# THE RING OPENING POLYMERIZATION OF RING STRAINED CYCLIC ETHERS

## DAVINDER PAUL SINGH RIAT

A thesis submitted for the degree of

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## SUMMARY

The kinetics and mechanisms of the ring-opening polymerization of oxetane were studied using cationic and coordinated anionic catalysts. The cationic initiators used were $BF_3OEt_2$/ethanol, $BF_3OEt_2$/ethanediol and $BF_3OEt_2$/propantriol. Kinetic determinations with the $BF_3OEt_2$/diol system indicated that a 1:1 $BF_3$:OH ratio gave the maximum rate of polymerization and this ratio was employed to determine the overall rates of polymerization.

An overall second-order dependence was obtained when the system involved ethanediol or propantriol as co-catalyst and a 3/2-order dependence with ethanol, in each case the monomer gave a first-order relationship. This suggested that two mechanisms accounted for the cationic polymerization. These mechanisms were investigated and further evidence for these was obtained from the study of the complex formation of $BF_3OEt_2$ and the co-catalysts by $^1H$ NMR.

Molecular weight studies (using size-exclusion chromatography) indicated that the hydroxyl ion acted as a chain transfer reagent when the [OH] > [$BF_3$]. A linear relationship was observed when the number average molecular weight was plotted against [oxetane] at constant [$BF_3$:OH], and similarly a linear dependency was observed on the $BF_3$:OH 1:1 adduct at constant oxetane concentration.

Copolymerization of oxetane and THF was carried out using $BF_3OEt_2$/ethanol system. The reactivity ratios were calculated as $r_{OXT} = 1.2 \pm 0.30$ and $r_{THF} = 0.14 \pm 0.03$. These copolymers were random copolymers with no evidence of oligomer formation.

The coordinated anionic catalyst, porphinato-aluminium chloride [(TPP)AlCl], was used to produce a living polymerization of oxetane. An overall third-order kinetics was obtained, with a second-order with respect to the [(TPP)AlCl] and a first-order with respect to the [oxetane] and a mechanism was postulated using these results.

The stereochemistry of [(TPP)AlCl] catalyst was investigated using cyclohexene and cyclopentene oxide monomers, using extensive $^1H$ NMR, 2-D COSY and decoupling NMR techniques it was concluded that [(TPP)AlCl] gave rise to stereoregular polymers.

KEY WORDS: RING-OPENING POLYMERIZATION, CATIONIC CATALYSTS, COORDINATED ANIONIC CATALYST, OXETANE, KINETICS, MECHANISMS

To my parents

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externally added Lewis bases.

# CHAPTER 1: INTRODUCTION

## 1.1.  General introduction

The ring-opening polymerization of cyclic ethers[1] is one of the oldest examples of the synthesis of macromolecules.  Most of the early work was carried out on ethylene oxide; Wurtz[2] in 1863 managed to synthesise oligomers of ethylene oxide.  Investigations by Staudinger[3,4] in 1929 established the polymerization of ethylene oxide to high molecular weight polymer and Levene[5] in 1927 and Meerwein[6] in 1937 reported the polymerization of propylene oxide and tetrahydrofuran respectively.  During this period the petrochemical industry developed, enabling the production of ethylene oxide and propylene oxide on a large scale.  Since then polymers and oligomers of these cyclic ethers have become some of the most important products to the synthetic chemical industry, widely used in the manufacture of surfactants, plasticizers, adhesives, coatings and raw material for the manufacture of urethane, elastomers, foams etc.  Polyepichlorohydrin is also produced industrially as a rubber material. The four membered cyclic ether 3,3-bis(chloromethyl)-oxetane produces a polymer which is an important engineering plastic and polymers of tetrahydrofuran of medium molecular weight and having hydroxyl end groups are used for making polyurethanes.

Around 1929, W.H. Carothers sub-divided synthetic polymers into two main groups so that a distinction could be made between polymers prepared by stepwise reaction of monomers and those formed by chain reactions. These he called:

(i)  Condensation Polymers - which involves elimination of a small molecule such as water or carbon dioxide during polymerization

(ii) Addition Polymers - where no loss of a small molecule occurs during polymerization.

While these definitions were perfectly adequate at the time it soon became apparent that notable exceptions existed and the term condensation polymerization was re-classified as step-growth polymerization.  This now included polymers such as polyurethanes, which grow by a step-wise reaction mechanism without elimination of a small molecule.  This also allowed the inclusion of ring-opening polymerizations since such polymer chains usually contained

funtional groups such as amide and ether linkages, which were conventionally synthesised by condensation processes.

Chain reaction polymerization occurs where a mechanism involves a series of steps, each step producing a reactive intermediate that causes the next step to occur. By this definition this also includes

(i) addition polymerization - includes vinyl monomers

(ii) ring opening polymerizations, which includes cyclic ethers, cyclic amides, lactones etc.

Depending upon the monomer, chain reaction polymerization occurs by several mechanisms. If addition polymerization is considered first, then the propagating species may be either free radical, cationic and anionic or it may involve a group transfer process as well as transition metal catalysts such as the Ziegler/Natta or metathesis types.

In addition polymerizations involving cationic and anionic initiators the formation and stabilisation of a carbonium ion or a carbanion depend largely on the nature of the group R in the vinyl monomer $CH_2=CHR$. For this reason cationic addition polymerization is usually limited to monomers with electron-donating groups which help to stabilise, by delocalisation, or an inductive effect, the positive charge of the active species. For example consider scheme 1.1

$$R^+ \; + \; CH_2=CHOBu^i \; \rightleftharpoons \; RCH_2\overset{+}{C}HOBu^i \; \longleftrightarrow RCH_2CH=\overset{+}{O}Bu^i$$

$$R^+ \; + \; CH_2=CMe_2 \; \longrightarrow \; RCH_2\overset{+}{C}(Me)_2$$
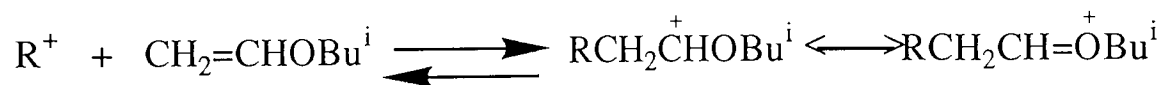
**Scheme 1.1. Stabilisation of the positive charge by delocalisation and by the inductive effect**

The species $R^+$ may be generated by a catalyst/cocatalyst systems, the details of which will be discussed later.

Anionic polymerization requires the monomer to possess electron-withdrawing substituents that promote the formation of a stabilised carbanion by resonance and inductive effects:
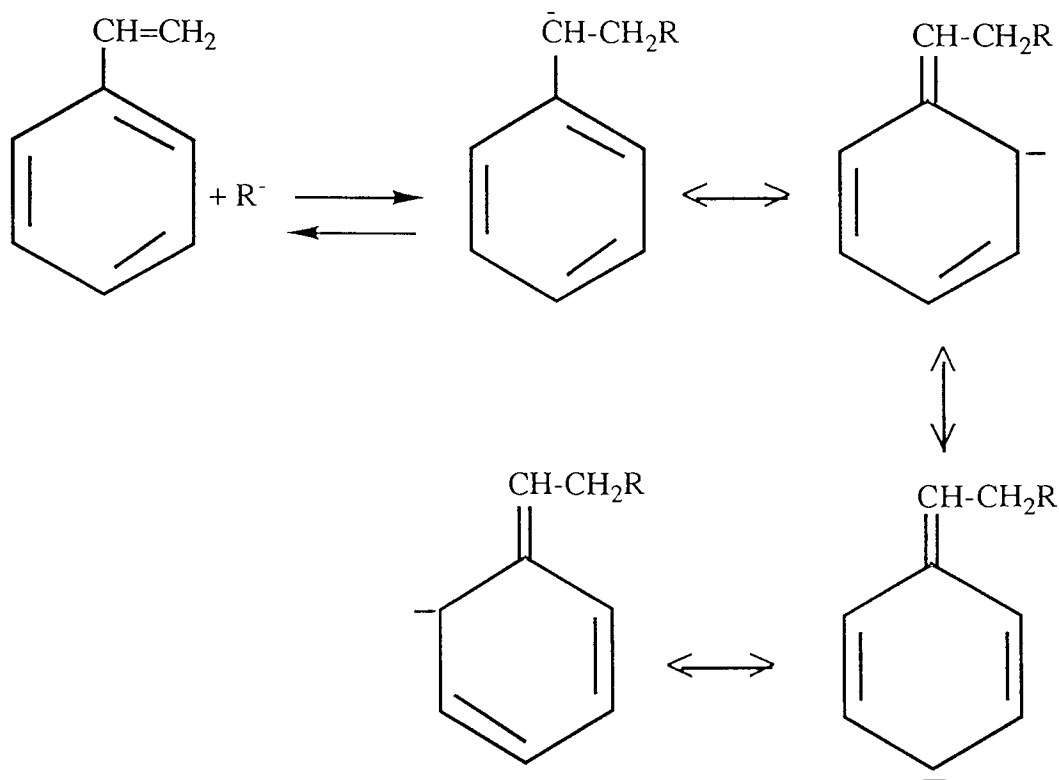


Scheme 1.2.   Resonance stabilisation of a carbanion

Organolithium compounds are examples of metal alkyl initiators which are typical sources of $R^-$ in scheme 1.2. The initiation involves addition to the double bond of the monomer as shown.

Initiation may also be achieved by charge transfer processes. The best known of these systems is that involving the charge transfer complex obtained from sodium and naphthalene as shown in scheme 1.3 below:

Na + (naphthalene) $\longrightarrow$ (naphthalene radical anion)$^{-}$ Na$^{+}$ $\longrightarrow$

(naphthalene radical anion)$^{-}$ + CH$_2$=CHPh $\longrightarrow$ (naphthalene) + $\cdot$CH$_2$$\bar{\text{C}}$HPh $\longrightarrow$

Na$^{+}$ [ Ph$\bar{\text{C}}$HCH$_2$CH$_2$$\bar{\text{C}}$HPh ] Na$^{+}$
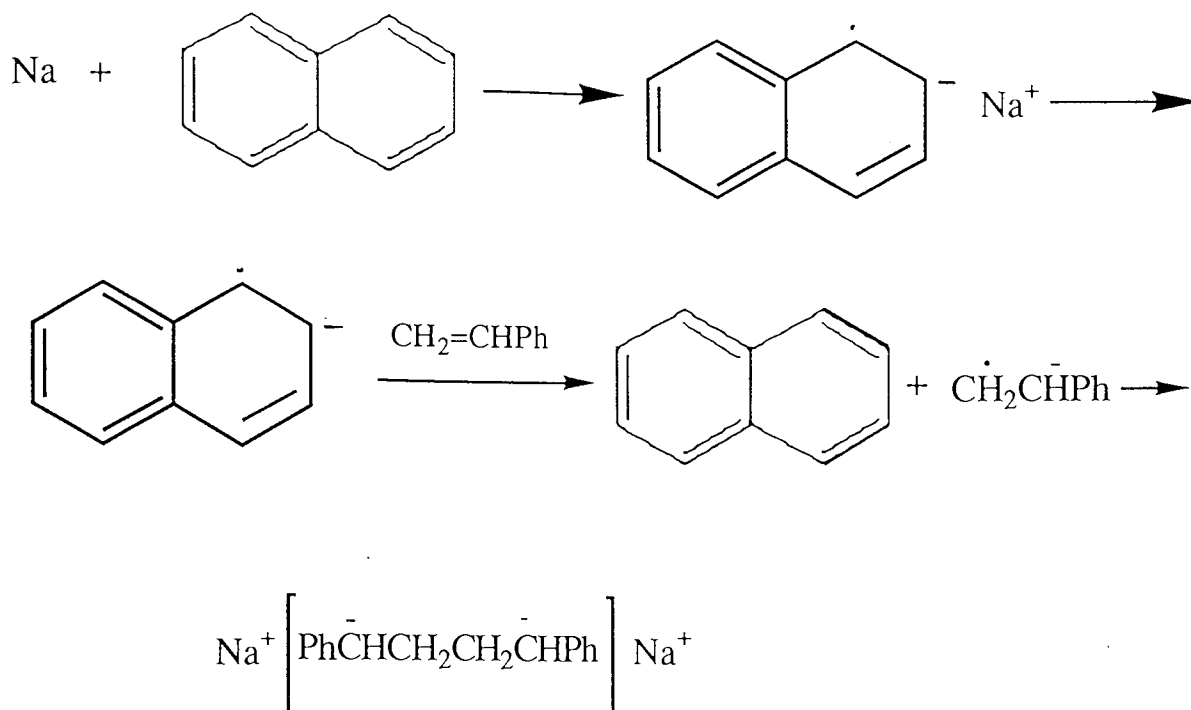
**Scheme 1.3. An example of charge transfer**

Ring-opening polymerizations are generally erroneously classified as condensation polymers due to the presence of functional groups such as the amide and ether linkages in the polymer chain. The tendency towards polymerization of a cyclic monomer depends upon the existence of ring strain, the initiator being used and the reactivity of the particular functional group within the ring. Propagating species may involve free radical, anionic, cationic or coordinate anionic catalysts. The type of mechanism involved largely depends upon the ring size and the chemistry of the functional group. For example, substituted cyclopropyl compounds, where the substituent is -CN, -COOH, -COCH$_3$ or -C$_6$H$_5$ are quite immune to the attack of free radicals, which would cause rapid polymerization of the corresponding substituted vinyl compounds[7]. In the case of cyclic ethers, the ether linkage is basic in the Lewis sense and as result, reports of the ring-opening polymerization of these cyclic ethers involve initiation by cationic species. Ethylene oxide and propylene oxide however can be polymerized by cationic, anionic or coordinate anionic initiators, owing to the high degree of ring strain in the small three membered ring.

Ring-opening polymerization is a mode of polymer formation which offers distinct advantages over conventional addition and condensation polymerizations. The polymer in most cases has

the same composition as the monomer and the polymerization takes place by a chain growth mechanism. In addition polymerization, the momomer requires an active site and must be able to replicate the propagating species. In the conventional condensation polymerization unfavourable equilibrium reactions between monomer, eliminated units and polymer exist, whereas equilibrium reactions in ring-opening polymerizations are more akin to those in addition polymerizations:

$$H^+ \; + \; \underset{\substack{\diagdown \diagup \\ O}}{CH_2\text{-}CH_2} \quad \rightleftharpoons \quad \underset{\substack{+O \\ | \\ H}}{CH_2\text{-}CH_2} \quad \xrightarrow[\;k_{-p}\;]{\;EO\;\; k_p\;}$$

ethylene oxide (EO)

$$HO\text{-}CH_2CH_2\text{-}\overset{+}{O}\underset{\diagdown}{\diagup}\!\!\!\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}$$

$$RO^- \; + \; \underset{\substack{\diagdown \diagup \\ O}}{CH_2\text{-}CH_2} \quad \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} \quad R\text{-}O\text{-}CH_2\text{-}CH_2O^-$$
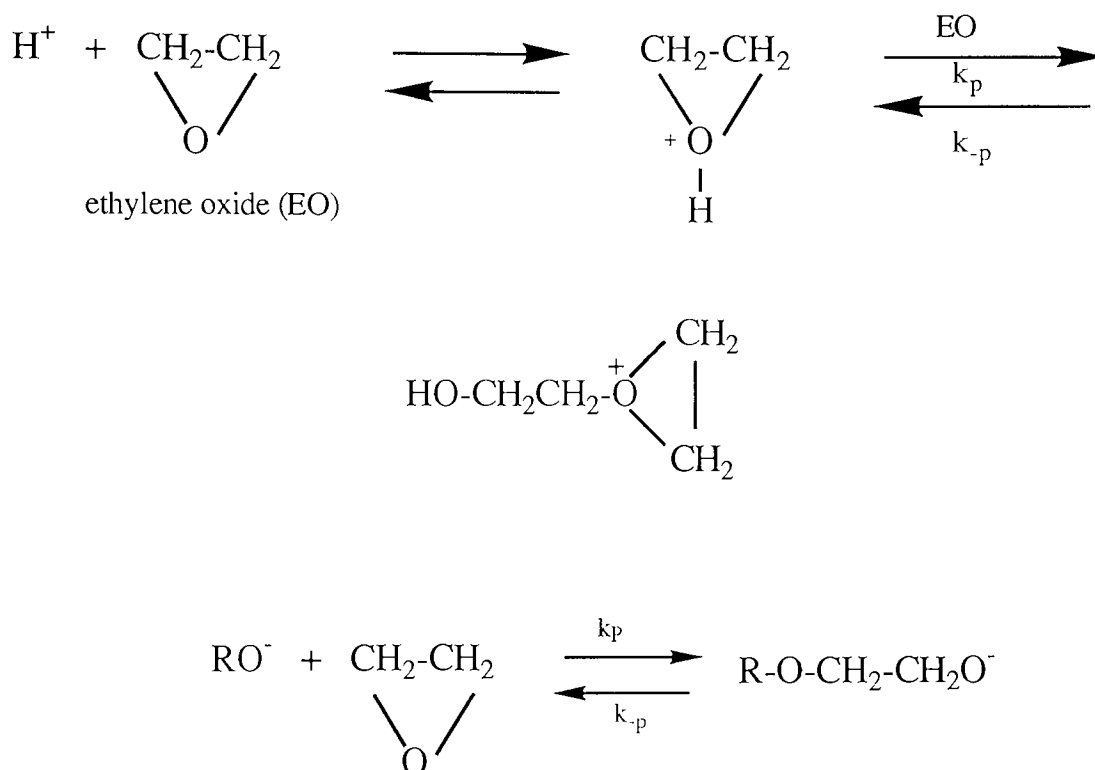
**Scheme 1.4. The equilibrium reactions involved in cationic and anionic initiation of ethylene oxide**

## 1.2. Thermodynamics of polymerization

The polymerization of monomers by addition, condensaton and ring-opening processes are normally characterised by a reversible reaction so that in any fundamental treatment of polymerizaton reactions leading to the elimination of monomer from a propagating species have to be considered, as in scheme 1.5 where Pn* represents any active species and M monomer:

$$P^*_n \; \longrightarrow \; P^*_{n-1} \; + \; M$$

**Scheme 1.5. Elimination of monomer from a propagating species**

Accordingly the propagation scheme for any reaction has to be amended as shown in scheme 1.6 below:

$$P^*_n + M \xrightarrow[\quad k_{-p} \quad]{\quad k_p \quad} P^*_{n+1}$$
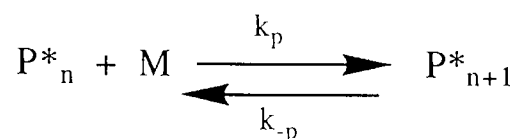
<u>**Scheme 1.6**</u>

Equilibrium reactions of this type may therefore be treated thermodynamically and the enthalpy, entropy and free energy of a polymerization may be measured.

In scheme 1.6, at equilibrium the forward reaction rate equals the reverse reaction rate, that is:

$$k_p[P^*_n][M]_e = k_{-p}[P^*_{n+1}]$$

i.e.
$$\frac{k_p[P^*_n][M]_e}{[P^*_{n+1}]} = k_{-p}$$

since
$$[P^*_n] \approx [P^*_{n+1}]$$

then
$$k_p[M]_e = k_{-p}$$

where $[M]_e$ = monomer concentration at equilibrium. The equilibrium constant for the reaction in scheme 1.6 is given by

$$\frac{k_p}{k_{-p}} = \frac{1}{[M]_e} = K \qquad\qquad 1$$

Since
$$\Delta G = -RT\ln K = \Delta H_p - T\Delta S_p \qquad\qquad 2$$

where $\Delta H_p$ and $\Delta S_p$ are the enthalpy and entropy changes taking place on polymerization. Therefore the equilibrium concentration of the monomer is given by:

$$\ln[M]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R}$$

**3**

The polymerization with which we are concerned exhibit negative values of both enthalpy and entropy. Then in the relationship

$$\Delta G = \Delta H - T\Delta S$$

$\Delta H > T\Delta S$ below a temperature known as the ceiling temperature ($T_c$) and $\Delta G < 0$. Above $T_c$ $\Delta H < T\Delta S$ and $\Delta G > 0$ and polymerization is impossible.

According to equation **3** $\ln[M]_e$ should be a linear function of $\frac{1}{T}$. An example of this was shown by Ofstead and Calderon[8] who determined the equilibrium monomer concentration for the polymerization of cyclopentene catalysed by the $WCl_6/EtOH/EtAlCl_2$ system at different temperatures. When $\ln[M]_e$ was plotted against $T^{-1}$ for the data obtained (figure 1.1), the values of -4.4kcal $mol^{-1}$ and -14.9cal $mol^{-1}$ $deg^{-1}$ were derived for $\Delta H_p^o$ and $\Delta S_p^o$ respectively. A ceiling temperature of 150°C was calculated by extrapolation.

## Fig 1.1

## Variation of monomer concentration with temperature for the polymerization of cyclopentene
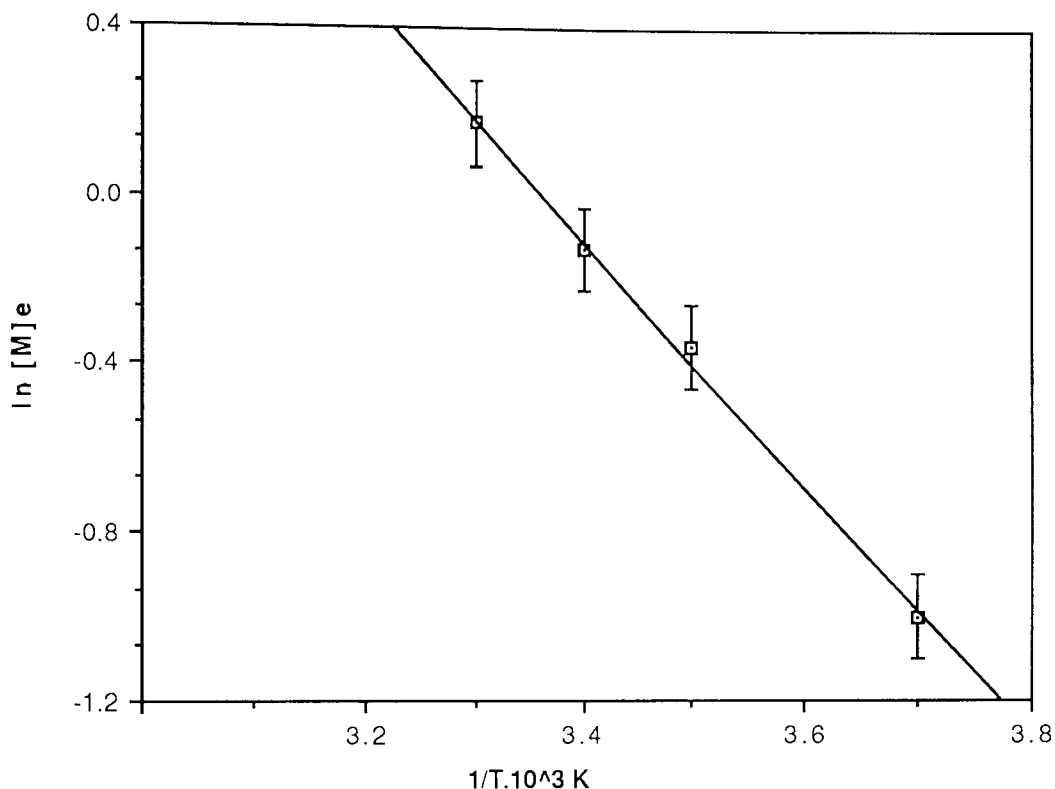


It was further noted that the enthalpy of polymerization calculated by Calderon corresponded to the estimated ring strain for cyclopentene (4.9 kcal mol$^{-1}$).

Since the standard free energy change associated with any ring-opening polymerization is made up of an enthalpy term and entropy term, $\Delta G^{o}_{p} = \Delta H^{o}_{p} - T\Delta S^{o}_{p}$, the values of these two terms and hence the magnitude and sign of $\Delta G^{o}_{p}$ is significant in determining polymerization. It must be noted that polymerization is possible only if $\Delta G^{o}_{p}$ is negative. There are a number of chemical and physical factors that influence $\Delta G^{o}_{p}$. The main chemical factors affecting $\Delta G^{o}$ are

(i) the size and the nature of the ring and hence steric strain,

(ii) substituents on the monomer,

(iii) whether the monomer is *cis* or *trans* i.e. geometrical isomerism,

(iv) tacticity in the polymer,

though (iii) and (iv) have a very small influence on $\Delta G^{o}p$. $\Delta H_p$ for ring-opening polymerizations is almost completely comprised of ring strain. Dainton and Ivin calculated the theoretical enthalpies and entropies of polymerization of a series of cycloalkanes varying in ring size from three to eight. Only cyclohexane showed the combination of positive enthalpy and negative entropy of polymerization, indicative of a monomer that is thermodynamically stable compared with the corresponding polymer. From these data the ceiling temperature and the equilibrium concentration $[M]_e$ can be calculated at any given temperature. These properties and their dependence on ring size are shown in table 1.1

## Table 1.1. Thermodyanamic of the Polymerization of Cycloalkanes*

| Ring size | $\Delta H^o$ (kcal mol$^{-1}$) | $\Delta S^o$ (cal mol$^{-1}$K$^{-1}$) | $\Delta G^o$ (kcal mol$^{-1}$) |
|---|---|---|---|
| 3 | -27 | -16.5 | -22.1 |
| 4 | -25.1 | -13.2 | -21.2 |
| 5 | -5.2 | -10.2 | -2.2 |
| 6 | 0.7 | -2.5 | 1.4 |
| 7 | -5.1 | -0.7 | -4.9 |
| 8 | -8.3 | -8.9 | -11.0 |

*Temperature 298K; 1cal = 4.184J

Generally values of $[M]_e$ for 3-, 4- and most 8- to 11- membered ring compounds are usually very small. This is because $\Delta H$ makes a large negative contribution to $\Delta G_p$. However for 5-, 6- and 7- membered rings $\Delta H$ values are small and $[M]_e$ values are then often in the range of 0.01 to 5M. The 7- membered rings are generally polymerizable but the sign of $\Delta G_p$ of polymerization of 5- and 6- membered rings is critically dependent on the nature of the ring. When polymerization is impossible the monomer contains very low ring strain energy.

The entropy change derives from two types of structural changes in the polymerization:

(i) the change due to translational entropy since the mobility of small rings is greatly reduced when incorporated into a polymer chain but for larger rings the translational motion is not

affected to any great extent and hence this negative value has a greater importance for smaller rings,

(ii) there is a reduction in the torsional and vibrational entropies (which are always positive) going from larger to smaller rings. As a consequence of this the overall entropy changes for ring-opening polymerization are generally positive to $\Delta G_p$ of polymerization which means that $\Delta H_p$ must contribute a small negative value if $\Delta G_p$ is to remain negative. This means ring-opening polymerization is possible only if the monomer contains ring-strain energy.

