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Anionic Ring-Opening Polymerization of Optically Active Epoxides

by

Wei Hong Yu

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

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The City University of New York

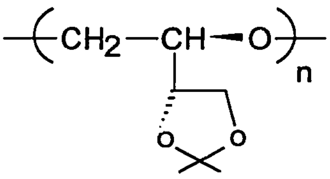
ABSTRACT

Anionic Ring-Opening Polymerization of Optically Active Epoxides

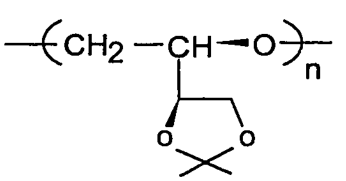
Wei Hong Yu

Advisers: Professors Howard Haubenstock and George Odian

Two new homopolymers, poly(2R,3S)-epoxide and poly(2S,3S)-epoxide have been synthesized via a ring-opening polymerization of (2R,3S)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol and (2S,3S)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol with potassium *tert*-butoxide or cesium hydroxide as initiators, and characterized by means of IR, 1-D and 2-D ^{1}H and ^{13}C NMR, GC, GPC and optical rotation measurement.



poly(2R,3S)-epoxide



poly(2S,3S)-epoxide

The poly(2R,3S)-epoxide only dissolves in very strong protonic solvents while the poly(2S,3S)-epoxide dissolves in some common solvents, such as chloroform, benzene, etc. Specific rotations of the poly(2S,3S)-epoxide have negative values in benzene and positive values in chloroform.

A linear increase in the molecular weights with conversions was observed in bulk polymerization of the (2S,3S)-epoxide with potassium *tert*-buoxide as initiator at 30°C. Molecular weight distributions of the polymers were relatively narrow. Polymerization mechanism of the (2S,3S)-epoxide prepared with *tert*-BuOK as initiator was revealed by the end-group analysis of the ^{13}C NMR spectrum.

Copolymerization of the (2R,3S)/(2S,3S)-epoxides and the (2R,3S)/(2S,3R)-epoxides at various ratios have been carried out. The studies showed that when copolymerizations of the (2R,3S)/(2S,3S)-epoxides were carried out starting with a monomer mixture consisting of (2R,3S)/(2S,3S) = 70/30 using *tert*-BuOK as initiator, (2R,3S)-monomer was incorporated into polymer chain preferentially over (2S,3S)-monomer.

ACKNOWLEDGMENTS

The author wishes to express sincere thanks to her mentors: Professor Howard Haubenstock and Professor George Odian for their guidance, support, and patience throughout this study. Appreciation is also expressed to Professor William Berkowitz for his time and helpful suggestions.

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I like to thank Dr. Hsin Wang for helping with the NMR experiments. My sincere thanks are also to Mr. Hugo Schimatz of the City College for his glass blowing work for the high-vacuum system and the polymerization tubes.

Without the support from my family, especially my parents, I can not finish this thesis. My many thanks are to my parents and my family.

Many people helped me in many ways, directly or indirectly. To all of them I wish to extend my sincere thanks.

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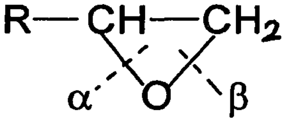
1.0 INTRODUCTION

The synthesis and application of optically active polymers are topics currently attracting much attention[1-8]. This may arise mainly from their chiral structure which is common to naturally occurring polymers. Most of the naturally occurring polymers are optically active and some of them show characteristics such as molecular recognition ability and catalytic activity, owing to their specific chiral structure as represented by genes and proteins. In synthetic polymer chemistry, it seems that one of the most challenging tasks is to construct functional polymeric systems that will be as effective as those in living systems, and the optically active synthetic polymers have today become of great interest and importance in this respect[1-4, 8-11].

Ring-opening polymerization of optically active cyclic ethers is a subject of fundamental as well as practical importance in connection with the reaction mechanism and with the properties of the polymer[12-15]. Most attention to stereochemical aspects has been paid in the polymerization of epoxides, mainly because of the formation of stereoregular polymers by some catalyst systems. The subjects of interest are: (1) the retention or inversion of configuration of the carbon atom at which the cleavage of the C-O bond takes place. (2) for unsymmetrically substituted epoxides, the ring-opening mode with respect to the two different C-O bonds (α or β scission),



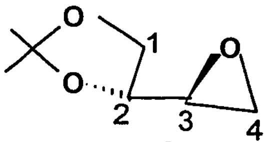
(3) for mixtures of enantiomeric epoxides, the random or selective incorporation of the optical enantiomers into a polymer molecule.

Stereoregular and optically active polyepoxides have been obtained starting from cyclic enantiomers and using anionic initiators since the ring-opening generally occurs through a regioselective attack on the CH_2, leading to β scission and giving an optically active polymer with units of the same absolute configuration as that of the monomer[16-24].

But generally, for epoxides, cationic polymerization does not occur with good regioselectivity, the ring opening taking place both by β-scission and α-scission, and the latter occurring with inversion of the configuration at the asymmetric carbon. This leads, for the polymerization of epoxides, to a lowering of the optical activities of polymers obtained from optically active monomers.[25] This is why most studies of stereospecific reactions have been carried out using anionic initiators, that more readily give stereoregular polymers.

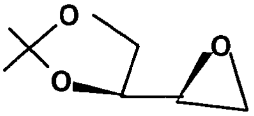
Chiral monomers often exist as racemic mixtures. Most of the initiators cannot distinguish between the enantiomers which are therefore incorporated into the polymer chain in a irregular manner. These initiators are called non-stereospecific initiators[12,16,26-28]. Some initiators possess stereospecific sites of R and S enantiomers, permitting the polymerization of R and S enantiomers at the same rate but without cross-propagation. However the isotactic polymer samples prepared with achiral initiators are optically inactive and consist of a racemic mixture of all-R and all-S polymer molecules. These initiators are called stereospecific initiators[12,16,26-28]. The polymerization of racemic monomers with stereospecific achiral initiators, resulting in the formation of stereoregular polymers, is called stereoselective polymerization. The polymerization of racemic monomers using chiral initiators may lead to the preferential polymerization of one of the two enatiomers. 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[12,16,26-28].

The study of this thesis involves the synthesis of optically active monomers, (2R,3S)-, (2S,3S)-, and (2S,3R)-3,4-epoxy-1,2-O-isopropylidene butane-1,2-diol:



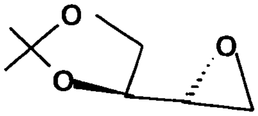
2R,3S-

(I)



2S,3S-

(II)

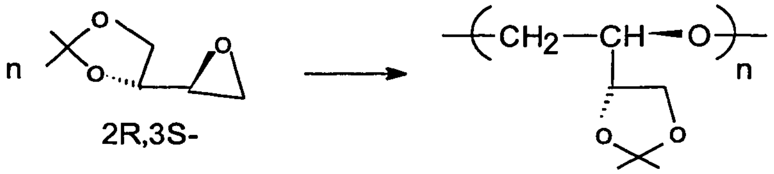


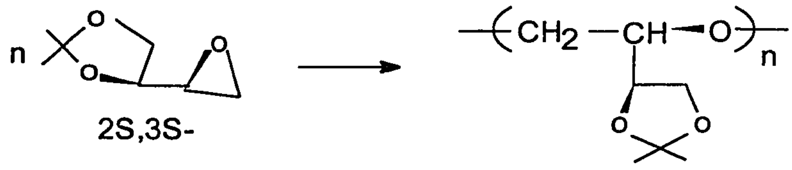
2S,3R-

(III)

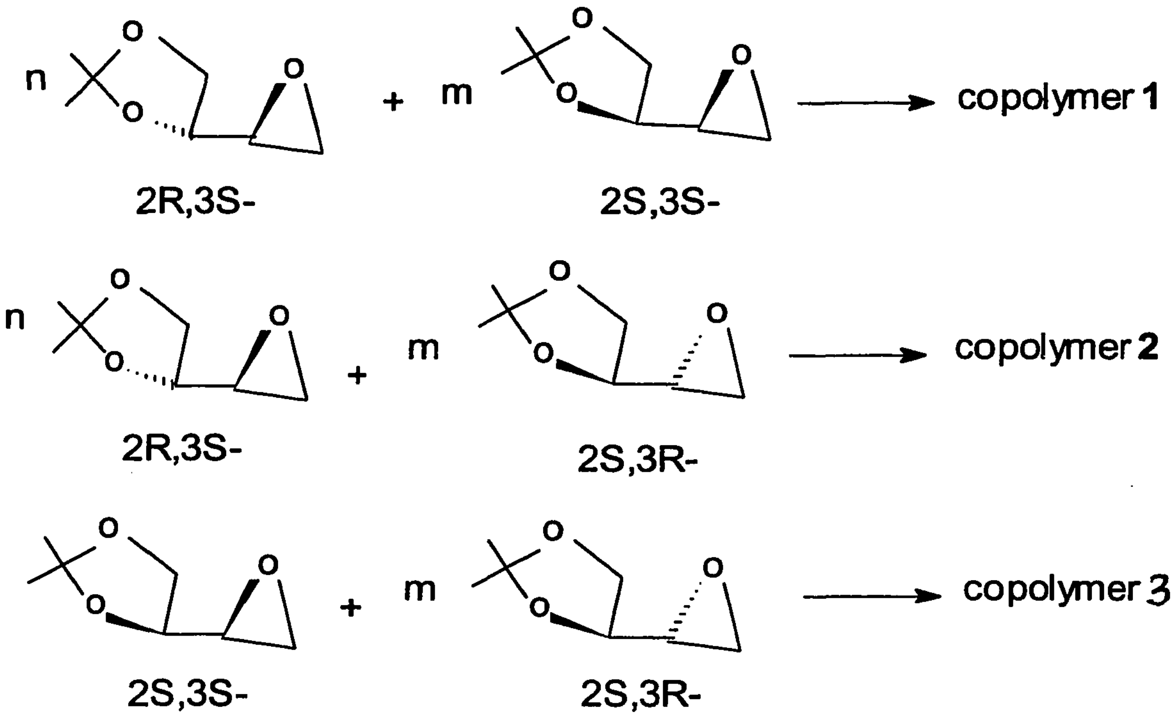
By anionic ring-opening polymerization of these epoxides, new optically active polymers can be obtained

:





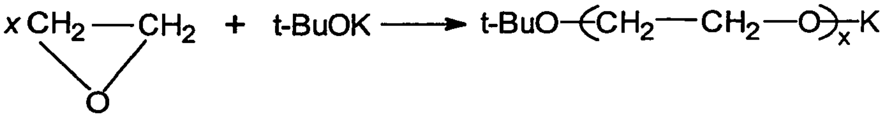
With these three different epoxides, different types of new copolymers can be prepared by anionic ring-opening polymerization:



2.0 BACKGROUND

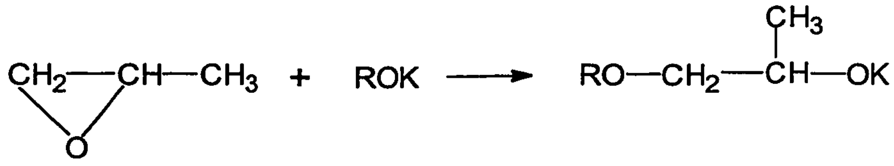
2.1 *Characteristics of Anionic Polymerization of Epoxides*

Epoxides can be polymerized by anionic initiators such as hydroxides, alkoxides, metal oxides, organometallic compounds, and other bases.[12,26,29,30] A representative catalyst belonging to alkali-metal-based catalyst is potassium *tert*-butoxide (*t*-BuOK). In the polymerization of ethylene oxide with *t*-BuOK in DMSO, the reaction proceeds stepwise by the repeated addition of a potassium *t*-butoxide to the epoxide.

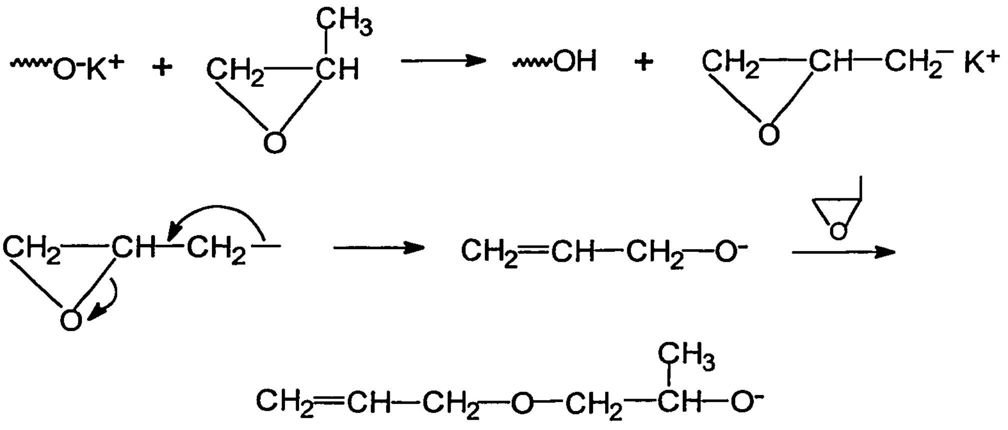


The molecular weight of the polymer increases with the extent of polymerization, and further addition of the monomer after completion of polymerization results in a further increase in the molecular weight,[31] indicating the ‘living’ nature of the polymerization. By a similar procedure, a block copolymer from ethylene oxide and propylene oxide may be prepared, which is useful as a non-ionic surfactant with hydrophilic as well as hydrophobic chains.

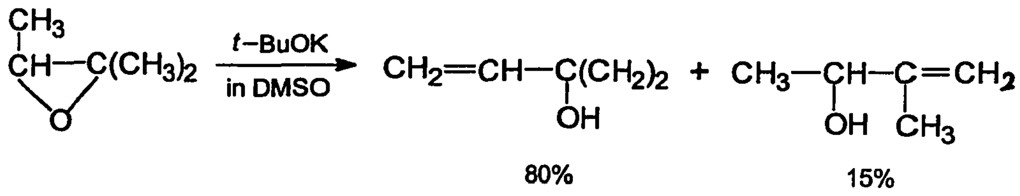
In the polymerization of unsymmetrical epoxides such as propylene oxide, the mode of ring opening is a matter of interest in connection with the reaction mechanism as well as the properties of the polymer formed. With propylene oxide, predominant cleavage of the methylene-oxygen bond, but not the methine-oxygen bond, is characteristic of the anionic mechanism.[32]

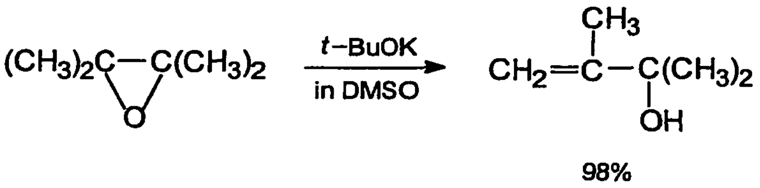


On the other hand, the molecular weight of propylene oxide polymer reaches a maximum value which is much lower than the calculated one. This observation is ascribed to the proton abstraction from the methyl group of the monomer by the growing alkoxide anion:[31,33]

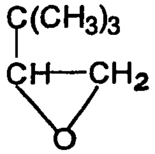


This type of chain transfer becomes more predominant with increasing number of methyl groups on the epoxide ring. For example, tri- and tetramethylethylene oxide give the corresponding alcohols in almost quantitative yield:[31]

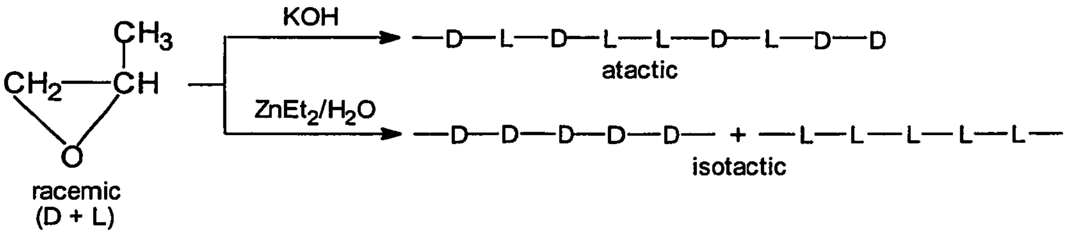




A linear increase in the molecular weight with conversion is observed in the polymerization of *t*-butylethylene oxide at 60° with *tert*-BuOK as initiator.[17] However, the rate of polymerization is very low.

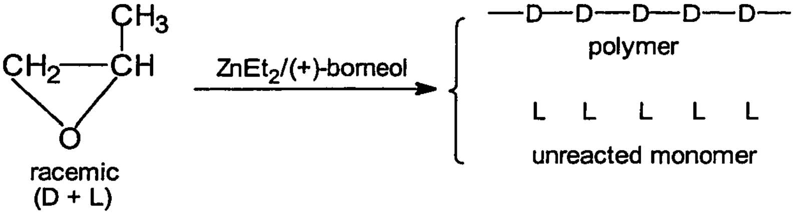


In the polymerization of racemic propylene oxide by alkali catalyst, the distribution of the steric structure with respect to the asymmetric carbon of the monomer unit in the polymer chain is random, the polymer being atactic. In contrast catalyst systems such as $FeCl_3$/propylene oxide,[34] $ZnEt_2/H_2O$,[35] and $AlEt_3/H_2O$/acetylacetone,[36] afford polymer with isotactic structure having long sequences in which the chiral centers of the monomer unit have the same absolute configuration.



Since propylene oxide has an asymmetric carbon, the formation of isotactic polymer from racemic monomer is the result of the selective incorporation of one of the optical antipodes of the monomer into a growing polymer molecule. In principle, there are two possible mechanisms for such a stereoselection in polymerization reactions. If a growing polymer terminal with , e.g. D-configuration, reacts preferentially with the monomer of the same D-configuration, an isotactic polymer will result (growing-chain control mechanism). On the other hand, an asymmetric structure of the catalyst, with which the monomer coordinates, may be responsible for the stereoselection. For the formation of isotactic poly(propylene oxide) catalyzed by $ZnEt_2/CH_3OH$, the latter mechanism (enantiomorphic catalyst site control) has been suggested.[37] More recently, the polymerization by a well-defined zinc complex with an asymmetric structure has been found useful in the interpretation of this mechanism at the molecular level.[38] On the other hand, the asymmetry of the growing polymer chain end is considered responsible for the enantiomeric selection observed in the polymerization of *t*-butylethylene oxide with *t*-BuOK.[17]

Although isotactic polymer of propylene oxide prepared from the racemic monomer is optically inactive because of the equal amounts of —D—D—D—D—D— And —L—L—L—L—L— sequences, the synthesis of optically active polymer from racemic monomer may be realized by using an optically active catalyst system such as $ZnEt_2$/(+)-borneol.[39-41] The selection of one of the monomer enantiomer is clearly demonstrated by the fact that unreacted monomer is rich in the enantiomer opposite to that incorporated preferentially into the polymer. Such a (partial) optical resolution of racemic monomers in the polymerization is called asymmetric-selective polymerization or stereoelective polymerization.



2.2 Living Polymerization of Epoxides

Living polymerization by a particular type of initiator is successful usually only for a limited type of monomer. In the polymerization of epoxide with anionic initiator, for example, propylene oxide can not afford the polymer with control molecular weight, because of the chain transfer to monomer. The following experimental criteria can be used to determine whether a given polymerization is a living polymerization.[42] (1) Narrow-molecular-weight distribution polymers are produced. (2) The number average molecular weight of polymer is a linear function of conversion. (3) Block copolymers can be prepared by addition of a second monomer after the completion of the polymerization of the first monomer.

In principal, living polymerizations provide the most versatile methodologies for the preparation of macromolecules with well-defined structures and low degrees of compositional heterogeneity.[43-48] Using these methodologies it is possible to synthesize macromolecular compounds with control of a wide range of compositional and structural parameters including molecular weight, molecular weight distribution, copolymer composition and microstructure, stereochemistry, branching, and chain-end functionality.[43-48]

Anionic polymerizations often provide convenient systems for the synthesis of living polymers. Polymerization of ethylene oxide is one of the earliest examples.[49] However, the earlier studies of this reaction involved chain-transfer because alcohol was added to solubilize alkoxides. Subsequently, it was found that controlled hydrolysis of organic ferric salts yields catalysts capable of polymerizing oxiranes to high molecular weight products.[50-52] Obviously, termination or transfer was greatly repressed in these systems.

Polymerization of ethylene oxide proceeding in the absence of alcohols was investigated by Figueruelo and Worsfold,[53] who chose hexamethyl phosphoric triamide as the solvent and sodium or potassium salts of $CH_3OC_2H_4OC_2H_4O^-$ as the initiator. The living character of this reaction was established.

Tsuneo et al. investigated bulk polymerization of (R)- and (S)- *tert*- butylethylene oxides initiated by potassium *tert*-butoxide.[17] The plots of the molecular weight of the polymer obtained versus the conversion gave a straight line . So they concluded that one polymer chain grows from each *tert*-BuOK without chain-transfer and termination, and that the copolymerization is a "living" copolymerization.

2.3. Stereochemistry of Ring-Opening Polymerization of Epoxides

2.3.1. Mode of Ring Opening

Propylene oxide has been most intensively investigated in relation to the stereochemical aspect of the polymerization. Propylene oxide has two different C-O linkages available for cleavage, i.e. the methylene-oxygen bond and the methine-oxygen bond. Model reactions,[54] the end groups of the polymer,[55] and the optical activity of polymer made from optically active monomer have all been discussed in connection with the mode of ring opening, but more direct evidence comes from the analysis of the dimeric degradation product of the polymer, and , more recently, from NMR studies on the polymers from deuterated monomers.

Both the amorphous , atactic poly (propylene oxide) made from racemic monomer using KOH as catalyst, and the crystalline isotactic polymer made using $Al(O\textit{i}\text{-}Pr)_3$ as catalyst, consist almost the exclusively of head-to-tail linkages. On the other hand, the non-crystalline fraction of the polymers obtained by $AlEt_3/H_2O$ catalysis contains considerable amounts of head-to-head, tail-to-tail linkages.

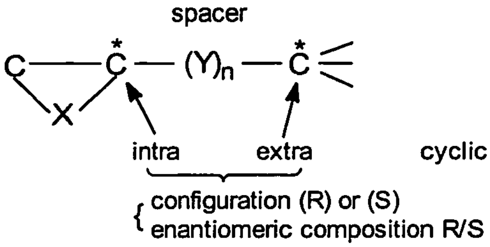
Similar results are the amorphous poly(propylene oxide) obtained from optically active (R or S) monomer using $ZnEt_2/H_2O$ and $FeCl_3$/propylene oxide as catalyst systems, indicating that cleavage occurs at methine-oxygen as well as methylene-oxygen bonds of the monomer in the polymerization, and that inversion of configuration takes place in the ring opening at the asymmetric carbon atom.[56]

^{13}C NMR spectroscopy of poly(propylene oxide) provides information as to the presence or the absence of head-to-head and tail-to-tail linkages,[57] in the polymers obtained by using *t*-BuOK, $ZnEt_2/H_2O$, $AlEt_3/H_2O$[57] and $Al(O\textit{i}\text{-}Pr)_3/ZnCl_2$[58] as catalyst. Therefore, ^{13}C NMR spectroscopy can be used to study the ring opening mode in polymerization of epoxides.

Inversion of the configuration of the carbon atom in the ring opening of epoxides suggested that the polymerization reaction may involve two or more metal atoms in a concerted, coordination mechanism, rather than a single metal atoms. In the latter, retention of the configuration would be more likely.

2.3.2. Influence on Stereoelectivity Due to the Monomer

The stereoelectivity of copolymerization of racemic epoxides is generally determined by initiator, monomer, microenvironment and chirality of the polymer chain. For a given initiator, the stereoelectivity depends on the nature of the monomer. When the bulkiness of the monomer substituent in α of the heteroatom is increased, the rate of polymerization decreases and the stereospecificity of the polymerization increases.[59] Different ways to increase the stereoelectivity were tried by acting on the "intracycle" and "extracycle" chirality of monomers.



The "intracycle" chirality concerns the asymmetric atom located in the cycle. When the starting material is enantiomerically enriched the stereoelectivity value r_R is increased.

The "extracycle" chirality assistance is promoted by using monomers bearing asymmetric centers in the substituent. This leads to the formation of diastereoisomers. The efficiency of the chiral assistance depends on the proximity of the two asymmetric centers, i.e. of the length of the spacer (n). When n=0, the two asymmetric centers being in vicinal positions, a very positive assistance effect was observed as demonstrated with (S)-secBu-(R,S)-oxirane for which a stereoelectivity of $r_R = 4.0$ was found.[60] This is much higher than the value found for methyloxirane ($r_R = 1.8$), for example. It is interesting to underline, that in spite of the opposite configuration (S) of the assistant asymmetric center the stereoelection works with enhancement effect.

2.3.3 Mechanisms of Steric Control and ^{13}C NMR Study of Tacticity of Copolymers

If the configuration of the monomer entering the polymer chain is independent of that of the last unit of the chain the distribution of configurational unit in the chain is random.

$$\cdots\!-\!R^* + R \xrightarrow{k_{RR}} \cdots\!-\!R^* \qquad \cdots\!-\!R^* + S \xrightarrow{k_{RS}} \cdots\!-\!S^*$$

$$\cdots\!-\!S^* + R \xrightarrow{k_{SR}} \cdots\!-\!R^* \qquad \cdots\!-\!S^* + S \xrightarrow{k_{SS}} \cdots\!-\!S$$

$$k_{RR} = k_{RS} = k_{SR} = k_{SS} \qquad r_R = \frac{k_{RR}}{k_{RS}} \qquad r_S = \frac{k_{SR}}{k_{SS}}$$

If the polymerization occurs with retention of configuration (i.e.

exclusive ring-opening in β-position) it is possible to correlate the proportion of different sequences (dyads, triads...) in the polymer chain with the ratio of concentration of the two enantiomers in the initial monomer mixture: p = S/R as established by Sepulchre et al.[61]. The calculated values for different triads are the following:

$$I = (p^3 + 1)/(p + 1)^3 \qquad S = H_i = H_s = \frac{p(p + 1)}{(p + 1)^3}$$

In the case of a racemic monomer, p = S/R = 1, the proportions of all triads are equal: $I = S = H_i = H_s = 25\%$. ($H = 2S = 50\%$). Experimentally, such values have been observed for the polymerization of propylene oxide using different purely anionic initiators such as KOH, t-BuOK.[62-64]

Another type of mechanism, called "growing chain-end control", has been considered in the case of ring-opening polymerization. In this particular case, the configuration of the entering monomer depends on the configuration of the last monomeric unit in the growing chain (Markovian statistics, 1-st order) or on that of the last n monomeric unit (n-th order Markovian).

If the control is carried out by the last unit, the following reactions with the corresponding rate constant must be considered:

$$\cdots\text{—R}^* + \text{R} \xrightarrow{k_{RR}} \cdots\text{—R}^* \qquad \cdots\text{—R}^* + \text{S} \xrightarrow{k_{RS}} \cdots\text{—S}^*$$

$$\cdots\text{—S}^* + \text{R} \xrightarrow{k_{SR}} \cdots\text{—R}^* \qquad \cdots\text{—S}^* + \text{S} \xrightarrow{k_{SS}} \cdots\text{—S}$$

$$(k_{RR} = k_{SS} \ddagger k_{RS} = k_{SR}) \qquad r = \frac{k_{RR}}{k_{RS}} = \frac{k_{SS}}{k_{SR}}$$

If $k_{RR} > k_{RS}$, the formation of isotactic sequences is favored. A tendency to the formation of stereoblocks is observed when $r \gg 1$. If $k_{RR} < k_{RS}$, syndiotactic sequences should be predominant.

Such a mechanism was proposed by Tsuruta et al.[17,18] in the case of bulk polymerization of *tert*-butyloxirane with *tert*-BuOK as initiator. It has been observed that when starting with an initial monomer mixture enriched in *R*-monomer, the latter was incorporated into the polymer chain preferentially over *S*-monomer ($k_{RR} > k_{RS}$). As the consequence, the enantiomeric excess of the unreacted monomer gradually decreased. The following proportions of triads have been found for a racemic poly(*tert*-butyloxirane)[23].

$$\text{I} = 32\% \qquad \text{H} = 48\% \qquad \text{S} = 20\%$$

$$\text{H} \neq 2\text{S} \qquad \text{and} \qquad \%\text{I} > \%\text{S}$$

This is significantly different from the random distribution found for poly(propylene oxide) prepared with the same initiator (I = S = H_i = H_s = 25%). This was explained by a growing chain control mechanism, *tert*-butyl group being bulky enough to make the chiral structure of the growing polymer chain able for the stereoelection of the chiral monomer. Similar effects have been observed in the case of anionic polymerization of styrene oxide by potassium alkoxides[65]. Therefore, some specific epoxides, with bulky substituent on the α-carbon, are possible to carry out stereoelective polymerization even with achiral chemical, such as *tert*-BuOK, as initiator.

Because NMR spectroscopy is sensitive to the configurational possibilities of the polymer sequences, the NMR measurement of tacticity of polymers is the important tool to understand the stereospecific polymerization mechanism. Copolymerization study between R- and S-monomer by ^{13}C NMR spectroscopy is useful for elucidation of the stereoselectivity or stereoelectivity mechanism. If the backbone methylene group of copolymers can be effectively isolated by spin decoupling or substitution on adjacent carbons, the relative number of tactic placements can be determined.[66] Having determined the number of tactic intensities it is possible to propose a statistics model of propagation and to calculate the probability parameters and average lengths of different stereo blocks.

2.4 End Group Analysis

Identification of end groups in the polymer chain can provide information on initiation and termination processes in various types of polymerization. In recent years a number of research teams have succeeded in obtaining qualitative and quantitative information concerning ends of polymer chains from ^{13}C NMR spectra. One approach is to synthesize low molecular weight fractions (typically of Mn 1000-4000), and to use as high concentration as possible to give an adequate signal-to-noise ratio. Johns at al.[67] characterized end groups in polystyrene prepared using di-t-butylperoxyoxalate as initiator. They showed that t-butoxymethyl groups in the polymer could be identified by means of signals at 27.3 ppm and 72.3 ppm.

End groups produced in the ring-opening polymerization of propylene oxide and its copolymerization with tetrahydrofuran have been studied by Mochel et al.[68]. The homopolymers prepared using boron trifluoride etherate as initiator contained both secondary and primary hydroxyl groups in approximately 2:1 ratio. The methyl end group resonance at 19.9 ppm is well resolved from that due to main-chain methyl groups at 17.5 ppm. In the copolymers, there are no resonances at 61.5 and 30.0 ppm to be expected if end groups arising from THF are present. The authors conclude that initiation of polymerization proceeds solely by attack of protonated propylene oxide on the two monomers.

The analysis of ^{13}C spin-lattice relaxation times T_1 provides a direct method for the assignment of ^{13}C NMR signals of end fragments of relatively low molecular weight polymeric molecules[69]. The method is based on the premise that ^{13}C T_1 values are generally longest at the chain ends and shortest at the middle of the molecule; intermediate carbons have intermediate T_1 values. This phenomenon is due to the higher freedom of motion at the chain ends relative to the internal segments. Slower tumbling in the middle of the chain facilitates the relaxation of internal carbons.[70] This effect is clearly seen for ^{13}C T_1 values in decane[71], with the largest T_1 values at chain end carbons in the middle of the chain:

T_1 (^{13}C, sec.) 8.74 6.64 5.71 4.95 4.36 4.36 4.95 5.71 6.64 8.74
$CH_3CH_2CH_2CH_2\ CH_2CH_2\ CH_2CH_2\ CH_2CH_3$

However in neat 1-decanol[72], the shortest T_1 values occur at the hydroxyl chain end:

$$T_1\ (^{13}C,\ \text{sec.})\qquad \overset{0.65}{HOCH_2}\ \overset{0.77}{CH_2}\overset{0.77}{CH_2}\overset{0.84}{CH_2}\ \overset{0.84}{CH_2}\overset{0.84}{CH_2}\ \overset{1.1}{CH_2}\overset{1.6}{CH_2}\ \overset{2.2}{CH_2}\overset{3.1}{CH_3}$$

This is attributable to aggregation effects involving hydrogen bridging at the hydroxyl groups which lessen the mobility of these chain ends and therefore lower T_1 at nearby carbons. This method also provides insight into specific interactions of end-groups and allows the detection of low molecular weight impurities.

2.5 Significance of the Project

At present, only a few examples have been observed of stereoelective processes using achiral initiators. One case is that the term "stereoelective" is applied to mixture of diastereoisomers rather than enantiomers. This example is the polymerization of diastereoisomers of (2R,3S) and (2S,3S) 3-Me-1,2-epoxy-pentane and 3-Me-1,2-epithiopentane, for which stereoelection occurred with t-BuOK, KOH and the $ZnEt_2/H_2O$ system.[73,74] Another example is the polymerization of enriched enantiomeric mixtures of t-butyloxirane for which stereoelection was observed with t-BuOK[21,22]. Stereoselectivity was also found in copolymerization of racemic t-butyloxirane with tert-BuOK as initiator[17,18].

In this work, the bulky epoxides with two chiral centers were chosen as monomers for anionic ring-opening polymerization. As mentioned above, the “intracycle” and “extracycle” chirality of these monomers may increase the stereoelectivity of the polymerization. It is interesting to investigate the stereoselectivity and stereoelectivity in copolymerization of these racemic, enriched enantiomeric or diastereoisomeric mixtures to compare with the existing examples.

Because t-BuOK dissolves in the epoxides to carry out homogeneous polymerization, t-BuOK has been chosen as the major anionic initiator to be investigated. For comparison, heterogeneous bulk polymerization of the epoxides with alkali hydroxide as anionic initiator was also investigated. For polyepoxide with acetal group, such as 1,1-diethoxypropane, the polymerization rate increases with the size of the counter ion, in the order of $Na^+ < K^+ < Cs^+$,[24] therefore CsOH was chosen as the catalyst to be studied.

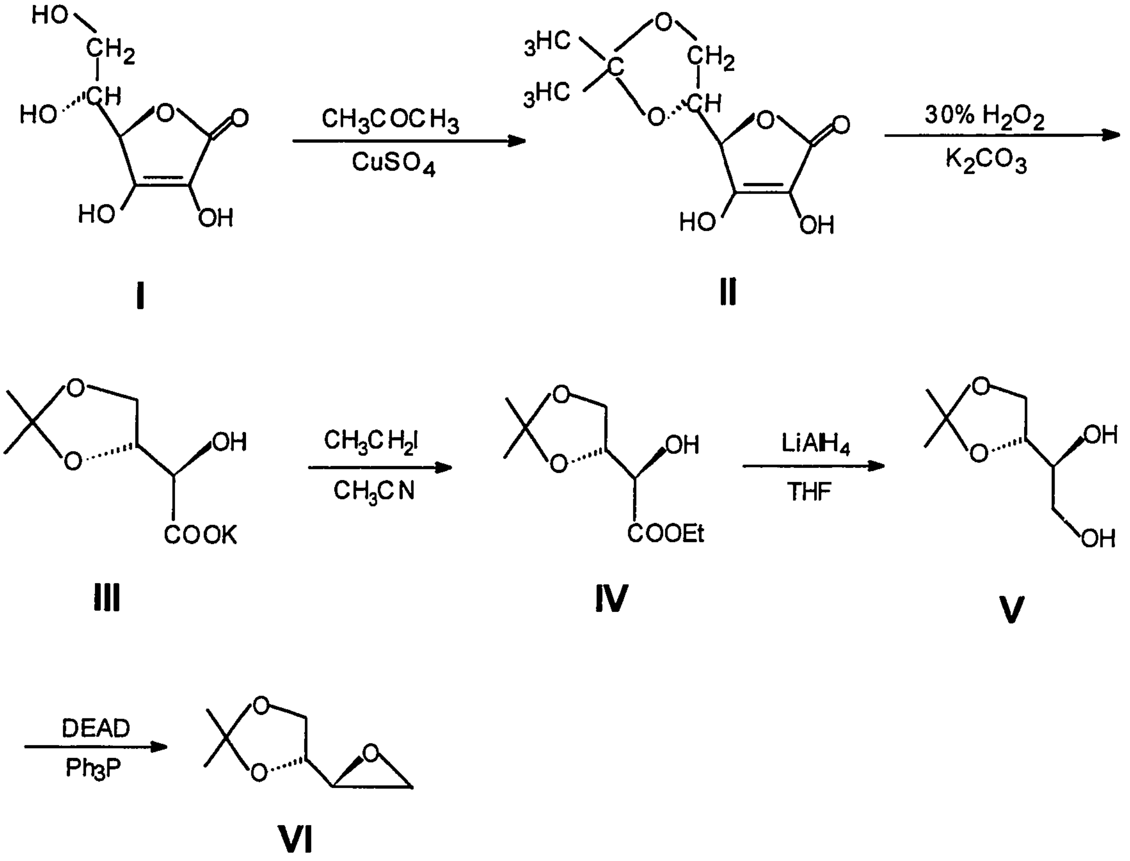
The homopolymerization of the epoxides were investigated in detail instead of the copolymerization in this work. However the analysis of the polymerization mechanism of the homopolymers, the ^{13}C NMR analysis of the end-groups and the tacticity of the homopolymers will be a great help in analysis of the tacticity of the copolymers from ^{13}C NMR, which may offer the information of the stereoselectivity or the stereoelectivity of the copolymerizations.

