be drawn about the relative rates of the initiation and propagation reactions.

Table 13, page 119, shows the second order rate constants found in the present work along with rate constants from previous studies. Because of large steric hindrance NPEO should polymerize much slower, under the same conditions, than either propylene or 1,2-butylene oxide. It can be seen that at 30°C and with the potassium counter ion, NPEO polymerizes about 30 times slower than propylene oxide reacted in DMSO(11) and about 65 times slower than a bulk propylene oxide polymerization.(6) The 1,2-butylene oxide was found to polymerize only about four times as fast as the NPEO.(14) It is interesting that the polymerization rate difference between

TABLE 13

COMPARISON OF REACTION RATES FOR ALKOXIDE AND HYDROXIDE INITIATED POLYMERIZATIONS

Monomer	Temperature °C	Initiator	Solvent	k_2 $\frac{\text{Liter}}{\text{Mole-Sec}} \times 10^4$
NPEO	30	t-BuOK	Bulk	0.04
NPEO	70	t-BuOK	Bulk	1.32
Propylene Oxide(11)	30	t-BuOK	DMSO(a)	2.5
Propylene Oxide(6)	30	KOH	Bulk	1.2
Propylene Oxide(8)	70	MeONa	Bulk(b)	1.36
1,2-Butylene Oxide(14)	30	t-BuOK	DME(c)	0.175
1,2-Butylene Oxide(14)	70	t-BuOK	DME	4.2
Ethyl Glycidyl Ether(14)	30	t-BuOK	DME	1.3
Ethyl Glycidyl Ether(14)	70	t-BuOK	DME	22.5
t-Butylethylene Oxide(12)	30	t-BuOK	DMSO	0.20
t-Butylethylene Oxide(12)	70	t-BuOK	DMSO	38.0

(a) Dimethyl Sulfoxide.

(b) Monomer contained between 0.37 and 1.39 mole/l MeOH.

(c) 1,2-Dimethoxyethane.

propylene oxide and 1,2-butylene oxide should be so great. However, if the propylene oxide were polymerized under the same conditions (i.e. same initiator, same solvent) this difference would probably decrease.

The effect that solvent has on the reaction rate can be seen with the polymerization of t-butylethylene oxide.(12) The t-butylethylene oxide was polymerized in dimethyl sulfoxide using t-BuOK as the initiator. The NPEO polymerization was also run using t-BuOK as the initiator but no solvent was used. Because of steric effects the rate of polymerization of t-butylethylene oxide should have been slower than the rate of polymerization of NPEO. However as can be seen from Table 13, page 119, the t-butylethylene oxide polymerized 5 times as fast at 30°C and 30 times as fast at 70°C as the NPEO. Temperature seemed to have a much greater effect on the t-butylethylene oxide polymerization than on the other polymerization. For NPEO on going from 30°C to 70°C the rate of polymerization increased 33 times, for 1,2-butylene oxide the rate increased 24 times while for t-butylethylene oxide the rate increased 190 times.

When propylene oxide was polymerized at 70°C, with MeONa initiator and in the presence of some methanol, the rate was decreased so much that it was almost equal to the NPEO polymerization rate at

TABLE 14

COMPARISON OF KINETIC DATA FOR ALKOXIDE INITIATED POLYMERIZATIONS

Monomer	Initiator	Solvent	Entropy of Activation cal/deg-mole	Activation Energy K cal/mole	Frequency Factor liter/mole-sec
Ethylene Oxide(7)	MeONa	1:4 Dioxan	-	17.8	2×10^8
Propylene Oxide(8)	MeONa	Bulk	-	17.4	10^7
Ethyl Glycidyl Ether(14)	t-BuOK	DME	-31.4 ± 2.1(A)	14.2 ± 0.6	2.4×10^6
1,2-Butylene Oxide(14)	t-BuOK	DME	-29.5 ± 3.4(A)	16.0 ± 0.7	2.3×10^6
NPEO	t-BuOK	Bulk	-25.9 ± 3.6(B)	17.9 ± 1.5	$4.3 \pm 0.6 \times 10^7$
t-Butylethylene Oxide(12)	t-BuOK	DMSO	-	24	-

(A) Calculated at 65°C
(B) Calculated at 60.0°C

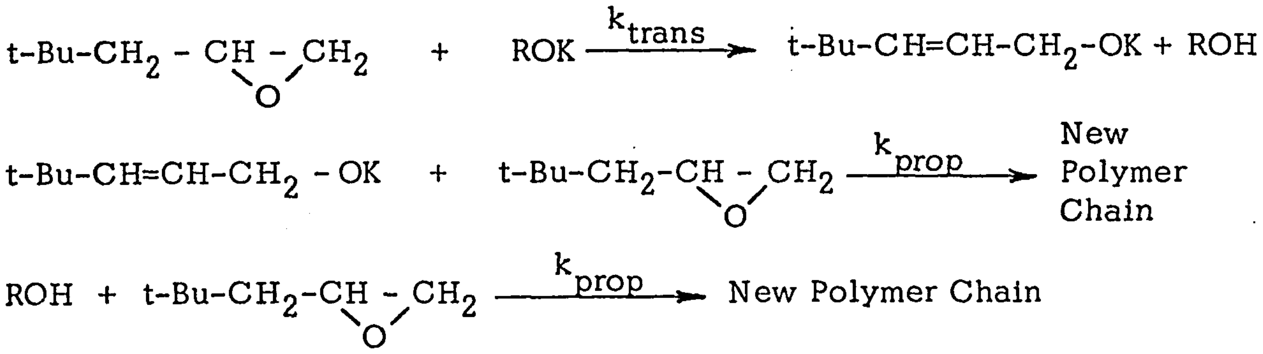
70°C.(8) This results because, as was discussed previously, going from one cation to a smaller one slows down the polymerization rate. Also the presence of alcohol has been shown by Snyder(5) to reduce the polymerization rate.

The activation energies, frequency fractors and entropies for various epoxides are shown in Table 14, page 121. It is difficult to draw any meaningful conclusions because of the limited data available. The table does show the expected increase in energies of activation, because of steric hindrance, when going from ethyl, to neopentyl to t-butyl side groups.

Large negative entropies were obtained in the polymerization of NPEO, ethyl glycidyl ether and 1,2-butylene oxide because of the lose of freedom when the S_N2 transition state was formed. These large negative entropies are typical of S_N2 type reactions.

E. Chain Transfer.

From previous work(5,6,8,9,11) done on propylene oxide it was expected that chain transfer would take place along with the propagation reaction. Table 15, page 124, shows the calculated and observed number average molecular weights for NPEO for different degrees of polymerization. The difference in the molecular weights at a certain reaction time indicates that chain transfer is taking place. Figure VII, page 125, shows how the difference in the theoretical and experimental number average molecular weight increases with time. For NPEO the chain transfer reaction would proceed by β elimination as shown below;



where R is any of the possible organic moieties. It can be seen that the transfer reaction does not terminate the polymerization but instead actually starts one new chain.

To calculate the energy of activation for the transfer reaction a

TABLE 15

CALCULATED AND OBSERVED $\overline{Mn}$ AND DEGREE OF POLYMERIZATION

Run No.	Time Hours	$\overline{Mn}$ (Obs)	$\overline{Mn}$ (Calc)	DP	DP_o
14	382	3400 ± 200	4750	29.2 ± 1.8	41
23	16	950 ± 50	1300	7.7 ± 0.4	10.8
23	24	1260 ± 50	1850	10.4 ± 0.4	15.7
23	34	1750 ± 80	2400	14.7 ± 0.7	20.5
23	46	2200 ± 150	3250	18.6 ± 1.3	28.0
23	58	2500 ± 150	4000	21.2 ± 1.3	34.6
23	75	2960 ± 150	4600	25.4 ± 1.3	40.0
23	97	3500 ± 500	5100	30.0 ± 4.4	44.4

Run 14 made at 39.9°C and Monomer/Initiator = 50/1
Run 23 made at 60°C and Monomer/Initiator = 50/1