In the case of the polymerization of cyclic ethers, where ring size varies from three to eight the trend is similar to cycloalkanes and cycloalkenes, where the 6-membered ring tetrahydropyran does not polymerize.

Substituents tend to stabilise the monomers thereby making $\Delta G_p$ less negative. In the case for cyclic ethers, the 4- membered rings (oxetanes) can be polymerized with the following substituents, bischloromethyl, halomethyl, dimethyl, benzene, sulphonyl methyl, ester, cyano and phosphorus substituents[9]. For the 5- membered tetrahydrofuran and other large rings polymerization does not occur with substituted groups.

The physical factors affecting $\Delta G_p$ include solvent, temperature, pressure, monomer concentration and the solubility of the resulting polymer in the reaction medium.

## 1.3. Initiators

Initiation of the polymerization of cyclic and acyclic monomers can be divided into three catagories, cationic, anionic and coordinated anionic. A general description of the initiators will be discussed in this section with the emphasis on cationic initiators for both vinylic and cyclic monomers. Anionic and coordinate anionic initiators will be limited to ring-opening polymerizations of cyclic ethers only.

## 1.3.1. Cationic polymerization

Polymerizations are generally classed as cationic when they involve a positively charged active species acting as an electrophile towards the monomer. These species may either appear in the transition state or as identifiable ionic species and are normally located at the end of the growing polymer molecule, where they are susceptible to attack by monomers which behave as nucleophiles. In some cases this situation is reversed if the monomer is initially activated by an acid. The types of monomers that have been polymerized cationically include:

(i) ethylenic monomers where the reactive intermediate is considered to be a carbocation (carbenium ion) in which the propagating intermediate may be in the form of:

$$-CH_2\overset{+}{-}CHR \quad X^- \xrightarrow{\quad CH_2=CHR \quad} -CH_2-CHR-CH_2-\overset{+}{CHR} \quad X^-$$

ii) heterocyclic monomers containing at least one heteratom (O, S, or P) in the ring and in this case the propagation involves an onium ion, for example the oxonium ion in the case for cyclic ethers:
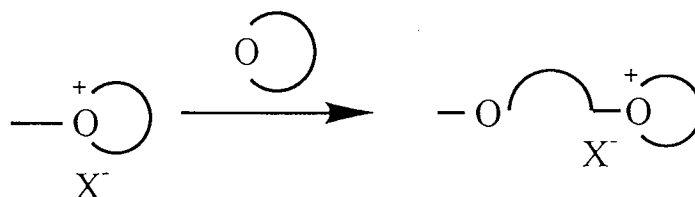


(iii) monomers of the aldehyde and acetal type, where propagation involves a non-classical carbenium ion, in which the charge is strongly delocalised:

R-O ... O⁺ ... :O ... O → $RO-CH_2CH_2-O-CH_2O$ ... O⁺

$RO-CH_2CH_2-O-CH_2O$ ... O: $\overset{+}{C}H_2$

$RO-CH_2CH_2-O-CH_2O$ ... O⁺ $CH_2$
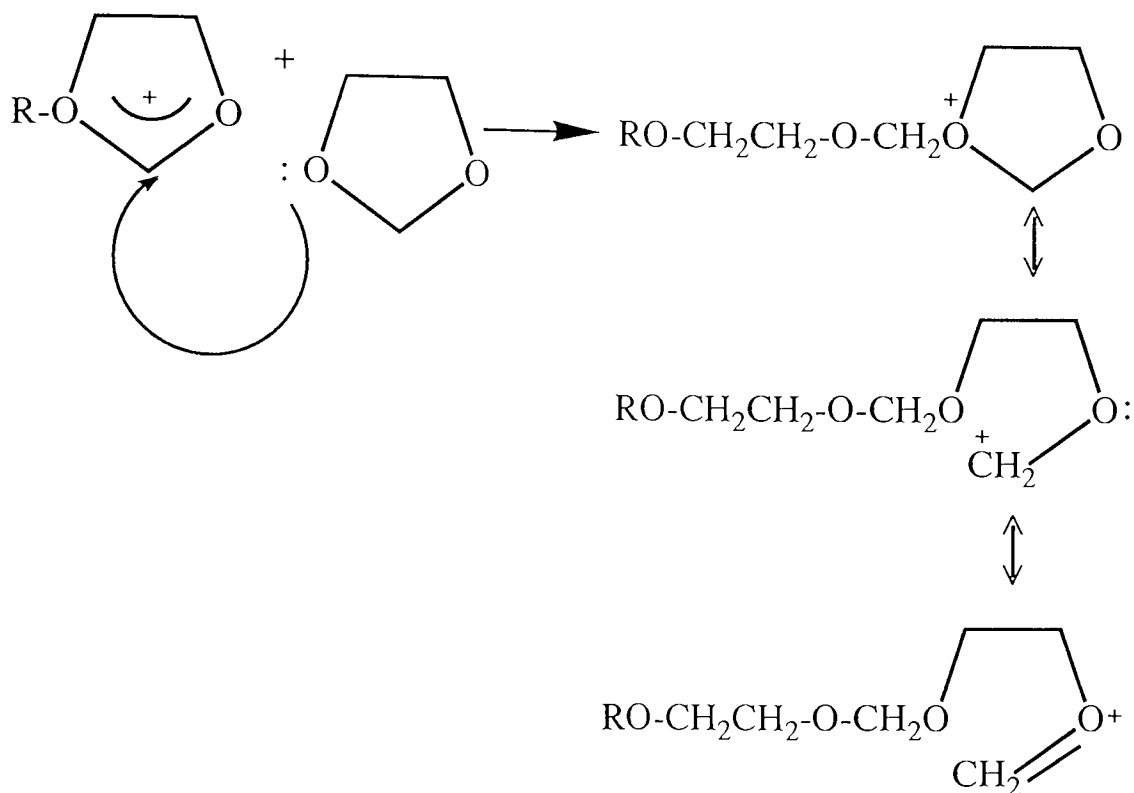
## 1.3.2. Cationic initiators for vinyl monomers

## 1.3.2.1. Initiation involving protonic acids

Bronsted acids have been used to polymerize vinylic monomers. The most reactive monomers generally give the most stable carbocationic species since the charge can be stabilised by resonance (aromatic systems) and/or by the electron-donating effects of the substituents(s). It has been found that very weak acids such as acetic acid or HCl ( in non-aqueous solvents) may polymerize a very reactive monomer such as vinyl carbazole.

Generally the most reactive acids for initiation are those with the highest acidities (i.e. the lowest pKa). This is because the counter-anion, being stable has a lower nucleophilicity and consequently is less reactive towards the carbocation. The most effective protonic initiators are trifluorosulphonic acid (triflic acid) and perchloric acid where termination by reaction with the counter-anion has been less important than the weaker acids. Measurement of the pKa values has been carried out in ethanoic acid and ethanenitriles[10] and table 1.2 illustrates this.

### Table 1.2. pKa of some Bronsted Acids in non-aqueous solvents

| Solvent / Acid | CH₃COOH | CH₃CN |
|---|---|---|
| $CF_3SO_3H$ | 4.7 | 2.6 |
| $HClO_4$ | 4.9 | 1.6 |
| $FSO_3H$ | 6.1 | 3.4 |
| $H_2SO_4$ | 7.0 | 7.3 |
| HCl | 8.4 | 8.9 |
| $CH_3SO_3H$ | 8.6 | 8.4 |
| $CF_3COOH$ | 11.4 | 10.6 |
| $CCl_3COOH$ | 12.2 | 12.7 |
| $CH_3COOH$ | 12.8 | 22.5 |

Unfortunately pKa data in the most commonly used solvents for cationic polymerization, such as alkyl chlorides, are not available.

Numerous reports on the polymerization of styrene using Bronsted acids have been published. Styrene has been polymerized in dichloromethane and methylene chloride using perchloric acid[11,12] and by triflic acid in dichloromethane[13,14]. α-methylstyrene and p-methoxystyrene gave rise to polymers when initiated with triflic acid. Other acids such as $ClSO_3H$ and $FSO_3H$ rapidly initiate the polymerization of styrene but limited yields are obtained , indicating that termination reactions become more predominant. Various solvents can be used for this particular polymerization including liquid $SO_2$, $PhNO_2$, $CH_2Cl_2$ and benzene[15,16]. Another sulphonic acid, $CH_3SO_3H$ has been used to polymerize p-methoxystyrene in $CH_2Cl_2$ at 30°C.

The polymerization of styrene by sulphuric acid is one of the oldest examples of a cationic polymerization. Yields of polymers depend on the concentration of $H_2SO_4$ used. It was presumed that initiation was fast, after which the rate began to decrease progressively involving a termination reaction that gave polystyryl bisulphate. Later it was observed that a

polymerization, with limited yield, could recommence again by addition of an excess of a weaker acid such as $CF_3SO_3H$ which normally did not polymerize styrene and that an ester of sulphonic acid was formed which was activated by $H_2SO_4$ acting as a solvent as shown in scheme 1.7.

Initiation:    M + HA $\longrightarrow$ HMA

HMA + HA $\longrightarrow$ HMA. HA

Propagation:  $HM_nA$. HA + M $\longrightarrow$ $HM_{n+1}A$. HA

Termination:  $HM_{n+1}$. HA + M $\longrightarrow$ $HM_{n+1}A$ + HMA
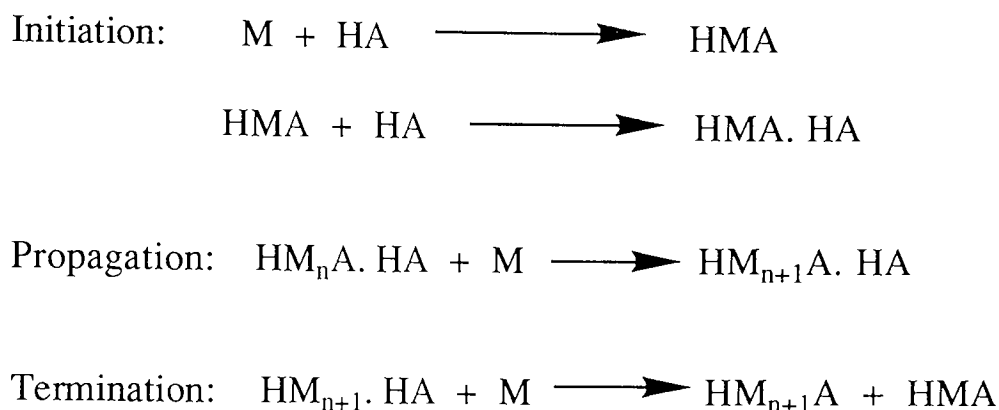
**Scheme 1.7. Mechanism of polymerization of styrene (M) by $H_2SO_4$ (HA)**

The excess concentration of the weaker acid ensured that esters remained active.

Hydrogen halides initiate the polymerization of reactive monomers such as vinyl ethers but low yields are normally produced. N-vinylcarbazole however can be polymerized by HCl, HBr and HI[17]. The initiation of styrene in $CH_2Cl_2$ has been shown to occur with high concentrations of dry HCl at -78°C but in liquid $SO_2$ the polymerization was unsuccessful[18]. HI was found to be an excellent initiator for isobutyl vinyl ether in toluene or in $CH_2Cl_2$ but in n-hexane the polymerization was slow[19]; HI also initiated the polymerization of *trans* anethole in $CH_2Cl_2$. Attempts have been made to polymerize isobutylene with hydrogen halides but the product is of low molecular weight containing also fragments of the catalyst. Recent work on isobutylenes using $HI/I_2$ initiators has been carried out and the significance of these results will be discussed later under the heading of recent developments in cationic polymerization.

Unsubstituted carboxylic acids have been reported to act as very weak initiators for N-vinyl carbazole. Trifluoroacetic acid is the most effective initiator among the haloacetic acids but

only in solvents with high dielectric constants where polymerization of styrene and isobutyl vinyl ethers has also been successsful.

## 1.3.2.2. Initiation of weak Bronsted acids by Friedel-Crafts acids

Generally weak Bronsted acids alone cannot initiate polymerization but when used conjunction with a Friedel-Crafts acid polymerization can take place. The mechanism of initiation was thought to involve a reaction of the alkene with a complex of the protogen with the Friedel-Crafts acid as illustrated in scheme 1.8 (a).

$$HA + MtX_n \longrightarrow H^+ [MtX_nA]^-$$

$$H^+[MtX_nA^-] + M \longrightarrow M^+H [MtX_nA]^-$$
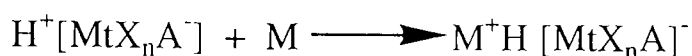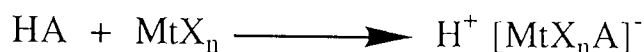
where Mt = metal, X=halogen (usually)

**Scheme 1.8(a). The initiation reactions of a Friedel-Crafts acid $MtX_n$ with a Bronsted acid HA**

A second proposal for the mechanism of initiation was made because the existence of stable complexes such as $H^+[MtXnA]^-$ only occurs in a few cases, for example $BF_3/H_2O$ system. They are not formed with hydrogen halides (e.g. $TiBr_4$ and HBr). A modified mechanism is shown in scheme 1.8 (b).

$$M + MtX_n \longrightarrow M. MtX_n$$

$$M. MtX_n + HX \longrightarrow M^+H [MtX_{n+1}]^-$$
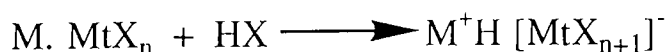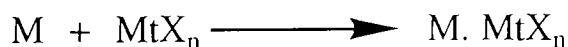
**Scheme 1.8 (b). Initiation involving hydrogen halides as the Bronsted acid**

This category of initiators involves a metal halide which is a strong Lewis acid in conjunction with a co-catalyst. Reports have shown that the metal halides include $AlBr_3$, $AlCl_3$, $AlEt_2Cl$, $AlEtCl_2$, $TiCl_4$, $TiBr_4$, $SnCl_4$, $BCl_3$, $BBr_3$, $BF_3$, $BF_3.OEt_2$ and $FeCl_3$. The co-catalysts,

usually sources of protons have included $Cl_3CCO_2H$, $ClCH_2CO_2H$, $MeCO_2H$, $MeNO_2$, PhOH, ROH, $H_2O$, HCl, HBr etc. Of these systems a few will be discussed in greater detail below.

## (a) Boron Trifluoride

Isobutylene was polymerized using a catalytic system $BF_3/H_2O$ and this was the first example of water acting as a co-catalyst. Because the reaction was vigorous, it was found that either a gaseous form of each catalytic component was required or the experiment had to be carried out at -80$^o$C. In each case the purity of the components had to be ensured for polymerization to occur. Since water was used in extremely small quantities, quantitative experiments were difficult to perform. To improve this situation water was replaced by other protonic sources such as ROH or $Cl_3CCO_2H$ and other co-catalysts mentioned above.

$BF_3.OEt_2$ has been most frequently employed for the polymerization of vinyl ethers because it readily produced high molecular weight polymers at low temperatures. Furthermore $BF_3$ or $BF_3.OEt_2$ was found to produce either crystalline or amorphous polymers of iso-butyl vinyl ether depending upon the reaction conditions. This was an important finding as this was the first experimental evidence for stereoisomerism of poly(vinyl ether)[20].

Styrene, $\alpha$-methylstyrene, indene, butadiene and isoprene have all been polymerized by $BF_3$/OH systems using various solvents and reaction conditions. The wide use of $BF_3$ as initiator is further enhanced by its ability to polymerize cyclic monomers, thus establishing its significance in cationic polymerization.

## (b) Aluminium based catalysts

Aluminium catalysts include $AlCl_3$, $AlBr_3$, $AlEt_2Cl$, $AlEtCl_2$ with protonic co-catalysts. It was found that $AlCl_3$ polymerized isoprene in the presence of chlorinated solvents[21], and later in 1951 butadiene was also polymerized by $AlCl_3$ in hexane, as solvent. Industrially $AlCl_3$ became one of the most important initiators since its was used in the manufacture of butyl rubber and polybutenes. Usually the purities of these monomers were not high and water was

the main contaminant which actually made polymerization possible. In 1961 styrene was found to be polymerized by $AlCl_3$ after the addition of water vapour[22] and isobutylene was also polymerized by the $AlCl_3/H_2O$ system. Other important aluminium catalysts include the aluminium alkyl chlorides. Kennedy et al.[23] concluded that the polymerization of isobutylene could be initiated with $AlEt_2Cl$ with which he measured the activity of various co-catalyst. He found that the ability to donate protons decreased in the following order $HCl \sim HBr > HF \sim H_2O > MeCOOH > MeOH > MeCOMe$ and the corresponding rates of polymerizations also decreased in the same order. $AlEt_2Cl/H_2O$ system was also used to polymerize isobutyl vinyl ether at -78°C in toluene giving rise to an atactic polymer, however, on addition of $O_2$ to this system a steroregular polymer was obtained[24]. With vinyl ethers, $AlEtCl_2$ gives isotactic polymers at low temperatures. Various other monomers have been polymerised using $AlEt_2Cl/OH$ systems, including isobutylene, styrene and α-methylstyrene. With $AlEtCl_2$ monomers such as styrene, isobutylene, α-methylstyrene and vinyl ethers have been polymerized but the mechanism of initiation is uncertain. Interesting studies were carried out on the addition of $^tBuCl$ to 2, 4, 4-trimethyl-1-pentene in $CH_3Cl$[25] and results showed that the order of decreasing reactivity of the Lewis acid was $Me_2AlCl > Et_2AlCl > Me_3 Al > Et_3Al$. This indicates that $Me > Et$ and $Al$-$Cl$ is a stronger Lewis acid compared to $Al$-$R$ system.


(c) Titanium (IV) catalyst

In terms of the work carried out using Ti (IV) catalysts $TiCl_4$ is the most important.


Plesch[26] carried out the polymerization of isobutylene using $TiCl_4/H_2O$ system in $CH_2Cl_2$ at various temperatures from -30 to -70°C. The experiments were repeated using $TiCl_4/HCl$ system and from the % conversion calculations it was apparent that HCl was not a co-catalyst at -30°C but acted as a co-catalyst at -70°C. This fact could not be explained until similar experiments were carried out on the polymerization of 1-butene[27] which indicated that HCl was not a co-catalyst at any temperature whilst $H_2O$ acted as a co-catalyst at all temperatures. It was concluded that scheme 1.8 (b) was the possible explanation for HCl and scheme 1.8 (a) for $H_2O$.

Various other experiments have been carried out including the polymerization of isoprene with $TiCl_4$ associated with other weak acids. Results indicated that the order of acidic activity was $CF_3COOH > CCl_3COOH > CF_3COO\text{-}s\text{-}Bu > CCl_3COO\text{-}s\text{-}Bu$[28], which had a direct effect on the rate of polymerization which also decreased in the same order.

Other unusual catalyst systems based on Ti include $Cl_3TiOBu^n$ n-butoxytrichlorotitanium which has been used for the polymerization of cyclopentadiene because the usual Friedel-Crafts catalysts produce cross-linked insoluble polymers unlike $Cl_3Ti\text{-}OBu^n$ which gives high molecular weight polymers in $CH_2Cl_2$[29].

## 1.3.2.3.  Initiation by Organic Cations

In this category, vinylic monomers can be initiated by the addition of an organic cation. Cations which are important here lie within a narrow margin of being neither too stable, i.e. unreactive or too reactive which normally lead to side reactions, usually involving the cation attacking the monomer and producing a different product. In between, the best compounds are triphenylmethyl (trityl, $Ph_3C+$) and cycloheptatrienyl (tropylium $C_7H_7^+$).

## (a)  Trityl Cations

Triphenyl methyl chloride in conjunction with Friedel-Crafts halides such as $SbF_5$, $SbCl_5$, $AsF_5$ in chlorinated solvents have been successsfully employed for the polymerization of many vinylic monomers, these include N-vinyl carbazole, isobutylvinyl ether, p-methoxystyrene, p-methylstyrene, cyclopentadiene, $\alpha$-methylstyrene, styrene, and indene[30-39]. In some cases strong Bronsted acids such as $HClO_4$ have replaced the Friedel-Crafts halides with similar results.

Initiation occurs by the addition of the trityl cation to the monomer, an example of this is shown in scheme 1.9:

$$Ph_3C\text{-}Cl \ + \ SbCl_5 \ \underset{\longleftarrow}{\longrightarrow} \ Ph_3C^+[SbCl_6]^-$$
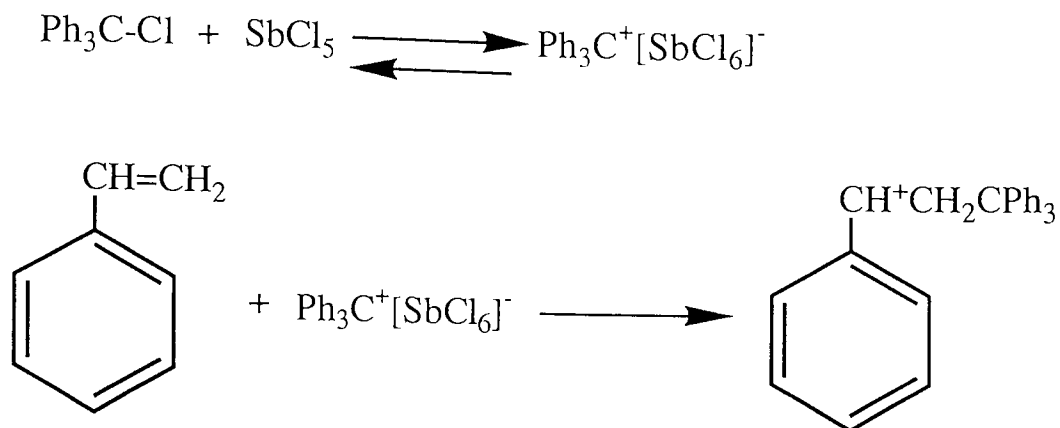


**Scheme 1.9.** **Initiation by the trityl cation**

However in the case of α-methylststyrene $Ph_3CH$ was detected[40] which indicates the following mechanism of initiation, scheme 1.10
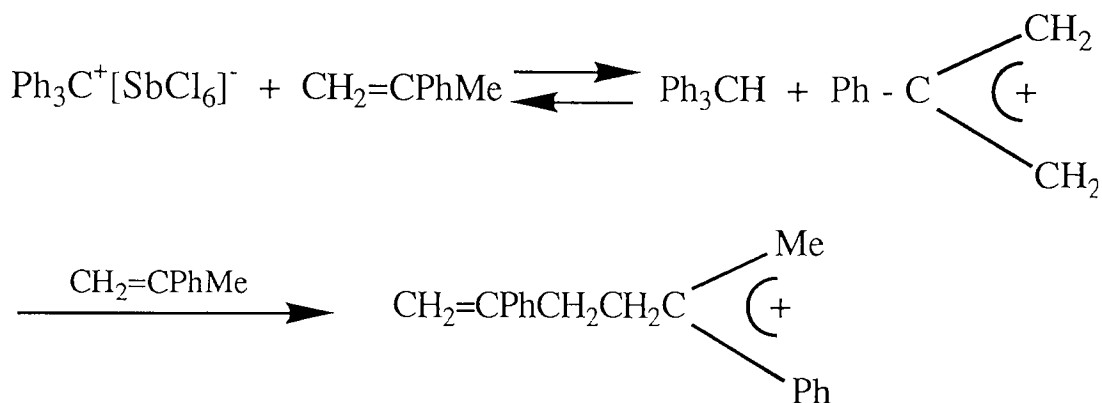


**Scheme 1.10.** **Initiation resulting from the hydride abstraction from the monomer by the trityl cation**

In scheme 1.10 the trityl cation initiates the polymerization by hydride abstraction from the monomer. This mechanism is possible because the resulting charge can be stabilised by resonance, similarly this mechanism was also proposed for the initiation of N-vinyl carbazole[41], scheme 1.11.
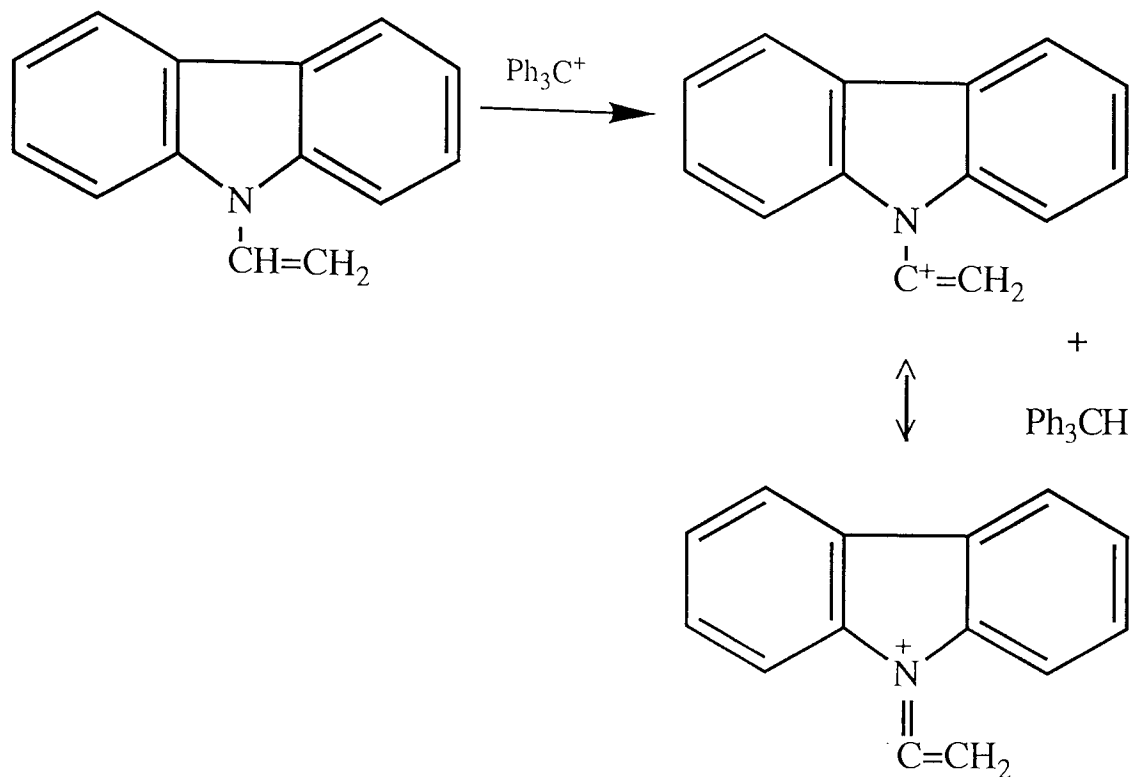
**Scheme 1.11. Initiation of N-vinyl carbazole by the trityl cation**

The polymerization of isobutylene could not be initiated by $Ph_3C^{+42}$ because an intramolecular reaction takes place as soon as the $Ph_3C+$ adds onto the double bond, the driving force for this is the cyclisation step as shown in scheme 1.12.
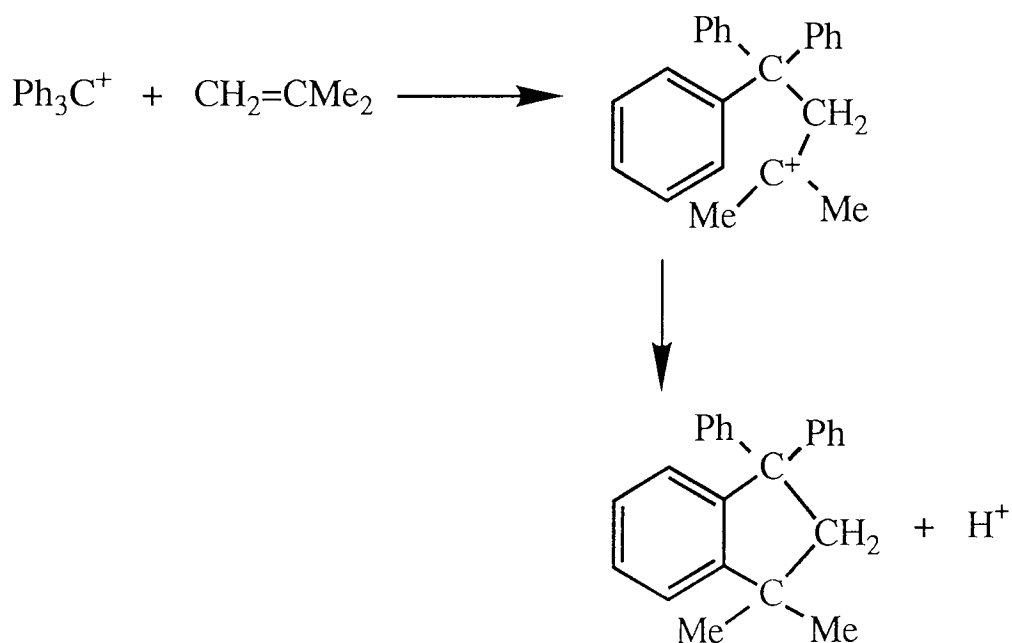


**Scheme 1.12. Termination by cyclisation**

## (b) Tropylium ion

Tropylium ions may be produced by interaction of cycloheptatriene with trityl cations shown by the equation below:

$$C_7H_8 + Ph_3C^+ \longrightarrow C_7H_7^+ + Ph_3CH$$

The tropylium ion is more stable than the trityl but it is still sufficiently reactive to polymerise isobutyl vinyl ether[43], N-vinyl carbazole[44] and p-methoxystyrene[45]. Initiation is usually direct, scheme 1.13.
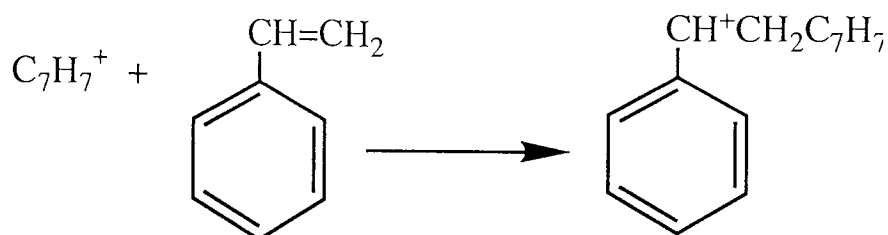


**Scheme 1.13.   Initiation by tropylium cation**

Other reactive organic cations include systems such as $SnCl_4/(R'Ph)(R^zPh)CHCl$, e.g.