From the practical point of view, the new optically active polymers with two chiral centers were prepared by anionic ring-opening polymerization. The synthesis of these products explores the potential in many fields: as chiral catalysts, as stationary phases for chromatographic resolution of optical antipodes, for the preparation of liquid crystals, and so on.

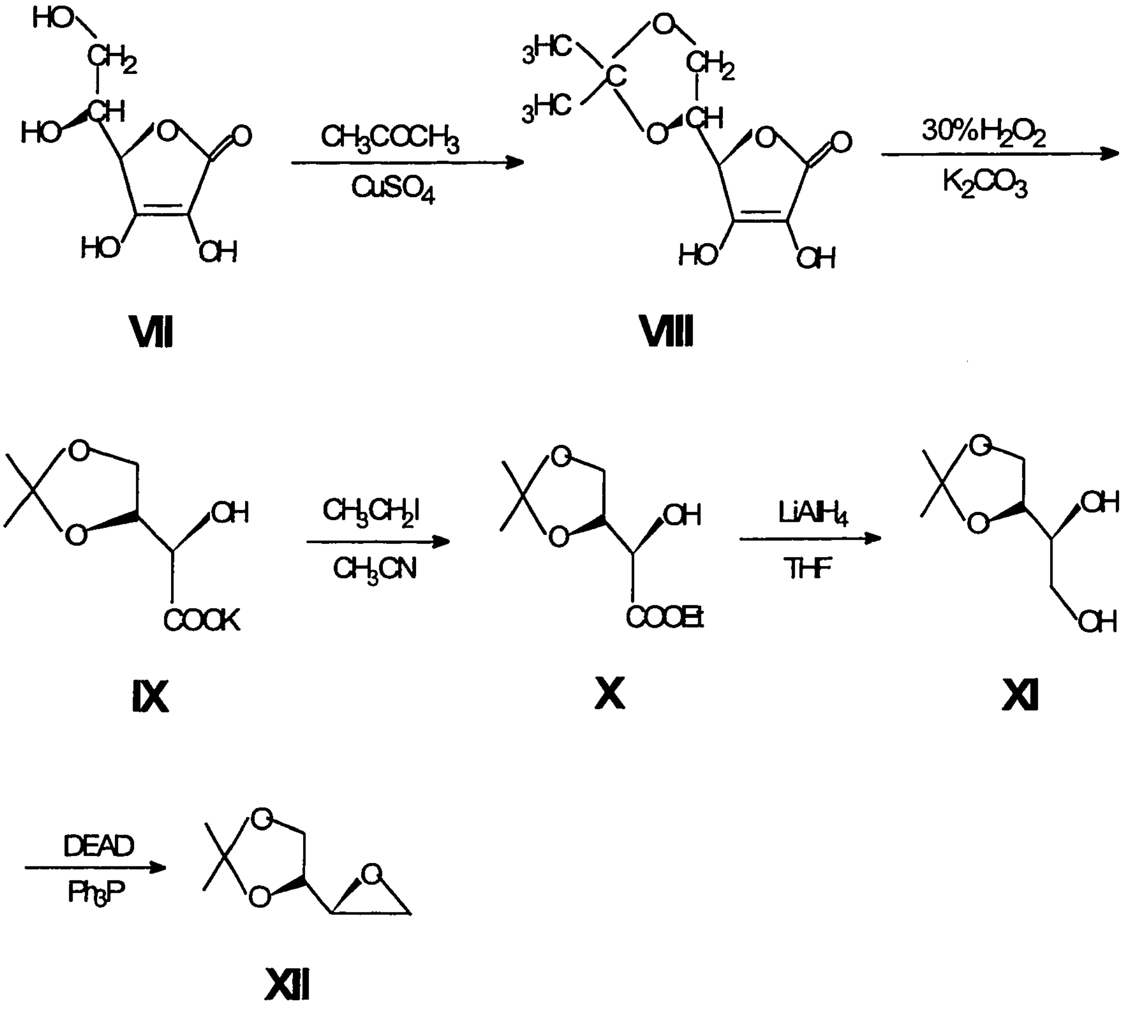
3.0 EXPERIMENTAL

3.1 Synthesis of monomers

Scheme I,

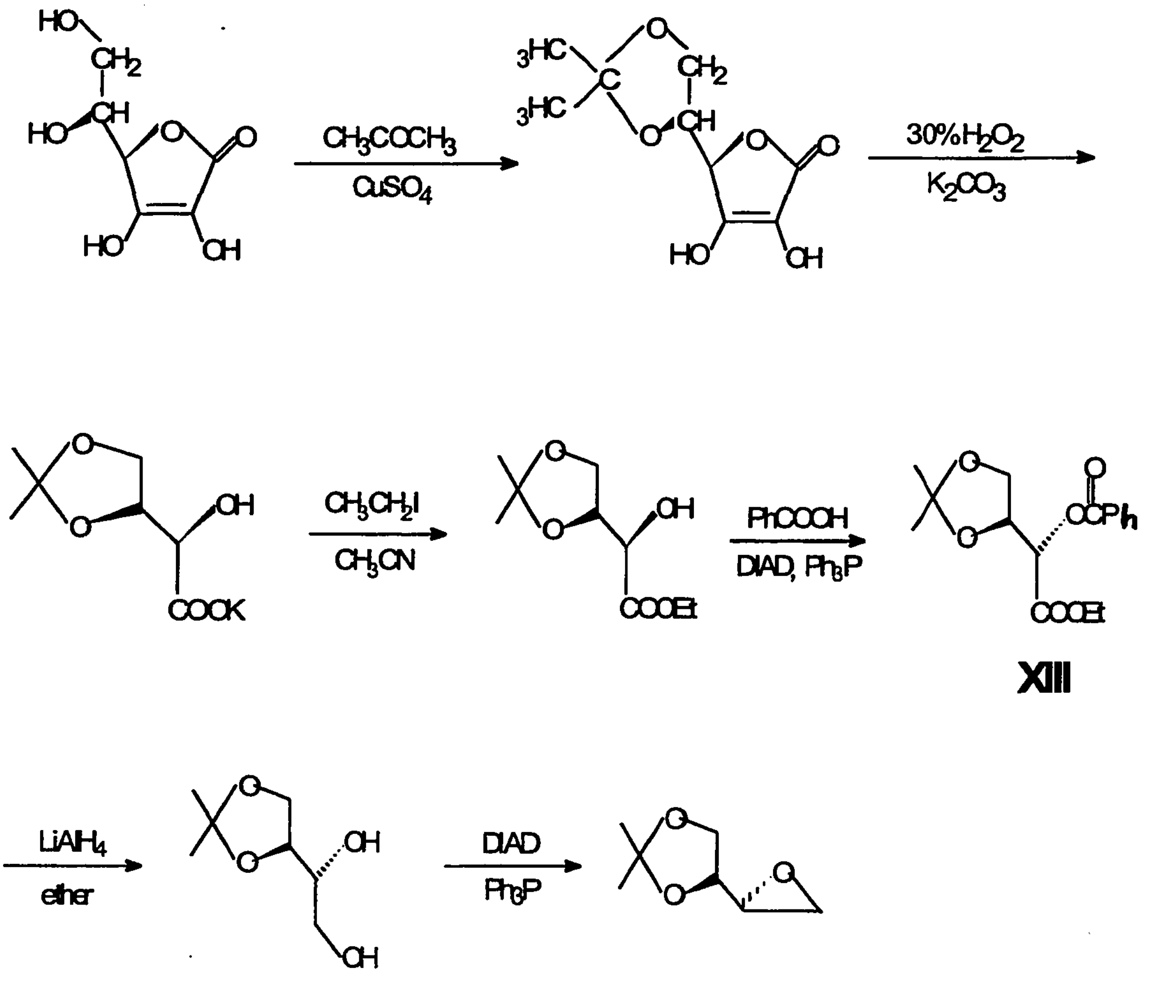

I
CH3COCH3
CuSO4
II
30% H2O2
K2CO3
III
CH3CH2I
CH3CN
IV
LiAlH4
THF
V
DEAD
Ph3P
VI

Scheme II:



VII
CH_3COCH_3
$CuSO_4$
VIII
$30\%H_2O_2$
K_2CO_3
IX
CH_3CH_2I
CH_3CN
X
$LiAlH_4$
THF
XI
DEAD
Ph_3P
XII

Scheme III:



XIII

XIV

XV

I: D-isoascorbic acid

II: 3,4-O-isopropylidene-D-isoascorbic acid

III: potassium (2R,3R)-3,4-O-isopropylidene-2,3,4-trihydroxy-butyrate

IV: ethyl (2R,3R)-3,4-O-isopropylidene-2,3,4-trihydroxy-butanoate

V: (2R,3S)-1,2-O-isopropylidenebutane-1,2,3,4--tetrol

VI: (2R,3S)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol

VII: L- ascorbic acid

VIII: 3,4-O-isopropylidene-L- ascorbic acid

IX: potassium (2R,3S)-3,4-O-isopropylidene 2,3,4-trihydroxy-butyrate

X: ethyl (2R,3S)-3,4-O-isopropylidene-2,3,4-trihydroxy-butanoate

XI: (2S,3S)-1,2-O-isopropylidenebutane-1,2,3,4-tetrol

XII: (2S,3S)- 3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol

XIII: ethyl (2S,3S)-2-O-benzoyl-3,4-O-isopropylidene-2,3,4-trihydroxybutanoate

XIV: (2S,3R)-1,2-O-isopropylidenebutane-1,2,3,4-tetrol

XV: (2S,3R)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol

DEAD: diethyl azodicarboxylate

DIAD: diisopropyl azodicarboxylate

3.1.1 Synthesis of 3,4-O-isopropylidene-D-isoascorbic acid (**II**)

A mechanically stirred suspension of 100 g (0.57 mol) of D-isoascorbic acid in acetone (2.25 L) was treated with 150 g of anhydrous $CuSO_4$. After the reaction was stirred at room temperature for 24 h, a second 150 g portion of $CuSO_4$ was added, and stirring was continued for an additional 24 h. The reaction was then filtered and concentrated, giving a near quantitative yield of the product.

3.1.2 Synthesis of potassium (2R,3R)-3,4-O-isopropylidene-2,3,4-trihydroxy-butyrate (**III**)

The isopropylidene derivative was dissolved in water (0.6 L) containing 156 g of K_2CO_3. This solution was chilled in an ice bath and stirred while 30% H_2O_2 (124.5 ml) was slowly added. During the addition the temperature was maintained below 20 °C. The solution was stirred while overnight and then concentrated in vacuum. The moist solid was extracted with boiling absolute EtOH (6 × 250 ml). After filtration and evaporation, the salt was dried under vacuum to provide 118 g of material. The yield was 97%.

3.1.3 Synthesis of ethyl (2R,3R)-3,4-O-isopropylidene-2,3,4-trihydroxy-butanoate (IV)

Treatment of a mechanically stirred suspension of the salt with EtI (120.5 g) in CH_3CN (0.75 L) at reflux for 24 h gave, after concentration and removal of the inorganic salt, 99 g of crude ester. Distillation under reduced pressure gave 94.15 g pure **IV** (NMR and TLC), 81% yield from D-isoascorbic acid; bp 70-110 °C/0.10 mmHg. A second distillation: bp 72 °C/0.0075mmHg. $[\alpha]_{589} = -22.25$ $deg.dm^{-1}.g^{-1}.cm^3$ ($c = 1.565$, CH_3OH

3.1.4 Synthesis of (2R,3S)-1,2-O-isopropylidenebutane-1,2,3,4-tetrol (V)

To a cooled, mechanically stirred suspension of powdered $LiAlH_4$ (13.1 g, 0.345 mol) in anhydrous taterahydrofuran (THF, 250 ml) was added dropwise a solution of **IV** (53.35 g, 0.26 mol) in anhydrous THF (100ml). After addition was complete the reaction was stirred for 1 h and then heated at reflux for 1 h. The excess $LiAlH_4$ was decomposed by sequential addition of water (12.5 ml), and water (35 ml). The mixture was filtered, and the solids were extracted (Soxhlet) with $CHCl_3$ for 24 h. The combined THF and $CHCl_3$ solutions were dried over anhydrous

$MgSO_4$ and then concentrated to furnish 40.3 g (95.3%) of **V**. Pure **V** was obtained by distillation under reduced pressure: bp 103-107°C /0.01mmHg. $[\alpha]_{589}$ 8.36 $deg.dm^{-1}.g^{-1}.cm^3$ (c = 4.17, C_2H_5OH)

3.1.5 Synthesis of (2R,3S)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol **(VI)**

Diethyl azodicarboxylate (DEAD, 2.58 g, 0.014 mol) was added dropwise to a stirred solution of **V** (2.17b g, 0.013 mol) and TPP (3.73 g, 0.014 mol) in dry ether (20 ml). An exothermic reaction was observed. After the mixture cooled to room temperature, the ether was removed under diminished pressure, and the remaining residue was distilled at 42°C/0.7mmHg to give 1.53 g (79.5%yield) of **VI**. $[\alpha]_{589}^{26}$ 11.93 $deg.dm^{-1}.g^{-1}.cm^3$ (c = 2.18, C_2H_5OH). Literature[75] $[\alpha]_{589}^{22}$ 11.47 $deg.dm^{-1}.g^{-1}.cm^3$ (c = 3.75, C_2H_5OH). The measurement of gas chromatography showed the purity of the epoxide as 96.5%.

3.1.6 Synthesis of 3,4-O-isopropylidene-L- ascorbic acid **(VIII)**

The procedure was the same as 3.1.1, except L-ascorbic acid instead of D-isoascorbic acid. The yield was 82 %.

3.1.7 Synthesis of potassium (2R,3S)-3,4-O-isopropylidene 2,3,4-trihydroxy-butyrate (**IX**)

The procedure was the same as 3.1.3. The yield was 84 %.

3.1.8 Synthesis of ethyl (2R,3R)-3,4-O-isopropylidene-2,3,4-trihydroxy-butanoate (**X**)

The procedure was the same as 3.1.4. The pure ester is colorless oil and the bp is 115-120°C/3mmHg. The yield was 78%, [α] = 19.11 (C 1.58, MeOH).

3.1.9 Synthesis of (2S,3S)-1,2-O-isopropylidenebutane-1,2,3,4-tetrol (**XI**)

The procedure was the same as 3.1.5. The yield was 86%. The crude product is light yellow viscous oil and [α] = 2.13 (C 4.20, EtOH).

3.1.10 Synthesis of (2S,3S)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol (**XII**)

The procedure was the same as 3.1.6. The yield was 84%. The pure epoxide is colorless oil and the bp is 72.5°C/15mmHg. $[\alpha]_{589}$ –7.76

deg.dm^{-1}.g^{-1}.cm^{3} (c = 1.20, $CHCl_3$). Literature[75] $[\alpha]_{589}^{22}$ – 6.54 deg.dm^{-1}.g^{-1}.cm^{3} (c = 1.88, $CHCl_3$).

3.1.11 Synthesis of ethyl (2S,3S)-2-O-benzoyl-3,4-O-isopropylidene-2,3,4-trihydroxybutanoate (**XIII**)

Benzoic acid (2.44 g, 20 mmol), triphenylphosphine (TPP, 5.3 g, 20 mmol), and compound **X** were dissolved in dry THF (100 ml). To this solution was added dropwise a solution of DIAD (4.2 g, 20 mmol) in THF (20 ml). After the mixture was stirred for 12 h at room temperature, the solvent was removed under diminished pressure and the residue taken up in ethyl ether. The solid precipitated was removed by filtration, the filtrate and washings were concentrated, and the resulting oil was chromatographed on a silica gel column. The column was eluted with hexane followed by hexane-ethyl acetate (95/5, v/v). The fractions containing UV positive material were pooled and furnished the intermediate **XIII** (2.2 g, 72%). [α] = -11.90 (C 4.88, EtOH).

3.1.12 Synthesis of (2S,3R)-1,2-O-isopropylidenebutane-1,2,3,4-tetrol (**XIV**)

To a cooled, stirred suspension of powdered $LiAlH_4$ (45 mg, 1.18 mmol) in anhydrous ethyl ether (10 ml) was added dropwise a solution of the benzoate **XIII** (241 mg, 0.78 mmol) in anhydrous ethyl ether (5 ml). After the addition was complete, the reaction mixture was stirred at room temperature for 1 h and then heated at reflux for 3 h. The excess $LiAlH_4$ was decomposed by sequential addition of water (0.1 ml), a 15% NaOH solution (0.1 ml), and water (2.2 ml). After filtration, the ethereal layer was dried over anhydrous sodium sulfate and concentrated to a light, yellow oil. The oil was distilled to provide **XIV** (120 mg, 90%): bp 110-120°C/0.3mmHg. $[\alpha]_{589}^{25}$ – 9.17 $deg.dm^{-1}.g^{-1}.cm^3$ (c = 5.81, C_2H_5OH). Literature[89] $[\alpha]_{589}^{25}$ – 7.61 $deg.dm^{-1}.g^{-1}.cm^3$ (c = 6.51, C_2H_5OH)

3.1.13 Synthesis of (2S,3R)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol (XV)

The procedure was the same as 3.1.6. The yield was 74%. **XV** is a colorless oil and the bp is 46°C/2.5 mmHg. $[\alpha]_{589}^{25}$ – 11.14 $deg.dm^{-1}.g^{-1}.cm^3$ (c = 2.59, C_2H_5OH). Literature[60] $[\alpha]_{589}^{25}$ – 10.96 $deg.dm^{-1}.g^{-1}.cm^3$ (c = 2.55, C_2H_5OH).

3.2 Anionic polymerizations

3.2.1 Vacuum Line Design and Operation

The designed high vacuum line illustrated in Figure 1 consists of a fore pump, diffusion pump, trap and manifold. To minimize the transfer of vibrations to the vacuum line, the fore pump is mounted on the floor and the connection between fore pump and the vacuum system is made with heavy walled vacuum tubing. The main high vacuum manifold is equipped with a high-vacuum gauge so the initial degree of evacuation can be measured. Standard high-vacuum stopcocks are employed. The working manifold includes one mercury-filled manometer for vapor pressure measurement, and one McLeod gauge for initial vacuum measurement. An arrangement of stopcocks is used to bypass the diffusion pump to make it unnecessary to wait for the diffusion pump to cool down when the main trap must be removed for cleaning or when the vacuum system is turned off and the fore pump is vented to the atmosphere.

To start a vacuum system, the clean main trap is fitted in place with an even coat of stopcock grease on the joint. A dewar partially filled with liquid nitrogen is raised around this trap, and the fore pump is immediately turned on. When the line has pumped down to less than 1 torr, the stopcocks are turned to route the gas through the diffusion pump, and the heater on the diffusion pump is then turned on. The progress of the evacuation is followed by means of an electronic vacuum gauge. The line is evacuated for several hours before use to permit the desorption of moisture and a thorough check on the performance of the line.

To shut the system off, stopcock next to (F) and (I) are turned to isolate the diffusion pump and to establish straight communication between the main trap (I), and the fore pump; also, the main valve to the vacuum system is closed. The following set of operations is then carried out in sequence and without delays between each step: the fore pump is switched off, stopcock (D) is opened to bring the system to atmospheric pressure, the liquid nitrogen filled Dewar on trap (I) is lowered, and trap (I) is removed and placed in a hood. The diffusion pump heater can then be switched off.

3.2.2 Bulk Homopolymerization

Polymerization of the epoxides were carried out in bulk typically at 30°C using t-BuOK or CsOH as initiator. Pre-dried $CsOH{\cdot}H_2O$ was weighed inside a dry-box and was added to a polymerization tube through a long neck glass funnel then the polymerization tube was attached to a high vacuum system. $CsOH{\cdot}H_2O$ was dried inside the polymerization tube under high vacuum at 180°C (oil bath) for 4 hours to remove the water[52] before introduction of the monomer.

Potassium *tert*-butoxide was purified by sublimation and transferred to a small vial. Then the vial containing the catalyst was weighed in a balance inside a dry-box. The catalyst was transferred to a polymerization tube through a long neck glass funnel in the dry-box. After that, the glass funnel, containing a trace amount of catalyst on the wall, and the empty vial were weighed separately. Then the clean and dried funnel were weighed again. The mass of the catalyst was calculated by all the above data as following:

Mass of Catalyst = Mass of Vial Containing Catalyst - (Mass of Empty Vial + Mass of Catalyst in the Glass Funnel)

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

Prior to polymerization, the epoxide was dried over calcium hydride by refluxing under vacuum and then was distilled.

After the polymerization tube, containing the catalyst, was attached to a high vacuum system, the t-BuOK was further dried at 80°C (oil bath) under high vacuum for 4 hours (CsOH was dried at 180°C for 4 hours). Then the dried epoxide was transferred to the polymerization tube with a long needle syringe. The monomer was deoxygenated by three freeze-pump-thaw cycles. Then the polymerization tube was sealed under high vacuum (1.0×10^{-4} mm Hg) and kept at 30°C for a specified amount of time. Some polymerizations were carried out at different temperatures.

3.2.3 Removal of Unreacted Monomer and 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. The unreacted monomer was recovered under high vacuum at room temperature using a dual trap shown in Figure 2. The system was kept under vacuum until there was no visible change in the escape of the monomer from 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. 2). The optical activity of the unreacted monomer was measured in chloroform or benzene while the temperature was maintained at 25°C by circulating water from a thermosat. A 2.0 g/dL solution of the epoxide was prepared in a 2 mL volumetric flask. The epoxide was weighed in the volumetric flask with an analytical balance, then solvent was added to the volumetric flask. The optical activity of pure epoxide was also measured at the same concentration at 25°C.

3.2.4. Determination of Polymer Yield

3.2.4.1. Determination of Polymer Yield by High Vacuum System

After removing the unreacted monomer, the polymerization tube was weighed. The polymer was then dissolved in chloroform 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 from a speedvac at around 40°C 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 = 9.3231 g
Weight of the tube after removing unreacted monomer = 9.2885 g
Weight of unreacted monomer (9.3231 - 9.2885) = 0.0346 g
Weight of empty tube and stirrer = 9.1267 g
Weight of initiator = 0.0120 g
Weight of polymer (9.2885-9.1267-0.0120) = 0.1498 g
Weight of monomer used (0.1498+0.0346) = 0.1844 g
%yield = (0.1498 / 0.1844) × 100 % = 81.2 %

3.2.4.2 Determination of Polymer Yield by GPC

Crude poly(2S,3S)-epoxides prepared with t-BuOK as initiator at different conversions were dissolved in THF respectively. The THF solutions were filtered, then directly analyzed for polymerization yield with GPC. The polymerization conversions of the crude polymers were calculated by the relative area of the polymer peak and the unreacted monomer peak in the GPC measurement. The calibration curve was described by ratio of the area of purified polymer peak to the area of monomer peak in GPC measurement vs the ratio of weight of purified polymer to weight of the monomer (Figure 3).

3.2.5. Isolation and Purification of Homopolymers

The crude poly(2R,3S)-epoxide was dissolved in hot CF_3CH_2OH, then was precipitated into ether. The precipitate was washed with ether three times, with distilled water twice, then was dried in a speedvac under vacuum at about 40°C until the weight is constant.

The crude poly(2S,3S)-epoxide was dissolved in hot chloroform , then precipitated into cold hexane. The precipitate was washed with hexane three times, with distilled water twice, then was dried in a speedvac under vacuum at about 40°C until the weight is constant.

3.2.6 Bulk Copolymerization

The treatment of catalyst and the polymerization was the same as the method used in homopolymerization. The recovered molar ratio of (2R,3S) / (2S,3S)-epoxide was determined by gas chromatography or by quantitative analysis of ^{1}H NMR of the comonomer. The initial molar ratio of (2R,3S) / (2S,3R)-epoxide was determined by weighing the monomers.

The crude poly(2R,3S) / (2S,3S)-epoxides were isolated and purified by dissolved in chloroform and precipitated in solvent mixture of methanol and water, then washed with the same solvent mixture for three times. The purified copolymers were dried in a speedvac under vacuum at about 40°C.

The crude poly(2R,3S) / (2S,3R)-epoxides prepared with t-BuOK as initiator were isolated and purified by dissolved in cold chloroform and precipitated in methanol. The precipitate was washed with cold methanol for three times then was dried in a speedvac until constant weitht.

3.2.7 Solution Copolymerization

Solution copolymerization of (2S,3S)–epoxide-(S)-propylene oxide in *N,N'* – dimethylpropyleneurea (DMPU) was investigated. DMPU was stirred at 60°C over CaH_2 for 1 hour, and then distilled at reduced pressure (b.p. 71 - 72°C / 0.1mmHg) before use. A polymerization tube containing weighed purified t-BuOK was connected to the high vacuum system and was heated in a 80°C oil bath for 2.5 hours under high vacuum. Then the polymerization tube was flushed with nitrogen gas and DMPU was added through a long needle syringe. After that the polymerization tube was degassed and (2S,3S)-epoxide was added through a long needle syringe. The solution was degassed under high vacuum then the tube was sealed. Then the sealed tube was heated at 30°C for 48 hours to ensure the polymerization complete. The sealed tube containing poly(2S,3S)-epoxide solution was opened and (S)-propylene oxide was added in a dry-box. The reaction tube with stirring was kept in the dry-box at 30°C for 48 hours.

The copolymer was isolated by stripping off the DMPU in a speedvac at 40°C under vacuum for 48 hours, then purified with the same method as for homopolymers of poly(2S,3S)-epoxide.

3.2.8 Characterization of the Recovered Unreacted Monomer

The recovered monomers were analyzed by ^{1}H NMR, ^{13}C NMR, GC, GPC and optical rotation measurements.

3.3 Molecular weights measurement

3.3.1 Gel Permeation Chromatography (GPC)

GPC of crude and purified polymers were carried out on a Waters 150C instrument with Millennium 2010 Chromatography Manager for purpose of determining the molecular weight and molecular weight distribution of the polymers. THF (dried over CaH_2 then distilled) was used as the mobile phase at a flow rate of 1.0 mL/min at 40°C. The stationary phase consisted of four ultrastryagel columns of 10^5, 10^4, 10^3, and 5×10^2 A sizes. The GPC calibrations were based on polystyrene standards.

3.3.2 Vapor pressure osmometer (VPO)

It was carried out on a Jupiter model 833 vapor pressure osmometer in o-dichlorobenzene at 126°C. Calibration of the vapor pressure osmometer was carried out with sucrose octaacetate in toluene at 50°C.

3.3.3 Carbon-13 nuclear magnetic resonance spectroscopy

^{13}C NMR was also used to determine the number average molecular weight of the polymers by the sum of the integral value for the methyl of *tert*-butoxide end-group with the main chain methyl signals. In using this procedure an assumption that each polymer molecule contains one *tert*-butoxide end group was made.

3.4 Spectroscopy analysis

3.4.1 Nuclear magnetic resonance (NMR) spectroscopy

3.4.1.1.a ^1H and ^{13}C NMR spectra

Proton (^1H) and carbon (^{13}C) NMR spectra were obtained at 25°C on an IBM WP 200SY FTNMR spectrometer using a 5-mm dual $^{13}C/^1H$ probe for ^1H and a 10-mm dual $^{13}C/^1H$ probe for ^{13}C, operating at 200 MHz for ^1H and 50 MHz for ^{13}C. ^1H and ^{13}C spectra of the polymers were obtained, respectively, in 5% and 10% (w/v) solutions of deuterated benzene-d_6, C_6D_6 at 25°C or 60°C. The spectra were referenced to the solvent signals, 7.15 ppm for the proton spectra and 128.0 ppm for the carbon spectra.

3.4.1.1.b Distortionless enhancement by polarization transfer (DEPT)

The DEPT spectra for the polymers were obtained in 10% (w/v) solution in benzene-d_6 at 25°C in order to determine the multiplicities of each ^{13}C resonance. The following standard pulse sequence was used (where D1 is the relaxation delay):[76]

^{1}H: D1 — 90° — ½ $J_{c\text{-}h}$ — 180° — ½ $J_{c\text{-}h}$ — PO — ½ $J_{c\text{-}h}$ — BB

^{13}C: ———————— 90° ———— 180° ———————— FID

PO is a variable depending on the desired multiplicities selection; i.e. for PO = 135° signals of positive intensity represent methyl and methine carbons and signals of negative intensity represents methylene carbons. For all reported DEPT results PO was chosen as 135°. $J_{c\text{-}h}$ is the one bond J scalar coupling constant between carbon and hydrogen. A value of 135 Hz was used for the experiments. Quaternary carbons have zero intensity. A relaxation delay, D1, of 2 seconds was used between pulses.

3.4.1.1.c ^{1}H and ^{1}H correlated spectroscopy (COSY)

The COSY spectrum was obtained by the use of the standard pulse sequence:[77]

^{1}H: D1 — 90° — D0 — 90° — FID

The COSY spectrum was recorded in a Varian Unity 200 spectrometer using 5% (w/v) solution in benzene-d_6 with benzene-d_6 as internal reference at 25°C. The experiment employed a recycle time of 4.0 s, with 8 transients being collected for each t_1 value. A total of 256 spectra, each consisting of 2048 data points, were accumulated, and the data matrix was zero-filled to 1024 by 2048 points with a frequency range of 2500 Hz in both dimensions. The pulse sequences included a four-step phase-cycling routine. For quadrature detection the phase cycles together with the receiver reference phase are incremented by $\pi/2$ every four accumulations to compensate for phase and amplitude errors in the receiver channels. The resulting interferogram were processed by using a phased shifted sine apodization factor with a phase of 0.5, endpoint of 1 and an integer exponent of 2, followed by zero-filling to 512 data points before the second Fourier transformation. The spectrum was symmertrized and plotted as a contour map.

3.4.1.1.d ^{1}H and ^{13}C correlated spectroscopy - Pulse Field Gradient[78-82] Heterronuclear Multiple-Quantum Correlation (GHMQC)

The essence of the HMQC experiment is the cancellation or elimination of the signals from protons attached to ^{12}C, leaving only signals from protons attached to ^{13}C contributing to a ^{13}C-^{1}H chemical shift correlation spectrum. With pulsed field gradients, coherence pathway can be selected by combining r.f. pulses and pulsed field gradients in one pulse sequence.. This yields artifact free H,C correlation spectra in a fraction of the time needed previously, since the receiver gain of the proton channel can be set to a very high value.

The spectra were recorded on a Varian Unity*plus* 600 Spectrometer using 10% (w/v) solution in benzene-d_6, which was as internal reference (7.15 ppm vs. Me_4Si for ^{1}H and 128.0 ppm vs. Me_4Si for ^{13}C), at 40°C.

The data for the spectrum was processed using Varian VNMR software; the data were forward extended in *f*1 to twice the original size using linear prediction (48 complex points were used to calculated 12 coefficients), zero filled to 4096×8196, and sine-bell weighted in both dimensions. The spectra is plotted in absolute-value mode with five contours spaced at intervals of 3. The data were obtained by averaging of 64 transients for each of 220 t1 increments; 90° pulse widths were 6.2

and 14.0 μs for ^{1}H and ^{13}C, respectively, and the gradients pulses were 2.0 ms in duration and were about 0.30 and 0.22T/m (for the first and second pulses, respectively).

3.4.1.1.e ^{1}H and ^{13}C correlated spectroscopy - Pulse Field Gradient Heteronuclear Multiple-Bond Correlation (GHMBC)[79-81]

The spectra were recorded on a Varian Unity*plus* 600 Spectrometer using 10% (w/v) solution in benzene-d_6, which was as internal reference (7.15 ppm vs. Me_4Si for ^{1}H and 128.0 ppm vs. Me_4Si for ^{13}C), at 40°C. The experiments employed the same pulse sequence as the GHMQC, only simply set the delay d2 to 50 ms, corresponding to a spin coupling constant of 10 Hz to obtain long-range H,C correlations via ^2J(C,H) and ^3J(C,H).

The data for the spectrum was processed using Varian VNMR software and forward extended in *f*1 to twice the original size using linear prediction (48 complex points were used to calculated 12 coefficients), zero filled to 4096×8196, and sine-bell weighted in both dimensions. The spectra is plotted in absolute-value mode with five contours spaced at intervals of 3. The data were obtained by averaging of 64 transients for each of 220 t1 increments; 90° pulse widths were 6.2 and 14.0 μs for ^1H and ^{13}C, respectively, and the gradients pulses were 2.0 ms in duration and were about 0.30 and 0.22T/m (for the first and second pulses, respectively).

3.4.1.2 Gas Chromatography

Gas chromatography analysis were carried out with a Hewlett-Packard 5890 Series II plus gas chromatograph using a flame ionization detector. The description of the typical GC experiment is shown below:

Column: diethylene glycol succinate (6 ft. × ¼ in.)

Detector: flame ionization

Injection temperature: 250°C

Detector temperature: 350°C

Run Table

Oven temperature initial value = 85°C

Oven temperature initial time = 10 min

Oven temperature program rate = 20°C/min

Oven temperature final value = 250°C

Oven temperature final time = 25 min

3.4.1.3 Infrared spectroscopy (FT-IR)

Infrared spectra of the polymers and monomers were recorded on a Magna-IR^{TM} 550 spectrometer using KBr pellet samples. The scanning range was generally from 4000 to 400 cm^{-1} with a 300 cm^{-1}/min. The absorption band position were calibrated with standard polystyrene film. All measurements were made at room temperature.

3.5 End group analysis

3.5.1 Acytylation of purified poly(2S,3S)-epoxide

0.1 g of polymer was dissolved in 2 ml of $CHCl_3$ and 0.03 g pyridine added with stirring. 0.03 g CH_3COCl in 1 ml $CHCl_3$ was added with stirring to the polymer solution at room temperature.[82] After the reaction mixture was stirred for 4 hour, it was added to hexane. Pyridine salt was precipitated but the polymer was not. The clear solution was concentrated then the solid was dissolved in $CHCl_3$. The $CHCl_3$ solution was added to mixture of MeOH/H_2O and the resulting precipitate filtered off, washed with water, and dried overnight in a speedvac at around 40°C.

3.5.2 Nuclear magnetic resonance spectroscopy

3.5.2.1 Carbon-13 NMR

^{13}C NMR spectra were obtained at 25°C on 10% (w/v) solutions in benzene-d_6 as described in Section 3.5.1.1.a.

3.5.2.2 Distortionless enhancement by polarization transfer (DEPT)

The spectra were obtained via the method described in section 3.5.1.1.b on the polymer samples in a 10% (w/v) solution in benzene-d_6 at 25°C.

3.5.2.3 Quantitative analysis[83-85]

The ^{13}C NMR spectra were recorded on a Varian Unity 200 spectrometer operating at 50 MHz with and without relaxation agent (0.1%) depending on the particular experiment. Samples were dissolved in benzene-d_6, 10% (w/v) in 5 mm tubes with benzene-d_6 as internal reference at 25°C. Decoupling was begun just before the pulse, and was gated off during a relaxation delay between pulses, then the Overhauser effect has to be suppressed, only decoupling effects should be seen. The other experimental conditions chosen to maximize signal-to-noise ratio were:

(i) pulse angle 90°;
(ii) pulse delay 9.00 sec;
(iii) acquisition time 1.50 sec;
(iv) spectral width 7561 Hz; and
(v) number of accumulations: 10000-15000

3.5.2.4 T1 measurement of ^{13}C NMR of the polymer[77,86,87]

T1's were determined by the inversion-recovery experiment with the following pulse sequence:

$$\pi - \tau - \pi/2 - \text{Acquire}$$

where π and $\pi/2$ are a π pulse and a $\pi/2$ pulse, τ is a delay which is under the control of the operator.

The ^{13}C NMR spectra were recorded on a Varian Unity 200 spectrometer operating at 50 MHz. Samples were dissolved in benzene-d_6, 10% (w/v) in 5 mm tubes with benzene-d_6 as internal reference at 60°C. The other experimental conditions chosen were: acquisition time 3.00 sec; pulse delay 5.00 sec; spectral width 7561 Hz. Thirteen d2 values were chosen ranging from 10 ms to 64 seconds for carbon resonances, 2000 acquisitions were accumulated for each d2 value. A single exponent was used to fit the relaxation data and regression analysis to calculate T_1's and the errors. The average errors were ~ 3%, and in no case did they exceed 10%.

