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Stereoelective polymerization of propylene oxide with a chiral aluminum alkoxide initiator

Panchalingam, Vaithilingam, Ph.D.

City University of New York, 1993

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STEREOELECTIVE POLYMERIZATION OF PROPYLENE OXIDE WITH A CHIRAL ALUMINUM ALKOXIDE INITIATOR

By

VAITHILINGAM PANCHALINGAM

A dissertation submitted to the Graduate Faculty in chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1993

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

Stereoelective Polymerization of Propylene Oxide with a Chiral Aluminum Alkoxide Initiator

By

Vaithilingam Panchalingam

Advisers: Professors Howard Haubenstock and George Odian.

The polymerization of propylene oxide (PO) was studied with an initiator prepared by the reaction of R-(-)-3,3-dimethyl-1,2-butanediol (DMBD) with aluminum hydride. When mixed with an equimolar amount of zinc chloride, the initiator was found to be highly reactive and also stereoelective in the polymerization of PO, preferentially incorporating R-(+)-PO into the polymer chain. Analysis of the polymer structure by ^{13}C-NMR spectroscopy showed that chlorine, hydroxy, and one type of alkoxy end groups derived from the initiator were present in the polymer prepared in bulk at 80°C. An additional alkoxy end group was identified in the polymer prepared at room temperature. Fractionation of poly(propylene oxide) (PPO) in acetone at -30°C gave about 10% insoluble PPO shown to be isotactic by ^{13}C-NMR. The soluble, largely atactic fraction contained irregular head-to-head (h,h) and tail-to-tail (t,t) structures. In the absence of coinitiator zinc chloride the PPO product was completely soluble at -30°C and contained a greater proportion of irregular h,h and t,t structures. The ^{13}C-NMR peak assignments

were made for the methine and methylene carbons in the irregular h,h and t,t linkages in PPO by the use of DEPT (Distortionless Enhancement by Polarization Transfer) experiment.

An attempt was made to fit the stereoelective behavior of this initiator system to a kinetic scheme. It was found that the system follows a second order monomer consumption. An initiator prepared by the reaction of aluminum hydride and N-methyl-l-ephedrine in a 1:3 molar ratio was also used for the polymerization of PO to check its stereoelective potential. This initiator system was found to be poor and its efficiency was not improved very much even by the use of zinc chloride as a coinitiator. However, this initiator preferentially elected the S-enantiomer from the racemic PO as opposed to the preferential election of R-enantiomer by the initiator derived from DMBD.

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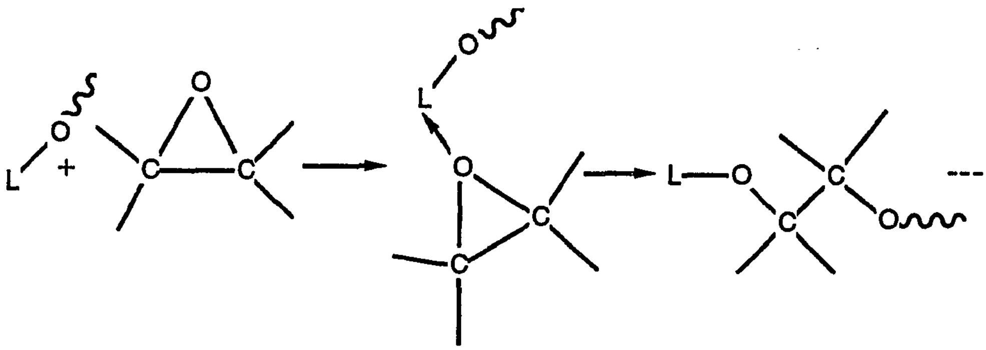
1.0 INTRODUCTION:

The formation of polyethers from oxirane (epoxide) monomers has been and continues to be a fertile area for investigation. Oxiranes can be polymerized by three distinct mechanisms: anionic or base initiated; cationic or acid initiated; and coordination polymerization.[1-4] This last process involves coordination of the oxirane oxygen atom by a Lewis acid moiety (L) at the catalytic site followed by nucleophilic attack on the activated monomer by alkoxide bound to the site as schematically shown in eq. 1-1.



---(1-1)

The remarkable reactivity of oxiranes is attributable to the oxygen atom contained in a strained three-membered ring. However the preparation of high molecular weight polymer is restricted by structural considerations of the particular monomer and the type of initiator chosen.[1]

Chiral monomers often exist as racemic mixtures. Most of the initiators cannot distinguish between the enantiomers which are therefore incorporated into the polymer chain in a irregular manner. These initiators are called non-stereospecific initiators.[3-7] Some initiators possess stereospecific sites (enantiomorphic catalyst sites) for R and S enantiomers, permitting the polymerization of R or S enantiomers selectively and form stereoregular polymers as shown in eq.1-2 and 1-3.

R monomer ---------> ∿∿∿R-R-R-R-R∿∿∿ -----------(1-2)

S monomer ---------> ∿∿∿S-S-S-S-S∿∿∿ -----------(1-3)

These initiators are called stereospecific initiators.[3-7] The polymerization of racemic monomers with stereospecific achiral initiators resulting in the formation of stereoregular polymers is called stereoselective polymerization. In general, there are non-specific sites which incorporate both R and S enantiomers to form atactic polymer. Stereoselective polymerization of oxiranes leading to stereoregular polymers has been observed with anionic[1,10,11] as well as cationic[1,12] initiators in special cases. The occurrence of stereoselective coordination polymerization has been generally observed with a variety of initiators. The polymerization of racemic monomers using chiral initiators may lead to the preferential polymerization of one of the two enantiomers. This is called stereoelective or asymmetric selective polymerization. An important feature in the stereoelective polymerization is the enrichment of the opposite enantiomer in the unreacted monomer. Thus, stereoelective polymerization may be used to resolve racemic monomers with suitable initiators.

The most widely studied monomer is propylene oxide (PO) which exists as a mixture of enantiomers. Stereospecific initiators synthesized by the reaction of diethyl zinc with chiral alcohols[13]or amino acids[14] have been shown to be stereoelective in the polymerization of oxiranes and thiiranes.[13,14] A highly effective chiral component for the stereoelective ring opening polymerization of oxiranes and thiiranes has been found to be the reaction product of diethyl zinc and DMBD taken in 1:1 molar proportion.[15-17]

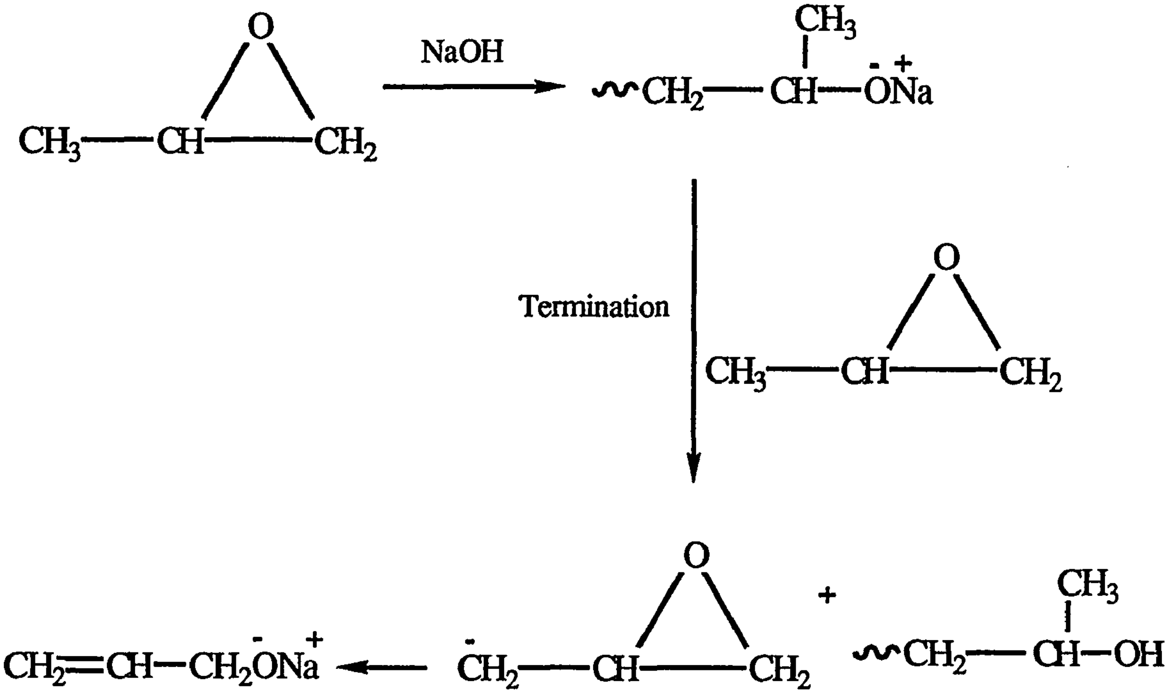
Aluminum based initiators have been ineffective in the stereoelective polymerization of epoxides and have not been extensively studied. An initiator system aluminum tris(l-3-menthyloxide)-zinc chloride was not stereoelective in the polymerization of PO since the recovered monomer was optically inactive.[18] While atactic polymer obtained with this initiator was optically active, it was shown that this was due to the presence of end groups.[18] An optically active polymer was reported in the copolymerization of PO and ethylene oxide with triethylaluminum-diethyl l-glutamate initiator.[19] An initiator prepared by the partial hydrolysis of the $FeCl_3$-PO complex was used to polymerize PO in the presence of d-bornyl ethyl ether. The unreacted monomer showed optical rotation, while the isolated crystalline polymer showed no optical rotation.[20]

The modification of $LiAlH_4$ with certain chiral alcohols has led to new reagents for the successful asymmetric reduction of prochiral ketones. For example the use of N-methyl-*l*-ephedrine has been studied thoroughly and successfully applied to asymmetric reductions of arylketones[21] and α-acetylenic ketones.[22] Often achiral components are introduced in addition to the chiral alcohol. In favorable cases, % enantiomeric excess of 75-90% have been realized.[22] The use of 2,2'-dihydroxy-1,1'-binaphthyl with diethyl zinc as an initiator for the polymerization of propylene sulfide at room temperature resulted in 80% optical purity in the unreacted monomer in 50% conversion and 92% optical purity in 67% conversion. However, with PO this initiator was found to be very inactive.[23] We have therefore investigated the polymerization of propylene oxide using a chiral aluminum alkoxide containing the chiral diol, DMBD as the chiral moiety. The chiral aluminum alkoxide was prepared by the reaction of the chiral diol, DMBD with aluminum hydride. The objective was to prepare the chiral aluminum alkoxide initiator and investigate its reactivity as a polymerization initiator as well as its stereoelective potential.

2.0 Background

2.1 General

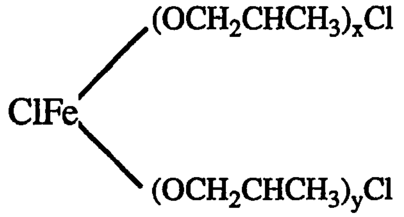
Epoxides can be polymerized by anionic initiators such as hydroxides, alkoxides, metal oxides, organometallic compounds, and other bases.[1-4] The polymerization of propylene oxide (PO) with NaOH results in lower molecular weight polymer. This was attributed to termination reactions shown in Scheme I.[4]



Scheme I

Price *et al.*[1,10,11] attempted the polymerization of *tert.* butyl propylene oxide which does not have α-protons and will not involve such termination reactions. The resulting polymer had an iso-syndio sequence in the polymer main chain. Price attributed this structural behavior to a chiral chain end control mechanism.[1,10,11] This iso-syndio sequence structure was later disputed by Tsuruta on the basis of ^{13}C-NMR studies.[24,25]

The first stereoselective polymerization of PO was carried out by Pruitt and Baggett.[26] They used a catalyst prepared by the reaction of PO and $FeCl_3$. The active species of this catalyst was suggested to be:



x + y ~5

Price *et al.* [27] studied the polymerization of PO with aluminum alkyl systems. Colclough *et al.*[28] found that the addition of a catalytic amount of water to the aluminum alkyl catalyst increased the molecular weight of the polymer. They suggested that the active species in this catalyst system is $R_2Al\text{-}O\text{-}AlR_2$ based on the amount of methane evolved during the reaction. Ueyama *et al.*[29] prepared the $R_2Al\text{-}O\text{-}AlR_2$ catalyst by the reaction of R_2AlOLi and R_2AlCl in a 1:1 molar ratio. This catalyst resulted in faster polymerization and increased crystalline polymer than the aluminum alkyl/water catalyst. They suggested that in the $AlR_3\text{-}H_2O$ system, the conversion of $AlR_3\text{-}H_2O$ to $R_2Al\text{-}O\text{-}AlR_2$ is not complete. Price *et al.*[30a] studied the polymerization of PO using aluminum isopropoxide. They found that the addition of anhydrous $ZnCl_2$ increased the polymerization rate and the amount of crystalline polymer. On the other hand, $ZnCl_2$ itself is not an efficient initiator for the polymerization of propylene oxide.[30b] An initiator prepared by the reaction of α, β, γ, δ-tetraphenylphorphine and diethylaluminum chloride has been shown to be an efficient initiator for the polymerization of epoxides.[31-33] This initiator produces living polymer chains and yield polymers with narrow and controllable molecular weights.[31-33] A novel platinum complex initiated ring opening polymerization for epoxides has been discovered recently.[34] These initiators function at levels of 10-20 ppm and often need a coinitiator containing a Si-H bond.[34] Tsuruta *et al.*[3] investigated the polymerization of PO with $ZnEt_2$-H_2O and $ZnEt_2$-ROH. The zinc initiated polymerizations have been extensively investigated and the early work has been reviewed.[3] Cadmium salts are reported to be efficient initiators for the polymerization of thiiranes. However, they are not effective for epoxides. This was attributed to the soft-hard acid-base theory. In this respect, cadmium is a soft acid and thiiranes are soft bases. Epoxides are not as soft bases as are thiiranes.[6,7] While details differ among the various initiators, it appears that they share certain important features. The polymer can be fractionated into acetone soluble (amorphous) and acetone insoluble (crystalline) components at ~-30°C. In all cases the major portion of the product consists of amorphous polymer and the crystalline content is ~10%.[30a]

Catalyst site control or chain end control mechanisms have been discussed for the polymerization of PO. An investigation of the polymerization of optically active PO samples of varying optical purities with diethylzinc-methanol initiator showed no change in the optical purity of recovered monomer.[3,35] This result cannot be explained by a chain-end control mechanism since this would predict a tendency toward racemic recovered monomer with increasing conversion. Tsuruta[3,35] explained the observation by assuming active sites with R- or S-selectivity toward monomer. If R_i^* and S_i^* represent growing species located at active sites with a certain degree i of R- and S-nature, then it may be shown that the ratio of the consumption of the enantiomers at R_i^* and S_i^* species at low degrees of polymerization is given by eq. (2-1)

$$\frac{d[R]_i}{d[S]_i} = \frac{\rho_i[R_i^*] + [S_i^*]}{[R_i^*] + \rho_i[S_i^*]} \cdot \frac{[R]}{[S]} \qquad (2\text{-}1)$$

where R and S represent monomer enantiomers and

$$\rho_i = \frac{k^i_{RR}}{k^i_{SR}} = \frac{k^i_{SS}}{k^i_{RS}} \qquad \text{------------}(2\text{-}2)$$

The rate constants refer to the processes

$$R_i^* + R \xrightarrow{k^i_{RR}} R_i^*$$

$$R_i^* + S \xrightarrow{k^i_{RS}} R_i^*$$

$$S_i^* + R \xrightarrow{k^i_{SR}} S_i^*$$

$$S_i^* + S \xrightarrow{k^i_{SS}} S_i^*$$

The above rate constants may contain factors related to adsorption of the monomers at the active species.[20] The identity of optical rotations of recovered and initial monomer requires that

$$\frac{\Sigma_i\, d[R]_i}{\Sigma_i\, d[S]_i} = \frac{[R]}{[S]} \text{ and } \frac{\Sigma_i\{\rho_i[R_i^*] + [S_i^*]\}}{\Sigma_i\{[R_i^*] + \rho_i[S_i^*]\}} = 1 \qquad (2\text{-}3)$$

Since the formation of isotactic polymer excludes $\rho_i = 1$, eq. (2-3) may be satisfied by assuming $[R_i^*] = [S_i^*]$. This suggests a symmetrical distribution of active sites with varying R and S nature. The presence of specific R and S active sites has been shown by the partial resolution of racemic poly(propylene oxide) through a column supported with poly[(-)-menthyl glycidyl ether].[36] A partial resolution was also achieved for poly(methyl thiirane) through a column supported with poly (S)-3-methyl-1-pentene.[37] An organozinc complex, $Zn(OCH_3)_2.(C_2H_5ZnOCH_3)_6$ as a model for enantiomorphic catalyst sites has been prepared for propylene oxide and the mechanism of polymerization has been discussed.[38]

2.2. Stereoelective Coordination Polymerization

The equal distribution of R- and S-selective active sites normally present in an achiral initiator can be altered by using a chiral initiator. In this way the stereoelective polymerization of racemic propylene oxide was first achieved by using a diethylzinc-(+)-borneol initiator which afforded an optically active polymer dextrorotatory in chloroform and levorotatory in benzene.[39] Recovered monomer is levorotatory due to preferential polymerization of the R-(+)-enantiomer.[40,41] The polymerization of propylene oxide was carried out with initiators prepared from diethylzinc and a variety of terpenic alcohols as well as simple alcohols such as (+)-2-butanol and (+)-3-octanol.[13] It was found that only the alcohols with rigid structures such as (+)-borneol and (-)-isoborneol were effective in inducing stereoelection. Alcohols with less rigid structures such as (-)-menthol, (+)-neomenthol, (+)-citronellol as well as several other cyclic alcohols showed little or no stereoelection capability. A possible explanation[42] is that the hindered bornyl group is prevented from migrating from the catalyst site L (see eq. 1-1) during the ring-opening propagation step while less bulky groups migrate to become end groups in the polymer.[27,39,41]

Furukawa *et al.* derived a linear relationship (eq.2-4) between the optical activity of recovered monomer and conversion in a stereoelective polymerization.[20]

$$\alpha = -\alpha_0 \frac{r-1}{r+1} \ln(1-x) \tag{2-4}$$

α = optical rotation of recovered monomer

α_0 = optical rotation of pure enantiomer, taken as 15.0° for PO [7]

x = conversion

r = stereoelectivity ratio (see below)

The eq. 2-4 is valid for low conversion x or low optical rotation of recovered monomer. The derivation of eq. 2-4 is based on a model involving reversible adsorption of monomer at the active site followed by ring opening propagation (eq. 2-5). It assumes that the rate of propagation is proportional to the concentration of adsorbed monomer which is small compared with the total monomer concentration (because the concentration of active sites and the equilbrium constants are both small).

$$R \xrightleftharpoons{K_R} R_{ad} \xrightarrow{k_R} \text{polymer}$$

$$S \xrightleftharpoons{K_S} S_{ad} \xrightarrow{k_S} \text{polymer}$$

------- (2-5)

R, S represent free R-, S-monomer

R_{ad}, S_{ad} represent adsorbed R-, S-monomer

K_R, K_S are equilibrium constants of adsorption

k_R, k_S are rate constants for ring opening

The stereoelective ratio r_R in eq. 4 is defined as

$$r_R = \frac{k_R K_R}{k_S K_S} \tag{2-6}$$

Furukawa *et al.* studied the polymerization of PO by an initiator prepared by partial hydrolysis of the $FeCl_3$ -PO complex in the presence of (+)-bornyl ethyl ether(BEE).[20] The recovered monomer was found to be (+)-PO, and a plot of $[\alpha]_D$ vs -ln(1-x) gave a reasonable straight line going through the origin in accordance with eq. 2-4. From the slope of the line, r_R values were obtained which varied from 1.004 to 1.71 depending on the molar ratios of the initiator components. The results of an adsorption experiment of PO on the initiator ($FeCl_3$ -PO)-H_2O-(+)-BEE quantitatively correlated with the preferred consumption of PO enantiomer during the stereoelective polymerization and led to the conclusion that $k_R = k_S$, so that $r_R = \frac{K_R}{K_S}$ and the adsorption step is decisive in controlling the propagation enantioselectivity.[20]

Initiator systems prepared from diethylzinc ($ZnEt_2$) and a variety of L-α amino acids have been studied in the polymerization of racemic PO.[14] It was found that (-)-PO polymerized preferentially regardless of the sign of rotation of amino acid. Equation (2-4) was applied to these polymerization systems and r (r_R or r_S) values varying from 1.02 to 1.20 could be calculated from the data. The most stereoelective initiator in this study was prepared from L-(-)-β-phenylalanine.

The highest stereoelectivity observed in the polymerization of PO was with an initiator prepared by the reaction of (R)-(-)-3,3-dimethyl-1,2-butanediol (DMBD) with $ZnEt_2$.[15] It was found that

R-(+)-PO is preferentially incorporated into the polymer chain with a stereoelectivity ratio $r_R = 1.8$. Unlike the amino acids-$ZnEt_2$ initiator systems for which the first order monomer consumption stereoelective law (eq. 2-4) is valid at low conversion (x) or low optical purity ($\alpha/\alpha_0 \ll 1$), the first order kinetic law had been verified to high conversions and high optical purity for the DMBD-$ZnEt_2$ initiator system. For this system, the eq. (2-4) takes the form [16]

$$(1-x)^{r-1} = \frac{1+\alpha/\alpha_0}{(1-\alpha/\alpha_0)^r} \quad \text{-------------------------(2-7)}$$

This eq. (2-7) was also satisfied by propylene sulfide with the same initiator system preferentially consuming the R-enantiomer. The stereoelectivity r_R (because R enantiomer selected preferentially) was 2.4 which is higher than found for propylene oxide with this initiator. It should be noted that with propylene sulfide, the preferentially elected monomer had the same absolute configuration as the chiral initiator. There was no such correlation found for the stereoelective polymerization of PO (ie. the absolute configuration of the selected enantiomer and the absolute configuration of the chiral catalytic moiety). The higher stereoelectivity and the election of monomer with the same absolute configuration as that of the initiator was probably due to the increased steric control in the sulfur atom compared to the smaller oxygen atom.

A second order monomer consumption equation (2-8) was established for the stereoelective polymerization of *tert.* butyl thiirane with $ZnEt_2$ -DMBD (1:1 molar) initiator system[43]:

$$\frac{1}{(1-x)(1+\alpha/\alpha_0)} = \frac{P_R}{(1-x)(1-\alpha/\alpha_0)} + (1-P_R) \quad \text{--------(2-8)}$$

Where P_R = Stereoelective ratio for the second order monomer consumption; x, α and α_0 has the same definition as in the first order monomer consumption.

The experimental data found for racemic $-CH_3$, $-C_2H_5$, CH_3CH_2O- thiiranes and $-CH_3$, CH_3CH_2O- oxiranes, using the $ZnEt_2$ -DMBD (1:1 molar) initiator were found to fit the first order stereoelective equation with respective stereoelectivity values (r_R) equal to 2.4, 2.4, 1.6, 1.8 and 2.0.[6] The isopropyl and *tert.* butyl thiiranes were found to fit the second order stereoelective equation with stereoelectivity values (r_R) both equal to 8 at 20°C.[43,44] The stereoelective behavior of tert.butyl oxirane with this initiator system was not successfully determined due to lower optical rotation of the unreacted monomer and sluggish polymerization rates.[7] It is interesting to compare the stereoelective behavior of various racemic monomers with different initiators. Since thiiranes showed higher stereoelectivity with the initiator prepared by the reaction of $ZnEt_2$ and DMBD in a 1:1 molar ratio at room temperature, the comparisons will be made with specific interest on thiiranes in the following sections.

2.2-1 Effect of Initiator on Stereoelectivity

It has been found that the polymerizations of Me, Et, iPr and tBu thiiranes and oxiranes with $ZnEt_2$-DMBD (1:1 molar) initiator system lead to the preferential election of R-enantiomer which is the same absolute configuration of DMBD.[6] The initiator prepared with $ZnEt_2$-α-amino acids also preferentially elected the enantiomer having the same absolute configuration as that of the amino acid.[14] The polymerization of methyl thiirane with $ZnEt_2$ and chiral alcohols containing more than one chiral center also resulted in the preferential election of enantiomer having the same absolute configuration as that of the chiral alcohol center.[45] However, no such correlation has been found for the polymerization of methyl oxirane with these chiral alcohols containing more than one chiral center.[3] The chemical composition of the initiator also played a decisive role in the enantiomeric choice. In the case of methyl thiirane, when the initiator was prepared such that monoalkoxy species predominated over dialkoxy species, the initiator system preferentially elected the enantiomer the configuration of which is opposite to to that of its chiral ligand.[45] Thus the ratio

I_s= R-M-OR*/ RO-M-OR*

Where M= metal (Zn, Cd); -OR* = chiral alkoxy ligand had to be considered and the following rule was found:

$I_s \leq 2$ homosteric choice (same absolute configuration)

$I_s > 3$ antisteric choice (opposite configuration)

For example, when $ZnEt_2$ was reacted at room temperature with DMBD in a 1:1 molar ratio, this system preferentially elected the dextrorotatory methylthiirane (homosteric choice; I_s= 0.44). When the same reagents were reacted in 1:0.5 molar ratio, the choice was opposite (antisteric; I_s=4).[45] No mechanistic expanations are offered for these changes.

The nature of the hydroxy ligand associated with the organometallic compound also influences the stereoelective efficiency of the initiator. The optical purity of recovered monomer at half reaction, $(\alpha/\alpha_o)_{x/2}$ can be used as a criterion of stereoelective efficiency. Thus, when racemic methyl thiirane was polymerized using different initiators prepared from the reaction of $ZnEt_2$ with chiral alcohols and glycols under homosteric conditions (I_s<1), the following order of efficiency was found:

Ligand : t-Bu-CHOH-CH_2OH > t-Bu-CHOH-CH_3 > t-Bu-CHOH-CH_2OCH_3
$(\alpha/\alpha_o)_{x/2}$: 30% 12% 2.5%

Within the 1,2-diol series, the following order of efficiency was found:

1,2-diol substituent: t-Bu = iPr > Ph > Me
$(\alpha/\alpha_o)_{x/2}$: 30% 28% 20% 8%

2.2-2 Effect of the Nature of the Monomer on Stereoelectivity

Oxiranes and thiiranes can be polymerized by the same type of initiator, $ZnEt_2$-DMBD (1:1molar) and comparison of their behavior using the optical yields at half reaction, $(\alpha/\alpha_o)_{x/2}$ can be easily made. The following results were observed for several thiiranes and oxiranes[6]:

Thiiranes	Substituent:	t-Bu= iPr >	Et = Me >	CH_3CH_2O
	$(\alpha/\alpha_o)_{x/2}$:	46%	30%	16%
Oxiranes	Substituent :	CH_3CH_2O >	CH_3	
	$(\alpha/\alpha_o)_{x/2}$:	25%	20%	

It appears that in general the stereoelectivity is higher for thiiranes than for oxiranes. In addition, the kinetic behavior of monomer consumption in the stereoelective polymerization was also dependant on the nature of the monomer, the details of which are described above.

The degree of stereoselectivity determined by measuring the stereoregularity of the polymer was also dependant on the nature of the monomer. For example, the polymerizations at room temperature with the $ZnEt_2$-DMBD (1:1 molar) initiator, the percentage of crystalline isotactic fraction was 20% for methyl oxirane[15], 35% for methyl thiirane[6] and almost 100% for t-butyl thiirane.[17]

2.2-3 Effect of the Enantiomeric Composition of the Initial Monomer on the Stereoelectivity

One of the most interesting features observed with methyl thiirane has been the strong effect of the enantiomeric purity of the starting monomer on stereoelectivity. A large increase in stereoelectivity value (r_R) was observed when the R content of the initial monomer increased, and it was possible to prepare a pure enantiomer by selective consumption of its antipode in a "cascade" process in which the residual monomer was used for a new stereoelective polymerization with fresh initiator.[6] As an example methyl thiirane with 98% optical purity was obtained in three steps with an overall yield of 11.5% from the racemic compound. A monomer of the same optical purity could be obtained in a simple experiment only at conversions higher than 98% with less than 2% yield. The first order law was also verified for the polymerizations of enriched monomer samples. The same type of behavior was observed with ethyl and methoxymethyl thiiranes. But a result that is very difficult to explain is that when initial monomer was enriched in S enantiomer, the r_R values also increased. For methyl oxirane on the other hand, a variation of r_R with the optical purity of the monomer was also observed, but led to a decrease of r_R from 1.8 to 1.3. These last two results illustrate the complexity of the nature of chiral centers responsible for stereoelection with those chiral initiators. For the stereoelective polymerization of t-butyl thiirane with the standard initiator ($ZnEt_2$/DMBD), there exists a limiting value for the optical activity of the unreacted monomer[46] as shown in eq. (2-9) derived from the 2nd order kinetic rate law:

$$\frac{\alpha_{limit}}{\alpha_o} = \frac{P_R - 1}{P_R + 1} \qquad (2\text{-}9)$$

The limiting value, $(\alpha/\alpha_o)lim = 0.78$ $\{[\alpha]_D^{25}$ limit = -32.7° (neat, dm) $\}$ was calculated using a stereoelectivity value of 8.[43] When starting with a monomer having an optical purity close to this limit value, i.e., by using a monomer of $\alpha_D^{25} = -30°$ (neat, dm), optical purity =0.71, the kinetic follows the same second order law. The limiting value is reached in 50% conversion and the stereoelectivity remained the same. The polymerization was also carried out with an initial monomer optical activity $[\alpha]_D^{25} = -34°$ (neat, dm), optical purity =0.81, slightly higher than the limit value (-32.7°). To satisfy the second order monomer consumption and the limiting value, the optical rotation of the unreacted monomer should have been decreased. However, the unreacted monomer showed increased optical rotation with conversion.[46] The kinetics could roughly fit the second order law with a stereoelectivity ratio 21 , which is much higher than the value 8 previously observed.[43]

2.2-4 Effect of Polymerization Temperature on the Stereoelectivity

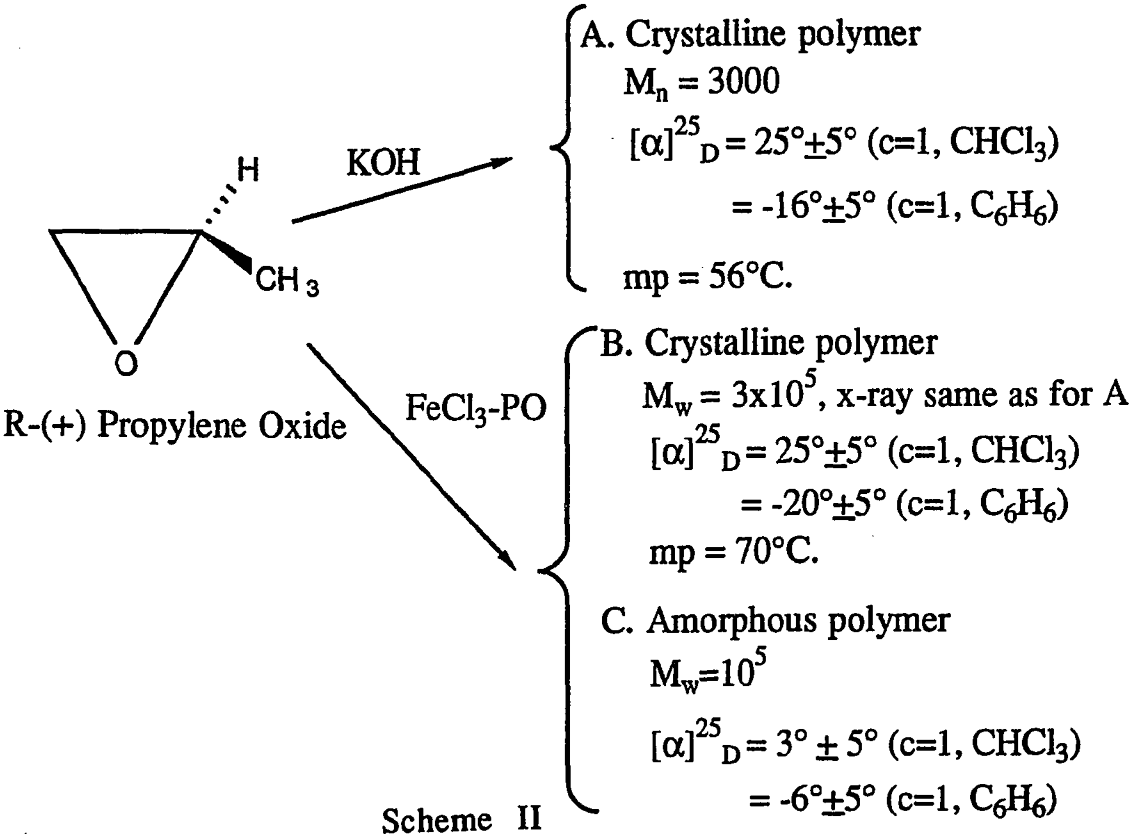
In the case of methyl oxirane and methyl thiirane, the stereoelectivity was not affected by changing the temperature, while the stereoselectivity of the process increased by lowering the temperature of polymerization as demonstrated by methyl oxirane.[15] The temperature showed a strong effect in the polymerization of t-butyl thiirane.[47] The stereoelectivity P_R doubled in value when the temperature was lowered from 20 to -3°C and on the contrary P_R decreased with increasing temperatures and at temperatures higher than 115°C the choice of the enantiomer was reversed.

2.2-5 Effect of Solvents and Additives on the Stereoelectivity

It was shown in the polymerization of methyl thiirane that the addition of tetrahydrofuran decreased the stereoelectivity, a competition occuring between the monomer and the solvent for the coordination on the metallic atom.[48] No such decrease was observed in the non-polar solvents such as toluene or heptane. Sepulchre[49] has shown the possibility to increase substantially the stereoelectivity by modifying the initiator with chiral agents such as optically active thioethers and amines or by using chiral solvents such as limonene.

2.3 Mechanism of Ring Opening Polymerization of Epoxides

The first work on the stereochemistry and mechanism of epoxide polymerization was reported by Price and Osgan[50], who polymerized a pure R(+)-propylene oxide [Scheme II].

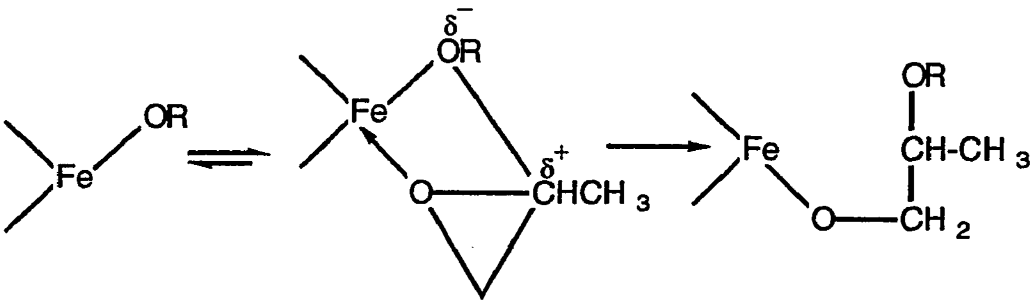


Scheme II

With an ordinary base catalyst, KOH, the R-monomer gave a low molecular weight, optically active crystalline polymer, as compared with the liquid, low molecular weight polymer obtained under comparable conditions with racemic monomer. This crystalline polymer from R-monomer was a stereoregular, isotactic polymer, and the liquid PPO from racemic monomer was evidently a stereorandom polymer. Since Gee *et al.*[51,52] had shown that nucleophilic attack on epoxides occurs preponderantly (>97%) at primary rather than secondary carbon, the asymmetric carbon in the optically active crystalline polymer was presumed to have the same configuration as in the optically active monomer.