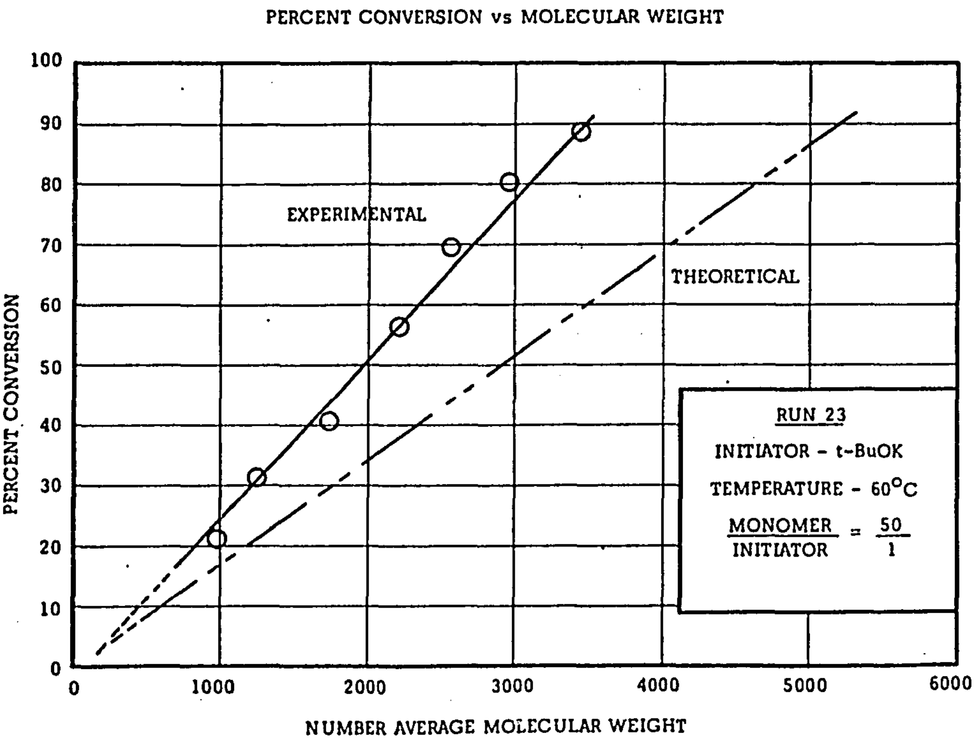

PERCENT CONVERSION vs MOLECULAR WEIGHT
PERCENT CONVERSION
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
NUMBER AVERAGE MOLECULAR WEIGHT
EXPERIMENTAL
THEORETICAL
RUN 23
INITIATOR - t-BuOK
TEMPERATURE - 60°C
MONOMER / INITIATOR = 50 / 1

FIGURE VII

method similar to that proposed by Gee et al$^{(8)}$ was used. For their calculations the molar concentrations of monomer and polymer chains were used. They derived the following equations;

$$-d[M]/dt = k_p\,[M]\,[C_o] + \alpha\, k_p\,[M]\,[C_o] \tag{1}$$

$$dn/dt = \alpha k_p\,[M]\,[C_o] \tag{2}$$

Combining and integrating these two equations gives,

$$n = n_o + \frac{\alpha}{1+\alpha}\,([M_o] - [M]) \tag{3}$$

where; $[M]$ = Concentration of Monomer (initially $[M_o]$).
$[C_o]$ = Initiator Concentration.
k_p = Polymerization Rate Constant.
αk_p = Chain Transfer Rate Constant.
n = Concentration of Chains (initially n_o).

The first term on the right hand side of equation (1) represents the amount of monomer consumed due to polymerization, while the second term represents the amount of monomer consumed due to chain transfer. Equation (2) represents the amount of new chains formed due to chain transfer.

The number-average degree of polymerization (DP) with chain transfer is given by,

$$DP = \frac{([M_o] - [M])}{n_o + \frac{\alpha}{1+\alpha}([M_o] - [M])} \tag{4}$$

In the absence of chain transfer,

$$DP_o = \frac{([M_o] - [M])}{n_o} \tag{5}$$

The following formula was then obtained,

$$\frac{1}{DP} = \frac{1}{DP_o} + \frac{\propto}{1 + \propto} \tag{6}$$

where $\propto$ = the ratio of k_{trans}/k_{prop}. A plot of $\frac{1}{DP}$ vs $\frac{1}{DP_o}$ when extrapolated to zero would yield the value of $\frac{\propto}{1+\propto}$. The main assumptions for these calculations was that chain transfer introduced one more chain initiator but had no effect on the polymerization rate and that the degree of polymerization had no effect upon the rate of chain transfer.

For the present work the values of DP and DP_o were obtained by the following formulas. For no chain transfer,

DP_o = % polymerization x ratio monomer to initiator

and using the experimentally determined number average molecular weight, $\overline{M}n$,

$$DP = \frac{\overline{M}n - \text{wt. initiator in polymer}}{\text{molecular weight of monomer}}$$

The values of DP and DP_o are listed in Table 15, page 125.

When Gee et al(8) derived their formula for DP they neglected the consumption of monomer as a chain initiator. This difference can be taken into account in the following manner.

Using Equation (1)

$$-d[M]_{total}/dt = k_p [M] [C_o] + k_p [M] [C_o] \tag{1}$$

for the rate of monomer consumed and,

$$-d[M]_{c.t.}/dt = \alpha k_p [M] [C_o] \tag{7}$$

where $[M]_{c.t.}$ is the amount of monomer consumed due to chain transfer. Combining and integrating equations (1) and (7) gives,

$$[M]_{c.t.} = \frac{1}{1+\alpha} ([M_o] - [M]) \tag{8}$$

which is the amount of monomer consumed in the chain transfer reaction.

For the new degree of polymerization with chain transfer the following ratio was used,

$$DP = \frac{\text{monomer consumed in polymerization}}{\text{concentration of polymer chains}}$$

which equals,

$$DP = \frac{([M_o] - [M]) - \frac{\alpha}{1+\alpha} [M_o]}{n_o + \frac{\alpha}{1+\alpha} ([M_o] - [M])} \tag{9}$$

Combining with DP_o and reducing this becomes,

$$\frac{1}{DP} = \frac{1}{DP_o}(1+\alpha) + \alpha \tag{10}$$

and solving for α gives,

$$\alpha = \frac{(DP_o - DP)}{DP\,(DP_o + 1)} \tag{11}$$

The values of α were calculated using equation (11) for runs 14 and 23 and are listed in Table 16, page 130. Figure VIII, page 131, shows a plot for $1/\alpha$ vs. the change in monomer concentration. It can be seen that there is a definite slowing in the rate of chain transfer with the degree of polymerization. Therefore the rate of chain transfer is decreasing relative to the rate of polymerization. Since both reactions are dependent on the concentration of the monomer and the number of end groups, as shown in the two equations below, the change in the reaction medium seems to be affecting the chain transfer reaction

$$\text{Rate of polymerization} = k_{prop}\,[M]\,[RO^-]$$
$$\text{Rate of chain transfer} = \alpha k_{prop}\,[M]\,[RO^-]$$

more than the propagation reaction.