3.5.2.5 GHMBC of poly(2S,3S)-epoxide

The spectra were obtained at 25°C on 10% (w/v) solutions in benzene-d_6 as described in Section 3.5.1.1.e.

3.6 Melting point measurements

Melting points of the polymers were tested with Fish Johns melting point apparatus.

3.7 Optical rotation measurements

Optical activity measurements were made with a Jasco model DIP-370 digital polarimeter.

4.0 RESULTS AND DISCUSSION

4.1 Characterization of the Monomers

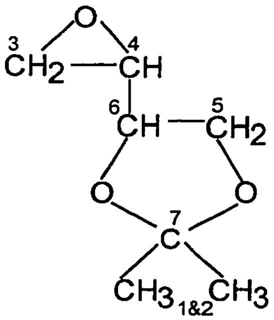
4.1.1 ^{13}C NMR Assignments of the Monomers

^{13}C NMR spectra of (2S,3S)-, (2R,3S)- and (2S,3R)-epoxides are shown on Figure 4, 5 and 6, respectively. Tables 1 shows the chemical shift values of the monomers. DEPT-135° spectrum of the (2S,3S)-epoxide is shown on Figure 7. Because the five-member ring contains two oxygens, the chemical shifts of its CH_2 and CH are more downfield than the epoxide ring. From the DEPT-135° spectrum, peak 3 and 5 are known as methylene carbons , while peak 4 and 6 as methine carbons. Therefore, the ^{13}C NMR for all three epoxides are assigned as in the Table 1 and the Scheme IV (The chemical shifts of (2S-3R)-epoxide is the same as the (2R,3S)-epoxide's):

Table 1 Chemical Shifts of the ^{13}C NMR Spectrum of the (2R,3S)- and (2S,3S)-Epoxide

Carbon Number	Chemical Shift (ppm)	
	(2R,3S)-	(2S,3S)-
1	25.51	25.65
2	26.7	26.44
3	45.05	42.81
4	51.91	51.54
5	66.75	65.94
6	76.82	76.23
7	109.62	109.76

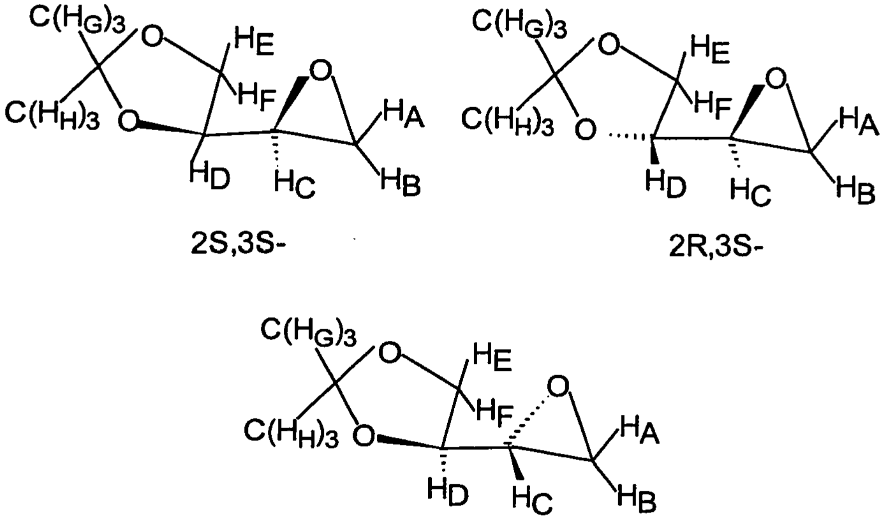
Scheme IV,



4.1.2 ^{1}H NMR Spectra Assignments

Figure 8, 9 and 10 show the ^{1}H spectrum of the(2R,3S)-epoxide, the (2S,3S)-epoxide the (2S,3R)-epoxide, respectively. Table 2 shows δ values of the spectra (The chemical shifts of the (2R,3S)-epoxide and the (2S,3R)-epoxide are the same). The signal assignments shown in Scheme V were based on the observed splitting pattern and chemical shift values in relation to those for protons in analogous environments, obtained either by calculation or from model compounds.[93,94] In the HMQC technique, the ^{13}C shifts are correlated to the shifts of the adjoining ^{1}H nuclei thus permitting the rapid assignments of either the ^{1}H or the ^{13}C spectrum whenever the other is known. GHMQC spectrum of the (2S,3R)-epoxide recorded on a 600 NMR spectroscopy (Figure 11) shows that multiplet Ha and Hb in the ^{1}H dimension correlate with the five-member ring methylene carbon in the ^{13}C dimension. Similarly, multiplet Hc correlates with five-member ring methine carbon, multiplet He & Hf correlate with three-member ring methylene carbon, and multiplet Hd correlates with three-member ring methine carbon. GHMBC spectrum of the (2S,3R)-epoxide (Figure 12) shows that multiplet Hd, He and Hf correlates with five-member ring quaternary carbon (3-bond correlation), which means that Hd, He and Hf are five-member ring protons. GHMQC and GHMBC spectra of the (2S,3S)-epoxide (Figures 13 and 14) are similar to the spectra of the (2S,3R)-epoxide. All these 2-D NMR spectra prove the assignments in Scheme V.

Scheme V,



2S,3S-

2R,3S-

2S,3R-

Table 2

Chemical Shifts of the ^{1}H NMR Spectrum of the (2S,3S)-Epoxide and (2R,3S)-Epoxide

Proton	Chemical Shift (ppm)	
	(2S,3S)-	(2R,3S)-
Hg & Hh	1.37 &1.45	1.37&1.49
Ha	2.66-2.70	2.26-2.30
Hb	2.78-2.82	2.43-2.47
Hc	3.01-3.07	2.82-2.88
Hd	3.85	3.86-3.92
He	4.00	
Hf	4.10	
He&Hf		3.65-3.80

4.2 Homopolymerization of the Epoxides

4.2.1 Homopolymerization of (R,S)-epoxide

4.2.1.1 Homopolymerization of (R,S)-epoxide with CsOH

4.2.1.1.a Solubility and Melting Point Analysis

$CsOH \cdot H_2O$ was dried inside the polymerization tube under high vacuum at 180°C for 4 hours. Under high vacuum, the $CsOH \cdot H_2O$ monohydrate begins to decompose below its melting point (180°C). Thus when CsOH is dried at 180°C, the amount of remaining water can possibly act as a transfer agent then is decreased. The polymerization of the epoxide was investigated in bulk in sealed evacuated tubes under high vacuum over a temperature range at -78 -60°C (Table 3). The polymerization was also carried out at constant temperature (35°C) and at different period time, which result is summarized in Table 4. The reaction mixture was a light orange solid. The polymer

Table 3

Bulk Polymerization of (2R,3S)-Epoxide

With CsOH at Various Temperatures

Sample #	Temp. (C)	Reaction Time	Yield (%)
1	-78	10 hour	3.0
2	0	10 hour	37.6
3	30	10 hour	81.4
4	60	10 hour	100

[I]/[M] = 8%

Table 4

Bulk Polymerization of (2R,3S)-Epoxide at Different Time

With CsOH as Initiator

Sample #	Reaction Time	Yiled (%)
1	17 h 40 min	27.6
2	25 h	30.8
3	42 h	35.3

[I]/[M] = 6% Temp.=35°C

was isolated by stirring the orange solid over hot 2,2,2-trifluoroethanol followed by precipitation into diethyl ether at room temperature. The purified polymer became a white powder. The measurement of gas chromatography of unreacted monomers (Figure 15) showed there was no obvious dimers or trimers and the purity of the unreacted monomer was 96.3%. The ^{1}H and ^{13}C NMR analysis of unreacted monomers of the sample 1, 2 and 3 in Table 4 also showed there were no evidence of dimers or trimers.

The polymer was insoluble in any common organic solvents such as DMSO, DMF, THF, DMA, nitrobenzene, methylene chloride, acetonitrile, dioxane, and chlorobenzene, etc. at room temperature or near the boiling point of the solvents employed. Some swelling was observed but less than 0.5% weight loss of the sample were found in these cases. The only good solvents for this polymer are strong protonic solvents such as hexafluoroacetone in water, O-chlorophenol at room temperature, hexafluoro-2-propanol at 30°C and 2,2,3,3-tetrafluoroethanol, 2,2,2-trifluoroethanol at 60°C. Melting point of the polymers was about 165-170°C depending on the polymerization conditions of the polymers.

4.2.1.1.b ^{1}H NMR Spectroscopy

A saturated solution of poly (2R,3S)-epoxide made with CsOH in C_6D_6 was analyzed by ^{1}H NMR at 60°C. The Figure 16 shows that the epoxide protons could not be well resolved. The chemical shifts are summarized in Table 5.

Table 5

Chemical Shifts of the ^{1}H NMR Spectrum of the Poly(2R,3S)-Epoxide With CsOH as Initiator

Proton Number	Chemical Shift (ppm)
1	1.35 (CH3)
2	1.55 (CH3)
3	3.40-3.85 (3H)
4	3.85-4.32 (3H)

4.2.1.1.c ^{13}C NMR Spectroscopy

Figure 17 shows ^{13}C NMR spectrum of poly(2R,3S)-epoxide in o-chlorophenol at 80°C. The carbon number and chemical shifts are summarized in Table 6.

Table 6

Chemical Shifts and Chemical Type of the ^{13}C NMR Spectrum of the Poly(2R,3S)-Epoxide With CsOH as Initiator

Carbon Number	Chemical Shift (ppm)	Chemical Type
1	25.36	CH3
2	26.78	CH3
3	66.91	CH2
4	71.86	CH2
5	76.03	CH
6	81.48	CH
7	109.92	C

Figure 18 shows DEPT-135° edited spectrum. The result is shown in Table 6.

4.2.1.2 Homopolymerization of (2R,3S)-epoxide with Potassium *tert*-Butoxide

The polymerizations were carried out in sealed glass tubes evacuated on a high vacuum apparatus at 30°C. The reaction mixture was a light orange solid. The polymer was isolated by stirring the orange solid over hot 2,2,2-trifluoroethanol followed by precipitation into diethyl ether at room temperature. The purified polymer became a white powder. The polymer is insoluble in any common organic solvents such as DMSO, DMF, THF, DMA, nitrobenzene, methylene chloride, acetonitrile, dioxane, and chlorobenzene, etc. at room temperature or near the boiling point of the solvents employed. Some swelling was observed but less than 0.5% weight loss of the sample were found in these cases. The only good solvents for this polymer are strong protonic solvents such as hexafluoroacetone in water, O-chlorophenol at room temperature, hexafluoro-2-propanol at 30°C and 2,2,3,3-tetrafluoroethanol, 2,2,2-trifluoroethanol at 60°C.

With the same ratio of initiator to monomer, the molecular weight of the polymer with potassium *tert*-butoxide as initiator seems to be higher than one with CsOH as initiator, therefore the polymer with potassium *tert*-butoxide was even more insoluble in organic solvents than that with CsOH as initiator. There were no ^{1}H and ^{13}C NMR spectra of this polymer obtained because of the insolubility. Melting point of the polymer was 165-170°C.

4.2.2 Homopolymerization of (2S,3S)-epoxide

4.2.2.1 Homopolymerization of (2S,3S)-epoxide with CsOH

4.2.2.1.a Solubility and Melting Point Analysis

The polymerization of the epoxide was investigated in bulk in sealed evacuated tubes under high vacuum over a temperature range at 0 -80°C (Table 7). The reaction mixture was a light orange solid. The polymer

Table 7

Bulk Polymerization of the (2S,3S)-Epoxide With CsOH at Various Temperatures

Sample #	Temp. (C)	Reaction Time	Yield (%)
1	0	60 hour	0
2	30	60 hour	77.7
3	60	60 hour	78.8
4	80	60 hour	67.4

[I]/[M] = 8%

was isolated by stirring the orange solid over hot chloroform followed by precipitation into hexane at room temperature. The purified polymer became a white powder.

The polymers were soluble in some common organic solvents such as DMSO, DMF, chlorobenzene, and hot chloroform, THF, benzene, but is insoluble in cold hexane, cold methanol and water. Melting point of the polymers was about 112-116°C depending on the polymerization conditions.

4.2.2.1.b Infrared Spectroscopic Characterization

FT-IR spectrum of poly (2S,3S)-epoxide prepared with CsOH is shown in Figure 19. The strongest absorbance was due to the C-O-C asymmetric stretching vibrations of the ethereal and acetal functions at 1270-1040 cm^{-1}.[72] A broad, weak absorbance was found at ~ 3500 cm^{-1} due to stretching vibration of the terminal OH- groups. The strong absorbances at 2996, 2930 and 2891 cm^{-1} were due to C-H stretching vibrations from CH_3, CH_2 and CH type of structures, respectively, while the absorbances at 1380 & 1477 cm^{-1} were due to CH_3- bending vibrations.[72]

4.2.2.1.c ^{1}H NMR Spectroscopy

Poly (2S,3S)-epoxide in C_6D_6 solution was analyzed by ^{1}H NMR at 40°C. The Figure 20 shows that the epoxide protons could be well resolved to compare with the spectrum of poly(2R,3S)-epoxide (Figure 16). The chemical shifts are summarized in Table 8.

Table 8

Chemical Shifts of ^{1}H NMR Spectrum of the Poly(2S,3S)-Epoxide With CsOH as Initiator

Proton Number	Chemical Shift (ppm)
1	1.42 (3H)
2	1.54 (3H)
3	3.40-3.60(1H)
4	3.68-4.00(3H)
5	4.00-4.20(1H)
6	4.20-4.38(1H)

4.2.1.1.d ^{13}C NMR Spectroscopy

Figure 21 shows ^{13}C NMR spectrum of poly (2S,3S)-epoxide in deuterial benzene at 40°C with benzene as reference. The carbon number and chemical shifts are summarized in Table 9.

Table 9

Chemical Shifts and Chemical Type of ^{13}C NMR Spectrum of the Poly(2S,3S)-Epoxide With CsOH as Initiator

Carbon Number	Chemical Shift (ppm)	Chemical Type
1	25.92	CH3
2	26.94	CH3
3	66.39	CH2
4	71.89	CH2
5	77.92	CH
6	81.12	CH
7	109.12	C

The DEPT-135° edited spectrum of the (2S,3S)-epoxide is similar to the spectrum of the (2R,3S)-epoxide. The result is shown in Table 9.

4.2.2.1.e Molecular Weight and Molecular Weight Distribution

The molecular weight of the poly(2S,3S)-epoxide were measured by Gel Permeation Chromatography (GPC) and Vapor Pressure Osmometer(VPO). The molecular weight distribution were determined by GPC. The result is summarized in Table 10.

Table 10

Molecular Weights and Molecular Weight Distribution of

The Poly(2S,3S)-Epoxide with CsOH as Initiator

Sample	Yield (%)	GPC Data			VPO
		Mw	Mn	Mw/Mn	Mn
1	77.7	3669	3167	1.18	4909
2	78.8	4192	3540	1.16	5283
3	67.4	1885	1598	1.18	3333

4.2.2.1.f The Optical Rotations of Poly(2S,3S)-Epoxide with CsOH

The optical rotations of poly(2S,3S)-epoxide were analyzed in benzene solution at 40°C. The result is listed in Table 11.

Table 11

Optical Rotations of the poly(2S,3S)-epoxide with CsOH As Initiator

Sample	Polymerization Temperature	Mn	
		VPO	[α]
1	30	3333	-8.92
2	60	5283	-6.60
3	80	4909	-7.64

Solvent = benzene

The optically active polymers may rotate the plane of polarized light more than, or less than, the monomeric analogue, and both effects have been found in the Table 11. This is apparent from the fact that the optical activity depends on the scalar product of electric and magnetic dipoles of the molecule in the excited state, which may be enhanced or diminished by the conformational distribution and configurational arrangement of the optically active units on the polymer molecule.

4.2.2.2 Homopolymerization of (2S,3S)-epoxide with Potassium *tert*-Butoxide

4.2.2.2.a Solubility and Melting Point Analysis

The polymerizations were carried out in sealed glass tubes evacuated at a high vacuum (1.0×10^{-4} mm Hg) apparatus at 30°C. In polymerization, the reaction mixture changed from green to dark orange liquid then to orange solid. The polymer was purified by dissolved in hot chloroform then precipitated in cold hexane. The purified polymer became white powder. The solubility of the polymer is similar to the solubility of the polymer prepared with CsOH as initiator. Melting point of the polymers was about 104-109°C depending on the polymerization conditions.

4.2.2.2.b ^{1}H NMR Spectroscopy

Poly (2S,3S)-epoxide in C_6D_6 solution was analyzed by ^{1}H NMR at 40°C. The Figure 22 shows that the epoxide protons could be well resolved. The chemical shifts are summarized in Table 12.

Table 12

Chemical Shifts of ^{1}H NMR Spectrum of the Poly(2S,3S)-Epoxide With Potassium *tert*-Butoxide as Initiator

Proton Number	Chemical Shift (ppm)
a	1.37 (3H)
b	1.50 (3H)
c	3.45 (1H)
d	3.78 (1H)
e&e'	3.86 (2H)
f	4.07(1H)
g	4.25 (1H)

4.2.2.2.c ^{1}H-^{1}H Correlated Spectroscopy (COSY) of Poly(2S,3S)-Epoxide with *tert*-BuOK

The COSY spectrum (Figure 23) of the poly(2S,3S)-epoxide was run in a 200 MHg NMR spectroscopy, which contains a computer generated 1-D spectrum along the F1 and F2 axes in order to aid in the interpretation of ^{1}H NMR spectrum. Cross peaks shows that proton multiplet 1 is coupled with multiplet 2, 3, 4, multiplet 2 is coupled with multiplets 1 and 3; multiplet 3 is coupled with multiplets 1, 2, 4; and multiplet 4 is coupled with multiplets 1 and 3.

4.2.2.2.d ^{13}C NMR Spectroscopy

Figure 24 shows ^{13}C NMR spectrum of poly (2S,3S)-epoxide in deuterial benzene at 40°C with benzene as reference. The carbon number and chemical shifts are summarized in Table 13.

The DEPT - 135° edited spectrum of the poly(2S,3S)-epoxide is similar to the spectrum of the poly(2R,3S)-epoxide. The result is shown in Table 13.

Table 13

Chemical Shifts and Chemical Type of ^{13}C NMR Spectrum of the Poly(2S,3S)-Epoxide With *tert*-BuOK as Initiator

Carbon Number	Chemical Shift (ppm)	Chemical Type
1	25.90	CH3
2	26.88	CH3
3	66.38	CH2
4	71.87	CH2
5	77.92	CH
6	81.15	CH
7	109.07	C

4.2.2.2.e Gradient-Selected Heteronuclear Multiple Quantum Correlation (GHMQC) Spectrum of Poly(2S,3S)-Epoxide with *tert*-BuOK

The GHMQC spectrum of poly(2S,3S)-epoxide (Figure 25), taken at 600 MHz spectroscopy, shows that multiplet 1 in the ^{1}H dimension correlates with the methine carbon near δ 78 ppm in the ^{13}C dimension. Similarly, multiplet 4 in the ^{1}H dimension correlates with the methine carbon near δ 81 ppm. At the higher magnetic field multiplet 3 separates into two multiplets, 3', a 2H multiplet centered near δ 3.85 ppm and 3", a 1H multiplet centered near δ 3.78 ppm. Multiplet 3" and one proton of multiplet 3' represent diastereotopic methylene protons which correlate with the methylene carbon near δ 72 ppm in the ^{13}C dimension. The other proton in multiplet 3' and the proton in multiplet 2 represent diastereotopic methylene protons which correlate with the methylene carbon near δ 66 ppm in the ^{13}C dimension.

4.2.2.2.f Gradient-Selected Heteronuclear Multiple Bond Correlation (GHMBC) Spectrum of Poly(2S,3S)-Epoxide with *tert*-BuOK

The GHMBC spectrum of poly(2S,3S)-epoxide (Figure 26), taken at 600 MHz spectroscopy, shows a correlation between multiplets 2 and 3' in the ^{1}H dimension with the quaternary carbon near δ 109 ppm in the ^{13}C dimension. These methylene protons must therefore be the dioxolane ring protons representing a 3-bond separation from the quaternary ring carbon. The chain methylene protons are further away (5-bond) from the quaternary carbon. Therefore the carbon peak at δ 66.38 ppm represents the methylene carbon in the dioxolane ring and the carbon peak at δ 71.87 ppm represents the chain methylene carbon.

From the COSY spectrum it is apparent that the multiplet 2 proton is coupled with the methine proton of multiplet 1, therefore multiplet 1 must represent the dioxolane ring methine proton. Since multiplet 1 correlates with the carbon peak near δ 78 ppm, the methine carbon peak at δ 77.92 ppm corresponds to the ring methine carbon and the peak at δ 81.15 ppm corresponds to the chain methine carbon , and correlates with multiplet 4 in the ^{1}H dimension of the GHMQC spectrum. It is interesting that the diastereotopic ring methylene protons are separated in chemical shift by about 0.2 ppm, while the chain methylene protons are separated by about 0.1 ppm.

4.2.2.2.g Assignment of ^1H NMR and ^{13}C NMR Spectra of Poly(2S,3S)-Epoxide with *tert*-BuOK

Summarizing the analysis of the COSY, DEPT, GHMQC and GHMBC spectra mentioned above, the ^1H NMR and ^{13}C NMR spectra of the poly(2S,3S)-epoxide can be assigned as in Scheme VI, Table 14 and Scheme VII, Table 15.

Scheme VI (assignment of ^1H NMR in Fig. 22),

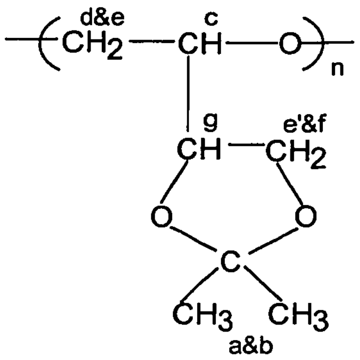


Table 14 Assignments of ^1H NMR Spectrum of the Poly(2S,3S)-Epoxide with *tert*-BuOK as Initiator

Proton	Chemical Shift (ppm)
Ha & Hb	1.37 &1.50
Hc	3.45
Hd	3.78
He & He'	3.85
Hf	4.06
Hg	4.25

Scheme VII (assignment of ^{13}C NMR in Fig. 23),

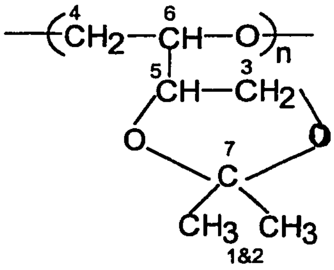


Table 15

Assignments of ^{13}C NMR Spectrum of the Poly(2S,3S)-Epoxide With *tert*-BuOK as Initiator

Carbon Number	Chemical Shift (ppm)
1	25.90
2	26.88
3	66.38
4	71.87
5	77.92
6	81.15
7	109.07

4.2.2.2.h Molecular Weights and Optical Rotations of Poly(2S,3S)-Epoxide Prepared with Potassium *tert*-Butoxide

The (2S,3S)-epoxide was polymerized in bulk at 30°C at different period time with different conversions. Then the polymers were isolated by stirring over $CHCl_3$ and precipitated into cold hexane. The molecular weights and optical rotations of the purified polymers were measured and the results are summarized in Table 16.

Table 16

Conversions and Molecular Weights of the Poly(2S,3S)-Epoxide

With *tert*-BuOK as Initiator

Conversion	Mn	Mw/Mn	$[\alpha]_{589}$ (C1.0)	
			C6H6	CHCl3
42.00	2331	1.06	_	_
44.00	2473	1.07	_	_
66.00	3567	1.12	-8.35	_
81.00	4529	1.13	-6.74	6.15
85.00	4717	1.11	-6.32	6.10
90.00	4811	1.13	-5.80	4.18
95.00	4940	1.13	-5.82	4.02

a %yield of crude product prepared with molar ration [M]/[I] = 17

b Determined by vapor phase osmometry

c Determined by gel permeation chromatography

It is of interest that the specific rotations of poly(2S,3S)-epoxide samples have negative values in benzene and positive values in chloroform. The specific rotation of its monomer shows similar behavior, with the sign of rotation being solvent-dependant, $[\alpha]_{589}^{25}$ 4.98 deg. $dm^{-1}.g^{-1}.cm^3$ (c = 1.0, C_6H_6); $[\alpha]_{589}^{25}$ – 7.8 deg. $dm^{-1}.g^{-1}.cm^3$ (c = 1.15, $CHCl_3$). Similar solvent-dependant behavior had been observed with poly ((R)-(+)-propylene oxide)[95]. This has been attributed to changes in the order of atom polarizabilities caused by specific solvent-solute interactions with poly (propylene oxide)[18,96]. This is probably the explanation for this polymer, since the monomer as well as the polymer shows solvent-dependant sign of rotation.

The (2S,3S)-epoxide was polymerized in bulk at 80°C for several days to reach almost 100% conversion for different molar ratios of initiator over monomer. The crude polymers were purified and then analyzed for molecular weights and optical rotations. The result is listed in Table 17.

Table 17

Molecular Weights and Optical Rotations of Poly(2S,3S)-Epoxide With *tert*-BuOK as Initiator

Sample	[I]/[M] (%)	GPC Data			VPO	[α]
		Mw	Mn	Mw/Mn	Mn	(C1.0)
1	8	3670	3266	1.12	5262	-9.66
2	6	3779	3370	1.12	5406	-7.96
3	4	5162	4376	1.18	6798	-8.08
4	2	5073	4353	1.16	6767	-9.62

$[\alpha]_{589}^{25}$ were determined in benzene

From the results it can be seen that the molecular weights of the polymers increase with the ratio of the concentration of the initiator to the monomer decrease up to [I]/[M] < 4%; the optical rotation of the polymers have the opposite sign compared with the monomer; the molecular weight distribution of the polymers are narrow.

4.2.2.3 End Groups Analysis of Poly(2S,3S)-Epoxide with Potassium *tert*-Butoxide as Initiator

4.2.2.3.a ^{13}C NMR and Quantitative Analysis of ^{13}C NMR of Poly(2S,3S)-Epoxide

Quantitative analysis of ^{13}C NMR of different molecular weights of poly(2S,3S)-epoxide indicates that the intensities of low intensity peaks of a, b, c, d, e, and f increase with molecular weights. T1 of these small peaks in ^{13}C NMR are shorter than 1.4 seconds, which means that these low intensity peaks are associated with end-group peaks rather than impurities[69]. These peaks were readily typed as methylene or methine carbon by DEPT-135° spectrum (Figure 27 and Table 18).

Table 18

Assignments of DEPT-135° Spectrum of End-Groups of the Poly(2S,3S)-Epoxide with *tert*-BuOK as Initiator

Carbon Number	Chemical Type
a	CH
b	CH2
c	CH2
d	CH
e	CH2
f	CH2

Figure 28 shows ^{13}C NMR spectra of low intensity peaks area of different polymers. The sample 1 is the polymer prepared with cesium hydroxide as initiator. The sample 2 is the polymer prepared with *tert*-BuOK as initiator which was weighed outside a dry box before polymerization. The sample 3 is the polymer prepared with *tert*-BuOK as initiator, which was weighed inside a dry box before polymerization. The DEPT-135° spectrum of sample 3 (Figure 29) shows that the chemical type of the end-group peaks are same as ones of sample 2, except that sample 3 has less low intensity peaks than sample 2.

To compare the spectra of sample 1 (Figure 21) with sample 2 (Figure 24), the spectrum of sample 1 is similar to one of sample 2, however peak *f* is absent in the spectrum of sample 1. The chemical shift of peak *f* is close to the value of 64 ppm assigned previously to the corresponding end-group carbon in poly(*tert*-butyloxirane)[18]. Therefore peak *f* can be assigned to the carbon α associated with the *tert*-butoxy end group.

Sample 2 prepared with potassium *tert*-butoxide initiator which had been exposed briefly to air showed ^{13}C NMR spectra containing all the peaks observed in spectrum of hydroxide (sample 1) and *tert*-BuOK initiated polymers (sample 3). This reflects the moisture sensitivity of potassium *tert*-butoxide , which leads to initiation with both hydroxide and *tert*- butoxide ions. The intensity of peak *c* in sample 3 is lower than one in sample 2 (from quantitative analysis of the ^{13}C NMR spectra). DEPT-135° spectrum of sample 3 (Figure 29) shows that peak *c'* (72.9 ppm) corresponds to a quaternary carbon, while DEPT-135° spectrum of sample 2 reveals peak *c* (72.8 ppm) as methylene carbon. Therefore the peak *c* in sample 2 must involve two peaks overlap, one of which is methylene carbon of peak *c*, another of which is quaternary carbon of peak *c'*. The chemical shift for peak *c'* agrees with the value (73 ppm) assigned for the quaternary carbon of the *tert*-butoxide end group in poly(*tert*-butyloxirane)[18]. Obviously peak *c'* can be assigned to the quaternary carbon associated with the *tert*-butoxy end group.

By comparising the spectra of all three samples, it can be seen that peaks *a, c* and *e* are absent in sample 3 but appear in sample 1 and sample 2, which predicts that these three peaks are associated with hydroxymethylene chain ends. Since peak *a* is a methine carbon, it can be assigned to the carbon β associated with the hydroxymethylene end group. From the chemical shifts of peaks *e* and peak *c*, peak *e* can be tentatively assigned as the α - carbon connected to the hydroxyl end group, while peak *c* might be the γ - carbon connected to the hydroxyl end group.

Peaks *b* and *d* appear in all three spectra, which can be tentatively assigned to the carbons associate with another chain end — hydroxylmethine end groups. Since peak *b* is methylene carbon, peak *b* is assigned to the carbon β connected to hydroxylmethine end group; peak *d* is methine carbon, it is assigned to the carbon α connected to hydroxylmethine end group. Peak *d* is shifted *ca.* 10 ppm upfield from the corresponding chain interior methine carbons (81 ppm). A carbon α to an alkoxy group is generally deshielded by about 8-10 ppm relative to a carbon α to a hydroxyl group [96], however this effect does not appear to hold for a *tert*-butoxyl ether structures[97].

4.2.2.3.b Acetylation of Purified Poly(2S,3S)-Epoxide Prepared with Potassium *tert*-Butoxide

The purified poly(2S,3S)-epoxide was acetylated with CH_3COCl in chloroform solution in order to aid in the assignment of the end group signals. The polymer was not acetylated 100% effectively as can be seen in the ^{13}C NMR spectrum (Figure 30), however, the effect of the acetyl group is clearly evident.

Figure 31 is ^{13}C NMR spectrum of poly(2S,3S)-epoxide with potassium *tert*-butoxide as initiator before acetylation. Figure 32 shows DEPT-135° spectrum of acetylated polymer. To compare Figures 30 and 31 with 32, it can be seen that after acetylation, one low intensity signal appears further downfield than peak *a* at 75.3 ppm (signal 1), two low intensity signals appear at 72.7 (signal 2) and 70.4 ppm (signal 3) respectively. DEPT spectrum shows that signal 1 and 2 are methine carbons while signal 3 is methylene carbon. The peak *a, b, c* and *d* remain the same chemical shift but their intensities became relatively lower because of the incomplete acetylation due to the steric hindrance of the side chain rings.

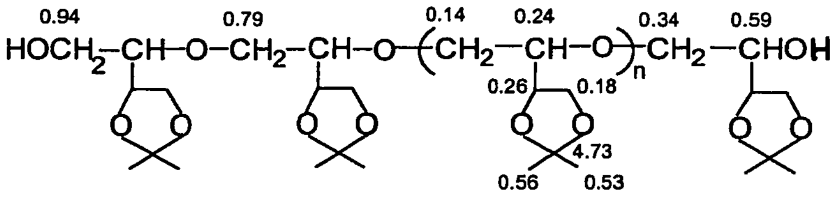
Acetylation of alcoholic hydroxyl groups causes characteristic downfield α shift 1.5 to 4 ppm and upfield β shift 1 to 5 ppm, carbon nuclei further from the carboxyl function are essentially unaffected within experimental uncertainty[85]. From the DEPT spectrum, it can be seen that there is no methine carbon signal in the upfield region of near peak *d* and there is no methylene carbon signal in downfield region near peak *b*. Therefore peak *d* must not be β carbon of the hydroxyl end group and peak *b* must not be α carbon of the hydroxyl end group. These results are consistent with the assignments from the NMR spectra of unacetylated polymers.

4.2.2.3.c T_1 Measurement of Poly(2S,3S)-Epoxide

Spin-lattice relaxation times T_1 can be useful as an aid in assigning end-group resonances in relatively low molecular weight polymeric molecules[46]. The method is based on the premise that ^{13}C T_1 values are generally longest at the chain ends and shortest at the interior carbons of a chain. The magnitude of ^{13}C T_1 values depends in part on the inverse of the correlation time τ_c at a particular carbon. Thus a small molecule in a nonviscous medium will have a short τ_c and a correspondingly large T_1 value while T_1 values for a viscous polymer will be relatively small.[70] This effect is clearly seen for ^{13}C T_1 values in decane[98], with the largest T_1 values at chain end carbons and smallest T_1 values at carbons in the middle of the chain. However in neat 1-decanol[99], the shortest T_1 values occur at the hydroxyl chain end. This is attributable to aggregation effects involving hydrogen bridging at the hydroxyl groups which lessen the mobility of these chain ends and therefore lower T_1 nearby carbons.

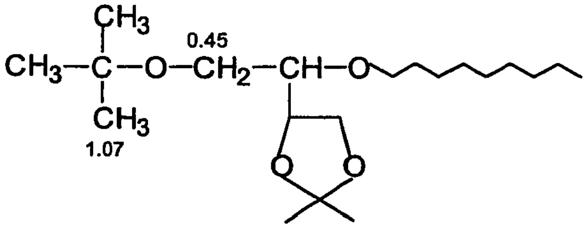
The poly(2S,3S)-epoxide, prepared with potassium *tert*-butoxide initiator which had been exposed briefly to air, was studied by partially relaxed ^{13}C NMR in terms of the spin-lattice relaxation behaviors in order to aid in assignment of the end group signals. The T_1 measurement of ^{13}C NMR spectrum of poly(2S,3S)-epoxide is shown on Figure 33. The ^{13}C T_1 values of poly(2S,3S)-epoxide, formed by hydroxide initiation, corresponding to the assignment of the chemical shifts of the signals are shown in Scheme VIII.

Scheme VIII:



T_1 values corresponding to *tert*-BuOK initiated chain ends are shown in Scheme IX.

Scheme IX:



Methylene carbons within the chain follow the expected pattern with interior carbons having lower mobility and smaller T_1 values and carbons near chain ends having greater mobility and larger T_1 values. Methine carbons as expected have larger T_1 values than methylene carbons. Aggregation effects involving hydroxyl groups are not apparent, similar to the observation of Lubnin and Kennedy[69] with hydroxyl-capped polyisobutylenes. This is attributable to a relatively low concentration of hydroxyl groups in solution.

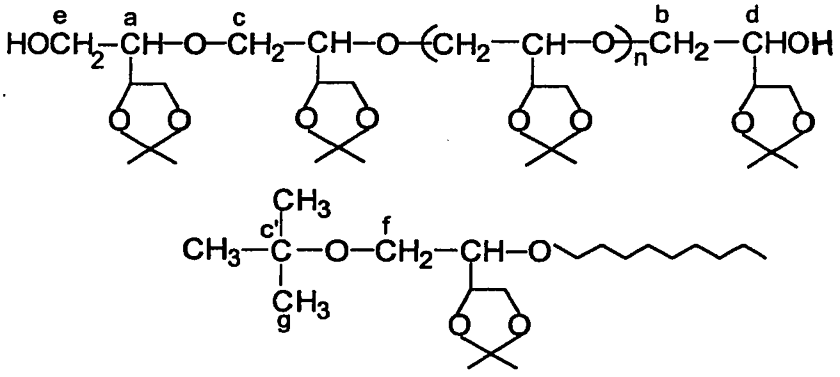
4.2.2.3.d GHMBC Analysis of Poly(2S,3S)-Epoxide with *tert*-BuOK

From the GHMBC spectrum of poly(2S,3S)-epoxide (Figure 26), it can be seen that the peak *c'* signal correlates with the protons of methyl end group peak, which is two bond correlation of quaternary carbon with methyl proton. The peak *d* on ^{13}C dimension has a strong cross peak with the proton at about 1.6 ppm on ^{1}H dimension, which might be a hydroxyl end group signal only revealed weakly. Therefore this correlated contour can be tentatively assigned as two bond correlation between signal *d* carbon with the proton of hydroxyl end group.

The signal *f* does not show up a correlated contour with protons because the long range ^1H-^{13}C J coupling are too weak to be observed. Similarly, the signal *d* has no correlated contour.