With the $FeCl_3$-PO catalyst and R-propylene oxide, Price obtained two different high molecular weight PPO, one an optically active crystalline polymer and the other a largely racemized amorphous polymer [Scheme II]. The optically active crystalline polymer made with the iron catalyst was identical, except for molecular weight, to the optically active crystalline polymer made with the KOH catalyst in both its x-ray pattern and its sign and magnitude of optical rotation. These observations showed that the asymmetric carbon in the crystalline polymer made with the iron catalyst had the same configuration as in the monomer from which it was derived, i.e, the propylene oxide polymerized with retention of configuration of its asymmetric carbon atom.

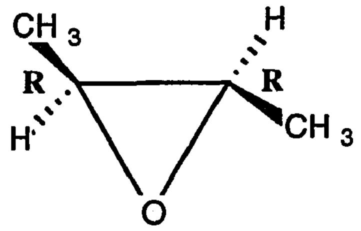
As a result of these findings, Price *et al.*[50] proposed a mechanism for the action of the iron catalyst [Scheme III].



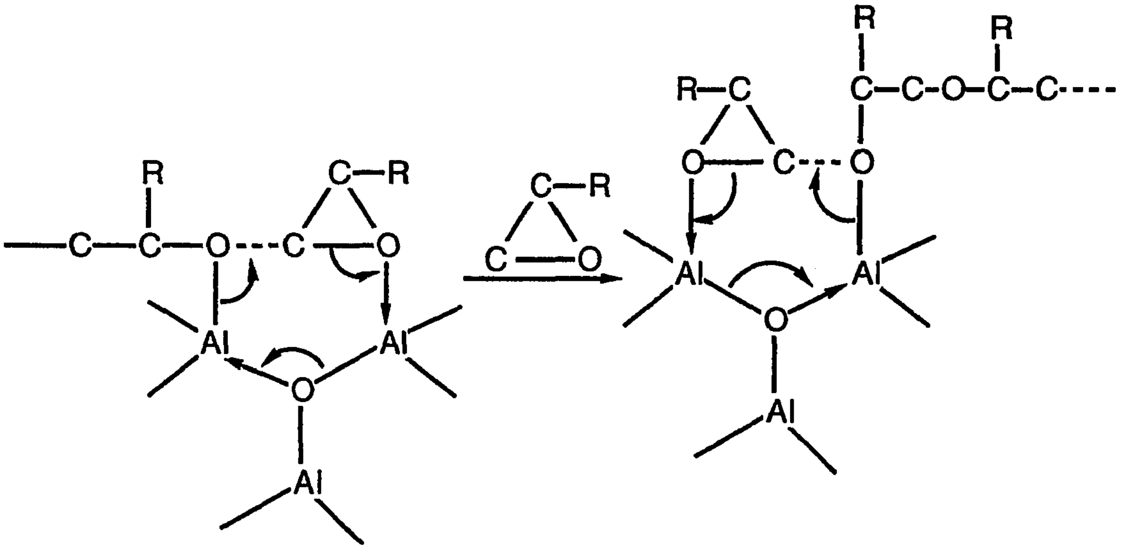
Scheme III

This mechanism had several important features: first, coordination of the epoxide and growth of the polymer on one metal atom; second, ring opening at the secondary carbon atom by a front side attack and retention of configuration; third, a possible racemization of the asymmetric carbon atom during ring opening due to free carbonium ion formation under some conditions to explain the amorphous optically inactive fraction. Later work by Vandenburg[53] showed that most of these features are incorrect.

Ring opening at a primary carbon of a monosubstituted epoxide is not going to reveal information regarding the inversion of configuration. Vandenburg[53] used symmetrically disubstituted epoxides to study the mechanism of ring opening polymerization. The resulting poly(epoxides) were treated with amylsodium or butyllithium to prepare monomer, dimer, and trimer diols. The stereochemistry of these diols clearly showed inversion of configuration during the ring opening polymerization of epoxides. He polymerized optically active trans epoxide with i-Bu_3Al-0.5H_2O catalyst at -78°C.

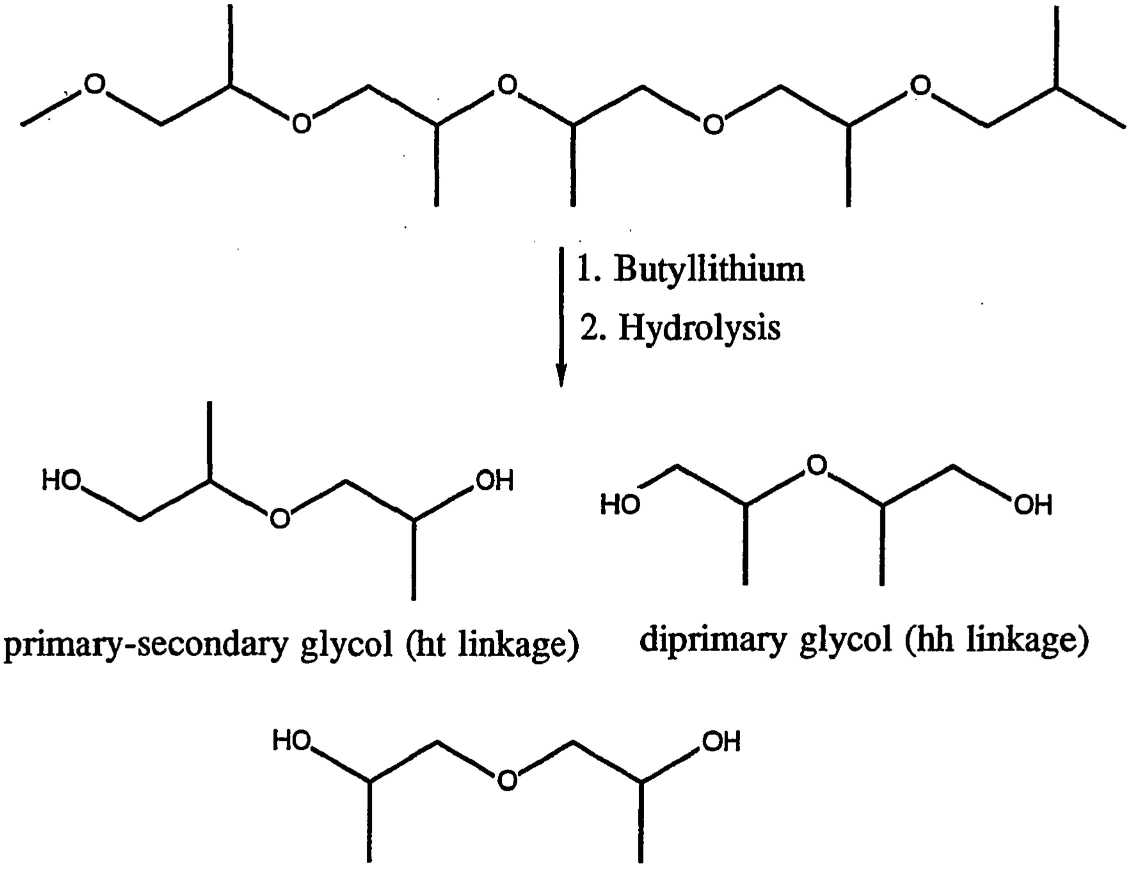


The resulting polymer showed no optical activity even though the monomer had a high optical rotation.[53] This result elegantly showed the inversion of configuration during the ring opening polymerization of epoxides. From these studies, Vandenburg concluded that the coordination polymerization of epoxides cannot propagate through a four membered ring intermediate containing a single metal atom, since such an intermediate cannot accommodate the essentially linear, three-centered transition state necessary for inversion at carbon. If propagation involves making and breaking metal-oxygen bonds, as commonly postulated for coordination, the catalytic species must contain at least two or probably more than two metal atoms. To accommodate the inversion of configuration and making and breaking bonds during coordination polymerization, Vandenburg formulated a mechanism as shown in Scheme IV.



Scheme IV

In this mechanism, the ring opening occurs by a rearward attack on the primary carbon and explains the retention of configuration at the asymmetric center. The coordination bonds in the catalyst structure are needed to move the growing polymer chain from one metal to an adjacent one without altering the valence of the metal. Although two four-coordinate aluminum atoms are shown in this mechanism, more than two aluminum atoms and/ or five or six coordinate aluminum may be required to fit all the experimental facts. Thus, more than two aluminum atoms may be needed to facilitate sterically a rearward attack on the epoxide. The fifth and sixth coordinate positions of aluminum may be needed, at least under some conditions, since effective catalysts are obtained when all of the fourth coordinate positions are occupied by a chelating agent such as acetylacetone.[53] The mechanism shown for aluminum, can also apply for other metal catalyst and other monomer systems such as episulfides. The requirement of more than two metal atoms in the catalyst for coordination polymerization of epoxides resulted in the preparation of μ-alkoxides (Metal---oxygen---metal linkage/μ-bridge) for the stereoregular polymerization of propylene oxide and other epoxides by Teyssie *et al*.[54] The formation of optically inactive PPO formed in the polymerization of R-propylene oxide with the iron catalyst was explained by the ring opening at both primary and secondary carbon atoms by the non-specific catalyst sites.[53] Vandenburg[53] also studied the cleavage of the amorphous poly(propylene oxide) formed by the coordination and cationic initiators using amylsodium and butyllithium. The amylsodium was used to prepare monomer diols and the butyllithium was used to prepare the dimer and trimer diols. His studies showed the presence of head-to-head (hh) and tail-to-tail (tt) linkages in addition to the regular head-to-tail linkages (ht) as shown by the presence of diprimary, disecondary and primary-secondary glycols in the prepared dimer glycols as shown in Scheme V[53]:



primary-secondary glycol (ht linkage)   diprimary glycol (hh linkage)

disecondary glycol (tt linkage)

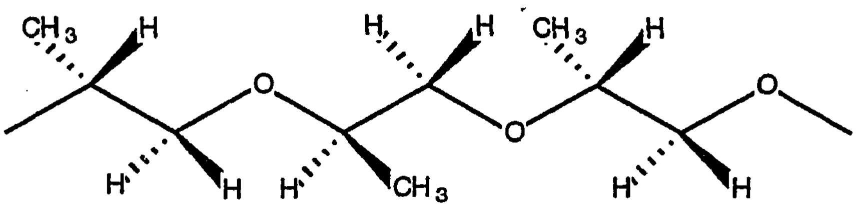
Scheme V

Similar cleavage studies have been used recently, to show that aluminum 5,10, 15, 20-tetraphenylphorphine (TPP)AlX (X=SPr or OCH_3) or zinc 5,10, 15,20-tetraphenyl-21-methylphorphine (NMTPP)ZnX (X=SPr or OCH_3) initiators also result in the inversion of configuration of the 2, 3-epoxybutanes in the ring opening polymerization.[55]

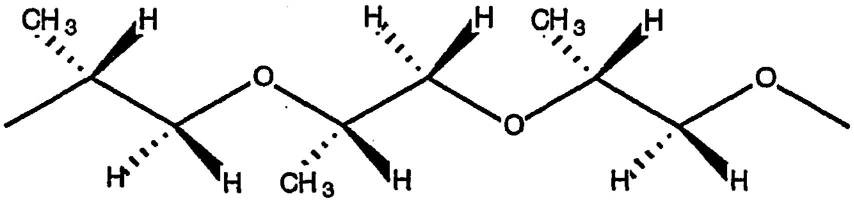
The presence of irregular hh and tt linkages in the amorphous PPO and stereoregularity in the PPO prepared by various initiators are now conveniently analysed by ^{13}C-NMR spectroscopy.

2.4 Microstructure Analysis of Poly(propylene oxide) by ^{13}C-NMR Spectroscopy.

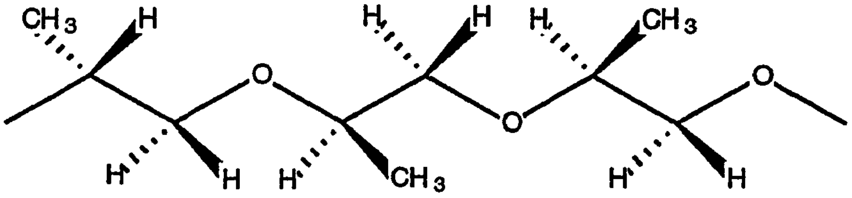
Assuming polymerization involves cleavage of only one of the C-O bonds in PO, it is possible to obtain four distinct stereochemical triads containing regular head to tail linkages (h-t) in the polymer. These h-t triads are presented in planar zigzag projection in Figure 1 a.[56]



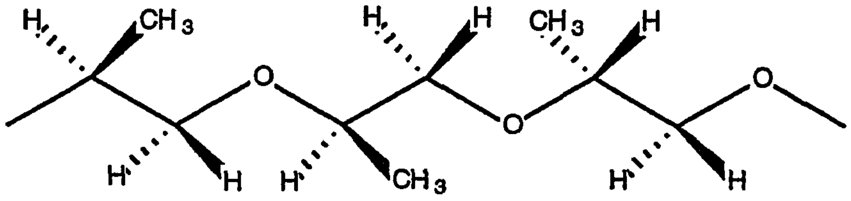
Isotactic, RRR or SSS



Syndiotactic, RSR or SRS



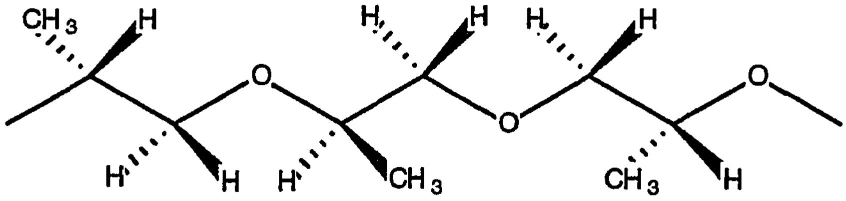
Heterotactic-1, RRS or SSR



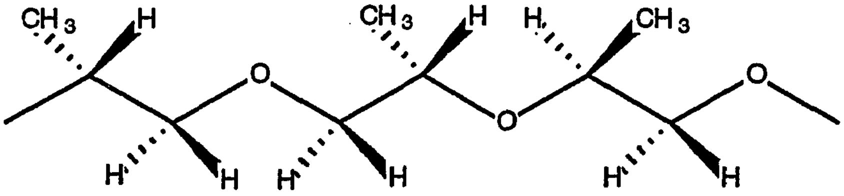
Heterotactic-2, SRR or RSS

Figure 1a. Stereoisomers of poly(propylene oxide) arising from regular head to tail linkages.

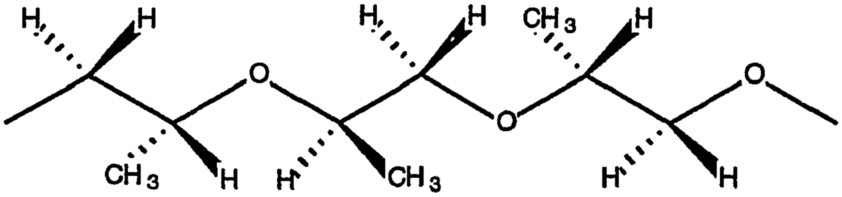
If both C-O bonds in PPO are subject to cleavage[56], then an additional three triads are possible for PPO. These are illustrated in Figure 1 b for all- R isomers, where H-T, H-H, and T-H refer to the direction of neighboring monomers and H is the methine end and T is the methylene end of the monomer unit.



(T-H : T-T) (T= CH_2 ; H= CH-CH_3)



(T-T : H-H)



(H-H : T-H)

Figure 1b. Isomers of poly(propylene oxide) arising from irregular head to head and tail to tail linkages.

The individual triads shown in Figure 1b, can give rise to four triads as shown in Figure 1a. Therefore, a total of sixteen triads are possible for the PPO containing h-t, h-h, and t-t linkages in the polymer main chain. The methine and methyl carbons are expected to be sensitive to triad sequences, and the methylene carbon is expected to be sensitive to diad sequences (meso and racemic).

The ^{13}C-NMR spectrum of PPO was first investigated by Shaffer.[57] Single carbon signals were found for methine, methylene and methyl carbons in the isotactic PPO. Tani *et al.*[58] also investigated the ^{13}C-NMR spectrum of PPO using isotactic polymer. The use of proton coupled spectrum allowed the assignment of the individual methine, methylene and methyl carbon resonances. The atactic PPO containing regular head-to-tail linkages (shown by cleavage to dimer glycols)[53] showed three peaks for methine carbon; two peaks for methylene carbon; and one peak for methyl carbon. The methine carbon in the regular head-to-tail linkage was deshielded compared to the methylene carbon. The three signals for the methine carbon were assigned to the isotactic, heterotactic and syndiotactic triads respectively with decreasing chemical shift. The two signals for the methylene carbon were assigned to meso and racemic diads. The racemic diad appears at a lower field than the meso diad. These assignments were made by comparing isotactic, crude and amorphous polymer fractions containing regular head to tail linkages. The polymer containing irregular head to head and tail to tail linkages showed a number of peaks for the methine and methylene carbons and no specific assignments were made. It should be noted that only one signal was observed for the two distinct heterotactic triads of the methine carbon. The methyl carbon also showed only one signal despite the possible four triads in the PPO containing regular h-t linkages. The ^{13}C-NMR peak assignments allowed the speculation of polymerization mechanism in propylene oxide. Thus, Jedlinsky *et al.* [58] reported the presence of h-h and t-t linkages in the PPO prepared with aluminum isopropoxide initiator and almost exclusive formation of regular h-t linkages with the same initiator when $ZnCl_2$ was used as a coinitiator in a 1:1 molar ratio. Therefore, ^{13}C-NMR spectroscopy can be used to study the ring opening mode in PO with our potential initiator systems. In addition, the end groups derived from the initiator can also be identified by ^{13}C-NMR spectroscopy to elucidate the mechanism of polymerization of PO with our initiator system.

2.5 End Group Analysis

Identification of end groups in the polymer chain helps to elucidate the polymerization mechanism. In the polymerization of ethylene oxide with aluminum isopropoxide (AIP)/$ZnCl_2$ initiator system (Al:Zn = 1:1 molar ratio), it was found that the polymer contains chlorine and hydroxy terminals in a 1:2 molar ratio.[30b] The IR spectrum showed absorbance at 1383 and 1368 cm^{-1} characteristic of the isopropoxy group.[30b,76b] The mechanism of polymerization of chlorophenylglycidyl ethers by AIP and $ZnCl_2$ was investigated by chlorine analysis and radioactivity measurements for the ^{14}C-labelled isopropoxy group. It was reported that the isotactic polymer fraction contained only isopropoxy moiety and proposed a mechanism of polymerization involving a complex formation between AIP and $ZnCl_2$.[60] The isotactic polymer was reported to propagate on the aluminum.[55] An initiator prepared by the reaction of α, β, γ, δ-tetraphenylphorphine with diethylaluminum chloride contained CH_3CHCl- group as the main end group in the polymerization of propylene oxide.[31] Consequently, the mechanism of polymerization involves the insertion of the epoxide into the Cl-Al bond of the initiator to give an aluminum alkoxide as the propagating active species.[31]

2.6 Aluminum Alkoxides

2.6-1 Preparation of Aluminum Alkoxide by Alcohol Interchange Reaction

An aluminum alkoxide has to be prepared as initiator for the polymerization of propylene oxide. Alcohol interchange was used to prepare high aluminum alkoxides by interchanging the appropriate alcohol with aluminum isopropoxide.[62] The resulting isopropyl alcohol was azeotropically distilled using benzene as solvent. Thus the preparation of aluminum t-butoxide and aluminum t-amyloxide showed that whereas the latter compound was obtained in more or less one charge, more than one charge of t-butyl alcohol was required in the case of aluminum t-butoxide and the interchange had to be continued over a longer period of time. The +I inductive effect of the t-amyl group is slightly higher than that of t-butyl group. However the steric factor should remain the same. Moreover the binary azeotropes of 2-propanol and t-butyl alcohol with benzene boil at a close range of temperature, with a little thermodynamic forward push for interchange in question; t-amyl alcohol solution boils at a higher temperature, effecting the interchange, seemingly at a faster rate. The disadvantage of this method is the use of larger amounts of appropriate alcohol and rigorous purifications in the case of incomplete reaction. Aluminum analysis and determination of isopropoxy group content reveal complete substitution of isopropoxy groups.[62]

2.6-2 Preparation of Aluminum Alkoxides by the Reaction of Aluminum hydride with Alcohols

The chemistry of compounds containing Al-H bonds is of considerable interest due to the utility of these hydrides as reducing agents. While aluminum hydride itself acts as a reducing agent, its alkoxy- or (aryloxy) aluminum hydride derivatives are used as selective reducing agents. For these purposes, aluminum hydride and alcohols were reacted in 1:1 or 1:2 molar ratio respectively to prepare the selective reducing agents.[63] The reaction of AlH_3 in THF with methanol, ethanol, 2-propanol, 1-butanol, and t-butyl alcohol in a 1:1 molar ratio resulted in the formation of the desired product $AlH_2(OR)$.[63] However, on standing these hydride solutions undergo disproportionation to give $AlH(OR)_2$ as shown in eq. (2-10).

$$2\ ROAlH_2 \text{--------}> (RO)_2AlH + AlH_3 \qquad (2\text{-}10)$$

The reaction of AlH_3 with the above alcohols in a 1:2 molar ratio was also studied and formation of $(RO)_3Al$ occured due to disproportionation as shown in eq.(2-11).

$$2\ (RO)_2AlH \text{------}> (RO)_3Al + ROAlH_2 \qquad (2\text{-}11)$$

These reactions of AlH_3 and alcohols in a 1:1 and 1:2 molar ratio suggest that the reaction of AlH_3 with alcohols in a 1:3 molar ratio can be used to prepare an aluminum alkoxide initiator for the polymerization of propylene oxide. In this preparation, hydrogen evolved is easily removed from the reaction medium and the aluminum alkoxide formed may stay in solution or precipitate facilitating the isolation of the product.

Ether or THF solutions of AlH_3 are prepared by the reaction of $LiAlH_4$ and anhydrous $ZnCl_2$.[64] The reaction product, ZnH_2, precipitates in this preparation and has to be destroyed before cleaning the glassware. However, the AlH_3 can also be prepared by the reaction of $LiAlH_4$ and 100% H_2SO_4 in ether or THF.[64] In this preparation, the reaction product Li_2SO_4 is unreactive and precipitates from the reaction medium making it a convenient way of preparing AlH_3. Solutions of AlH_3 in THF have been observed to slowly lose hydride with the formation of 1-butanol.[65] Consequently, the preparation of AlH_3 in diethyl ether is preferred over its preparation in THF. The solutions of AlH_3 are standardized by the method of Felkin[66] and further characterized by its infrared spectrum.[64,67] The infrared spectra of $LiAlH_4$, AlH_3 and alkoxy aluminum hydrides exhibit distinct Al-H stretching vibration (see Table 1) and can be used to characterize any alkoxyaluminum hydride species which may form in the reaction of AlH_3 and alcohols.

Table 1: Al-H Stretching Vibrations (υ_{Al-H}) in the Infrared Spectra of Hydride Solutions.[67]

Hydride Species	Solvent	Conc.[a]	υ_{Al-H} , cm^{-1}
$LiAlH_4$	Et_2O	0.10-0.31	1736-1739
		1.6	1740
		4.4	1725
	THF	4.0	1655
AlH_3	Et_2O	0.4	1783
AlH_2OR[b]	Et_2O	0.2	1845
$AlH(OR)_2$[b]	Et_2O	0.07-0.08	1883

[a] Concentrations refer to the molarity of "hydride," e.g., 0.1M $LiAlH_4$ would be 0.4M in "hydride".

[b] R= 2,4-dimethyl-3-pentyl.

The infrared spectra of solutions of various AlH_3 -Lewis base complexes have been reported to show a shift of the Al-H absorption in monotrimethylamine-AlH_3 complex to a lower frequency when a second molecule of trimethylamine is added.[68a] Dautel and Zeil[68b] prepared several mono-and bis-Lewis base-AlH_3 complexes, including several mixed bis-complexes with Lewis bases such as THF, dioxane, and trimethylamine. A shift in the Al-H absorption of a mono-adduct on dissolving it in a second Lewis base was observed. The Al-H absorptions were correlated with the coordination number of aluminum in the complexes, the higher frequency being considered as characteristic of tetracovalent aluminum, while the lower frequency was associated with the pentacovalent state.[68a,b] The infrared data for AlH_3 -Lewis base complexes are summarized in Table 2.

Table 2: Infrared Data for AlH_3 -Lewis Base Complexes.[68a,b]

Lewis base	AlH_3 :base ratio	Solvent	Al-H absorption, cm^{-1}
Et_2O	-	Et_2O	1801
Et_2O	1:4	Benzene	1804, shoulder at 1800
THF	-	THF	1724
THF	1:1	Benzene	1786
THF-Et_2O	1:1:1	Benzene	1710, shoulder at 1695
Trimethylamine	1:2	Et_2O	1695, shoulder at 1739
Trimethylamine	1:2	THF	1695
Trimethylamine	1:2	Benzene	1690
Trimethylamine	1:1	Et_2O	1770(strong), 1724(weak)
Trimethylamine	1:1	THF	1710,1695, shoulder at 1770
Trimethylamine	1:1	Benzene	1786

3.0 MATERIALS AND METHODS

Propylene oxide (Aldrich, 99%) was refluxed over KOH, distilled, and then fractionally distilled through a Nester Faust spinning band distillation column. The fraction b.p. 34.5°C was collected. Prior to use in polymerization studies, the propylene oxide was refluxed over calcium hydride and distilled. Diethyl ether (anhydrous, Fisher ACS certified) was refluxed over calcium hydride and distilled under dry nitrogen. The ether was then refluxed over lithium aluminum hydride and distilled under nitrogen. Zinc chloride (Fisher, 98%) was dried by refluxing with thionyl chloride (eq. 3-1)[69] which was distilled over quinoline to remove the yellow colored impurity. Excess thionyl chloride was removed at room temperature

$$ZnCl_2.xH_2O \ + \ xSOCl_2 \text{ -------->} \ ZnCl_2 \ + \ xSO_2 \ + \ 2xHCl \quad \text{----(3-1)}$$

under vacuum and residual traces removed at 90°C (2 torr). Pinacolone (Aldrich, 95%) was fractionally distilled. Bromine (Fischer, liquid), sucrose (Aldrich), Baker's yeast (ICN chemical Co.), formaldehyde (Fischer, 40% w/w), formic acid (Fisher, 85% w/w) and benzene (Fischer, ACS-reagent grade) were used as received. Acetone (Fischer, reagent grade) was dried over activated molecular sieves (3Å).

Lithium aluminum hydride (Alfa-Ventron, 95%) was dissolved in ether and filtered under nitrogen. Aluminum hydride in ether was prepared by the slow addition of 100% sulfuric acid to a stirred solution of standard lithium aluminum hydride at 0°C[64] (eq. 3-2).

$$2LiAlH_4 + H_2SO_4 \text{ -------> } Li_2SO_4 + 2AlH_3 + 2H_2 \text{ -----(3-2)}$$

Sulfuric acid (100%) was prepared by the slow addition of fuming sulfuric acid (30% SO_3) to 96% sulfuric acid with stirring at 10.3-10.4°C until the contents froze.[70] The aluminum alkoxide initiator for the polymerization was prepared by the reaction of alcohol with aluminum hydride. The progress of the hydride reaction with alcohol and the preparation of aluminum hydride according to eq. (3-2) were followed by measuring the hydrogen evolution by a "Precision" wet test meter manufactured by Precision Scientific Co., Chicago. Standardization of $LiAlH_4$ and AlH_3 solutions were carried out by iodine titration,[66] (eq. 3-3, 3-4 & 3-5) titration of lithium as LiOH,[71] (eq. 3-6) as well as aluminum analyses by EDTA titration and

$$LiAlH_4 + 2I_2 \text{ (excess) --------> } LiI + AlI_3 + 2H_2 \text{ ---------(3-3)}$$

$$2AlH_3 + 3I_2\text{(excess) --------> } 2AlI_3 + 3H_2 \text{ ---------------(3-4)}$$

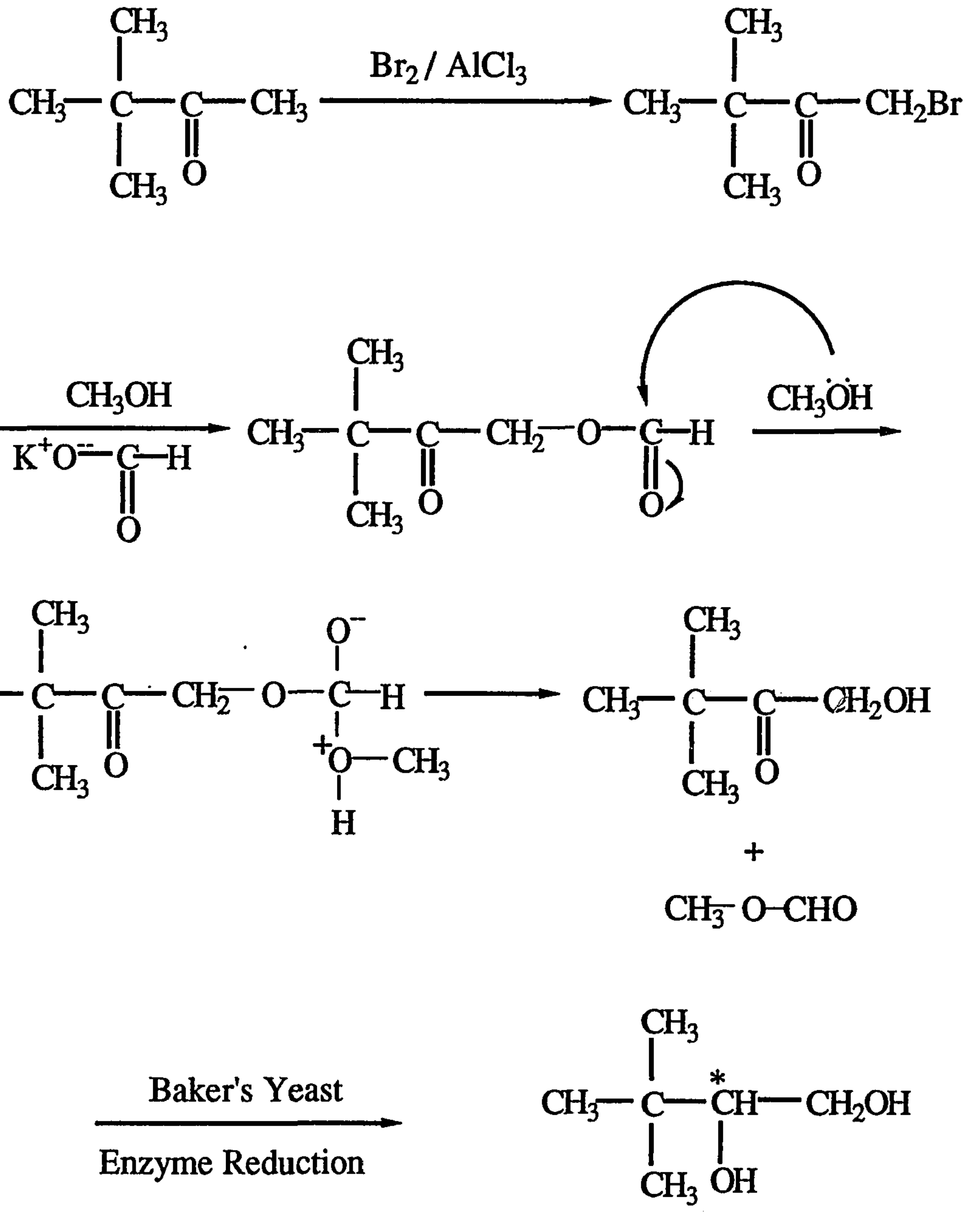
$$I_2\text{(excess)} + 2S_2O_3^{2-} \text{ -------> } S_4O_6^{2-} + 2I^- \text{ -----------------(3-5)}$$

$$LiAlH_4 + 4H_2O \xrightarrow{\text{ROH/water}} LiOH \text{ (base)} + Al(OH)_3 \text{ (neutral)} + 4H_2 \text{ (3-6)}$$

complexometric titrations with 8-hydroxyquinoline.[72] The glassware for the preparation of hydride solutions in ether and the reaction of hydride with alcohols were flame dried under vacuum.

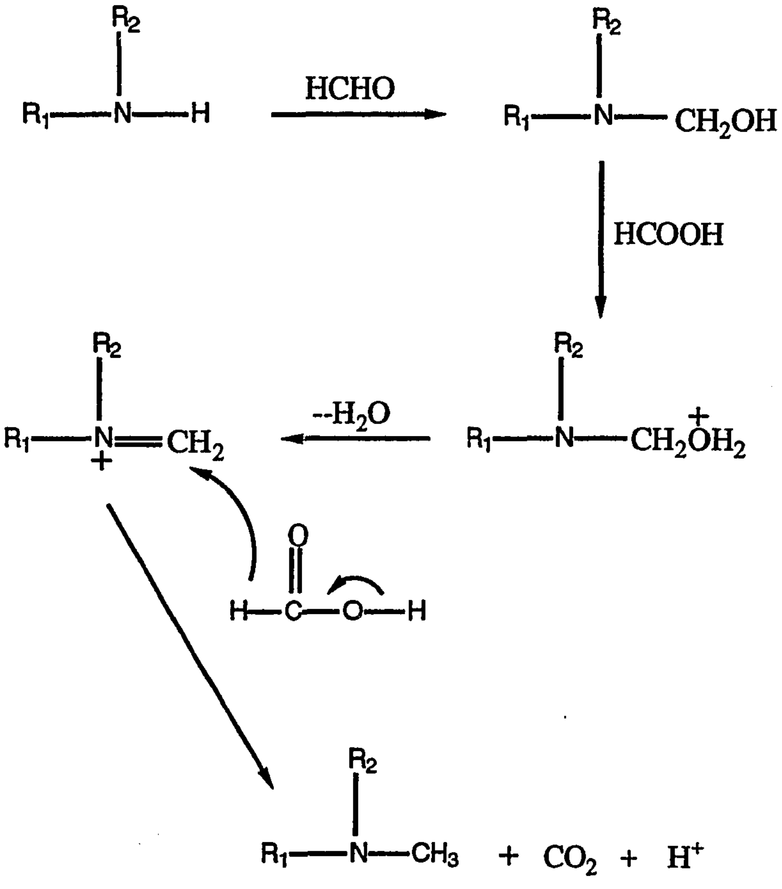
R(-)-3,3-dimethyl-1,2-butanediol (DMBD) was prepared according to reaction scheme VI.[73]

SCHEME V I



N-methyl ephedrine was prepared from l-ephedrine according to the Eschweiler-Clark method[74] as shown in scheme VII.

SCHEME VII



The progress of the methylation reaction was monitored by thin layer chromatography on a silica gel plate. The developing solvent system was the upper layer from the solvent mixture of butanol, acetic acid and water taken in 4:1:5 proportion respectively The staining agent was ninhydrin which shows a pink color with secondary amines and a purple color with tertiary amines.