2-methyl-1-pentene



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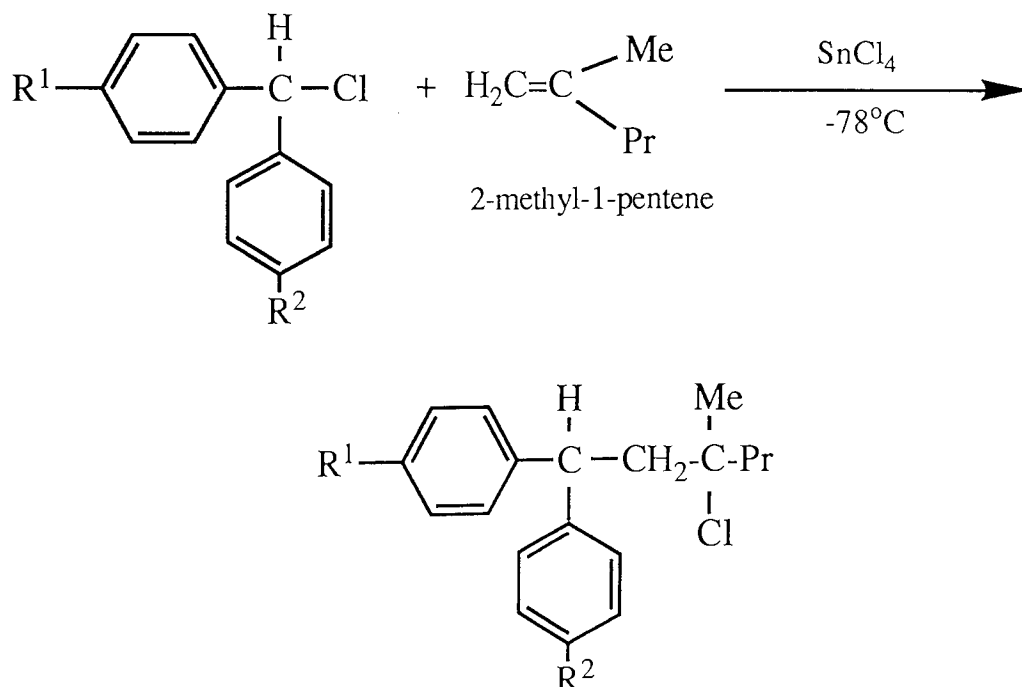
where Kennedy et al.[46] discovered that increasing the donating effect of $R^1$ and $R^2$ yielded more rapid initiation. In some cases, the complex $BF_3.OEt_2$ has been shown to initiate polymerization by the ether acting as catinogen i.e.

$$BF_3OEt_2 \rightleftharpoons [BF_3OEt_2]^- Et^+ + M \longrightarrow [BF_3OEt_2]^- EtM^+$$
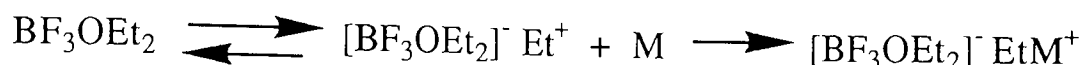
however the mechanism is unknown even though there is some evidence that styrene can be initiated by $BF_3.OEt_2$ under absolute anhydrous conditions[47].

The reaction of acyl/aryl chlorides with a Friedel-Crafts acid gives an oxocarbenium salt which has been used to initiate the polymerization of styrene and acenaphthylene[48] i.e.
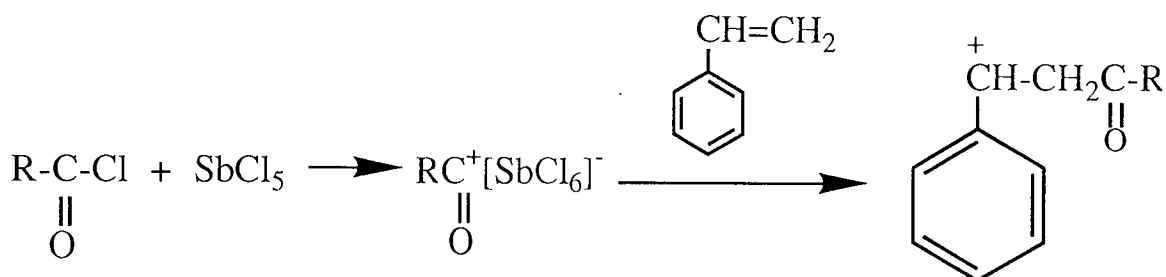


Dialkylcarbenium ions and dioxolenium ions act as alkylating agents and with counteranions such as $BF_4$ or $SbCl_6^-$ they can initiate ring-opening polymerizations of cyclic ethers. However evidence suggests that 2-methyl styrene and isobutyl vinyl ether could be initiated by these systems:



$$\longrightarrow HCO_2H + CH_2=CH_2 + MeC^+Ph_2$$
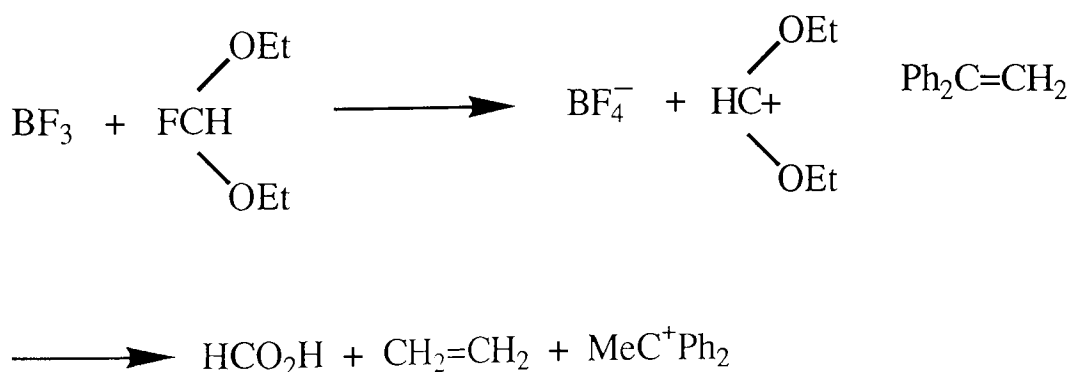
## 1.3.2.4. Vinyl ethers

Most of the initiators for vinyl ethers have been explained in the above sections however there are some initiators which polymerize vinyl ethers only. These include:

(a) Halogens

Historically iodine was the first initiator for the polymerization of vinyl ethers[49]. The rate of polymerization of n-butyl vinyl ether with these initiators decreases in the order $I_2 > ICl > IBr > Br_2$.

(b) Metal halides

Nucleophilic monomers such as ketene acetals $CH_2=C(OR)_2$ can be polymerized by weakly acidic metal halides e.g. $ZnCl_2/H_2O$.

(c) Metal oxides

This includes $Cr_2O_3$ and $Al_2O_3$ which are solid catalysts and consist of Lewis acid sites, e.g. electron deficient metal atoms . Isobutyl vinyl ether has been polymerized using these initiators.

(d) Photoinitiators

These involve iodenium and sulphonium salts which decompose upon UV and visible light irradiation to form cations which can add to vinyl ethers i.e.

$$Ar_2I^+X^- \qquad Ar = Ph, C_6H_4OMe, \qquad X = SbF_6^-, AsF_6^-$$

$$Ar_3S^+X^- \qquad Ar = Ph, C_6H_4OMe, \qquad X = SbF_6^-, AsF_6^-$$
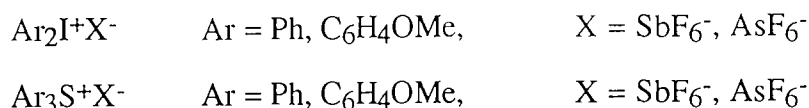
The progress made in the understanding of the mechanism of cationic polymerization and the developments in photochemistry have led to the initiation of cationic polymerization by photochemical techniques.

Crivello et al.[50] reported a group of salts which are active as photoinitiators for cationic polymerization. These recent findings include the following salts; diaryliodenium (I), triarylsulphonium (II), dialkylphenacylsulphonium (III), dialkyl-4-hydroxyphenylsulphonium salts (IV) and triarylselenium salts (V).

$$\left[ \begin{array}{c} Ar \\ \diagdown \\ Ar \diagup \end{array} I^+ \right] X^- \qquad \left[ \begin{array}{c} Ar \\ | \\ Ar - S^+ \\ | \\ Ar \end{array} \right] X^- \qquad \left[ \begin{array}{c} R \\ | \\ Ar\text{-}C\text{-}CH_2\text{-}S^+ \\ \| \quad \; | \\ O \quad \; R \end{array} \right] X^-$$

<div align="center">

(I)             (II)             (III)

</div>

$$\left[ \begin{array}{c} Ar \\ | \\ Ar - Se^+ \\ | \\ Ar \end{array} \right] X^-$$

<div align="center">

(IV)                    (V)

</div>
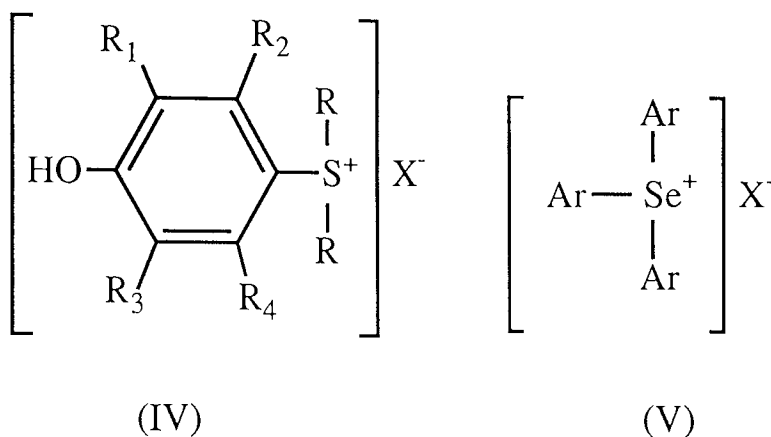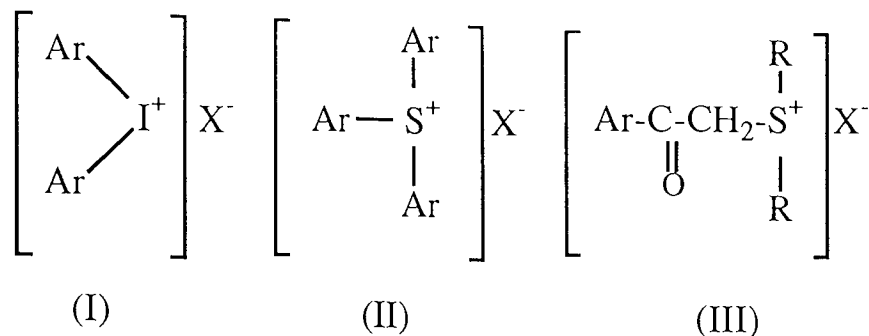
where $X^- = AsF_6^-, PF_6^-, SbF_6^-, BF_4^-$

Normally in the absence of light these salts are stable even at high temperatures. On irradiation a photochemical process occurs, which involves the homolytic cleavage of a bond such as the carbon-iodine bond in the case of diaryliodenium salt to produce a strong acid HX (i.e. $HBF_4$, $HAsF_6$, $HPF_6$ or $HSbF_6$). These extremely strong acids are excellent initiators for cationic polymerization. The following mechanism is thought to occur, scheme 1.14,

Major: $Ar_2I^+ X^- \xrightarrow{h\upsilon} [Ar_2I^+ X^-]^* \longrightarrow Ar\text{-}I^{+\bullet} + Ar^\bullet + X$

$Ar\text{-}I^{+\bullet} + Y\text{-}H \longrightarrow Ar\text{-}I^+\text{-}H\text{-}Y \longrightarrow Ar\text{-}I + H^+$
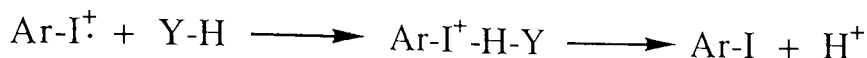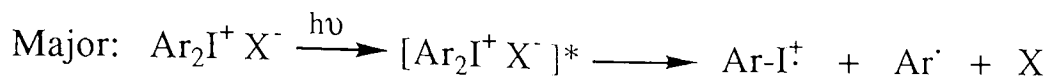
(where Y is a solvent or monomer)

Minor: $[Ar_2I^+ X^-]^* + Y\text{-}H \dashrightarrow [Ar\text{-}Y\text{-}H]^+ + ArI + X^-$

$$\downarrow$$

$$Ar\text{-}Y + H^+$$
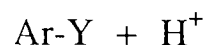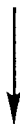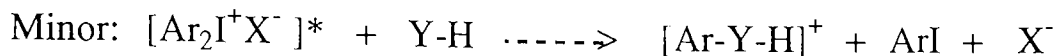
**Scheme 1.14.   Mechanism of initiation with photochemically active compounds**

Successful polymerizations at room temperature of vinylic monomers, styrene, $\alpha$–methyl styrene and vinyl ethers, and heterocyclic monomers, cyclic epoxides, oxetanes, THF, trioxanes propylene sulphides, thietane, lactones and spirobicyclic orthoesters have been reported, using light of wavelengths less than 360nm.

Dyes such as acridine orange, acridine yellow phosphine R, benzoflavin and setoflavin T can be used to obtain photodecomposition of diaryliodium salts at wavelengths longer than 360nm[51]. Triarylsulphonium dialkylphenacylsulphonium and dialkyl(4-hydroxyphenyl) sulphonium salts were sensitized by perylene and other polynuclear hydrocarbons[52,53]. Under these conditions polymerization took place by ambient sunlight.

The rate of polymerization depends upon both the monomer reactivity and the nucleophilicity of the counteranion of the initiator salt. The order of reactivity of photoinduced polymerization correlates well with the known relative nucleophilicities of the anions, that is, $SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$.

It must also be noted that during photodecomposition free radical species ($Ar\cdot$ and $Y\cdot$) are also produced as transient intermediates. This means that both free radical and cationic

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polymerizations can take place, simultaneously in some cases. Irradiation of equimolar mixtures of 1,4-cyclohexene oxide and methylmethacrylate with $Ph_3S^+SbF_6^-$ yielded two homopolymers, polycyclohexene oxide (cationic) and polymethylmethacrylate (free radical). These polymerizations took place independently. The same system containing 2,6-di-tert. butyl-4-methylphenol, which acts as an inhibitor gave only polycyclohexene oxide. Conversely, the system with triethylamine which acts as a poison for cationic polymerization yielded only polymethylmethacrylate. The multi-functional nature of the sulphonium salts could therefore be extended by using monomers which contain functional groups of cationic and free radical polymerizations to give a cross-linked insoluble polymer.

Ledwith proposed a different mechanism from Crivello[54] by which photoinitiation by triarylamonium, sulphonium and iodenium salts occurs, considers scheme 1.15:

$Ar_3N^{+\cdot}$ ⇌ $Ar_2N=⟨⟩(+)-R$ ⇌

$Ar_2\dot{N}=⟨⟩(+)-R$ $\xrightarrow{\text{O}}$

$Ar_2\dot{N}=⟨⟩-R$ $\xrightarrow{Ar_3N^{+\cdot}}$
$H \quad ^+O$

$Ar_2N-⟨⟩-R$ + $Ar_3N$ + $H^+$
$^+O$
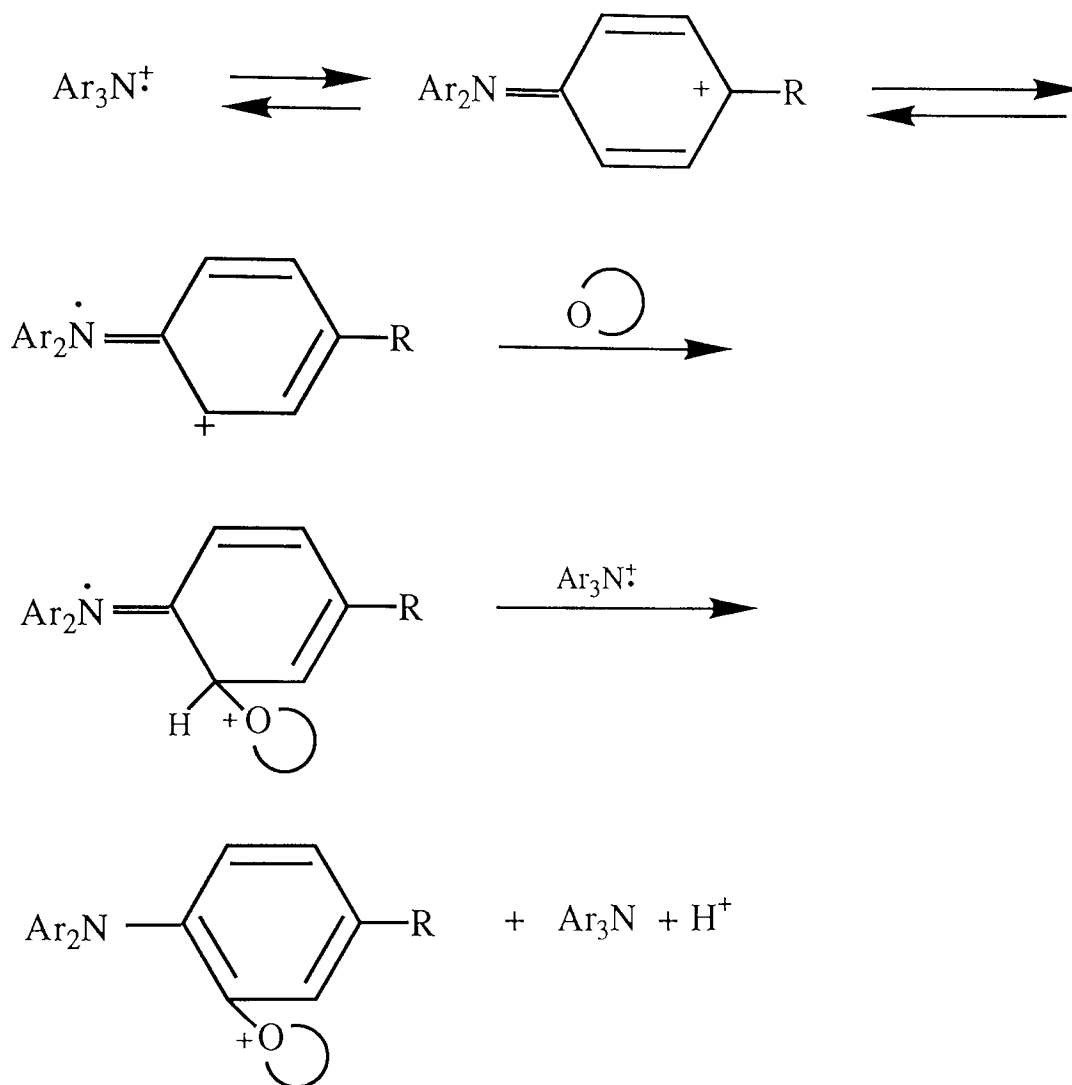
**Scheme 1.15. Ledwith's mechanism of initiation**

Both cationic radicals and protons are responsible for the photoinitiation with these initiators. Stable cation radicals based upon trialkylpyrylium, thiopyrylium and phenothiazine have been found to be excellent initiators for different heterocyclic monomers[55].

## 1.3.3. Cationic initiators for cyclic monomers

The majority of the initiators described for cationic vinyl polymerizations are also able to initiate the ring-opening polymerization of cyclic monomers. The cyclic monomers of particular interest in this section contain a single heteroatom, these are the cyclic ethers.

## 1.3.3.1. Initiation of cyclic ethers

There are three possible routes of initiation of cyclic ether polymerization, these are:

(i) direct addition of the initiator to the monomer molecule

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(ii) abstraction of a hydride ion ($H^-$) from the monomer and

(iii) formation of zwitterion between initiator and monomer.

Examples of these initiating systems are described below.

(a) Friedel-Crafts type initiators (e.g. $BF_3$, $AlEt_2Cl$, $AlBr_3$, $AlCl_3$, $SbF_5$, $SnCl_4$, $FeCl_3$ and $PF_5$) in presence of suitable coinitiators ($H_2O$, $HX$) may form oxonium ions which then act as the propagating species, as shown in scheme 1.16 (a).

$$BF_3 + H_2O + O \longrightarrow H - \overset{+}{O} \quad [BF_3OH]^-$$
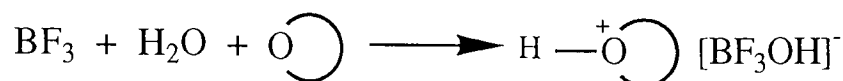
**Scheme 1.16(a). Formation of the oxonium ion**

With epoxides, $BF_3$ alone may lead to the formation of a zwitterion. The addition is direct because of the high degree of ring strain, scheme 1.16(b).

$$\overset{-}{B}F_3 \longleftarrow :\overset{+}{O} \triangleleft \overset{O\triangleleft}{\longrightarrow} \overset{-}{B}F_3O \sim\!\!\sim \overset{+}{O}\triangleleft$$
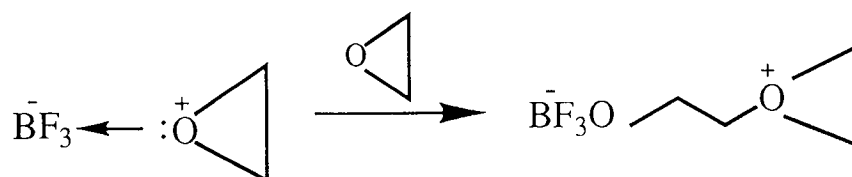
**Scheme 1.16(b). Initiation involving a zwitterion**

(b) Protonic acids and their derivatives (anhydrides, esters), oxycarbenium and oxonium salts initiate the polymerization of cyclic ethers by direct addition, as shown schematically in scheme 1.17.

$$CF_3SO_2OH + O \longrightarrow H - \overset{+}{O} \quad SO_3CF_3^-$$

$$R\overset{O}{\overset{\|}{C}}{}^+A^- + O \longrightarrow R\overset{O}{\overset{\|}{C}} - \overset{+}{O} \quad A^-$$

$$R_3O^+A^- + O \longrightarrow R - \overset{+}{O} \quad A^- + R_2O$$
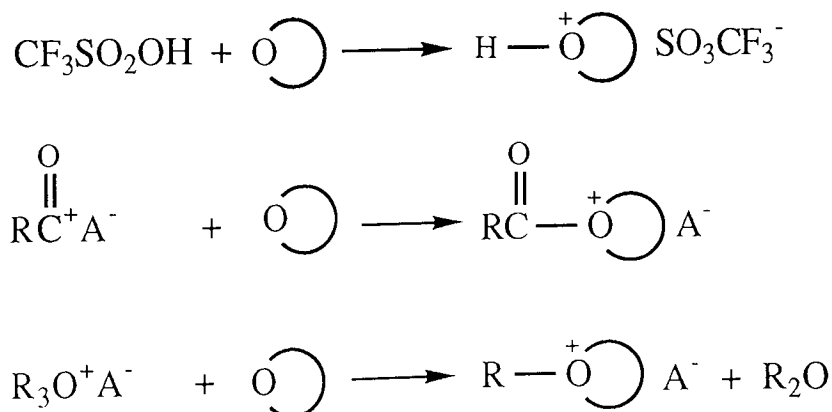
**Scheme 1.17. Initiation of cyclic ethers by direct addition of acids**

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(c) Trityl ions may initiate the polymerization of cyclic ethers by addition followed by hydride ion abstraction[56,57]. The mechanism is shown in scheme 1.18:

$$Ph_3C^+A^- + \quad \underset{O}{\bigcirc} \quad \rightleftharpoons \quad \underset{\underset{Ph_3C}{|}}{\overset{+}{O}} \quad A^-$$

$$\underset{\underset{Ph_3C}{|}}{\overset{+}{O}} \quad A^- \quad + \quad \underset{O}{\bigcirc} \quad \xrightarrow{\text{slow}} \quad Ph_3C^+A^- + \quad \underset{O}{\bigcirc}$$

$$\downarrow \text{fast}$$

$$Ph_3CH \quad + \quad \underset{O}{\overset{+}{\bigcirc}}CH$$
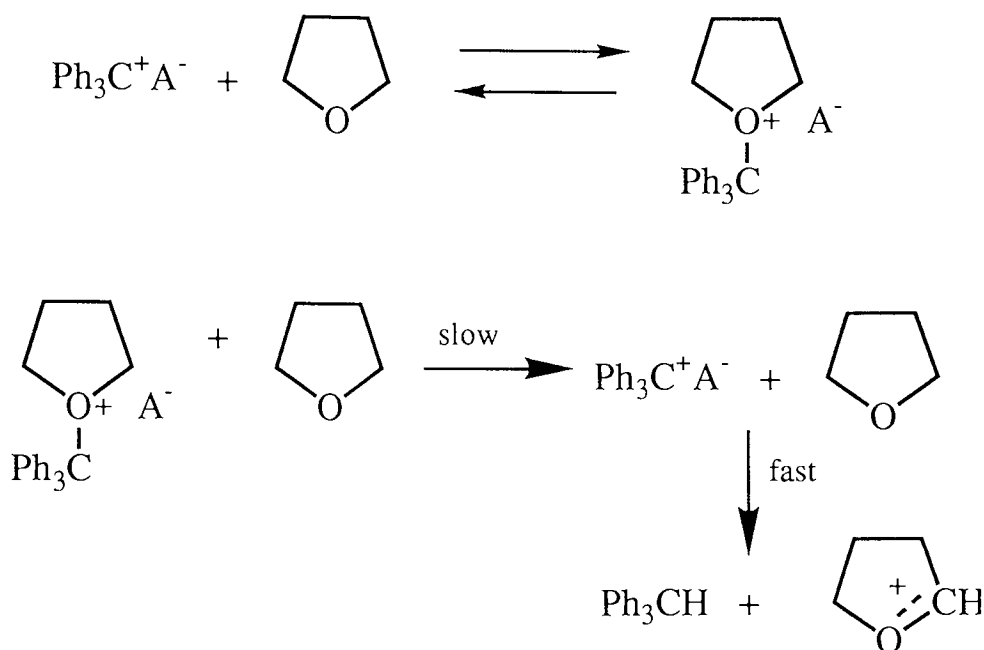
**Scheme 1.18.   Initiation involving a hydride abstraction**

The evidence for scheme 1.18 came from the studies involving $^{14}$C-labelled catalyst and it was shown that the resulting polymer did not carry any end group originating from the initiator[58].