In summary, all above technical analysis are consistence with end group signals assignment of ^{13}C NMR as shown in Scheme X.

Scheme X:



4.2.2.4 Polymerization Mechanism of Poly(2S,3S)-Epoxide Prepared with Potassium *tert*-Butoxide

4.2.2.4.a Living nature of the polymerization

Poly(2S,3S)-epoxide samples at different conversions were purified and molecular weights then measured by GPC. Molecular weight variation with conversion for the purified samples is shown in Figure 34.

Unpurified crude polymers at different polymerization time were also measured of molecular weights with GPC, the polymerization conversions were calculated by the area of the polymer peak verse the monomer peak in the GPC result from the calibration curve (Figure 3). Molecular weight variation with conversion for the crude samples is shown in Figure 35. As shown in Figure 34 and 35, the plots of the molecular weight of the polymer obtained versus the conversion gave a straight line and the molecular weight distributions are relatively narrow. During polymerization of the (2S,3S)-epoxide, reaction mixture changed to dark orange color liquid from green then orange solid. Although the reaction was over, the orange color persisted, suggesting that perhaps the reactive species has remained in the system. These characteristics are generally associated with a living polymerization system. The degree of polymerization (DP) varies from 16 to 34. These values are generally little higher than the values calculated from the monomer / initiator molar ratios, indicating that not all of the initiator was effective. This may due to impurities present in the polymerization tube were destroyed by the initiator before the onset of polymerizations and difficulty in placing all weighted initiator into the narrow polymerization tube in contact with monomer (Trace of them remained on a wall of the polymerization tube). However the loss of initiator does not affect molecular weight distributions.

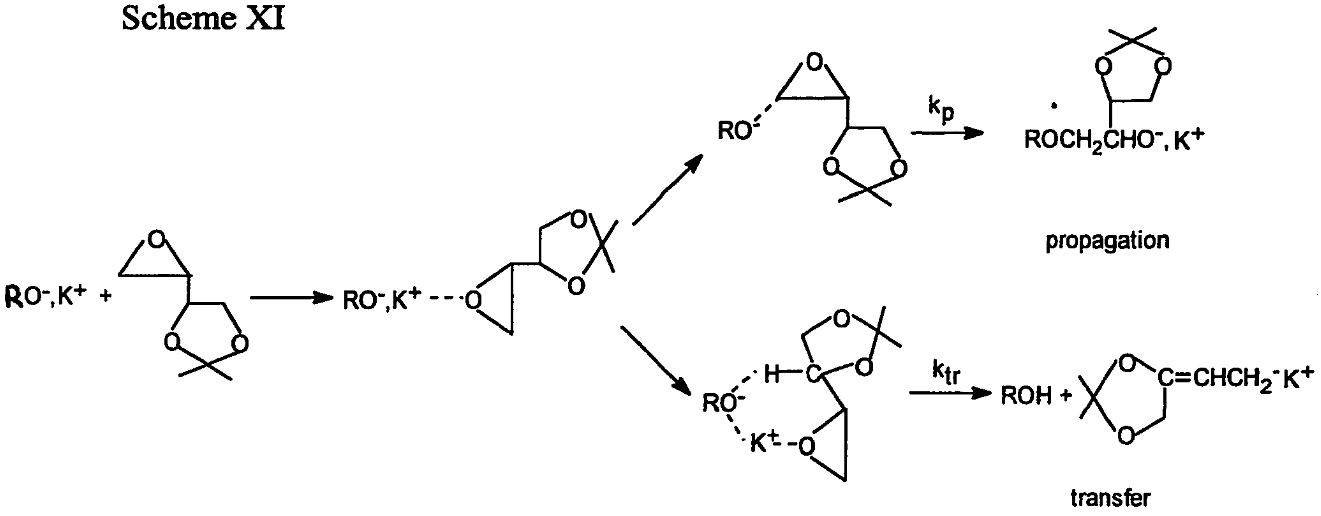
To prove the living polymerization mechanism, block-copolymerization of the (2S,3S)-epoxide / S-propylene oxide was carried out in *N,N'*-dimethylpropyleneurea (DMPU) solution. Since alcohols act as chain-transfer agents, to overcome difficulties caused by lack of solubility of initiator and polymer, the polymerization can be performed in aprotic but powerfully solvating media because termination and chain-transfer might be avoided in those solvents. (DMPU has been shown to be an excellent replacement for the carcinogenic HMPA, hexamethyl phosphoric triamide[100,101]) The (2S,3S)-epoxide was added to *tert*-BuOK / DMPU solution with molar ratio of monomer to initiator as 15 at concentration of 0.9 mol/L. After the polymerization completed, S-propylene oxide was added to the poly(2S,3S)-epoxide solution with the molar ratio of S-propylene oxide to (2S,3S)-epoxide as about 1/3. The isolated material could not be precipitated in hexane (The poly(2S,3S)-epoxide made with same molar ratio of monomer to initiator was easily precipitated in hexane). This result proved that no poly(2S,3S)-epoxide was left after addition of propylene oxide, that is all of the original polymers were living and eventually produced block polymers of (2S,3S)-epoxide-(S)-propylene oxide.

For comparison, random copolymerization of (2S,3S)-epoxide / S-propylene oxide was also carried out in DMPU solution. The polymerization conditions were the same as above, except S-propylene oxide and the (2S,3S)-epoxide were added to the *tert*-BuOK / DMPU solution at the same time and the molar ratio of S-propylene oxide to (2S,3S)-epoxide as about 3.

Figure 36 shows the ^{13}C NMR spectrum of crude poly[(2S,3S)-epoxide-block-(S)-propylene oxide] copolymer and Figure 37 shows the ^{13}C NMR spectrum of purified random copolymer of (2S,3S)-epoxide / (S)-propylene oxide. In Figure 37, the peaks of the main chain carbon obviously separate to two peaks (methine carbon splits to 80.8 and 80.4 ppm, methylene carbon splits to 71.7 and 69.6 ppm) because of two types of connection of each main chain carbon, while the peaks of side chain carbons remain singled as in the homopolymer. In Figure 36, the peaks of the main chain carbon almost were undisturbed by poly[(S)-propylene oxide] chain, which confirms the copolymer as block copolymer. That means that poly(2S,3S)-epoxide solution system does initiate the polymerization of (S)-propylene oxide to obtain the block copolymer. This further proves that the polymerization of (2S,3S)-epoxide with t-BuOK as initiator possesses characteristics of living polymerization.

To check occurrence of chain-transfer reaction in the polymerization, the ^{1}H spectra of the polymers at 4.5-6.0 ppm region and the ^{13}C spectra of the polymers at 110-140 ppm region were carefully expanded, but there were no any peaks to be found in these regions, which means there was no any olefinic end-groups in the polymers. According to the literature[12,44,45], the propagation occurs mainly through the free alkoxide anions, the chain transfer to the monomer occurs through the ion pairs with the intervention of K^+ cations. Scheme XI shows the propagation and the chain transfer in the polymerization of the epoxides. Obviously, the steric hindrance in the transition state of chain transfer is much higher than one of propagation. Combining these results, it can be concluded that one polymer chain grows from each *tert*-BuOK without chain-transfer and termination.

Scheme XI



4.2.2.4.b Regioselectivity in the polymerization of (2S,3S)-Epoxide with *tert*-BuOK

The bulkiness of the alkyl substituent exerts an enormous influence upon the nature of stereoselective polymerization of alkylepoxides. The ^{13}C spin-lattice relaxation times for the polymer of (2S,3S)-epoxide are listed in Table 19 to compare with the literature data of the three polyepoxides, in which n denotes the number of hydrogen atom bound to the relevant carbon atom. The result of Table 19 shows that the mobility of carbons of a monomer group on a polymer molecule in order of increasing mobility is given by CH$_2$ (backbone) < CH (side group) < CH (backbone) < CH_2 (side group) < CH_3 (side group) < C (side group). It is somewhat surprise that the methine carbon of the side group is so restrict in benzene solution. Because the bulkier the alkyl substituent, the smaller nT_1 values were obtained, the polymer of (2S,3S)-epoxide has the bulkiest substitutent in all these polyepoxides. That means the polymer chain of (2S,3S)-epoxide has slower segmental motion owing to the enhanced rigidity of the macromolecule possessing bulkier substituents than the other polyepoxides.

The assignment of the main peaks and the minor peaks in the ^{13}C NMR spectrum of the polymer has revealed that each carbon signal is a sharp singled and no extra signals due to irregular structure can be observed, indicating that the poly(2S,3S)-epoxide is stereoregular, isotactic polymer, and that the amounts of head-to-head and tail-to-tail sequences are too small, if any, to be detected by ^{13}C NMR. Therefore, the bulk polymerization of the (2S,3S)-epoxide was concluded to proceed to form head to-tail sequences under the exclusive cleavage at either of the O-CH bond (α-opening) or the O-CH_2 bond (β-opening).

The assignment of the end-group peaks in the ^{13}C NMR

Table 19 ^{13}C Spin-Lattice Relaxation Times, nT_1 (sec)

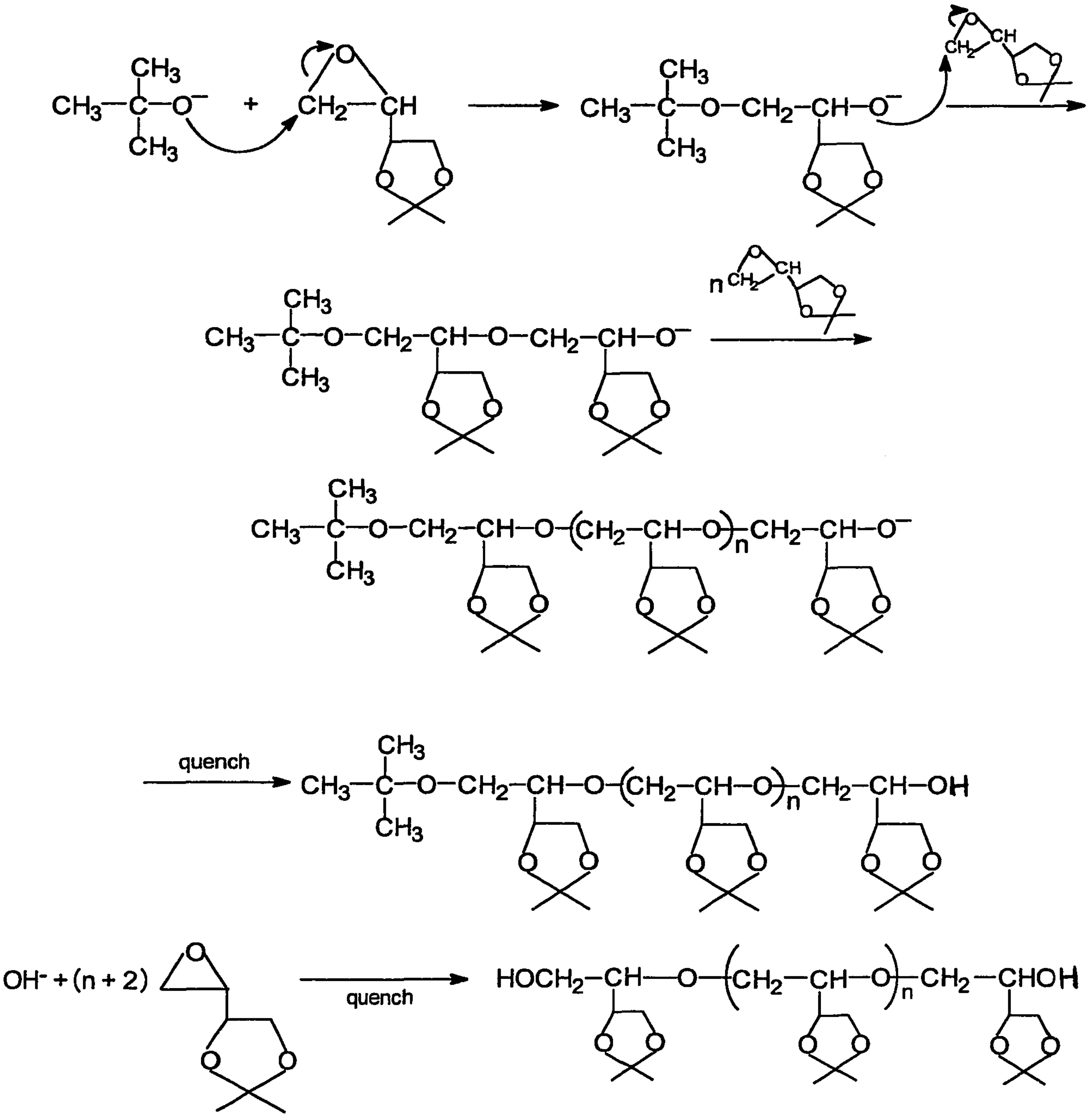
Polymer	CH	CH2	substitutent			
			C	CH	CH2	CH3
Me a	2.2	3.0	_	_	_	6.9
isoPr a	0.84	0.98	_	0.84	_	3.9
t-Bu a	0.52	0.54	4.0	_	_	2.0
dioxyring	0.24	0.14	4.73	0.18	0.26	0.53,0.56

in C_6D_6: Conc. *Ca* 10 w/v %, at 60°C.   a: from reference 4

spectrum of the polymer unambiguously confirmed that the bond cleavage of the (2S,3S)-epoxide takes place exclusively at O-CH_2 bond during the polymerization process with *tert*-BuOK as initiator. Therefore the polymers had the same configuration as in the monomer from which they were derived, i. e., the polymers polymerized with retention of configuration of its asymmetric carbon atom. The regioselectivity of the polymerization mainly comes from the bulkiness of the five-member ring substituent of the oxyethylene unit, in another word, the polymerization is the steric control ring-opening polymerization.

In summary, the polymerization initiation involves a nucleophilic attack of the initiator potassium *tert*-butoxide at the methylene carbon of the epoxide ring; hydroxide ion initiation also occurs with potassium *tert*-butoxide exposed to air; quenching of the polymerization results in hydroxyl end groups. The mechanism is shown in Scheme XII:

Scheme XII,



4.3 *Copolymerization of the Epoxides*

4.3.1 Bulk Copolymerization of the (2R,3S) / (2S,3S)-Epoxides Prepared with CsOH

Bulk copolymerization of equal molar ratio of (2R,3S) / (2S,3S)-epoxides was studied at 35°C. The initial ratio of the comonomer and the final ratio of the recovered comonomer after the copolymerization were measured by gas chromatography. The optical rotation of the initial comonomers and the recovered comonomers also are measured. The results show that the molor ratio of (2R,3S) / (2S,3S)-epoxides and the optical rotation of recovered comonomer did not obviously change. The copolymers are yellow viscous oils, easily dissolved in common organic solvents. The polymerization yields with different polymerization time are listed in Table 20, which shows that the rates of copolymerization are lower than the rates of homopolymerization.

^{13}C NMR spectrum of the copolymer (Figure 38) shows that it is an atactic copolymer, which means the reaction is a random copolymerization.

Table 20

Bulk Copolymerization of the (2R,3S)/(2S,3S)-Epoxides

With CsOH as Initiator

Sample	[I]/[M] (%)	Time Hour	Temp. C	Yield (%)
1	8	23	35	20.0
2	14.8	17	35	59.8

4.3.2 Copolymerization of the Epoxides Prepared with t-BuOK

4.3.2.1 Bulk Copolymerization of the (2R,3S) / (2S,3S)-Epoxides

Bulk copolymerizations of the (2R,3S) / (2S,3S)-epoxides with molar ratio of 50/50 and 70/30 were investigated respectively. The reactions were carried out at 30°C with molar ratio of initiator to comonomer as 6%. The polymer system developed a green color in the beginning then changed to dark orange gradually. The copolymers were isolated by dissolving in $CHCl_3$ then precipitating into cold hexane. After quenching in methanol, the precipitate of the copolymer became white from orange color. The yield of copolymer with initial molar ratio of 50/50 was 60.7% after reaction of 4.5 hours, while the yield of copolymer with initial molar ratio of 70/30 was 43.4 % after reaction of 3.5 hours. Figure 39 shows the ^{13}C NMR of poly[(2R,3S) / (2S,3S)-epoxides] with molar ratio of 70/30. In the spectrum, the peaks of the side chain carbons split to two, the chemical shifts corresponding to (2R,3S)- and (2S,3S)-epoxide segments respectively, while the peaks of the main chain carbons are overlapped because of the random arrangement of the comonomers in the polymer chain.

For investigating the reactivity of the (2R,3S)-epoxide and (2S,3S)-epoxide in the copolymerization, the molar ratio of (2R,3S) / (2S,3S) epoxides before the copolymerization and after the copolymerization were studied by ^{1}H NMR. The solvents of the supernatant from the precipitation of the copolymer were removed, then C_6D_6 was added to the recovered comonomers for the ^{1}H NMR measurement. The ^{1}H NMR (Figure 40) revealed that the molar ratio of (2R,3S) / (2S,3S) epoxides of recovered comonomer changed from 70/30 to 60/40 (2.33 to 1.56) at 43.4% conversion. That means when the copolymerization of the (2R,3S)/(2S,3S)-epoxide of was carried out starting with a monomer mixture consisting of (2R,3S)/(2S,3S) = 70/30 using *tert*-BuOK as initiator, (2R,3S)-monomer was incorporated into polymer chain preferentially over (2S,3S)-monomer. This may be explained that the rigid and bulky five-member ring attached to the growing polymer terminal will restrict the modes of relative orientation of an entering monomer molecule onto the growing chain. In this case, the only element for stereoelection should be the chirality of the growing chain.

4.3.2.2 Bulk Copolymerization of the (2R,3S) / (2S,3R)-Epoxides With *tert*-BuOK

Bulk copolymerization of (2R,3S) / (2S,3R)-epoxides with different initial molar ratio of comonomers were studied at 30°C. The optical rotation of the initial comonomer and recovered comonomers were analyzed and the results are summarized in Table 21.

Table 21

Bulk Copolymerization of the (2R,3S)/(2S,3R)-Epoxides

With *tert*-BuOK as Initiator

Sample	RS/SR	Initial [α]	Final [α]	Time (h)	Yield (%)
1	50/50	-0.087	-0.72	3.3	85.2
2	65/35	3.45	3.06	11.2	54.0
3	70/30	5.19	4.67	3.3	95.8

a: initial molar ratio of comonomers
b: $[\alpha]_{589}^{25}$ C = 2.0, EtOH
c: initial [M]/[I] = 16
d: initial [M]/[I] = 31

It is interesting that a stereoelective effect was found in the polymerization of unbalanced mixture of R/S-*tert*-butyloxide and R/S-styrene oxide using t-BuOK as initiator. But the above data are not enough to conclude the obvious stereoelective effect in this copolymerization system.

The optical rotations of copolymer 2 in Table 21 and its comonomer before polymerization were measured in chloroform and benzene respectively. The result is summarized in Table 22.

Table 22

Optical Rotation of the Copolymer **2** and Its comonomer

Comonomer [α], C =1.0		Copolymer [α], C = 1.0	
CHCl3	C6H6	CHCl3	C6H6
3.95	9.84	10.36	1.15

From the Table 22 it can be seen that although the optical rotation of the starting comonomer and the recovered comonomer are similar in ethanol , the optical rotation of the copolymer changed to 10.36 from 3.95 in chloroform, and changed to 1.15 from 9.84 in benzene. That means the change of the optical rotation of the copolymer from the comonomer did not come from the change of the molar ratio of the (2R,3S) / (2S,3R)-epoxide in the copolymer, but most probably come from the interaction between the copolymer main chain and solvent molecules. It is can also be seen that the copolymer possesses lower degrees of solvent interaction in benzene and possesses higher degrees of solvent interaction in chloroform.

4.3.3 ^{13}C NMR spectra analysis of the copolymers

Copolymerization study between R- and S-monomer by ^{13}C NMR spectroscopy is a useful tool for elucidation of the stereoselectivity or stereoelectivity mechanism. If the backbone methylene group of copolymers can be effectively isolated by spin decoupling or substitution on adjacent carbons, the relative number of tactic placements can be determined.[54]

For tacticity studies, the ^{13}C NMR spectra of the copolymers from bulk copolymerization of (2R,3S) / (2S,3R)-epoxides with molar ratios of 50/50, 65/35 and 70/30 were investigated respectively and shown on Figure 41, 42 and 43. It can be seen that from the ^{13}C NMR spectrum of the racemic polymer and isotactic polymer, the methylene carbon and methine carbon peaks for the isotactic polymer are sharp but not for the racemic polymer. Since the structure of the magnetic resonance peaks of a polymer, which is in sufficiently dilute solution, is determined only by carbons on the same molecule or in the solvent, and is not sensitive to interaction with other polymer molecules, it is evident that the racemic polymer is a (2R,3S)- / (2S,3R)- mixture on a single chain, and not a mixture of (2R,3S)- and (2S,3R)- molecules. It can also be seen that the backbone methylene carbon region is the most sensitive to tacticity and six peaks in this region were observed, which might be assigned to tetrad tacticity peaks[23]. As compared with isotatic homopolymer and copolymers with different ratios of (2R,3S) / (2S,3R)-epoxides, a complete tetrad assignment of the methylene signals might be possible[23,66]. From the observed peak areas with an aid of curve fitting and calculated areas according to n-order statistic, stereoelectivity mechanism of the copolymerization might be resolved[66].

5.0 CONCLUTIONS

1. The new optically active homopolymers can be prepared by ring-opening polymerization of (2R,3S)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol and (2S,3S)-3,4-epoxy-1,2-O-isopropylidenebutane-1,2-diol, respectively, with potassium *tert*-butoxide or CsOH as initiator.
2. The copolymers of the (2R,3S)/(2S,3R)-epoxides, (2R,3S)/(2S,3S)-epoxides and (2S,3S)/(2S,3R)-epoxides can also be prepared by ring-opening polymerization with potassium *tert*-butoxide or CsOH as initiator.
3. The ^{13}C NMR spectra of the homopolymers show that the homopolymers are stereoregular, isotactic polymers, and that the polymerization was proceed to form head-to-tail sequences under

the exclusive cleavage at either of the O-CH bond or the O-CH_2 bond.

4. The end-group analysis results of the homopolymer of (2S,3S)-epoxide confirmed that the bond cleavage of (2S,3S)-epoxide takes place exclusively at the methylene-oxygen bond during the polymerization process. The polymers polymerized with retention of configuration of its asymmetric carbon atom.
5. The ^{13}C NMR spectrum of the poly(2S,3S)-epoxide prepared with potassium *tert*-buoxide as initiator was assigned by DEPT, COSY, GHMQC and GHMBC NMR techniques.
6. The bulk polymerization of (2S,3S)-epoxide with potassium *tert*-buoxide as initiator possesses characteristics of living polymerization. This 'living' polymerization nature means that one polymer chain grows from each *tert*-BuOK without chain-transfer and termination.
7. The specific rotations of the polymer of (2S,3S)-epoxide have negative values in benzene and positive values in chloroform. This solvent effect is most probably due to the interaction between polymer main chain and solvent molecules.

8. When copolymerization of the (2R,3S)/(2S,3S)-epoxide was carried out starting with a monomer mixture consisting of (2R,3S)/(2S,3S) = 70/30 using *tert*-BuOK as initiator, (2R,3S)-monomer was incorporated into polymer chain preferentially over (2S,3S)-monomer.
9. Due to the different chirality of the main chain, the homopolymers of (2R,3S)-epoxide and (2S,3S)-epoxide have different chemical properties and physical properties: the poly(2R,3S)-epoxide only dissolved in very strong protonic solvents and the epoxide protons are overlapped in its ^{1}H NMR spectrum, while the poly(2S,3S)-epoxide dissolves in common organic solvents and the epoxide protons are well resolved in its ^{1}H NMR spectrum.

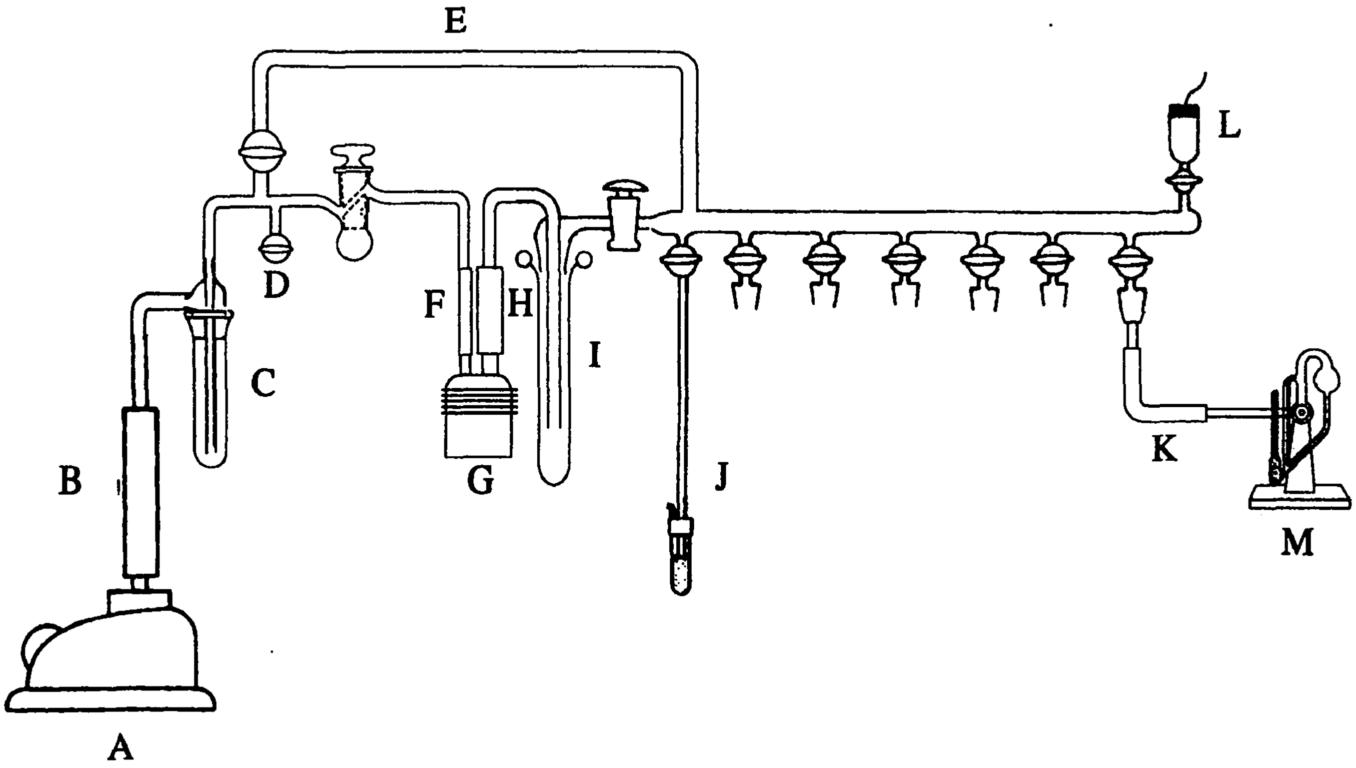


Figure 1 High vacuum line. (A) Mechanical fore pump; (B), (F), (H), (K) vacuum tubing; (C) dry-ice trap; (D) stopcock for venting system when fore pump is turned off; (E) bypass; (G) diffusion pump; (I) main trap; (J) Hg manometer; (L) thermocouple vacuum gauge; (M) McLeod gauga.

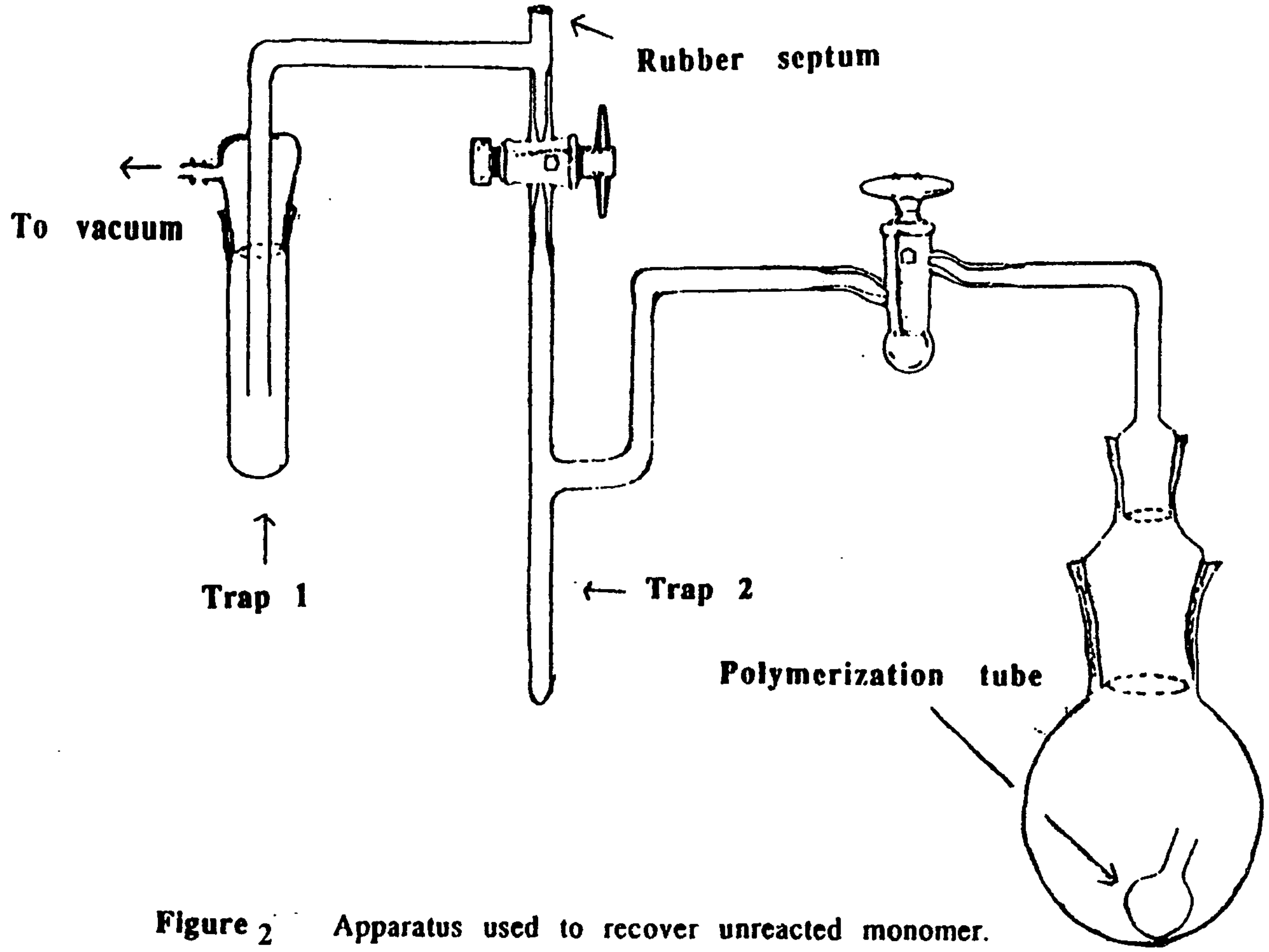


Figure 2 Apparatus used to recover unreacted monomer.