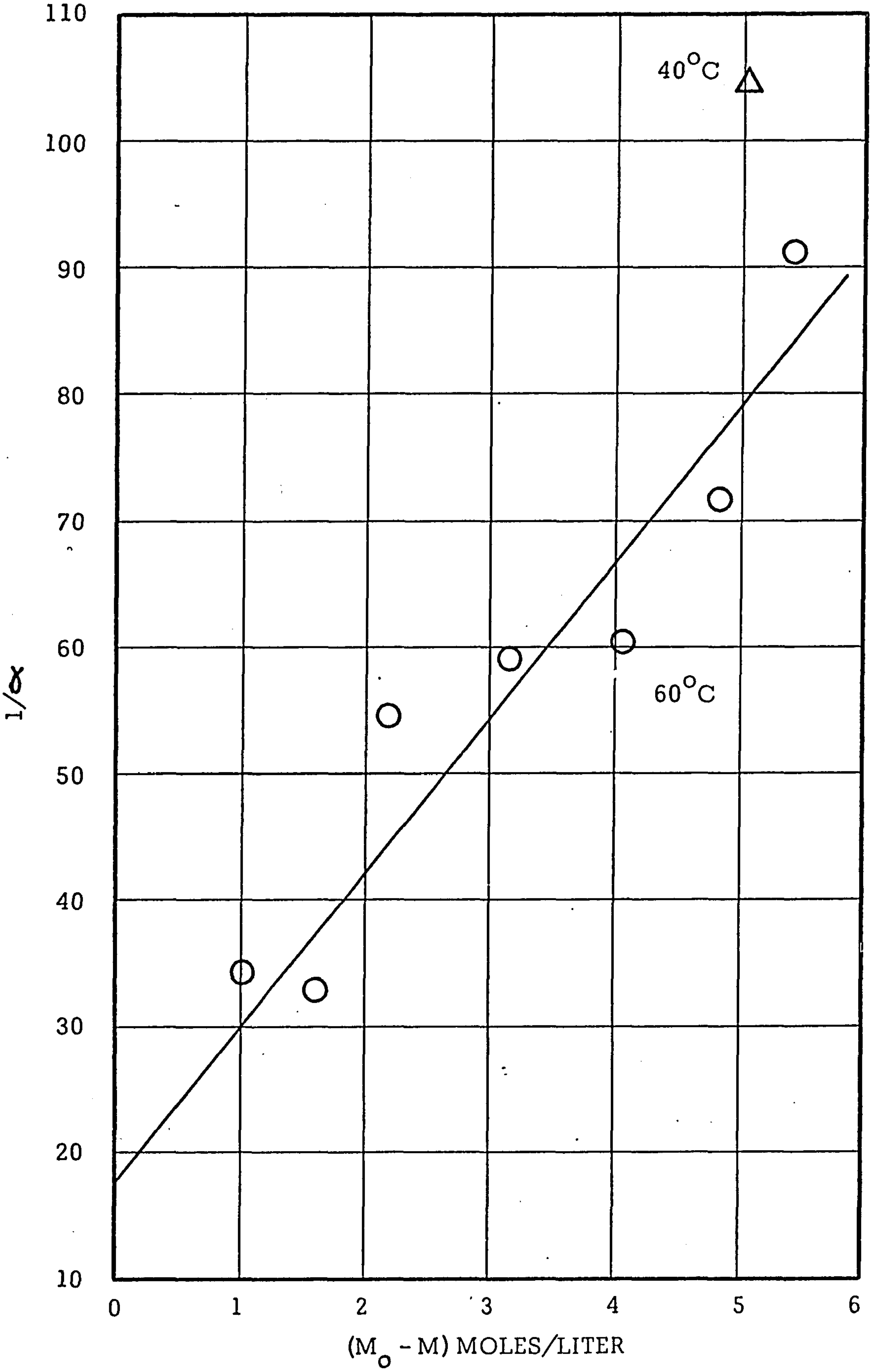
There is also the possibility that the chain transfer reaction is not second order. This was checked into by making a plot of log monomer concentration versus log chain transfer rate. This plot had a slope of

TABLE 16

NPEO CHAIN TRANSFER CALCULATIONS

Run No.	Time Hours	$M_o - M$ Moles/Liter	α	$1/\alpha$
14	382	5.048	.0096 ± 0.0005	104 ± 6
23	16	1.026	.033 ± 0.004	30.5 ± 3.7
23	24	1.615	.031 ± 0.002	32.3 ± 2.1
23	34	2.215	.018 ± 0.002	55.5 ± 6.1
23	46	3.186	.017 ± 0.002	58.8 ± 6.9
23	58	4.081	.016 ± 0.002	62.5 ± 7.8
23	75	4.833	.014 ± 0.001	71.4 ± 5.1
23	97	5.442	.011 ± 0.003	90.8 ± 24.0

FIGURE VIII



RATE OF CHAIN TRANSFER vs MONOMER CONCENTRATION

1.5 indicating that instead of the chain transfer reaction being first order with respect to monomer it was a 1.5 order reaction.

Substituting this value back into equations 1 and 7 gives,

$$-d[M]_{total}/dt = k_p [M] [C_o] + \alpha k_p [M]^{1.5} [C_o] \tag{1a}$$

and

$$-d[M]_{c.t.}/dt = \alpha k_p [M]^{1.5} [C_o] \tag{7a}$$

Solving for α gives,

$$\alpha = \frac{DP_o - DP}{[M]^{0.5} (DP) (DP_o + 1)} \tag{12}$$

Calculating the α's by equation 12 for the different reaction times in run 23 gave a fairly constant value of about 0.0115. However within the present work it could not be determined whether α was varying because of the change in the reaction medium or if α was constant with the chain transfer reaction being a 1.5 order reaction with respect to monomer concentration. Because of previous work by Gee et al(8), where α was found to be constant in a medium that did not change much throughout the reaction, it was decided that α was changing because of the changing reaction medium.

The values of $1/\alpha$, listed in Table 16, page 130, are plotted against monomer concentration for two different temperatures in Figure VIII, page 131. From this figure it can be seen that the value of $1/\alpha$ is larger at 40°C than at 60°C for the same percent conversion. This indicates that the rate of chain transfer increases with increasing temperature as was mentioned on page 94.

The chain transfer rate constants were calculated by taking the values of α for the 39.9°C and 60°C, at 75% conversion, and multiplying them by the 39.9°C and 60°C propagation rate constants. The chain transfer rate constants were found to be $.97 \pm 0.5 \times 10^{-7}$ liter/mole-sec at 39.9°C and $7.7 \pm 0.6 \times 10^{-7}$ liter/mole-sec at 60°C. The energy of activation for the chain transfer reaction was then determined by plotting the log of the rate constants versus the reciprocal of absolute temperature. From the slope of this plot the energy of activation was found to be 21,500 ± 1,500 cal/mole. Therefore, at 75% conversion, the energy of activation for the chain transfer reaction is from 3-4 K cal/mole greater than the energy of activation for the propagation reaction. More molecular weights would be needed from the 40°C run so that the difference in the values of $1/\alpha$, and thus the chain transfer activation energy, could be determined at the beginning of the polymerization.

Table 17, page 135, lists the ratios of the propagation rate to the chain transfer rate obtained from the polymerization of various epoxides. Where possible for the bulk polymerizations the percent conversion of monomer is also given because of the change in chain transfer rate with percent polymerization found for NPEO run in bulk. With polymerizations run in various solvents the percent conversion was not given.

The effect that the reaction medium had on the rate of chain transfer can be seen when propylene oxide was polymerized in dimethyl sulfoxide (DMSO) and in bulk. The amount of chain transfer was five times as great when propylene oxide was polymerized in DMSO. DMSO has been shown to markedly speed up the breaking of C–H bonds.(52) The rest of the propylene oxide polymerizations gave consistent results.

When comparing the amount of chain transfer, at room temperature, for propylene oxide and NPEO it was found that the ratios of $k_{2(prop)}$ to $k_{2(trans)}$ were about the same for both. However, propylene oxide has three protons α to the epoxide ring while NPEO only has two. Therefore, the number of eliminations per hydrogen is greater for NPEO (46 compared to 34). This is consistent with the fact that branched chain compounds undergo elimination reactions faster than straight chain

TABLE 17

COMPARISON OF AMOUNT OF CHAIN TRANSFER IN EPOXIDE POLYMERIZATIONS

Monomer	Solvent	Initiator	Temperature	$\frac{k_2 (\text{prop})}{k_2 (\text{trans})}$
Propylene Oxide(11)	DMSO	t-BuOK	Room Temp.	20
Propylene Oxide(5)	Bulk	t-BuOK	Room Temp.	103(a)
Propylene Oxide(5)	Bulk	KOH	25°C	95
Propylene Oxide(6)	Bulk	KOH	30°C	98(b)
Propylene Oxide(8)	Bulk	MeONa	70°C	77(c)
Propylene Oxide(8)	Bulk	MeONa	93°C	32(c)
1,2-Butylene Oxide(14)	DME	t-BuOK	Room Temp.	133(d)
1,2-Butylene Oxide(14)	DME	t-BuOK	65°C	40(d)
Ethyl Glycidyl Ether(14)	DME	t-BuOK	65°C	13(d)
NPEO	Bulk	t-BuOK	Room Temp.(f)	92(e)
NPEO	Bulk	t-BuOK	39.9°C	80(e)
NPEO	Bulk	t-BuOK	60°C	60(e)
t-Butylethylene Oxide(12)	DMSO	t-BuOK	60°C	(g)

Notes for Table 17 on following page.

Notes for Table 17

(a) 75% conversion.

(b) Calculated from the number of mmoles of unsaturation in polymer formed at 60% conversion.

(c) Values were said to be independent of percent conversion.