(d) Oxycarbenium ions thus formed can act as initiators, as protons may be released and the formation of a double bond within the monomer may result[57,58] i.e.

$$\underset{\underset{A^-}{O}}{\overset{+}{\bigcirc}}CH \quad \longrightarrow \quad \underset{O}{\bigcirc} \quad + \quad HA$$
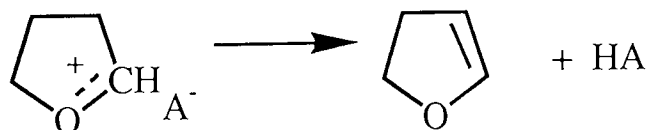
The 3-, 4- and 5-membered cyclic ethers are of major interest since they contain substantial ring strain energy necessary for polymerization to occur. Six-membered cyclic ethers do not polymerize and higher cyclic ethers have been studied less extensively but are known to have been polymerized cationically. For this reason individual discussion of the initiation of 3-, 4- and 5- membered cyclic ethers will be described.

## 1.3.3.2. Initiation of oxiranes (3-membered systems)

The polymerization of the three membered cyclic ethers can be treated as irreversible due to the high degree of ring strain. Substituents decrease the polymerizability but the release of ring strain energy during polymerization compensates the conformational strain.

Generally, cationic mechanism for the polymerization of oxiranes involve addition of the initiating cation or the formation of zwitterions[59,60]. The action of the Lewis acids are considered to give rise to zwitterions without the use of a co-catalyst. Of the many Lewis acids examined the most common are $BF_3$, $SnCl_4$, $FeCl_3$, $TiCl_4$ and $ZnEt_2$ which is a less strongly Lewis acid but is still able to polymerize oxiranes. There is no information of $ZnEt_2$ acting as a catalyst for larger cyclic ethers.

Results in the literature concerning the initiation of oxiranes by protonic acids, carbenium, oxonium or oxocarbenium salts are scarce. Furthermore hydride abstraction from the monomer molecule is difficult as oxiranes are poor $H^-$ donors. However there is some conclusive evidence that the trityl ion initiates oxirane polymerization by addition[61]. This reaction is shown in scheme 1.19.
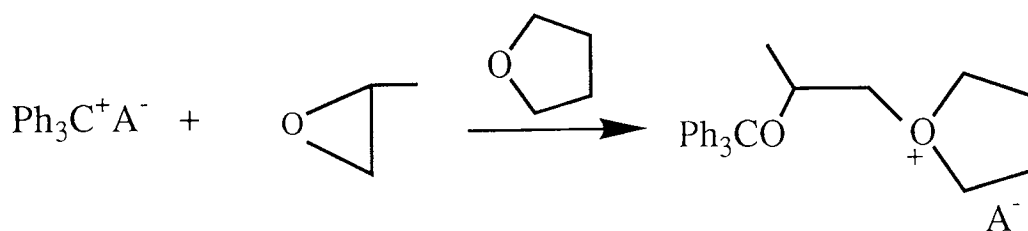


Scheme 1.19. Initiation of an oxirane by a trityl ion

Photoinitiator involving iodenium, sulphonium and selenonium salts have been shown to polymerize oxiranes.

## 1.3.3.3. Initiation of oxetanes (4-membered systems)

The ring strain energy of the 4-membered oxetane ($107 kJmol^{-1}$) is slightly lower than that of oxirane ($114 kJmol^{-1}$) and the polymerization is regarded as irreversible because $[M]_e$ is negligible. If the oxetane ring possesses bulky substituents such as 3,3-dimethyloxetane and

3,3-bis (chloromethyl)-oxetane (BCMO) these monomers are able to polymerize unlike the corresponding substituted compounds of tetrahydrofuran (THF), the 5-membered system, which will be discussed in the next section.

Conventional protonic acids are not suitable for polymerizing cyclic ethers (oxiranes, oxetanes, THF) because only very low molecular weight products are obtained. However superacids such as $FSO_3R$, $CFSO_3R$ are able to polymerize cyclic ethers to high molecular weight. For example ethyl triflate, $EtSO_3CF_3$, polymerized BCMO[62] though there is no record of oxetane being polymerized by this method.

The majority of the cationic initiators for oxetanes involve the Friedel-Crafts acids with the use of a suitable co-catalyst. The reaction is shown in scheme 1.16(a). The Friedel-Crafts acids $BF_3$, $BF_3.OEt_2$, $SnCl_4$, $SbCl_5$, $AlCl_3$, $FeCl_3$ and $PF_5$ have been commonly used for the polymerization of oxetanes. Initial work carried out by J.B. Rose[63] on the polymerization of oxetane using $BF_3$ indicated that the use of a co-catalyst was necessary and he concluded that the rate of polymerization of oxetane using $BF_3$ initiator was proportional to the amount of water added and polymerization would not occur with $BF_3$ under absolutely anhydrous conditions which contrasts with the polymerizations of oxiranes. Later Farthing and Reynolds[64] also concluded that water was necessary for the polymerization of BCMO. Suitable co-catalysts included the following, $Cl_3CCO_2H$, $H_2O$, HCl, HBr, ROH, $MeCO_2H$ etc.

Another group of initiators involves the aluminium alkyls ($AlR_3$) which are also Lewis acids. For the polymerization of oxiranes, oxetanes and THF, these so called 'Vandenburg catalysts' are only active in the presence of water which produces an even stronger Lewis acid. It has be be noted most Vandenburg's catalysts have been extensively employed for the polymerization of oxetane and BCMO[65-67].

Another type of additive (or co-catalyst) in the Lewis acid catalysed polymerization of oxetane (and THF) is termed 'promotor'[68-72] which refers to a cyclic ether (usually an epoxide) having a higher ring-opening activity towards the Lewis acid in comparison with the monomer itself.

The interaction of promotor and the Lewis acid provides the initiating oxonium ion. An example of this type of polymerization includes the initiation of BCMO in either the presence of $BF_3$, $AlCl_3$ or $SnCl_4$ with promotor molecules such as epichlorohydrin and propylene oxide[72]. This is illustrated in scheme 1.20.
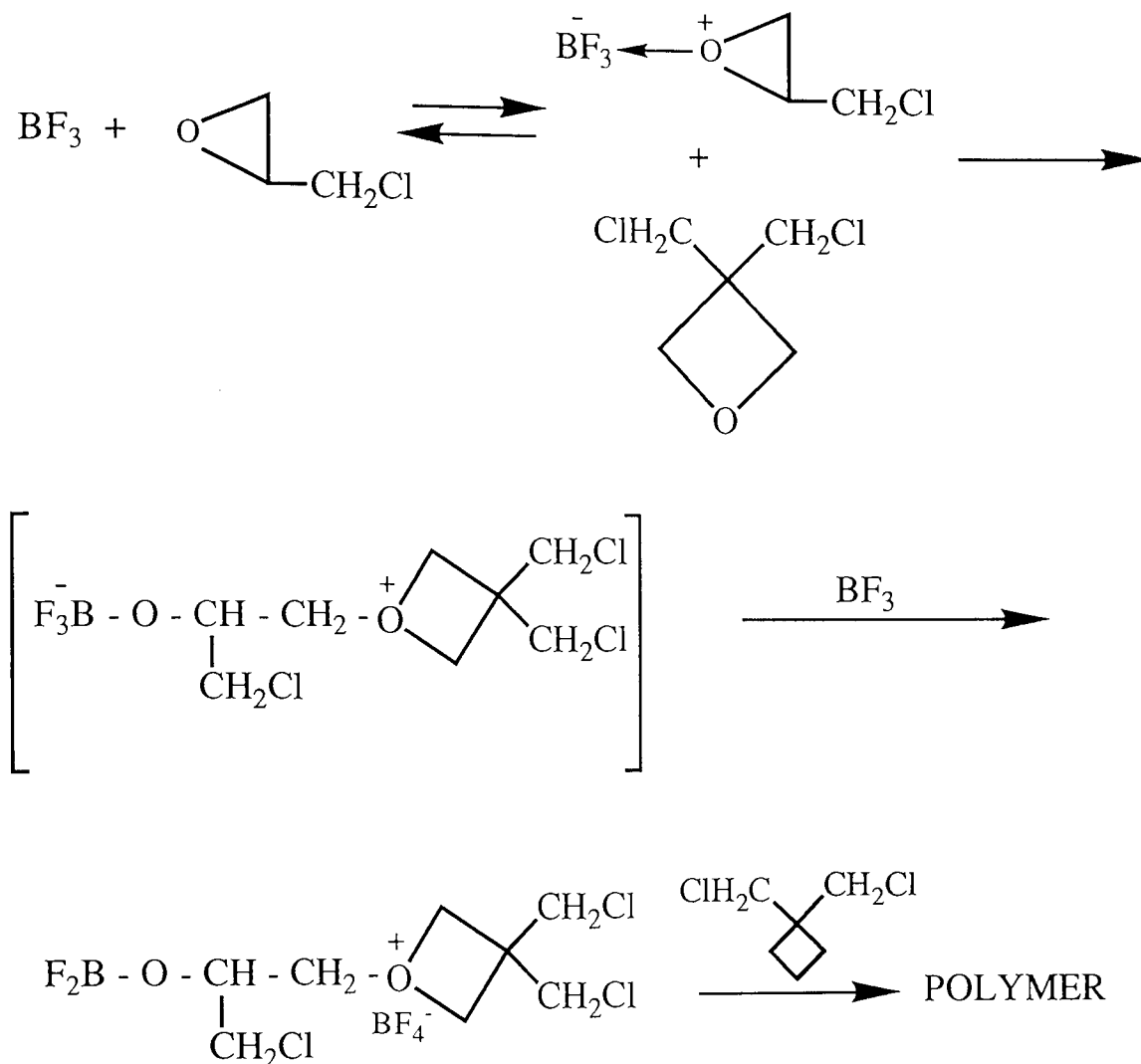
**Scheme 1.20. The use of a 'promotor' molecule for the initiation of BCMO**

The promotors have two distinct advantages, (i) there is no need for a co-catalyst, (ii) the actual concentration of the Lewis acid required for polymerization is lower compared with the normal circumstances of Lewis acid/co-catalyst systems because of the higher degree of interaction of the promotor molecule with the Lewis acid.

Cationic polymerization involving photoinitiators has been carried out on BCMO but there is no record of these being used for polymerization of oxetane.

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## 1.3.3.4. Initiation of tetrahydrofuran (THF) 5-membered system

The polymerizability of a monomer may be characterised by

(i) the enthalpy and entropy of polymerization, or

(ii) the ceiling temperature for the polymerization of bulk monomer.

Because the ring strain energy of THF is considerably lower than that of oxetane or oxirane ($23kJ\ mol^{-1}$), the ceiling temperature for the polymerization of bulk monomer is $80^{\circ}C$. Therefore the polymerization of THF is considered reversible since the equilibrium monomer concentration at normal polymerization temperatures is considerable. Ideally $[THF]_e$ should be independent of reaction conditions but this is not the case, $[THF]_e$ strongly depends on the nature of the solvent and the concentrations used[73].

THF is one of the most studied monomers among the cyclic ethers along with ethylene oxide, propylene oxide and epichlorohydrin. The conventional cationic initiators of THF will be discussed in this section.

Friedel-Crafts acids such as $BF_3$, $FeCl_3$, $SnCl_4$ or $AlCl_3$ can act as initiators of THF polymerization but only in the presence of strong alkyl hakides such as chloromethyl methyl ether, 2,3-dihydrofuran or acyl halides. Direct initiation involving alkyl or acyl cations is considered in such systems:

$$BF_3 + CH_3OCH_2F \rightleftharpoons BF_4^-\ CH_3OCH_2^+$$

$$FeCl_3 + CH_3COCl \rightleftharpoons FeCl_4^-\ CH_3CO^+$$
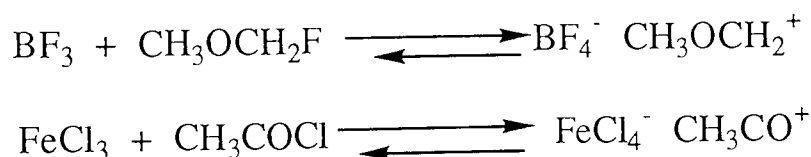
However when Friedel-Crafts acids are used in the presence of protonic acids (co-catalysts) such as $H_2O$, ROH, $CH_3COOH$ etc, polymerization of THF does not occur. This is because unlike the case of the oxirane and oxetanes the secondary oxonium ion produced upon protonation is less reactive towards the monomer due to the lower ring strain associated with THF.

Polymerization of THF in the presence of promotors using Friedel-Crafts acids is possible; systems such as $BF_3$/(epichlorohydrin or propylene oxide) have been used, other systems

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have included AlEt$_3$/H$_2$O with either epichlorohydrin, propylene oxides, β-propiolactone or diketene promotors[71,72]. AlEt$_3$/H$_2$O alone does not initiate the polymerization of THF. There are a few exceptional cases where action of Friedel-Crafts catalysts alone are enough to promote the polymerization of THF, such acids are strong and include PF$_5$ and SbCl$_5$[74-76] Further systems include the hydride abstraction or proton elimination mechanisms which involve

(i)  carbenium ions R$_3$C+ (Ph$_3$C$^+$A$^-$)

(ii)  alkoxycarbenium ions ROCH$_2$$^+$ (CH$_3$OCH$_2$$^+$A$^-$).


(i)  The carbenium ion mechanisms

The polymerization of THF by carbenium ions tropylium and p-chlorophenyl cation has been reported[77,78]. The mechanism of initiation with trityl salts has been studied and it was found that the initiation reaction is not a direct addition to THF to form the oxonium ion, instead the Ph$_3$C+ abstracts α-hydrogen of the THF and the protonic acid that is produced initiates the polymerization as shown in scheme 1.21:
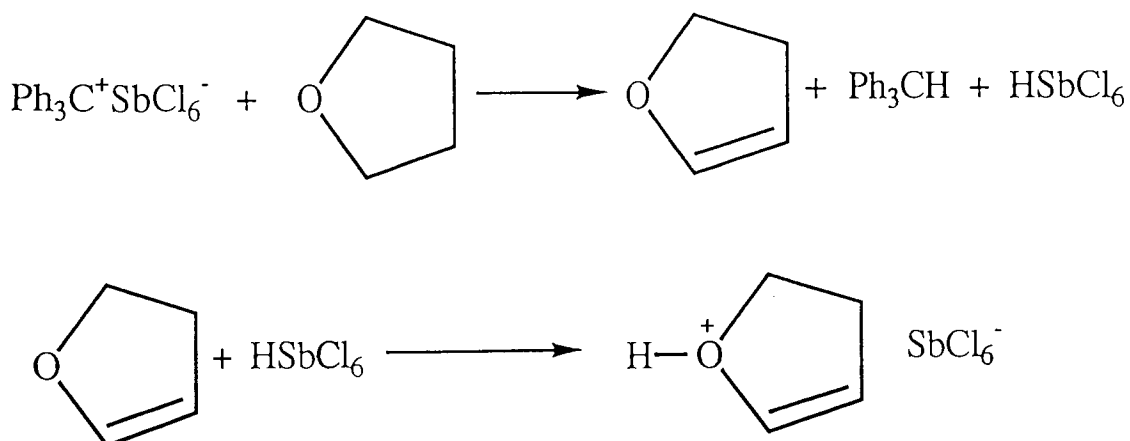


Scheme 1.21.  Trityl cation initiation via a hydride abstraction mechanism


In some cases when AgSbF$_6$/PhCH$_2$X is used where X=Cl initiation of THF occurs by a proton which is eliminated from the PhCH$_2$$^+$ cation i.e.

$$PhCH_2Cl + AgSbF_6 \longrightarrow AgCl + PhCH_2^+ SbF_6^-$$

$$PhCH_2^+ + \text{(tetrahydrofuran ring, O)} \longrightarrow H\!-\!\overset{+}{O}\text{(ring)} + 2C_6H_5\text{-}\overset{\cdot\cdot}{C}\text{-H}$$

$$\downarrow$$

$$C_6H_5 - CH{=}CH - C_6H_5$$

If in the above case X=Br then direct addition would take place:

$$PhCH_2Br + AgSbF_6 \longrightarrow AgBr + PhCH_2^+ SbF_6^-$$

$$PhCH_2^+ + \text{(tetrahydrofuran ring, O)} \longrightarrow PhCH_2\!-\!\overset{+}{O}\text{(ring)}$$

## (ii) Alkoxycarbenium ions

Triphenylmethylium salts react with dioxalane by hydride transfer to form the corresponding dioxolenium salts, which react with nucleophiles exclusively by addition. Dioxolenium salts can be considered derivates of dialkyloxycarbenium ions and are exellent initiators for ring opening polymerization of THF, consider scheme 1.22:

$$Ph_3C^+SbCl_6^- + \text{(dioxolane ring)} \longrightarrow Ph_3CH + \text{(dioxolenium ring, }C^+\text{)} SbF_6^-$$

$$\text{(dioxolenium ring, }C^+\text{)} SbF_6^- + \text{(THF ring, O)} \rightleftharpoons CHO\text{-}O\text{-}CH_2CH_2\!-\!\overset{+}{O}\text{(ring)} SbF_6^-$$

Scheme 1.22. Initiation of THF by dioxolenium salts

Bisdioxolenium salts were used by Yamashita et al.[79] to produce dicationically growing poly(THF), thus:

$$ClCH_2CH_2OCO\text{-}(CH_2)_8\text{-}OCOCH_2CH_2Cl + 2AgClO_4 \longrightarrow$$



$$+ 2AgCl$$

(iii) Onium ions: RnX ($(C_2H_5)_3O^{\pm}A^-$)

Trialkyloxonium ions ($R_3O^+A^-$) are the most important initiators for cationic ring-opening polymerizations of all classes of heterocycles (cyclic ethers, acetals, sulphides, lactones, phosphates and amines). Generally they can be prepared by the mechanism shown below developed by Penczek et al.[80] - scheme 1.23:



**Scheme 1.23. Formation of trialkyloxonium ions**

Trialkyloxonium ions are strongly alkylating agents consequently initiating the polymerization of THF and other heterocyclic monomers by simple alkylation at the most nucleophilic site of the monomer. Initiation takes place without any side reactions and occurs quantitatively. The advantage of these initiators is that they are useful for kinetic work; THF again has been polymerized using these initiators[81] and the initiation was analysed by direct NMR spectroscopy. Other monomers have also been examined namely cyclic sulphides and cyclic esters of phosphoric acid.

$$(C_2H_5)_3O^+ \ BF_4^- \ + \ O \text{(cyclic)} \longrightarrow C_2H_5-O^+ \text{(cyclic)} \ BF_4^- \ + \ (C_2H_5)_2O$$

## (iv) Covalent ions

Strong alkylating agents such as esters of superacids ($CF_3SO_3R$, $FSO_3R$ and $ClSO_3R$) are able to initiate directly again without any side reactions[82,83]. Where alkylating compounds are concerned the initiation depends both on the ability of the initiator to form a cation and on the monomer nucleophilicity.

$$C_2H_5OSO_2CF_3 \ + \ O \text{(cyclic)} \longrightarrow C_2H_5-O^+ \text{(cyclic)} \ CF_3SO_3^-$$

Weak cationating agents such as alkyl iodine and benzyl halides are able to initiate the polymerization of strong nucleophilic monomers such as cyclic amines and cyclic imino ethers.

## 1.3.4. Initiation of ring-opening anionic polymerization

A number of heterocyclic monomers including epoxides, lactones, lactams, cyclic ureas and cyclic siloxanes can be polymerized by an anionic mechanism. Catalysts for anionic ring-opening polymerizatons involve the following types of compounds; amides, hydrides, alkoxides, hydroxides, pyridine, tertiary amines and organometallics of the alkali metals Na and K.

Work carried out on the polymerization of epoxide with hydrogen compounds such as phenols, carboxylic acids, alcohols and amines have shown that the polymerizaton not only depends on the acidity of the active hydrogen compounds but also on the nature of the solvent and catalyst. Boyd and Marle[84] carried out the reaction between ethylene oxide or propylene oxide and substituted phenols in 98% ethanol, using the sodium salt of a substituted phenol. From the rate constants the Hammett reaction constants $\rho$ were found to be -0.95 and -0.77 for ethylene and propylene oxides respectively, suggesting an anionic mechanism. The initiation takes the form shown in scheme 1.24.

**Scheme 1.24. Anionic initiation of ethylene oxide using the sodium salt of a substituted phenol**

Lowe and Weibull[85] explained that the rate of initiation step can be represented by the rate equation below and that an additional molecule of phenol takes part in the rate determining step:

$$\frac{-d[C_6H_5OH]}{dt} = k[C_2H_5OH][C_2H_4O][C_6H_5ONa]$$

Sakai and Ishii[92] studied the reactions of ethylene oxide with many different hydrogen compounds such as substituted phenols and determined reaction rates by following the reaction dilatometrically. They proved that the rates of the first step, and the subsequent steps, could be expressed by an equation similar to that above. Electron-donating substituents on the phenol gave higher rate constants than the electron-withdrawing substituents. The catalyst potassium phenoxide was found to be present in all subsequent reactions which behaved as an ion-pair species.

In the reaction of higher alcohols with ethylene oxide using different kinds of alkoxide catalysts, various rate constants were observed, depending upon the kind of alkoxide. Rate constants were higher with more basic alkoxides, t-BuOK > t-BuONa > KOH > RONa > CH$_3$ONa > NaOH[87]. Unlike cationic initiation there is no need for a co-catalyst primarily because the three membered epoxide are extremely reactive compounds. Various solvents have been used such as n-butanol, nitrobenzene, 98% ethanol, xylene and carbon tetrachloride.

## 1.3.5. Initiation of ring-opening coordination anionic polymerization

Ethylene oxide and propylene oxide can be polymerized to very high molecular weight polymers under mild conditions using coordinate anionic polymerization. The propagating species is anionic in nature e.g. metal alkoxide. The monomer first coordinates with the catalyst prior to propagation. The same name was previously applied to polymerization of olefins by Ziegler/Natta catalysts.

The coordinate polymerization of epoxides originated from work carried out by Pruitt and Baggett[88] in 1955. They obtained very high molecular weight polypropylene oxide polymers using $FeCl_3$ catalyst.

Following the invention of Pruitt and Baggett many related catalyst systems were discovered. Examples include $Fe(OEt)_3/H_2O$[89], $ZnEt_2/H_2O$[90,91], $ZnEt_2/ROH$[92], $AlR_3/H_2O/acetylacetone$[93], $Al(OR)_3/ZnCl_2$[94], $Al(OR)_3/Zn(OAc)_2$[95] and $Et_2AlCl/porphine$[96,97]. Various solvents have been used namely benzene, dioxane, dichloromethane, chloroform and diethyl ether.

## 1.4. Mechanisms of ring-opening polymerization of cyclic ethers

## 1.4.1. Cationic ring-opening polymerization of cyclic ethers

This section will discuss the cationic polymerization mechanism of cyclic ethers, and the mechanism of oxetane will be discussed in detail though it must be emphasised that the general principles apply to other cyclic ethers as well.

The cationic polymerization of oxetane, first recorded by Farthing[98] in 1955 gave linear polymers of high molecular weight. J.B. Rose extended Farthings work[63] and reported that cationic polymerization would not occur under absolutely anhydrous conditions when $BF_3$ is used as an initiator. Water was the essential co-catalyst. Furthermore he observed the rate of polymerization of oxetane initiated by $BF_3$ was proportional to the amount of water added. Farthing and Reynolds[64] reported that the polymerization of 3,3-bis(chloromethyl)-oxetane by $BF_3$ initiator occurred when a small amount of water was introduced to the system. On the other hand, 3-membered cyclic ethers such as ethylene oxide, propylene oxide and

epichlorohydrin are vunerable to the action of the Lewis acid and are polymerized by the Lewis acid alone. However in all cases the polymerizations are not 'clean' and there are many side reactions. This makes the kinetics and, in turn, the mechanism difficult to understand. There have been several attempts to describe the mechanism but as yet there is no clear-cut evidence to say which is correct.