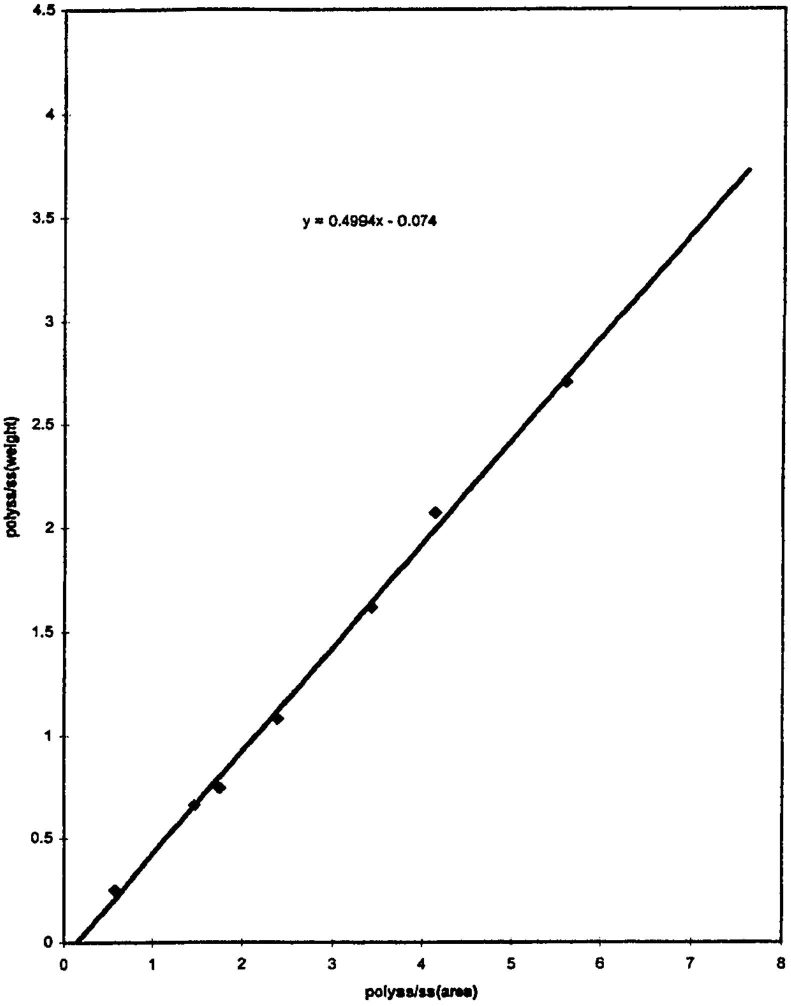


Figure 3 GPC Calibration Curve of Poly(2S,3S)-epoxide vs (2S,3S)-epoxide

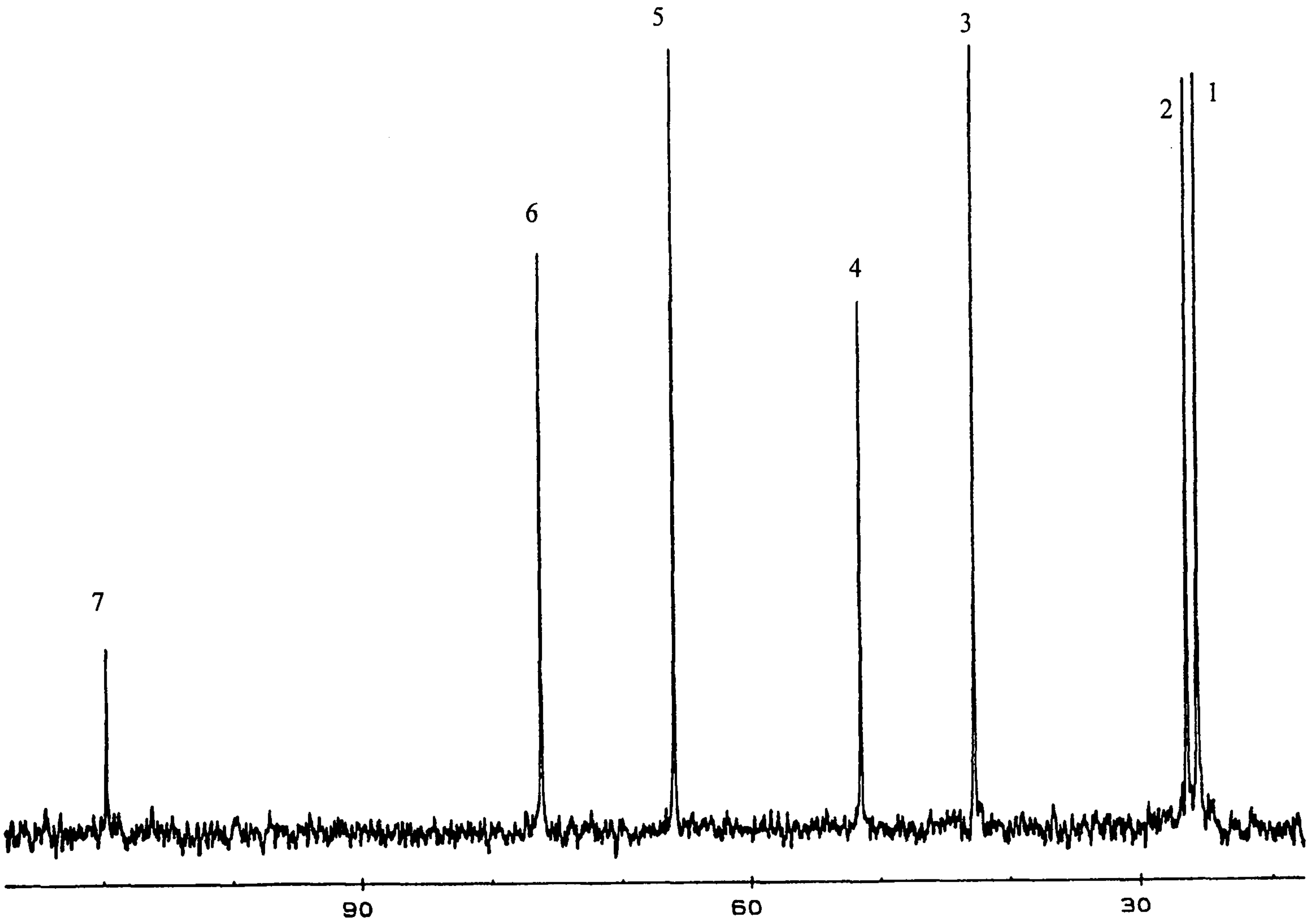


Figure 4 ^{13}C NMR spectrum of (2S,3S)-epoxide monomer, in C_6D_6, 40°C

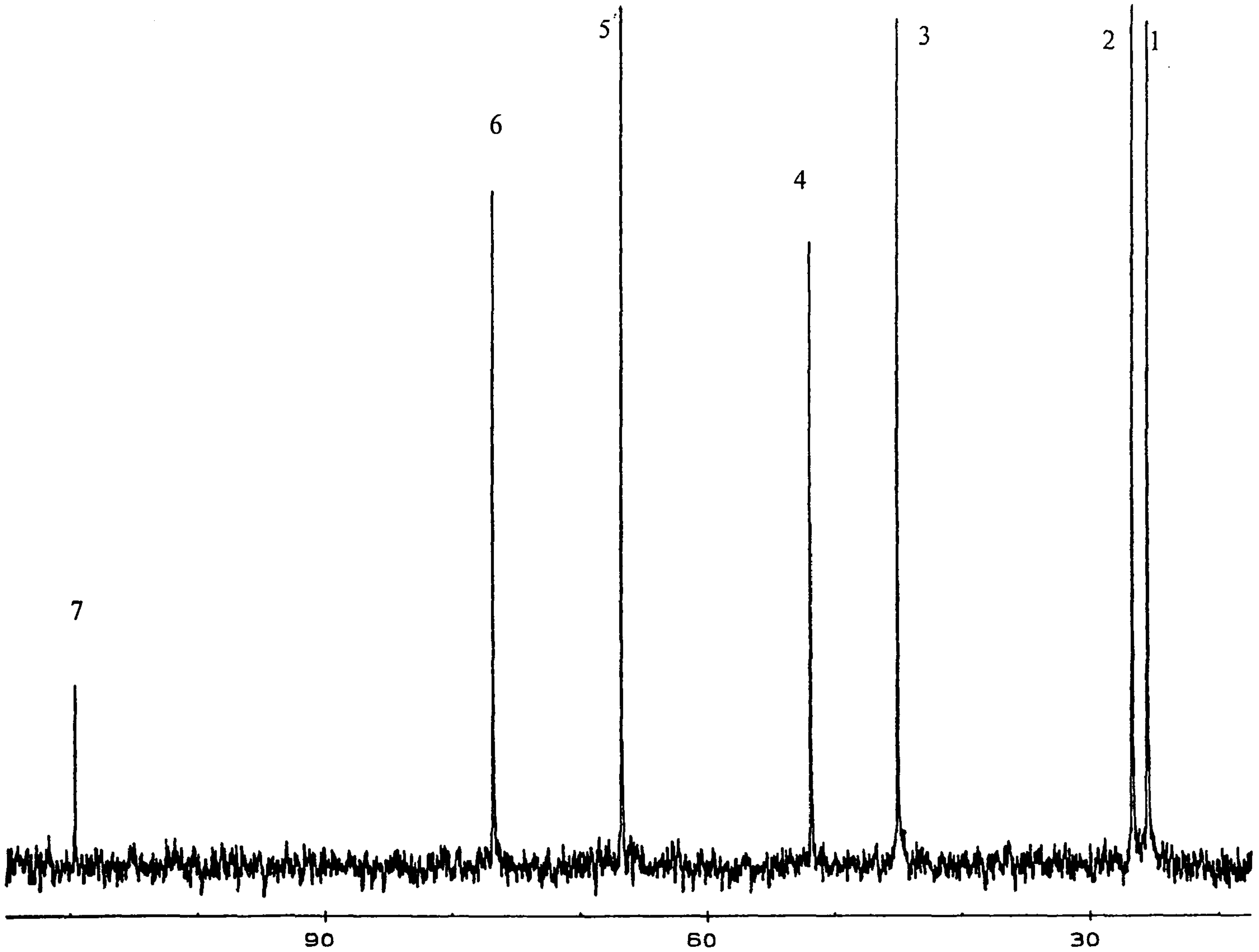


Figure 5 ^{13}C NMR spectrum of the (2R,3S)-epoxide monomer, in C_6D_6, 40°C

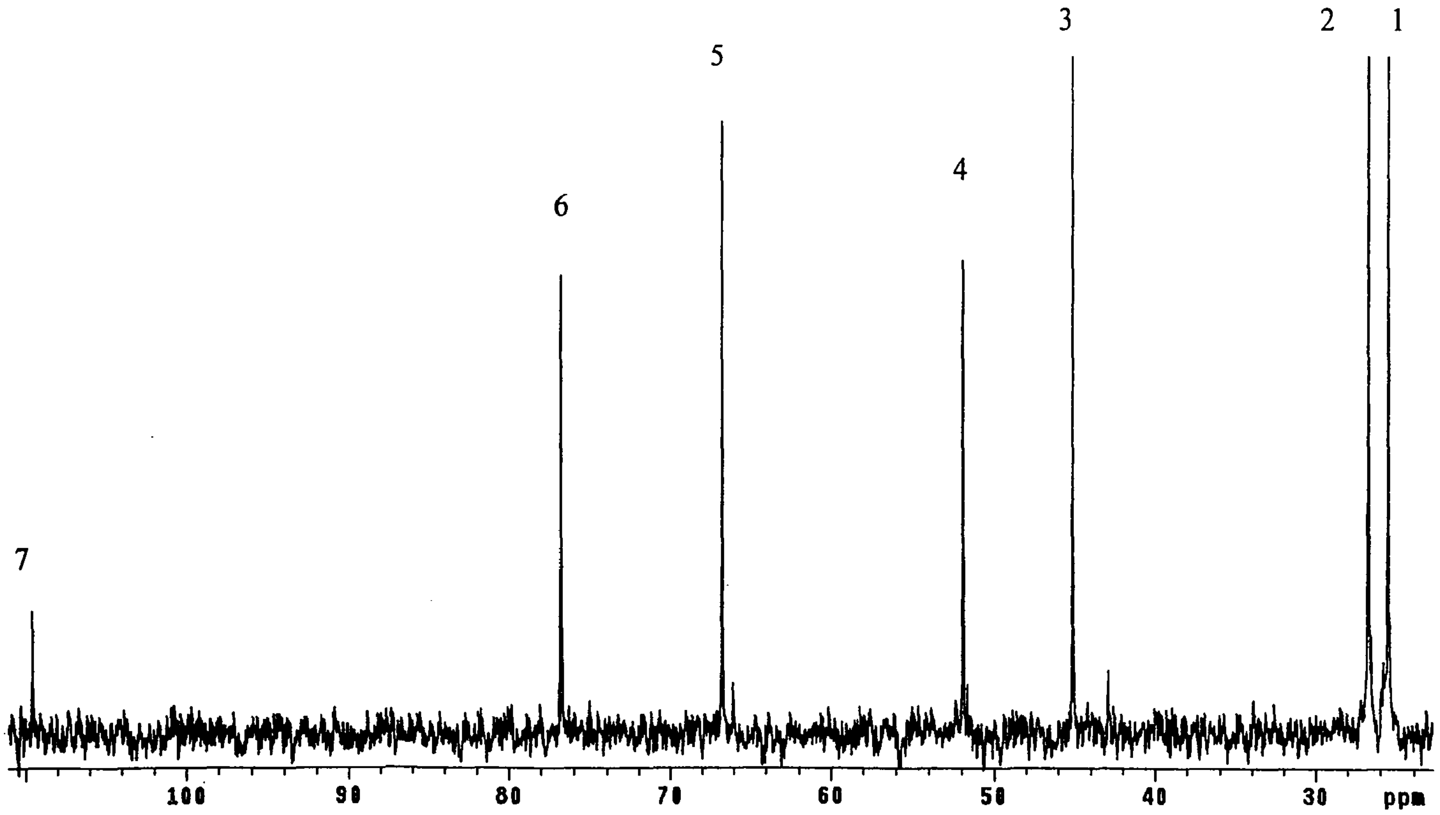


Figure 6 ^{13}C NMR spectrum of the (2S,3R)-epxoide monomer, in C_6D_6, 25°C

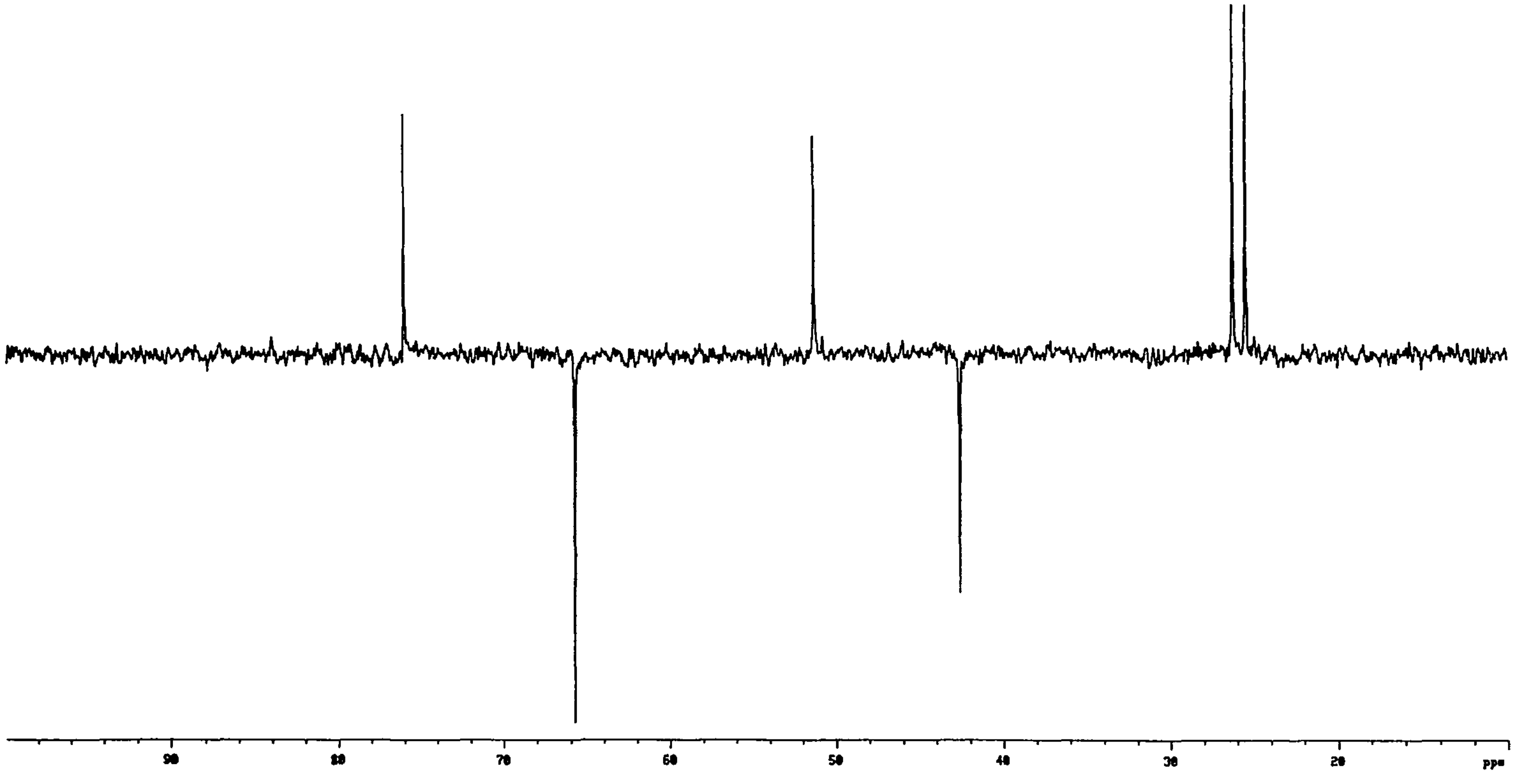


Figure 7 DEPT-135° of the (2S,3S)-Epoxide monomer, in C_6D_6, 40°

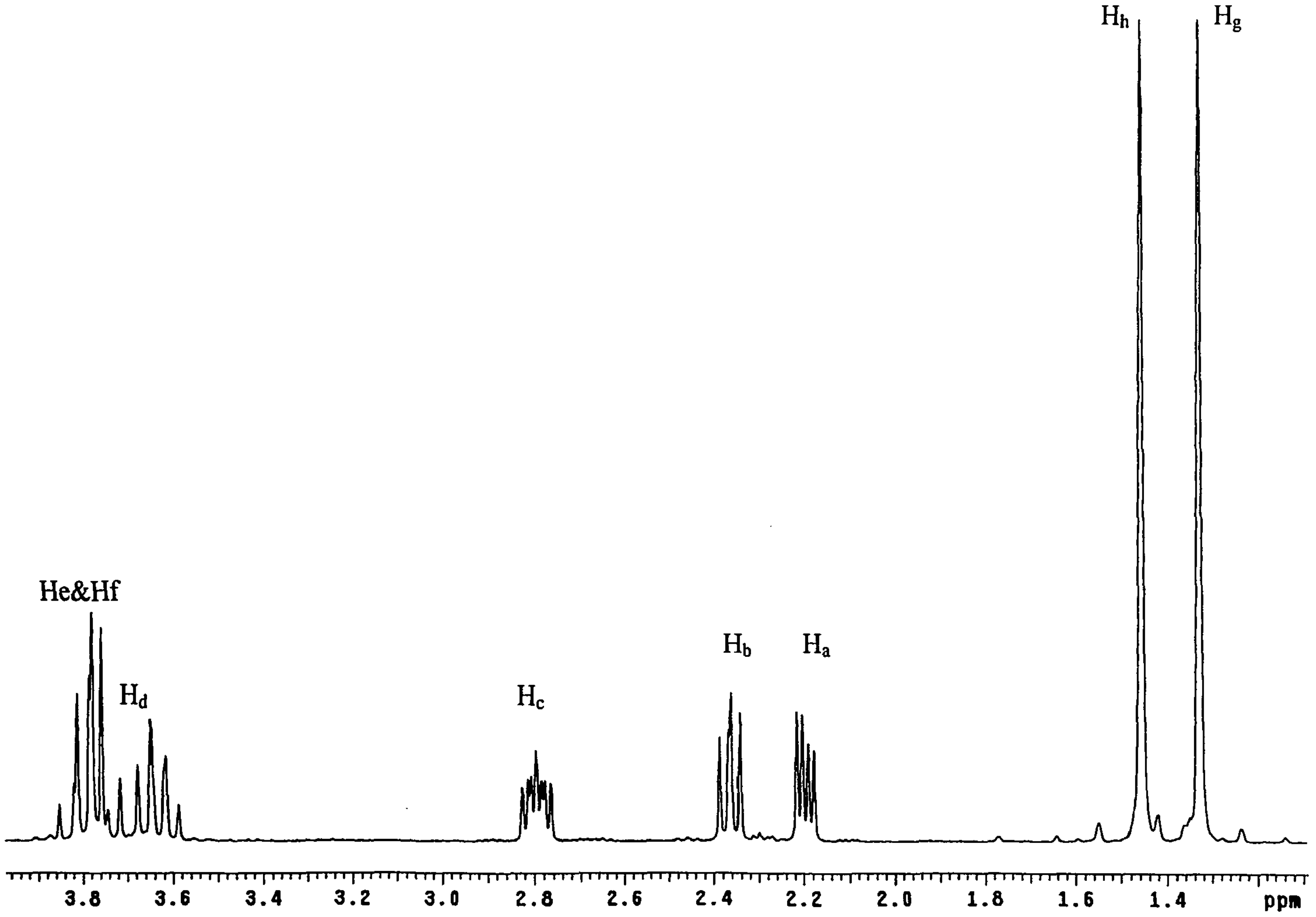


Figure 8 ^{1}H NMR spectrum of the (2R,3S)-epoxide, in $CDCl_3$, 25°C

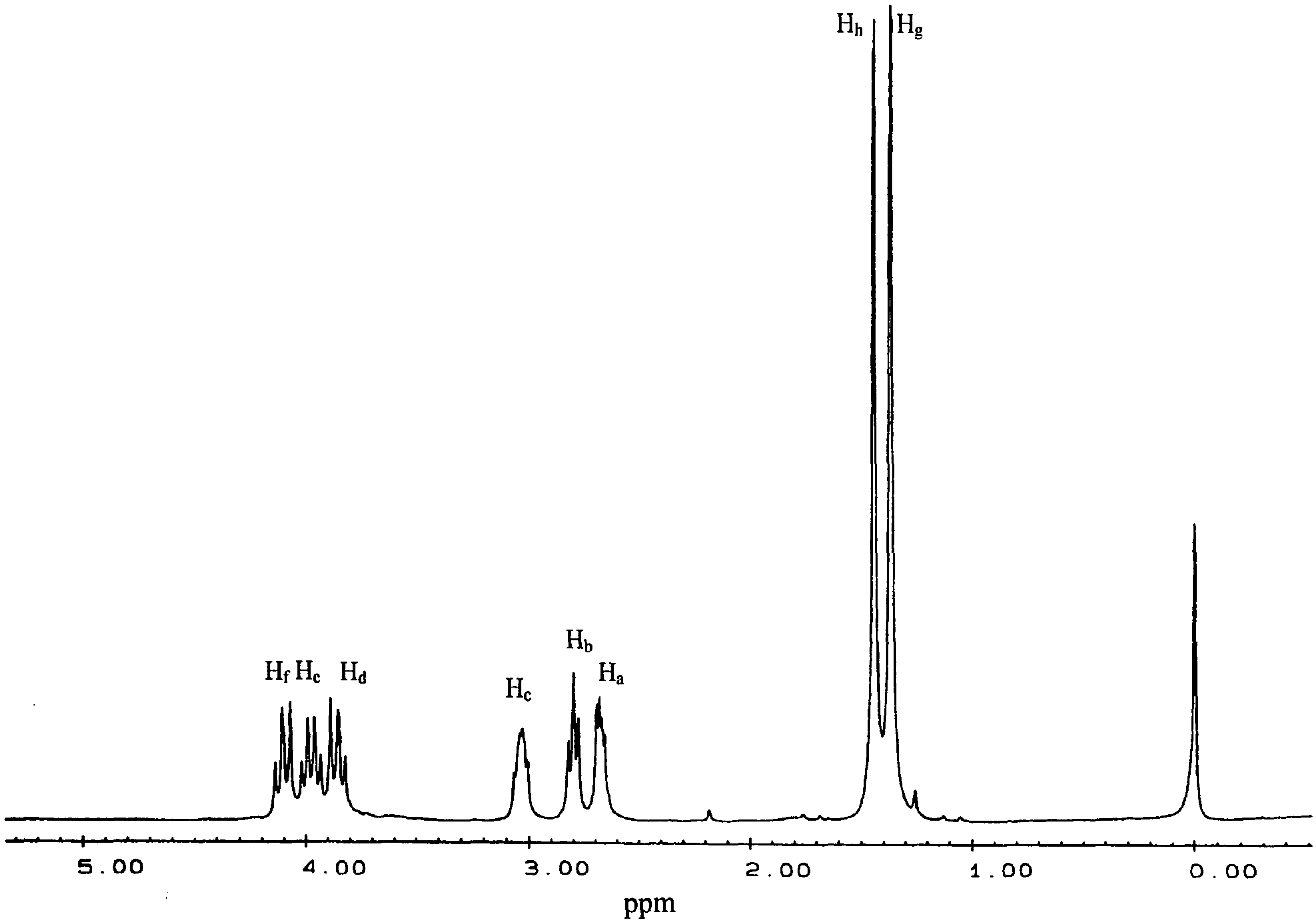


Figure 9 ^{1}H NMR spectrum of the (2S,3S)-epoxide , in $CDCl_3$, 25°C

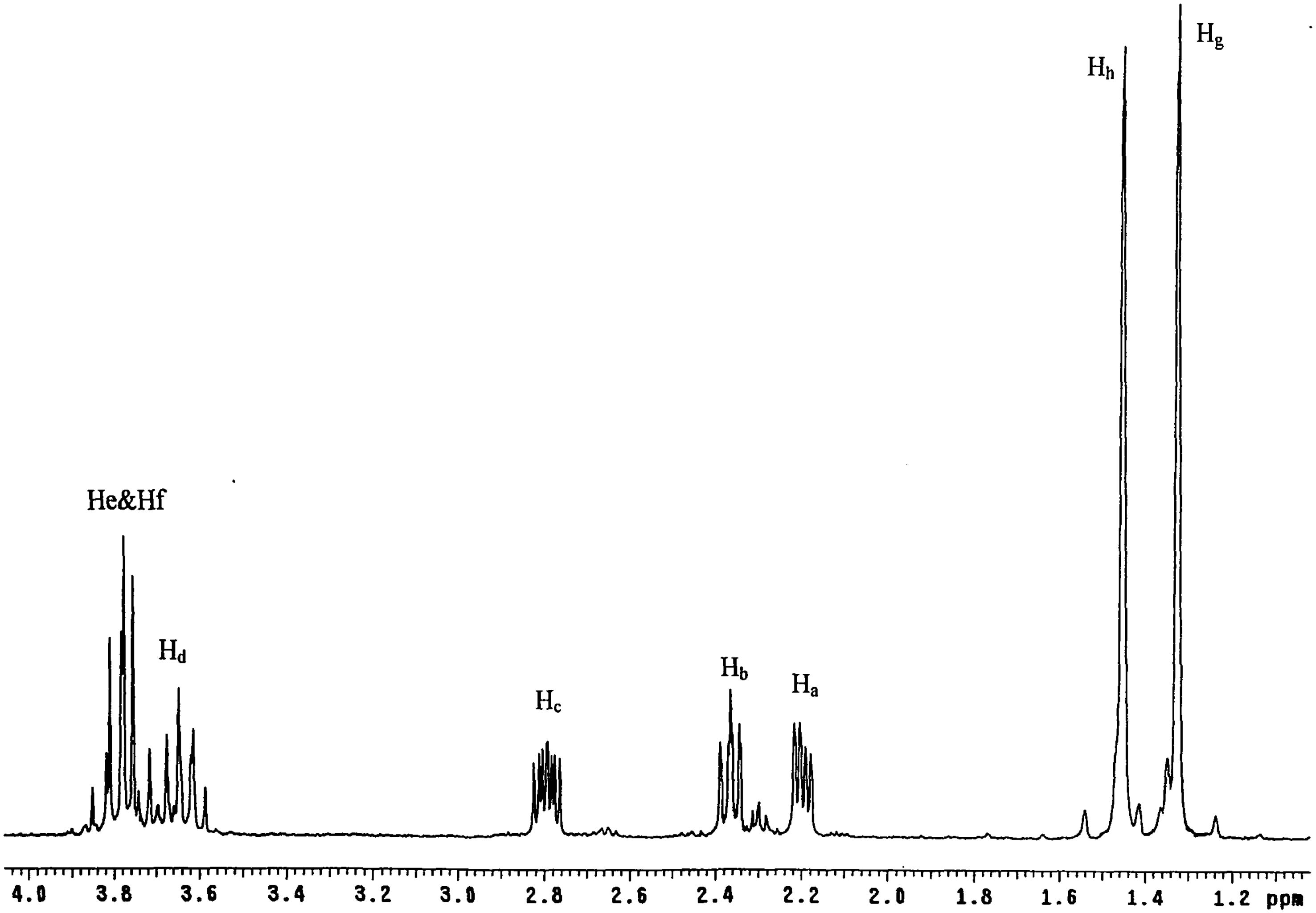


Figure 10 ^{1}H NMR spectrum of the (2S,3R)-epoxide , in $CDCl_3$, 25°C

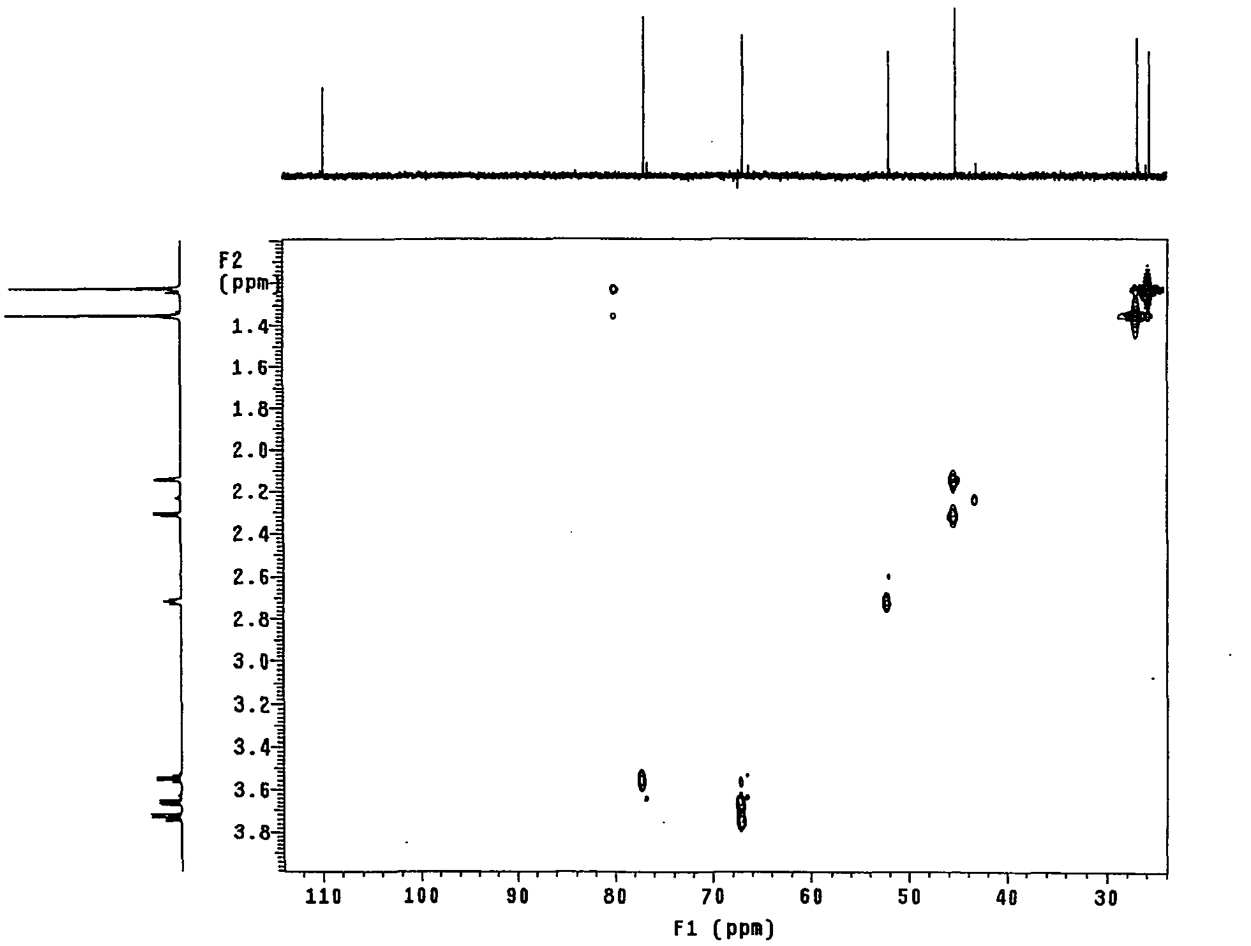


Figure 11 GHMQC NMR spectrum of the (2S,3R)-epoxide monomer In C_6D_6

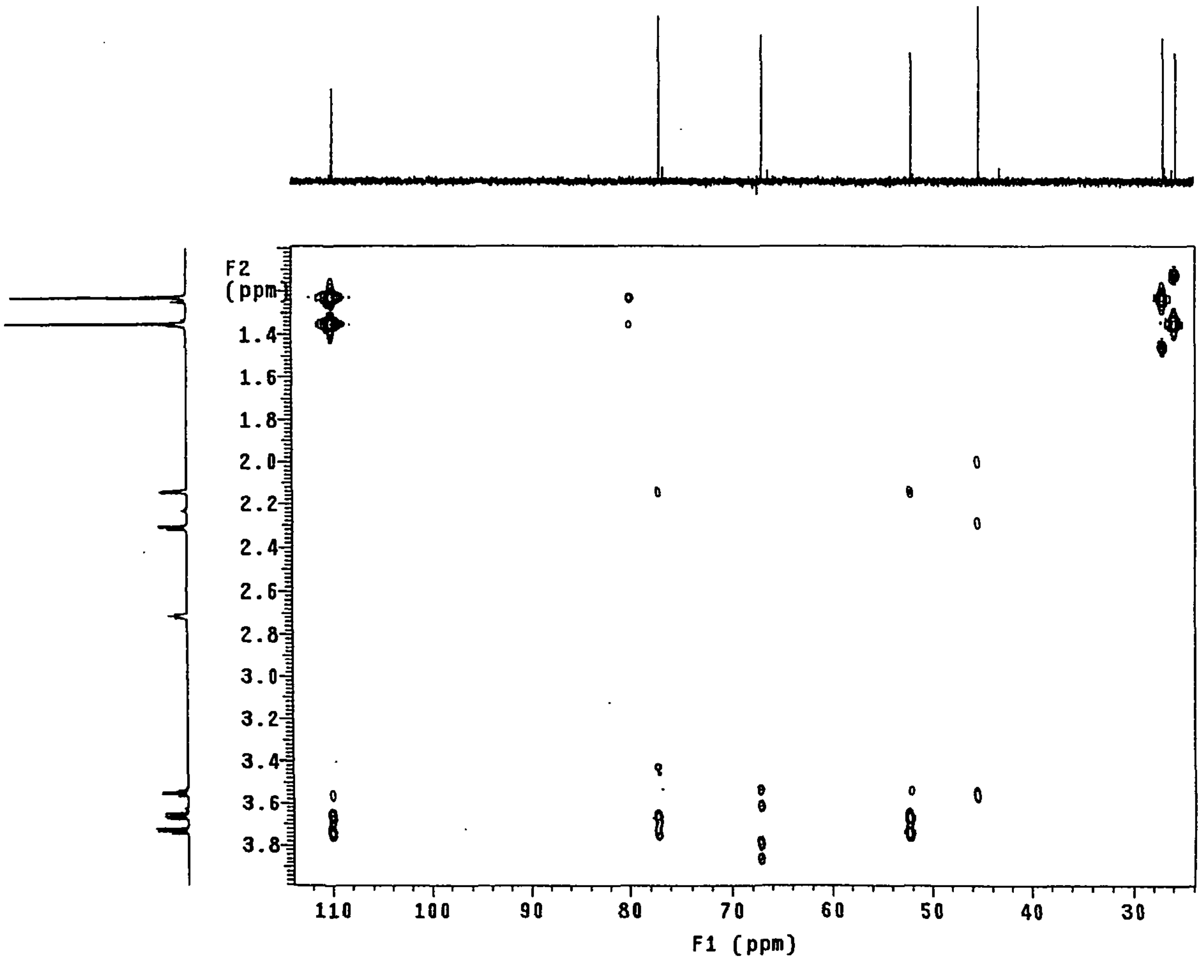


Figure 12 GHMBC NMR spectrum of the (2S,3R)-epoxide monomer In C_6D_6

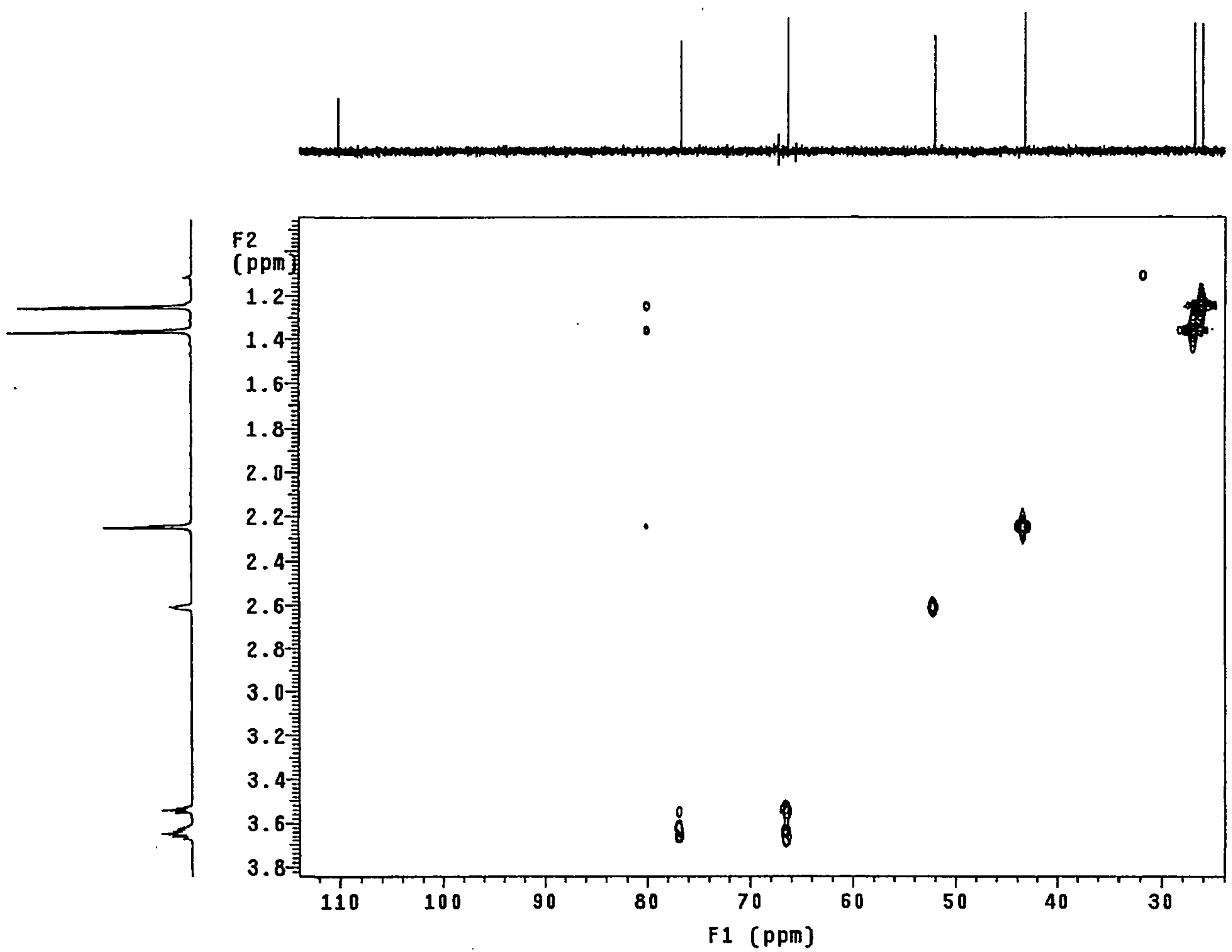


Figure 13 GHMQC NMR spectrum of the (2S,3S)-epoxide monomer In C_6D_6

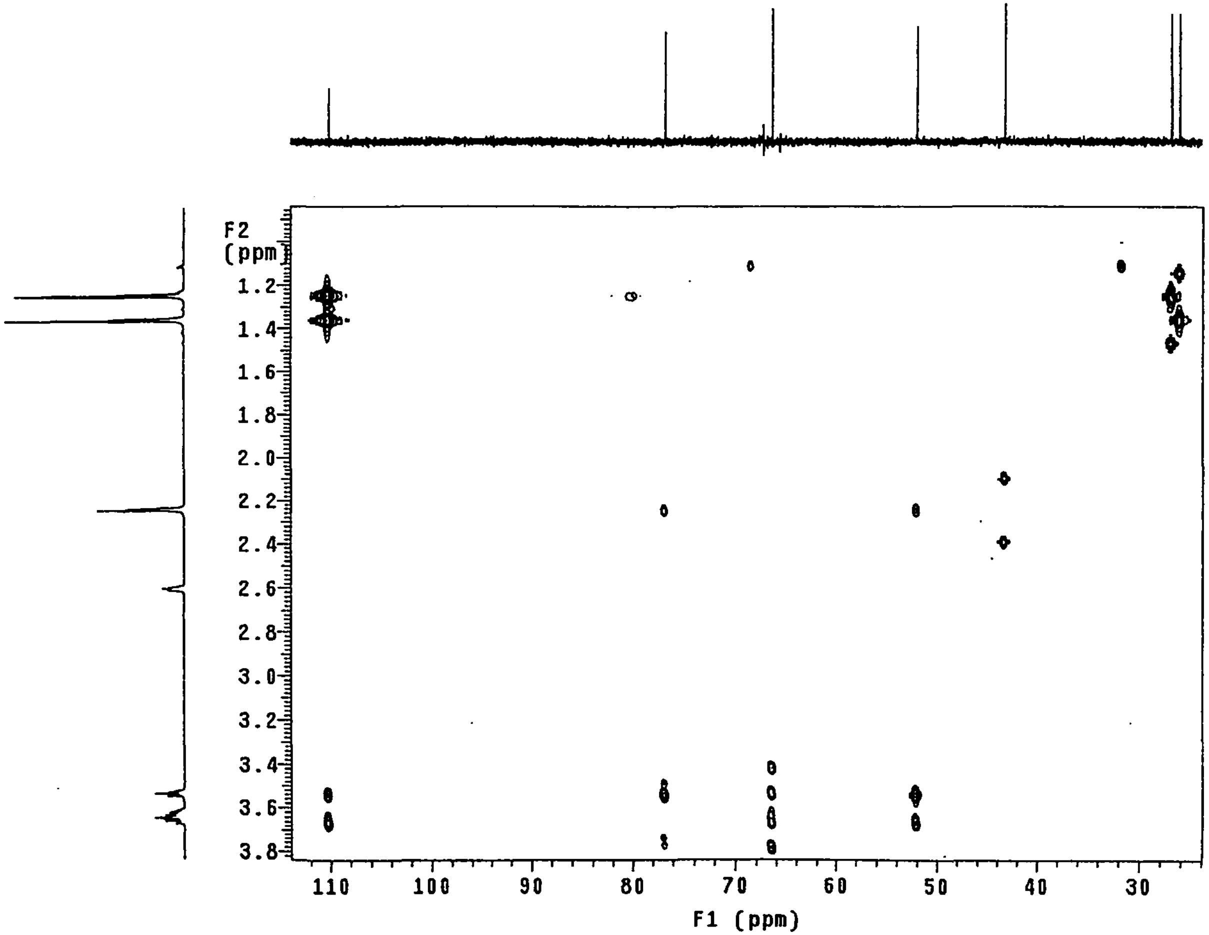