Infrared spectra were recorded on a Beckman 4260 model spectrophotometer. Spectra of solutions were obtained in $CHCl_3$ or in CCl_4 at concentrations of 5-10% (w/w). Spectra of polymer samples were obtained as a thin films cast from benzene. Spectra of the reaction products of aluminum hydride and alcohols were obtained as a thin mull in nujol. The mulls were prepared in a dry box. NMR spectra were recorded on an IBM WP 200 FTNMR spectrometer operating at 50.3 MHz for carbon and 200.1 Mz for proton. Polymer samples for NMR analysis were used as 20% w/w in C_6D_6 or in C_6D_6-C_6H_6 mixtures. All chemical shifts (δ) reported were referenced to tetramethylsilane. Gas chromatographic (GC) analyses were carried out with a Hewlett-Packard 5880A instrument using a flame ionization detector. Optical rotation measurements were carried out with a Perkin-Elmer model 141 polarimeter. Number-average molecular weights of acetone soluble polymer fractions were determined using a Hewlett-Packard model 302B vapor pressure osmometer. Measurements were made in toluene at 53°C using benzil (MW=210.18) as a calibration standard.

4.0 Experimental

4.1 Synthesis of R(-)-3,3-dimethyl-1,2-butanediol (DMBD)

4.11 Synthesis of Bromopinacolone from pinacolone[73]

Bromine (1155 g, 7.2 mol) was added dropwise over 6 h. at 0°C to a stirred solution of pinacolone (725 g, 7.2 mol) in 1.5 L of anhydrous ether containing 9 g of anhydrous $AlCl_3$. The solution was stirred for another 4 h at room temperature. Then water (200 mL) was added to this solution to remove HBr and $AlCl_3$. An exothermic reaction occured during the addition of water. The organic layer was isolated and dried over anhydrous $MgSO_4$. The concentrated product was fractionally distilled. Yield 1012 g (78.5%); bp 50.0-50.5°C (0.8-0.9 mm) [lit. [73] bp 75°C (15 mm)]. The product was a colorless liquid and its purity was checked by infrared spectroscopy. A strong IR absorbance at 1360 cm^{-1} characteristic of pinacolone disappeared in the IR spectrum of bromopinacolone.

4.12 Synthesis of 3,3-dimethyl-1-hydroxy-2-butanone[73] (ketole)

Ethyl formate (855 g, 11.5 mol) was added to KOH (643 g, 11.5 mol) in anhydrous methanol (3L) and refluxed for 1 h. to generate potassium formate. Bromopinacolone (947 g, 5.3 mol) was slowly added into the stirred potassium formate solution. An exothermic reaction occured and KBr precipitated. The clear solution was transferred into another flask and the contents were refluxed for 11 h. Methanol was removed by rotoevaporation and diethyl ether was added to precipitate any remaining KBr. The concentrated product was fractionally distilled. Yield 432 g (70%); bp 34°C (1.5mm) [lit. [73] bp 64°C (25 mm)]. The product was a colorless liquid and its purity was checked by IR spectroscopy. Two characteristic bands at 1160 cm^{-1} and 690 cm^{-1} (C-Br stretching) for bromopinacolone disappeared in the IR spectrum of 3,3-dimethyl-1-hydroxy 2-butanone.

4.13 Synthesis of R(-)-3,3-dimethyl-1,2-butanediol (DMBD)[73]

Baker's yeast (250 g) was stirred in water (1L) in a 5L flask connected to a gas trap. Sucrose (250 g) in water (1L) at 30°C was slowly added to the yeast. Carbon dioxide evolution started immediately and the system was maintained at 35°C for 0.5 h. 3,3-Dimethyl-1-hydroxy-2-butanone (25 g, 0.216 mol) was then added to the reaction mixture. The contents were mixed well and maintained at 35°C for 3 days. The reduction was repeated 5 times. Yeast was removed from the combined reaction mixtures by centrifugation. Water was removed by rotoevaporation at a temperature below 50°C. The concentrated product was extracted with a mixture of ethanol and water taken in 3:1 proportion respectively. The extract was dried over anhydrous $MgSO_4$ and the solvents were removed by rotoevaporation. The resulting honey like product was fractionally distilled. Yield 30%; bp 93-95°C (10 mm); $[\alpha]_D^{25}$ =-26.2° (c=0.69, $CHCl_3$). The product was further purified by spinning band distillation, bp 87°C (9 mm); mp. 38-41°C; $[\alpha]_D^{25}$ =-26.6° (c=0.69, $CHCl_3$)[lit.[73] bp 95°C (12 mm); $[\alpha]_D^{25}$=-28.1° (c=0.69, $CHCl_3$)].

The optical purity of our DMBD product was 95% [(-26.6/-28.1)100=95] based on the observation that glycol obtained by enzymatic reduction of the corresponding ketol was enantiomerically pure. The GC analysis of DMBD showed trace amount of two impurities and they are shown to be not due to the precursor ketol as exemplified by the spiking experiment (Fig. 2 a & b). The GC analysis also showed greater than 99.6% purity in the sample. ^1H-NMR spectrum of DMBD in D_2O (Fig.3) also showed only a trace amount of impurity as shown by a small peak near the peak due to the tert. butyl group. ^{13}C-NMR ($CDCl_3$) (Fig. 4) : δ 33.6 (quaternary C); 25.9 (CH_3); 63.2 (CH_2); 79.8 (CH). These signal assignments were confirmed using a DEPT editing sequence[75] which distinguishes CH and CH_3 groups (peaks positive) from CH_2 groups (peaks negative). The DEPT spectrum is shown in Fig. 4 (insert). These assignments are useful in the identification of any end groups in poly(propylene oxide) derived from the DMBD.

The infrared spectrum of DMBD is shown in Figure 5 for the C-C-O asymmetric stretching region (1100-1000 cm^{-1}). The IR spectrum in CCl_4(Fig. 5a) shows three strong peaks in this region. The peak at 1045 cm^{-1} (corrected) was assigned to the primary hydroxy functionality of DMBD by comparing its precursor ketol. This assignment is in agreement with reported values for C-C-O asymmetric stretching of primary alcohols.[76] The peak at 1090 cm^{-1}

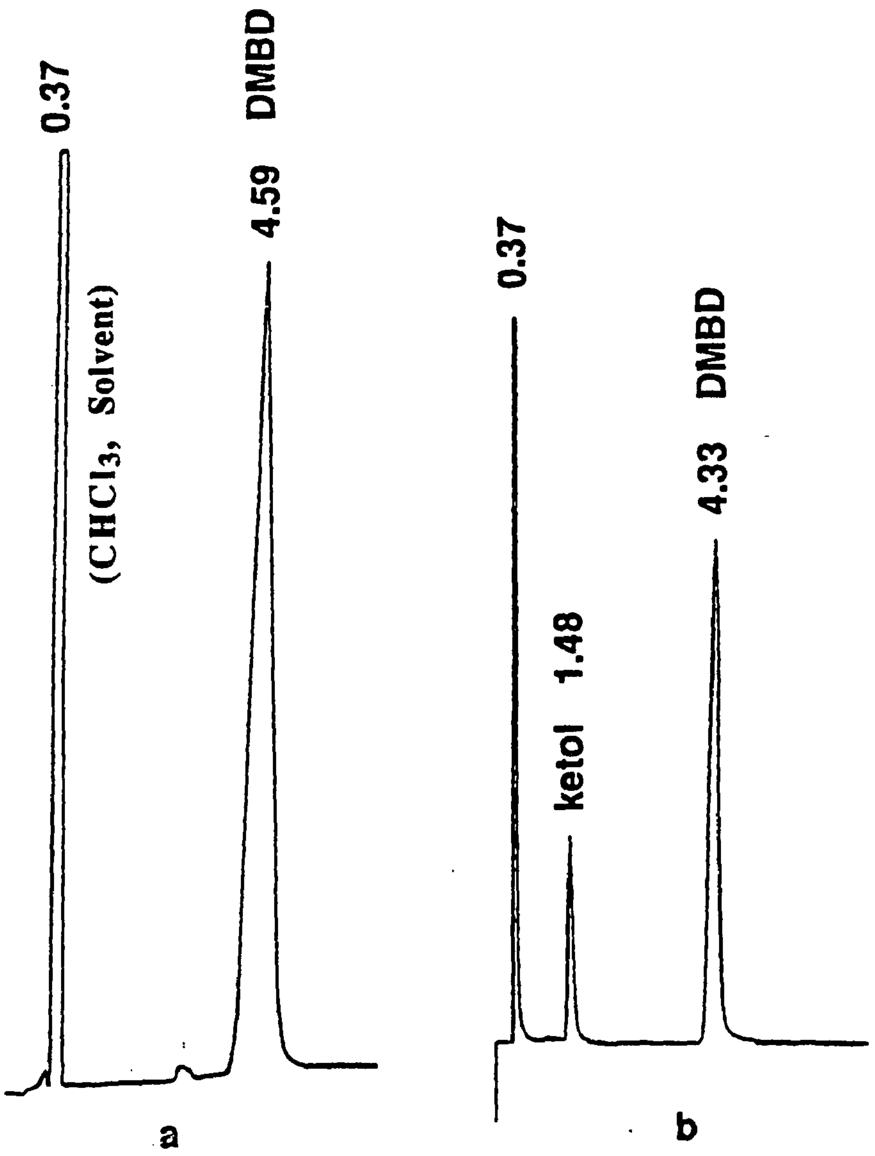


Figure 2. Gas chromatograph of (a) DMBD, and (b) DMBD spiked with precursor ketole.

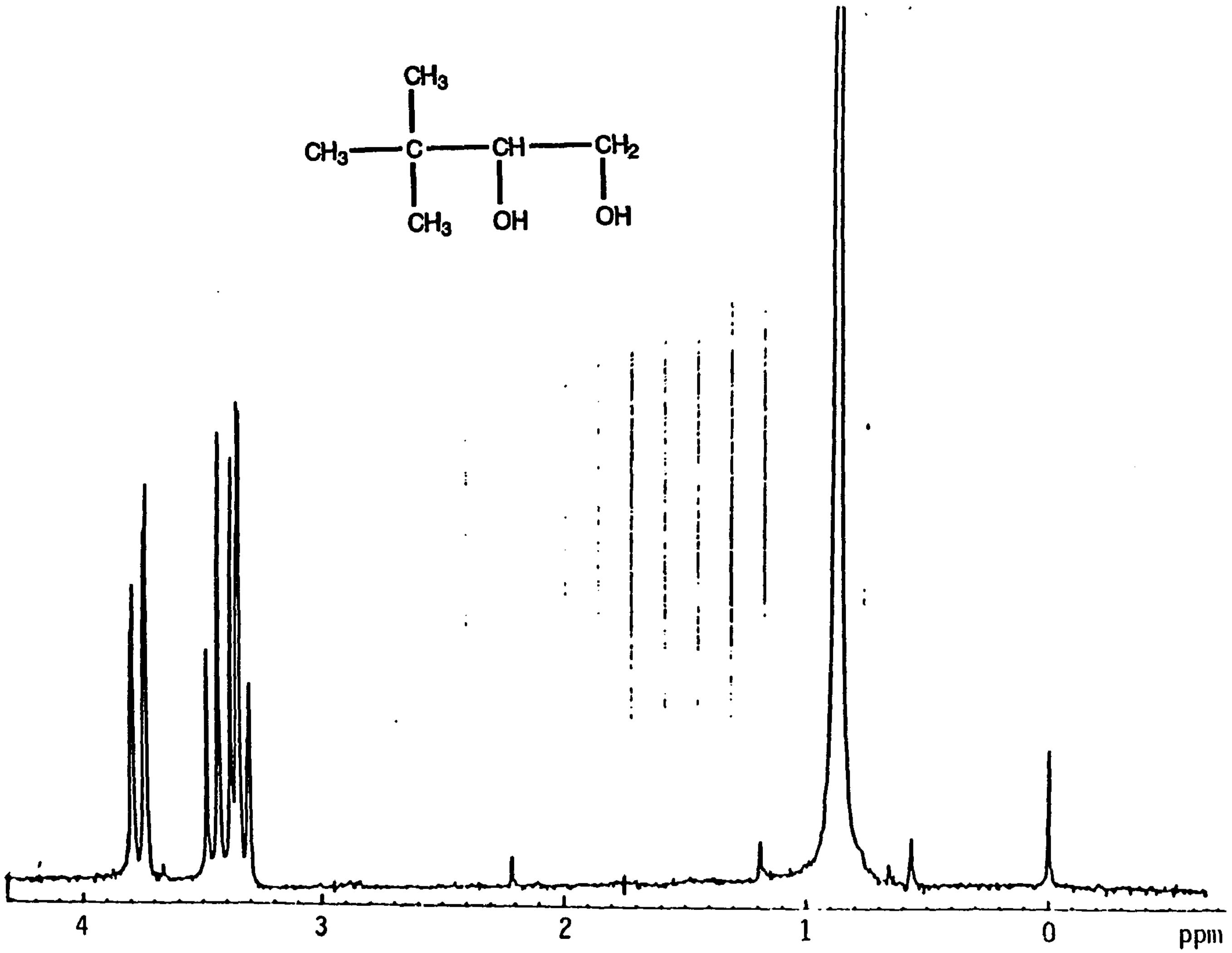


Figure 3. 200 MHz ^{1}H-NMR spectrum of DMBD in D_2O (10% wt/wt).

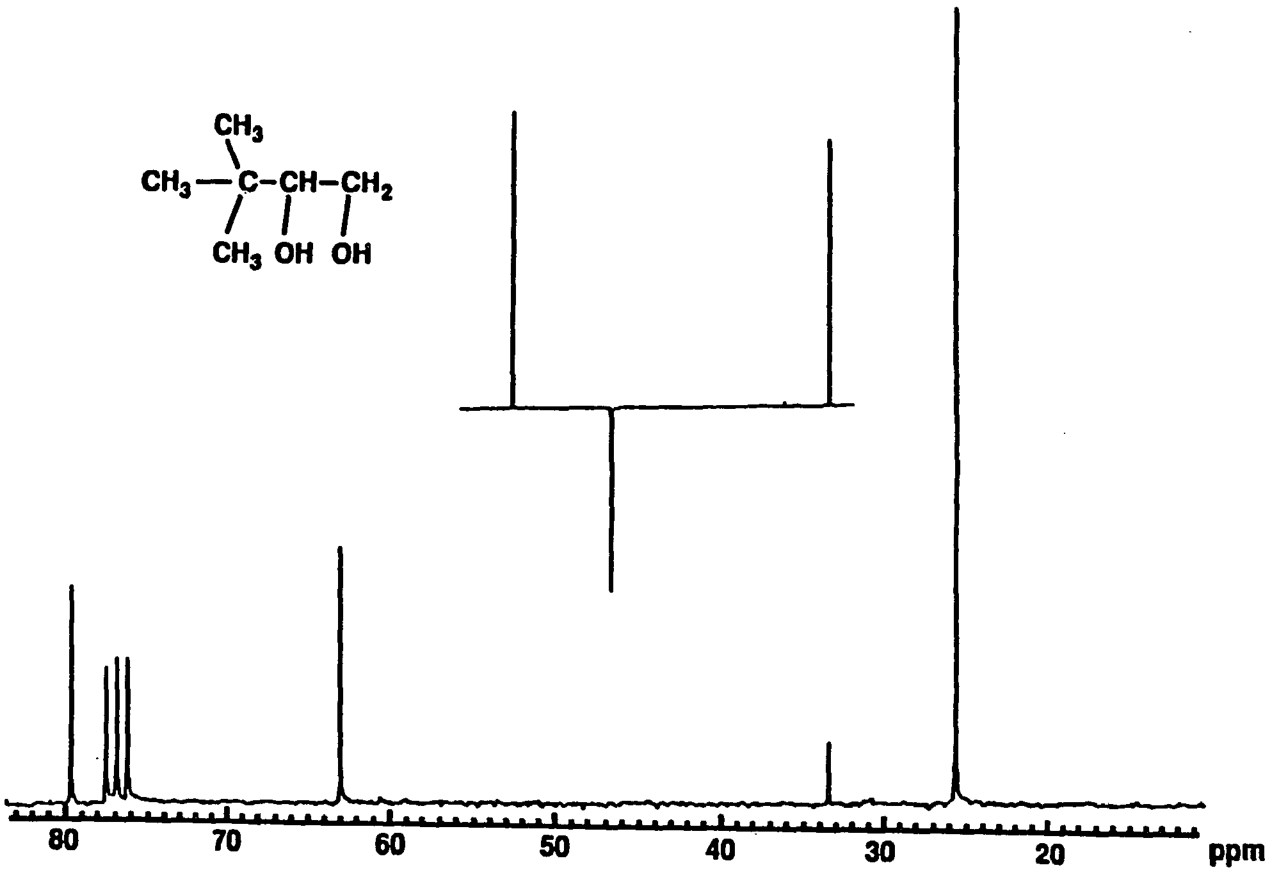


Figure 4. 200 MHz ^{13}C-NMR spectrum of DMBD in $CDCl_3$ (10% wt/wt, insert DEPT spectrum).

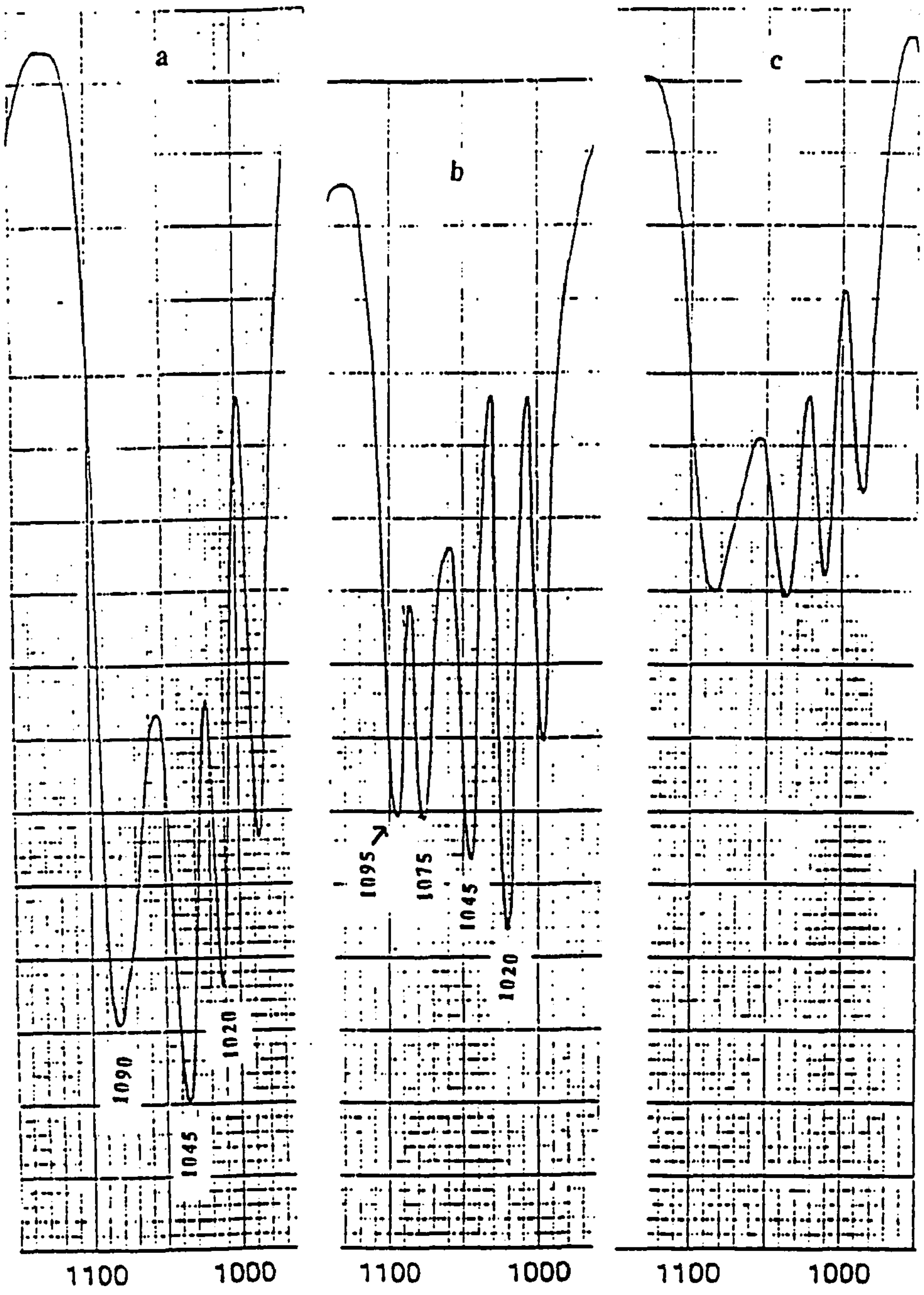


Figure 5. Infrared spectrum of DMBD (C-O stretching region) (a) in CCl_4 (10% wt/wt), (b) in nujol, and (c) in nujol with trace amount of water.

(corrected) may be due to the secondary hydroxy functionality, because the C-C-O asymmetric stretching in a secondary alcohol generally appears at a higher frequency than that of a primary alcohol.[76] It is interesting to note that the peak at 1090 cm^{-1} in CCl_4 split into two peaks at 1095 cm^{-1} and 1075 cm^{-1} (corrected) in nujol (Fig. 5b). The addition of a trace amount of water to the nujol mull causes the two peaks to collapse to a single peak at 1090 cm^{-1}(Fig. 5c). Consequently, the collapsing of the two peaks to a single broad peak at 1090 cm^{-1} was attributed to an inter molecular hydrogen bonding of the alcohol with the chlorinated solvent as shown in eq.(4-1).

--C-Cl + H-O-R --------> --C-Cl ---H-O-R -----------(4-1)

These two peaks at 1095 cm^{-1} and 1075 cm^{-1} were tentatively assigned to the C-C-O asymmetric stretching of the secondary hydroxy group. Further comments about these two peaks will be discussed in the IR spectrum of the reaction product of DMBD and AlH_3. The peak at 1020 cm^{-1} was not assigned to any particular vibration.

4.2 Synthesis of N-Methyl-l-ephedrine

4.21 Synthesis of N-Methyl-l-ephedrine Hydrochloride[74]

Formaldehyde(15 g, 0.2 mol, 40% w/w in water) and formic acid (23.25 g, 0.45 mol, 90% w/w in water) were added to l-ephedrine (15 g, 0.91 mol). The reaction mixture was refluxed at 100°C. Vigorous carbon dioxide evolution started when the temperature reached 90°C and slowed down in 0.5 h. Thin layer chromatographic analysis indicated that the reaction is complete in 1.5 h.

Concentrated HCl (9 mL) was added to make the amine salt and the product was concentrated by rotoevaporation. Ethanol was added in the final stages to facilitate the removal of the high boiling azeotropic mixture of formic acid and water. The product was recrystallized from methanol giving 17 g of NME-HCl (87%), mp 192.5-193.5°C; $[\alpha]_D^{25}$= - 29.7°(c=5.7, water) [lit.[77] mp 183°C; $[\alpha]_D^{25}$= -29.8° (c=5.7, water)].

4.22 Synthesis of N-Methyl-l-ephedrine from its hydrochloride salt.[74]

N-methyl-l-ephedrine hydrochloride (5.5 g, 25.5 mmol) was dissolved in water (50 mL) and 10% KOH was added dropwise until no further precipitation occured. Ether (75 mL) was then added to dissolve the free amine and the contents were transferred into a separatory funnel. Additional 10% KOH was added until no further precipitation occured in the aqueous layer. The system was thoroughly mixed and the addition of KOH was repeated until no further precipitation occured in the aqueous layer. The organic layer was washed with 3 x 30 mL saturated sodium chloride solution, dried with anhydrous magnesium sulfate and the solvent removed by rotoevaporation. The product was recrystallized from petroleum ether giving a 75% yield, mp 87-88°C; $[\alpha]_D^{25}$= 29.5° (c=4.5, methanol) [lit.[77] mp. 87-88°C; $[\alpha]_D^{25}$= 29.5° (c=4.5, methanol)]. ^{13}C-NMR ($CDCl_3$) : d 142.93, 127.87, 126.63, 125.89 (benzene ring); 72.52 [Ph (H) $\underline{C}$-OH]; 65.58 (H-$\underline{C}$-CH3); 42.71 [N($\underline{C}H_3)_2$]; 9.50 ($\underline{C}$H3).

4.3 Preparation of a Solution of Aluminum Hydride in Ether.[64]

Lithium aluminum hydride (179 mmol,1175 mL of 0.15M ether solution) was transferred into a 2L three neck flask equipped with two addition funnels (100 mL and 500 mL) and a reflux condenser under a dry nitrogen atmosphere. The lithium aluminum hydride was initially transferred from the stock solution by a transfer needle under a positive nitrogen pressure into the calibrated 500 mL funnel and then added into the three neck flask to aid in the measurement of the volume of solution. Sulfuric acid (100%, 89.5 mmol) was weighed in a vial inside a dry box and transferred into the 100 mL addition funnel by a syringe. The syringe and vial were rinsed with ether (25 mL) and the rinse were added into the 100 mL funnel. The reaction flask was cooled to 0°C, ice water was run through the condenser to facilitate the condensation of ether vapor, and the system was then connected to a wet test meter to measure the hydrogen evolution. The pressure of the system was allowed to equilibrate. The ether solution of 100% sulfuric acid was slowly added to the magnetically stirred solution of lithium aluminum hydride over a period of 8 h. The progress of the reaction was followed by gas analysis and 185 mmol hydrogen was evolved during the reaction (theoretical 179 mmol). The solution was allowed to settle at room temperature under a nitrogen atmosphere. The clear supernatent solution was filtered by syringe technique into a dry flask and stored under nitrogen for future use.

The gas analysis made for aluminum hydride preparations in different batches were compiled in Table 3. The theoretical and observed amount of hydrogen are in good agreement to justify the accuracy of the gas analysis by the wet test meter. It is important to note that these gas analyses were later used to measure the extent of the reaction of aluminum hydride with DMBD to prepare the aluminum alkoxide initiator.

Table 3: Gas analysis results using wet test meter to check the accuracy of measurements[a]

Room temp. (°C)	Atmospheric pressure(torr)[b]	Amount of hydrogen evolved (mmol)	
		Theoretical	Observed[c]
20.2	745.0	9.48	9.58 (1.1)
22.8	744.2	17.71	17.91 (1.1)
28.4	731.7	41.20	41.90 (1.7)
26.0	737.8	31.60	33.60 (6.3)
24.0	740.4	50.55	50.94 (0.8)
20.6	736.8	76.69	78.06 (1.8)
19.2	751.1	209.44	212.93 (1.7)
22.0[d]	738.2	192.80	203.40 (5.5)
21.5[d]	729.0	178.00	185.50 (4.2)

(a) Volume of evolved hydrogen in the reaction of lithium aluminum hydride and sulfuric acid (eq.1) was measured.
$2LiAlH_4 + H_2SO_4 \text{--------}> Li_2SO_4(s) + 2AlH_3 + 2H_2(g)$ (4-2)

(b) Corrected for moisture

(c) Values within the bracket indicate the % excess.

(d) Reaction temperature 0°C; All the other reactions are at room temperature.

The infrared spectrum of 0.1 M AlH_3 in ether (Fig. 6) showed strong bands at 1786 cm^{-1} (Al-H stretching) and at 752 cm^{-1} (Al-H bending) (lit. [64] 1788 cm^{-1} and 765 cm^{-1} respectively). Infrared spectral analysis of the reaction product of lithium aluminum hydride and sulfuric acid is a convenient method for the characterization of aluminum hydride. However, this is not a sensitive method for judging the composition of the hydride solution. The aluminum hydride prepared by the above mentioned method cannot be further purified by conventional methods. The composition is essential for the use of this hydride as a substrate for the preparation of aluminum alkoxide initiator. Consequently the aluminum hydride solution was further characterized by aluminum and hydride analyses. Standardization of AlH_3 and $LiAlH_4$ was carried out by iodine titration[66], titration of lithium as a base (LiOH)[71] , as well as aluminum analyses by EDTA titration and complexometric titrations with 8-hydroxyquinoline.[72] These various methods gave results in excellent agreement with each other as shown in Table 2. Gas analysis was also carried out for the reaction of aluminum hydride solutions with methanol. For example, the addition of 150 mL of 0.1 M AlH_3 in ether to a stirred ether solution of methanol (44.7 mmol) at 0°C produced 45.1 mmol of H_2 (theoretical 44.7 mmol). The aluminum methoxide product showed 22.4% Al (8-hydroxyquinoline; theoretical 22.5%). These results show that AlH_3 present in solution reacts with methanol completely in accordance with eq.(4-3). They also serve as an additional standardization method for AlH_3 solutions.

$$AlH_3 + 3CH_3OH \text{ --------> } Al(OCH_3)_3 + 3H_2 \text{ ------ } (4\text{-}3)$$

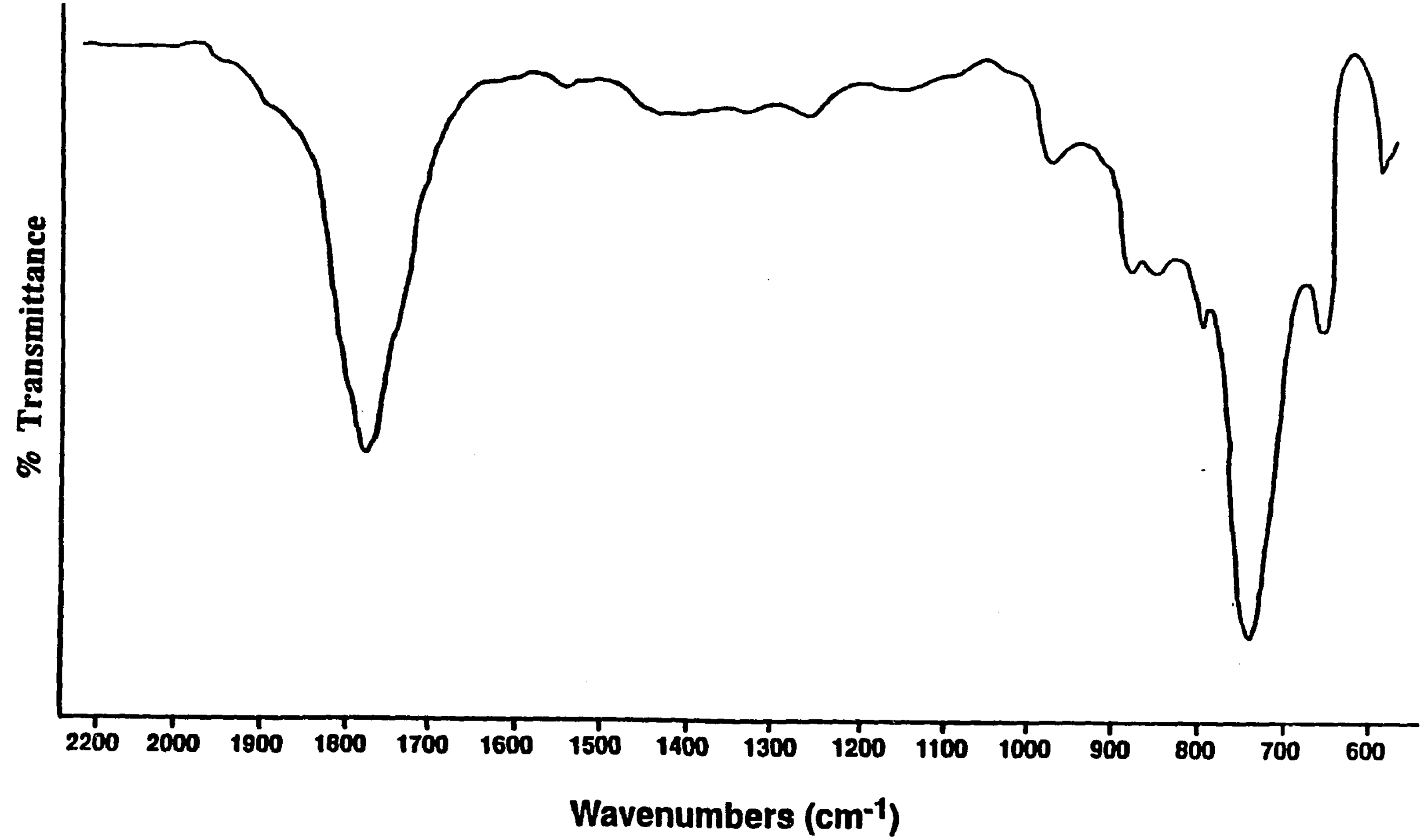


Figure 6. Infrared spectrum of an ether solution of AlH_3 (0.1 M).

The experimental details of these standardization and titration methods are described in the following sections.

4.31 Standardization of aluminum hydride and lithium aluminum hydride solutions by iodine titration[66]

Ether solution of aluminum hydride (10.0 mL) was added to an iodine solution in toluene (15.0 mL, 0.2 M). Several drops of glacial acetic acid were added to the resulting precipitate followed by 10.0 mL of water. Sodium thiosulfate (0.1 M) was slowly added to the stirred solution until a yellow solution was obtained. Starch indicator solution (2 mL) was then added and the solution was further titrated with sodium thiosulfate until the color changes from blue to colorless. A similar procedure was used in the standardization of lithium aluminum hydride solutions.

4.32 Standardization of lithium aluminum hydride by titration of lithium as a base [71]

Lithium aluminum hydride solution (5.0 mL) was added to hexane(25.0 mL). The resulting cloudy solution was slowly reacted with a mixture of hexane and ethanol (1:1 v/v). Water (25.0 mL) was added to this solution and the resulting lithium hydroxide was titrated with 0.1 N HCl with continuous stirring. A pH meter was used to follow the titration and the addition of HCl was continued until the pH of the solution remained at 6.6 for several minutes.

4.33 Aluminum Analysis

4.33-1 Aluminum analysis using 8-hydroxyquinoline (oxine)[72]

Aluminum analysis by this method was carried out for $KAl(SO_4).12H_2O$ as a reference compound according to the standard procedure.[72] Standard solutions of oxine and the reference compound were also prepared according to the standard procedure in the literature.[72]

4.33-2 Aluminum analysis of the ether solution of aluminum hydride

An ether solution of aluminum hydride (10.0 mL) was transferred into a flask and the hydride was allowed to react in the air. The resulting precipitate was dissolved in dil.HCl. The solution was diluted to 150 mL and the pH was made to 4.3 using a pH meter. The solution was heated to 50-60°C on a water bath and 20% excess oxine solution was added to precipitate the aluminum as a complex salt. The precipitation was completed by the addition of 4 g of ammonium acetate. The solution was allowed to cool and filtered through a sintered glass funnel and washed with water until the filtrate became colorless. The precipitate was then dissolved in hot conc.HCl and few drops of 0.1% methyl orange indicator and 0.5 g KBr were added. The solution was titrated with 0.1 N potassium bromate solution until a yellow color solution appeared. A premature color change occurs and more indicator solution was added as needed. Then the solution was diluted with 2 N HCl and 10 mL of 10% KI was added to this solution. Finally the solution was titrated with 0.1 N sodium thiosulfate using starch as indicator.

4.33-3 Aluminum analysis of $Al(OCH_3)_3$

The analytical sample was the reaction product of aluminum hydride and methanol treated in a 1:3 molar proportion respectively. Approximately 0.08 g of sample was transferred into a vial inside a dry box and was weighed on an analytical balance. The sample was dissolved in dil.HCl and a similar procedure used for the analysis of aluminum hydride solution was carried out for the remainder of the analysis.

4.34 Aluminum analysis using EDTA titration[72]

Standard 0.01 M EDTA (ethylene diamine tetra acetic acid-disodium salt) and 0.01M $ZnSO_4.7H_2O$ were prepared.[72] The procedure used for the aluminum analysis of $KAl(SO_4)_4.12H_2O$ was adopted for the aluminum analysis of aluminum isopropoxide (as a reference compound) and aluminum hydride.