Kinetic chain polymerizations are characterized by three main stages, initiation, propagation and termination. Rose proposed the following mechanism for the polymerization of oxetane based upon detailed investigation of the kinetics of the $BF_3$-catalysed system.

Initiation



Scheme 1.25. Cationic initiation of oxetane

The complex role of water as a co-catalyst required the postulation of a two step initiation process. The secondary oxonium ion (I), which exists as an ion pair, is much less active than the tertiary oxonium ion (II)[63].

$$H[O(CH_2)_3]_n \longrightarrow \overset{+}{O} \quad :O \qquad \xrightarrow[S_N2]{k_p}$$

$$[BF_3OH]^-$$

$$H[O(CH_2)_3]_{n+1} \longrightarrow \overset{+}{O}$$

$$[BF_3OH]^-$$

**Scheme 1.26. Propagation reaction of the polymerizaton of oxetane**

The chain propagates by a nucleophilic attack of the oxygen atom of the monomer on the $\alpha$-carbon of the tertiary oxonium ion. The propagation step is thought to occur by an $S_N2$ type mechanism. $[BF_3OH]^-$, the gegenion, presumed to be formed in initiation, maintains its integrity during propagation. It should be noted however that similar inorganic complexes are known to be unstable. Under the reaction conditions, $[BF_3OH]^-$ may disproportionate or it may react further with $BF_3$ to give $BF_4^-$.

Termination

Termination is the least well understood of the three reactions. That termination occurs is indicated by the fact that the polymerization of oxetane is not a living system.

One possible termination reaction involves chain transfer to water (or co-catalyst) as shown in scheme 1.27.

$$H[O(CH_2)_3]_n \longrightarrow \overset{+}{O} \quad + \; HOH \xrightarrow{k_{tr}} H[O(CH_2)_3]_{n+1} \longrightarrow OH$$

$$[BF_3OH]^- \qquad\qquad\qquad\qquad H^+[BF_3OH]^-$$

**Scheme 1.27. Termination involving chain transfer to the co-catalyst**

Studies have shown that the intrinsic viscosity of the polymer produced decreases with an increase in the concentration of co-catalyst, water or alcohol.

Chain transfer may also occur by the following intramolecular reaction shown in scheme 1.28:

$$H\,[O(CH_2)_3]_n \overset{+}{\underset{[BF_3OH]^-}{O}} \xrightarrow{k_{tr}'}$$

$$H[O\text{-}(CH_2)_3]_{n-3}\overset{+}{\underset{[BF_3OH]^-}{O}}\begin{array}{c}(CH_2)_3\text{-}O\text{-}(CH_2)_3\\ \\(CH_2)_3\text{-}O\text{-}(CH_2)_3\end{array}O$$

**Scheme 1.28. Chain transfer reaction by an intramolecular reaction**

The product of this reaction is purported to be strain free and is presumed to be relatively unreactive until it comes into contact with a terminating group or monomer. Cyclic tetramer is then formed. However copolymerization studies[64,99-101] indicated that the strain in the trialkyl oxonium ion is not the key factor but the basicity of the attacking monomer controls the rate of reaction. Thus the strainless oxonium ion could not react to form free tetramer and generate a growing chain.

Rose pointed out that the tetramer could be produced by the process of back-biting, i.e. scheme 1.29.

$$HO(CH_2)_3[O(CH_2)_3]_2\text{-}\overset{+}{\underset{[BF_3OH]^-}{O}} \longrightarrow O\begin{array}{c}(CH_2)_3\text{-}O\text{-}(CH_2)_3\\ \\(CH_2)_3\text{-}O\text{-}(CH_2)_3\end{array}\overset{+}{O}\text{-}H \quad [BF_3OH]^-$$

**Scheme 1.29. Tetramer formation by the back-biting process**

To complicate this issue further no tetramer could be formed with 2-methyloxetane and 3, 3-bis(chloromethyl)-oxetane, (BCMO). However later Arimatsu[102] did record the production of a tetramer with BCMO when triethyl aluminium was used as catalyst.

It is interesting to note that both chain transfer and back-biting processes involve the generation of $H^+$ which can be subsequently be utilised by an incoming monomer to reproduce the active centre and consequently another polymer chain. It is because of this feature there is no formal termination, unlike free radical polymerization, when a pair of free radicals react together and as a result a dead polymer is formed with no other free radical generated in the process. This reaction can be regarded as a true termination step. The mechanism proposed by Rose is now known as the ACTIVE CHAIN END mechanism since the active centre, oxonium site appears at the end of the growing polymer and the attacking nucleophile is the uncharged monomer.

Furtherwork done in this area has shown that the polymerization of BCMO with a Lewis acid ($BF_3$, $SnCl_4$ or $AlCl_3$) may be possible without the use of the usual co-catalyst. Instead epichlorohydrin or propylene oxide may be used as 'promotors'. This has already been discussed in section 1.3.3.3.

Until 1984, it was thought that the activated chain end (A.C.E) mechanism was the sole mechanism by which cationic ring opening polymerization of cyclic ethers could be achieved. A second mehanism was then proposed by Penczek[103] which was entitled 'Activated Monomer Mechanism' (A.M.M). This mechanism consists of the step-by-step addition of the protonated monomer, or monomer activated in some other way, to the growing macromolecule that possesses a nucleophile end group (e.g. hydroxyl end group) e.g. scheme 1.30

$$-O\text{-}CH_2CH_2OH \ + \ \underset{\underset{\underset{H}{|}}{\overset{\displaystyle CH_2\text{-}CH_2}{\diagdown\diagup}}}{O+} \longrightarrow -O\text{-}CH_2CH_2\text{-}O\text{-}CH_2CH_2OH \ + \ H^+$$

anion omitted

Scheme 1.30. The activated monomer mechanism

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The roles of the two species are therefore reversed when compared with A.C.E..

So far work on the application of this mechanism has been limited to ethylene oxide, propylene oxide and epichlorohydrin. Polymerization by this mechanism may be accompanied by the usual A.C.E cationic growth, involving tertiary oxonium ions (back-biting) and chain transfers.

Conditions have to be found that enhance A.M.M and simultaneously supresses A.C.E mechanism. It is also important to realise that by its very nature A.M.M leads to a reduction in back-biting and consequent formation of cyclic oligomers.

Penczek considered the initiation of polymerization of an oxirane catalysed by an alcohol in the presence of a protonic acid to take place by the mechanism shown in scheme1.31. Superficially these polymerizations of oxirane would appear to be under identical conditions but this is not the case. The conventional A.C.E mechanism would apply if the protonic acid catalyst were added to a solution of oxirane. In this case the added alcohol would act as a transfer agent during the course of the polymerization. To polymerize oxirane by an A.M.M, however, the procedure must be changed. In this case a solution of the alcohol is produced in the solvent for polymerization and the protonic acid catalyst is added to this solution. The monomer is then admitted slowly into the solution so that at any instant its concentration is only of the order of that of the initiator. The proton from the acid catalyst preferentially protonates the monomer, as would be the case in the A.C.E. mechanism. However because the concentration of monomer is so low the only nucleophile present capable of attacking the hydroxonium compound is the alcohol.

Scheme 1.31. Comparison of the A.M.M and A.C.E. mechanisms

From the above reaction schemes to encourage A.M.M, the [ROH] has to be increased whilst the monomer concentration to be decreased. The main advantage Penczek deduced is that with the A.C.E mechanism there is approximately 40% of the cyclic tetramer formed by either back-biting or by chain transfer, whilst with A.M.M tetramer formation is less than 1% when slow addition of the monomer takes place. Side reactions that do appear are the direct result of some A.C.E propagation which is an inherited property of A.M.M. The study of A.M.M is still in its infancy and it will be interesting to see the application of this mechanism to larger cyclic ethers such as oxetanes, THF etc.

## 1.4.2. Living polymerizations

The reaction schemes for cationic polymerization usually contain no formal termination step and if all the non-propagating side reactions such as chain transfer and back-biting are excluded from the system then consumption of the monomer should continue until all has been consumed leaving the active centres still intact and if more monomer is then introduced the active end would continue its growth. If the initiation reaction is fast the polymers obtained in living polymerizations are of narrow molecular weight distribution, because propagation reactions proceed uniformally with respect to all growing polymer molecules. The number of polymer molecules is the same as that of the initiator and it does not change. These polymers are termed 'Living' and the molecular weight increases with conversion[104,105]. If the rate of initiation is slow the molecular weight distribution is broader than that obtained with a rapid initiation system. Living polymerizations may be terminated by the addition of a reagent such as a protic acid $H_2O$, ROH, depending on the nature of the active centre. In a conventional cationic ring-opening polymerizations termination occurs by transfer through back-biting or chain transfer, and for this reason these polymerizations are referred to as 'Pseudo-living Polymerizations', because the system still possesses an active centre but $DP_n \neq [M]_t - [M]_o/[I]$

where

$DP_n$ = average degree of polymerization

$[M]_t$ = concentration of monomer at time t

$[M]_o$ = concentration of monomer at time 0

$[I]$ = concentration of initiator


The most well known example of a living polymerization is the anionic polymerization of styrene in THF initiated by metal alkyls or sodium naphthalide, wherein only initiation and propagation occur.


## 1.4.3. Recent developments in living cationic polymerizations
## 1.4.3.1. Developments in living cationic ring-opening polymerizations

Traditionally cationic ring opening polymerization has been described as unpredictable, unreliable and above all uncontrollable. A living system, however can ensure controllability to

a larger extent.  As a result, research in polymer chemistry in the 1980's has been focused on living systems.

THF[106] and oxepane[107] give rise to living polymerizations using cationic initiators such as 1,3 dioxolan-2-ylium hexafluoroantimonate (X)

$$\begin{array}{c} \text{O} \quad\quad \text{O} \\ \diagdown\;\diagup \\ \text{C+} \quad \text{SbF}_6^- \\ | \\ \text{H} \end{array}$$

(X)

Cyclic acetals, namely 1,3 dioxalane and 1,3 dioxepane have been found to polymerize under living conditions.  Other monomers include oxazines and oxazolines, where chain transfer does not occur because the nucleophilicities of the heteroatoms in the polymer chain are lower than those in the corresponding monomer molecules due to the presence of the alkyl substituents on the  polymer heteroatoms.  Further analysis has shown that certain cyclic sulphides, amines and cyclic esters of phosphonic acid give rise to living polymers[108-110]; in these cases the number of substituents on the monomer becomes a major factor since kinetic studies indicated the bulkier monomer undergoes a living  polymerization.  Finally, as already discussed earlier the activated monomer mechanism proposed by Penczek et al.[103] also gives rise to living polymers of epoxides, as yet, however no other groups of monomers have been polymerized.


## 1.4.3.2.  Developments in living catonic vinyl polymerizations

The main focus with cationic vinyl polymerization in the last decade has been directed towards obtaining polymers of controlled structures.  To achieve this the techniques of living cationic systems has been extensively involved.

In 1984, Higashimura et al.[111] reported a truly living cationic system with alkyl vinyl ethers (CH$_2$=CHOR;  R=alkyl) when the polymerization was carried out using a mixture of hydrogen

iodide and iodine at 0°C. According to Higashimura HI is the initiator and the iodine serves as the co-catayst consider scheme 1.32:

$$CH_2=CH-OR \xrightarrow{\text{HI}} H-CH_2-CH-I \xrightarrow{I_2} H-CH_2-\overset{+}{C}H \cdots \overset{-}{I} \cdots I_2$$

with OR substituents, and addition of $CH_2=CH-OR$ leading to:

$$H(CH_2-CH)_nCH_2-\overset{+}{C}H \cdots \overset{-}{I} \cdots I_2 \quad \text{(Living polymer)}$$

**Scheme 1.32. Polymerization of vinyl ether using HI/I$_2$ system**

In the 'initiator/activator' mechanism shown above the interaction of the molecular iodine (activator) with I⁻ is electrophilic. Thus it acts as a Lewis acid that 'modifies' the nucleophilicity of the iodine anion. These considerations, in turn, suggest that not only the HI/I$_2$ system but other combinations of a nucleophilic anion (from an initiator) and a Lewis acid (activator) may induce living cationic polymerization.

'Mild' metal halides as Lewis acid activators other than iodine ZnX$_2$ and SnX$_2$; (X=I, Br, Cl) are useful· In particular the HI/ZnI$_2$ initiating system permits living cationic polymerization of alkyl vinyl ethers to occur at room temperture or above[112]. Other substrates other than hydrogen iodide that act as initiators include the following (in conjunction with iodine or ZnI$_2$): diaryl phosphates (e.g. HOP(O)(OPh)$_2$)[114], trimethylsilyl iodide[115] and MeSiOCH$_2$CH$_2$OCH$_2$I (from trimethylsilyl iodide and 1,3 dioxalane)[116]. Unlike the latter two which degenerate the iodide counteranion, as does hydrogen iodide, the HOP(O)(OPh)$_2$/ZnI$_2$ system provides the first example of living cationic processes that are mediated by phosphate anions.

Metal halides of strong Lewis acidity such as $AlEtCl_2$ polymerise vinyl ethers rapidly, but the polymerizations are not living - most probably because these Lewis acids form counteranions that are not sufficiently nucleophilic to stabilise carbocations. Aoshima and Higashimura found that adddition of an appropriate Lewis base to such non-living system leads to living cationic polymerization[117,118]. A typical example involves $CH_3$-CH(OiBu)-OCOCH$_3$ (initiator), $AlEtCl_2$ (activator) and 1,4 dioxane (added base)[119]. This mechanism is illustrated in scheme 1.33.



**Scheme 1.33. Example showing the significance of 1,4 dioxane to induce a living polymerization**

Table 1.3 below shows some reported examples of added Lewis base living cationic polymerization of vinyl ethers, along with initiating systems that are employed in the presence of these bases[117-122].

## Table 1.3.  Initiating systems for living cationic polymerization of vinyl ethers with externally added Lewis bases

| Initiator/Activator | Added Lewis base | Ref. Nº |
|---|---|---|
| $H_2O/AlEtCl_2$ | $CH_3COOEt$ | 117 |
| $H_2O/AlCl_3$ | $PhCOOEt$ | 119 |
| $CH_3COOH/AlEt_2Cl$ | $EtOCOOEt$ | 119 |
| $CH_3CH(OiBu)OCOCH_3/AlEtCl_2$ | 1,4 dioxane, THF | 118,120 |
| $CH_3CH(OiBu)OCOCF_3/AlEtCl_2$ | 2,6 dimethylpyridine | 121 |
| $CF_3SO_3H$ | $Me_2S$, $Et_2S$ | 122 |

In 1986, Faust and Kennedy reported the living cationic polymerization of isobutylene, employing tertiary acetates (initiators) in conjunction with boron trichloride ($BCl_3$; activator or coinitiator).  Since then a number of initiating systems have been developed for the living cationic polymerization of isobutylene.  These systems are listed below:

(a)  carbocation stabilisation with nucleophilic anions

tertiary ester/$BCl_3$[123-133]

tertiary ether/$BCl_3$[134-139]

tertiary alcohol/$BCl_3$[140,141]

(b)  carbocation stabilisation with added Lewis bases

cationogen (initiator)*/$BCl_3$/Lewis base[142,143]

cationogen*/$TiCl_4$/Lewis base[144,145]

(* tertiary chloride, esters, ethers, alcohols)

It has been difficult to achieve living processes for styrene derivates which are less reactive and form propagating carbocations less stable than those from vinyl ethers.  A series of living cationic polymerizations has recently been developed for some of these aromatic monomers (Table 1.4)[146-155].

## Table 1.4. Initiating systems for living cationic polymerization of styrene derivates (p - R-C$_6$H$_4$-CH=CH$_2$)

| R | Initiating system | Ref |
|---|---|---|
| | Initiator/Activator | |
| H (syrene) | $p$ -CH$_3$C$_6$H$_4$CH(CH$_3$)-OCOCH$_3$/BCl$_3$ | 146 |
| | C$_6$H$_5$CH(CH$_3$)Cl/SnCl$_4$ | 147 |
| | HSO$_3$CH$_3$/SnCl$_4$ (+ n Bu$_4$NCl) | 148 |
| CH$_3$ | CH$_3$CO-ClO$_4$/none (+ n Bu$_4$NCl) | 149 |
| | HI/ZnCl$_2$ | 150 |
| 2,4,6-trimethyl | C$_6$H$_5$C(CH$_3$)$_2$-OCOCH$_3$/BCl$_3$ | 151 |
| OCH$_3$ | HI/ZnI$_2$ | 152,153 |
| OC(CH$_3$)$_3$ | HI/ZnI$_2$ | 154 |
| Cl | CH$_3$C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$Cl/TiCl$_4$ | 155 |

The addition of tetra-n-butylammonium chloride (n BuNCl) in the cases listed in table 1.4 is able to afford living polystyrene with very narrow molecular weight distributions (Mw/Mn ~1.1).

### Quasi-living cationic polymerization

Before the discovery of truly living cationic polymerizations Kennedy et al. devised an interesting approach for controlling molecular weight and molecular weight distribution. The process termed 'quasi-living polymerization'[155-164] involves a polymerization to be carried out an extremely low concentration of monomer. This is achieved by slow but continuous monomer addition into a solution of an initiating system and resultant growing species. These conditions resemble a truly living polymerization i.e. Mn increases progressively with, and often proportionally to the total weight of reacted monomer. The molecular weight disstribution is fairly narrow (1.3-1.8). Kennedy however uses the prefix 'quasi' to differentiate from truly living polymerization as the former involves a reversible termination

$$( \text{e.g.} \quad \text{-}C^+ \text{- - - -}BCl_4 \rightleftharpoons C\text{-}Cl + BCl_3)$$

and in some cases a reversible or irreversible chain transfer as well[156]. Systems which generate 'quasi-living polymerization' include cumyl chloride/$BCl_3$ (or $TiCl_4$) and dicumyl chloride/$AgSbF_6$. Monomers which have been polymerized with these systems include $\alpha$-methylstyrene[157,158], t-butylstyrene[159], 2,4,6-trimethylstyrene[160], indene[161], isobutylene[162], isobutylvinyl ether[163] and methylvinyl ether.

## 1.4.4.  Mechanisms of anionic ring-opening polymerizations

The mechanism of anionic ring-opening polymerization can be divided into two catergories. In the first category, the anionic propagating end attacks the monomer to open the ring. Ethylene oxide can be polymerized by this mechanism using alkali-metal based catalyst; scheme 1.34,



**Scheme 1.34.  Mechanism of polymerization of ethylene oxide using RONa**

Potassium t-butoxide (t-BuOK) has been used to polymerise ethylene oxide in DMSO and it was found that the molecular weight of the polymer increased linearly with the molar ratio of the monomer consumed to the catalyst[165], a characteristic of living polymerizations. However when propylene oxide was polymerized by the same technique the maximum molecular weight was lower than the calculated value. This was because propylene oxide acted as a transfer agent and a proton from the methyl group could be abstracted by the growing alkoxide anion, consider scheme 1.35,

**Scheme 1.35.** **Example of an anionic polymerization involving a proton abstraction from the monomer by the growing alkoxide anion**

This type of chain transfer involves the protons $\alpha$ to the ring since the incidence of such reactions increases with the number of methyl groups on the epoxide ring. If these protons are substituted by methyl groups such as t-butyl-ethylene oxide a living polymerization is obtained although the rate of polymerization is low[166].

The initiators below have also been used to initiate the living polymerizations of ethylene oxide in THF:



The mechanism is known to proceed by the following route

$$2 \left[ \text{naphthalene} \right]^{\bar{\cdot}} M^+ \quad + \quad \underset{O}{CH_2 - CH_2} \quad \xrightarrow{THF}$$



Other catalysts giving rise to living systems include:



and



cryptated

In this case the mechanism of initiation is bifunctional whereas the initiator was monofunctional i.e. scheme 1.36

**Scheme 1.36.  Bifunctional initiation of ethylene oxide**

Depending upon the substituent group, R, (for example in the above case R = H) the degree of polymerization $DP_n = 2[M]_0/[Cat]_0$ where as if R = $CH_3$ then $DP_n = [M]_0/[Cat]_0$. This will therefore show different molecular weights of poly(ethylene oxide) and is a direct consequence of different mechanisms of initiation[167].

The second category of anionic ring-opening polymerization is concerned with the polymerizations of lactams and N-carboxy-α-amino acid anhydrides (NCA). The initiation and propagation of lactams is shown in scheme 1.37.

$$NaX \ + \ HN\text{-}C\text{=}O \longrightarrow Na^+N^-\text{-}C\text{=}O \ + \ HX$$

'activated monomer'

$$NaN^-\text{-}C\text{=}O \ + \ HN\text{-}C\text{=}O \longrightarrow HN \ C\text{-}N\text{-}C\text{=}O$$

$$HN \ C\text{-}N\text{-}C\text{=}O \xrightarrow[HN\text{-}C\text{=}O]{} H_2N \ C\text{-}N\text{-}C\text{=}O \xrightarrow{Na^+N^-\text{-}C\text{=}O}$$

$$H_2N \ C\text{-}N\text{-}C\text{-}N\text{-}C\text{=}O \longrightarrow H_2N \ C\text{-}N \ C\text{-}N\text{-}C\text{=}O \xrightarrow{HN\text{-}C\text{=}O}$$

$$H_2N \ C\text{-}N \ C\text{-}N\text{-}C\text{=}O \xrightarrow{Na^+N^-\text{-}C\text{=}O} etc$$

Scheme 1.37. The mechanism of polymerization of lactams

The above mechanism illustrates the following points:

(i) the opening of the lactam ring to produce the amide anion

(ii) hydrogen abstraction from the monomer by the amide anion to produce the activated monomer, and

(iii) the nucleophilic attack of activated monomer on the acylated lactam ring at the propagating end.

NCA have been polymerized using a tertiary mine catalyst by a similar mechanism.


## 1.4.5. Mechanisms of coordinate anionic polymerization

### (a) A brief introduction

Since Pruitt and Baggett[88] obtained high molecular weight polypropylene oxide polymers using $FeCl_3$ in 1955, Price[168] proposed the 'coordinate anionic mechanism', in which the monomer was coordinated to the catalyst and activated towards nucleophilic attack, providing orientation of reacting molecules, leading to sterospecific polymerization. The mechanism is shown in scheme 1.38 below:

$$Fe\text{-}OR_n \;+\; CH_2\text{-}CH_2\diagdown O\diagup \longrightarrow \quad \overset{\delta-}{Fe-OR_n} \quad \longrightarrow \quad Fe\text{-}O\text{-}C\text{-}C\text{-}OR_n$$

**Scheme 1.38. The coordinated anionic mechanism of the polymerization of ethylene oxide**

The repeated attack of the $OR_n$ group on a ring carbon atom of coordinated epoxide resulted in coordination anionic propagation without formation of an ion pair.

An interesting feature of these coordinated anionic catalysts is that stereoregular polymers can be obtained. For example when a racemic mixture of propylene oxide was polymerized using $ZnEt_2$/MeOH system two homopolymers of (+) polypropylene oxide and (-) polypropylene oxide were produced. An 'enantiomeric site' has been proposed by Sheldon et al.[169] and by Tsuruta[170] where the catalyst system consist of two different sites which are in a mirror-image relationship stereochemically. One site selects one enantiomer and the other site selects the other. During propagation the ring opens at the $CH_2$-O bond which results in the retention of

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the configuration of the chiral carbon. Without the asymmetric component present in the catalyst system the concentrations and the activities of both sites are the same which leads to asymmetrical polymer.

The coordinated anionic catalysts tend to give rise to living polymerizations. The $ZnEt_2/H_2O$ system[171] when used to polymerize propylene oxide it was found that the molecular wight increased as did the % conversion by the addition of further monomer to the reaction mixture after polymerization was complete. It must be noted that though these systems give living polymerizations the molecular weight distribution is not narrow ($M_w/M_n = 3$). In general, coordinate catalysts of the type mentioned above are not favourable for the synthesis of polymers with controlled length. This is because the catalysts have different sites with different reactivities forming broad molecular weight distributions.

(b)  Further developments in coordinated anionic catalysts - metalloporphyrins as intiators

In 1978, novel initiators were produced and found to be extremely effective for the living polymerizations of epoxides to give polymers with controlled chain length and narrow molecular weight distribution[104,105]. These initiators are the metalloporphyrins of particularly zinc, aluminium and manganese. The work involving these initiators has been extensively carried out on ethylene oxide and propylene oxide. Larger ring systems have not been studied.

The catalyst is prepared by using 5, 10, 15, 20 tetraphenylporphine - 21H,23H (TPPH$_2$) dissoved in a suitable solvent e.g. $CH_2Cl_2$ and reacted with diethylaluminium chloride, $AlEt_2Cl$. This gives rise to a product known as (5,10,15,20-tetraphenyl porphinato) aluminium chloride [(TPP)AlCl], consider scheme 1.39.

(TPPH$_2$)

AlEt$_2$Cl/CH$_2$Cl$_2$

Room temp

[(TPP)AlCl]

$$+ \ 2C_2H_6 \uparrow$$

**Scheme 1.39. Preparation of the [(TPP)AlCl] catalyst**

Substituted porphyrins can also be used to prepare the following initators.

[(TPP)AlCl] is the most active catalyst of the metalloporphyrins studied. Others include the following:

(i)  TPPH$_2$ $\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{AlEt}_3}$ (TPP)AlEt $\xrightarrow[\text{65°C}]{\text{CH}_3\text{OH}}$ (TPP)Al-OCH$_3$

(ii)  TPPH$_2$ $\xrightarrow[\text{CHCl}_3]{\text{Mn(OAc)}_2}$ (TPP)Mn-OAc



p - Cl.TPPH$_2$

p - OCH$_3$.TPPH$_2$ is substituted by Ph-OCH$_3$

(iii)   p - Cl.TPPH$_2$ $\xrightarrow[\text{CH}_2\text{Cl}_2/\text{RT}]{\text{AlEt}_2\text{Cl}}$ (p - Cl.TPP)AlCl + 2C$_2$H$_6\uparrow$

(iv)   p - CH$_3$O.TPPH$_2$ $\xrightarrow[\text{CH}_2\text{Cl}_2/\text{RT}]{\text{AlEt}_2\text{Cl}}$ (p - CH$_3$O.TPP)AlCl + 2C$_2$H$_6\uparrow$

(v)



Etioporphyrin (Etio H$_2$)

$\downarrow$ AlEt$_2$Cl

CH$_2$Cl$_2$/RT

(Etio)AlCl + 2C$_2$H$_6\uparrow$

(vi)



$$\downarrow \text{ZnEt}_2$$
$$\text{CH}_2\text{Cl}_2$$



$$+ \text{ C}_2\text{H}_6 \uparrow$$

Zinc N-methyl and phenyl-5, 10, 15, 20-tetraphenylporphyrin

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These initiators also give rise to living polymers of β-lactones[172], episulphides[173]. Block copolymers can also be synthesised and the living nature of the system ensures control over the chain length of each segment. Examples of copolymerizations include ethylene oxide with propylene oxide[174] and propylene oxide with carbon dioxide[175].