Figure 14 GHMBC NMR spectrum of the (2S,3S)-epoxide monomer In C_6D_6

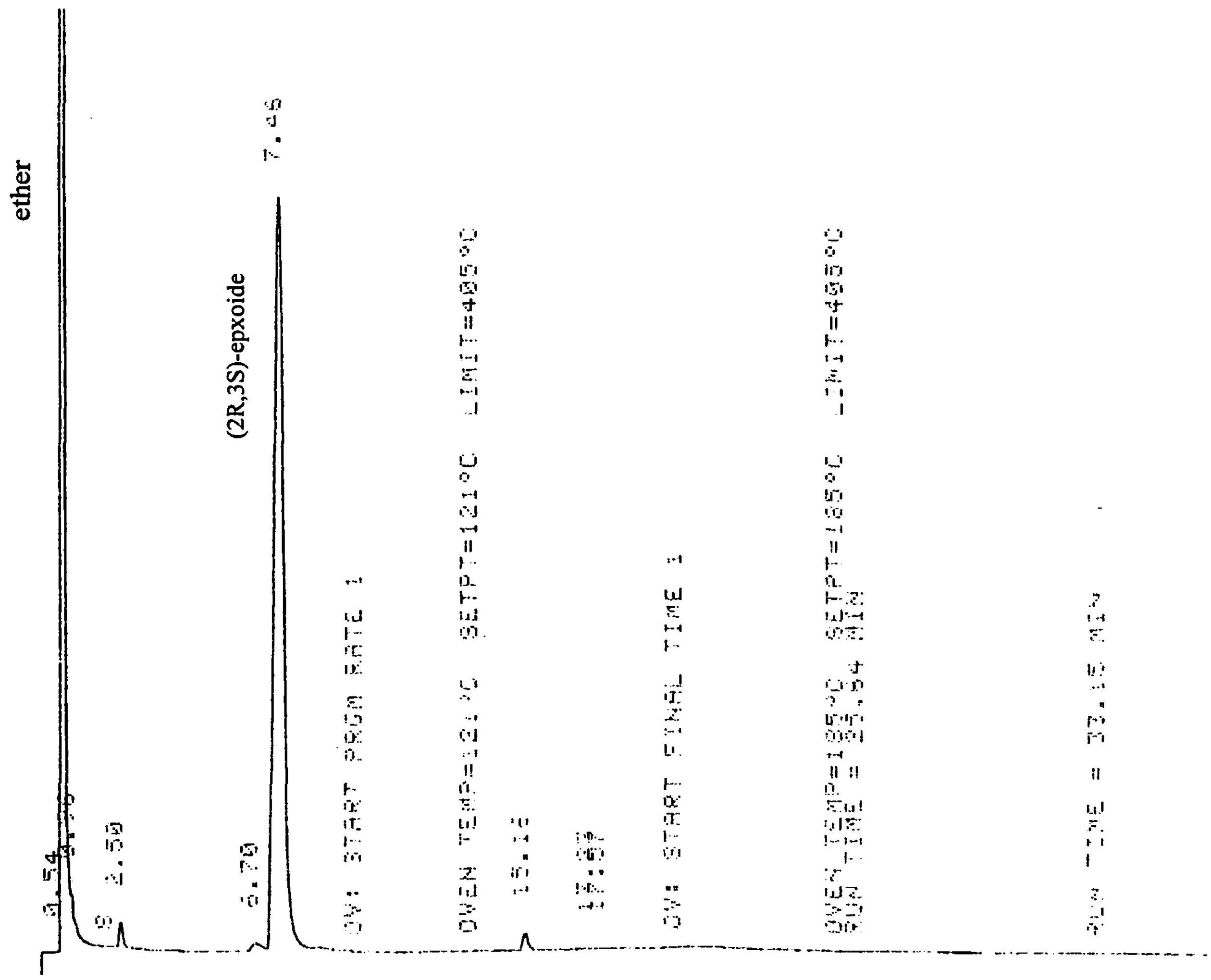


Figure 15 GC spectrum of recovered (2R,3S)-epoxide from the polymerization system with CsOH as initiator

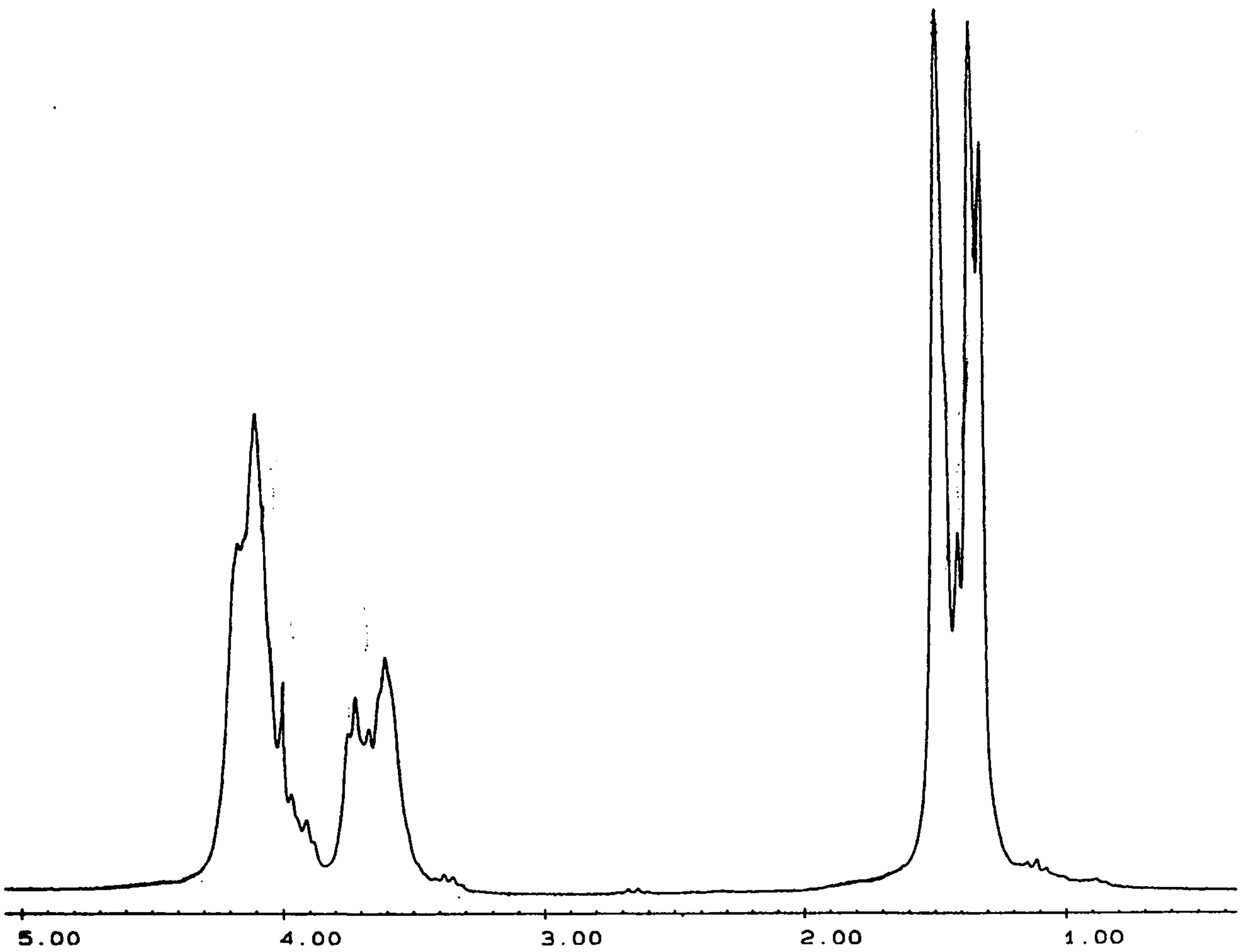


Figure 16 ^{1}H NMR spectrum of the poly(2R,3S)-epoxide with CsOH as initiator, C_6D_6, 60°C

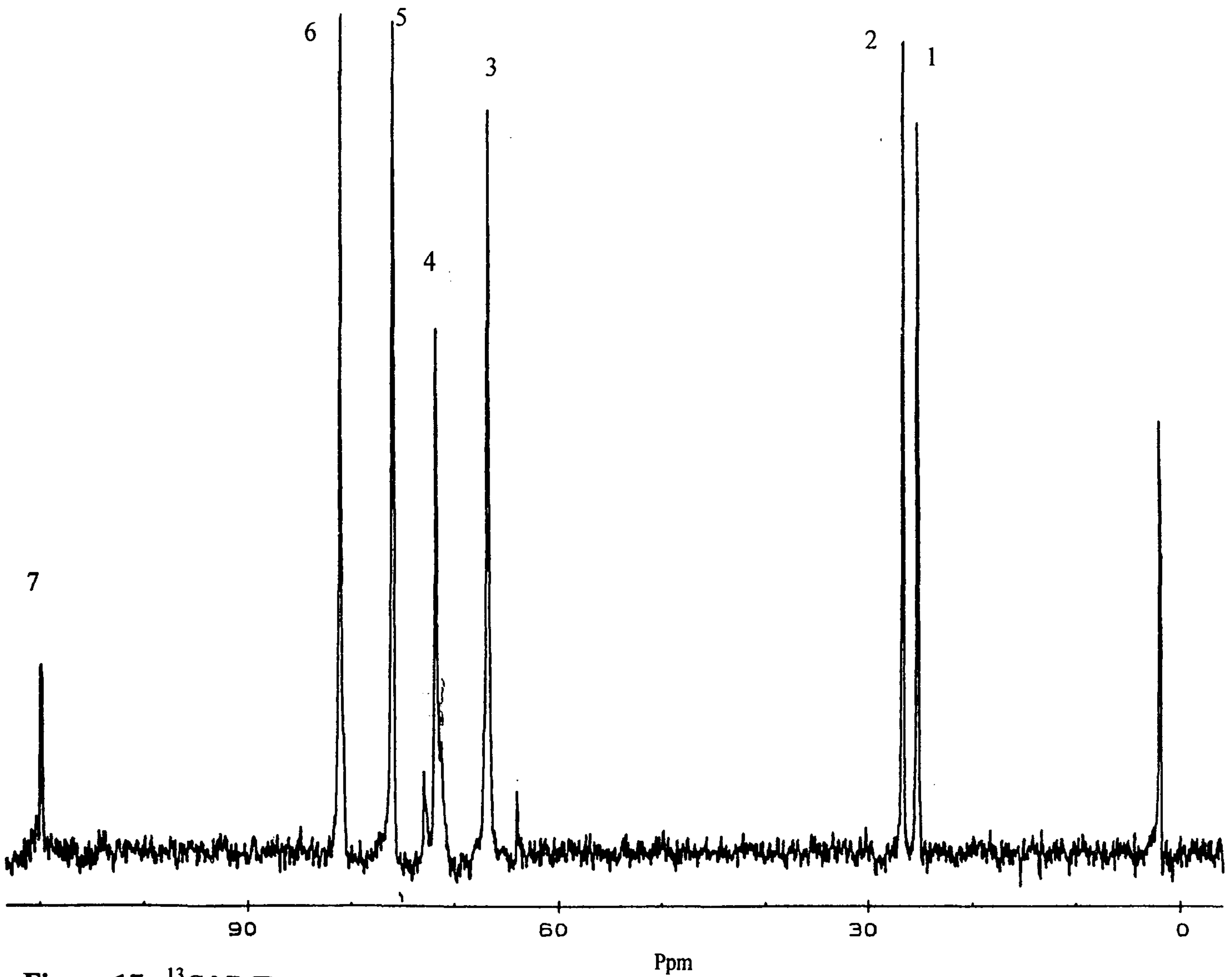


Figure 17 ^{13}C NMR spectrum of the poly(2R,3S)-epoxide with CsOH as initiator, in o-chlorophenol, 80°C

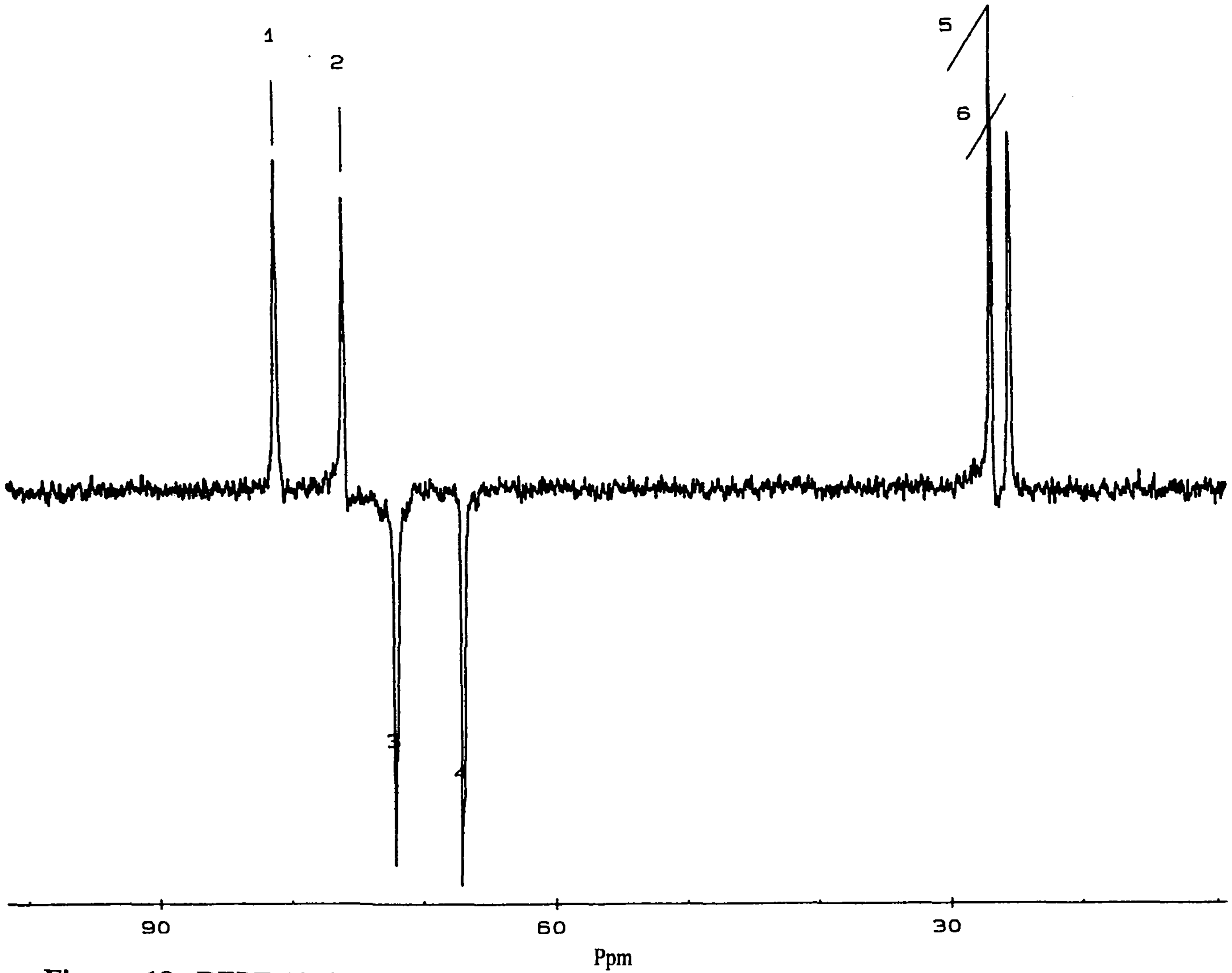


Figure 18 DEPT-135° of the poly(2R,3S)-epoxide with CsOH as initiator

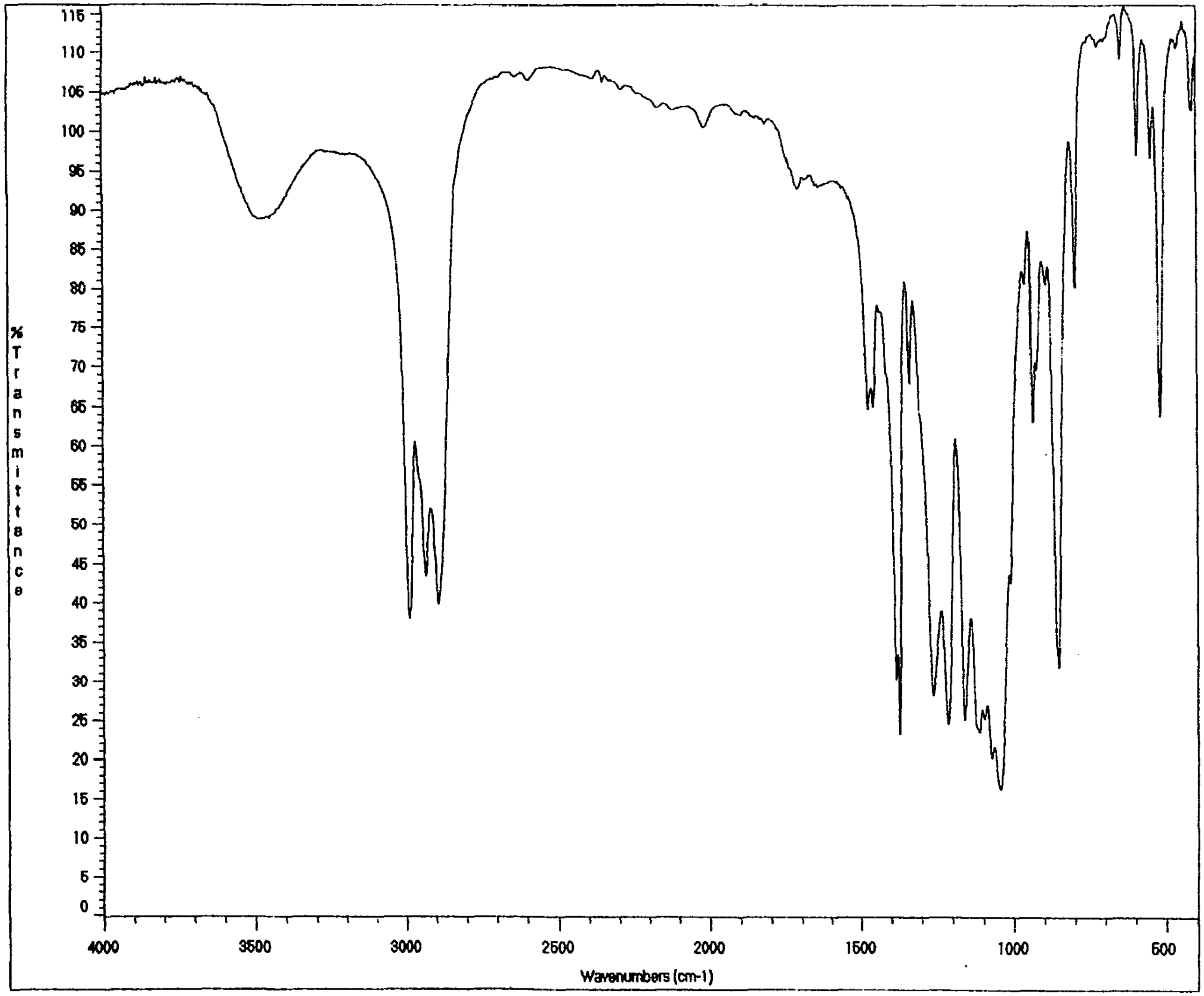


Figure 19 IR Spectrum of the Poly(2S,3S)-Epoxide with CsOH as Initiator

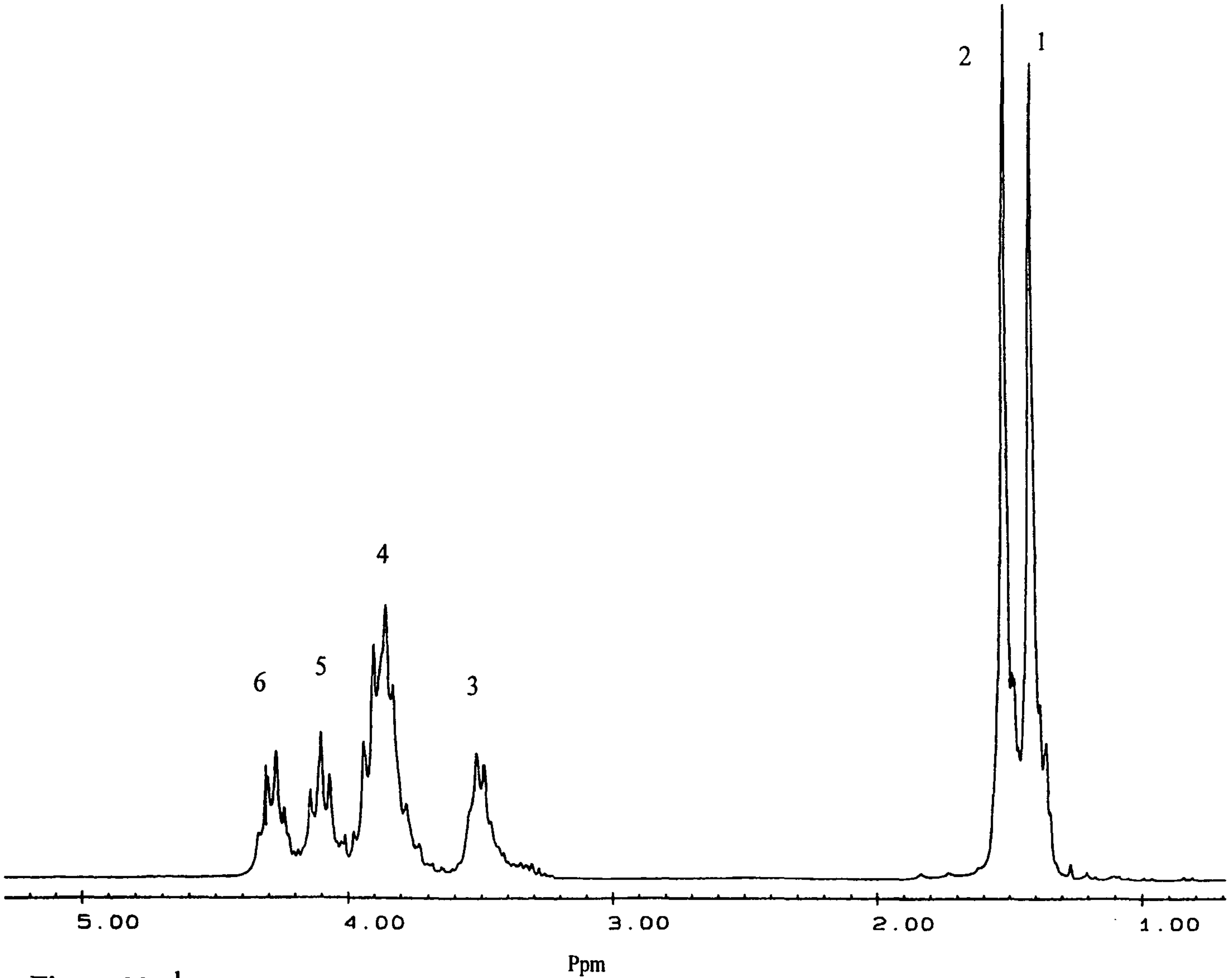


Figure 20 ^{1}H NMR spectrum of the poly(2S,3S)-epoxide with CsOH as initiator, in C_6D_6, 40°C

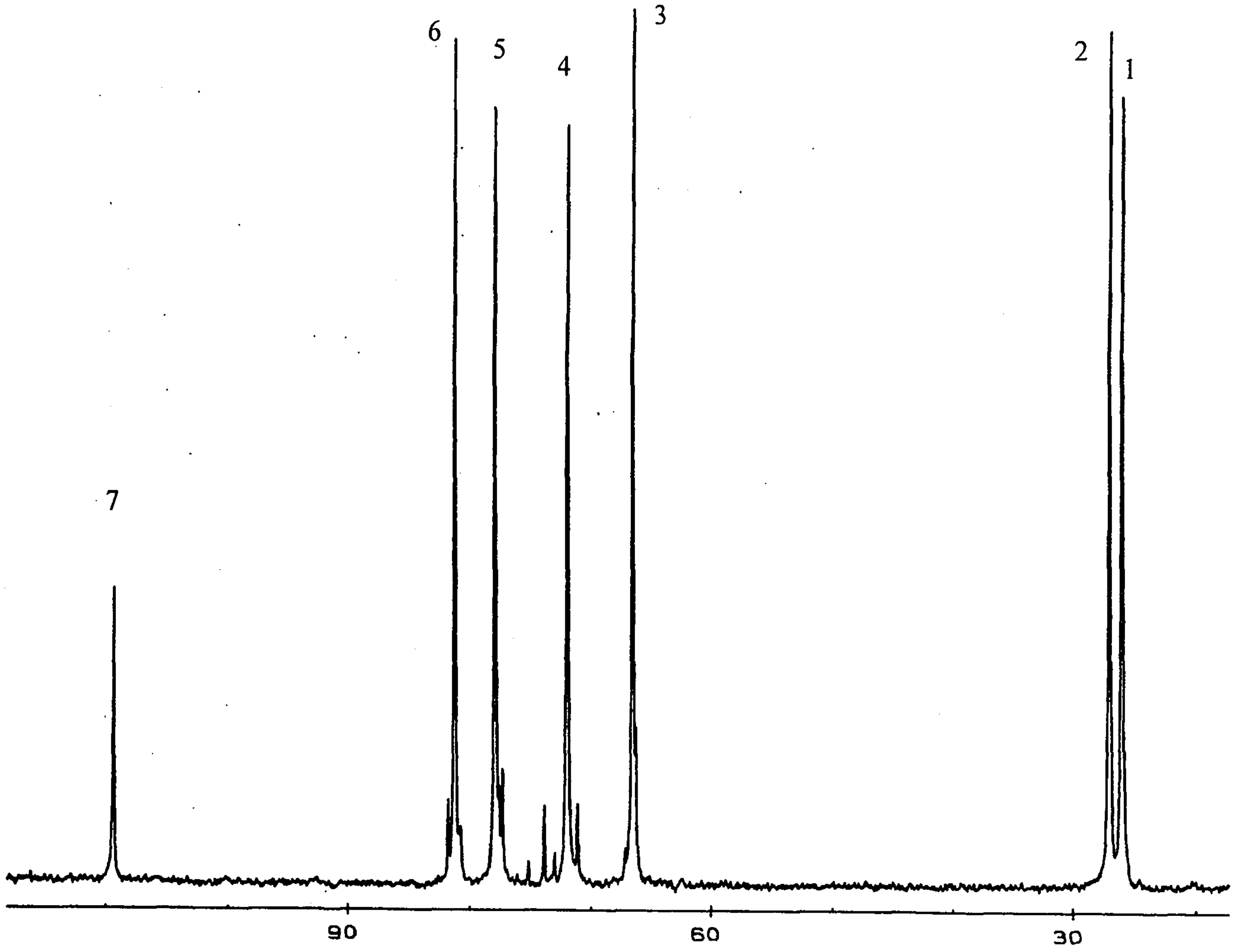


Figure 21 ^{13}C NMR spectrum of the poly(2S,3S)-epoxide with CsOH as initiator, in C_6D_6, 40°

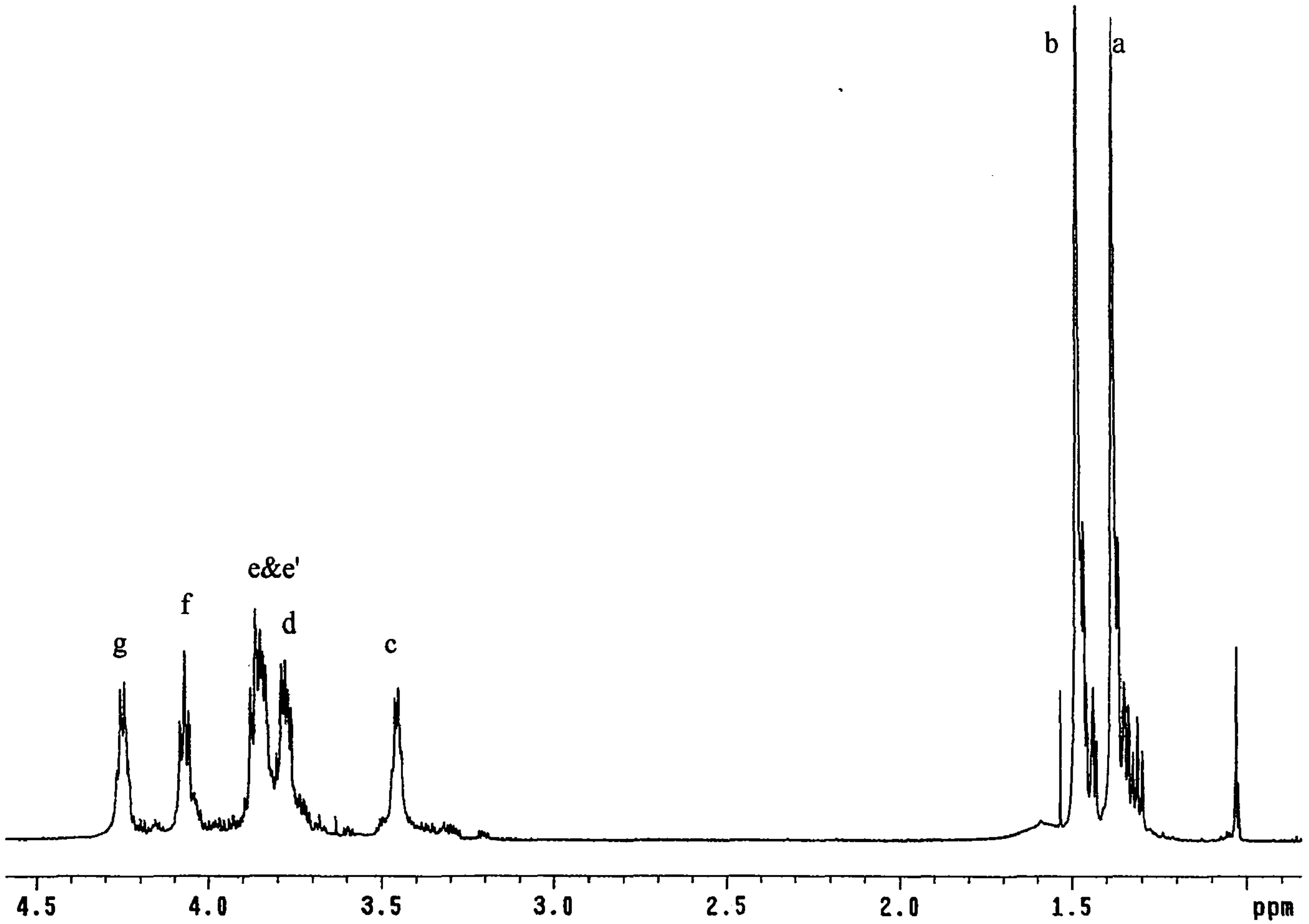


Figure 22 ^{1}H NMR spectrum of the poly(2S,3S)-epoxide with *tert*-BuOK as initiator, in C_6D_6, 25°C

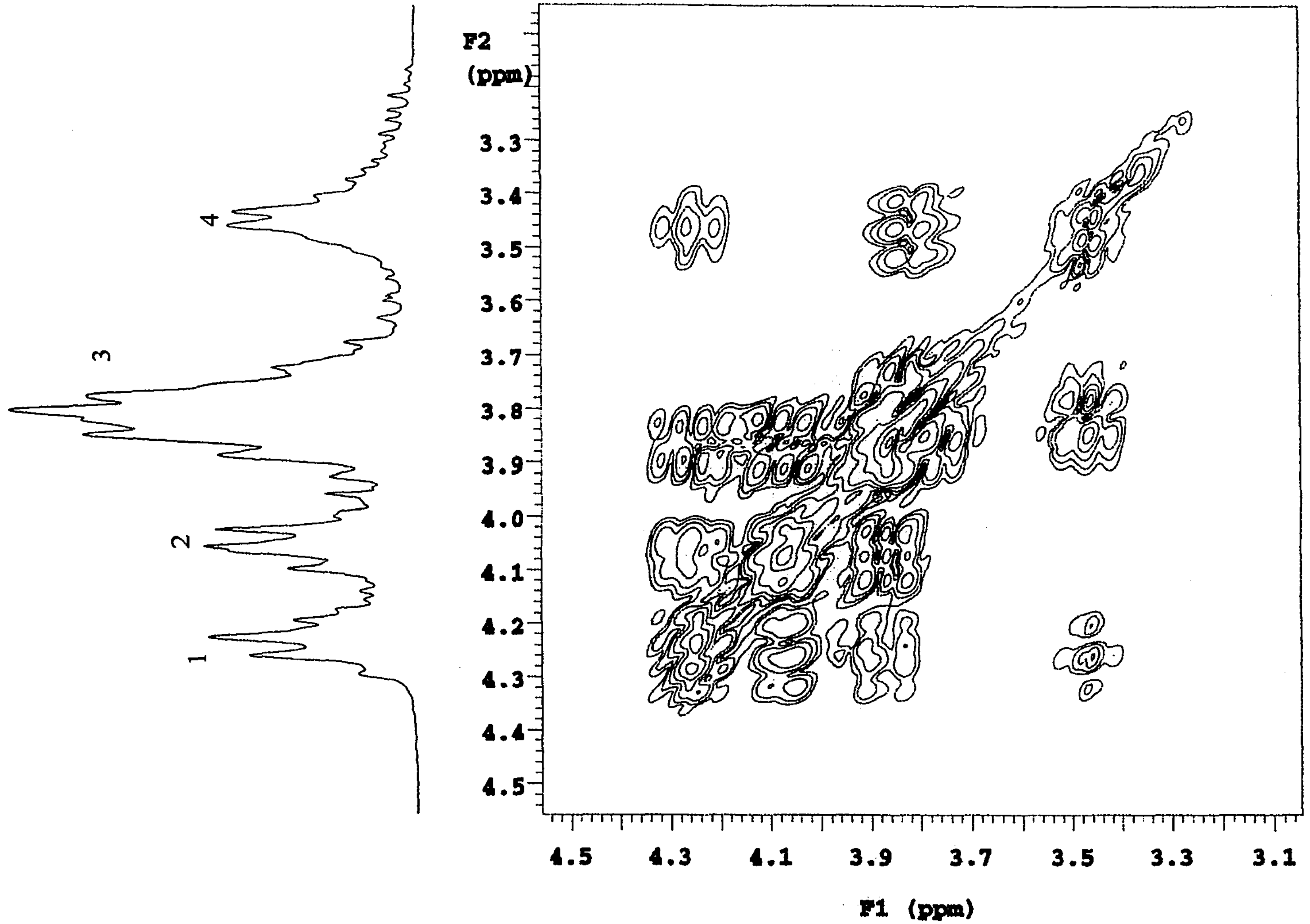


Figure 23 COSY Spectrum of the Poly(2S,3S)-Epoxide with *tert*BuOK as Initiator, in C_6D_6, 25°C