(d) Estimated from Number Average molecular weights.

(e) 60% conversion.

(f) Extrapolated from measured values on a log k vs $1/T^{o}K$ plot.

(g) See page 137.

compounds.(40) This can also be seen from the fact that, while NPEO and 1,2-butylene oxide have the same number of α to the ring hydrogens, the 1,2-butylene oxide undergoes less chain transfer than NPEO. The energy of activation for the chain transfer reaction of 1,2-butylene oxide was estimated from the number average molecular weights obtained by Joyce.(14) This value was found to be about 23 ± 3 K cal/mole or about 7 K cal/mole higher than the propagation activation energy. This is larger than the 3-4 K cal/mole difference found for NPEO.

The effect of an oxygen atom on the rate of chain transfer was found to be very great. When ethyl glycidyl ether and 1,2-butylene oxide were polymerized at the same conditions the ethyl glycidyl ether was found to undergo three times as much chain transfer as the 1,2-butylene oxide.

The effect of temperature on the rate of chain transfer can be seen in the results from the polymerization of NPEO. As the temperature is raised the proportion of chain transfer reactions becomes greater. This is to be expected because of the higher energy of activation required for the chain transfer reaction.

Price and Carmelite (11) polymerized t-butylethylene oxide in DMSO using potassium t-butoxide as the initiator. They reported that the resulting polymer showed no infrared absorption indicative of unsaturated end groups. However they reported a large difference between the observed molecular weight (1123) and the calculated molecular weight (2000). In a later article, Price and Fukutani(12) reported that all their polymers of t-butylethylene oxide had lower molecular weights than the theoretical values. Chain transfer was not expected with t-butylethylene oxide because there are no hydrogens α to the ethylene oxide group. When the polymerizations were carried out in DMSO sulfoxide endgroups were formed in the polymer. Chain transfer also occurred when the polymerization was carried out in diglyme and in bulk. However no definite conclusions were drawn about the type of chain transfer reactions taking place.

CHAPTER IV

CONCLUSIONS

The bulk polymerization of neopentylethylene oxide followed pseudo first order kinetics up to about 60% conversion of monomer to polymer. After about 60% conversion the polymerization became second order. The energy of activation for the propagation reaction was found to be about 17.9 ± 1.5 K cal/mole.

Large steric requirements for the neopentyl group resulted in a very large negative entropy for the S_N2 propagation reaction. This value was found to be -25.9 ± 3.6 e.u./mole @ 60.0°C. The frequency factor was found to be around $4.3 \pm 0.6 \times 10^7$ liter/mole-sec.

Neopentylethylene oxide underwent a chain transfer reaction along with the propagation reaction. The energy of activation for the chain transfer reaction was found to be 21.5 ± 1.5 K cal/mole, at 75% conversion of monomer to polymer, or about 3-4 K cal/mole greater than the energy of activation for the propagation reaction. The rate of chain transfer was found to decrease with decreasing temperature and increasing percent conversion. At 75% conversion and 40°C there were about .95 transfer reactions per 100 propagation reactions while at 60°C and the same percent conversion there were about 1.3 transfer reactions per 100 propagation reactions. Also for the polymerization run at 60°C there were 6.5 transfer reactions per 100 propagation reactions at zero percent conversion.

Most of the data obtained collaborated the existing theory that increasing the initiator counter ion size increases the rate of the propagation reaction. Thus the rate of polymerization increased when the initiator was changed from t-BuOLi to t-BuOK to t-BuORb.

In the preparation of optically active monomers the separation of diastereomers by gas chromatography seems to be limited by the molecular weight of the compounds. The molecular weight of the diastereomers prepared in this study was 391. This is probably too high to be vaporized in a gas chromatograph column without some sort of decomposition taking place.

In trying to separate enantiomers by gas chromatography using the right column material is critical, with finding this material a matter of trial and error for each particular compound. Preparation of enough optically active monomer by gas chromatography for polymerization studies would probably be very laborious because sample size would have to be small to get an effective separation.

CHAPTER V

RECOMMENDATIONS

For Kinetic Work

1. Polymerizations of other 1,2-epoxides would be of help in gaining a more thorough understanding of the propagation and chain transfer reactions. Especially in determining why the rate of chain transfer decreased with increased percent polymerization.

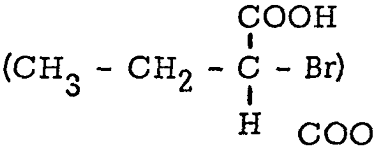
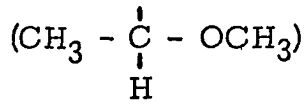
2. It would probably be better to run future polymerizations of NPEO and other 1,2-epoxides at lower concentrations to avoid the large density change that was encountered in this study.

3. More NPEO molecular weight data is required at polymerization temperature other than 60°C to more accurately calculate the chain transfer energy of activation.

4. It would be of interest to try and find out what the solid was that precipitated after the monomer and t-BuOK initiator were mixed and to see if this solid had any connection with the slow initiation reaction.

5. It would also be interesting to do some additional polymerizations of NPEO with KOH to clear up some of the unusual results obtained with this initiator.

For Preparation of Optically Active Monomer

1. For distillation and gas chromatographic work on the separation of diastereomers a lower molecular weight optically active acid should be used to react with the bromohydrin. For example either d or l - α - bromobutyric acid  $(CH_3 - CH_2 - \overset{COOH}{\underset{H}{C}} - Br)$ (M.W. - 167) or the methyl ether of lactic acid  $(CH_3 - \overset{COOH}{\underset{H}{C}} - OCH_3)$ (M.W. - 104) could be used. Both these compounds have one reactive group and a lower molecular weight than the l-menthoxyacetic acid (M.W. - 212) used in this study.

2. Instead of trying to prepare the optically active monomer by resolution of enantiomers or diastereomers it might be better to try to synthesize the optically active epoxide from readily available compounds.

3. Rerun the gas chromatograph with the 20% L-(-)- arabitol on Chromosorb W column. Inject the bromohydrin enantiomers at the lowest temperature (130°C) that was tried before. These conditions should give two peaks which can be collected and analyzed to see if any separation of the enantiomers is obtained.

APPENDIX A

TABLE 18

EXPERIMENTAL DATA RUN NUMBER 14

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 50/1
2. Reaction Temperature: 39.9°C
3. Initiator: 7.83 Weight Percent, 1.88 Molar Potassium t-Butoxide

Reaction Time Hours	Density gms/ml	Monomer Equivalents/gm Sample	Monomer Moles/Liter
0	0.8127	0.00775	6.298
8	0.8155	0.00756	6.165
21	0.8210	0.00721	5.919
33	0.8248	0.00698	5.757
50	0.8350	0.00629	5.252
75	0.8405	0.00587	4.934
120	0.8455	0.00534	4.515
166	0.8570	0.00460	3.942
220	0.8693	0.00354	3.077
290	0.8785	0.00274	2.407
382	0.8933	0.00140	1.250

TABLE 19

EXPERIMENTAL DATA RUN NUMBER 15

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 50/1
2. Reaction Temperature: 80.3°C
3. Initiator: 7.89 Weight Percent, 1.88 Molar Potassium t-Butoxide

Reaction Time Hours	Density gms/ml	Monomer Equivalents/gm Sample	Monomer Moles/Liter
0	0.7770	0.00798	6.200
1	0.7812	0.00752	5.875
2	0.7882	0.00734	5.785
3	0.7959	0.00698	5.555
6	0.8158	0.00534	4.356
9	0.8350	0.00457	3.816
12	0.8504	0.00327	2.781
14	0.8600	0.00252	2.167
17	0.8655	0.00198	1.714
20	0.8753	0.00124	1.085
24	0.8813	0.00073	0.643

TABLE 20

EXPERIMENTAL DATA RUN NUMBER 18

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 20/1
2. Reaction Temperature: 39.9°C
3. Initiator: 16.9 Weight Percent, 1.94 Molar Potassium t-Butoxide

Reaction Time Hours	Density gms/ml	Monomer Equivalents/gm Sample	Monomer Moles/Liter
0	0.8193	0.00715	5.858
3	0.8213	0.00705	5.790
10	0.8250	0.00675	5.569
24	0.8317	0.00625	5.198
41	0.8417	0.00565	4.756
46	0.8435	0.00499	4.209
55	0.8483	0.00445	3.775
72	0.8560	0.00382	3.270
96	0.8663	0.00276	2.391
136	0.8793	0.00170	1.495
168	0.8870	0.00121	1.073
220	0.8935	0.00054	0.482