4.34-1 Aluminum analysis of aluminum isopropoxide

Approximately 0.05 g of sample was transferred into a small vial inside a dry box and was weighed on an analytical balance. The sample was dissolved in dil. HCl and the pH was made to 7-8 using ammonium hydroxide. EDTA (0.01 M) was added from a burette, the amount of which is more than to react all the aluminum in the solution. The solution was boiled for several minutes to react all the aluminum , cooled, the pH was adjusted again to 7-8, and titrated with 0.01M Zn^{2+} solution using Eriochrome Black-T as the indicator. The color change was from blue to pink.

4.34-2 Aluminum analysis of ether solutions of aluminum hydride

Aluminum hydride in ether (5.0 mL) was transferred into a flask using a syringe and reacted with a mixture of ether and ethanol. The resulting precipitate was dissolved in dil.HCl. The remainder of the procedure for the analysis was similar to the analysis of aluminum isopropoxide as described above. The results of all the aluminum analyses and hydride titrations with iodine for aluminum hydride are presented in Table 4; the results for lithium aluminum hydride are presented in Table 5; the results for the reference compounds are presented in Table 6.

Table 4. Molarity of ether solutions of Aluminum Hydride Determined by Various Titration Methods.

M(EDTA)	M(Iodine)	M(8-Hydroxyquinoline)
0.1069	0.1033	0.0975
0.1041	0.1040	0.1021
0.1021	0.1023	0.0987
0.1011	0.1036	0.1017

Table 5. Molarity (M) of $LiAlH_4$ determined by various methods:

Run #	M (Iodine)[a]	M (EDTA)[b]	M (LiOH)[c]
1	0.128	0.133	0.134
2	0.131	0.144	0.135
3	0.130	0.137	0.132
4	0.130	0.135	0.138
5	0.131	0.134	-

a) Molarity determined by iodine titration (experimental section 4.31)

b) Molarity determined by EDTA titration(experimental section 4.34).

c) Molarity determined by titration of lithium as a base (experimental section 4.32).

Table 6. Aluminum analysis of some reference compounds

sample	method of analysis	% Al observed	calculated
Aluminum isopropoxide	EDTA	12.85±0.06	13.24
$Al(OCH_3)_3$	8-hydroxy quinoline	22.42±0.27	22.49
$KAl(SO_4)_4.12H_2O$	8-hydroxy quinoline	4.09±0.03	4.05

4.4 Preparation of Chiral Aluminum Alkoxide Initiator (Al.DMBD)

DMBD (12.6 g, 106.7 mmol) was added to a 2L three neck flask equipped with a reflux condenser, addition funnel and a rubber septum under a dry nitrogen atmosphere. An ether solution of aluminum hydride (0.11 M, 71 mmol) was transferred into the addition funnel. Ice water was run through the condenser and the system was then connected to a wet test meter. The pressure of the system was allowed to equilibrate and the hydride solution was added over 11 h to the magnetically stirred DMBD solution. Hydrogen evolution was measured by the wet test meter and corresponded quantitatively to the volume of AlH_3 added up to 81% addition. At that point hydrogen evolution ceased and no further hydride was added. After stirring overnight the reaction mixture was filtered under nitrogen atmosphere. The precipitate was washed with ether and dried at 90°C (2 mm), giving 14.3 g (~100% based on AlH_3) of initiator. The solid product was insoluble in a variety of common solvents tested. This product was used in the polymerization experiments and will be referred to as Al.DMBD. The IR spectrum of the concentrated filtrate showed no peaks characteristic of any organic material. The IR spectrum of the solid product in nujol (Fig. 7) show a strong broad band around 1100 cm^{-1}. This peak is probably due to the combined Al-O and C-C-O stretching of the aluminum alkoxide initiator.[76] It should be noted that the peak at 1045 cm^{-1}(Fig. 5) which was previously assigned to the C-C-O stretching of the primary hydroxy functionality was absent in the reaction product. The peaks at 1095 cm^{-1} and at 1075 cm^{-1} (Fig. 5)

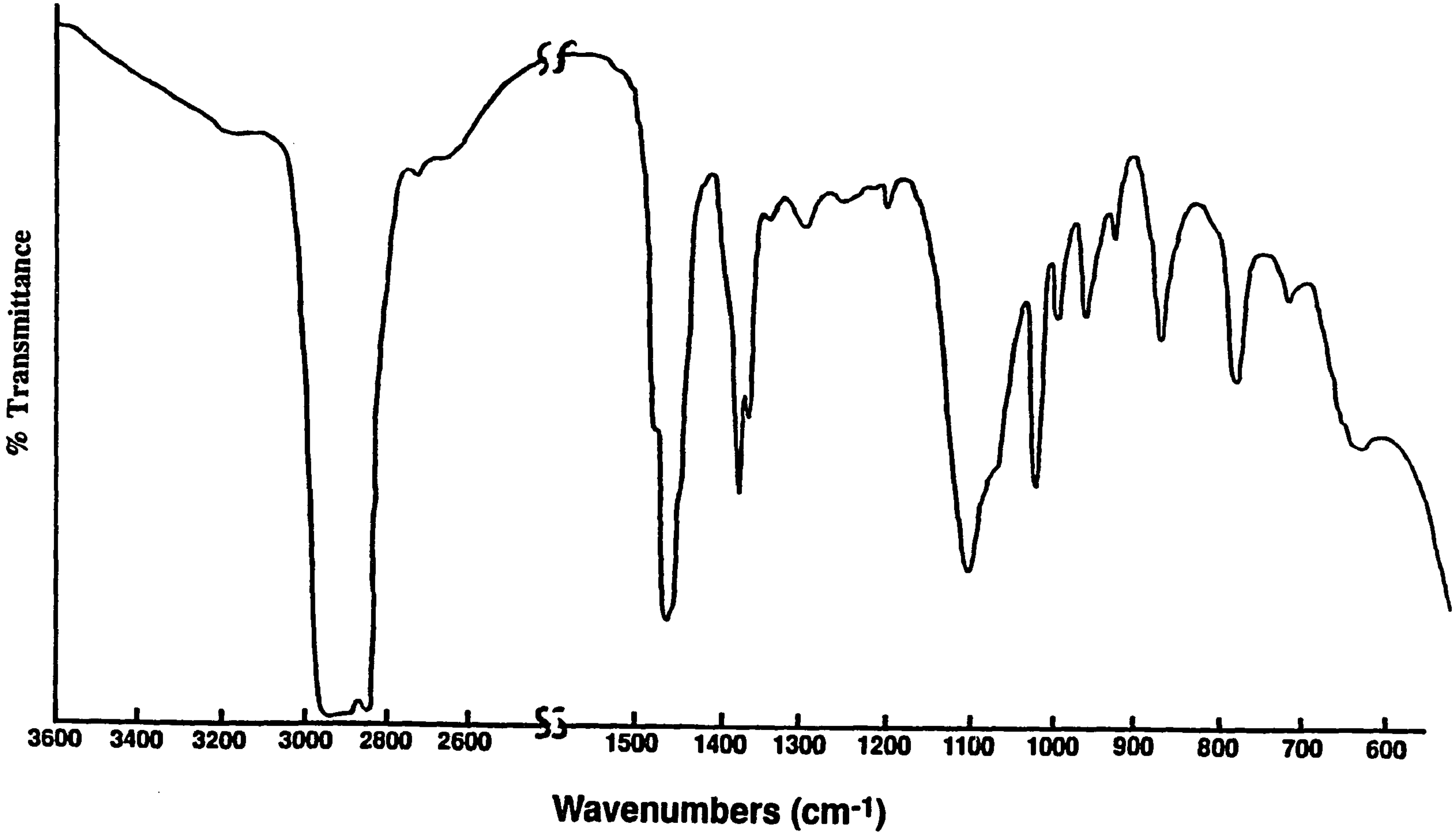


Figure 7. Infrared spectrum (nujol mull) of Al.DMBD prepared by the addition of AlH_3 to DMBD (AlH_3 : DMBD = 2:3 molar ratio) up to gas evolution ceases.

which were also previously assigned to the secondary hydroxy functionality of the DMBD are probably appearing as shoulders in the IR spectrum of the product (Fig. 7). An estimation of the extent of the reaction of the secondary hydroxy group with AlH_3 is difficult from the IR spectral analysis. This is due to the presence of the strong broad absorption around 1100 cm^{-1}.

In a repeat experiment for the preparation of chiral aluminum alkoxide initiator, an ether solution of AlH_3 (0.13 M, 275 mL, 356 mmol) was added over 11 h to a stirred solution of DMBD (6.3 g., 53.4 mmol) in 300 mL ether, in a manner similar to the above preparation. The gas evolution ceased after 82% hydride addition with 82% of the theoretical hydrogen evolution observed even though the remaining hydride solution was added. After stirring overnight, the reaction product was filtered under a positive nitrogen atmosphere. The solid product was washed with ether until the filtrate showed no solid residue upon evaporation. The product was dried at 90°C (2 mm) giving 6.7 g (92%) initiator. This product was also used for the polymerization of PO and will be referred to as Al.DMBD*. The IR spectrum of the concentrated filtrate (Fig. 8) exhibits a peak at 1730 cm^{-1} due Al-H stretching. This peak is not due to unreacted aluminum hydride, because other peaks due to organic materials are seen in the spectrum. The IR spectrum of the solid product in nujol (Fig. 9) exhibits a peak at 1830 cm^{-1} also characteristic of Al-H stretching vibration in an alkoxy substituted aluminum hydride. The differences in the Al-H absorption frequencies of the filtrate and the solid product are due to the

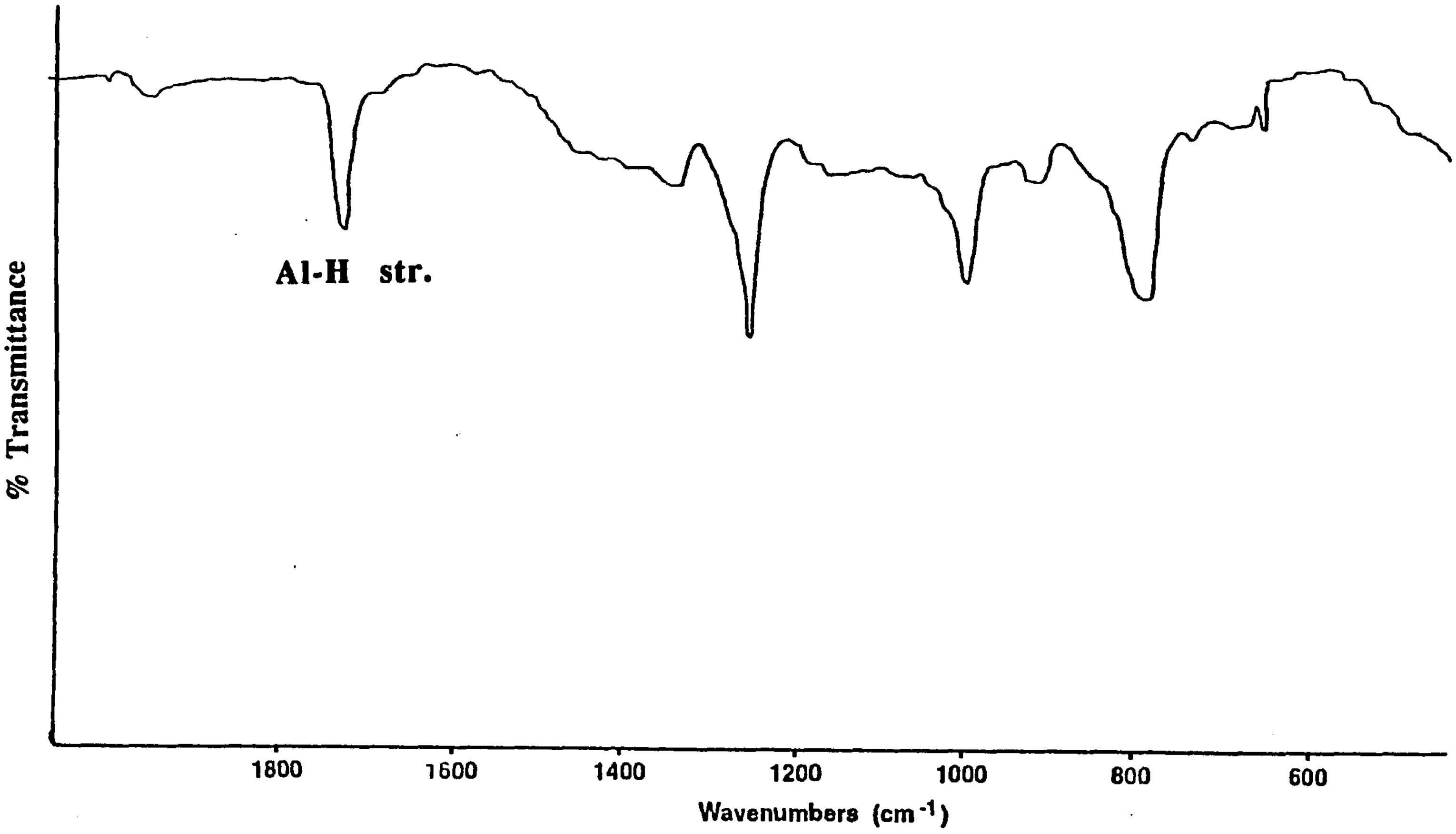


Figure 8. Infrared spectrum of the concentrated filtrate (ether) resulted in the complete addition of AlH_3 to DMBD (AlH_3 : DMBD = 2:3 molar ratio) despite gas evolution ceased. ~81% reaction.

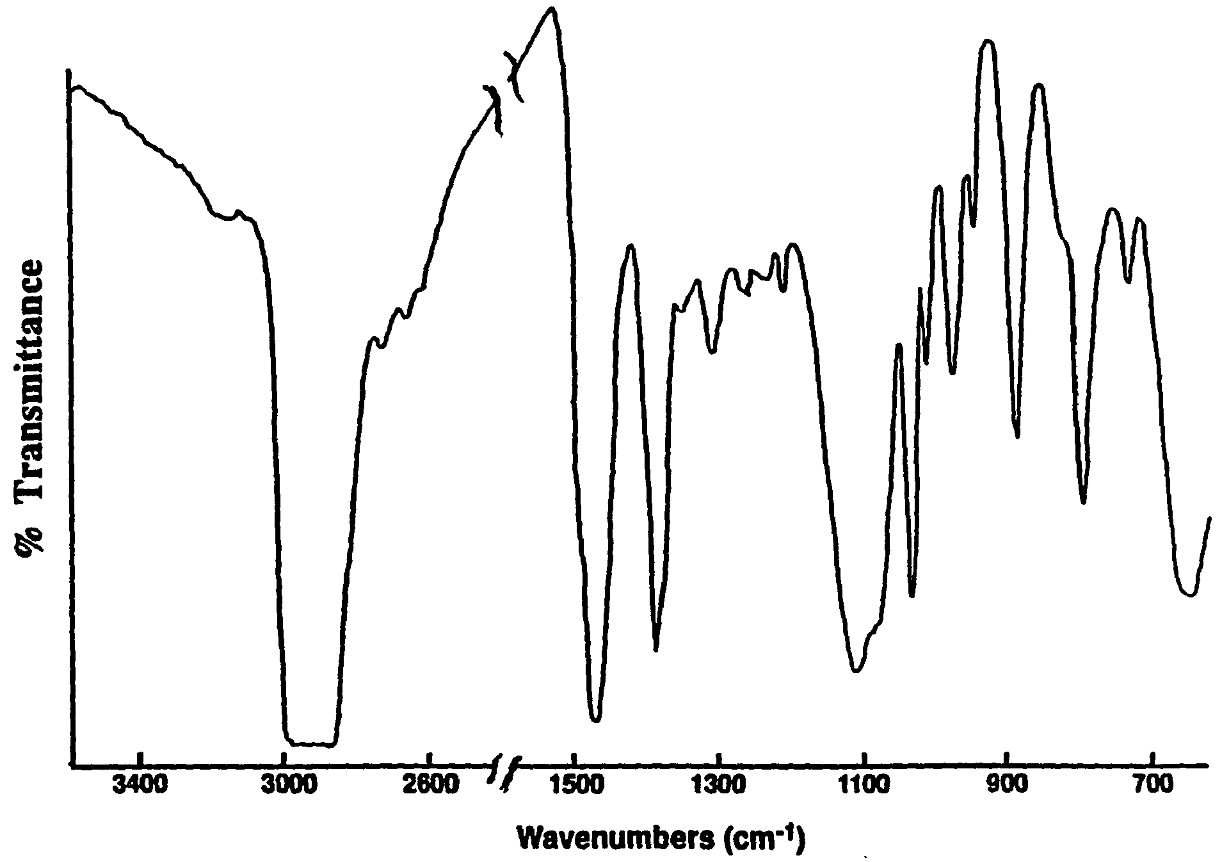


Figure 9. Infrared spectrum (nujol mull) of Al.DMBD prepared by the complete addition of AlH_3 to DMBD (AlH_3 : DMBD = 2:3 molar ratio) despite gas evolution ceased ~81% reaction.

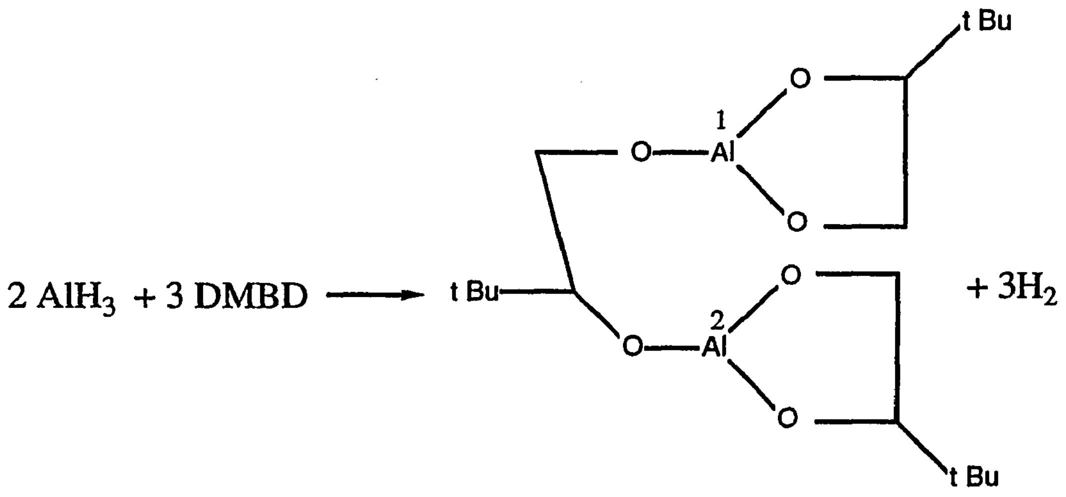
physical nature of the samples (solution compared to solid) or the number of alkoxy substituents attached to the aluminum. The formation of soluble and insoluble hydride products due the addition of AlH_3 after the gas evolution had ceased is probably due to a disproportionation reaction as in eq. 4-4.

$$\underset{}{AlH_3} + Al(OR)_3 \text{ ------> } \underset{\substack{\text{insoluble}\\\text{in ether.}}}{AlH(OR)_2} + \underset{\substack{\text{soluble}\\\text{in ether}}}{AlH2(OR)} \text{ ------(4-4)}$$

These kinds of disproportionation reactions have been used to prepare mono and disubstituted aluminum hydrides by controlling the amount of aluminum hydride and aluminum trialkoxide at a lower temperature.[63]

The cessation of hydrogen evolution after approximately 81-82% of the AlH_3 solution had been inversely added suggests that no free DMBD remained in solution at that point. Further, hydrogen evolution did not occur in the experiment where additional AlH_3 was added suggesting that residual hydroxy groups were unreactive, possibly attributable to steric hindrance related to the environment of the neopentyl type secondary hydroxy groups in the product.

A complete reaction between AlH_3 and DMBD can be represented as in eq. (4-5). It should be noted that the structure of



-------------- (4-5)

the aluminum alkoxide in eq. (4-5) is over simplified for convenience. The actual structure may be polymeric in nature as suggested by the insolubility of this material in a variety of common organic solvents. The Al(1) in eq. (4-5) is reacted with two primary hydroxy groups and a secondary hydroxy group. On the other hand, the Al(2) in eq. (4-5) has to react with one primary hydroxy group and two secondary hydroxy groups. This is sterically unfavorable and only five out of the six available hydroxy groups are reacting to form the aluminum alkoxide. Such a reaction will lead to the evolution of 83% hydrogen as observed(81-82%). However, such a reaction will require the addition of all the AlH_3. The hydrogen evolution corresponded quantitatively to the volume of AlH_3 added up to 81-82% which suggests that the reaction between AlH_3 and DMBD in a 2:3 molar proportion respectively cannot be explained by the reaction of only five out of the six available hydroxy groups.

Little information is available on the reactions of aluminum hydride with alcohols. Aluminum hydride has been reacted with alcohols such as methanol, ethanol, propanol, and tert. butyl alcohol to prepare substituted aluminum hydrides.[63] There appears to be a correlation between the incomplete reaction of aluminum hydride with alcohols and the degree of steric hindrance. Sterically less hindered propylene glycol was reacted with aluminum hydride in a manner similar to the preparation of the chiral aluminum alkoxide initiator as described previously. The concentrated filtrate of this reaction product showed an IR absorption peak at 1730 cm^{-1} due to Al-H stretching vibration. The IR spectrum of the solid product in nujol (Fig. 10) showed a peak at 1830 cm^{-1} also due to Al-H stretching vibration as in Fig. 9. These IR spectral analysis show that the reaction of aluminum hydride and propylene glycol also results in the formation of soluble and insoluble products as observed in the same type of reaction with DMBD. However, propylene glycol reacted more completely with AlH_3 giving 95% of the expected hydrogen evolution. Under similar conditions, methanol reacted completely with AlH_3 and the IR spectra of concentrated filtrate and the solid product in nujol showed the absence of any hydride species. The gas analysis results of the reaction of AlH_3 with DMBD, propylene glycol and methanol are summarized in Table 7 for comparison. The hindered 2,4,6-tri-*tert.*-butylphenol was shown to react with only two equivalents of hydride on refluxing with AlH_3 in ether.[78] However, N-methyl-l-ephedrine which contain a bulky phenyl substituent completely reacted with aluminum hydride (miscellaneous experiments).

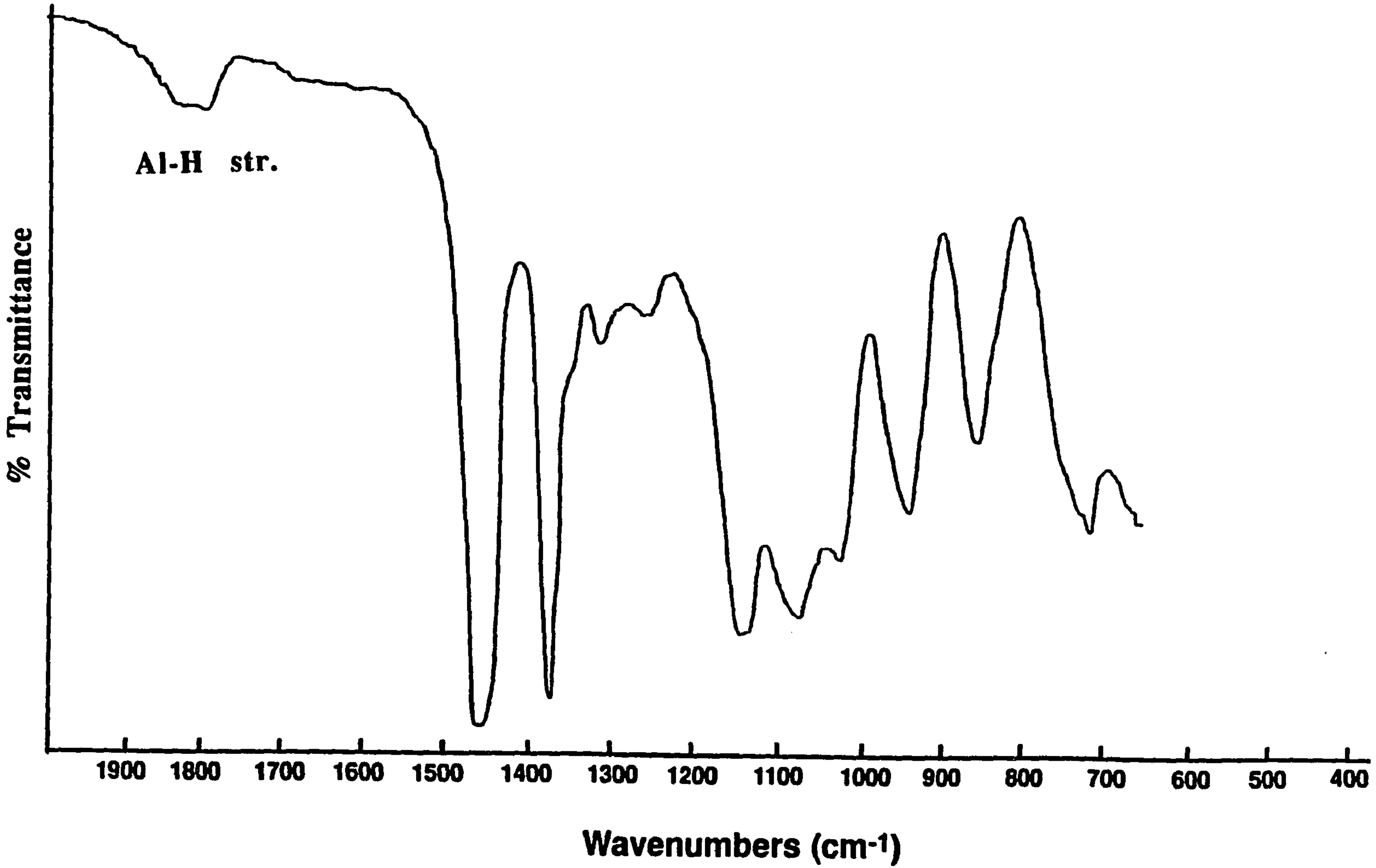


Figure 10. Infrared spectrum (nujol mull) of the product prepared by the complete addition of AlH_3 to propylene glycol (AlH_3 : propylene glycol = 2:3 molar ratio).

Table 7: Reaction of Aluminum hydride with diols and methanol

Alcohol (mmol)	AlH_3 (mmol)	Extent of Reaction	
		Volume of hydride added, %	Hydrogen evolution, %
DMBD[a](106.70)	71.10	62	63
		66	67
		70	72
		73	75
		78	78
		80	79
		81	-b-
DMBD[a](53.40)	35.60	22	25
		31	32
		33	34
		46	50
		51	53
		60	63
		64	66
		67	71
		71	73
		78	81
		81	82
		100	82
Propylene glycol(13.89)	9.26	13	9
		34	32
		47	44
		67	65
		81	81
		100	95
Methanol (44.58)	14.86	100	100

(a) R(-) 3,3-dimethyl-1,2-butanediol.

(b) Reaction slowed down and no further hydride solution was added.

4.5 Polymerization of Propylene Oxide

4.51 Sample Preparation for Polymerization

Polymerizations of propylene oxide (PO) were carried out in bulk at 80°C using the initiator Al.DMBD alone or with $ZnCl_2$ as a coinitiator. The latter initiator will be referred to as Al.DMBD-$ZnCl_2$. Polymerization tubes were specifically made for drying $ZnCl_2$ as well as transferring monomer by vacuum techniques as shown in Figure 11a. The straight arm of the polymerization tube had a 24/40 female joint (A) to attach a condenser for drying $ZnCl_2$ with thionyl chloride under reflux. The side arm (B) of the tube had a break seal and a constriction to facilitate the sealing of the polymerization tube under vacuum. A quantitative amount of Al.DMBD initiator and predried $ZnCl_2$ (see materials and methods) were transferred into small vials inside a dry box. The predried , preweighed $ZnCl_2$ was added to the polymerization tube inside the dry box using a long plastic funnel to avoid the adhering of any solid material on the tube wall. Thionyl chloride (3 mL) was added to the polymerization tube and refluxed under nitrogen atmosphere for 2 h with stirring. The excess thionyl chloride was removed at room temperature under vacuum and residual traces at 90°C (2 mm) for 0.5 h. The tube under vacuum was then taken to a dry box and the preweighed Al.DMBD initiator was added again using a long plastic funnel. Then the tube was sealed under vacuum. It is important to make sure there are no solid particles adhered onto the walls of the polymerization tube during the transfer of initiator into the tube or adhering due to static charges inside the dry box. The adhered solid

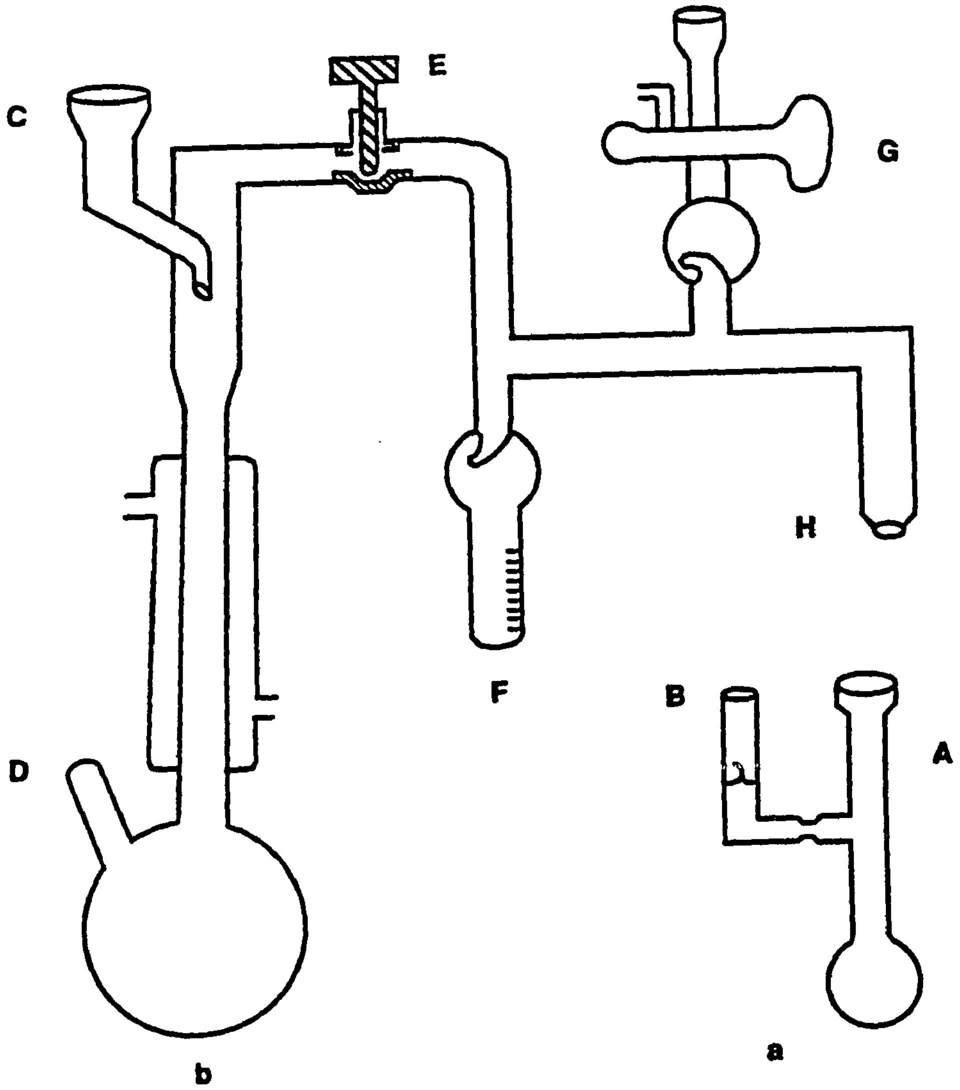


Figure 11. Apparatus used for the polymerization of propylene oxide. (a) polymerization tube, and (b) monomer purification and distillation unit.

particles created holes during the sealing of the polymerization tube and the monomer leaked out of the tube during polymerization.

Prior to polymerization, propylene oxide was dried over calcium hydride by refluxing under vacuum using the apparatus shown in Figure 11b. The two piece set up contained a 500 mL round bottom flask fused with a condenser. The top end of this unit had a 24/40 female joint (C) to attach the other unit. The calcium hydride drying agent was added to the round bottom flask through the side arm D and it was sealed. The other part of this set up contained two vacuum valves. The valve E is used to control the amount of PO distilled into the fused graduated cylinder (F). The other two way vacuum valve (G) is used to connect the system to a vacuum line and to open the system to atmospheric pressure where necessary. The side arm B (Fig. 11a) is used to seal the polymerization tube to this unit (end H).

Before sealing the polymerization tube to this set up, the purified PO was distilled into the round bottom flask through the side arm C under nitrogen atmosphere and then it was stoppered. The PO was deoxygenated by freeze-pump-thaw cycles and the system was refluxed under vacuum. The PO was stored in this system by closing the valve E. A small magnet was attached above the break seal of the polymerization tube and it was sealed to the main set up at the end H (Fig. 11b). After checking for leaks, the system was dried by flaming under vacuum. A controlled amount of PO was distilled into the graduated cylinder under vacuum. This was achieved by cooling the graduated cylinder with liquid nitrogen. Approximately 4 mL frozen PO corresponded to 5 mL liquid and the exact amount of monomer was determined after the polymerization. The break seal of the polymerization tube was then broken and the known amount of monomer was then condensed into the polymerization tube by cooling with liquid nitrogen. Then the polymerization tube was sealed under vacuum and kept at 80°C for a specified amount of time. Some polymerizations were carried out at room temperature for an extended period of time.

Propylene oxide was also polymerized with an aluminum isopropoxide (AIP)-$ZnCl_2$ initiator (1:1 molar ratio) in bulk at 80°C for comparison purposes.

Initial polymerizations were carried out with PO using Al.DMBD initiator and $ZnCl_2$ coinitiator in which $ZnCl_2$ was introduced as an ether solution. A quantitative amount of ether solution of $ZnCl_2$ was introduced into polymerization tubes and the ether was initially removed under vacuum. The remaining ether from the residual paste like material was removed by heating under vacuum. The rest of the procedure was same as previously described. The Al.DMBD and Al.DMBD* (experimental section 4.4, p60 and p62) initiators were used for these polymerizations.