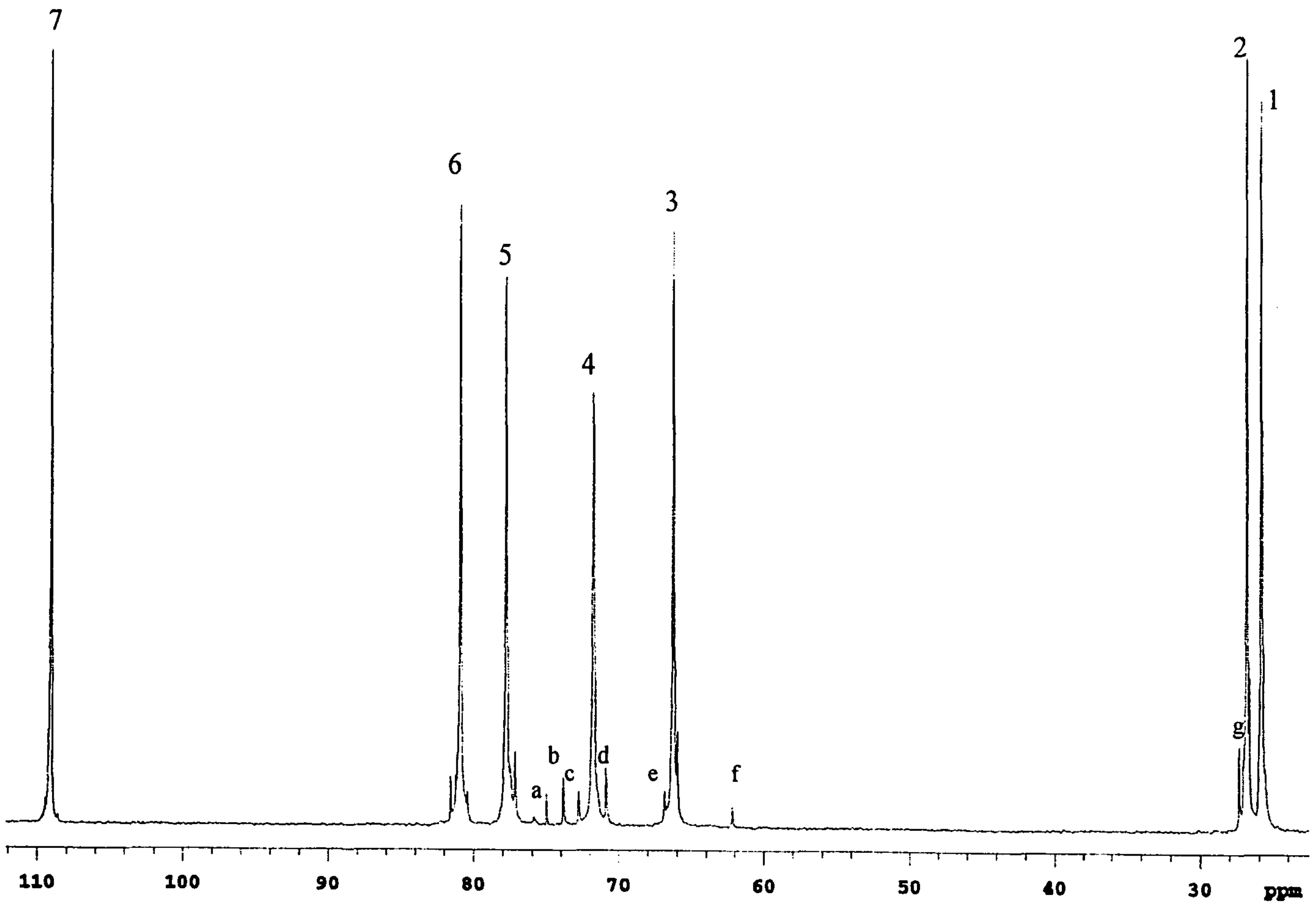


Figure 24 ^{13}C NMR spectrum of the poly(2S,3S)-epoxide with *tert*-BuOK as initiator, in C_6D_6, 40°C

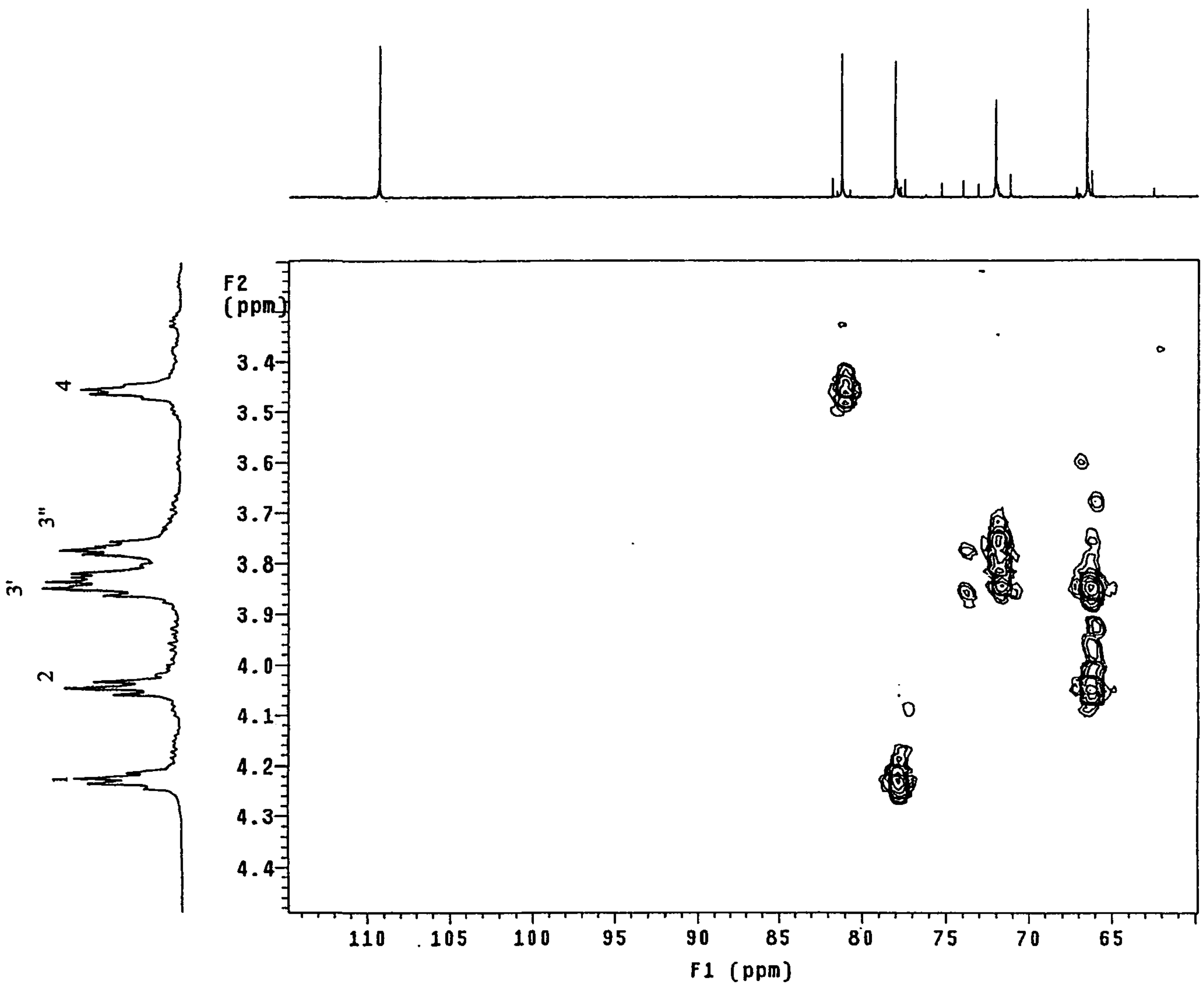


Figure 25 GHMQC Spectrum of the Poly(2S,3S)-Epoxide with *tert*BuOK as initiator, in C_6D_6, 40°C

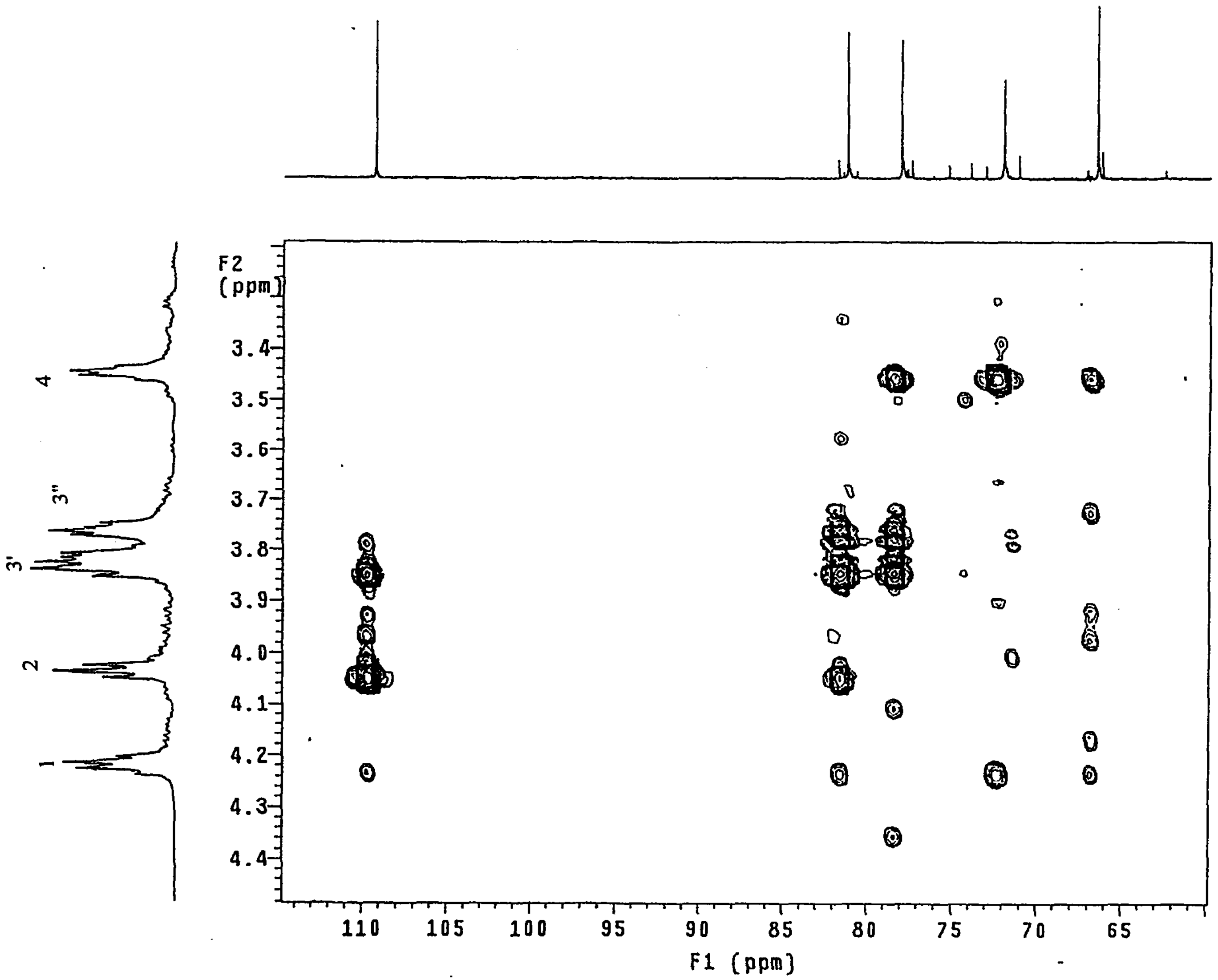


Figure 26 GHMBC Spectrum of the Poly(2S,3S)-Epoxide with *tert*-BuOK as initiator in C_6D_6, 40°C

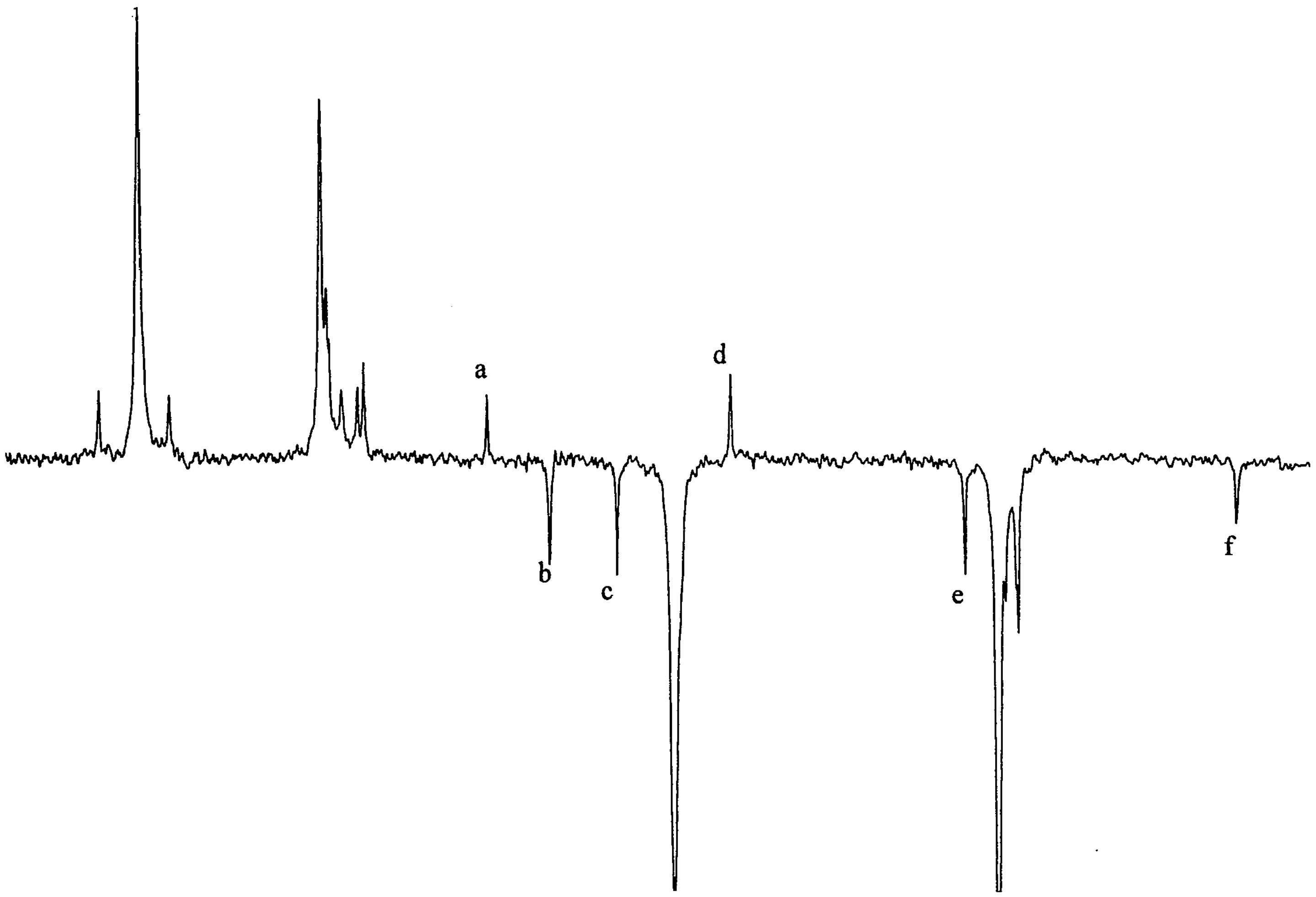


Figure 27 DEPT-135° spectrum of the poly(2S,3S)-epoxide with *tert*-BuOK as initiator, in C_6D_6, 40°

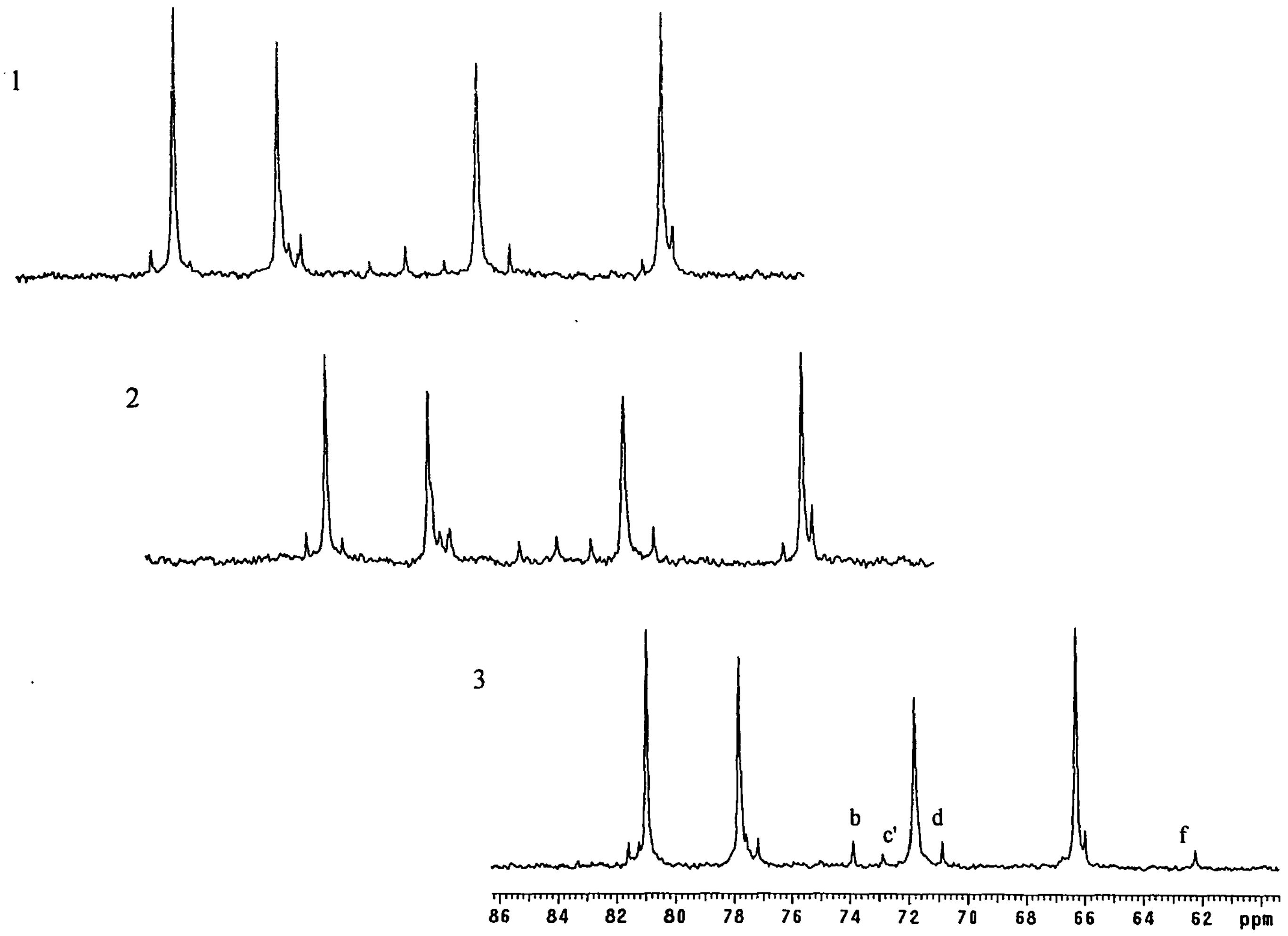


Figure 28 ^{13}C NMR spectra of the poly(2S,3S)-epoxide. (a) with CsOH as initiator, b&c: with *tert*-BuOK as initiator, (b) *t*-BuOK weighed outside a dry-box, (c) *t*-BuOK weighed inside a dry-box

Figure 29 DEPT-135° spectrum of the poly(2S,3S)-epoxide with *tert*-BuOK which was weighed inside a dry-box, in C_6D_6, 40°C

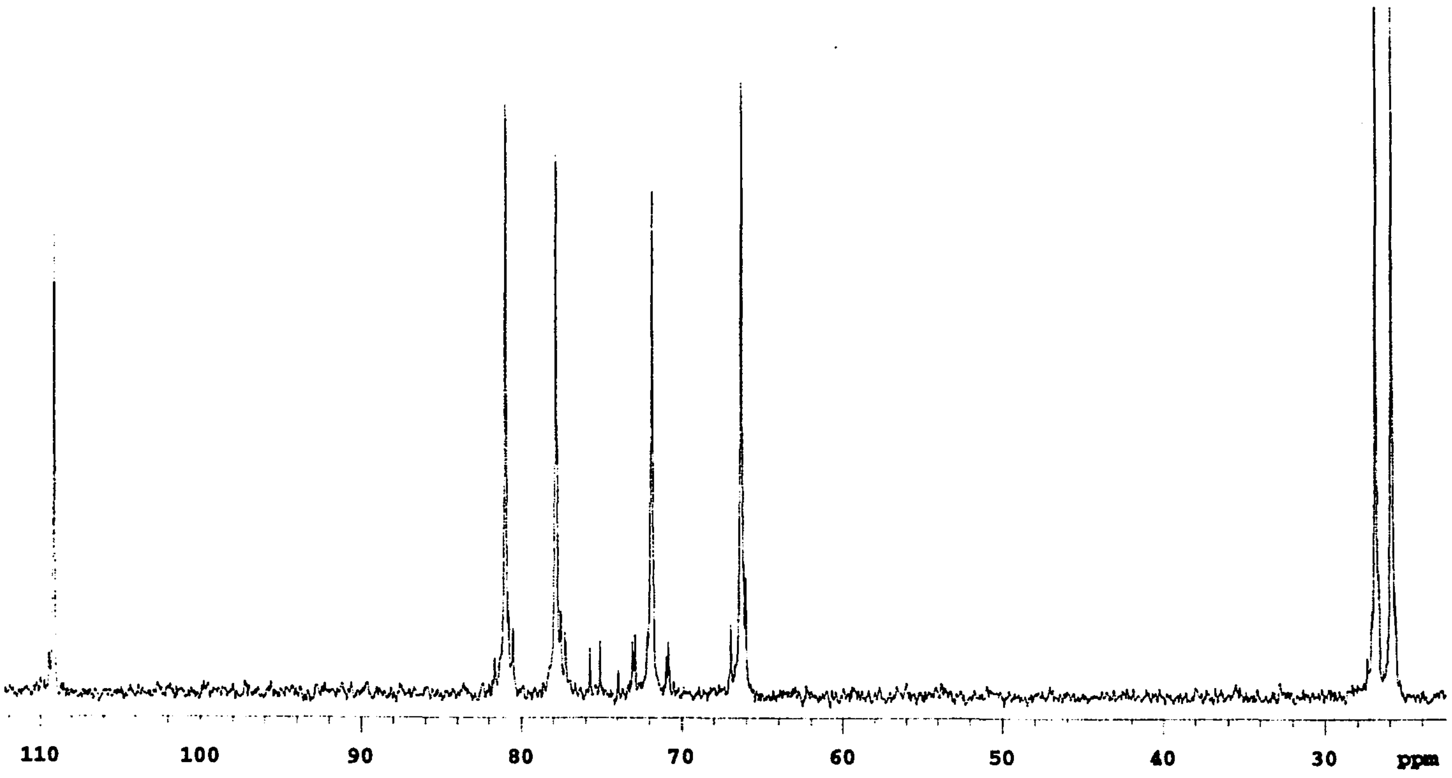


Figure 30 ^{13}C NMR Spectrum of the Poly(2S,3S)-Epoxide After Acetylation, in C_6D_6, 40°C

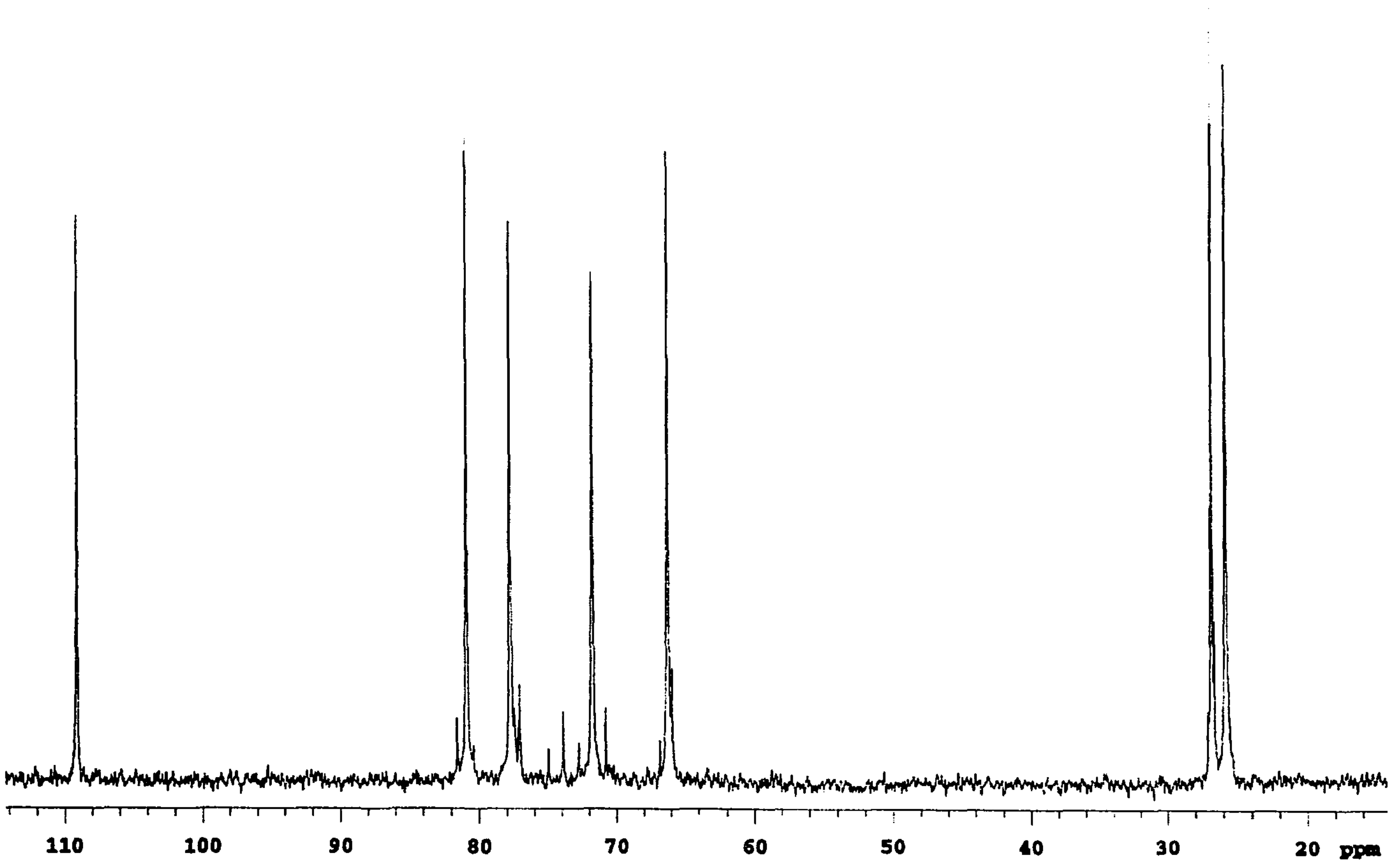


Figure 31 ^{13}C NMR spectrum of the poly(2S,3S)-epoxide before acetylation, with *tert*-BuOK as initiator, in C_6D_6, 40°C

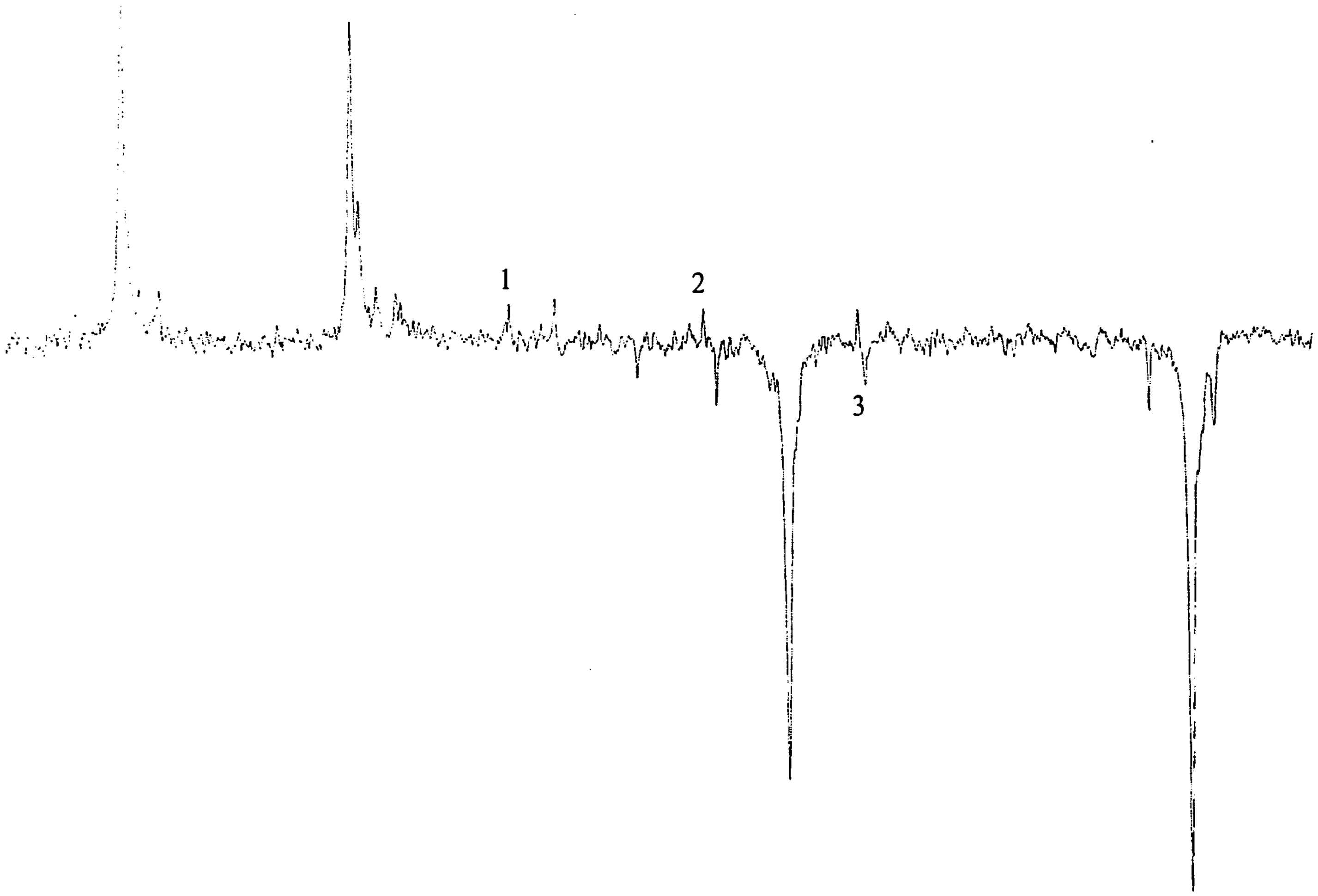


Figure 32 DEPT-135° of Poly(2S,3S)-Epoxide with *tert*-BuOK as Initiator After Acetylation

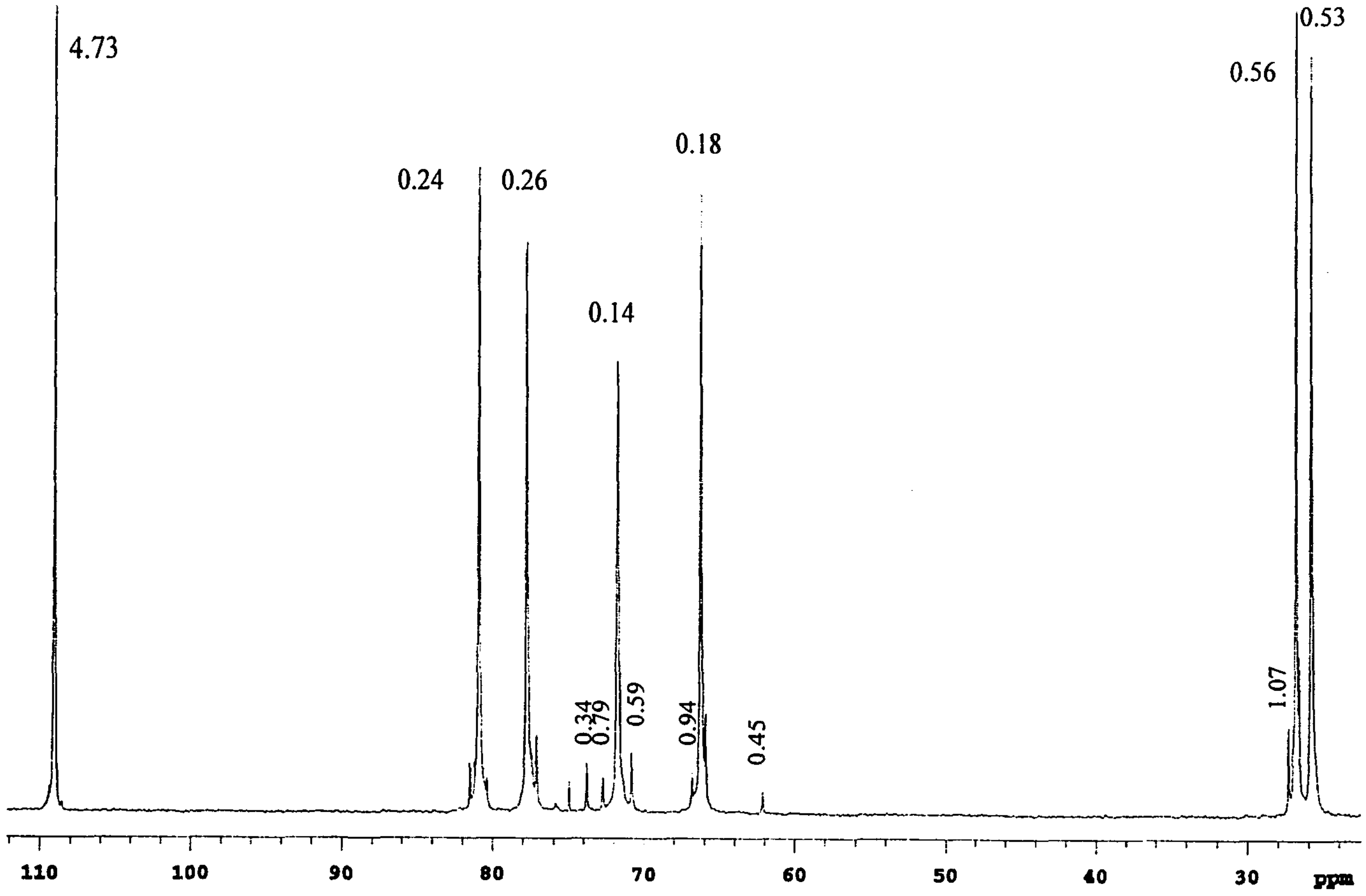


Figure 33 T[1] measurement of ^{13}C NMR of the poly(2S,3S)-epoxide with *tert*-BuOK as Initiator, in C_6D_6, 40°C