TABLE 21

EXPERIMENTAL DATA RUN NUMBER 19

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 20/1
2. Reaction Temperature: 80.3°C
3. Initiator: 16.9 Weight Percent, 1.94 Molar Potassium t-Butoxide

Reaction Time Hours	Density gms/ml	Monomer Equivalents/gm Sample	Monomer Moles/Liter
0	0.7825	0.00715	5.595
0.25	0.7839	0.00702	5.503
0.5	0.7867	0.00691	5.436
0.75	0.7884	0.00666	5.251
1	0.7924	0.00628	4.976
1.5	0.7994	0.00599	4.788
2	0.8068	0.00518	4.179
2.5	0.8140	0.00476	3.875
3.5	0.8254	0.00363	2.996
5	0.8413	0.00247	2.078
7	0.8551	0.00131	1.120
10	0.8653	0.00048	0.415

TABLE 22

EXPERIMENTAL DATA RUN NUMBER 20

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 20/1
2. Reaction Temperature: 80.3°C
3. Initiator: 16.95 Weight Percent, 1.94 Molar Potassium t-Butoxide

Reaction Time Hours	Density gms/ml	Monomer Equivalents/gm Sample	Monomer Moles/Liter
0	0.7825	0.00718	5.618
0.5	0.7867	0.00682	5.365
1	0.7924	0.00616	4.881
1.5	0.7994	0.00563	4.501
2.25	0.8107	0.00474	3.843
3.5	0.8254	0.00374	3.087
5	0.8413	0.00224	1.885
7.5	0.8585	0.00143	1.228

TABLE 23

EXPERIMENTAL DATA RUN NUMBER 21

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 5/1
2. Reaction Temperature: 60.0°C
3. Initiator: 32.82 Weight Percent, 3.33 Molar Potassium t-Butoxide

Reaction Time Hours	Density gms/ml	Monomer Equivalents/gm Sample	Monomer Moles/Liter
0	0.839	0.00592	4.967
1/4	0.843	0.00576	4.856
1/2	0.850	0.00544	4.624
1	0.8575	0.00510	4.373
2	0.864	0.00451	3.897
4	0.877	0.00386	3.385
6	0.880	0.00296	2.605
8 1/2	0.895	0.00184	1.647
10	0.902	0.00144	1.299
12	0.905	0.00068	0.615

TABLE 24

EXPERIMENTAL DATA RUN NUMBER 22

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 20/1
2. Reaction Temperature: 60.0°C
3. Initiator: 16.99 Weight Percent, 1.94 Molar Potassium t-Butoxide

Reaction Time Hours	Density gms/ml	Monomer Equivalents/gm Sample	Monomer Moles/Liter
0	0.7964	0.00701	5.582
0.5	0.7975	0.00705	5.622
1	0.7992	0.00702	5.610
2	0.8014	0.00675	5.417
3	0.8037	0.00627	5.039
5	0.8083	0.00585	4.729
8.5	0.8190	0.00524	4.292
12	0.8325	0.00415	3.455
16	0.8435	0.00328	2.767
21	0.8562	0.00228	1.952
26	0.8657	0.00156	1.350

TABLE 25

EXPERIMENTAL DATA RUN NUMBER 23

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 50/1
2. Reaction Temperature: 60.0°C
3. Initiator: 7.71 Weight Percent, 1.84 Molar Potassium t-Butoxide

Reaction Time Hours	Density gms/ml	Monomer Equivalents/gm Sample	Monomer Moles/Liter
0	0.7930	0.00787	6.241
2	0.7963	0.00772	6.147
5	0.8007	0.00748	5.989
10	0.8097	0.00698	5.652
16	0.8200	0.00636	5.215
24	0.8320	0.00556	4.626
34	0.8425	0.00478	4.027
46	0.8581	0.00356	3.055
58	0.8710	0.00248	2.160
75	0.8810	0.00161	1.418
97	0.8891	0.00090	0.799

TABLE 26

EXPERIMENTAL DATA RUN NUMBER 23

REACTION CONDITIONS

1. Mole Ratio Monomer/Initiator: 50/1
2. Reaction Temperature: 60.0°C
3. Initiator: 7.71 Weight Percent, 1.89 Molar Potassium t-Butoxide

Reaction Time Hours	Percent Conversion By Polymer Workup	Percent Conversion By Titration	Number Average Molecular Wt.
16	19.37	21.5	990
24	29.5	31.4	1260
34	39.5	41.0	1750
46	55.8	56.1	2220
58	68.94	69.4	2570
75	80.17	80.1	2960
97	93.0	88.9	3450

TABLE 27

PHYSICAL PROPERTIES OF OLEFIN AND OXIDE

4,4-Dimethyl-1-Pentene	From Present Study	From Literature
Specific Gravity	0.6785 @ 30°C	0.6827 @ 20°C (29)
Boiling Point	72.5°C (760 mm)	72.35°C (760 mm) (29)
Refractive Index		n_D^{20} 1.3911 (29)

Neopentylethylene Oxide		
Specific Gravity	0.814 @ 30°C	0.829 @ 25°C (31)
Boiling Point	124.9 ± 0.2°C @ 744.5 mm	126-128°C (31) @ 744 mm
Refractive Index		n_D^{24} 1.4089 (31)

APPENDIX B

SAMPLE DETERMINATION OF MOLECULAR WEIGHT

Polymer From Run 23, t-BuOK Initiator

Temperature = 60°C, Time = 24 Hrs.

$$\frac{\text{Monomer}}{\text{Initiator}} = \frac{50}{1}$$

$$\text{Molecular Weight} = \frac{\text{Gms Solute} \times \text{M.W.Solvent} \times (K - R)}{R \times \text{Solvent Weight}}$$

K = Cell Constant = 22,000
R = Resistance

$$\text{Molality} = \frac{\text{Moles}}{1000 \text{ Gms Solvent}} = \frac{\text{Gms Solute} \times \frac{\text{Mole}}{\text{Gms Solute}}}{\text{Gms Solvent}} \times 1000$$

Solution 1, Resistance 1.

0.0517 Gms Polymer/1.8222 Gms Benzene
Resistance = 41

$$\text{Molecular Weight} = \frac{0.0517 \text{ Gms Pol.} \times 78.1 \times (22{,}000 - 41)}{41 \times 1.8222 \text{ Gms Benzene}}$$

$$= 1195$$

1/Molecular Weight = 0.000837

$$\text{Molality} = \frac{0.0517 \text{ Gms Pol.} \times \frac{1 \text{ Mole}}{1195 \text{ Gms}}}{1.8222 \text{ Gms Benzene}} \times 1000$$

Molality = 0.0237

Solution 1, Resistance 2,3, & 4.

0.0517 Gms Polymer/1.8222 Gms Benzene
Resistance = 40,40,43
Molecular Weight = 1214,1214,1130
1/Molecular Weight = 0.000824, 0.000824, 0.000885
Molality = 0.0234, 0.0234, 0.0251

Solution 2, Resistance 1,2,3,4, & 5.

0.0847 Gms Polymer/1.7606 Gms Benzene
Resistance = 76,78,78,74,84
Molecular Weight = 1084, 1057, 1057, 1112, 982
1/Molecular Weight = 0.000923, 0.000947, 0.000947, 0.000900, 0.00102
Molality = 0.0443, 0.0455, 0.0455, 0.0433, 0.0490

Solution 3, Resistance 1,2,3, & 4.

0.1007 Gms Polymer/1.3505 Gms Benzene
Resistance = 125, 126, 133, 128
Molecular Weight = 1020, 1012, 957, 996
1/Molecular Weight = 0.000980, 0.000988, 0.001045, 0.001002
Molality = 0.0737, 0.0736, 0.0778, 0.0749

Solution 4, Resistance 1,2,3,4, & 5.