The mechanism of these polymerizations is thought to involve a coordinated anionic step; an illustration of this mechanism is shown in scheme 1.40:

**Scheme 1.40.   Mechanism of polymerization of ethylene oxide with [(TPP)AlCl] catalyst**

It is believed that polymerization takes place by activation of the Al-Cl bond by first coordinating the monomer to the Al atom, which is electron deficient, by way of the electron rich oxygen atom of the monomer. Nucleophilic attack of the chloride ion on the α-carbon of the monomer follows and the ring then opens to form the propagating structure. During propagation further coordination of the monomer occurs in a similar way. However nucleophilic attack at the α-carbon is thought to occur by the ethereal oxygen atom which is directly linked to the Al atom as shown in scheme 1.40.

The type of mechanism that takes place with the metalloporphyrins is dependent upon the monomer in question. In 1986, Inoue et al.[176] discovered that living polymerization of methacrylic esters by (porphinato)aluminium methyl, (TPP)Al-Me, took place at room temperature upon irradiation with visible light (> 420nm). The reaction did not proceed substantially in the dark. This indicates the complexity associated with these types of catalysts. There is an obvious need for much further progress to be made in order to understand the mechanism in relation to the type of catalyst and the type of monomer used.

## 1.4.6. Immortal polymerization

More recently, Inoue proposed a new concept of 'Immortal Polymerization' for the ring opening polymerization epoxides and $\beta$-lactones[177]. Living polymerization does not ensure immortality as termination can take place by addition of protonic reagents.

Using the aluminium porphyrins such as (TPP)Al-Cl, as described in the above section, it was found that the polymerization still continued even in the presence of a protic acid. This is remarkable considering that the growing polymer is of a nucleophilic nature and compounds such as water, HCl, ROH were unable to terminate polymerization. The reaction gives a polymer with a narrow molecular weight distribution and unlike living polymerization the number of polymer molecules is greater than that of the initiator. The immortal polymerization can be accounted for by the unusual reactivity of the aluminium atom-axial ligand bond (Al-X).

When propylene oxide was polymerized using (TPP)Al-Cl, a living system was observed. Addition of hydrogen chloride should have terminated the living polymerization, but instead it actually assisted the polymerization as further addition of propylene oxide was polymerized as well[177].

The reaction scheme below indicates how the protic reagent might participate in the polymerization:

$$(TPP)Al\text{-}OR + HCl \rightleftharpoons (TPP)Al\text{-}Cl + H\text{-}OR$$

$$(TPP)Al\text{-}Cl + n\ CH_2\text{---}CH_2 \rightleftharpoons (TPP)Al\,(OCC)_n\,Cl$$

(with the epoxide O bridging the CH₂–CH₂)

$$(TPP)Al\,(OCC)_n\,Cl + H\text{-}OR \rightleftharpoons (TPP)Al\text{-}OR + H(OCC)_n\,Cl$$

The addition of HCl generates the original catalyst which can be utilised to polymerize a further batch of monomer if re-introduced into the system. The chain transfer reactions shown above are reversible and occur much more rapidly than chain growth . The consequence of this is that narrow molecular weight distribution of polymers are obtained. It has been estimated that the chain transfer reactions are about 8-10 times faster than the propagating reaction[177]. Thus with immortal polymerizaton the number of polymer molecules is not limited by the amount of initiator but can be increased if required by the addition of a protic acid.

## 1.5. Kinetics of ring-opening polymerizations

## 1.5.1. Kinetics of cationic ring-opening polymerizations

The propagation process of cationic ring-opening polymerizations is thought to occur via an $S_N2$ type mechanism. This occurs between the active chain end which holds the positive charge and the monomer itself. Thus:

The rate of the propagating step can be expressed by the second-order equation (1):

$$R_p = k_p[P^+][M] \tag{1}$$

where $k_p$ is the propagation rate constant, and $[P^+]$ and $[M]$ are the concentrations of the propagating onium ion (or the $3°$ oxonium ion in the case of cyclic ethers) and monomer respectively. The oxonium propagating species may either exist as an ion-pair of various

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degrees of association or as a free ion. Work carried out on THF[178,179] and oxepane[180] indicates that the rate constants for propagation by the free ion ($k_p+$) and by the ion pair ($k_p\pm$) are approximately the same. Since $k_p\pm \approx k_p+$, the $k_p$ in equation (1) may be taken to repesent the overall kinetic reactivity. This finding is contrary to anionic systems where $k_p+ > k_p\pm$.

Using equation (1) $k_p$ can be calculated but in order to do so [P$^+$] must be determined first. Two methods have been developed to calculate the concentrations of the active centres. The methods are based upon the end-capping techniques, namely, the 'Phenoxyl End Capping' and the 'Phosphine-End-Capping' have been used.

In the Phenoxyl End-Capping, the active centres are converted to the phenyl ether by reaction with sodium phenoxide. The concentrations of the phenoxyl end groups are then determined by U.V absorption at $\lambda_{max}$ =273nm[181]:

$$ \overset{+}{-O} \bigcirc \quad + \text{ NaOPh} \longrightarrow \quad \text{-CH}_2\text{-O-Ph} $$
$$ \text{A}^- $$

This reaction is fast and quantitative and has been applied to the polymerization of oxetane and its substituted derivatives[182]. THF[183], oxepane[184] and 7-oxabicyclo (2.2.1)heptane derivates[185,186]. This method was later modified by using sodium picrate instead of sodium phenoxide[187]. The advantage this had was the picryl ether group has a higher extinction coefficient, $\varepsilon = 1.36 \times 10^4$ litre mol$^{-1}$cm$^{-1}$ compared with the phenyl ether $\varepsilon = 1.93 \times 10^3$ litre mol$^{-1}$cm$^{-1}$.

The Phosphine End Capping is based upon the following reaction:

$$ \overset{+}{-O} \bigcirc \quad + \text{ PR}_3 \longrightarrow \quad \text{-CH}_2\text{-P}^+\text{-R}_3 $$
$$ \text{A}^- \qquad\qquad\qquad\qquad \text{A}^- $$

The concentration of the phosphonium ion can be calculated using $^{31}$P FT. NMR.

Apart from the end-capping techniques, direct NMR observations have been used to determine the concentration of the active centres, THF, oxepane, 6-membered cyclic phosphates, 3,3-dimethylthietane and 2-oxazoline have been examined[188-193].

Using the data available the following conclusions about the rate constants for propagation of ring-opening polymerizations are obtained

(i) $k_p$ at 0°C covers a wide range of values from $10^{-8}$ to 18 $dm^3mol^{-1}s^{-1}$

(i) $k_p$ is higher for monomers with higher ring strains which indicates that the ring-opening activity is far more significant than the nucleophilicity of the incoming monomer.

(iii) The general order of $k_p$ values for rings of similar strain:

cyclic ether > cyclic sulphide > cyclic amine > cyclic imino ether

This order is opposite to that of the stabilities of the corresponding onium chain ends. This can be explained by the electronegativities of the particular heteroatom involved, the higher the electronegativity of the heteroatom the more strain exists on the cyclic onium.

## 1.5.2. Kinetics of anionic ring-opening polymerization

Gee et al.[194,195] studied the polymerization kinetics of ethylene oxide in dioxane, using sodium methoxide as catalyst with small excess of free methanol. The polymerization rate equation (2) is shown below:

$$\frac{-d[E]_0}{dt} = k\, C_0\, [EO] \qquad (2)$$

[EO] = ethylene oxide concentration and $C_0$ = initial concentration of NaOMe; k = rate constant.

The presence of free alcohol in the polymerization system in polar solvent and/or at higher reaction temperature may give rise to the series of reactions shown in equation 3 below, in which x and y represent all integral values from zero to infinity.

$$CH_3(OC_2H_4)_xONa + CH_3(OC_2H_4)_yOH$$

$$\updownarrow$$

$$CH_3(OC_2H_4)_xOH + CH_3(OC_2H_4)_yONa \qquad (3)$$

This means that each alcohol molecule, as well as each alkoxide, would be a growing end of a polymer molecule. The degree of polymerization $DP_n$ at time t can be expressed by equation (4) below in which the subscripts o and t indicate initial time and time t and $[CH_3OH]_o$ is the initial concentration of free methanol.

$$DP_n = \frac{([EO]_o - [EO]_t)}{([CH_3OH]_o + [catalyst]_o)} \qquad (4)$$

Gee found that the $DP_n$ values from equation (4) agreed with the experimental values he obtained[195]. Gee suggested that the rate equation was not dependent upon the concentration of free methanol. However the activation energy was found to be higher with the presence of free methanol which indicated a termolecular mechanism prevailed in this case. The rate equation can be expressed as shown below:

$$\frac{-d[EO]}{dt} = k_3 \, C_o \, [EO][CH_3OH]_o$$

The inclusion of methanol in the above expression indicates that it has a direct effect on the dielectric constant.

## 1.6. Molecular weight distribution in polymerization

Information regarding the course of polymerization reactions may be obtained from the study of the molecular weight and molecular weight distribution changes that take place during the polymerization. It has been found that the number average and weight average molecular weights may or may not change during the course of a polymerization, depending upon the kinetics and mechanisms of reaction. An examination of how the different types of mechanism affect molecular weight and molecular weight distribution will be discussed below; these

include the following mechanisms, stepwise (condensation), free radical addition, ionic living and ring-opening polymerizations. These discussions will be limited to the formation of linear polymers only.

## 1.6.1. Stepwise polymerization

The classic example to report here involves a series of experiments carried out by Flory in 1939. He described the kinetics of polyesterification of a reaction between 1,6-hexandioic acid and ethanediol over a wide range of temperature using $\underline{p}$ - toluenesulphonic acid as catalyst. The kinetics of this reaction was determined by the rate of disappearance of carboxylic acid groups by titrating the reaction mixture with methanolic KOH.

The kinetics revealed by Flory suggest that the reaction is fast and a high average chain length is obtained. The kinetics expression therefore becomes

$$\frac{-d[COOH]}{dt} = k[COOH][OH][H^+] = k'[COOH][OH]$$

where k' includes the rate constant k and the [catalyst] which also remains constant, hence

$$\frac{-dc}{dt} = k'c^2$$

integration gives
$$C_0k't+1 = \frac{1}{(1-p)}$$

where p = extent of reaction.

Therefore a plot of $\frac{1}{(1-p)}$ against time gives a linear plot as shown in fig 1.2.

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$$\frac{1}{1-p}$$

time

**Fig 1.2. Relationship between $\frac{1}{(1-p)}$ and time in a stepwise polymerization**

The formation of long chain polymers in stepwise polymerizations is a random process leading to chains of widely varying length. Due to this random nature the distribution of chain length obtained in a given sample can be calculated using statistics. The problem is to calculate the probability of finding a chain composed of x basic structural units in the reaction mixture at time t for either of the two reactions

$$x\ A\text{-}A\ +\ xB\text{-}B \longrightarrow A\text{-}A\!\!\left[\text{B-AB-A}\right]_{x-1}\!\!B\text{-}B \qquad \text{or}$$

$$xA\text{-}B \longrightarrow A\!\!\left[\text{BA}\right]_{x-1}\!\!B$$

To calculate the probability that a functional group A or B has reacted, the probability for one of the groups has to be determined say group A at a time t.

The probability that (x-1) A groups have reacted to form a chain is given by

$$p^{x-1}, \text{ where p is the extent of reaction}$$

Carothers defined p as $\quad p = \dfrac{(N_0\text{-}N)}{N}$

where p = extent of reaction at time t

$N_0$ = original number of molecules in an A-B monomer system

N = is the number of all molecules remaining at time t.

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Since $X_n$ (number average chain length) $= N_0/N$ then the above expression for p can be re-written as

$$X_n = \frac{1}{(1-p)} \qquad (1)$$

where (1) is known as Carothers equation

It follows that if A groups remain unreacted the probability this uncondensed group is (1-p) and so the probability $P_x$ of finding one chain x units long (i.e. an x-mer) is

$$P_x = (1-p)p^{x-1} \qquad (2)$$

Since the fraction of x-mers in any system equals the probability of finding one, the total number $N_x$ present is given by

$$N_x = N(1-p)p^{x-1} \qquad (3)$$

where N = total number of molecules present in the reaction. Substituting the Carothers equation (1) into (3) gives

$$N_x = N_0(1-p)^2p^{x-1} \qquad (4)$$

The variation of $N_x$ for values of p and x are shown in figure 1.3. If equation (4) is expressed in terms of mass fractions w (4) becomes

$$w_x = x(1-p)^2p^{x-1} \qquad (5)$$

Equations (4) and (5) suggest that large sized chains are only obtained with high conversions, as p exceeds 0.95 the fraction of low molar mass material decreases.

FIGURE 1.3. (a) Number fraction distribution curves for linear step growth polymerizations. Curve 1, $p = 0.9600$; Curve 2, $p = 0.9875$; Curve 3, $p = 0.9950$. (b) Corresponding weight fraction distributions for the same system.

Number average and weight average can be calculated as follows

$$M_n = N_x \Sigma \, (M_0/N_x)/N = M_0/(1-p) \quad \text{and}$$

$$M_w = M_0(1+p)/(1-p)$$

where $M_0$ is the molar mass of the repeat unit

$$\text{The polydispersity} = \frac{M_w}{M_n} = \frac{M_0(1+p)/(1-p)}{M_0(1+p)} \doteq \frac{(1+p)}{(1-p)} \qquad (6)$$

Since $DP_n$ i.e. the average degree of polymerization is defined as

$$DP_n = \frac{\text{Number of molecules initially present}}{\text{Number of molecules present at time t}} = \frac{C_0}{C}$$

$$\therefore DP = \frac{1}{(1-p)}$$

From Flory's work $1/1-p$ against time i.e. conversion is a linear increase, since $DP_n \propto M_n$ also increases linearly with conversion. Finally polydispersity which is a measure of the range of polymer of different molecular weights increases with % conversion according to equation (6).

## 1.6.2. Free radical addition polymerization

The kinetics of free radical addition polymerization can be summarised in equation (1) below

$$R_p = k_p \left( f\frac{k_d}{k_t} [I] \right)^{1/2} [M] \qquad (1)$$

where $R_p$ = rate of polymerization ie propagation

$k_p$ = rate constant for the polymerization of propagation

f = initiator efficiency

$k_d$ = rate constant of initiation

[I] = concentration of initiator

$k_t$ = rate constant of termination which includes combination i.e. coupling of two chains $kt_c$ and disproportionation $kt_d$

[M] = concentration of monomer


Free radical polymerization can be distinguished from step-wise condensation polymerization by the fact that the active species is short lived. The rate of polymerization and $DP_n$ are then kinetically controlled.


The kinetic chain length $v$ and the average degree of polymerization $DP_n$ can be derived using equation (1). The kinetic chain length $v$ is the measure of the average number of monomer units with its life time and is related to $X_n$ ($DP_n$) through combination. Thus combination leads to $DP_n = 2v$ if however the only mechanism of termination is disproportionation then $DP_n = v$. Under steady state conditions

$$v = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p^2[M]^2}{2k_t R_p} \qquad (2)$$

where $R_p$ = rate of polymerization

$R_t$ = rate of termination

$R_i$ = rate of initiation


From equation (2) it can be seen that $v$ is proportional to $[M]^2/R_p$. Any change in $v$ with conversion reflects a change in $[M]^2/R_p$ with reaction. Consider figure 1.4.

DP$_n$ (vertical axis)

% conversion (horizontal axis)

**Figure 1.4.  Dependence of DP$_n$ on % conversion in a free radical polymerization**

This plot differs greatly from the corresponding plot shown in stepwise polymerization where it was observed that 1/(1-p) against conversion gave a linear increase.

This means that a high molar mass polymer is formed immediately the reaction begins and both DP$_n$ and M$_n$ show little variation throughout the course of the reaction; Long reaction times only increases the polymer yield (% conversion) but not M$_n$.

### 1.6.3.  Ionic polymerization

For simplicity, a general kinetic scheme will be described which will adequately explain both cationic and anionic kinetics chain processes.  Consider the mechanism:

$$I + M \xrightarrow{k_i} M^*$$

$$M_n^* + M \xrightarrow{k_p} M^*_{n+1}$$

$$M^*_n \xrightarrow{k_t} P_n + X$$

From the above scheme, the overall rate of polymerization for such ionic process is given by

$$R_p = k_p [M][M^*] \tag{1}$$

where $R_p$ = rate of polymerization

$k_p$ = rate constant of propagation

[M] = concentration of monomer

[M*] = concentration of active species

Since
$$R_i = k_i [I][M] \tag{2}$$

where $R_i$ = rate of initiation

$k_i$ = rate constant of initiation

[I] = initiator concentration

[M] = monomer concentration

and
$$R_t = k_t[M^*_n] \tag{3}$$

then assuming steady state

$$R_i = R_t$$

$$[M^*] = \frac{k_i}{k_t} = [I][M] \tag{4}$$

substituting (4) into (1) gives an overall polymerization

$$R_p = k_p[M][M^*]$$

$$R_p = \frac{k_p \, k_i}{k_t} [I][M]^2 \tag{5}$$

Since the chain length $(X_n)$ is given by

$$X_n = \frac{R_p}{R_t} \qquad\qquad X_n = \frac{k_p}{k_t} [M]$$

If termination is obtained only through chain transfer then

$$X_n = \frac{k_p}{k_{tr}}$$

and since the chain length will be statistically controlled the molecular weight distribution will be broad.

## 1.6.4. Living polymerizations

For the purposes of this discussion, living polymerizations exhibit initiation and propagation reactions only; termination chain transfer and back-biting do not take place. This means that propagation should continue until all the monomer has been consumed, leaving the active centre intact and able to propagate, or 'alive'. Further additions of fresh monomer will result in the growth of the active centre. Termination should only be possible by the addition of a substance that reacts with the propagating centre. There are two types of living polymerization which can be distinguished by the kinetics, depending on whether the rate of initiation is fast compared with the rate of propagation, or whether it is of similar or lower rate. If $R_i \gg R_p$ the active centres are produced in a very short time and polymers of narrow molecular weight reactions proceed uniformly with respect to all growing polymer molecules. Furthermore the number of polymer molecules is the same as that of the initiator. This would suggest the following:

(i) $M_n$ would increase linearly with increasingly % conversion and

$$DP_n = \frac{[M]_0 - [M]_t}{[I]} \times n$$

where n is an integer that depends on the mechanism of initiation, for example the initiation of styrene with naphthalide/Na n = 2 i.e.



$$2 \left[ \overset{\bullet}{C}H_2\overset{-}{C}HPh \right] \longrightarrow Ph\overset{-}{C}HCH_2CH_2\overset{-}{C}HPh$$

(ii) $M_n$ would also increase linearly with increasing [monomer]:[catalyst] ratio.

(iii) The polydispersity would remain low (~ 1.10-1.50) throughout the course of the polymerization.

(iv) Initiator efficiency would ~ 100%.

There are a few examples of living polymers where $R_i < R_p$ i.e. the active centres are produced slowly. However because there is no formal termination step these are also classed as living. The consequence of this is that

(i) $M_n$ would increase with % conversion but the distribution would broaden over a period of time.

(ii) the number of polymer molecules would not necessarily equal the number of initiator molecules.

(iii) initiator efficiency is conversion dependent.


## 1.6.5. Ring-chain equilibria

When the monomer used in a polymerization is a cyclic molecule, then, in addition to the factors described in section 1.6 to 1.6.4, controlling molecular weight and molecular weight distribution, ring-chain equilibria may exist. This is best illustrated by the polymerization of oxirane (E.O). During the activated complex cationic polymerization of EO, the propagating centre is believed to exist as the oxonium ion. This ion may propagate by reaction with a monomer molecule, or may undergo an intramolecular reaction, leading to cyclic oligomer formation - consider scheme 1.41.

**Scheme 1.41:** **Example of a ring-chain equilibrium reaction. Known to exist in the polymerization of ethylene oxide**

Such polymerizations are normally described by having the same functional group in the monomer and polymer; in this case ethereal oxygen.

Under certain conditions the polymerization of oxetane[63,196] and ethylene oxide[197], cyclic oligomer may account for up to 35%. Tetrahydrofuran however may account for only 3%. Furthermore, polymerizations of the monomers

$$\boxed{-O\text{-}CH_2\text{-}(OCH_2CH_2)_z}$$

where $z = 3,4,5$ have been carried out cationically and a series of cyclooligomers were observed[198,199]. For example when $z = 3$ macrocycles containing 220 ring atoms have been observed.

The presence of the bimodal distribution obtained by size exclusion chromatography and the detection of macrocycles by chemical means for both ring opening polymerizations and ring opening metathesis polymerization are explained by the theory of ring-chain equilibria postulated by Jacobson and Stockmayer in 1950.

The theory states that above the equilibrium concentration for polymer formation, the relative concentrations the oligomers are independent of the initial concentrations of the monomer and the catalyst; only a slight dependency on temperature is observed, and above the equilibrium concentration of monomer the [polymer]/[oligomer] ratio increases with increasing concentration of monomer. The equilibrium between open chain polymer and each cyclic oligomer ($M_x$) may be summarised as:

$$A\text{-}M_y\text{-}B \rightleftharpoons A\text{-}M_{y-x}\text{-}B + M_x$$

$$\text{chain} \rightleftharpoons \text{chain} + \text{ring}$$

$$\therefore \qquad P_x = \frac{(x_w - 1)}{(x_w + 1)} \qquad \text{(for } x_w \gg 1, \text{ i.e. high conversion of}$$

$$\text{monomer to polymer)}$$

where $P_x$ is the fraction of the equivalent initial monomer converted at equilibrium;

and $X_w$ is the weight average degree of polymerization of linear polymer.

The equilibrium constant ($K_x$) for the formation of the cyclic oligomer ($M_x$) may be written as

$$K_x = \frac{[A\text{-}M_{y-x}\text{-}B][M_x]}{[A\text{-}M_y\text{-}B]} = \frac{[M_x]}{[P_x]} = [M_x]$$

According to the Jacobson-Stockmayer equation relating to such equilibria the concentration $[M_x]$ of a single species in the distribution should be proportional to $X^{-2.5}$ which is correct for a constant characteristic ratio $C_x$ ($C_\infty$) according to the following equation

$$[M_x] \approx K_x = (\frac{3}{2\pi})^{3/2} \frac{1}{2} N_A (nC \times 1^2)^{-3/2} X^{-2.5}$$

where $N_A$ = Avogadro's number.

n = is the number of bonds per monomer unit.

$$\therefore [M_x] = K_x \propto X^{-2.5}$$

$$\therefore \ln [M_x] \propto -2.5 \log x$$

This means that plots of $\ln[M_n]$ against $\ln x$ for a series of different ring size cyclic monomers should give a linear relationship with gradient of -2.5. The intercepts of such plots also show the predicted dependence on ring size.

It should be noted that the concentrations of certain oligomers particularly tetramers, appear to deviate from predicted behaviour.

## 1.7. Scope of this work

The aims of this project were:

(i) To investigate the kinetics and the mechanisms of the polymerization of oxetane using three different cationic systems. $BF_3OEt_2$/ethanol, $BF_3OEt_2$/ethanediol, $BF_3OEt_2$/propantriol.

(ii) To copolymerize oxetane and THF cationically and to investigate the molecular weight distribution differences compared with that of the homopolymerization of oxetane.

(iii) To produce a living polymerization of oxetane and other substituted oxetanes using a metalloporphyrin catalyst. An investigation of the kinetics and mechanism of this polymerization.

(iv) To investigate the control of stereoregularity by the metalloporphyrin catalyst in the polymerization of cyclic ethers.

# CHAPTER 2: EXPERIMENTAL

## 2.1. Vacuum techniques

The intermediates involved in ring-opening polymerizations such as onium ions (cationic) or alkoxide ions (anionic) are known to be very sensitive and are particularly sensitive towards oxygen and moisture. The same is true of the catalyst components used in this project. For this reason the purification and preparation of monomers, solvents and catalyst solutions as well as most polymerizations were carried out using either high vacuum techniques or in an atmosphere of argon to exclude these impurities.

## 2.1.1. The vacuum line

The vacuum line is shown in figure 2.1. It is constructed from glass and consisted of a manifold (A) with an adjoining bulb (B) which enabled the volume of the manifold to be increased during degassing procedures, together with four greaseless taps (C). A greased tap (D) enabled the connection of the manifold to two vacuum pumps in series, an Edwards rotary pump (E) which produced a pressure of $10^{-3}$ torr and a mercury diffusion pump (F) to lower the pressure even further to approximately $10^{-5}$ torr. The pressure inside the system was measured by a vacustat (G). Liquid nitrogen traps (H) were situated either side of the mercury diffusion pump to prevent the escape of vapours into the laboratory and to protect the Edwards rotary pump during evacuation.

**KEY**

| | | |
|---|---|---|
| ▨ Ground glass joints | | ▨ Mercury |
| ▨ Liquid nitrogen | | ▨ Water |
| ⊗ Greaseless tap | | |

**Figure 2.1. The high vacuum line**

## 2.1.2. Treatment of glassware

All the glass apparatus was cleaned thoroughly by soaking over night in a concentrated solution of sodium hydroxide and ethanol which removed any residual high vacuum silicon grease. Chloroform was also used to remove any polymer residue and finally the apparatus were left in an oven at 240°C for a period of 24 hours prior to use.

## 2.1.3. Freeze-thaw degassing of solvents

The degassing of the liquids prior to distillation was carried out by attaching the solvent flask (figure 2.2 (a)) to the vacuum line with the main tap (D) closed. A Dewar vessel filled with liquid nitrogen was placed around the flask. When frozen, the appropriate taps were opened and the sysem evacuated. The main tap was then closed and the solvent allowed to thaw. This procedure was repeated until no further difference in vacuum was observed between freezing stages of the freeze and thaw processes.

## 2.1.4. Trap to trap distillation

The degassed solvent (or monomer) could then be transferred to another flask using the high vacuum line. An empty receiver flask, which had been dried in an oven at 240°C was attached to the vacuum line and evacuated. This was then immersed into liquid nitrogen. By closing the main tap (D) and opening the appropriate taps the contents of the solvent (monomer) flask were allowed to distill into the receiver flask.

## 2.1.5. Apparatus

The use of a high vacuum storage system required specially designed glass vessels for storage of monomers and catalysts. Solvents and liquid monomers were dried under argon or vacuum using flasks of the type shown in figure 2.2 (a). If the solvents or monomer were required in a polymerization vessel then they were collected in flasks shown in figure 2.2 (b) which could be attached to the polymerization vessel.

Catalyst solutions were prepared and stored under argon in flasks of the type shown in figure 2.2 (c). The solution was stored in bulb (X) and when required small amounts were transferred into (Y) by opening tap (A) (keeping (B) closed). A dry argon supply was connected at (Z), tap (A) was closed and then the vessel was inverted and tap (B) removed, the required quantity of solution could then be withdrawn from the vessel using a syringe.