4.52 Removal of Unreacted Monomer for Optical Activity Measurement.

The polymerization tubes were removed from the oil bath after the specified times and cleaned. The polymerization tube was opened and its weight recorded. It was found that the unopened tube had a slightly larger weight than the opened tube probably due a slight vacuum in the sealed tube. Consequently, the weights of the polymerization tubes were recorded after opening. The unreacted monomer was recovered under vacuum (2 mm) at room temperature, or at 80°C using a dual trap shown in Figure 12. When the polymer conversion was low, a lower vacuum was initially applied to avoid splashing of the polymer. When the polymerization was carried out to high conversion, removal of unreacted monomer was not complete at room temperature. The system was heated to 80°C under vacuum and at one point the polymer in the small polymerization tube will come out as a bubble and the unreacted monomer released. If necessary, the amount of vacuum and heating had to be controlled to avoid splashing of the polymer. The system was kept under vacuum until there is no visible change in the escape of the monomer from the polymer and there is no change in the height of the unreacted monomer in the trap. The monomer was removed from the trap by a syringe through the rubber septum (Fig. 12). The optical activity of the unreacted monomer was measured in benzene, and also as the neat liquid where possible at 25°C. The temperature was maintained at 25°C by circulating water from a thermostat. A 24 g/dL solution of PO in benzene was prepared in an nmr tube. This was done, for example, by introducing 3.1 cm of

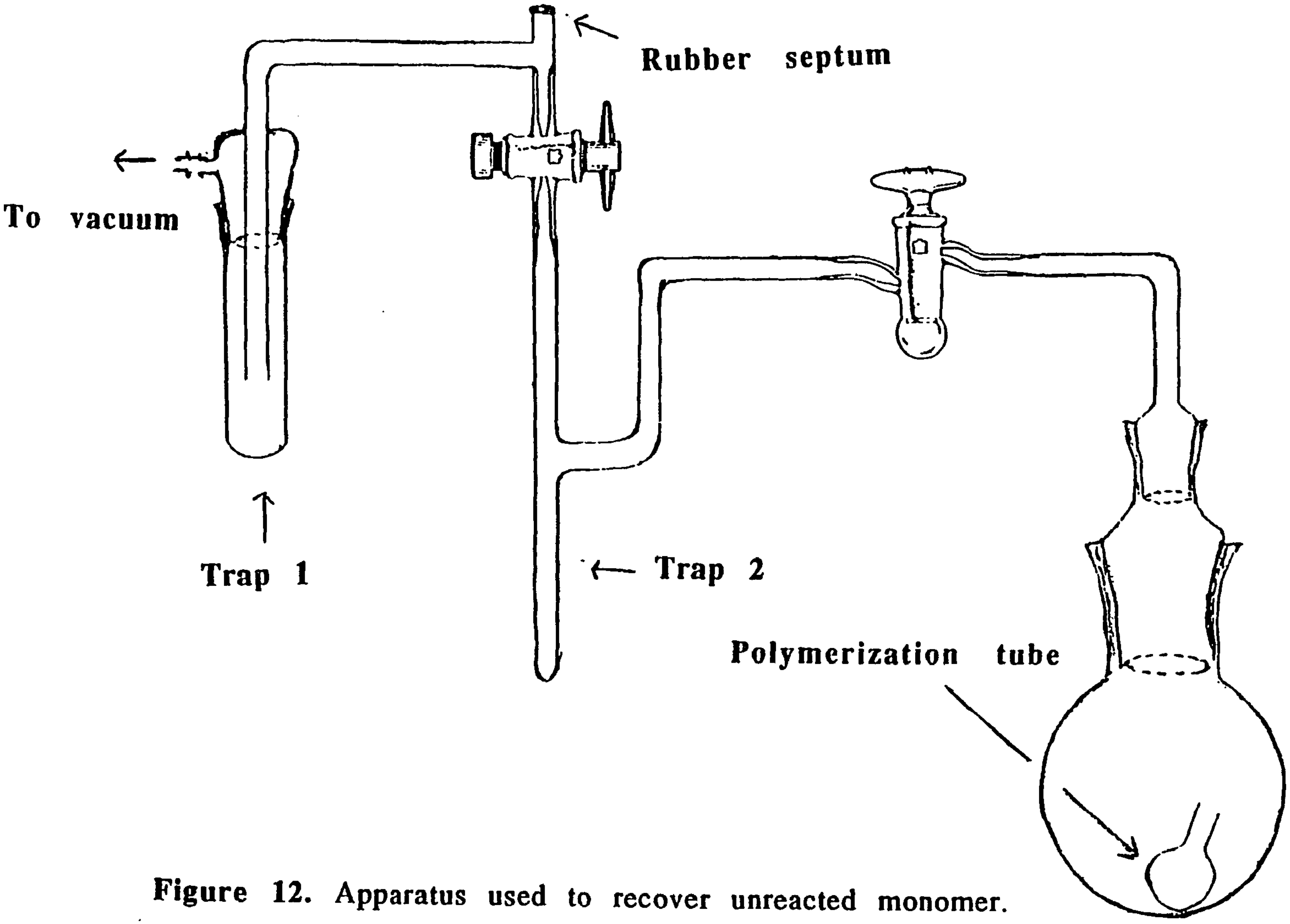


Figure 12. Apparatus used to recover unreacted monomer.

unreacted monomer into a flat bottom 5 mm diameter nmr tube and diluting the monomer with benzene to 10.8 cm. The following calculation shows the concentration of the unreacted monomer in g/dL:

Density of propylene oxide = 0.83 g/mL at 25°C
Volume of propylene oxide = height x (22/7) x r^2
=3.1 cm x (22/7) x $(5/2)^2$ cm^2
Mass of propylene oxide = 0.83 g/mL (density) x Volume
Total volume of the solution = 10.8 cm x (22/7) x $(5/2)^2$ cm^2
Concentration of propylene oxide = mass/volume
= 0.24 g/mL
= 24 g/dL

The optical activity of pure S-propylene oxide (Aldrich, 99%) was also measured in benzene at the same concentration and as neat liquid.at 25°C.

4.53 Determination of Polymer Yield.

After removing the unreacted monomer, the polymerization tube was weighed. The polymer was then dissolved in benzene and the tube was cleaned. The dry weight of the tube and the small stirrer bar were recorded. The polymer yield was then calculated. The solvent was removed from the polymer solution by freeze drying technique and the polymer yield was again calculated. The monomer recovery was complete by the above method as shown by almost the same yield of polymer in both cases. A typical calculation of the polymer yield is illustrated below:

Total weight of the polymerization tube =24.6725 g

Weight of the tube after removing unreacted monomer =23.1695 g

Weight of unreacted monomer (24.6725-23.1695) = 1.5030 g

Weight of empty tube and stirrer =16.2192 g

Weight of initiator = 0.4844 g

Weight of polymer (23.1695-16.2192-0.4844) = 6.4659 g

Weight of monomer used = (6.4659+1.5030) = 7.9689 g

% Yield = (6.4659/7.9689)x 100 =81.1

4.54 Characterization of the Recovered Unreacted Monomer.

The ^{1}H-NMR spectrum of the unreacted monomer in $CDCl_3$ shown in Figure 13 exhibits a small peak at 0.9 ppm. The spectrum recorded with a small amount of added DMBD (Fig. 13b) suggests that this small peak is due to free DMBD or DMBD moiety in the poly(propylene oxide) oligomers present in the recovered monomer. The GC of a recovered monomer shown in Figure 14a exhibit several impurities. The spiking experiment (Fig. 14b) with a small amount of DMBD suggest that the peak around 9.85 min. is probably due to free DMBD in the recovered monomer. The first peak around 0.37 min. is due to the propylene oxide. The peaks appearing after 4.0 minutes are plotted with increased intensity (100 times). Almost all the unreacted monomers showed the same type of impurities irrespective of their recovery temperatures (80°C or room temperature). The amounts of impurities are found to be less than

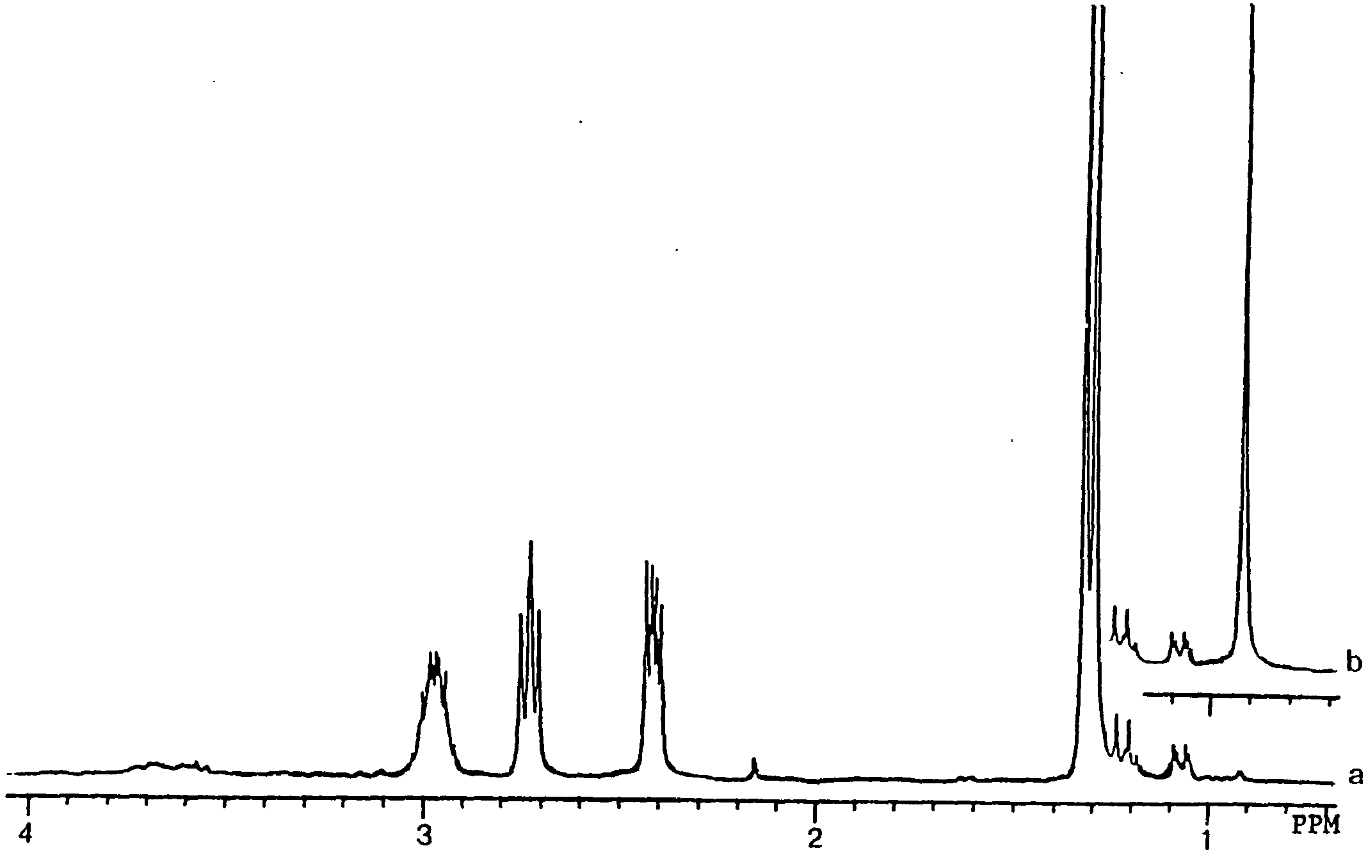


Figure 13. 200 MHz ^{1}H-NMR spectra of (a) recovered unreacted propylene oxide, and (b) with spiked DMBD in $CDCl_3$.

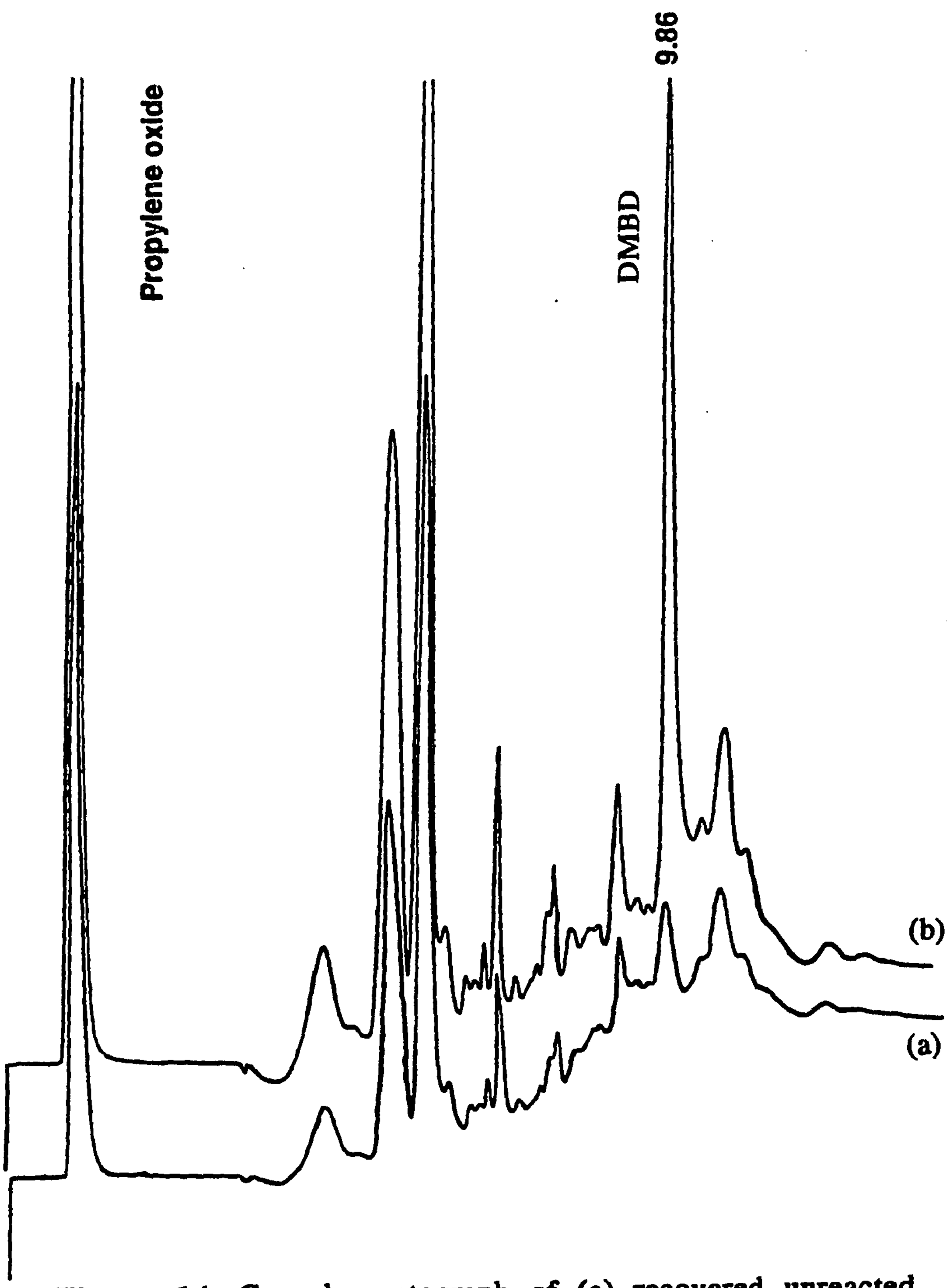


Figure 14. Gas chromatograph of (a) recovered unreacted propylene oxide, and (b) with spiked DMBD.

1% by integration. The description of the GC experiment is shown below:

Column : Diethylelene glycol.succinate (6ft. x 1/4 in)
Detector : Flame ionization
Injection Temperature : 175°C
Detector Temperature : 250°C
Run Table
Oven Temperature Initial Value =35°C
Oven Temperature Final Value = 4 min.
Oven Temperature Program Rate= 29°C/min.
Oven Temperature Final Value = 170°C
Oven Temperature Final Time = 7 min.

For comparison purposes, samples of racemic propylene oxide containing known amounts of DMBD from 0.013 to 0.20% (w/w) were prepared and their optical activities were measured at 25°C and also examined by GC analysis using the above temperature programing. The results are summarized in Table 8.

Table 8: Gas chromatographic and optical rotation results of racemic propylene oxide containing known amounts of DMBD.

Concentration of DMBD (% w/w)	Observed optical rotation(°, dm)[a]	Area % of DMBD by GC analysis
0.2	-0.047	0.348
0.1	-0.023	0.157
0.05	-0.014	0.108
0.025	-0.009	0.037
0.013	0	-

[a]Direct reading from the polarimeter.

The GC analysis showed that the presence of free DMBD in the recovered unreacted monomer (Fig. 14) to be 0.009-0.116%(w/w), and the monomer is at least 99% pure. A direct comparison of this % of DMBD with the results in Table 8 suggests that the contribution of DMBD to the measured optical rotation of recovered monomer is negligible.

4.55 Fractionation of Polymers into Crystalline and Amorphous Components

The remainder of the product after the removal of unreacted monomer was dissolved in benzene and initiator residues were removed by stirring with a small added quantity of methanol followed by centrifugation. The benzene solution was concentrated by rotoevaporation and polymer recovered by freeze drying. This was achieved by freezing the polymer in dry ice/acetone bath and rotating the flask so that the polymer solidifies as a thin film and then applying vacuum to remove benzene. Fractionation of polymers was carried out in two stages. The polymer was first dissolved in acetone (1 g/50 mL), cooled at -30°C for 0.5 h and centrifuged at -30°C. The precipitate was redissolved in benzene and freeze dried. It was then fractionated again at -30°C from acetone (1 g/450 mL). The soluble fractions were combined and the acetone removed by rotoevaporation. This soluble amorphous polymer was dissolved in benzene and rotoevaporated. Finally, both acetone soluble and insoluble fractions were freeze dried from benzene. Optical rotations of acetone insoluble polymer fractions were measured in benzene and in chloroform at 25°C.

5.0 Results and Discussion

5.1 Stereoelective Polymerization of Propylene Oxide

Preliminary studies showed that polymerization of PO with the chiral initiator Al.DMBD in bulk at 80°C in the absence of $ZnCl_2$ was slow, resulting in 85% reaction after 3 weeks. Furthermore, the optical rotation of unreacted monomer was very low { $[\alpha]_D^{25}$ = -0.049° (neat, dm) }. On the other hand , the Al.DMBD-$ZnCl_2$ initiator with Al:Zn = 1:1 molar ratio was found to be highly reactive and was stereoelective in the polymerization of PO in bulk at 80°C. The optical activity of recovered monomer was measured as a function of polymer yield (Table 9).

Table 9: Polymerization of Racemic PO with Al.DMBD-$ZnCl_2$ (Al:Zn = 1:1 molar ratio) Initiator[a]

		Optical rotation of unreacted monomer	
Polymerization time, hr.	Polymer yield, %	$[\alpha]_D^{25}$ (neat)	$[\alpha]_D^{25}$ (c= 24, benzene)
4	15	-0.035	-0.072
7	28	-0.102	-0.162
11	43	-0.252	-0.434
14	48	-0.259	-0.470
18	63	-0.349	-0.629
20	71	-0.471	-0.888
22	81	-0.675	-1.180
33	84	-0.700	-1.360
42	98	-	-1.940

---

[a] Polymerizations were carried out in bulk at 80°c with 1 mol % initiator. $ZnCl_2$ was predried with thionyl chloride, weighed and transferred into polymerization tube, then further dried with thionyl chloride.

Polymer yield increased with reaction time and there was a monotonic increase in optical rotation of the unreacted monomer with increasing polymer yield.

5.1-1 First Order Kinetic Analysis of the Polymerization of Racemic PO with the Al,DMBD-ZnCl$_2$ initiator System.

The conversion, optical rotation data was treated by the first order in monomer relationship,

$$\alpha = - \alpha_0 \; [(r-1)/ \; (r+1)] \; \ln \; (1-x) \qquad \text{-------------(5-1)}$$

derived by Furukawa *et al.*[20] In the above equation α is the specific rotation $[\alpha]^{25}_{D}$ (c=24, benzene) of unreacted monomer, $[\alpha_0]^{25}_{D}=$ 24.0°(c=24, benzene) measured using pure S-enantiomer (Aldrich) and x is the conversion to polymer. In fact, the S-enantiomer has a negative rotation and the sign of rotation was changed to satisfy the rotation of the R-enantiomer which is required in the actual equation. The data for the first order kinetic scheme are presented in Table 10. The plot shown in Figure 15a gave a stereoelective ratio r= 1.06 with a correlation coefficient of 0.993 for the data up to 84% conversion. The data was also plotted using the specific rotation of unreacted monomer measured as a neat liquid. An $[\alpha_0]^{25}_{D}=$ 15.0°(neat, dm)[79] was used for the optical activity of pure R-enantiomer. The plot shown in Figure 15b gave a stereoelective ratio r = 1.05 with a correlation coefficient of 0.991. A consequence of this first order kinetic behavior is the limiting value of α . As x---> 1, $\alpha \longrightarrow - \alpha_0$.[43] In this case as x---> 0.98 (98% conversion), the specific rotation of unreacted monomer reaches a value of -1.94 rather than -24.0 measured for pure S-enantiomer. The calculated value of the specific rotation at this conversion was -5.34 using the stereoelective ratio r=1.06. This leads to the conclusion that a first order kinetic relationship is unsatisfactory for this system.

Table 10: Data for the first order kinetic behavior

sample Ref. #	Fraction of monomer polymerized (x)	-ln (1-x)	$[\alpha]_D^{25}$ (neat)	$[\alpha]_D^{25}$ (C=24, benzene)
C-283-1	0.15	0.16	0.035	0.072
C-283-2	0.28	0.33	0.102	0.162
C-283-3	0.43	0.56	0.252	0.434
C-252-5	0.48	0.65	0.259	0.470
C-283-4	0.63	0.99	0.349	0.629
C-283-5	0.71	1.24	0.471	0.888
C-252-4	0.81	1.66	0.675	1.180
C-283-6	0.84	1.83	0.700	1.360
C-252-1	0.98	3.91	-	1.940

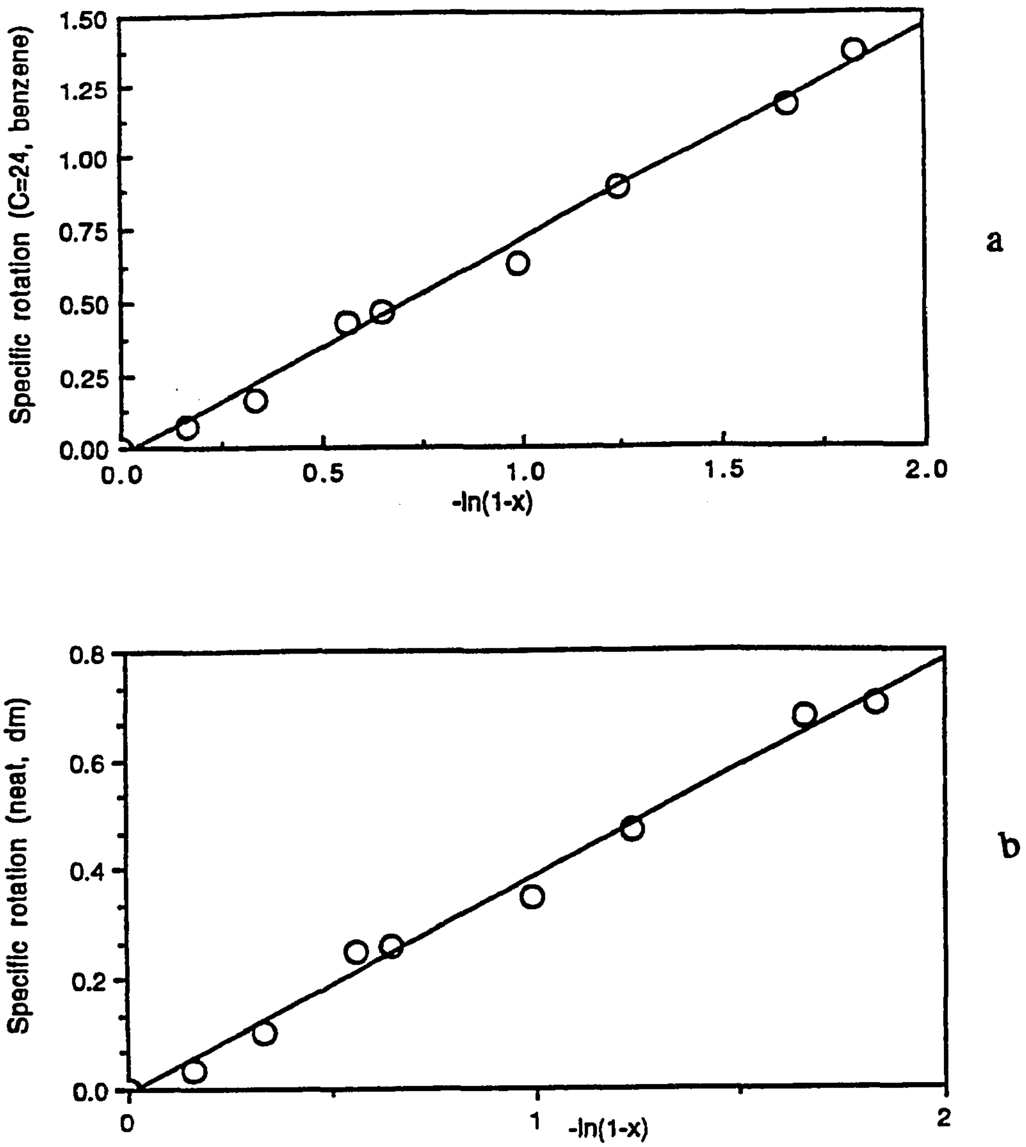


Figure 15. First order kinetic plot for the data obtained by the polymerization of racemic propylene oxide with Al.DMBD-ZnCl$_2$ initiator: (a) unreacted monomer was used as a solution in benzene (c=24 g/dL), and (b) as a neat liquid.

5.1-2 Second Order Kinetic Analysis of the Polymerization of Racemic PO with the Al.DMBD-ZnCl$_2$ initiator System.

The optical rotation, conversion data was treated by the eq. (5-2) derived by Dumas *et. al.*[43]

$$\frac{1}{(1-x)(1+\alpha/\alpha_0)} = \frac{P_R}{(1-x)(1-\alpha/\alpha_0)} + (1-P_R) \quad \text{-----------------} \quad (5\text{-}2)$$

Here P_R is the stereoelective ratio for the second order monomer consumption kinetic scheme; α, α_0 and x have the same definition as in the first order kinetic scheme discussed above. The second order kinetic data are presented in Table 11. The plot shown in Figure 16 gave the following results for the data up to 84% conversion:

Table 11: Data for the second order kinetic behavior

sample Ref. #	Fraction of monomer polymerized (x)	$[\alpha]_D^{25}$ (C=24, benzene)	$\frac{1}{(1-x)(1+\alpha/\alpha_0)}$	$\frac{1}{(1-x)(1-\alpha/\alpha_0)}$
C-283-1	0.15	-0.072	1.16	1.15
C-283-2	0.28	-0.162	1.39	1.37
C-283-3	0.43	-0.434	1.80	1.74
C-252-5	0.48	-0.470	1.96	1.89
C-283-4	0.63	-0.629	2.77	2.64
C-283-5	0.71	-0.888	3.60	3.35
C-252-4	0.81	-1.180	5.56	5.05
C-283-6	0.84	-1.360	6.58	5.88
C-252-1	0.98	-1.940	54.33	46.31

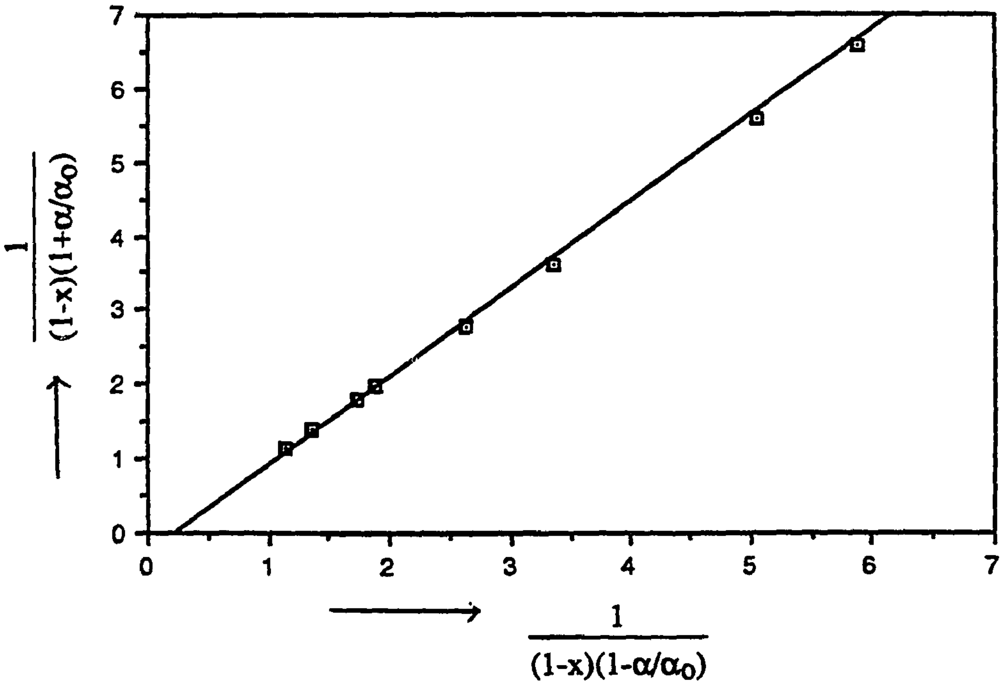


Figure 16. Second order kinetic plot for the data obtained by the polymerization of racemic propylene oxide with Al.DMBD-$ZnCl_2$ initiator; unreacted monomer was used as a solution in benzene (c=24 g/dL).

$C = 1\text{-}P_R = -0.196 = \text{Intercept}$

$M = P_R = 1.144 = \text{Slope}$

Correlation Coefficient =0.9998.

The average stereoelective ratio was calculated from the slope and intercept to be 1.17. The eq. (5-2) can be rewritten as

$$\frac{1}{(1-x)(1+\alpha/\alpha_0)} = \frac{P_R}{(1-x)(1-\alpha/\alpha_0)} + (1-P_R) \quad \text{---------------} \quad (5\text{-}2)$$

$$(\alpha/\alpha_0)^2\,(1-x) + (\alpha/\alpha_0)[\,P_R+1]\,/\,[\,P_R-1] + x = 0 \quad \text{---------------}(5\text{-}3)$$

One consequence of this kinetic law is the existence of a limiting value for the optical purity of unreacted monomer at complete conversion.[43] This limit (α/α_0) is equal to $(P_R-1)/(P_R+1)$, when x---> 1. This can be envisioned from eq. (5-3):

As x--->1, the eq. 5-2 can be written as

$$(\alpha/\alpha_0)[\,P_R+1]\,/\,[\,P_R-1] + 1 = 0 \quad \text{-------------------}(5\text{-}4)$$

$$\text{ie)}\ (\alpha/\alpha_0) = [\,P_R-1]\,/\,[\,P_R+1] \quad \text{-----------------}(5\text{-}5)$$

In this polymerization,

$$(P_R-1)/(P_R+1) = (1.17-1)/(1.17+1) = 0.08$$

At 98% conversion,

$$(\alpha/\alpha_0) = 1.94/24 = 0.08$$

$$\text{ie)}\ (\alpha/\alpha_0) = [\,P_R-1]\,/\,[\,P_R+1]$$

Consequently it appears that the polymerization of racemic PO with Al.DMBD-$ZnCl_2$ initiator system follows a second order kinetic scheme. A definite conclusion cannot be made as to whether the system follows a first or second order kinetic scheme due to the observed low stereoelectivity.

An attempt was made to calculate the theoretical values of the optical rotation of the recovered unreacted monomer, α, at various conversions for the first and second order monomer consumption schemes. The eq. (5-1) along with the stereoelective ratio, r_R of 1.06 was used to calculate the value of α for the first order monomer consumption. The stereoelective ratio, P_R, of 1.17 and $[\alpha_0]^{25}_{D}=$ 24.0°(c=24, benzene) were used to calculate the value of α for the second order monomer consumption. The second order kinetic equation (5-3) was rearranged to equation (5-6). A computer program was used to solve the quadratic eq. (5-6). The calculated results are

$$(1-x).\alpha^2 + \alpha_0 . [\,P_R +1] \,/\, [\,P_R-1].\,\alpha + x \,.\alpha_0^2= 0 \qquad (5\text{-}6)$$

$$A\alpha^2 + B\alpha + C=0 \qquad (5\text{-}7)$$

presented in Tables 12 and 13 for the first and second order kinetic schemes respectively. The plots of the experimental and theoretical values of the optical rotation of the unreacted monomer (α) as a function of polymer conversion (x) are presented in Figures 17a (first order kinetics) and 17b (second order kinetics) respectively. It appears from the Tables 12, 13 and Figures 17a and b, that the observed optical rotations are lower than the calculated values. The calculated value at 98% conversion corresponding to a first order kinetics scheme is -5.319. The observed specific rotation is

-1.940 suggesting that a first order kinetic is unsatisfactory. However, for a second order kinetic scheme, the calculated value (-1.842) and observed value (-1.940) are in better agreement than for the first order kinetic scheme. In fact, the calculation shows that the limiting value for the optical rotation of the recovered monomer is reached. The observed optical rotations up to 84% conversion are lower than the calculated values except satisfying the requirement for the limiting value. Therefore, caution should be made in these justification. However, the analysis indicate, how these data can be manipulated, if a better stereoelectivty is obtained.

Table 12: Calculated optical rotation for a first order monomer consumption.

Conversion,x	-ln(1-x)	$[\alpha]^{25}_{D}$	
		Calculated	Observed
0.10	0.11	-0.150	-
0.15	0.16	-0.218	-0.072
0.20	0.22	-0.300	-
0.28	0.33	-0.449	-0.162
0.43	0.56	-0.762	-0.434
0.48	0.65	-0.884	-0.470
0.63	0.99	-1.346	-0.629
0.71	1.24	-1.686	-0.888
0.81	1.66	-2.258	-1.180
0.84	1.83	-2.489	-1.360
0.90	2.30	-3.128	-
0.95	3.00	-4.080	-
0.98	3.91	-5.319	-1.940
0.99	4.61	-6.269	-
0.999	6.908	-9.395	-
0.9999	11.513	-15.658	-

Table 13: Calculated optical rotation for a second order monomer consumption[a,b].

Conversion,x	C=576x	A=1-x	$[\alpha]^{25}_{D}$	
			Calculated	Observed
0.10	57.60	0.90	-0.188	-
0.15	86.40	0.85	-0.282	-0.072
0.20	115.20	0.80	--0.376	-
0.28	161.28	0.78	-0.527	-0.162
0.43	247.68	0.57	-0.809	-0.434
0.48	276.48	0.52	-0.903	-0.470
0.63	362.88	0.37	-1.186	-0.629
0.71	408.96	0.29	-1.336	-0.888
0.81	466.56	0.19	-1.524	-1.180
0.84	483.84	0.16	-1.579	-1.360
0.90	518.40	0.10	-1.692	-
0.95	547.20	0.05	-1.786	-
0.98	564.48	0.02	-1.842	-1.940
0.99	570.24	0.01	-1.861	-
0.999	575.42	0.001	-1.878	-
0.9999	575.94	0.0001	-1.888	-

[a] $B=\alpha_0 \cdot [P_R + 1] / [P_R - 1] = 306.48$ was used in the calculation.
[b] A, B, C are defined in equations (5-6) and (5-7).