0.1255 Gms Polymer/1.2172 Gms Benzene
Resistance = 210, 207, 192, 195, 201
Molecular Weight = 837, 848, 915, 901, 874
1/Molecular Weight = 0.001195, 0.001178, 0.001093, 0.00111, 0.001143
Molality = 0.123, 0.122, 0.113, 0.114, 0.118

The intercept, which gives the number average molecular weight, was determined by the method of least squares using all the molecular weights calculated above. The error in the intercept was found for each calculated molecular weight and the average of all these errors was used as the error in the number average molecular weight. The calculations of intercept and percent error were made with a computer program.

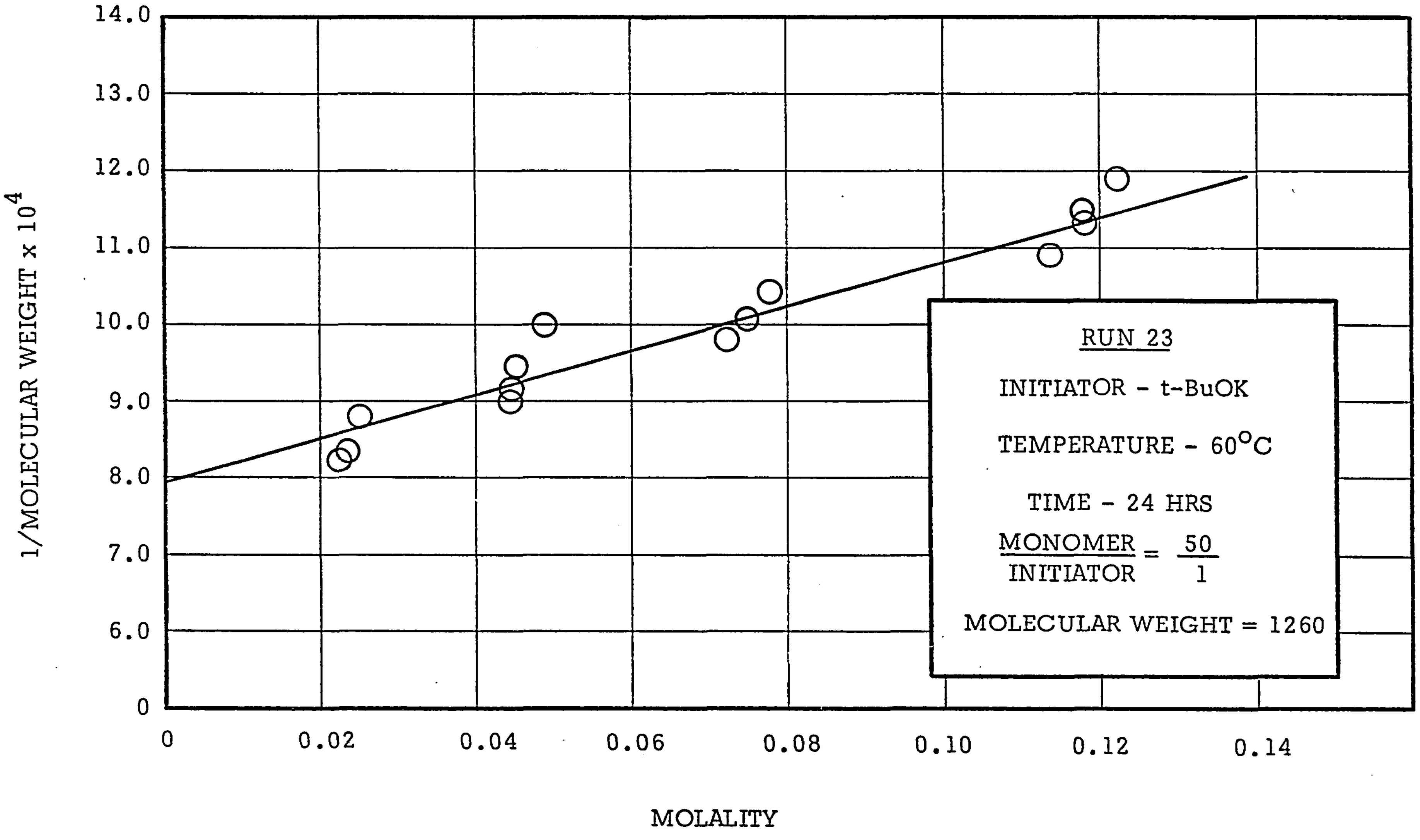
SAMPLE DETERMINATION OF MOLECULAR WEIGHT
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
0
1/MOLECULAR WEIGHT x 10^4
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
MOLALITY
RUN 23
INITIATOR - t-BuOK
TEMPERATURE - 60°C
TIME - 24 HRS
MONOMER / INITIATOR = 50 / 1
MOLECULAR WEIGHT = 1260

FIGURE IX

Number Average Molecular Weight

$$\text{Intercept} = \frac{1}{\text{M. W.}} = 7.94 \times 10^{-4}$$

Average Error in Intercept = 3.2%

Molecular Weight = 1260 ± 50

CHEMICALS USED

Prep. of Olefin

1. 2-Chloro-2-methylpropane, B.P. 50-51°C, Matheson, Coleman and Bell.
2. 3-Bromopropene, B.P. 69-71°C, Matheson, Coleman and Bell.
3. Magnesium metal turnings (for Grignard reactions) Analytical Reagent, Mallinckrodt.

Prep. of Bromohydrin

4. N-Bromosuccinimide, Fisher Scientific Company.
5. 4,4-Dimethyl-1-Pentene, City Chemical Corporation.

Prep. of Oxide

6. Potassium Hydroxide, U.S.P. Pellets, Approx. 85% KOH, Mallinckrodt.

Initiators

7. 1,2-Dimethoxyethane (Ethylene Glycol Dimethyl Ether) Matheson, Coleman and Bell.
8. Potassium, sticks, Matheson, Coleman and Bell.
9. t-Butyl Peroxide, (Di-tert-Butyl Peroxide) Practical, Matheson, Coleman and Bell.
10. Zinc Chloride, dry-granular, Fisher Scientific Company, Reagent.
11. Cesium Hydroxide, 99.7% min. City Chemical Corporation.
12. Rubidium t-Butyl Oxide, MSA Research Corporation.
13. Lithium t-Butyl Oxide, MSA Research Corporation.

For Titrations

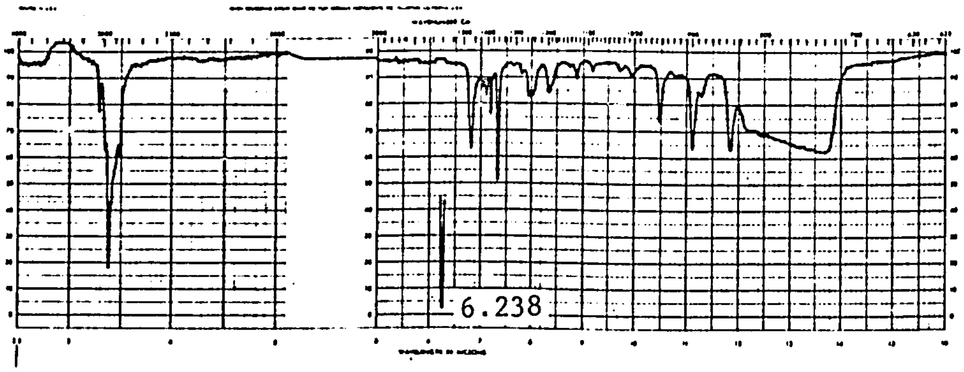
14. 1-Dodecanethiol, (Dodecyl Mercaptan) practical, Matheson, Coleman and Bell.
15. Acetic Acid, 99.7% min, M.P. 16.0-16.6°C, Matheson, Coleman and Bell.
16. Isopropyl Alcohol, Merk, Reagent grade.
17. Iodine Solution, Harleco, N/10.

Others

18. Benzene, Baker Analyzed Reagent (Thiophene free).
19. Chloroform, Baker Analyzed Reagent.
20. Carbon Tetrachloride.
21. 1-Menthoxyacetic Acid, City Chemical Corporation.