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**Figure 2.2 (a).  Solvent drying flask**



**Figure 2.2 (b).  Solvent storage flask**

**Figure 2.2 (c).   Catalyst storage flask**

## 2.2.   Preparation and purification of materials

### 2.2.1.   Monomers

### 2.2.2.   Oxetane

Oxetane was obtained from Aldrich Chemical Co and was placed over calcium hydride for 48 hours in a stoppered flask (figure 2.2 (a)) with the greaseless tap cracked open to allow hydrogen to escape.  The oxetane was then degassed using freeze-thaw technique.

Slices of sodium metal were added to 10g of benzophenone in another flask of the same type, and the oxetane was then transferred to this flask by the trap-to-trap distillation procedure.  It was apparent that the oxetane was dry when a deep blue solution was produced with sodium benzophenone mixture:

$$\text{Na} \;+\; \underset{O}{\overset{\|}{\text{Ph-C-Ph}}} \;\longrightarrow\; \underset{\text{Ph}}{\overset{\text{Ph}}{\diagdown}}\!\dot{\text{C}}\text{-O}^-\,\text{Na}^+ \quad \text{blue (dry)}$$

$$\Big\downarrow \; H_2O$$

$$\text{NaOH} \;+\; \underset{\text{Ph}}{\overset{\text{Ph}}{\diagdown}}\!\dot{\text{C}}\text{-OH}$$

$$\Big\downarrow \; -1/2\,H_2$$

$$\underset{\text{Ph}}{\overset{\text{Ph}}{\diagdown}}\text{C=O}$$

The blue colour resulted form the production of a sodium benzophenone complex which will only develop in a completely dry environment. The oxetane was then distilled back into another dry flask by the trap-to-trap distillation method. This was carried out because a reaction between sodium and oxetane took place if the mixture was allowed to stand for sometime at room temperature. This reaction was accompanied by the evolution of a gas, presumably hydrogen and the consumption of the monomer.

### 2.2.3.   Tetrahydrofuran  (THF)

THF (hplc grade) was obtained from Fisons Chemicals Ltd.  The procedure carried out above for purification of oxetane was repeated for THF.  However there was no observed reaction between sodium and THF consequently there was no need to separate THF from the benzophenone complex.

### 2.2.4.   3,3-Dimethyl-oxetane

Exactly the same procedure was carried out as in section 2.2.1 for the preparation of this monomer.

### 2.2.5.   3-Methyl-3-oxetane  methanol

The monomer 3-methyl-3-oxetane methanol was obtained from Aldrich Chem. Co and was placed over $CaH_2$ for 48 hours in a stoppered flask with the greaseless tap cracked open to allow hydrogen to escape.  The monomer was then degassed using the freeze-thaw tecnique, and was ready for use.

### 2.2.6.   3-Methyl-3-nitratomethyl-oxetane

This monomer was supplied by the Ministry of Defence R.A.R.D.E division, as a 25% w/w solution in dichloromethane and used without further purification.

### 2.2.7.   Cyclohexene  oxide

Cyclohexene oxide was obtained from Aldrich Chemical Co.  and was placed over fresh $CaH_2$ for 48 hours.  The monomers was then degassed by the freeze-thaw technique and transferred to another dry solvent flask by the trap-to-trap distillation method.

### 2.2.8.   Cyclopentene  oxide

Procedure described as in section 2.2.7.

## 2.3.    Solvents

## 2.3.1.    Dichloromethane

Dichloromethane (high purity grade) was obtained from Romil Chenical Co. and placed over fresh $CaH_2$ for three days. It was then fractionally distilled under an inert atmosphere of argon. The distillation apparatus is shown in figure 2.3. The distillation was carried out in a closed system to prevent moisture contaminating the solvent. Before starting distillation the system was purged with argon for a period of twenty minutes after which valve X was closed and Y opened to entrap the argon distillation was then commenced.

Figure 2.3: Distillation apparatus
used for the purification of
dichloromethane.

A  Electric isomantle

C  Vigreux column

E  Condenser

G  Solvent flask

X } valves
Y

B  Round bottomed flask with a greaseless tap

D  Thermometer

F  Fraction cutter

H  Safety traps (one containing decalin)

## 2.3.2. THF

THF was used for size exclusion chromatography studies. The h.p.l.c. grade obtained from Fisons is expensive and therefore it was necessary to remove any peroxides by shaking each litre of solvent with $20cm^3$ of a ferrous salt solution made from 60g ferrous sulphate dissolved in $6cm^3$ of concentrated sulphuric acid and $110cm^3$ of water.

## 2.4. Catalyst

### 2.4.1 Boron trifluoride etherate

Boron trifluoride etherate, $BF_3OEt_2$ is a self-drying agent. It gives off toxic fumes on hydrolysis and has to be handled at all times in a fume cupboard.

The required concentration of $BF_3OEt_2$ solution was prepared in dried and distilled dichloromethane. The preparation was carried out in a dry box and the amount of $BF_3OEt_2$ was drawn out using a syringe into a catalyst flask already containing a known volume of dichloromethane. Depending upon the use either a 0.01M or 0.1 solution was prepared.

### 2.4.2. Ethanol

Ethanol was dried by refluxing $10cm^3$ under nitrogen gas over 1g of pure magnesium with a small amount of iodine, which converted the alcohol to the epoxide. At this stage an extra $120cm^3$ of the ethanol was added to the system and the mixture was allowed to reflux for a further 30 minutes:

$$Mg + C_2H_5OH \longrightarrow H_2 + Mg(OC_2H_5)_2$$

$$Mg(OC_2H_5)_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2C_2H_5OH$$

The alcohol was fractionally distilled under argon into another flask (using the system illustrated in fig. 2.3) containing activated molecular sieves (4Å), followed by degassing and storage under vacuum.

The required concentration of ethanol was made up in a catalyst flask already containing dried and distilled $CH_2Cl_2$. Again, either a 0.1M or a 0.01M solution was prepared.

### 2.4.3. Ethanediol

Ethanediol was initially placed over some fresh $CaH_2$ for a period of 24 hours, after which it was poured over dried (1g) magnesium (in a dry box) and left for 24 hours. The diol was followed by degassing and storage under vacuum. The required concentration of 0.1M or 0.01M was prepared in a catalyst flask again using $CH_2Cl_2$ as solvent.

### 2.4.4. Propantriol

Propantriol was dried by pouring over some activated molecular sieves (4Å). The molecular sieves were pre-heated at 600°C for a period of 24 hours, then placed in a dessicator containing anhydrous calcium chloride pellets. On cooling they were transferred into a solvent flask containing propantriol and left for a further 24 hours. Again the required concentration of propantriol was prepared using pure and dried $CH_2Cl_2$ as described above.

### 2.4.5. 5,10,15,20-Tetraphenyl-21H, 23H-porphine

5, 10, 15, 20-Tetraphenylporphine was purchased from Aldrich Chemical Co and was used withour further purification.

### 2.4.6. Aluminium diethyl chloride

Aluminium diethyl chloride was supplied from Schering Chemicals Ltd, in a specially constructed steel container stored under nitrogen as it reacts violently on contact with air or moisture. 0.05 molar solutions of aluminium diethyl chloride in $CH_2Cl_2$ were prepared by the following method.

The required quantity of dried $CH_2Cl_2$ was placed into the bulb (X) of the catalyst flask (figure 2.2(c)) in a dry box. The flask was then taken out of the dry box and inverted and clamped in a position with an argon line attached at Z, and subsequently tap A was removed.

The required quantity of aluminium diethyl chloride was then withdrawn by syringe from the steel cannister and injected into the dichloromethane through the barrel of tap A.

## 2.5.    Preparation of solutions

### 2.5.1.    Oxetane

The investigation of the kinetics of polymerization of oxetane using the conventional cationic catalysts required the use of both 10 and 20% w/w oxetane made up in pure, dried dichloromethane. The method to prepare these solutions is described below.

A clean solvent flask of the type shown in figure 2.2(b) was attached to the vacuum line and evacuated and then weighed. It was re-attached to the vacuum line and oxetane (pure/dried) was distilled into this flask from the storage flask using the trap-to-trap distillation method. After approximately 10g of oxetane had been collected the appropriate taps were closed and the vessels removed from the vacuum line. Dichloromethane was weighed into the solvent flask in the dry box to make up the required solution.

### 2.5.2.    Preparation of porphinato-aluminium chloride catalyst

The preparation of the porphinato-aluminium chloride catalyst was carried out in a solvent flask similar to that shown in figure 2.2(a). However instead of using a stopper a self-sealing rubber suba-seal was used. To the clean and dry flask 1.83g of 5,10,15,20-tetraphenyl-21H, 23H-porphine was added and the suba-seal was fitted tightly. The flask was then attached to the vacuum line and evacuated. It was then disconnected, after the vacustat indicated a good vacuum, and taken to the dry box where $50.0cm^3$ of pure/dried $CH_2Cl_2$ was added through the side-arm of the vessel. After about two hours, $10cm^3$ of 0.05 molar $AlEt_2Cl$ solution was added by syringe through the suba-seal to form the catalyst porphinato-aluminium chloride. The time allowed for the formation of the catalyst was about 8-10 hours, after which the vessel was re-connected to the vacuum line, the contents frozen, and re-evacuated to take away any gases that had formed during reaction between $AlEt_2Cl$ and porphyrin.

## 2.6. Polymerization techniques

## 2.6.1. Cationic homopolymerization of oxetane using calorimetry

The ring-opening polymerization of oxetane is an exothermic process ($\Delta H = -19.3$ kcal mol$^{-1}$). Therefore a system capable of measuring the change in temperature while the reaction is taking place in adiabatic condition could be used to measure rates of reaction for the system under study. For this reason the use of a calorimeter was employed.

### 2.6.1.1. Calorimeter Experiments

A modification of the technique described by Biddulph and Plesch[200] was used. The calorimeter is shown in figure 2.4. The temperature change associated with the ring-opening polymerization was measured by a thermistor, 2k$\Omega$ (GL23, RS Components Ltd), connected to a Knauer auto-potentiometer bridge adapted with a Serviscribe IS recorder.

In a typical experiment, the calorimeter was attached to the vacuum line through (C) with the monomer flask (figure 2.2 (b)) connected to (B). Tap (D) was closed and the whole system evacuated. After evacuation, tap (E) was closed and the required amount of monomer was transferred from the monomer flask attached at B. Tap (E) was opened to allow the oxetane solution into the bulb of the calorimeter and then re-closed. The calorimeter was placed on a magnetic stirrer and the thermistor was connected to the Knauer auto-potentiometer bridge. To ensure that the ambient temperature did not have an effect on the experiments, water at 30°C was continually passed through the double jacket. The balancing bridge was connected to a chart recorder which recorded the change in resistance of the thermistor as a function of a change in temperature.

The monomer solution which was added to the apparatus was left for 15 minutes to equilibrate until no more changes were registered by the potentiometric bridge. At this point the temperature of the monomer solution had risen from room temperature to 30°C. The bridge was then adjusted to zero and a stable base line was obtained on the chart recorder. The required amounts of catalyst solutions were injected through the rubber septum (J) using syringes, the co-catalyst being injected first. The bridge was calibrated and it was found that

the change in temperature associated with one full scale deflection (F.S.D) is equivalent to $12^{\circ}C$. Thus the rate of change in temperature during polymerization could be measured in units of $^{\circ}C$ $s^{-1}$, since the chart recorder was set at a constant speed of 2mm $s^{-1}$. The rates of polymerizations could be estimated from slopes of the lines obtained.

A , B , C  Glass joints

D, E, F, G, H  Greaseless joints

I  Ceramic probe

J  Rubber septum

K  Double jacket

L  Leads from probe

M  Magnetic follower



20 cm$^3$

Figure 2.4: Calorimeter

The rates in $^{\circ}C$ $s^{-1}$ were converted to conventional units mol $dm^{-3}s^{-1}$. This was carried out by plotting total deflection (mm) of each experiment against [oxetane] in m.mol $dm^{-3}$. A linear relationship with an intercept close to the origin was obtained and the slope was calculated to be $4.84 \times 10^{-3}$ mol $dm^{-3}$ $s^{-1}$ which is then multiplied by the rates in $^{\circ}C$ $s^{-1}$ x 17.6 to give the equivalent rate in mol $dm^{-3}$ $s^{-1}$. (The 17.6 figure arises from the calibration that a rise of $1^{\circ}C$ is equivalent to 17.6mm change from the base line).

## 2.6.2.   Cationic copolymerization of oxetane and THF

In this series of experiments a vessel similar to that shown in figure 2.2 (a) was used. The vessel was slightly modified as it was graduated and instead of a glass stopper a suba-seal was placed. The weighed vessel was attached to the vacuum line through the side arm and evacuated. Pure and dried oxetane was then transferred into the 'copolymerization' vessel by the trap-to-trap distillation method. The amount of oxetane transferred was then weighed. The vessel was re-attached to the vacuum line. The stock-bottle containing THF over sodium benzophenone was attached and the required amount of THF was transferred over to the copolymerization vessel by the usual trap-to-trap method. The vessel was taken off the vacuum line and $1cm^3$ of 0.1M ethanol and $BF_3.OEt_2$ solutions were injected through the suba-seal. These experiments were repeated using various ratios of oxetane and THF but the catalyst concentrations were kept constant.

## 2.6.3.   Coordinated anionic polymerizations

In this series of experiments the catalyst 5, 10, 15, 20-tetraphenylporphyrin was used to polymerize the following monomers; oxetane, 3, 3-dimethyloxetane, 3-methyl-3-oxetane methanol, 3-methyl-3-nitratomethyl-oxetane, cyclohexene oxide, cyclopentene oxide and THF.

The polymerization vessel used for these experiments is shown in figure 2.5. The flask was placed in a glovebox that had been filled with dry argon and 0.473g (0.77mmol) of 5, 10, 15, 20-tetraphenyl-porphine was introduced into the vessel. $15cm^3$ of 0.05 molar $AlEt_2Cl$

solution was then added by syringe through the suba-seal and reaction to form the catalyst for the polymerization, 5, 10, 15, 20-tetraphenyl-porphine aluminium chloride was allowed to take place for 4 hours. After this period approximately 17.5g (0.302 mol) of monomer was then distilled under vacuum into the vessel. The flask was subsequently removed sealed and removed from the vacuum line and polymerization was carried out at 55°C by immersing the flask in a bath at constant temperature. Samples of the polymerizing solutions were removed at regular intervals by syringe for molecular weight analysis. The rubber septum was renewed prior to each experiment.



**Figure 2.5. Vessel used for the polymerization using 5,10,15,20-tetraphenyl porphine catalyst**

## 2.6.4. Dilatometry

### (i). Principles

Dilatometry is a technique used to measure the contraction or expansion of liquids or solids. During a polymerization a contraction of material is usually observed as there is an increase in

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density while monomer is converted to polymer. It has been considered that this technique gives sensitive measurement of the extent of conversion. The accuracy of the technique depends upon the following factors:

(a) the temperature must be kept constant, which is achieved by carrying the experiment in a bath at constant temperature, into which the dilatometer is immersed to avoid thermal fluctuations in the meniscus,

(b) when the polymerization reaction is exothermic, the heat evolved should be readily conducted to the wall of the vessel. Reduction of monomer/catalyst concentrations usually enable this to be achieved,

(c) the capillary must be sufficiently small in diameter to enable a high sensitivity and also have a uniform diameter, and

(d) the extent of conversion must be kept low because a highly viscous medium could prevent the movement of the meniscus.

The decrease in volume that occurs during polymerization is due to the difference in densities between the monomer and the polymer produced. The density of the polymer indicates the density of the polymer in solution and not the solid polymer. This density error is almost negligible and small compared with the sources of error in the measurement of rates of polymerization.

Since the volume change originates solely from the conversion of monomer molecules to monomer units in the polymer chain, the dilatometric method can be a very useful procedure to study the polymerization kinetics.

(ii) Treatment of data

In a dilatometer if the meniscus moves between two points, $\Delta h$ apart, the decrease in volume ($\Delta V$) would be:

$$\Delta V = \pi r^2 \Delta h$$

where r is the radius of the capillary.

If m grams of monomer are completly polymerized to m grams of polymer, the volume of contraction would be

$$\Delta V = V_p - V_m = \frac{m}{\rho_p} - \frac{m}{\rho_m} = m\frac{\rho_m - \rho_p}{\rho_p \cdot \rho_m}$$

Then
$$m = \Delta V \frac{\rho_p \cdot \rho_m}{\rho_m - \rho_p}$$

where $V_p$ = volume of polymer

$V_m$ = volume of monomer

$\rho_p$ = density of polymer

$\rho_m$ = density of monomer

If $\Delta M$ is the number of moles of monomer polymerized then

$$\Delta M = \frac{m}{M_m} = -\frac{\Delta V}{M_m}\frac{\rho_p \cdot \rho_m}{\rho_m - \rho_p}$$

where $M_m$ = molecular weight of polymer.

Assuming that the volume of the dilatometer (V) is much greater than the total volume change, then any variation in the monomer concentration $\Delta[M]$ can be approximated to:

$$\Delta[M] = \frac{\Delta M}{V} = \frac{1}{V}\frac{\Delta V}{M_m}\frac{\rho_p \cdot \rho_m}{\rho_m - \rho_p} = \frac{\pi r^2 \Delta h}{V M_m}\frac{\rho_p \cdot \rho_m}{\rho_m - \rho_p}$$

where $\dfrac{\pi r^2}{V M_m}\dfrac{\rho_p \cdot \rho_m}{\rho_m - \rho_p}$ is a constant K for the system under study.

So that
$$\Delta[M] = K\Delta h$$

The rate of polymerization ($R_p$) can then be obtained from a plot of $\Delta h$ as a function of time since:

$$R_p = \frac{-d[M]}{dt}$$

so that $R_p$ is proportional to $\Delta h/\Delta t$.

<u>(iii) Experimental</u>

The dilatometer used in this project is shown in figure 2.6. The dilatometer was attached to the vacuum line at (H) and the monomer flask similar to the one shown in figure 2.2 (b) was connected at (I). The whole system was then evacuated. Tap (J) was then closed. The required amount of porphinato aluminium chloride catalyst (preparation described in section 2.5.2) was injected through the suba-seal D. Tap (J) was then re-opened to distill off the dichloromethane from the solid catalyst, via trap-to-trap technique. Tap (J) was then re-closed and the monomer was introduced into the dilatometer through (I). Tap (G) was then closed and the empty monomer flask removed. The dilatometer was removed from the vacuum line and manipulated until the oxetane and the solid catalyst mixed together i.e. a homogeneous solution. The dilatometer was then placed in a constant water bath set at 39°C the solution was allowed to equilibrate before tap (E) was closed so to obtain a meniscus in the capillary (K).

The rates were calculated as a change in height,h against time,t.The capillary of the dilatometer was 1.5mm and to convert the rates into mol dm$^{-3}$s$^{-1}$ the multiplication factor was

$\Delta h / \Delta t$ x.05123/3600 (height in cm,time in hours).

Figure 2.6:   Dilatometer

## 2.7. Analytical techniques

## 2.7.1. Size-exclusion chromatography

Size exclusion chromatography (S.E.C) is a technique used for the determination of molecular weight and molecular weight distribution of polymer samples, provided that the sample is soluble in the solvent used for S.E.C. The object of S.E.C is to separate a sample of a polymer into its component fractions according to their sizes i.e. hydrodynamic volume. The diagram of the S.E.C is shown in figure 2.7.

S.E.C consists of a stationary phase, which is usually cross-linked polystyrene beads, packed into a column or a series of columns. The beads swell when the solvent is introduced and they are constructed in such a way that pores are created on their surface when this occurs. The sythesis of the beads is carefully controlled to yield a narrow distribution of pore sizes. When the polymer is eluted along the column at a constant flow rate, the smaller molecules are able to permeate a larger fraction of the available pores, unlike the bigger molecules which permeate the largest pores and hence travel down the column faster.

The eluent used for S.E.C in this project was THF. The THF was delivered at 1ml per minute by a Perkin-Elmer series 10 liquid chromatography pump. Samples of the polymer made up in THF (1-2% w/v) were injected into the columns by a 100$\mu$l valve and loop injector system. The solution then enters a series of columns, in this case five $\mu$-PL gel columns (supplied by Polymer Laboratories), the first being a short pre-column to remove suspended material and the remainder having exclusion limits of $10^2$, $10^3$, $10^4$ and $10^5$ Å respectively. The eluent from the columns was analysed by Knauer differential refractometer and a Perkin-Elmer LC - 85B variable wavelength spectrometer, connected in series. The output of each detector was recorded on a dual-pen chart recorder. The differential refractometer continously monitors the refractive index (R.I) of the eluting solution and compares it with the R.I of the pure solvent. Any difference generates a deflection on a chart recorder which is proportional to the concentration of the eluting polymer at that time i.e. weight of polymer per unit volume. The uv/visible detector responds to chromophoric groups either attached to, or part of the polymer

Fig. 2.7: Schematic diagram of the apparatus used for SEC

KEY

A    Precolumn              D    $10^4$ Å column          OP  Output to plotter

B    $10^2$ Å column        E    $10^5$ Å column          P   Peristaltic Pump

C    $10^3$ Å column        G    Pressure guage           S   Solvent reservoir

                            L    Valve and loop injector

backbone, and the response the detector gives is proportional to the concentration of the solute present in the solution and the molar extinction coefficient of the solute at the set wavelength.

## 2.7.1.2. Calibration of the S.E.C

To estimate the average molecular weight it is necessary first to determine how the molecular weight of the eluted polymer varies over the range of elution volumes. For this purpose polystyrene and polyTHF samples of narrow molecular weight distribution and of known molecular weights were injected into the column in turn. The volume of the solvent pumped through the column required to elute the polymer of specific molecular weight was measured and a calibration curve plotted as shown in figure 2.8. By comparison of the retention volumes of different polymers it was possible to obtain either a polystyrene or a poly THF equivalent molecular weight, for most polymers.

Figure 2.8: Calibration curves for the SEC

Pst y=10.762-0.24351x

Pthf y=9.4858-0.21523x

Log Mwt

Elution vol/ml

## 2.7.1.3. Mathematics of calibration



Volume of solvent pumped through system (cm$^3$)

**Figure 2.9. Typical size exclusion chromatograph**

The average molecular weight may be calculated as follows:

By definition

$$M_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \quad \text{and} \quad M_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

where $M_n$ = number average molecular weight

$M_w$ = weight average molecular weight

$N_i$ = number of molecules of molecular weight Mi in a given sample

$M_i$ = molecular weight of a given sample

If $W_i$ is the weight of polymer of molecular weight $M_i$ in a given fraction then

$$N_i = \frac{W_i}{M_i}$$

$\therefore$
$$M_n = \frac{\Sigma W_i}{\Sigma W_i/M_i} \quad \text{and} \quad M_w = \frac{\Sigma W_i M_i}{\Sigma M_i}$$

Since R.I response is a measure of the concentration of polymer of molecular weight $M_i$ at a given height $h_i$, then $W_i$ may be substituted by $h_i$, hence

$$M_n = \frac{\Sigma h_i}{\Sigma h_i/M_i} \quad \text{and} \quad M_w = \frac{\Sigma h_i M_i}{\Sigma M_i}$$

## 2.7.2. Nuclear magnetic resonance spectroscopy

High resolution nuclear magnetic resonance spectroscopy was carried out using Bruker AC 300 spectrometer. Solutions of the samples were made by dissolving the solids in deuterated chloroform ($CDCl_3$) and adding a small quantity of tetramethylsilane (T.M.S) as reference to each solution.

# CHAPTER 3
## CATIONIC POLYMERIZATION STUDIES OF OXETANE AND THF

### 3.1. The study of the kinetics of the polymerization of oxetane

### 3.1.1. Introduction.

No significant work concerning the kinetics of the cationic polymerization of oxetane has been reported since Farthing[98] and Rose[63]. There has been a growing interest in the cationic ring-opening polymerization of cyclic ethers, but information regarding the mechanism of polymerization still needs to be acquired which can be investigated by establishing the kinetics of polymerization. The initiators of interest in these studies involve $BF_3OEt_2/OH$ systems, and three different hydroxyl co-catalysts have been examined, ethanol, ethanediol and propantriol.

So far, the collective work by Farthing and Rose has indicated that the mechanism of the polymerization of oxetane using $BF_3$-$H_2O$ system includes three main stages; initiation, propagation and termination. The mechanism has been discussed in chapter 1 section 1.4.1, however to summarise, they concluded that the propagation step is considered as an $S_N2$ step which is of second-order type kinetics. Termination was considered to take place by either a transfer reagent or by the process of back-biting.

The first objective of this project was to establish the kinetics of propagation of oxetane using $BF_3OEt_2$ as initiator in conjunction with the three main co-catalysts. Dichloromethane was used as the solvent and the calorimeter discussed in chapter 2 section 2.6.1.1 was used for this study. The effect of the three catalyst systems in the molecular weight of polymers was also examined

### 3.1.2. The effect of $BF_3$:OH molar ratio on the rate of polymerization

Before any study of the kinetics of the polymerization of oxetane could be carried out, an investigation of the molar ratio of $BF_3$:OH which gave the optimum rate was examined. This was carried out in order to investigate the ideal conditions under which the kinetic order with respect to the concentrations of the catalyst and the monomer can be established.

A series of experiments was carried out to study the effects on the rate of polymerization of oxetane of [OH] at constant [BF₃], and [BF₃] at constant [OH]. In a typical experiment 5.0cm³

of 10% w/w oxetane solution was used. 0.1M BF₃ and 0.18M ethanediol ($\equiv$ 0.36M [OH]) were prepared using pure, distilled dichloromethane. The required volumes of these solutions were added, the solution of diol first, to the solution of oxetane. The rise in temperature associated with polymerization was recorded by a chart recorder. A typical chart recorder trace is shown in figure 3.1. (The detailed description of the procedure is discussed in chapter 2 section 2.6.1.1). The rates of polymerization, which are related to $\Delta T/\Delta t$ could be determined from this plot using the gradients of the lines obtained, taking into account $1^\circ C \equiv 17.6$ mm deflection. The effect of [OH], and [BF₃OE₂] on $\Delta T/\Delta t$ are given in table 3.1.