It should be noted that while the DMBD-diethyl zinc initiator system exhibited a higher stereoelectivity (r=2.8), our system appeared to be more reactive. A chiral initiator system aluminum tris(l-3-menthyloxide)-$ZnCl_2$ was not stereoelective in the polymerization of PO since the recovered monomer was optically inactive.[18]

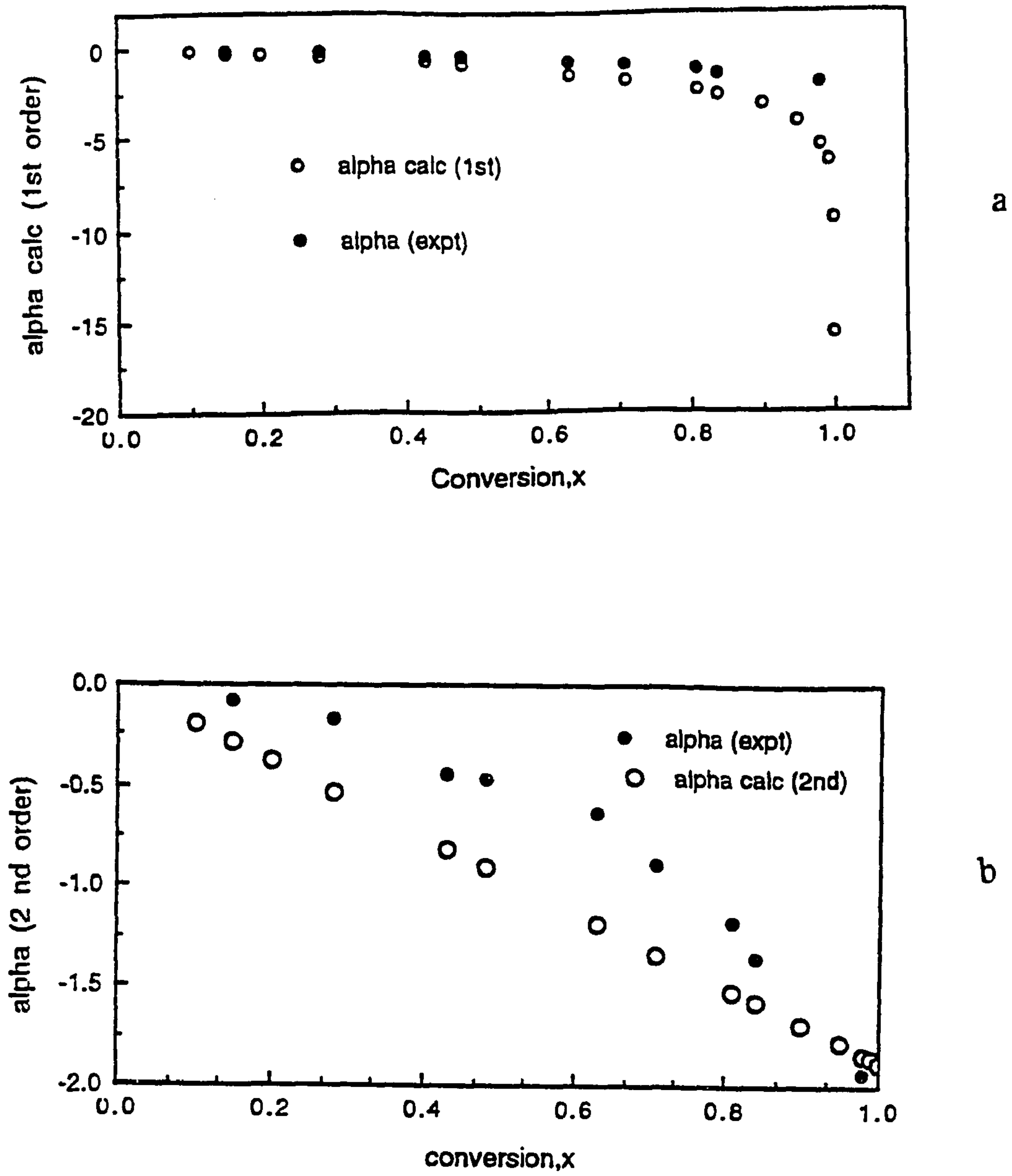


Figure 17. comparison of the calculated and observed optical rotation for (a) first order kinetics, and (b) second order kinetics.

The activity of the initiator and the corresponding polymer yield was found to depend on the manner in which the $ZnCl_2$ coinitiator was dried. Samples of $ZnCl_2$ which were weighed directly from a reagent bottle, transferred into a polymerization tube and then dried using thionyl chloride gave a less active initiator than samples which were predried, weighed, and further dried after transfer to a polymerization tube, as shown in Table 14.

Table 14: Check for Reproducibility in the Polymerization of Racemic Propylene Oxide[a]

Initiator				Optical rotation of the unreacted monomer	
Al.DMBD, mmol	$ZnCl_2$, mmol	mol %	Polymer yield, %	$[\alpha]_D^{25}$ (neat)	$[\alpha]_D^{25}$ (c = 24,benzene)
2.14	2.13[b]	0.96	85	-0.722	-
2.13	2.13[b]	0.98	85	-0.658	-
2.12	2.12[b]	0.98	81	-0.649	-
2.15	2.15[c]	0.94	96	-	-2.010
2.14	2.15c	1.08	95	-	-2.320
2.14	2.15c	0.88	95	-	-1.520

[a] Polymerization in bulk at 80°c for 36 hr.

[b] $ZnCl_2$ weighed and transferred into polymerization tube, then dried using thionyl chloride.

[c] $ZnCl_2$ predried with thionyl chloride, weighed and transferred into polymerization tube, then further dried with thionyl chloride.

The difference in initiator activity may be attributed to the moisture sensitivity of $ZnCl_2$ and to the actual amount of $ZnCl_2$ weighed and transferred in the two procedures.

The polymerization results were also found to depend on whether the coinitiator $ZnCl_2$ was used as an ether solution or dry solid. In these polymerizations, ether was removed by heating under vacuum. The initiator system is referred to as Al.DMBD-$ZnCl_2$(E). The results are presented in Table 15.

Table 15: Polymerization results of PO with Al.DMBD-$ZnCl_2$(E) (Al:Zn = 1:1 molar ratio) initiator at 80°C in bulk[a]

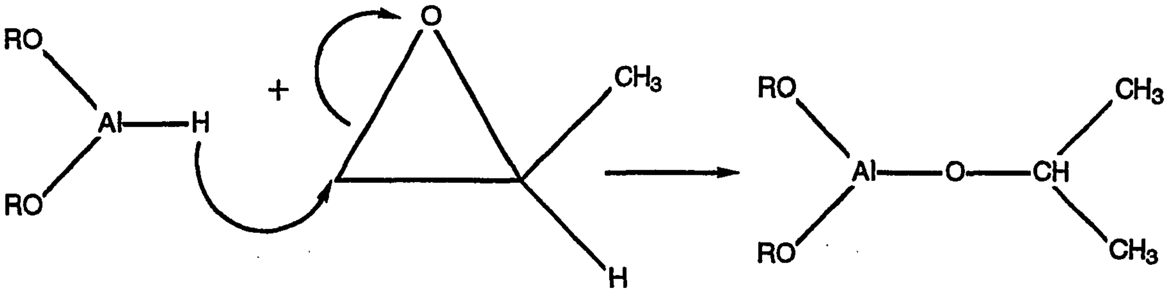
Reference #	Polymer Yield, %	Optical Rotation of Unreacted Monomer, $[\alpha]_D^{25}$ (neat)
C-217-1[b]	37	-0.378
C-217-2[b]	42	-0.434
C-217-10[b]	77	-0.570
C-217-3[c]	28	-0.148
C-222-2[c]	50	-0.245
C-222-1[c]	57	-0.198
C-222-3[c]	67	-0.154
C-217-4[c]	87	-0.965

[a] Polymerizations were carried out in bulk at 80°C with 1 mol% initiator for 36 h. $ZnCl_2$ was introduced as an ether solution and then removed by heating under vacuum.

[b] Aluminum alkoxide initiator component was Al.DMBD described in experimental section 4.4 (p60).

[c] Aluminum alkoxide initiator component was Al.DMBD* described in experimental section 4.4 (p62).

The results in Table 15 indicate that the polymerization by this method are irreproducible. It should be noted that the $ZnCl_2$ is very important coinitiator for this polymerization as previously noted. Heating the ether solution of $ZnCl_2$ which is a Lewis acid-base complex, leads to the destruction the active initiator. The exact amount and nature of the $ZnCl_2$ coinitiator is also not known in individual runs. These factors can explain these irreproducible results. With the Al.DMBD*-$ZnCl_2$ system, it was found that the initiator was almost dissolved in the monomer when the sealed polymerization tube was brought from liquid nitrogen temperature to room temperature. This is probably due to the presence of active aluminum hydride in the Al.DMBD* which may have reacted with PO as shown in equation (5-8):



---------------- (5-8)

Such reactions have been reported between AlH_3 and PO.[80] The above reaction can be confirmed by identifying an isopropyl end group in the polymer chain. Unfortunately, no ^{13}C-NMR spectrum was obtained for these samples due to their irreproducible results.

5.2 Fractionation of Poly(propylene oxide) PPO

PPO samples obtained with Al.DMBD-$ZnCl_2$ were fractionated into acetone soluble and insoluble fractions at -30°C as described in the Experimental Section. Approximately 10% of the polymer was found to be insoluble. On the other hand PPO obtained in the absence of $ZnCl_2$ was soluble in acetone at -30°C. Number- average molecular weights of the acetone soluble fractions were determined by vapor pressure osmometry and optical rotations of acetone insoluble fractions were measured in benzene as well as in chloroform solutions. The results are summarized in Table 16. The negative rotations in benzene and positive rotations in chloroform for the acetone insoluble fractions as well as the negative rotations of unreacted monomer indicate that R-(+)-PO is preferentially incorporated into the polymer, with retention of configuration at the chiral centers. The different signs of rotation of optically active PPO in benzene and in chloroform was first noted by Price and Osgan.[50] This interesting solvent effect has been subsequently studied and attributed to changes in the order of atom polarizabilities caused by specific solvent-solute interactions.[81,82] The observation of change in sign of optical rotation in benzene and chloroform of our samples of acetone insoluble isotactic PPO indicates that the observed optical rotation is a property of the polymer chains and is not due to the presence of chiral end groups. Such optical activity in the polymer has been observed due to chiral end groups in the polymerization of PO with aluminum tris(l-3-menthyloxide)-$ZnCl_2$ initiator system.[18] As expected, the optical rotation of the polymer in our system decreases with the extent of polymerization(Table 9) due to the incorporation of the of opposite enantiomer in the latter part of the polymerization.

Table 16: Fractionation of Poly(propylene oxide)

Polymer yield, %	Acetone insoluble fraction, %	M_n of acetone soluble fraction[a]	Optical activity of acetone insoluble $[\alpha]^{25}_{D}$ (c=1, benzene)	Optical activity of acetone insoluble $[\alpha]^{25}_{D}$ (c=1, $CHCl_3$)
43.4	6.2	1070	-3.2	1.6
48.0	11.7	910	-3.0	1.5
63.0	9.4	1490	-2.8	1.3
71.2	9.2	1760	-1.9	1.3
81.1	10.1	1760	-1.5	1.0
84.0	8.8	1720	-1.6	0.8
84.6	9.3	1730	-2.0	0.8
98.0	9.4	1370	-1.0	-

[a] M_n determined by vapor pressure osmometry.

5.3 Characterization of Poly(propylene oxide) (PPO)

5.31 Infrared Spectroscopic Characterization of PPO Fractionation Products

FT-IR spectra of acetone soluble and insoluble fractions of PPO prepared using the Al.DMBD-$ZnCl_2$ are shown in Figures 18 a and b respectively. For comparison, FT-IR spectrum of a PPO sample purchased from Aldrich Chemical Co. is also included in Figure 18c. The Aldrich sample is a liquid and soluble in acetone. The characteristic frequencies are tabulated in Table 17 and some tentative assignments are also shown in the Table. The strongest absorbance in all three samples were due to the C-O-C asymmetric stretching of the ether linkages at 1108 cm^{-1}.[76] A broad, weak absorbance was also found in all the samples ~ 3500 cm^{-1} due to stretching vibration of the terminal OH- groups. All three samples exhibited similar absorbances except additional bands were seen at 1478, 1331, 1242, and 922 cm^{-1} for the acetone insoluble fraction. The Aldrich sample is expected to contain hydroxy terminals arising from the NaOH initiator. The similarities of the three spectra indicate that chlorine or *t*-butyl end groups derived from the Al.DMBD-$ZnCl_2$ initiator are not detected in the IR spectra of our PPO samples.

Table 17 : Infrared spectroscopic data of acetone soluble, insoluble and an Aldrich PPO soluble in acetone[a,b]:

Aldrich	Acetone Soluble	Acetone Insoluble	Assignments
3467	ca 3500	ca. 3500	O-H str
2974	2970	2970	CH_3 str
2934	2932	ca. 2930	CH_2 str
2896	2897	2886	CH str
2872	2870	2874	CH_3 str
-	-	1478	CH_3 bend
1456	1454	1454	CH_3 bend
1374	1373	1377	CH_3 bend
1345	1346	1346	CH_2 bend
-	-	1331	
1297	1296	1296	
1260	1260	ca. 1260	
-	-	1242	crystalline-?
1108	1107	1107	C-O-C asym str.
-	-	1038	
1014	1015	1015	
929	930	934	
-	-	922	crystalline-?
866	866	868	
837	837	833	

[a] Most of the assignments were made according to reference 76.

[b] The additional absorbances for the crystalline fraction was also reported in reference 83.

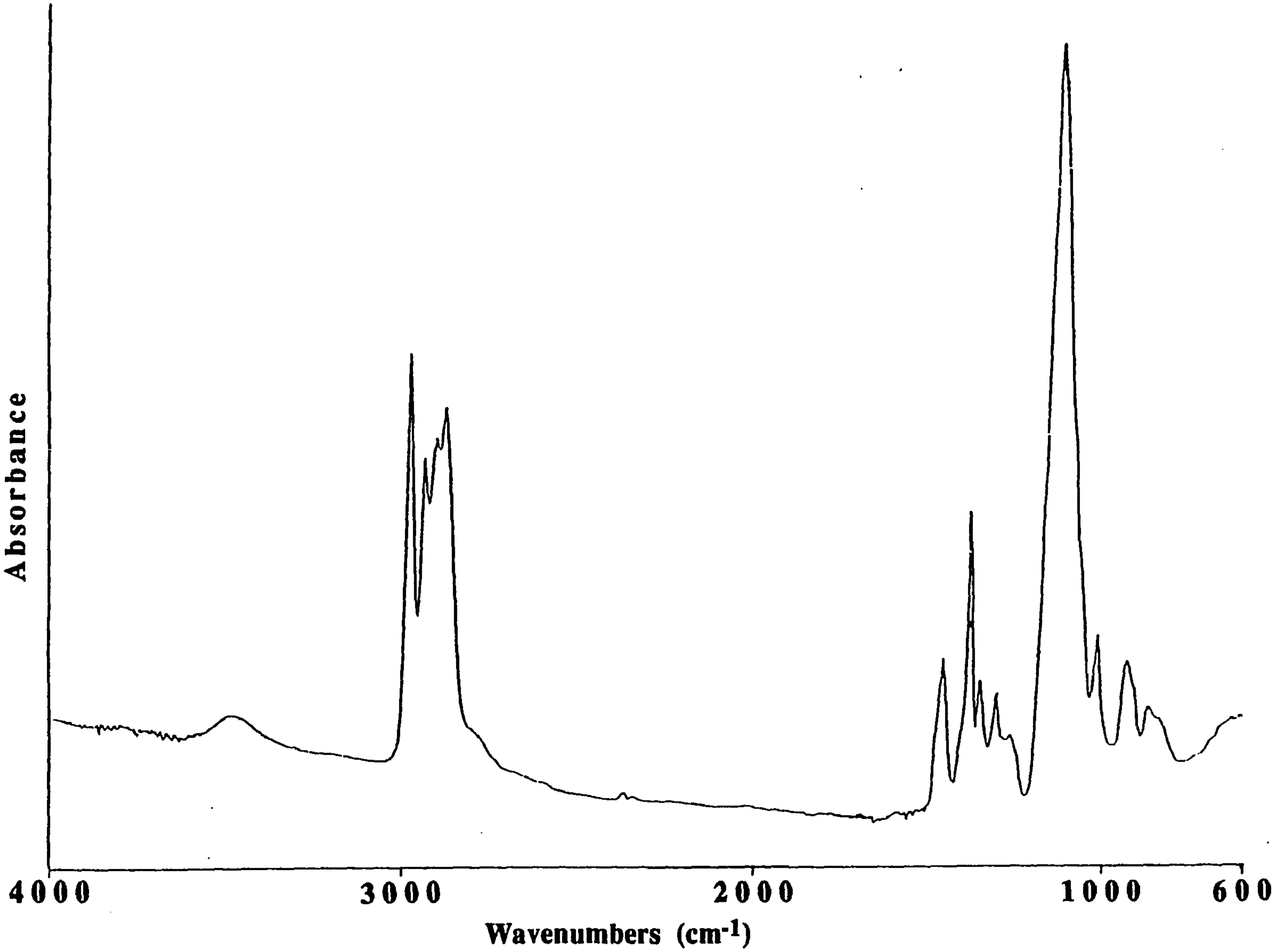


Figure 18a. FT-IR spectrum of acetone soluble PPO (film cast from benzene) prepared with Al.DMBD-ZnCl$_2$ at room temperature.

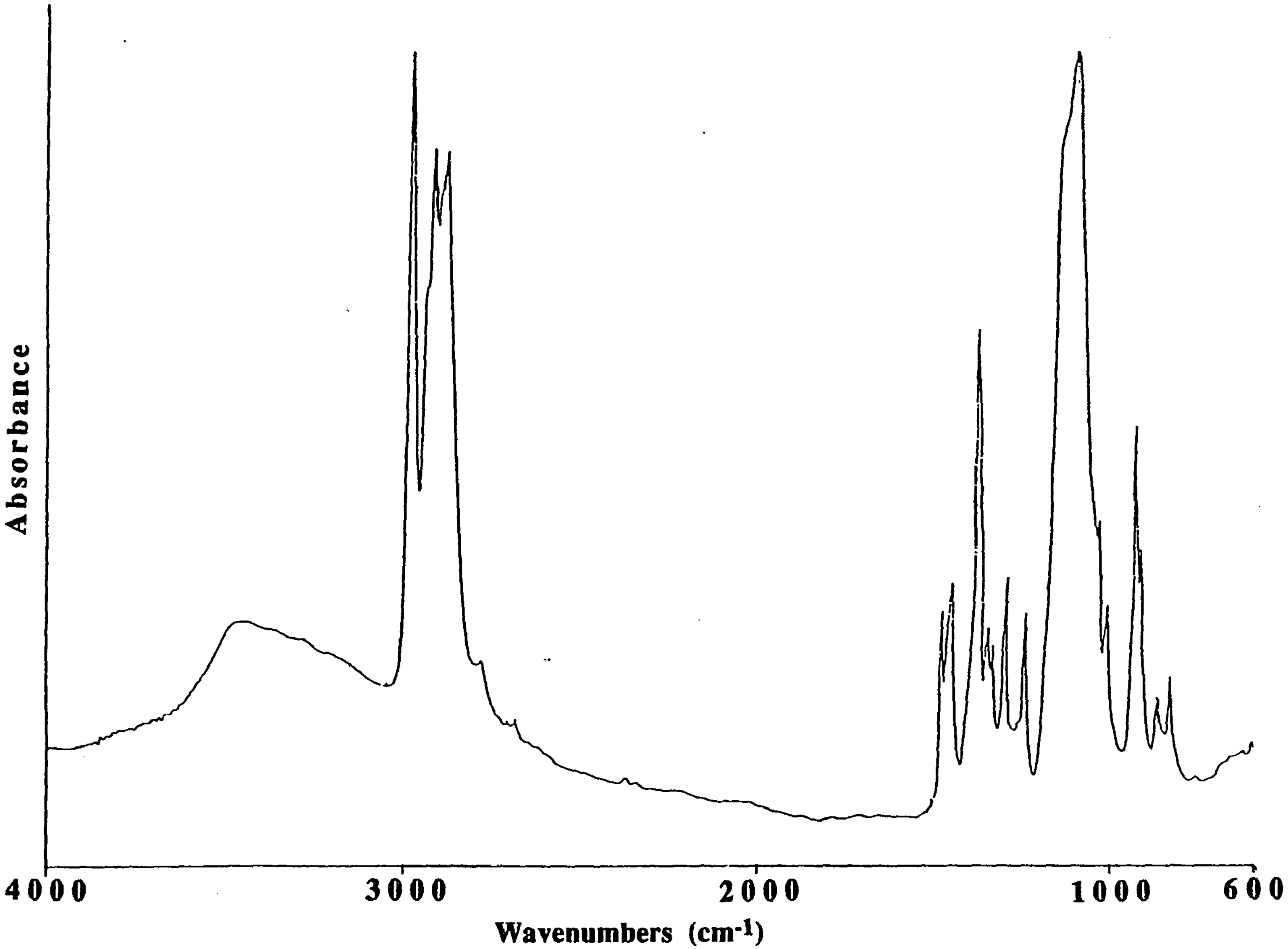


Figure 18b. FT-IR spectrum of acetone insoluble PPO (film cast from benzene) prepared with Al.DMBD-$ZnCl_2$ at room temperature.

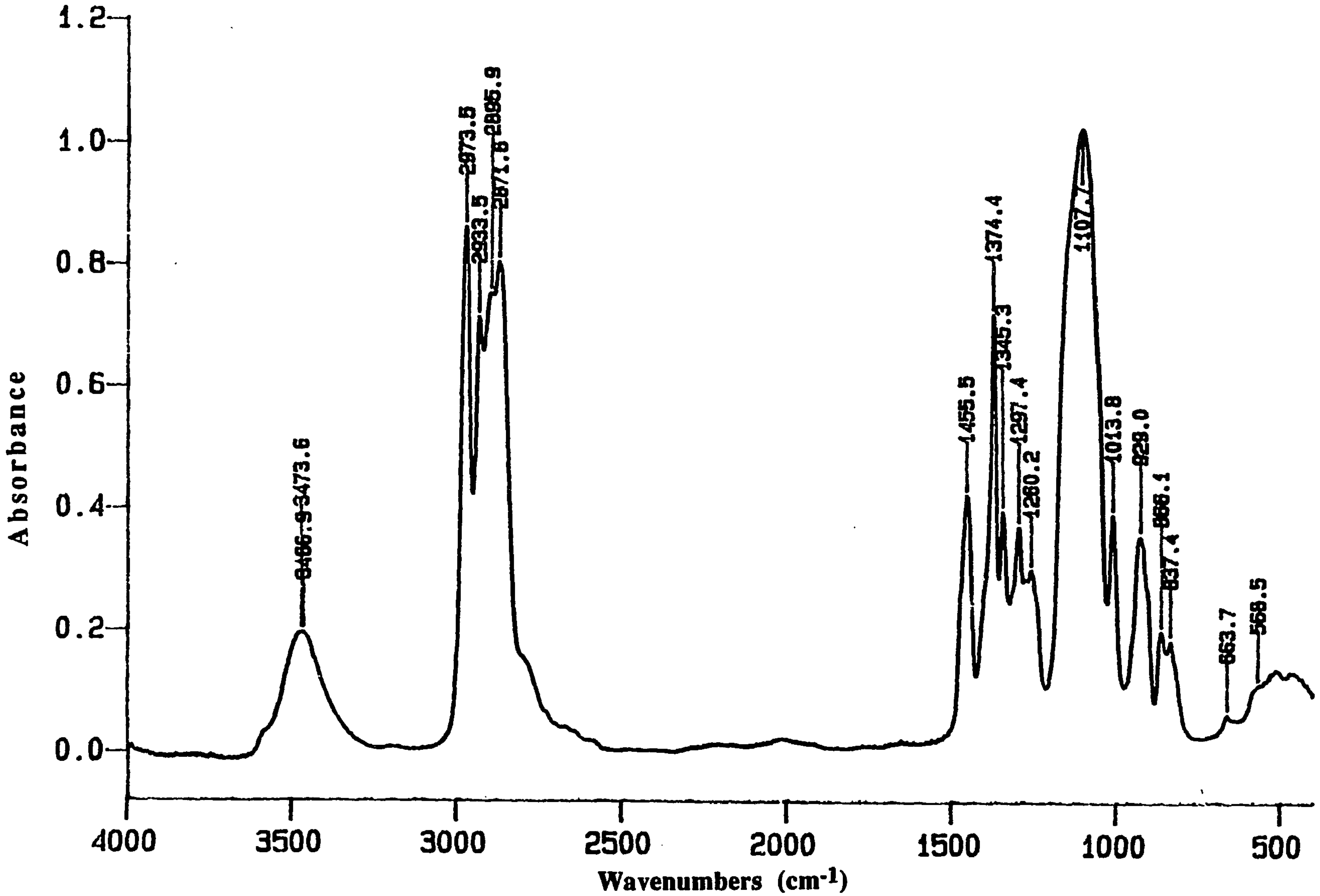
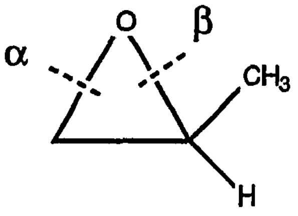


Figure 18c. FT-IR spectrum of acetone soluble PPO (Aldrich, film cast from benzene).

5.32 Stereochemistry and Head-to-Tail Structure.

The 50.3 MHz ^{13}C-NMR spectrum of acetone insoluble PPO is shown in Figure 19. Singlets at 75.8, 73.9, and 17.8 ppm are assigned to isotactic methine, methylene, and methyl carbons, respectively.[58] The acetone insoluble PPO fraction is therefore highly isotactic head-to-tail (h,t) polymer. The ^{13}C-NMR spectrum of an amorphous fraction, soluble in acetone at -30°C, prepared with Al.DMBD-$ZnCl_2$ initiator is shown in Figure 20. Three major signals at 75.8, 75.7, and 75.5 ppm are assigned to the isotactic, heterotactic, and syndiotactic triads, respectively, of the methine carbon in the polymer chain.[58] Two signals at 73.7 and 73.5 ppm are assigned to meso and racemic diads, respectively, of the methylene carbon. The peak at 17.7 ppm is assigned to the methyl carbon.[58] The relative areas for the various methine and methylene carbon signals indicate the acetone soluble polymer is essentially atactic although isotacticity may predominate over syndiotacticity.

These signals arise from regiospecific opening of the epoxide ring resulting in regular h,t linkages. Minor signals seen in the 73 to 76.5 ppm region are attributed to head-to-head (h,h) and tail-to-tail (t,t) linkages arising from both α- and β-ring opening of the epoxide (structure i),[58,59] or from units next to chain ends.



i

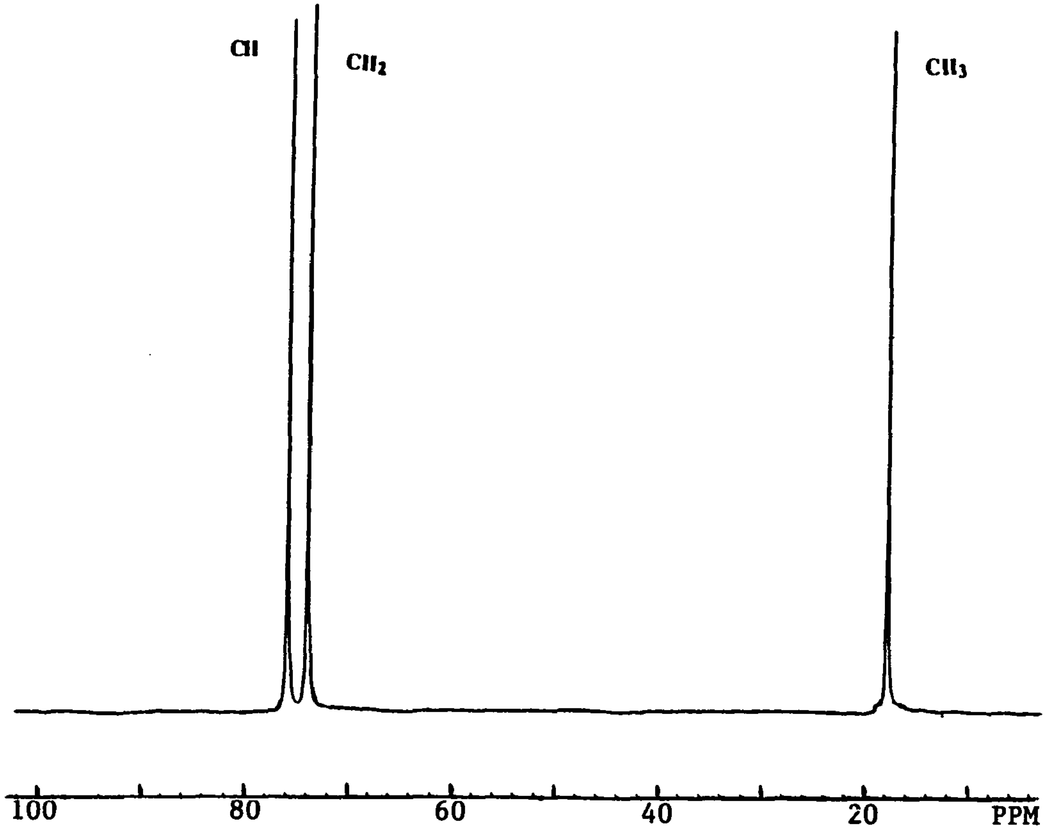


Figure 19. 50.3 MHz ^{13}C-NMR spectrum of acetone insoluble PPO prepared with Al.DMBD-ZnCl$_2$ initiator. Conditions: 30° pulse angle; 24°C; 29716 acquisitions.

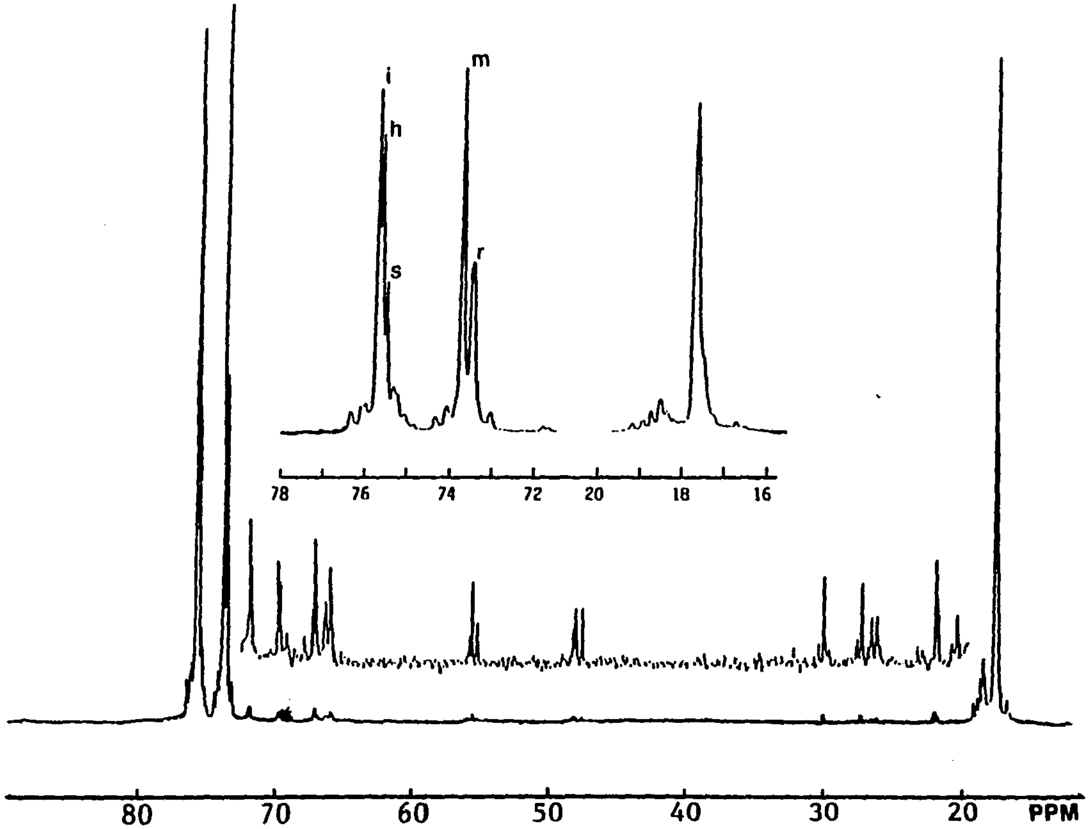


Figure 20. 50.3 MHz ^{13}C-NMR spectrum of acetone soluble PPO prepared with Al.DMBD-$ZnCl_2$ initiator. Conditions: 30° pulse angle; 24°C; 16365 acquisitions.

Figure 21 shows the ^{13}C-NMR spectrum of PPO prepared with the initiator Al.DMBD in the absence of $ZnCl_2$. A considerably larger proportion of irregular (h,h) and (t,t) polymer structures is evident compared with the amorphous polymer prepared with Al.DMBD-$ZnCl_2$ (Fig. 20). The lack of regioselectivity is characteristic of cationic polymerization of epoxides. The ^{13}C-NMR spectrum (Fig. 21) is similar to the spectra of PPO prepared with cationic initiators such as aluminum isopropoxide (AIP) and known to contain (h,h) and (t,t) linkages.[58] The effect of $ZnCl_2$ on Al.DMBD is similar to its effect on AIP[30,58] in speeding up the polymerization , giving a lower proportion of irregular linkages and producing isotactic polymer by a coordination process.[60]

A DEPT spectrum (CH_2 negative, CH, CH_3 positive) of the methylene and methine region for PPO prepared with the Al.DMBD initiator is shown in Figure 22. Methylene carbon signals are seen which are markedly deshielded relative to methylene carbon signals in regular (h,t) linkages. Peaks appearing at 75.93, 76.03, 76.23 and 76.28 ppm in the normal spectrum (Fig. 21, see Table in the insert) are seen to be CH_2 peaks in the DEPT spectrum. Methylene carbon signals in normal (h,t) main chain linkages appear at 73.41 and 73.66 ppm (racemic and meso diads, respectively) in Fig.21. The isotactic CH triad peak appearing at 75.68 ppm in Fig. 21 is seen in the DEPT spectrum to include underlying CH_2 peaks resulting in an apparent increased intensity of the isotactic CH peak. Other CH carbon signals in regular (h,t) main chain linkages appear at 75.45 and 75.58 ppm (syndiotactic and heterotactic triads, respectively) in Fig. 21. A peak

Peak Number	Chemical Shift (ppm)	Assignment
1	76.28	CH_2 (h.h, t.t)
2	76.23	CH_2 (h.h, t.t)
3	76.03	CH_2 (h.h, t.t)
4	75.93	CH_2 (h.h, t.t)
5	75.68	?
6	75.58	CH (h.t, syndio)
7	75.45	CH (h.t, hetero)
8	75.30	?
9	75.20	?
10	74.28	CH_2 (h.h, t.t)
11	74.03	CH_2 (h.h, t.t)
12	73.84	CH (h.h, t.t)
13	73.66	CH_2 (h.t)
14	73.41	CH_2 (h.t)
15	73.04	CH (h.h, t.t)

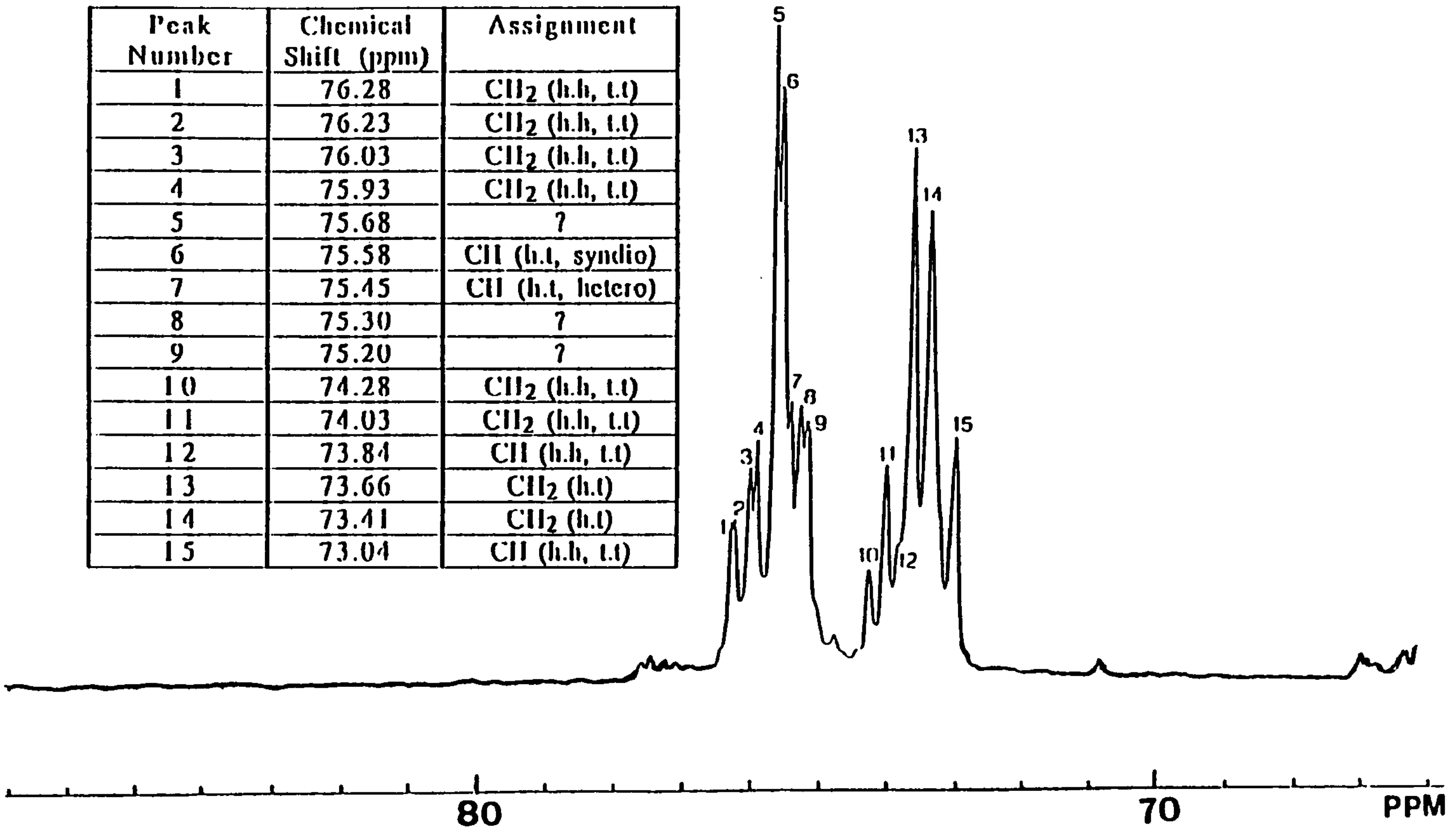


Figure 21. 50.3 MHz ^{13}C-NMR spectrum of PPO prepared with Al.DMBD initiator. CH and CH_2 region. Conditions: 30° pulse angle; 24°C; 3772 acquisitions; 10s relaxation delay.