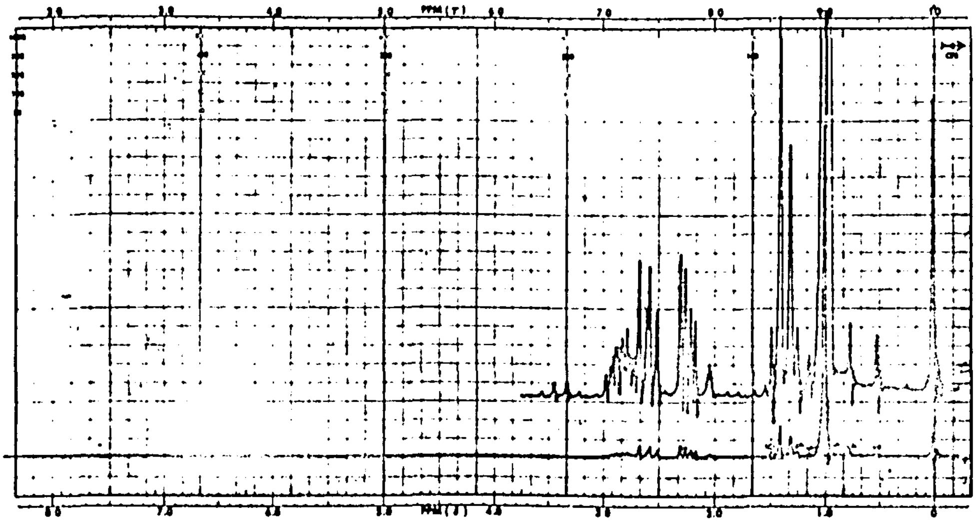
APPENDIX C

INFRARED SPECTRUM OF NEOPENTYLETHYLENE OXIDE
FIGURE X



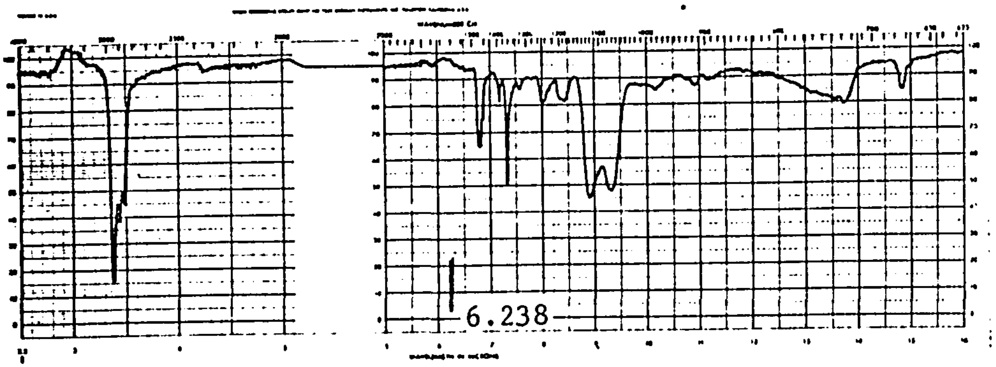
Solvent: CCl_4
Concentration: 2%
Path: 0.2 mm

60 MC NUCLEAR MAGNETIC RESONANCE SPECTRUM
FIGURE XI



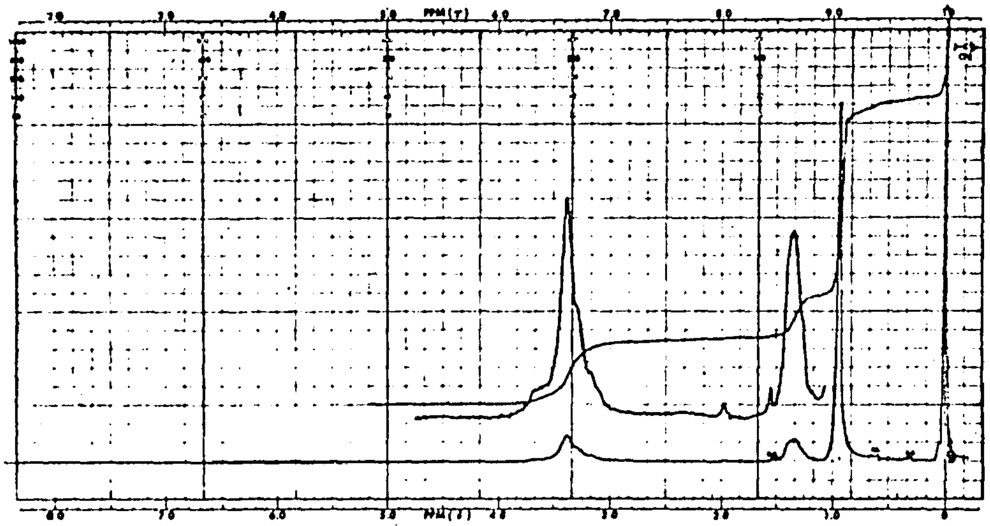
Sample:	Neopentylethylene Oxide
Solvent:	CCl_4
Temperature:	38°C
Filter Bandwidth::	4 cps
R.F. Field:	0.05 mG
Sweep Time:	250 sec.
Sweep Width:	500 cps
Spectrum Amp:	1.6
Integral Amp:	80

INFRARED SPECTRUM
POLY(NEOPENTYLETHYLENE OXIDE) RUN 3B
FIGURE XII



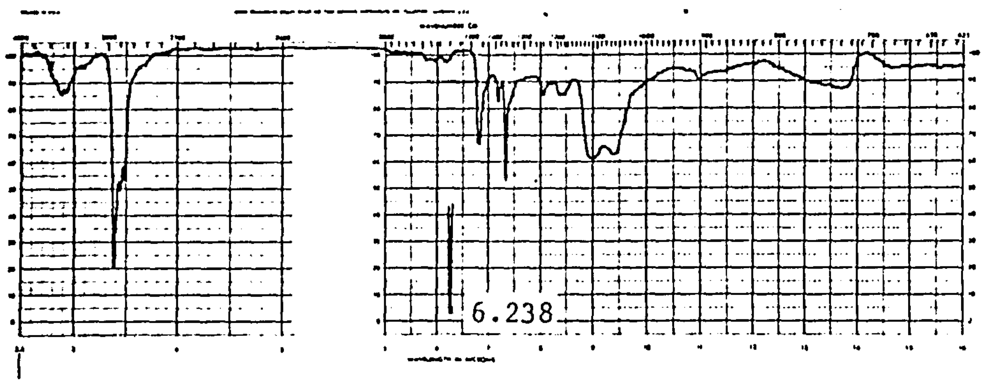
Solvent: CCl_4
Concentration: 1%
Path: 0.2 mm

60 MC NUCLEAR MAGNETIC RESONANCE SPECTRUM
RUN 3B
FIGURE XIII



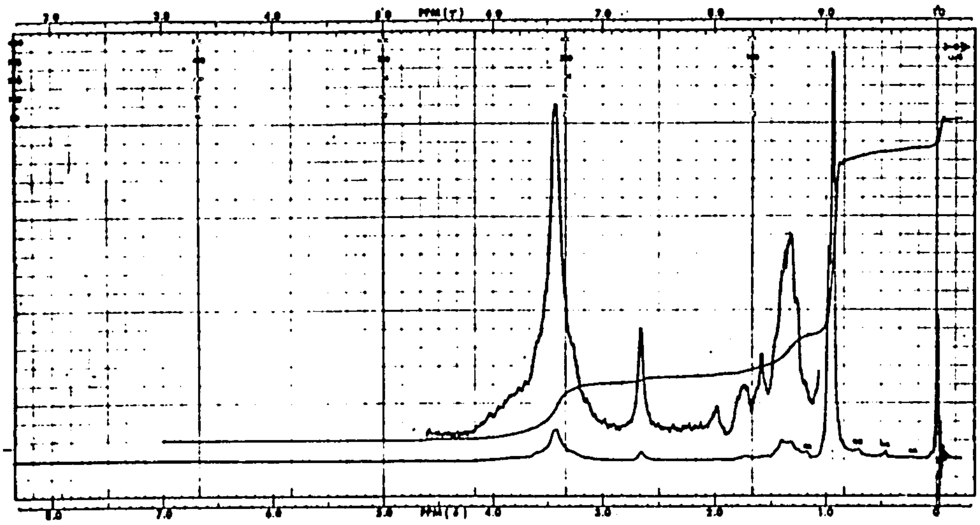
Sample: Poly(neopentylethylene oxide)
Solvent: CCl_4
Temperature: 38°C
Filter Bandwidth: 4 cps
R.F. Field: 0.05 mG
Sweep Time: 250 sec
Sweep Width: 500 cps
Spectrum Amp: 2.5