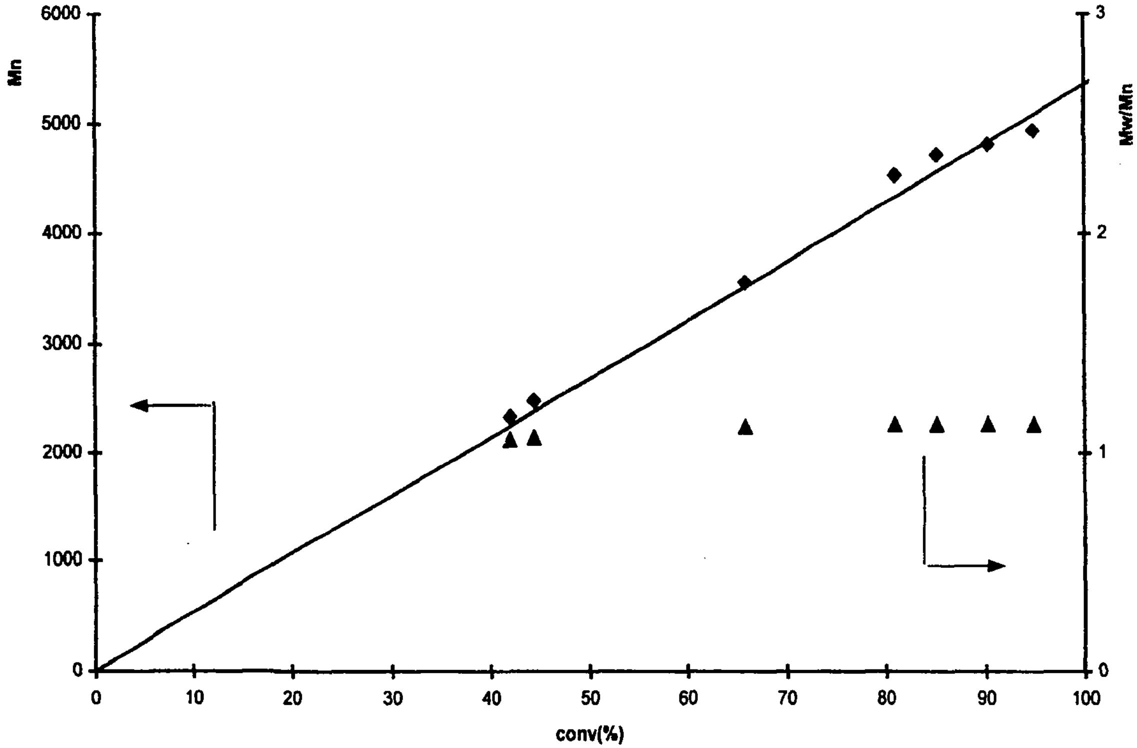


Figure 34 Mn of purified poly(2S,3S)-epoxide vs conversion in bulk polymerization with *tert*-BuOK at 30°C

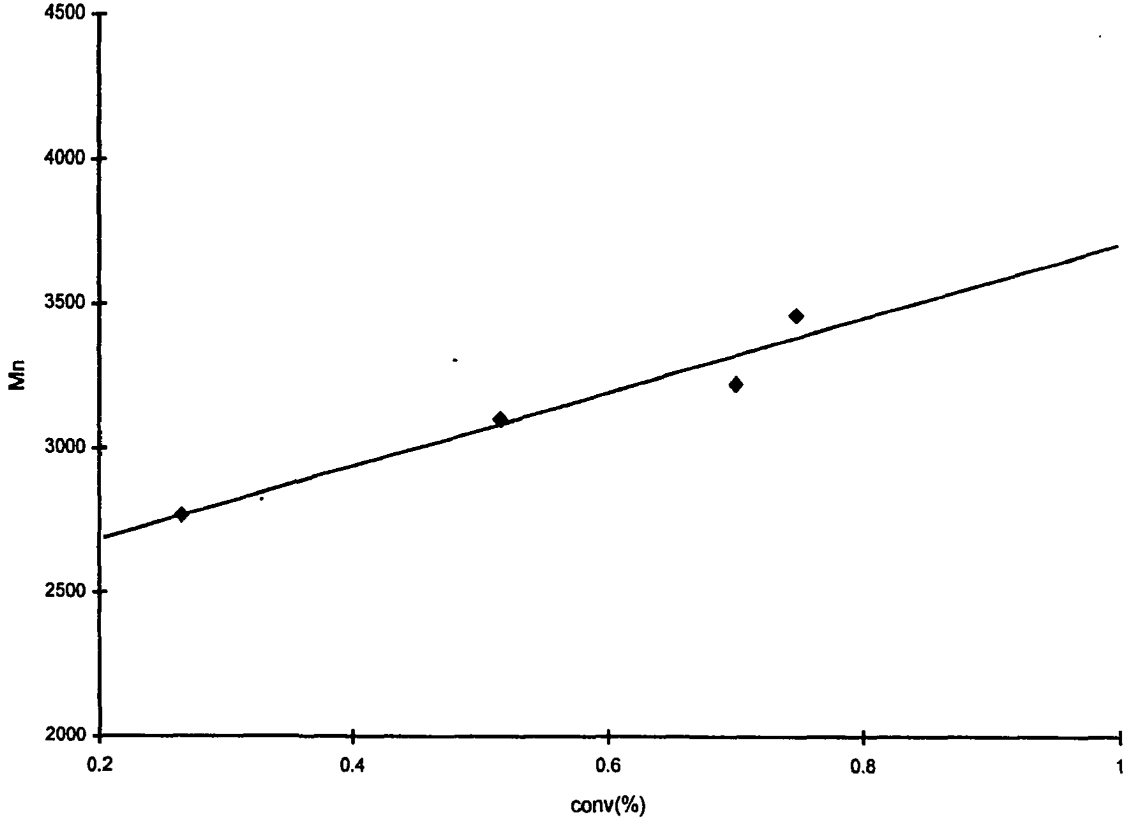


Figure 35 Mn of crude poly(2S,3S)-epoxide vs conversion in bulk polymerization with *tert*-BuOK as initiator at 30°C

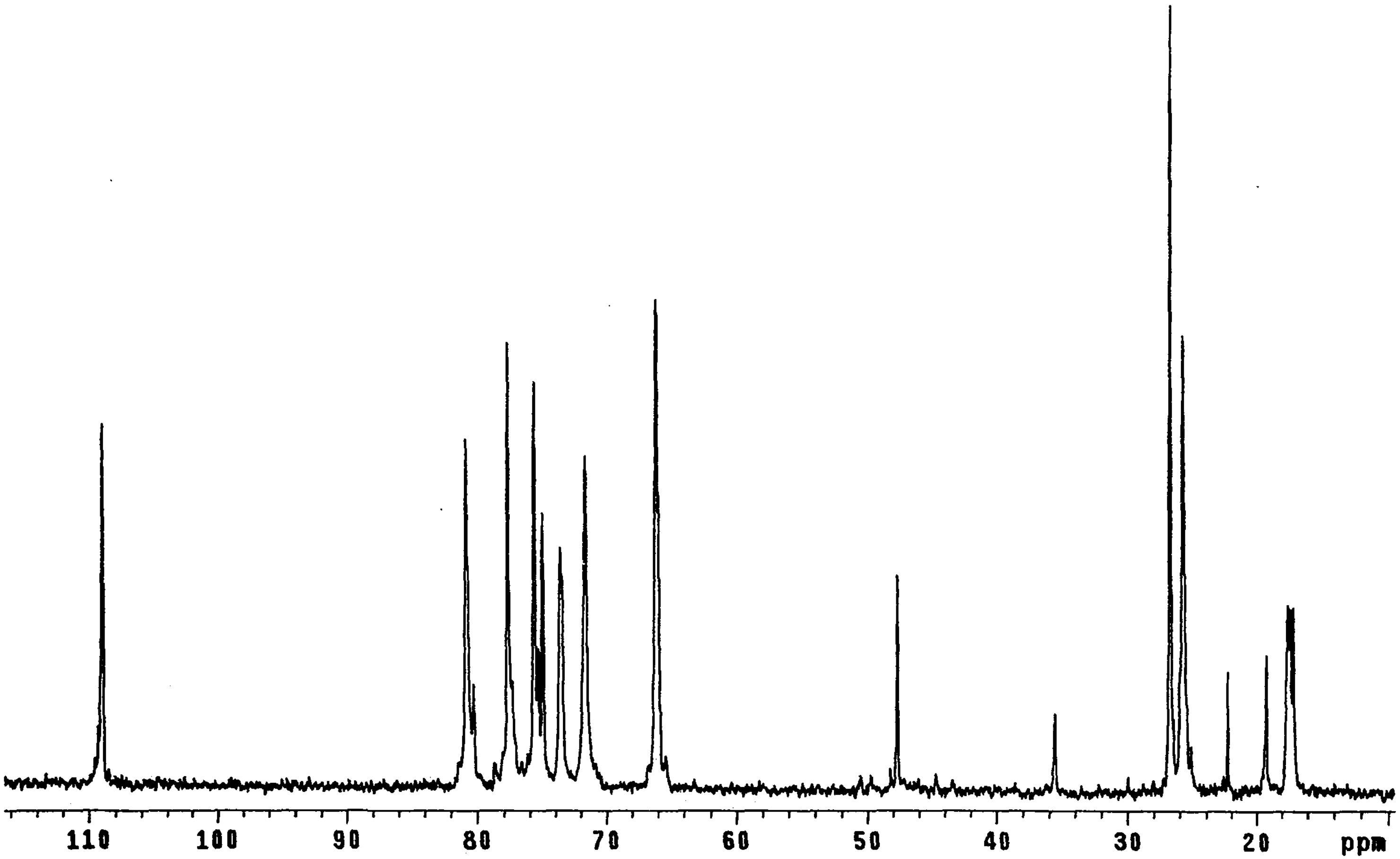


Figure 36 ^{13}C NMR spectrum of poly[(2S,3S)-epoxide-block-propylene oxide] copolymer with *tert*-BuOK as initiator, in C_6D_6, 40°C

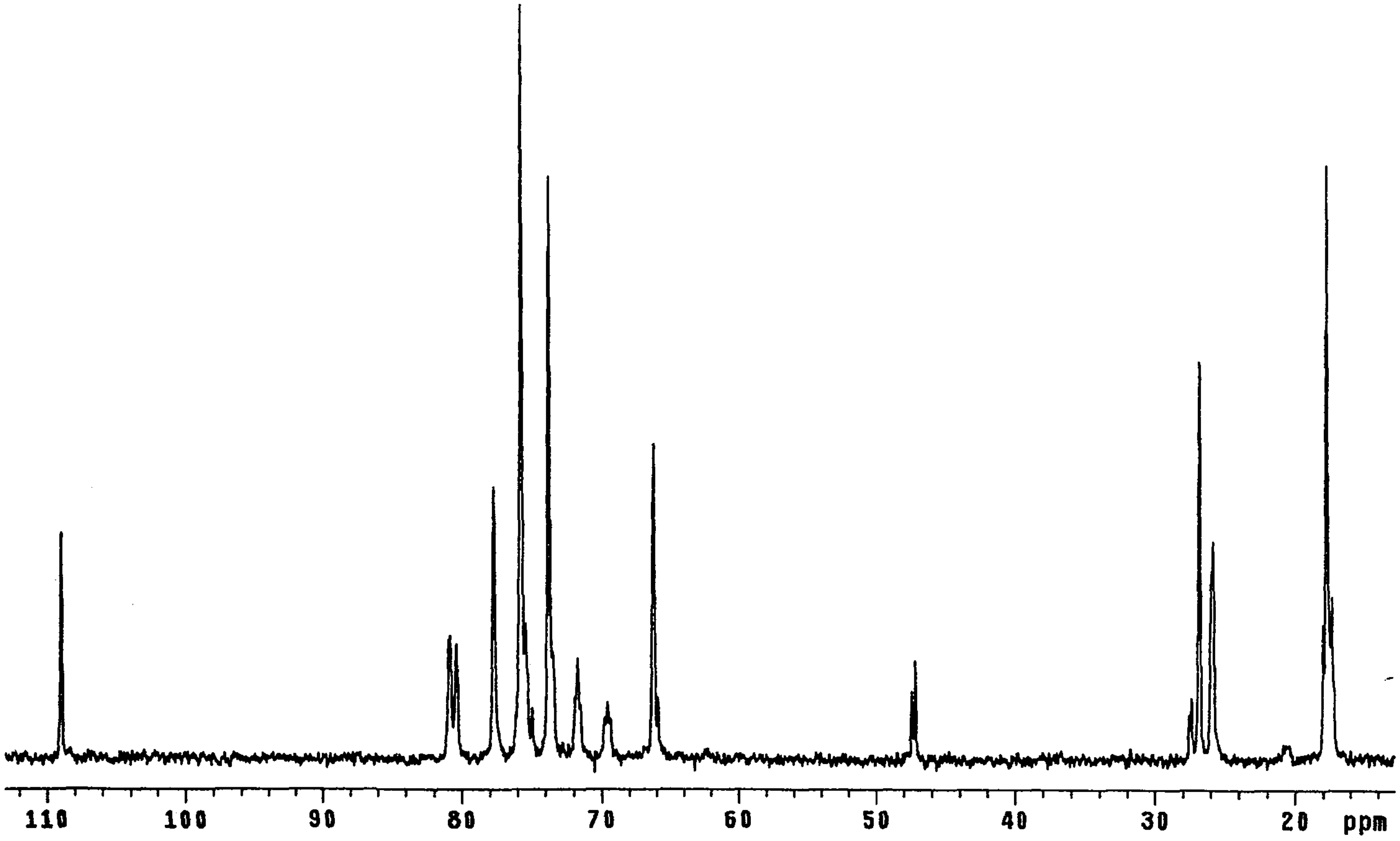


Figure 37 ^{13}C NMR spectrum of poly[(2S,3S)-epoxide-propylene oxide] random copolymer with *tert*-BuOK as initiator, in C_6D_6, 40°C

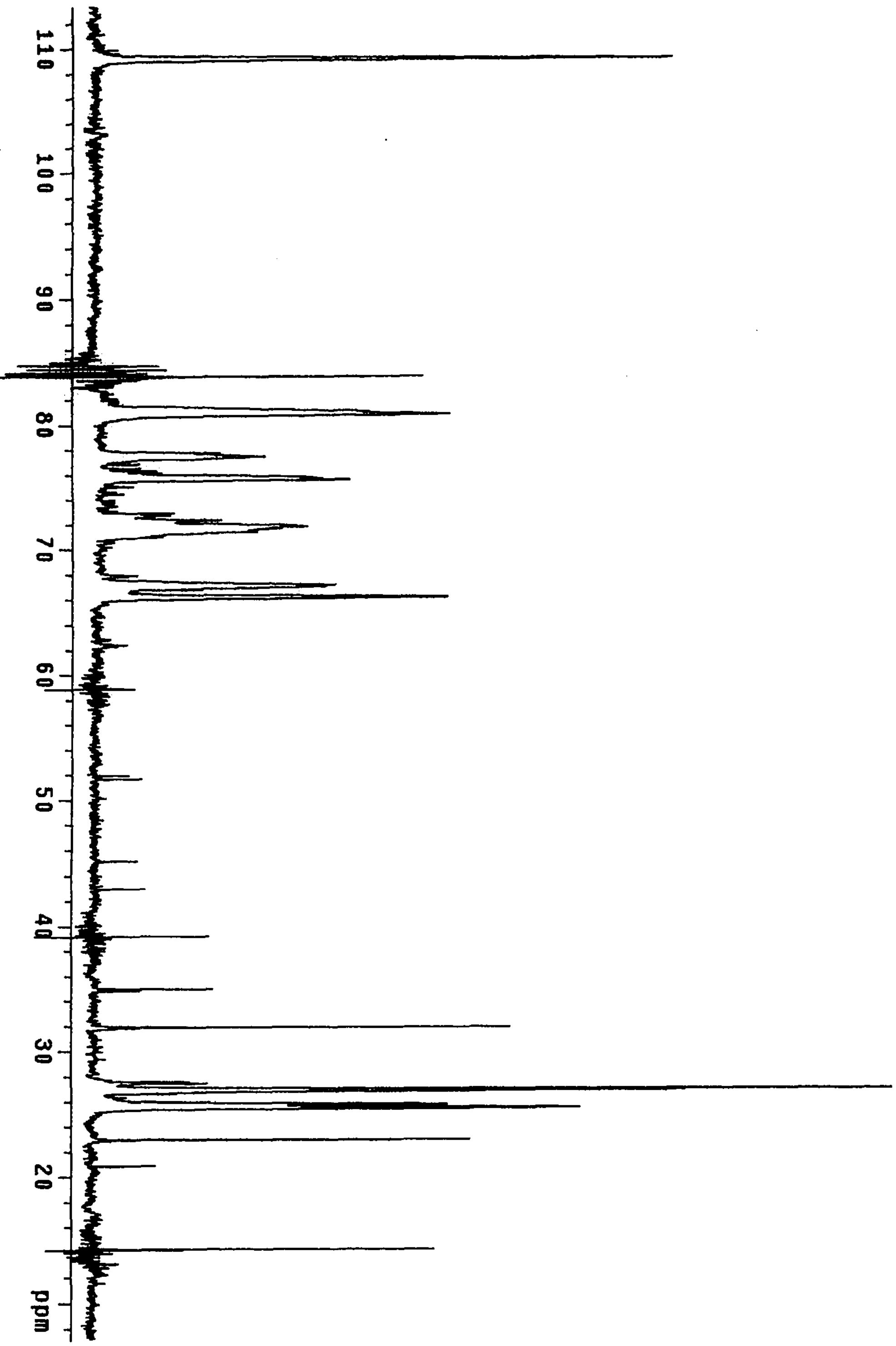


Figure 38 ^{13}C NMR spectrum of crude copolymer of (2R,3S)/(2S,3S)-epoxide (50/50) with CsOH as Initiator, in C_6D_6, 40°C

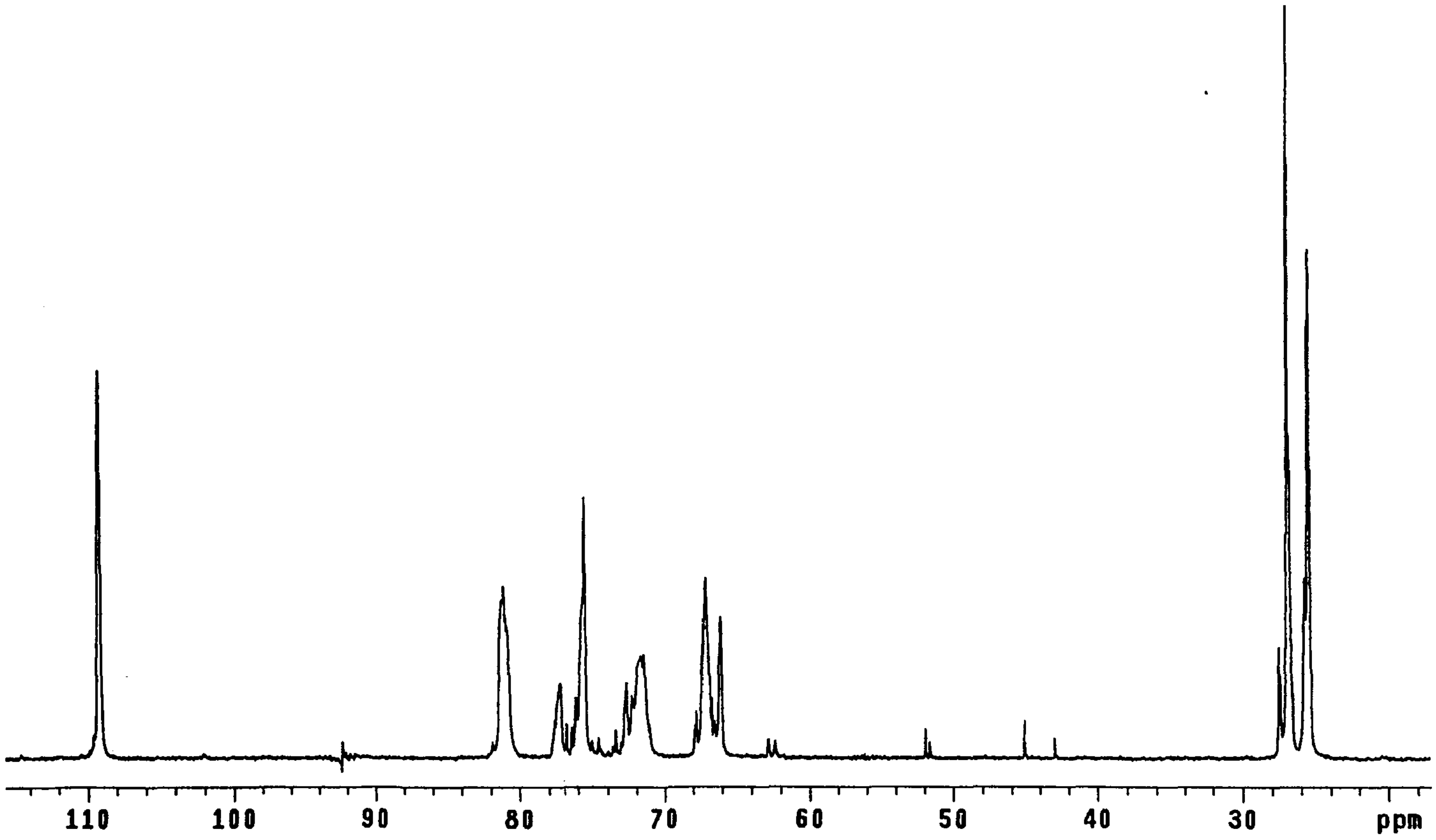


Figure 39 ^{13}C NMR spectrum of copolymer of (2R,3S)/(2S,3S)-epoxide (70/30) with *tert*-BuOK as Initiator, in C_6D_6, 40°C

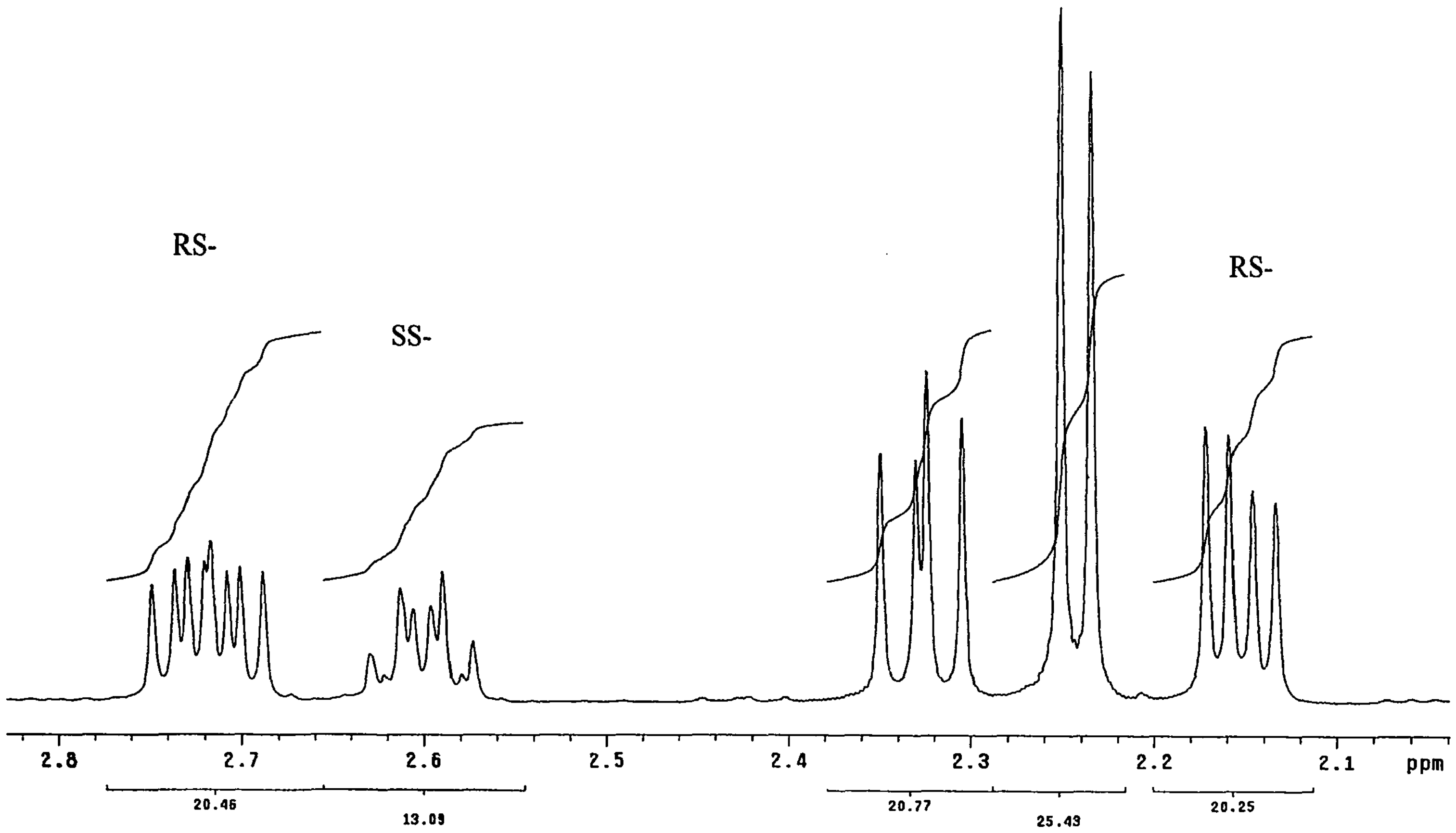


Figure 40 ^{1}H NMR spectrum of recovered comonomer from copolymerization of (2R,3S)/(2S,3S)-epoxide with initial ratio of 70/30, *tert*-BuOK as initiator

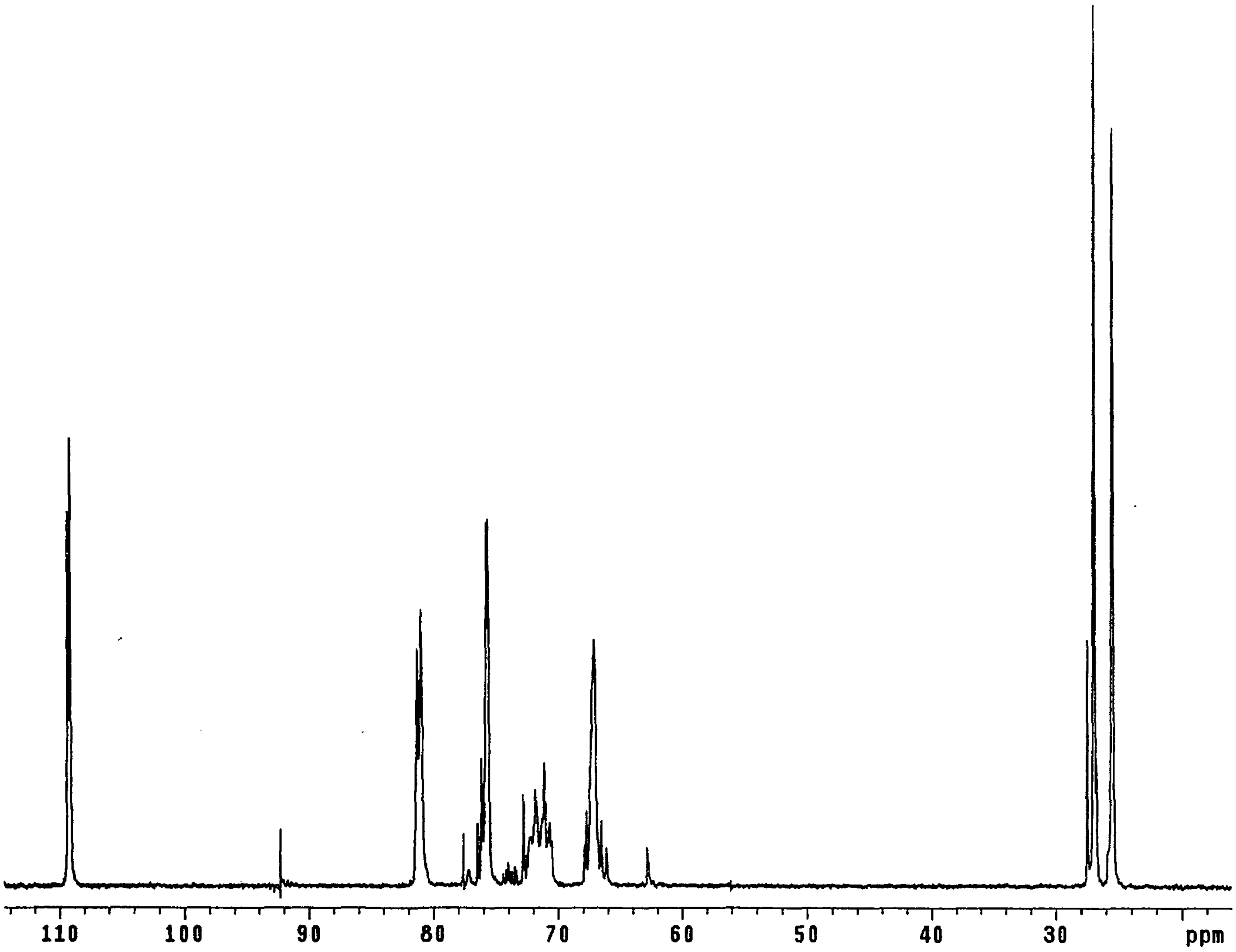


Figure 41 ^{13}C NMR spectrum of copolymer of the (2R,3S)/(2S,3R)-epoxide with initial ratio of 50/50 with *tert*-BuOK as initiator

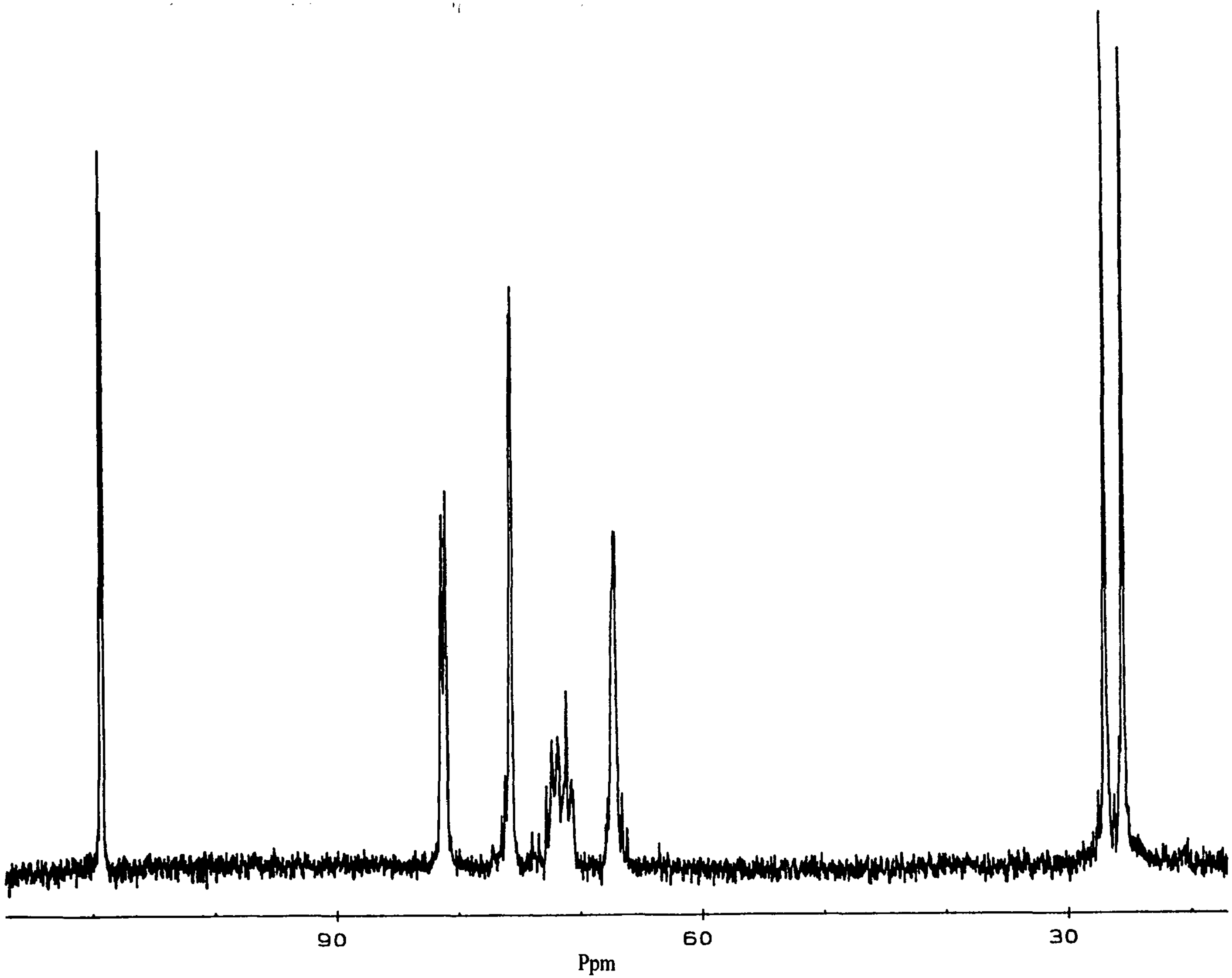


Figure 42 ^{13}C NMR spectrum of copolymer of the (2R,3S)/(2S,3R)-epoxide with initial ratio of 65/35 with *tert*-BuOK as initiator

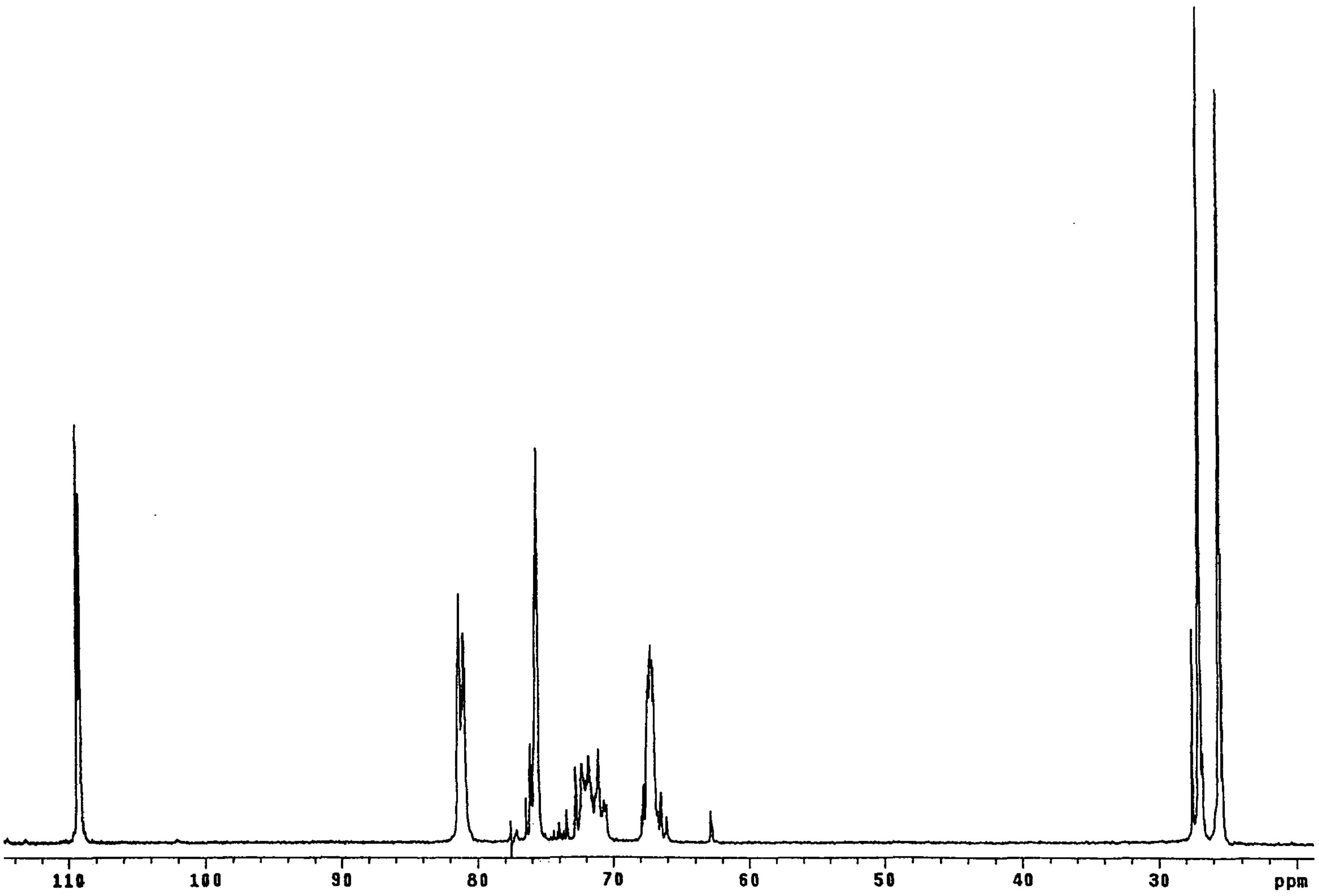


Figure 43 ^{13}C NMR spectrum of copolymer of the (2R,3S)/(2S,3R)-epoxide with initial ratio of 70/30 with *tert*-BuOK as initiator

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