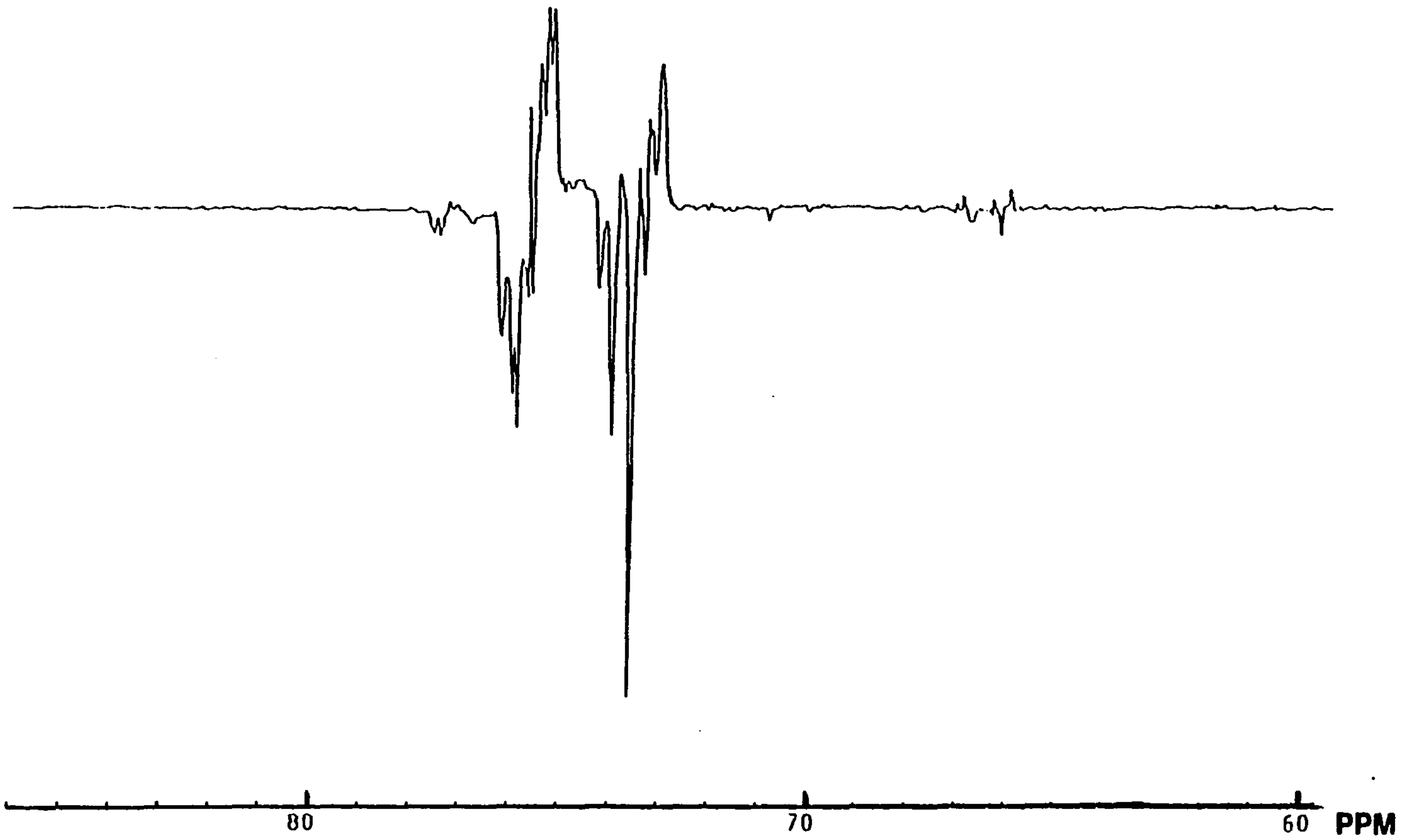


Figure 22. 50.3 MHz ^{13}C-NMR DEPT spectrum of PPO prepared with Al.DMBD initiator. CH (positive) and CH_2 (negative) region.Conditions: 30° pulse angle; 24°C; 3772 acquisitions; 10s relaxation delay.

at 73.04 ppm corresponds to a shielded CH signal as shown by the DEPT spectrum.

The racemic CH_2 diad peak at 73.41 ppm in the normal spectrum includes an overlapping CH peak as revealed in the DEPT spectrum. Thus the apparent intensities of the main chain (h,t) isotactic CH triad and racemic CH_2 diad peaks appear exaggerated.

The appearance of the various signals can be envisioned by considering the number and type of α, β, and γ substituents for these methine and methylene carbons. The various types of substituents are shown in Table 18 for the methine and methylene carbons in a h.t, h.h, and t.t linkages shown in Figure 23:

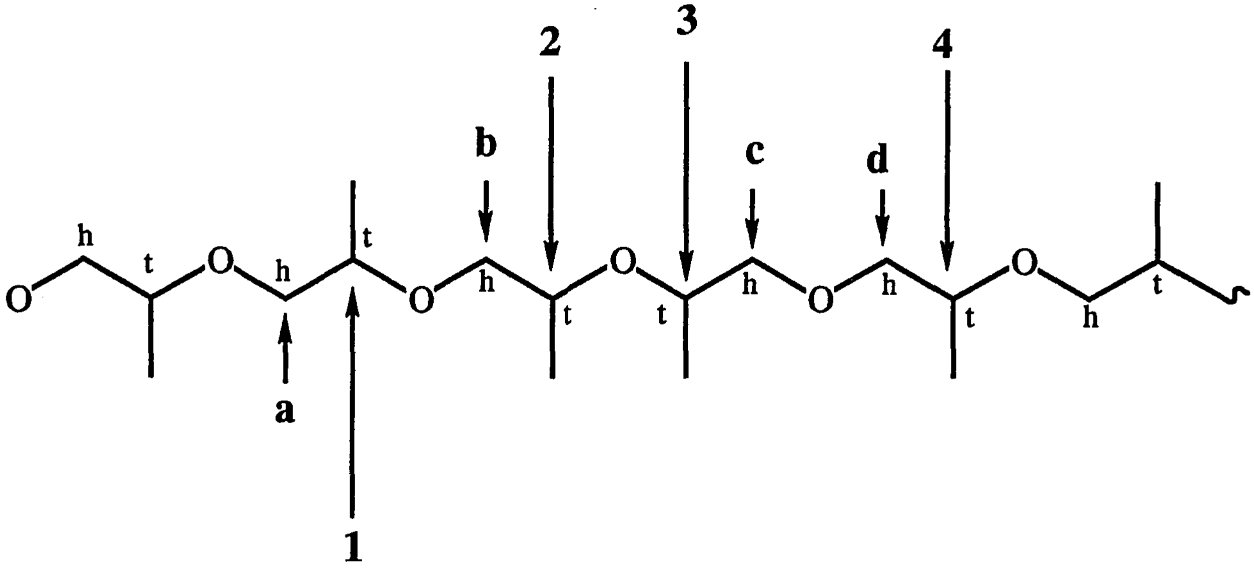


Figure 23. Poly(propylene oxide) with head to tail, head to head, and tail to tail linkages.

Table 18 : Substituents for CH and CH_2 carbons in h.t, h.h and t.t linkages in the PPO main chain.

Carbon Type	Substituents		
	α	β	γ
$-\overset{a}{CH_2}-$ (h.t)	O, CH	O, CH, CH_3	$2CH_2$,CH_3
$-\overset{b}{CH_2}-$	O, CH	O, CH, CH_3	CH, CH2, CH_3
$-\overset{c}{CH_2}-$ (t,t)	O, CH	O, CH_2, CH_3	2CH
$-\overset{d}{CH_2}-$ (t,t)	O, CH	O, CH_2, CH_3	CH, CH_2
$-CH^1-$ (h.t)	O, CH_2, CH_3	O, CH_2	2CH
$-CH^2-$ (h.h)	O, CH_2, CH_3	O, CH	CH, CH2, CH_3
$-CH^3-$ (h,h)	O, CH_2, CH_3	O, CH	$2CH_2$,CH_3
$-CH^4-$	O, CH_2, CH_3	O, CH_2	CH, CH_2

The ^{13}C-NMR chemical shift of a particular carbon is affected by the number and types of α, β, and γ substituents. The α and β substituents have deshielding effects and the γ substituent is shielding.[84] These carbon substituents (CH, CH_2, CH_3) gives the same contribution to the chemical shift of a particular carbon irrespective of its presence at α or β carbon. Consequently, all the methine and methylene carbons give rise to the same chemical shift by their α and β substituents. The difference occurs only on their γ substituents which is shielding. The γ substituent contributes ~1.5 ppm shielding effect when it is in a gauche conformation to the particular carbon in question.[76] For a first approximation, CH, CH_2, and CH_3 groups contribute equally to the shielding effect. Accordingly, -$\overset{a}{CH_2}$- (h.t, γ = 2 CH_2, and CH_3) and -$\overset{b}{CH_2}$- (γ = CH, CH_2, and CH_3) are more shielded than the -$\overset{c}{CH_2}$- (t.t, γ = 2 CH) and -$\overset{d}{CH_2}$- (t.t, γ = CH and CH_2).

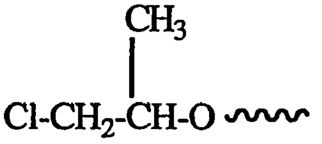
Similarly, -CH^2- (h.h, γ = CH, CH_2, and CH_3) and -CH^3- (h.h, γ = 2 CH2 and CH_3) are more shielded than -CH^1- (h.t, γ = 2 CH) and -CH^4- (γ = CH and CH_2). Overall, -$\overset{a}{CH_2}$- ((h.t), -$\overset{b}{CH_2}$-, -CH^2- (h.h), and -CH^3- (h.h) are more shielded than -$\overset{c}{CH_2}$- (t.t), -$\overset{d}{CH_2}$- (t.t), -CH^1- (h.t), and -CH^4-.

Within these two sets, the exact contribution of the shielding effect of γ substituent is dependant on the fraction of molecules in the gauche conformation. Such calculation needs information about the rotational isomeric states (RIS) models for the polymer in question.[84] This is beyond the scope of this work. The assignments and overlapping of CH and CH_2 peaks in regioirregular sequences and chain end structures of PPO have recently been discussed by Schilling and Tonelli.[56]

5.33 Identification of End Groups in PPO

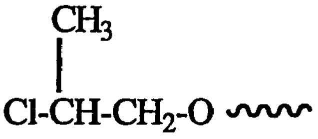
End groups derived from the $ZnCl_2$ coinitiator are incorporated into the polymer chain during the polymerization process. Two groups of signals at 48 and 55 ppm seen in the spectrum of acetone soluble PPO prepared with Al.DMBD-$ZnCl_2$ initiator (Fig. 20) are absent in the spectrum of PPO prepared without $ZnCl_2$ coinitiator (Fig.

21). No trace of the signals is evident in the latter spectrum on expansion and enlargement of this region. However, these signals appear in a spectrum of amorphous PPO prepared with an AlP-$ZnCl_2$ (1:1 molar ratio) initiator (Fig. 24). These two sets of signals are assigned to the chlorine containing end group structures ii and iii. On the basis of a DEPT spectrum (Fig. 25) the signals at 48 ppm are assigned to the CH_2 carbon of ii and the peaks at 55 ppm are assigned to the CH carbon of iii. The assignment of the 48 ppm signals is in agreement with that made by Aida *et al.* for the same end group in PPO prepared with a tetraphenylporphine-diethylaluminum chloride initiator.[31]



$Cl\text{-}CH_2\text{-}\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}}H\text{-}O\sim$

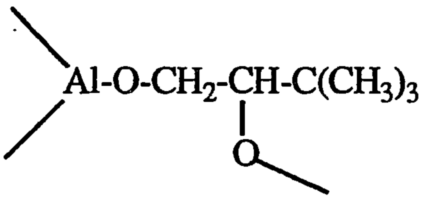
ii



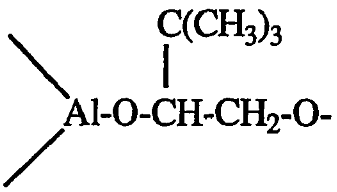
$Cl\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{-}CH_2\text{-}O\sim$

iii

The Al.DMBD initiator contains alkoxyaluminum fragments corresponding to structures iv and v. Alkoxy end groups derived from DMBD can be incorporated into the polymer. Vandenberg[63] has

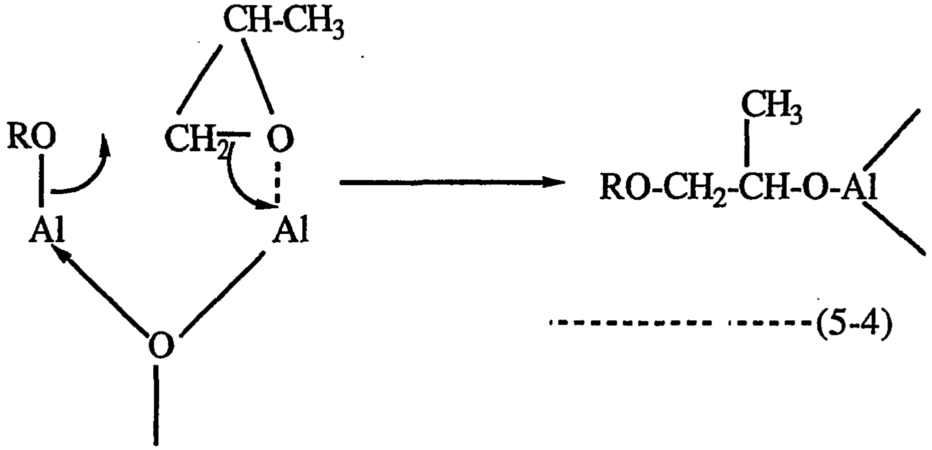


iv



v

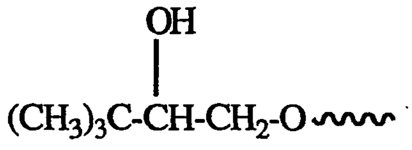
pointed out that the catalytic species in coordination polymerization must contain at least two metal atoms in order to accommodate the observed inversion of configuration in the ring opening propagation step (eq. 5-9).



..................(5-4)

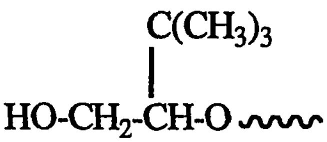
In eq. (5-9) the alkoxy moiety -OR may be the growing polymer chain or a DMBD derived group shown in structures xix and xx. Furthermore, in the presence of the coinitiator $ZnCl_2$, zinc atoms may be involved in the catalytic species.[60]

Cationic polymerization processes are possible, particularly in the absence of coinitiator $ZnCl_2$. Termination involving combination of a propagating oxonium ion with an alkoxy group derived from iv or v present as gegenion is a possibility.[4] Based on these considerations alkoxy end groups corresponding to structures iv and v are possible.



$(CH_3)_3C\text{-}\overset{OH}{CH}\text{-}CH_2\text{-}O\sim\sim$

vi

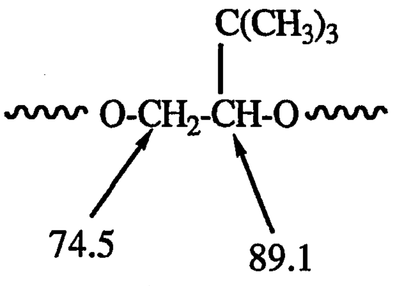


$HO\text{-}CH_2\text{-}\overset{C(CH_3)_3}{CH}\text{-}O\sim\sim$

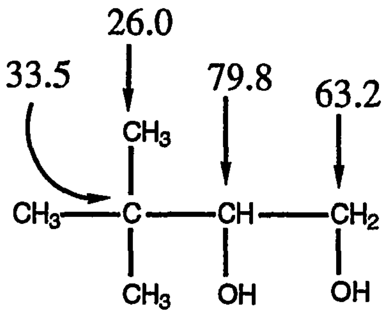
vii

The presence of alkoxy end groups is suggested by signals in the vicinity of 26 ppm in the ^{13}C-NMR spectrum of amorphous PPO (Fig. 20) since the methyl carbon chemical shift of the diol DMBD appears at 26 ppm. Furthermore, these signals are not present in the spectrum of amorphous PPO produced by AIP-$ZnCl_2$ (Fig. 24) although other end group signals are present.

The end group corresponding to structure vii could be expected to show a methine carbon signal at 89 ppm. This is based on the corresponding methine signal reported for poly(t-butyloxirane) (viii).[82] It may be noted that the conversion of an alcohol (-OH) substituent to an ether (-OR) functional group causes a deshielding effect on an α-carbon of approximately 10 ppm.[76] This effect can be seen in a comparison of the chemical shifts of the CH_2 carbon and CH carbon in DMBD (ix) at 63.2 ppm and 79.8 ppm respectively with those shown in poly(t-butyloxirane) (viii).



viii



ix

On expansion and amplification of the 78 to 108 ppm region of the spectrum shown in Figure 20, no signal is seen near 89 ppm. A weak signal at 34.68 ppm is assigned to the quaternary carbon of the

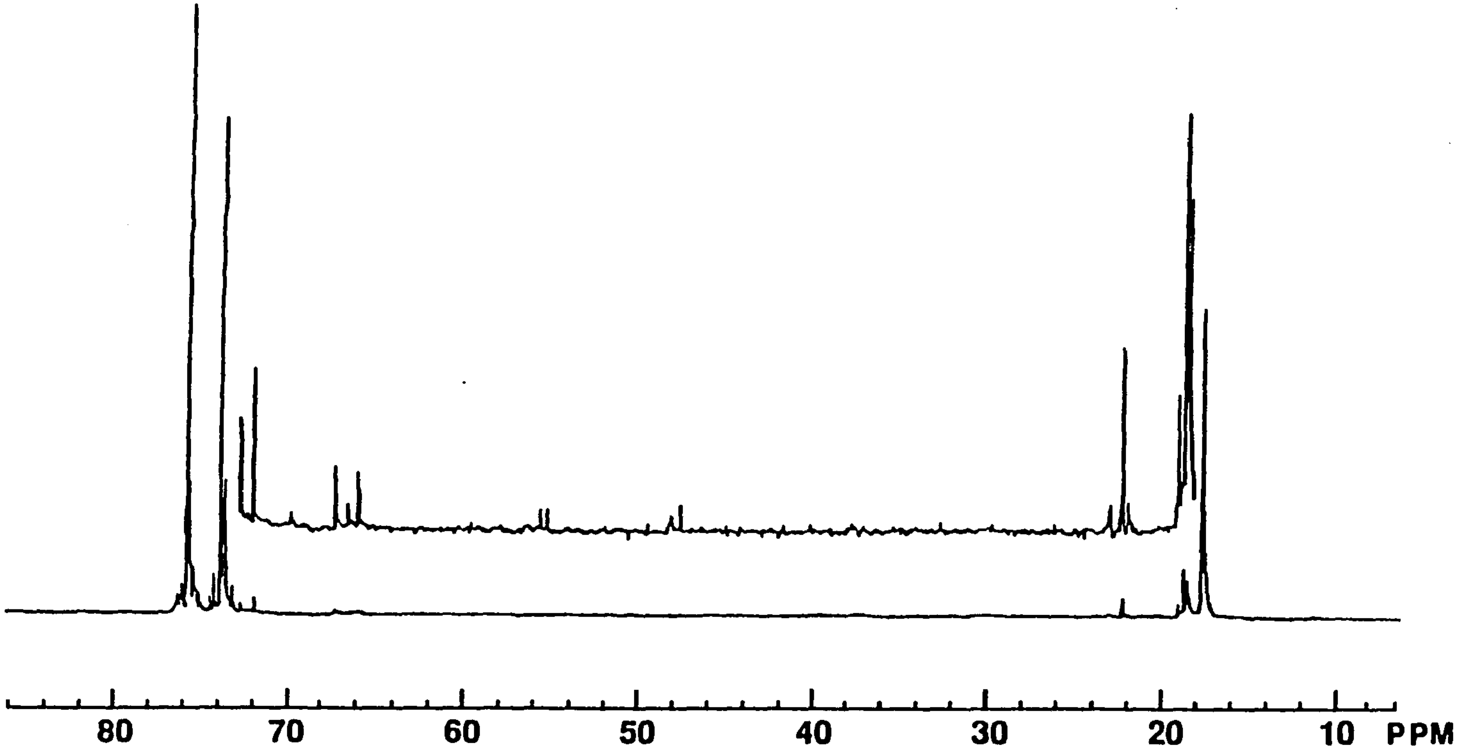


Figure 24. 50.3 MHz ^{13}C-NMR spectrum of PPO prepared with AlP-$ZnCl_2$ initiator (Al:Zn= 1:1 molar ratio). Conditions: 30° pulse angle; 24°C; 36175 acquisitions.

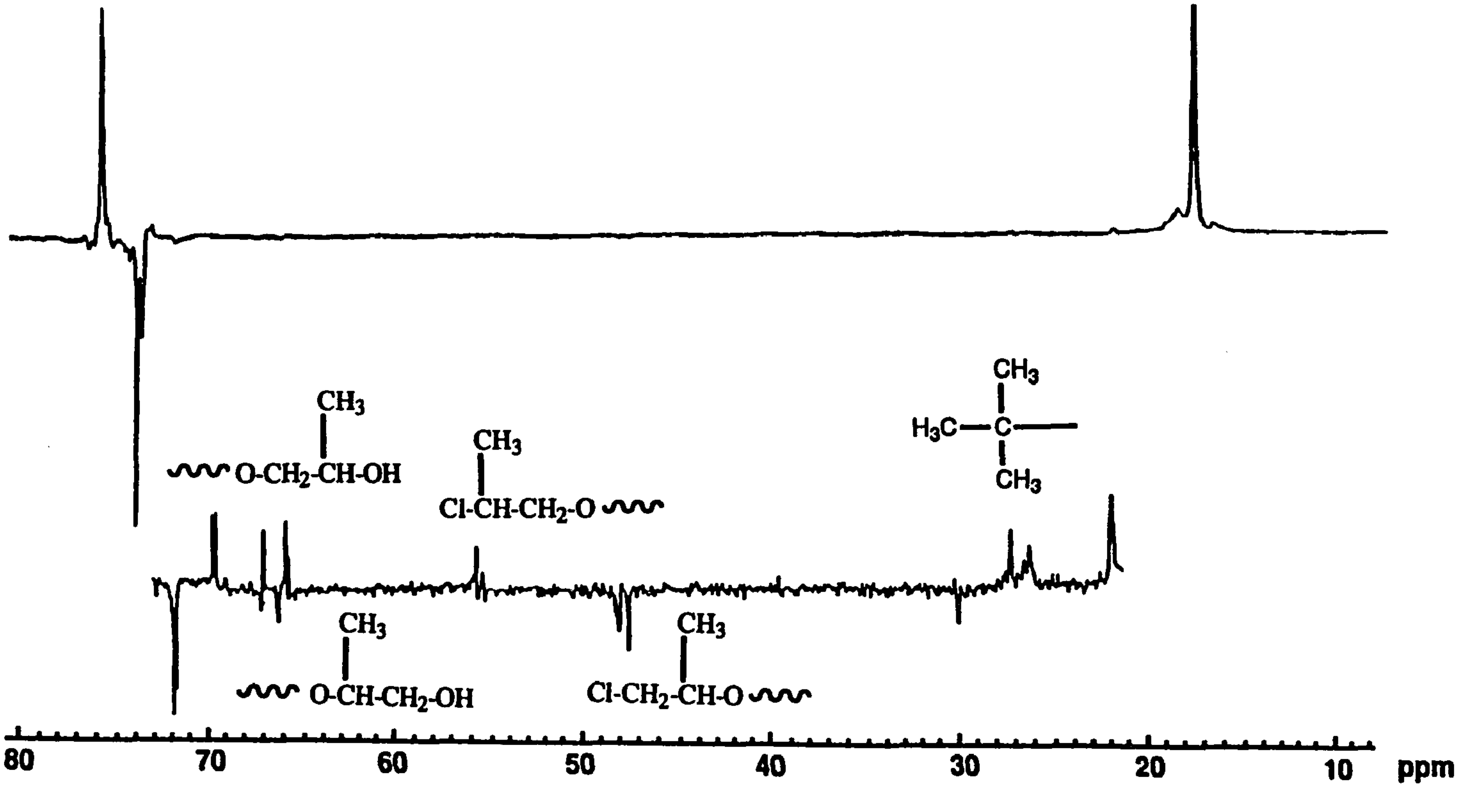


Figure 25. 50.3 MHz ^{13}C-NMR spectrum (DEPT) of acetone soluble PPO prepared with Al.DMBD-ZnCl$_2$ initiator (Al:Zn= 1:1 molar ratio).

t-butyl group. Signals are present in the 73-79 ppm region in Figures 20 and 21 may correspond to the CH_2 carbon in structure vi. Based on these considerations it appears unlikely that the end group of structure vii is present in the polymer. Based on the quantity of hydrogen evolved in the preparation of Al.DMBD, both types of alkoxy group iv and v are assumed to be present in the initiator. Alkoxy group transfer then occurs preferentially at an initiator site corresponding to structure iv rather than v, presumably due to steric hindrance in the latter neopentyl type structure.

The ^{13}C-NMR (75.45 MHz) spectrum of the acetone insoluble PPO prepared at room temperature is shown in Figure 26 (a and b). A signal at 88.4 ppm assignable to the neopentyl type structure (v) is seen in this sample. In addition, there are peaks at 48 and 55 ppm which are already assigned to the chlorine containing end groups ii and iii respectively. The signal due to the t-butyl end group at 26 ppm is also seen in this sample. It should be noted that end groups are not detected in the ^{13}C-NMR(50.3 MHz) spectrum of the acetone insoluble PPO prepared at 80°C (Fig.19). This is due to the sensitivity of the instrument operating at 75.45 MHz. The identification of both chlorine and alkoxy end groups suggest that the isotactic chain propagation occurs not only at the aluminum atom but also at the zinc atom. It should be noted that Jedlinski *et al.*[60] reported that isotactic propagation occurs at the aluminum alkoxy moiety rather than at the zinc alkoxy moiety in the polymerization of chlorophenylglycidyl ethers with aluminum isopropoxide-$ZnCl_2$ (1:1 molar) initiator system.

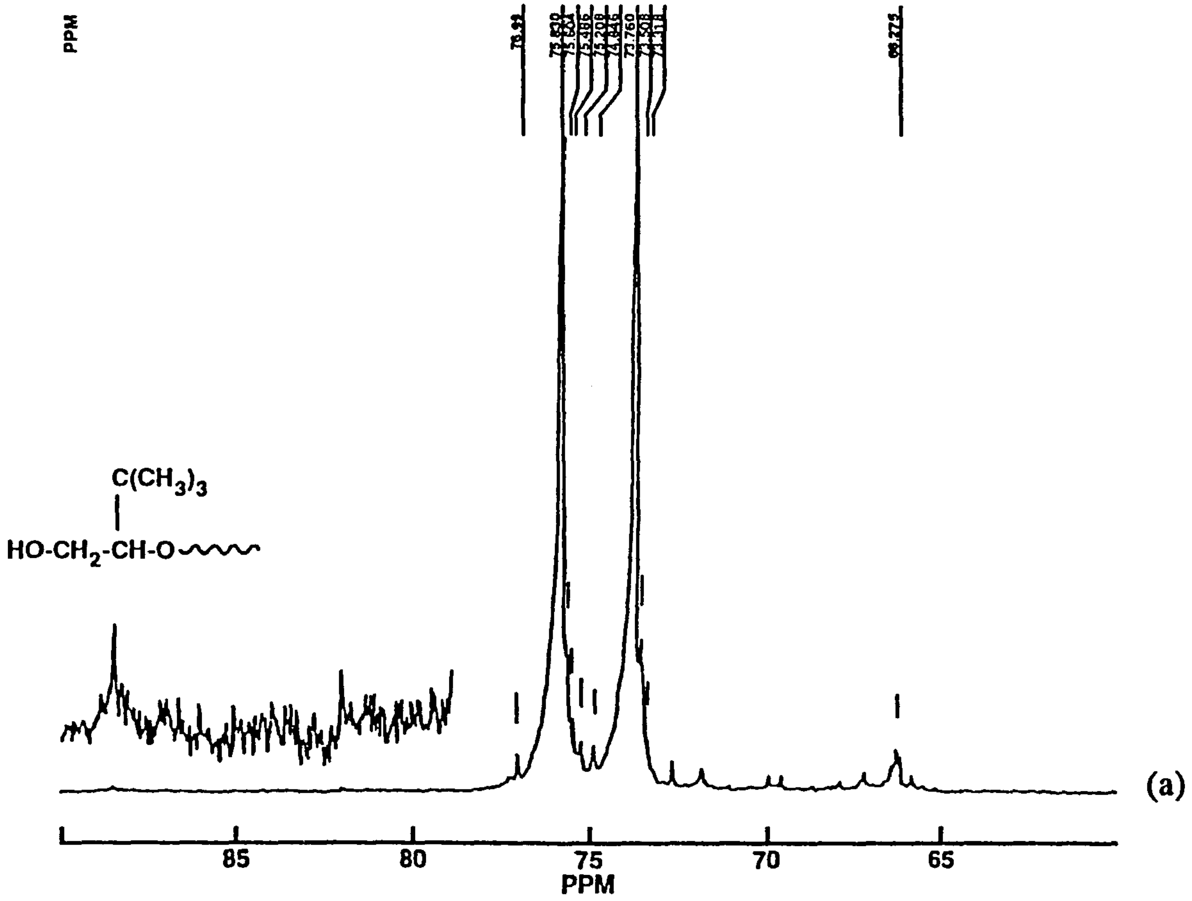


Figure 26 (a and b). 75.45 MHz ^{13}C-NMR spectra of acetone insoluble PPO prepared with A1.DMBD-ZnC12 initiator at room temperature. Conditions: 30° pulse; 24° C; 10000 acquisitions; 10s delay.

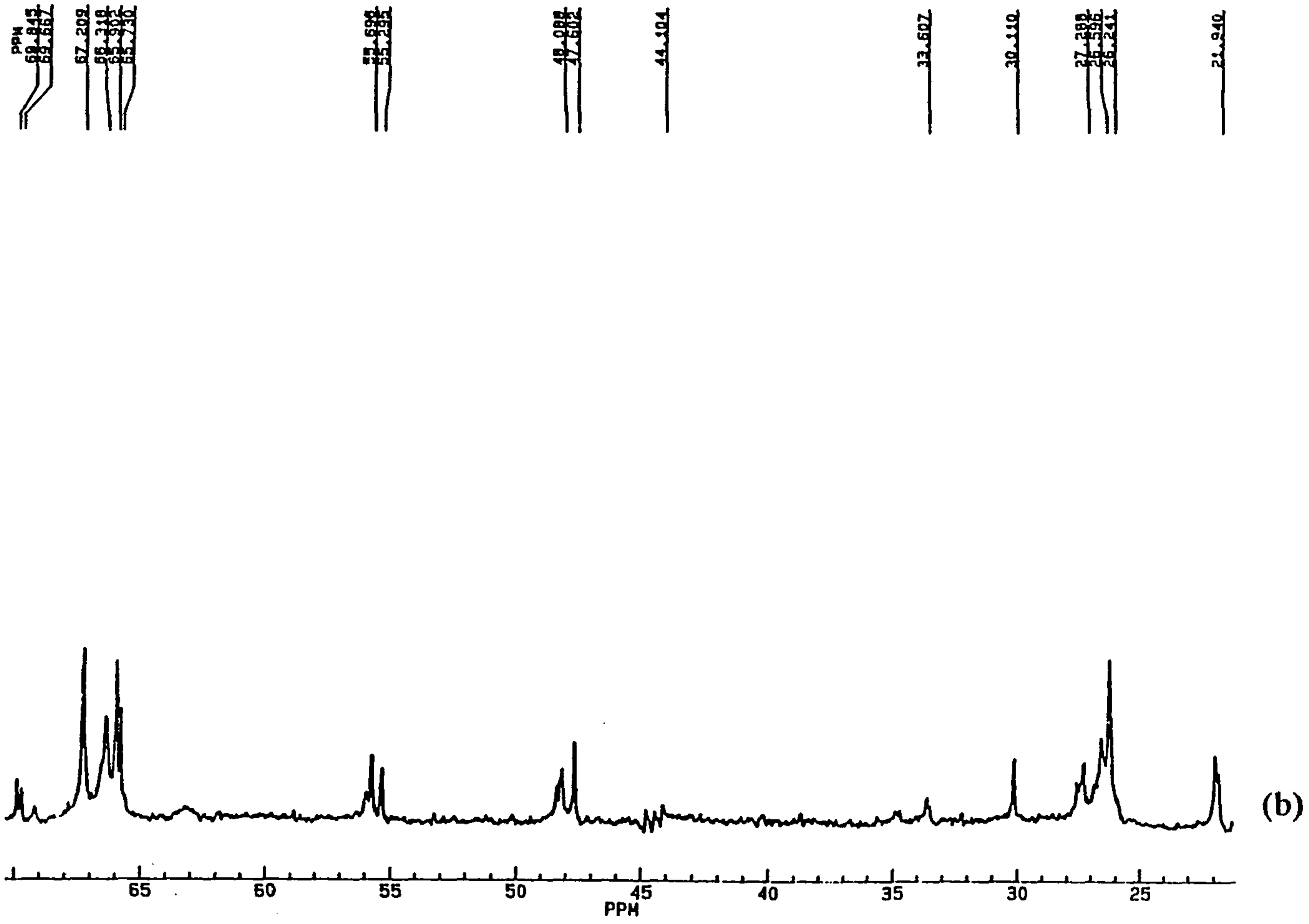
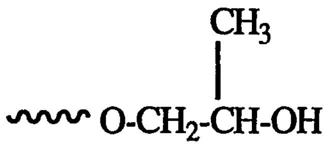


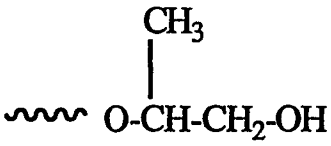
Figure 26 (a and b). 75.45 MHz ^{13}C-NMR spectra of acetone insoluble PPO prepared with Al.DMBD-ZnCl2 initiator at room temperature. Conditions: 30° pulse; 24°C; 10000 acquisitions; 10s delay.