INFRARED SPECTRUM
POLY(NEOPENTYLETHYLENE OXIDE) RUN 6
FIGURE XIV

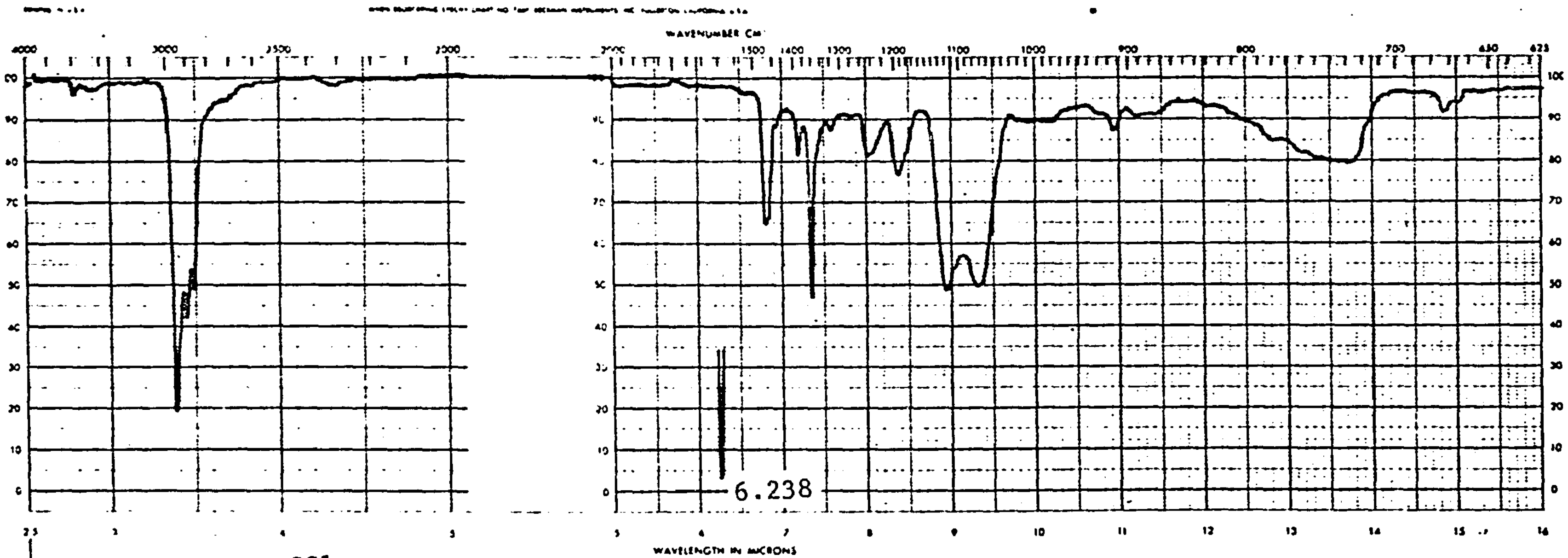


Solvent: CCl_4
Concentration: 1%
Path: 0.2 mm

60 MC NUCLEAR MAGNETIC RESONANCE SPECTRUM
RUN 6
FIGURE XV

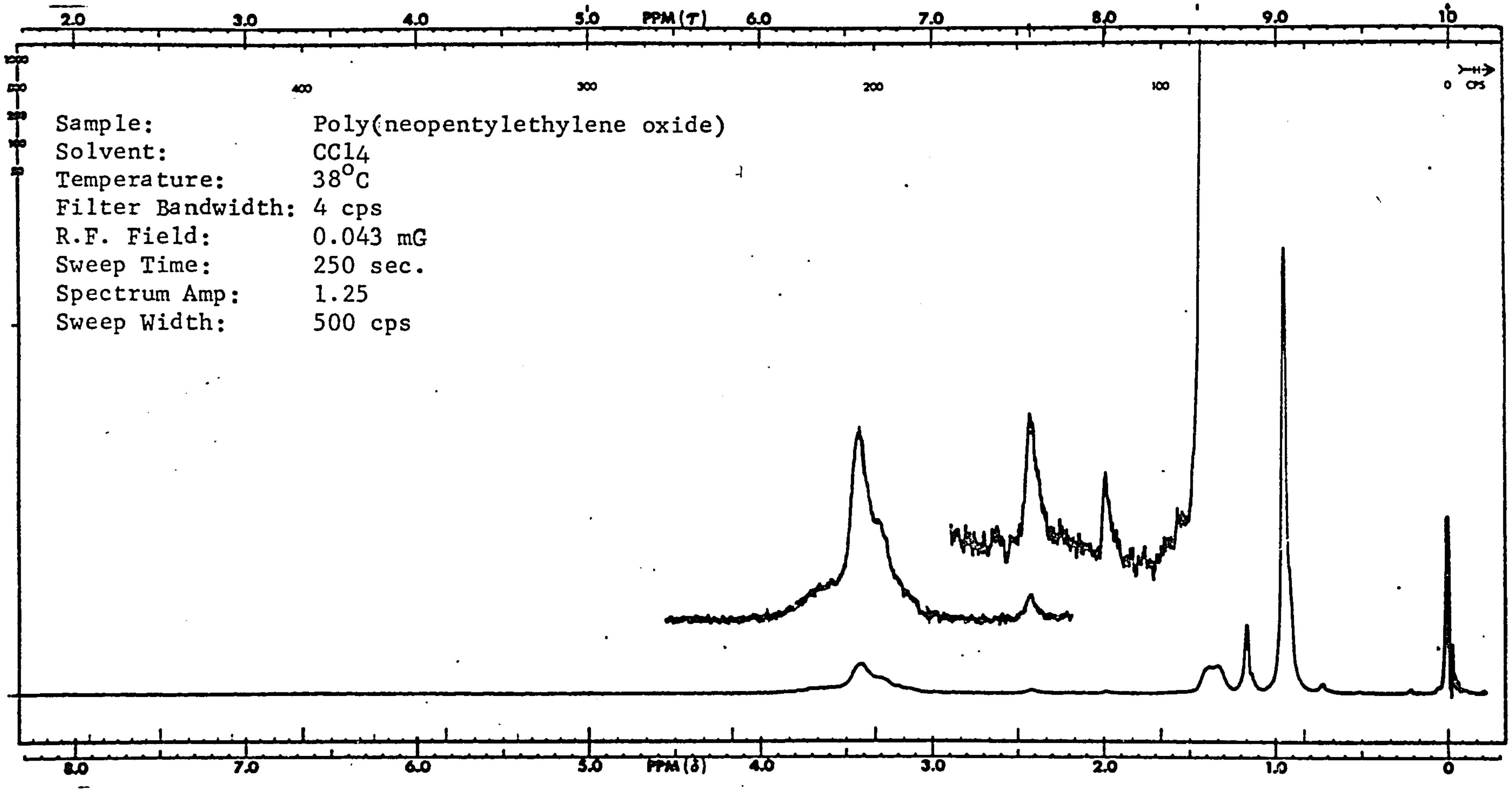


Sample:	Poly(neopentylethylene oxide)
Solvent:	CCl_4
Temperature:	38°C
Filter Bandwidth:	4 cps
R.F. Field:	0.05 mG
Sweep Time:	250 sec.
Sweep Width:	500 cps
Spectrum Amp:	4.0



Solvent: CCl$_4$
Concentration: 1%
Path: 0.2 mm

INFRARED SPECTRUM
POLY(NEOPENTYLETHYLENE OXIDE) RUN 13
FIGURE XVI



Sample: Poly(neopentylethylene oxide)
Solvent: CCl4
Temperature: 38°C
Filter Bandwidth: 4 cps
R.F. Field: 0.043 mG
Sweep Time: 250 sec.
Spectrum Amp: 1.25
Sweep Width: 500 cps

60 MC NUCLEAR MAGNETIC RESONANCE SPECTRUM
RUN 13
FIGURE XVII

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Newark College of Engineering	1963-67	D.Sc.	1970

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Summer, 1962	Alleghany Ballastics Laboratory, Cumberland, Maryland.
Sept., 1962-June, 1965	National Defence and Education Act Fellowship, Newark College of Engineering.
Sept., 1965-June, 1966	Assistant Instructor, Newark College of Engineering.
Present Position:	Esso Research and Engineering Co. Florham Park, New Jersey.