Two groups of signals appear in 66-67 ppm region in Figures 20 and 21. These arise from CH and CH_2 peaks as shown by DEPT spectra (Figs. 22 and 25) and are assigned to hydroxy containing end groups ix and x. A signal at approximately 66-67 ppm in the spectrum of poly(propylene glycol) has been assigned to the methine carbon in structure x.[56] These hydroxy end groups may be formed during methanolysis of initiator fragments in the polymer.



$\sim\!\sim O\text{-}CH_2\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{-}OH$

x



$\sim\!\sim O\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{-}CH_2\text{-}OH$

xi

No olefinic peaks were seen near 116 or 135 ppm which indicates the absence of vinyl end groups.[56] Vinyl end groups would result from chain transfer to monomer[85] in an anionic polymerization.

5.4 Comparison of Al.DMBD-$ZnCl_2$ Initiator with the other Initiator Systems for the Polymerization of Racemic PO.

The end group analyses show that the Al.DMBD-$ZnCl_2$ is a coordination type initiator similar to AIP-$ZnCl_2$ or to alcohol modified $ZnEt_2$ initiator. Polymerization of PO with Al.DMBD in the absence of $ZnCl_2$ is similar to AIP initiated polymerization, and appears to be cationic.[59]

The Al.DMBD-$ZnCl_2$ initiator is one of the very few chiral aluminum based initiators showing stereoelective behavior in the polymerization of racemic PO. The fractionation of polymer insoluble in acetone at -30°C was found be comparable to other aluminum initiator systems. Aluminum tris(l-3-menthoxide)-$ZnCl_2$ [18] and AIP-$ZnCl_2$ [30,59] initiators gave 10-14% polymer insoluble in acetone at -30°C. The DMBD-$ZnEt_2$ initiator[15] gave approximately 10% polymer insoluble in acetone at -20°C. The stereoelectivity of the DMBD-$ZnEt_2$ initiator is greater although the Al.DMBD-$ZnCl_2$ initiator was found to be more reactive.

6.0 CONCLUSIONS

1.0 A chiral aluminum alkoxide (Al.DMBD) initiator for the polymerization of PO was prepared by the addition of an ether solution of AlH_3 to a stirred ether solution of DMBD in a 2:3 molar ratio, respectively.

2.0 The gas evolution ceased after approximately 81-82% of the AlH_3 solution had been added to the DMBD solution which suggests that residual hydroxy groups were unreactive, possibly attributable to steric hindrance related to the environment of the neopentyl type secondary hydroxy groups in the product.

3.0 The bulk polymerization of racemic PO at 80°C with the Al.DMBD initiator leads to the preferential incorporation of R-enantiomer into the polymer chain. However, the rate and stereoelectivity was found to be very low.

4.0 The use of $ZnCl_2$ as a coinitiator (Al:Zn = 1:1 molar ratio) referred to as Al.DMBD-$ZnCl_2$, increased the rate and stereoelectivity of the polymerization of PO.

5.0 The Al.DMBD-$ZnCl_2$ initiator system was found to be more reactive than the DMBD-$ZnEt_2$ initiator system which is more stereoelective.

6.0 The polymer prepared with Al.DMBD alone as initiator was completely soluble in acetone at -30°C. The ^{13}C-NMR spectrum showed that this polymer contained irregular (h,h) and (t,t) linkages in addition to the regular (h,t) linkages in the polymer chain.

7.0 Approximately 10% of the polymer prepared with the Al.DMBD-$ZnCl_2$ initiator was insoluble in acetone at -30°C. The insoluble fraction was highly isotactic and the acetone soluble fraction was atactic as shown by ^{13}C-NMR spectroscopy. However, the acetone soluble polymer contained mainly regular (h,t) linkages in the polymer chain as opposed to the polymer prepared with Al.DMBD alone as initiator.

8.0 Two types of chlorine containing end groups due the initiation by $ZnCl_2$ and an alkoxy end group derived from DMBD were detected in the polymer prepared at 80°C with the Al.DMBD-$ZnCl_2$ initiator.

9.0 An additional sterically hindered alkoxy end group derived from the DMBD was detected in the polymer prepared at room temperature.

7.0 Miscellaneous Experiments

7.1 Preparation of Aluminum Hydride in Diglyme

In the preliminary investigations, volume measurements made using a gas burette, for the evolved hydrogen in the reaction of lithium aluminum hydride in ether with a limited amount of ethanol were found to be inaccurate. Gas analyses were found to be more accurate in diglyme due to its low volatility (bp 154°C). Consequently, the preparation of aluminum hydride in diglyme (eq. 7-1) was attempted with the objective of carrying out reactions with DMBD in this medium.

$$2LiAlH_4 + 4H_2SO_4 \xrightarrow{\text{Diglyme}} 2AlH_3 + Li_2SO_4 + 2H_2 \text{ ------(7-1)}$$

In a typical experiment, sulfuric acid (100%, 3.5 mmol) was added to a stirred diglyme solution of lithium aluminum hydride (0.2 M, 7.0 mmol). Hydrogen evolution corresponded to 7.3 mmol (calculated 7.0 mmol). The solution was allowed to settle and filtered under nitrogen atmosphere. The IR spectrum of $LiAlH_4$ (0.2M) in diglyme is shown in Figure 27. The IR spectrum of the filtrate shown in Figure 28 is almost identical to the spectrum of $LiAlH_4$, except that intensities of the signals were reduced. The IR data indicate that sulfuric acid reacted completely with $LiAlH_4$ in diglyme without AlH_3 is being formed as shown in eq. 7-2.

$$2LiAlH_4 + 4H_2SO_4 \xrightarrow{\text{Diglyme}} Li_2SO_4 + Al_2(SO_4)_3 + 4H_2 \text{ -------(7-2)}$$

However, there are some minor shoulders in the IR spectrum of the product in Figure 28.

The concentration of lithium and aluminum were determined before and after the reaction with sulfuric acid. The concentration of lithium was determined by titrating lithium as a base[71] (experimental section 4.32) and the concentration of aluminum was determined by EDTA titration[72] (experimental section 4.34). The results shown in Table 19 indicate that the concentrations of lithium and aluminum are equal before the reaction with sulfuric acid as expected for $LiAlH_4$. However, the concentrations of lithium and aluminum are not equal in the reaction product corresponding to unreacted $LiAlH_4$ as inferred from the IR spectral analysis. It appears that the reaction product contains $LiAlH_4$ (0.11 M) and AlH_3 (0.04 M) explaining the IR spectrum in Figure 28 and its minor shoulders. Aluminum hydride is formed initially and it appears that sulfuric acid reacts faster with aluminum hydride than with lithium aluminum hydride in a diglyme reaction medium. However, these reaction rates are reversed in ether or in THF allowing the preparation of aluminum hydride by this method.

Table 19: Results of AlH_3 Preparation in Diglyme by the Reaction of $LiAlH_4$ and 100% H_2SO_4.

	Before reaction with H_2SO_4		After reaction with H_2SO_4	
Run #	Molarity of Lithium[a]	Molarity of Aluminum[b]	Molarity of Lithium[a]	Molarity of Aluminum[b]
1	0.20	0.20	0.07	0.11
2	0.21	0.21	0.07	0.11

[a] Molarity of lithium was determined by titrating lithium as a base (experimental section 4.32).

[b] Molarity of aluminum was determined by EDTA titration (experimental section 4.34).

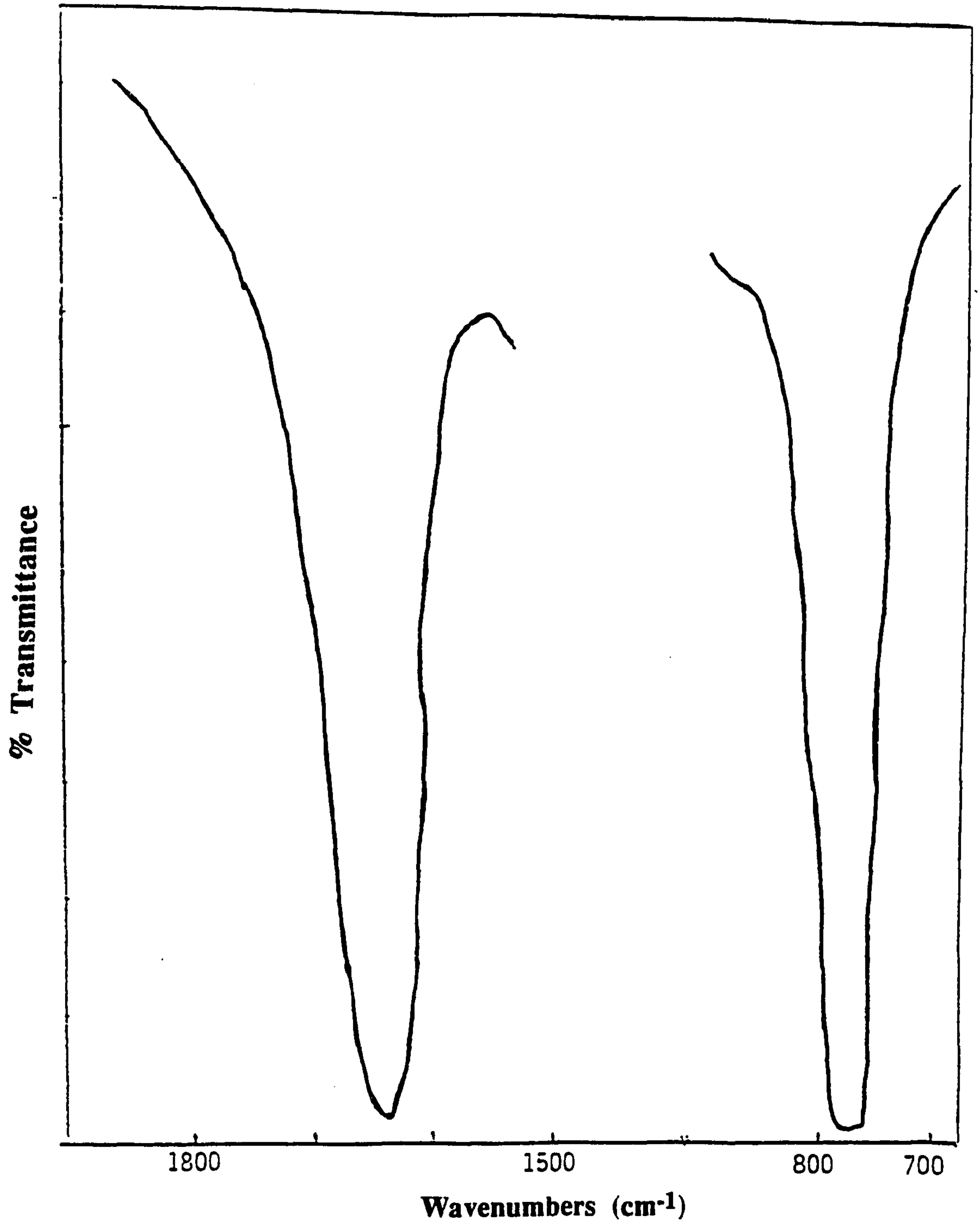


Figure 27. Infrared spectrum of $LiAlH_4$ (0.2 M) in diglyme.

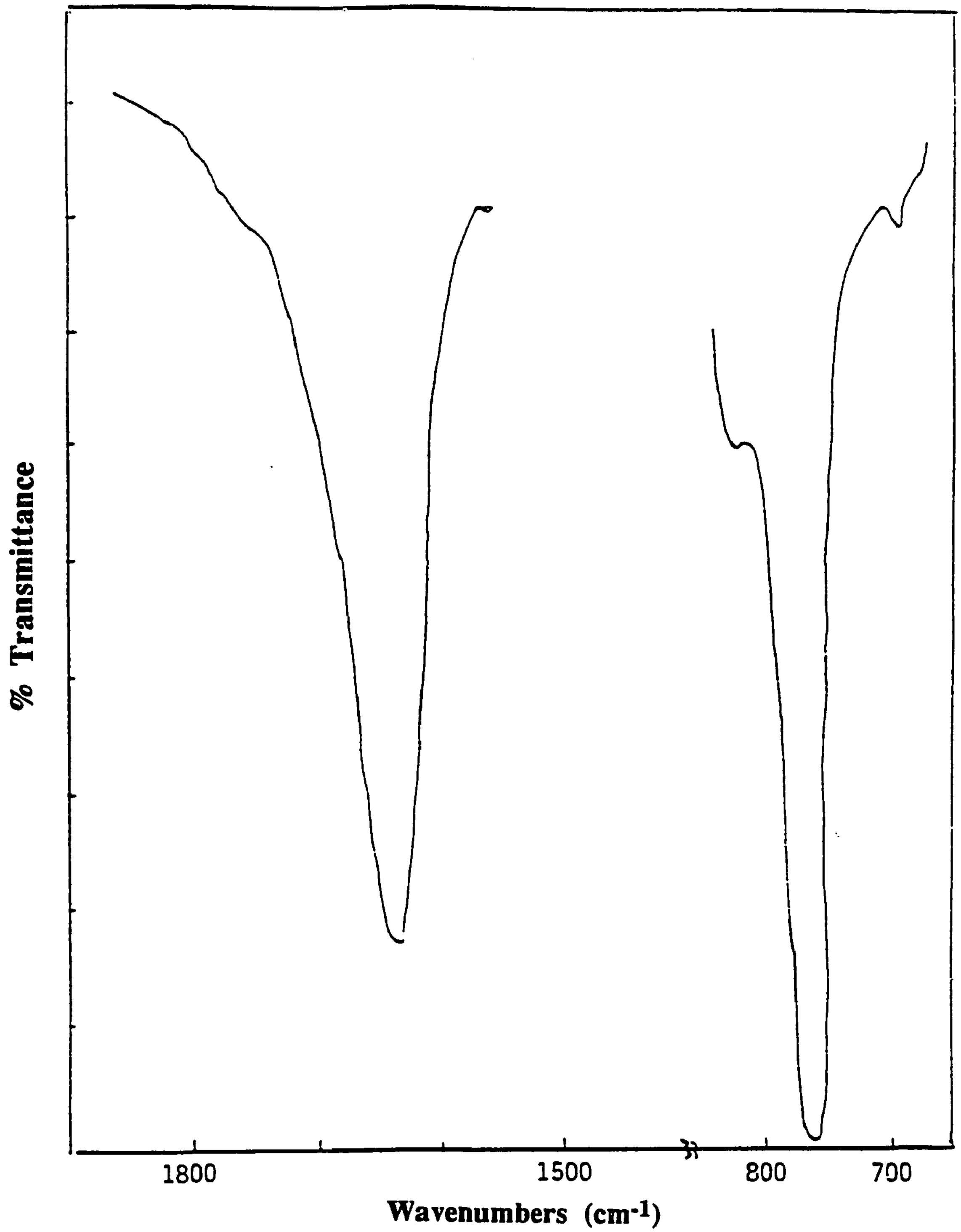


Figure 28. Infrared spectrum of the reaction product of $LiAlH_4$ and 100% H_2SO_4 in diglyme.

7.2 Preparation of AlH_3 in diglyme using $ZnCl_2$ [64]

The preparation of AlH_3 in diglyme was attempted using $ZnCl_2$ as shown in eq. 7-3 due to the failure of its preparation using sulfuric acid as shown in eq. 7-1.

$$2LiAlH_4 + ZnCl_2 \xrightarrow{\text{Diglyme}} 2AlH_3 + ZnH_2 + 2LiCl \quad \text{--------(7-3)}$$

In a typical reaction , a diglyme solution of zinc chloride (4.68 mmol, 80 mL) was slowly added to a stirred diglyme solution of lithium aluminum hydride (9.36 mmol, 0.82 M, 14.4 mL). The clear solution was filtered under nitrogen atmosphere .

Elemental analysis indicated that 4.65 mmol (calc. 4.68 mmol) of zinc was present in the solid residue by EDTA titration[72] (experimental section 4.34). Titration for chloride[72] showed the presence of only 0.42 mmol chloride ions in the solid residue as opposed to the use of 9.36 mmol of chloride as zinc chloride for the preparation of AlH_3. EDTA titration (experimental section 4.34) of the filtrate indicated a trace amount of zinc in the solution. The total concentration of aluminum and zinc in the solution were determined to be 0.10 M by EDTA titration. Since almost 99.4% of the original zinc was present in the solid residue, the concentration of zinc in the solution is negligible and hence the concentration of aluminum is 0.10 M (calc. 0.10 M for AlH_3). A flame test indicated the presence of lithium ions in solution and the chloride analysis had already shown that only a trace amount chloride is present in the solid residue. A solubility test indicated that 0.10 M solution of LiCl in diglyme can easily be made. All the above results indicated that the treatment of $LiAlH_4$ in diglyme with $ZnCl_2$ proceeded according to eq.(7-3) to form AlH_3 as observed in ether[64] and in THF.[65]

The IR spectrum of AlH_3 in diglyme as prepared by the above procedure is shown in Figure 29. There are 2 signals for Al-H stretching and bending. In general only one signal for Al-H stretching and one signal for Al-H bending has been observed for AlH_3 prepared in ether or in THF[64]. The IR spectrum of AlH_3 in ether is already shown in Figure 6 (experimental section). These two signals for Al-H stretching for AlH_3 in diglyme prepared by the reaction of $LiAlH_4$ and $ZnCl_2$ were definitely due to the presence of lithium cation in the solution. For this reason, AlH_3 in diglyme containing no lithium ions was prepared as shown in eq. 7-4.

AlH_3 (ether) ----> AlH_3 (ether, diglyme) ----> AlH_3 (diglyme) ---(7-4)

This was achieved by adding dry diglyme to an ether solution of AlH_3 and removing the ether under vacuum. The IR spectrum of this solution of lithium free AlH_3 in diglyme is shown in Figure 30. Interestingly there are again 2 signals in the Al-H stretching region [1765 cm^{-1} (m), 1710 cm^{-1} (w)]. The shoulder at 1640 cm^{-1} was apparently due to a trace amount of unreacted $LiAlH_4$. The intensities of these two main signals are reversed in AlH_3 in diglyme containing lithium ion (Fig. 29).

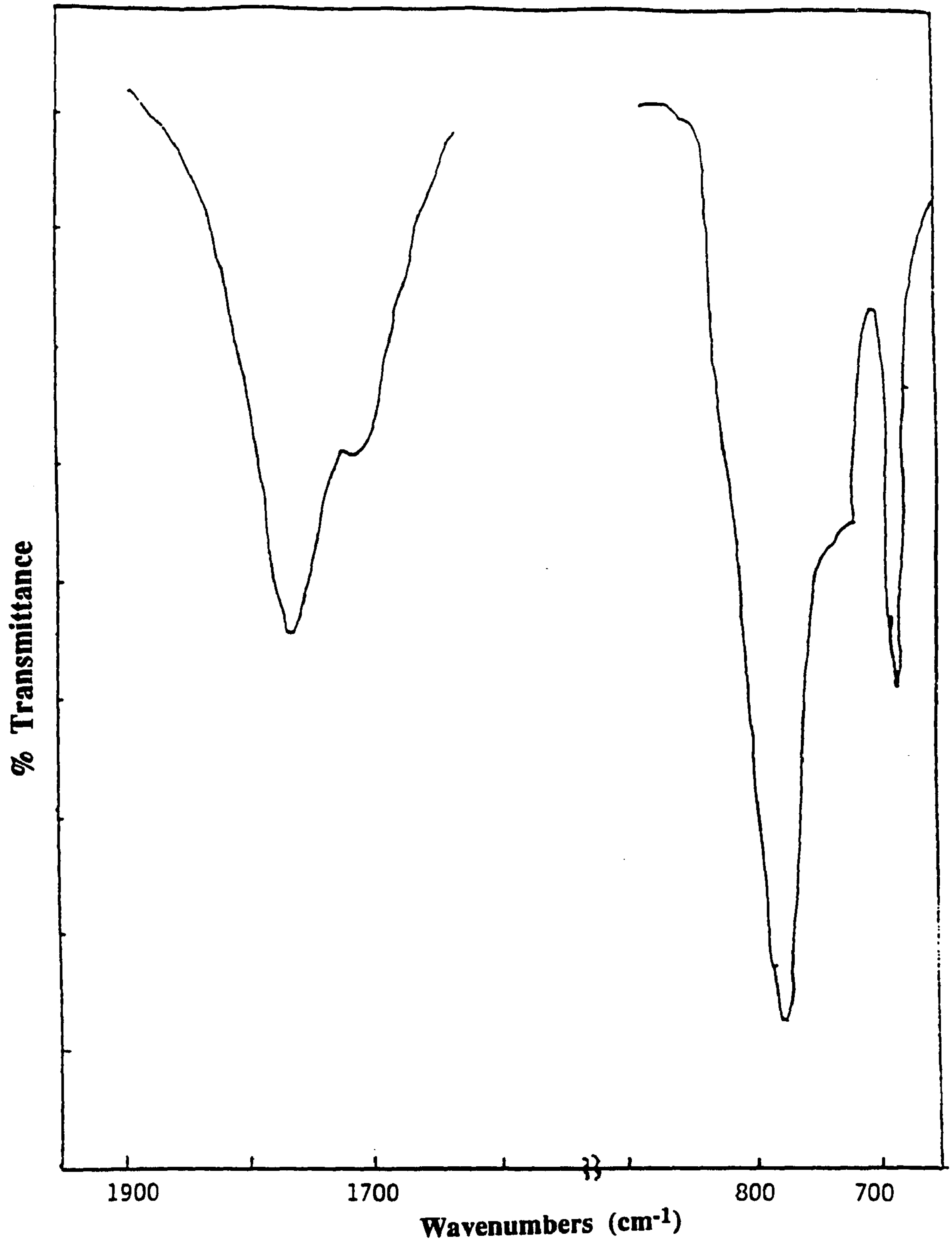


Figure 29. Infrared spectrum of AlH_3 in diglyme containing lithium ion in solution.

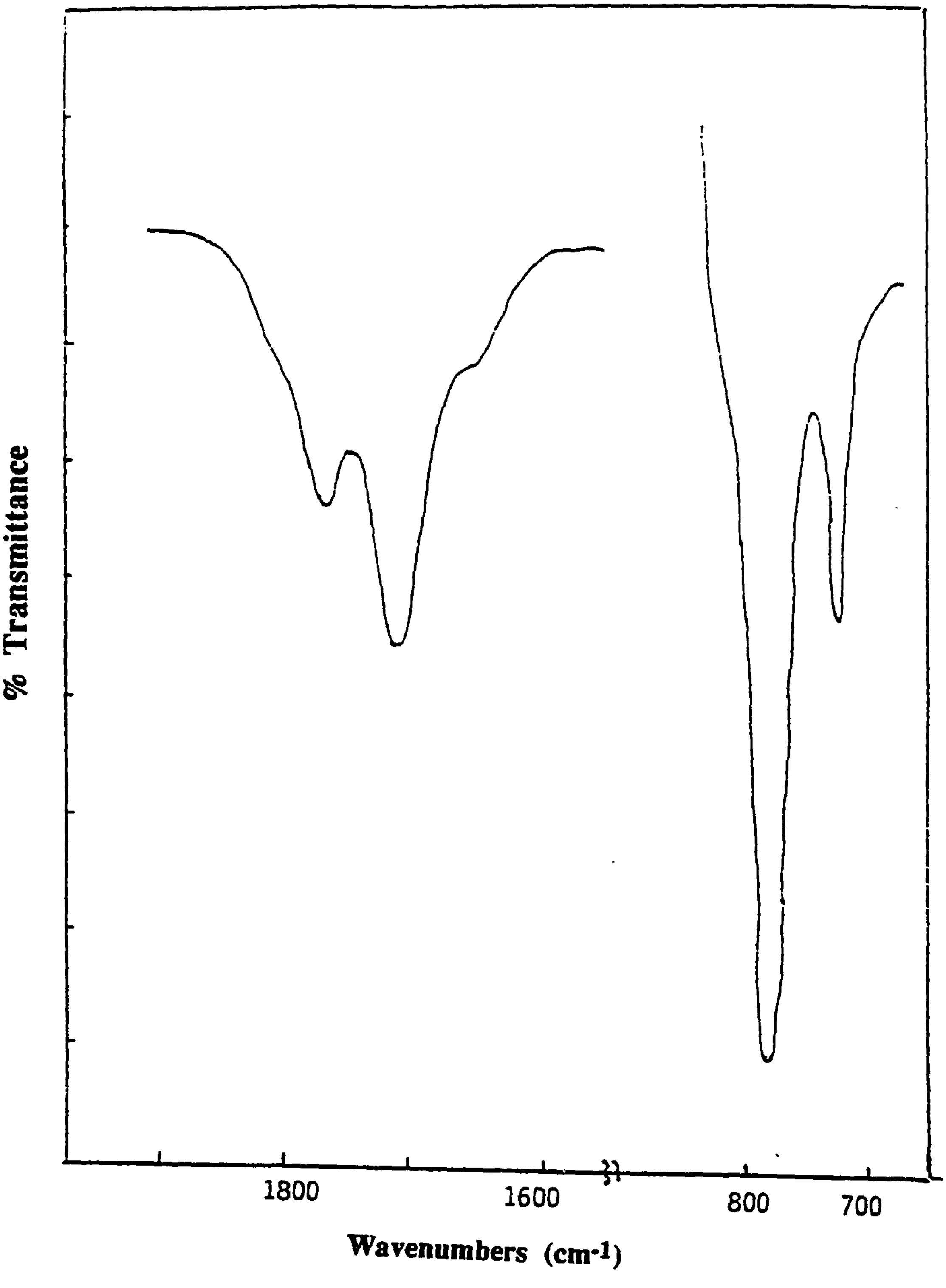


Figure 30. Infrared spectrum of AlH_3 in diglyme containing no lithium ion in solution.

This can be explained by assuming 4 and 5 coordinated aluminum hydride species in diglyme. The fourth and fifth coordinations arise from the the coordination of diglyme with aluminum. The chelating ability of lithium ion increases the concentration of 5-coordinated aluminum hydride by reducing steric hindrance for the coordination as illustrated in Figure 31.

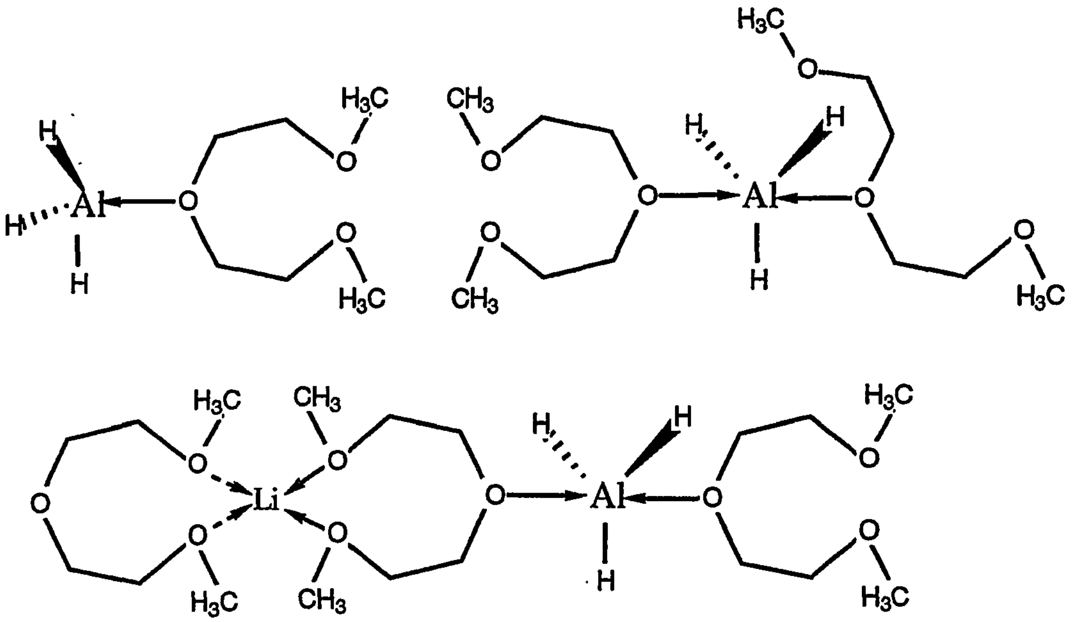


Figure 31. Four and Five coordinated AlH_3

In the diglyme solution of AlH_3 in the absence of lithium ion, the concentration of 5-coordinated species will be low. Hence, the signal at 1710 cm^{-1} (Al-H stretching) was assigned to a 5-coordinated AlH_3 species and the other signal at 1765 cm^{-1} (Al-H stretching) was assigned to a 4-coordinated AlH_3 by considering the relative intensities of these signals in Figures 29 and 30. Somewhat similar observations are seen in the Al-H bending region (signals at 777, 720 and 684 cm^{-1}). Aluminum hydride species with 4 and 5 coordinations were postulated to explain the IR spectra of $AlH_3.N(CH_3)_3$, $AlH_3.2N(CH_3)_3$ and related Lewis base complexes of aluminum hydride.[68] The preparation of AlH_3 in diglyme using $LiAlH_4$ and HCl gas dissolved in diglyme has been reported.[86] However, the IR spectrum of AlH_3 in diglyme has not been reported.

7.3 Reaction of AlH_3 with N-Methyl-l-ephedrine (NME)

An ether solution of AlH_3 and NME were reacted in a 1:3 molar ratio, respectively to prepare a potential chiral aluminum alkoxide initiator for the polymerization of propylene oxide (PO) as shown in eg. 7-5(R_1OH = NME).

$$AlH_3 + 3R_1OH \text{ --------> } Al(OR_1)_3 + 3H_2 \text{ --------------(7-5)}$$

In a typical preparation, an ether solution of AlH_3 (18.6 mmol) was added over 8h to a stirred solution of NME (55.9 mmol). Hydrogen evolution was measured by wet test meter and corresponded to 55.9 mmol (calc. 55.8 mmol). In a repeat experiment of the same scale corresponded to 56.7 mmol gas evolution. It should be noted that the NME reacted completely with AlH_3 as shown by the quantitative evolution of hydrogen despite the presence of a bulky phenyl substituent in this alcohol. The reaction was incomplete for the same type of reaction with DMBD (experimental section 4.4).

7.31 Properties of the reaction product of AlH_3 and NME.

The product, here after labelled as Al.NME, was soluble in the reaction medium (ether) unlike the reaction product of DMBD and AlH_3. The melting point of this product ranged 80-120°C and was irreproducible. The purification of this material was unsuccessful because of its solubility in common organic solvents. Addition of methanol to an ether solution of this product caused an immediate precipitation. Since $Al(OCH_3)_3$ is insoluble in ether, a possible reaction between methanol and Al.NME can be represented as shown in eq. 7-6.

$$3CH_3OH + Al(OR_{1})_3 \text{ ---->} Al\,(OCH_3)_3 + 3R_1OH \text{ -------}(7\text{-}6)$$

Reactions shown in eq. 7-6 had been used to prepare other substituted aluminum alkoxides by the interchange reaction of aluminum isopropoxide and other alcohols under refluxing conditions.[57] This type of interchange reaction is not used to prepare our Al.DMBD or Al.NME initiators because, such reactions require larger amounts of alcohols (NME and DMBD) and purification from the reaction mixture due to incomplete reactions.

7.4 Polymerization of Racemic Propylene Oxide using Al.NME and Al.NME-$ZnCl_2$ initiators.

Racemic propylene oxide (PO) was polymerized in bulk at 80°C with Al.NME alone and with $ZnCl_2$(Al:Zn =1:1 molar ratio) as a coinitiator. The latter initiator is referred to as Al.NME-$ZnCl_2$. The results are summarized in Table 20.

Table 20: Polymerization of Racemic PO with Al.NME and Al.NME-$ZnCl_2$ [a]

PO (mL)	Al.NME (mol %)	$ZnCl_2$ (mol %)	Polym. Time	Polymer Yield(%)	Optical Rotation of Unreacted Monomer
5.0	1.0	--	2 months	87	0.135° (33% w/w, benzene)
5.0	1.0	1.0	3 weeks	42	0.256° (neat, dm)

[a] Polymerizations were carried out in bulk at 80°C.

As seen in Table 20, the polymerization of PO with Al.NME initiator was very slow. The initiator was readily soluble in the monomer and a brown colored solution formed during the polymerization. The resultant polymer is readily soluble in water.

The use of $ZnCl_2$ as a coinitiator, increased the stereoelectivity of the system as shown by the optical rotation of the unreacted monomer (Table 20). The initiator dissolved in the monomer during the polymerization and again a brown colored solution was formed. After 18 h a colored complex precipitated. The complex precipitate slowly redissolved during the polymerization. This complex precipitate was readily soluble in water and no polymer was extracted from the aqueous layer using benzene as solvent.

It should be noted that this initiator system preferentially elected the S-enantiomer from the racemic PO as opposed to the preferential election of R-enantiomer by the chiral aluminum alkoxide initiator derived from the chiral diol DMBD.

The increase of polymerization temperature to 100°C or use of solvents such as DMF or ortho dichlorobenzene did not improve the initiator efficiency and hence no further polymerization studies were attempted with this initiator.

7.5 Conclusions

1. AlH_3 cannot be prepared by the reaction of a diglyme solution of $LiAlH_4$ and 100% sulfuric acid.
2. AlH_3 was prepared in diglyme by the reaction of $LiAlH_4$ and $ZnCl_2$ in a 2:1 molar ratio. The IR spectrum of AlH_3 in diglyme exhibits two types of Al-H stretching vibrations due to 4 and 5 coordinated species in the solution. The fourth and fifth coordination arise by the coordination of the solvent assisted by the chelating ability of lithium ion present in the solution.
3. A chiral aluminum alkoxide initiator Al.NME was prepared by the complete reaction of aluminum hydride and N-methyl-l-ephedrine in a 1:3 molar ratio.
4. The chiral initiator Al.NME polymerized racemic propylene oxide with the preferential election of S-enantiomer. However, this was found to be a poor initiator and its efficiency cannot be improved by the use of $ZnCl_2$ as a coinitiator.

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