## Table 3.1. Effect of BF₃:OH molar ratio on the rate of polymerization

| $10^5$ moles x BF₃OEt | $10^5$ moles x OH | Ratio B:OH | $\dfrac{\Delta T/\Delta t}{^\circ C s^{-1}}$ |
|---|---|---|---|
| 9.25 | 4.20 | 2.20:1 | 0.704 |
| 9.25 | 6.35 | 1.46:1 | 0.700 |
| 9.25 | 8.40 | 1.10:1 | 0.910 |
| 9.25 | 16.6 | 0.56:1 | 0.810 |
| 9.25 | 33.0 | 0.28:1 | 0.730 |
| 9.25 | 66.0 | 0.14:1 | 0.700 |
| | | | |
| 4.62 | 16.60 | 0.27:1 | 0.625 |
| 7.12 | 16.60 | 0.42:1 | 0.750 |
| 9.25 | 16.60 | 0.56:1 | 0.970 |
| 18.5 | 16.60 | 1.11:1 | 1.500 |
| 37.0 | 16.60 | 2.23:1 | 0.860 |
| 72.0 | 16.60 | 4.34:1 | 0.966 |
| 142.0 | 16.60 | 8.43:1 | 1.050 |

Initial temperature = 30°C     [oxetane]=0.62mol dm⁻³

Figure 3.1: Chart recorder output indicating heat rise during polymerization of oxetane

The results in table 3.1 would indicate the rate of polymerization of oxetane is a maximum when the molar ratio of $BF_3OEt_2$:OH is 1:1. When the concentration of $BF_3OEt_2$ is held constant, the concentration of the propagating centres increases up to a maximum when the concentration of the hydroxyl group reaches that of $BF_3OEt_2$. That the rate of polymerization reaches a maximum at this ratio suggests that the species responsible for initiation of the polymerization is a 1:1 complex of $BF_3OEt_2$ and an hydroxyl group.

If the results at constant concentration of hydroxyl groups are considered, the rate of polymerization reaches a maximum at a molar ratio of $BF_3$:OH of 1:1, which would indicate the formation of a 1:1 complex as the active initiating species. However the rate of polymerization decreased as the concentration of $BF_3OEt_2$ was increased above 1:1 mole ratio and so it would appear that the excess $BF_3OEt_2$ deactivates the system in some way. Figure 3.2 shows the results in a graphical form.



Figure 3.2:The effect of [BF₃]:[OH] ratio on the rate of polymerization of oxetane.

### 3.1.3: The efects of the concentration of $BF_3$ and OH on the number average molecular weight , $M_n$, of poly(oxetane)

The number average molecular weights of the polymers obtained in section 3.1.2 were analysed by size exclusion chromatography.

The chromatograph of a typical polymer, shown in figure 3.3, shows that the polymer has a broad molecular weight distribution and illustrates the presence of high molecular weight material and lower molecular weight oligomers. Previous work on the polymerization of oxetane suggests that the oligomers are cyclic and principally cyclic tetramer. The values of $M_n$ shown in table 3.2 ignore the presence of these oligomers. The results shown in table 3.2 indicate that, at constant concentration of hydroxyl groups, the number average molecular weight material is independent of the concentration of $BF_3OEt_2$. However, there is a marked dependence of the number average molecular weight on the concentration of hydroxyl groups. Analysis of these results shows that the number average molecular weight of the polymer exhibits a linear dependence on the reciprocal concentration of the hydroxyl group. This dependence shown in figure 3.4 and is indicative of the presence of transfer reactions. Although the dependence of $M_n$ on [OH] looks linear, a further plot of a function of $1/M_n$ against [OH] shown in figure 3.5 indicates that the increase of $M_n$ is no longer linear when the [OH] > [$BF_3$], therefore a 1st order type termination is being observed i.e.

$$M_n = \frac{R_p}{R_t + R_{tp}} \qquad \frac{1}{M_n} = \frac{R_t + R_{tp}}{R_p} = \frac{k_t}{k_p[M]} + \frac{k_{tr}\,[OH]}{k_p\,[M]}$$

**Table 3.2. The effect of [BF₃] and [OH] on the Mn of poly (oxetane)**

| Ratio<br>$BF_3$ : OH | Mn/g mol$^{-1}$<br>Poly (THF) equivalent |
|---|---|
| 1 : 0.45 | 4629 |
| 1 : 0.67 | 3829 |
| 1 : 0.90 | 2768 |
| 1 : 1.80 | 1593 |
| 1 : 3.60 | 1441 |
| 1 : 7.20 | 1175 |
|  |  |
| 0.27 : 1 | 1640 |
| 0.42 : 1 | 1652 |
| 0.56 : 1 | 1692 |
| 1.11 : 1 | 1549 |
| 2.23 : 1 | 1798 |
| 4.43 : 1 | 1801 |
| 8.43 : 1 | 1391 |

Initial temperature = 30°C   [oxetane]= 0.62mol dm$^{-3}$

(Mn values are normally quoted to an accuracy of $\pm$ 50 g mol$^{-1}$).

It must be noted that the s.e.c. does not give absolute values of Mn, especially with low molecular materials since the change in refractive index is not independent at low concentrations of the monomer. Thus there are two other techniques available, light scattering and osmometry.

Figure 3.3: Atypical s.e.c curve showing the eluted polymer and oligomers

Light scattering gives absolute Mw, Osmometry gives absolute Mn.

The s.e.c. gives the following results;

Mw (sec) > Mw (absolute)

Mn (sec) < Mn (absolute)

Polydispersity ( PD) s.e.c. > PD (absolute).

These results are due to a dispersion process which leads to an artificial broadening of the molecular weight distribution curve.

Figure 3.4:  Dependence of <M>n of poly(oxetane) on [OH] and [BF3]

130

10

8

6

4

2

0

$10^4 * <M>_n^{-1}$

0   10   20   30   40

$10^3 * [OH]/mol\ dm^{-3}$

Figure 3.5: Dependence of <M>n of poly(oxetane) on [OH]

### 3.1.4. Effect of the monomer concentration on the rate of polymerization and on Mn

A series of experiments was carried out using 0.01M $BF_3OEt_2$ and 0.01M OH solutions, and various volumes of 20% w/w oxetane. The volume of the monomer was varied from 1.0 cm$^3$ to 5.0 cm$^3$ and the total volume of each experiment was kept constant by adding dichloromethane. The effects of concentration of monomer on the rate of polymerization and Mn, were investigated employing a 1:1 molar ratio of $BF_3OEt_2$ and OH solutions using the three different catalyst systems, $BF_3OEt_2$/ethanol, $BF_3OEt_2$/ethanediol and $BF_3OEt_2$/propantriol. Table 3.3 and figure 3.6 show the effects of monomer concentration on the rates of polymerization and the effect of monomer concentration on Mn is shown in table 3.4 and figures 3.7-3.9.

**Table 3.3. The effect of monomer concentration on the rate of polymerization using three different co-catalysts, ethanol, ethanediol and propantriol in conjunction with BF$_3$OEt$_2$**

| Vol of 20% w/w oxetane /cm | [oxetane] mol dm$^{-3}$ | Vol (cm$^3$) of CH$_2$Cl$_2$ | Vol (cm$^3$) of 0.01 M BF$_3$OEt$_2$ | Vol (cm$^3$) of 0.01M OH | Rates x 10$^3$ / mol dm$^{-3}$ s$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| | | | | | BF$_3$OEt$_2$ ethanol | BF$_3$OEt$_2$ ethanediol | BF$_3$OEt$_2$ propantriol |
| 5.0 | 3.05 | 0.0 | 1.0 | 1.0 | 8.00 | 7.17 | 7.15 |
| 4.0 | 2.44 | 1.0 | 1.0 | 1.0 | 5.71 | 5.63 | 5.79 |
| 3.0 | 1.83 | 2.0 | 1.0 | 1.0 | 3.76 | 4.61 | 4.35 |
| 2.0 | 1.22 | 3.0 | 1.0 | 1.0 | 2.51 | 2.23 | 2.54 |
| 1.0 | 0.61 | 4.0 | 1.0 | 1.0 | 1.23 | 0.94 | 0.99 |

A linear relationship is observed when the rate of polymerization is plotted against the concentration of oxetane (figure 3.6). From this analysis it is apparent that the effect of the oxetane concentration on the rate of polymerization exhibits 1st order kinetics regardless of the nature of the catalyst system used.



Figure 3.6: Dependence of rate of polymerization on [oxetane].

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**Table 3.4.** The effect of monomer concentration on the number average molecular weight $M_n$ using the three different catalyst systems

| Vol of 20% w/w oxetane /cm$^3$ | [oxetane] mol dm$^{-3}$ | Vol of CH$_2$Cl$_2$ /cm$^3$ | Vol of 0.01M BF$_3$ /cm$^3$ | Vol of 0.01M OH /cm$^3$ | Poly (THF) $M_n$ g mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| | | | | | BF$_3$ ethanol | BF$_3$ diol | BF$_3$ triol |
| 5.0 | 3.05 | 0.0 | 1.0 | 1.0 | 3375 | 6662 | 11313 |
| 4.0 | 2.44 | 1.0 | 1.0 | 1.0 | 2949 | 6032 | 9089 |
| 3.0 | 1.83 | 2.0 | 1.0 | 1.0 | 1784 | 4879 | 7785 |
| 2.0 | 1.22 | 3.0 | 1.0 | 1.0 | 1440 | 3987 | 6654 |
| 1.0 | 0.61 | 4.0 | 1.0 | 1.0 | 641 | - | 4167 |

Similarly a linear relationship is obtained when the number average molecular weight, Mn is plotted against the concentration of oxetane for the three different catalyst systems (figures 3.7 - 3.9).

The Mn increases in the following order of the co-catalyst used propantriol > ethanediol > ethanol. It therefore seems apparent that the number of OH groups per molecule of co-catalyst has a significant bearing on Mn. Furthermore for the same concentration of oxetane the Mn increases approximately in a ratio of 1:2:3 when the co-catalyst used are ethanol, ethanediol and propanetriol respectively.

Figure 3.7: Dependence of <M>n of (poly)oxetane on [oxetane] using BF3:ethanol system.



Figure 3.8 : Dependence of <M>n of poly(oxetane) on [oxetane] using BF3:ethanediol system.

**Figure 3.9:Dependence of <M>n of (poly)oxetane on [oxetane] using BF3:propantriol system.**

### 3.1.5. Effect of the catalyst/co-catalyst complex concentration on the rate of polymerization and on Mn

The study described in section 3.1.2 has shown that the rate of polymerization of oxetane shows a maximum when the concentrations of BF3OEt2 and the OH group are identical. It was suggested that a 1:1 complex of BF3OEt2 and OH is formed and is the initiating species from which the active centre is derived. It seems reasonable, therefore to investigate the effect of concentration of this 1:1 complex on the rate of polymerization and Mn. Again the three catalyst systems used in study 3.1.4. were used.

A series of experiments was carried out to investigate the effect of the concentration of the 1:1 complex on the rate of polymerization. The experiment were carried out using a constant volume of a 20% w/w solution of oxetane in dichloromethane, equal volumes of 0.01M solutions of BF3OEt2 and the hydroxyl compounds in dichloromethane and additional dichloromethane to ensure that the overall volume of the polymerization system remained constant. The total volume of all polymerizations was maintained at $7.0cm^3$ which was made up of $3cm^3$ of 20% w/w solutions of oxetane in dichloromethane, between 0.5 and 2.0 $cm^3$ of solutions of the catalysts and between 3.0 and 0.0 $cm^3$ of additional dichloromethane.

Figure 3.10 shows a typical displacement time plot for this series of experiments. The slope generated by the chart recorder is not as steep as in those shown in figure 3.1 because the concentration of catalyst was reduced by a factor of ten. Unlike the rates calculated in table 3.1 which were quoted only as relative rates, the rates calculated in this study and in section 3.1.4 were in terms of the conventional units, mol dm$^{-3}$ s$^{-1}$, the conversion of $^{o}$Cs$^{-1}$ to mol dm$^{-3}$ is described in section 2.3.1.1. These results are shown in table 3.5. The number average molecular weight Mn were analysed for this study and the results are also shown in table 3.5.

Figure 3.10:   Typical time displacement plot for

the series of experiments described in

section 3.1.5.



BF$_3$OEt$_2$            OH

Addition of catalyst

| 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |

Time/s

| (Vol. of 20% w/w oxetane, cm³) | Vol. of CH2Cl2 cm³ | Vol. of 0.01M BF3 cm³ | Vol. of 0.01M OH cm³ | $10^3\frac{[BF_3OEt_2]}{:OH]}$ mol dm⁻³ | $10^3$ RATE OF POLYMERIZATION mol dm⁻³ s⁻¹ | | | $M_n$/g mol⁻¹ Poly THF | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\frac{BF_3}{ethanol}$ | $\frac{BF_3}{ethanediol}$ | $\frac{BF_3}{propantriol}$ | $\frac{BF_3}{ethanol}$ | $\frac{BF_3}{ethanediol}$ | $\frac{BF_3}{propantriol}$ |
| 3.0 | 3.0 | 0.50 | 0.50 | 0.71 | 2.30 | 2.13 | 3.32 | 1836 | 2522 | 12783 |
| 3.0 | 2.5 | 0.75 | 0.75 | 1.07 | 3.75 | 4.09 | 4.86 | 2330 | 5188 | 12400 |
| 3.0 | 2.0 | 1.00 | 1.00 | 1.43 | 4.86 | 5.28 | - | 2320 | 5045 | - |
| 3.0 | 1.5 | 1.25 | 1.25 | 1.79 | 5.28 | 7.36 | 8.09 | 2205 | 5822 | 14032 |
| 3.0 | 1.0 | 1.50 | 1.50 | 2.14 | 5.62 | 8.69 | - | 2223 | 4327 | - |
| 3.0 | 0.5 | 1.75 | 1.75 | 2.50 | 5.79 | 9.37 | 10.22 | 2323 | 4339 | 12992 |
| 3.0 | 0.0 | 2.00 | 2.00 | 2.86 | 6.13 | 10.22 | 10.73 | 2352 | 5464 | 12693 |

Table 3.5. The effect of catalyst/co-catalyst concentration on the rate of polymerization and on the $M_n$

It was found that the kinetic behaviour of BF₃OEt₂ : C₂H₅OH and the diol and triol catalyst systems were different. It can be seen from figure 3.12 that the rate of polymerization is half-order in the concentration of BF₃ : ethanol complex but first order in BF₃ : diol and BF₃ : triol systems (figure 3.11).



**Figure 3.11: Dependence of Rp on concentration of [BF3OEt2] for various cocatalysts**

Figure 3.12: Dependence of rate of polymerization on [BF3:ethanol] system

The correlation coefficient values for the BF$_3$/ETOH complex from figures 3.11 and 3.12 are 0.867 and 0.931 respectively, which favour the half order dependency.

### 3.1.6. Calculation of rate constants

(i) BF$_3$ : Diol and BF$_3$ : Triol catalysts systems

Analysis of the kinetic data for the polymerization of oxetane with BF$_3$ : diol and BF$_3$ : triol catalysts showed that the rate of polymerization may be described by the general equation

$$R_p = k[M][cat] \qquad\qquad \textbf{1}$$

Values for the rate constant for the reaction, which is quite possibly a composite rate constant, may be determined from figures 3.6 and 3.11. The slopes of the lines shown in figure 3.6 and 3.11 are as follows:

The gradients of the slopes in figure 3.6 are $2.52 \times 10^{-3} = k[catalyst]$ for the BF$_3$ : triol system and $2.55 \times 10^{-3} = k$ [catalyst] for the BF$_3$: diol system.

The values for the rate constant are shown in table 3.6

**Table 3.6. Shows the calculated rate constants for the catalyst systems BF₃:triol and BF₃:diol**

| Catalyst system | Variable | $k/dm^3 mol^{-1}s^{-1}$ |
|---|---|---|
| $BF_3OEt_2$/diol | [Monomer] | 2.05 |
| $BF_3OEt_2$/triol | [Monomer] | 1.87 |
| $BF_3OEt_2$/diol | [Catalyst] | 1.94 |
| $BF_3OEt_2$/triol | [Catalyst] | 1.76 |

average $k_{diol} = 2.0 \ dm^3 mol^{-1}s^{-1}$, $k_{triol} = 1.8 \ dm^3 mol^{-1}s^{-1}$

The consistency of these data and moreover the good straight lines obtained from each plot would seem to indicate that the equation (1) is a reasonable equation to describe the kinetics of the system. The differences in the values between the rate constant for the diol and triol systems will be discussed later.

(ii) BF₃ : Ethanol catalyst system

Kinetic analysis of the polymerizations initiated by this catalyst combination suggest that the rate equation for the polymerization is

$$R_p = k[cat]^{1/2}[M]$$

The slope of figure 3.6 is therefore $k[cat]^{1/2}$ and that of figure 3.12 is $k[M]$. Evaluation of the rate constant (k) from the two plots gave values of 0.07 and 0.08 $(dm^3 mol^{-1})^{1/2}s^{-1}$ respectivly. Therefore this gives $k_{ethanol} = 0.075 \ (dm^3 mol^{-1})^{1/2}s^{-1}$.

In conclusion it should be noted that there is a reasonable similarity, within experimental error, between the values of overall rate constant for initiation with BF₃:diol and BF₃:triol, but these were significantly different from the values obtained for the BF₃:ethanol system. This and the marked difference in the kinetic dependences of the rate of polymerization on the concentration of the catalyst will be explained shortly.

## 3.1.7. Mechanistic reaction schemes

Most polymerization reactions involve three main stages, initiation, propagation and termination. If a general reaction scheme can be developed based upon the early work done by J.B. Rose[63], then it is possible the mechanism may take the following form.

### Initiation

A Lewis acid will react with a base to form an active species $Pn^*$.

$$(\text{I}) \quad BF_3OEt_2 \;+\; ROH \;\;\underset{\longleftarrow}{\overset{k_i}{\longrightarrow}}\;\; \bar{B}F_3 \leftarrow \overset{+}{\underset{H}{O}}\text{-R} \;+\; OEt_2$$

$$(2) \quad \bar{B}F_3 \leftarrow \overset{+}{\underset{H}{O}}\text{-R} \;+\; \overset{O \rule[0.5ex]{1.2em}{0.4pt}}{\boxed{\phantom{xx}}} \;\;\overset{k_i{}'}{\longrightarrow}\;\; H\text{-}\overset{+}{O}\rule[0.5ex]{1.2em}{0.4pt}\boxed{\phantom{xx}}\;\; \bar{B}F_3OR$$

### Propagation

This involves the attack of the monomer (M) on the $\alpha$-carbon the active species $Pn^*$.

$$(3) \quad P_n^* \;+\; M \;\;\overset{k_p}{\longrightarrow}\;\; P_{n+1}^*$$

### Termination

This step may be achieved by several reactions

(a) There may be a simple termination step such as

$$(4) \quad P_n^* \;\;\overset{k_t}{\longrightarrow}\;\; P_n \;+\; I$$

where $P_n$ = polymer, I = initiator

(b) Termination via chain transfer reagent, such as excess OH as the results have indicated earlier.

$$(5)\;\;(i) \quad P_n^* \;+\; OH \;\;\overset{k_{tf}}{\longrightarrow}\;\; P_n \;+\; H^+$$

$$(ii) \quad H^+ \;+\; M \;\;\longrightarrow\;\; P_n^*$$

The above five steps give the overall general kinetic behaviour for the polymerization. Since

$$R_p = \frac{-d[M]}{dt} = k_p[P_n^*][M]$$

where

$R_p$ = rate of propagation

$k_p$ = rate constant for propagation

$[P_n^*]$ = concentration of active species/active polymer end

$[M]$ = concentration of monomer

An expression for $[P_n^*]$ must be found. To find $[P_n^*]$ the following assumptions are made, $d[Pn^*]/dt = 0$.

From this it can be stated that $[P_n^*]$ is dependent on (1) for its formation and not (2). Steady state conditions in the concentration of propagating species can then be applied, so using the scheme it can be said that

$$\frac{d[P_n^*]}{dt} = 0 = k_i[BF_3][OH] - k_t[P_n^*]$$

$$\therefore \quad k_i[BF_3][OH] = k_t[P_n^*]$$

$$\frac{k_i}{k_t}[BF_3][OH] = [P_n^*]$$

Thus an expression for $[P_n^*]$ is found which can be substituted into the rate equation

$$R_p = k_p[P_n^*][M]$$

hence

$$R_p = \frac{k_p k_i}{k_t}[BF_3][OH][M] \tag{x}$$

The above equation for $R_p$ suggests that the rate of polymerization is dependent upon the concentrations of $BF_3$, OH and the monomer. Furthermore this dependence is 1st order with each reagent. However it should be noted that the polymerization is only possible when both $BF_3$ and OH are present. In addition the rate of polymerization is dependent on the ratio of the

concentrations of these two components, being a maximum when the ratio of their molar concentrations is 1. It should be noted therefore that the kinetic data in section 3.1.5, the dependence of $R_p$ on catalyst concentration, refers to the product of [BF$_3$][OH]. Hence it is thought that it is reasonable to simplify equation (x) to

$$R_p = \frac{k_p k_i}{k_t} [BF_3 : OH][M]$$

This gives overall second order kinetics for the polymerization. This approach agrees with the derivations earlier concluded when the system employed consisted of ethanediol and propantriol as co-catalysts. In addition the assumption made for the steady state approximation has also been correct.

In order to explain the general kinetic dependence for the polymerization when ethanol was used as the co-catalyst, a modification should be applied to the above system. The most significant feature of the kinetics that has to be explained is the half-order dependence on the initiator concentration. There are a number of approaches that can be adopted here that should be considered. Firstly if the termination is second order, as found in free radical polymerization, this would give rise to a half-order dependence on initiator concentration. Ionic polymerizations are not generally characterised in such ways because this would imply two like charges approaching one another, and termination described as

$$P_n^* + P_n^* \longrightarrow \text{Polymer}$$

This can almost certainly be ruled out.

Another approach is to consider that the kinetics are similar to the KNH$_2$/liq.NH$_3$ polymerization of styrene. In this case the 1/2 order dependence arise because of an equilibrium between the initiating amide ion and the initiator KNH$_2$ in the solvent

$$KNH_2 \rightleftharpoons K^+ + NH_2^-$$

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$$\text{NH}_2^- + \text{CH}_2=\text{CHPh} \longrightarrow \text{NH}_2\text{-CH}_2\text{-}\overset{-}{\text{C}}\text{HPh}$$

This cannot be ruled out and it is possible that the scheme for initiation should be written as

$$\overset{-}{\text{B}}\text{F}_3\overset{+}{\underset{\displaystyle |\atop\displaystyle H}{\text{O}}}\text{Et} \underset{\xleftarrow{\hspace{1cm}}}{\xrightarrow{\hspace{0.5cm}K\hspace{0.5cm}}} \text{EtO}\overset{-}{\text{B}}\text{F}_3 + \text{H}^+$$

Then $\qquad\qquad K = [\text{H}^+][\text{EtOBF}_3^-]/[\text{BF}_3^-\text{ HO}^+\text{ Et}]$

and since $\qquad\quad [\text{H}^+] = [\text{EtOBF}_3^-]$

$$[\text{H}^+] = K^{1/2}[\text{EtOH}^+\text{BF}_3^-]^{1/2}$$

However, because the solvent is dichloromethane, such dissociations are unlikely and would be just as likely to occur within the diol and triol systems. This then leaves a third alternative the possibility that the propagating centre is formed by the dissociation of an associated dimer.

The distinction in the kinetics of polymerization is believed to be caused by a difference in the structures of the propagating centres. It is simplest to consider first of all the propagating centre for the diol catalyst, which is believed to be a monomeric structure. It is thought that when ethanediol is involved the following complex is formed for the anion.



which can be written as

The driving force for this to occur is the possibility of forming a 5-membered structure in the complex with the empty $sp^3$ orbital of the B atom overlapping with $sp^3$ lone pairs of the oxygen atom. With propantriol a similar structure can be envisaged.

Now if the complex with ethanol is considered then only the following can take place

$$F_3\bar{B}\text{-O-CH}_2CH_3$$
$$P_n^+$$

and it seems likely therefore that this species will dimerise as does polystyryllithium in cyclohexane by association of dipoles.



Because there is no second OH group, the ion pairs i.e., the active centre and the gegenion can dimerise. This is not likely with ethanediol and propantriol as their respective OH groups are involved in forming the stable 5-membered structure. Based upon this, the mechanism of polymerization involving ethanol as co-catalyst may take the following form:

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## Initiation

(1) $BF_3OEt_2 + ROH \underset{\longleftarrow}{\overset{k_i}{\longrightarrow}} \overset{-}{B}F_3\text{-}\overset{+}{O}\text{-}R + OEt_2$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | $

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H$

(2) $BF_3\text{-}\overset{+}{O}\text{-}R + $ $O\!\!\square$ $\underset{\longleftarrow}{\overset{k_i'}{\longrightarrow}}$ $H\text{-}\overset{+}{O}\!\!\square \; \overset{-}{B}F_3OR$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \underbrace{\qquad\qquad\qquad\qquad\qquad}$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad P_i^+ \qquad\quad X^-$

## Propagation

(3) $\quad 2\,P_i^+\,X^- \underset{\longleftarrow}{\overset{\longrightarrow}{\qquad\qquad}} (P_1^+X^-)_2 \qquad$ DIMERIZATION

(4) $\quad P_n^+\,X^- + M \overset{k_p}{\longrightarrow} P_{n+1}^+\,X^-$

## Termination

$\qquad\qquad P_n^+\,X^- \longrightarrow P_n + I$

$\qquad$ (i) $\;P_n^+\,X^- + OH \longrightarrow P_n + H^+$

$\qquad$ (ii) $\;H^+ + M \longrightarrow P_n^*$

It is important to note that polymerization does not occur when the active centre and the gegenion are involved in the dimerised state. For this reason the kinetics involving ethanol are slower and give rise to the half-order dependency.

### 3.1.8. NMR studies on $BF_3OEt_2/ROH$ complexes

In order to provide further evidence for the mechanisms described in section 3.1.7, detailed NMR analysis was carried out to elucidate the structures of possible complexes formed when $BF_3OEt_2$ was reacted with the three co-catalysts. A series of solutions were prepared in which the ratio of $BF_3$:OH was varied from 1:1 to 1:3 respectively the $^1H$ NMR spectra of the resulting complexes were recorded. The results are shown in tables 3.7-3.10 and the spectra are shown in appendix 1.

**Table 3.7.** **Chemical shifts of $^1$HNMR spectra of the BF$_3$OEt$_2$ and the three co-catalysts**

| COMPOUND | $^1$H CHEMICAL SHIFT ppm |
|---|---|
| BF$_3$ ◄── O(CH$_2$CH$_3$)$_2$ | CH$_2$ (quartet) 3.543-3.614<br><br>CH$_3$ (triplet) 1.149-1.196 |
| BF$_3$ ◄── O$^+$H$_2$ | O$^+$H$_2$ (singlet) 10.107 |
| CH$_3$CH$_2$OH | CH$_2$ (quartet) 3.50-4.00<br><br>CH$_3$ (triplet) 1.10-1.40<br><br>OH (singlet, broad) 2.2-2.5 |
| CH$_2$OH<br>\|<br>CH$_2$OH | CH$_2$ (singlet) 3.500<br><br>OH (singlet) 5.230 |
| CH$_2$OH<br>\|<br>CHOH<br>\|<br>CH$_2$OH | CH$_2$<br><br>    3.40-4.00<br><br>CH<br><br>OH (singlet) 4.70 |
| CH$_3$CH$_2$OCH$_2$CH$_3$ | CH$_2$ (quartet) 3.4-3.5<br><br>CH$_3$ (triplet) 1.2 |

**Table 3.8.** **Shows the chemical shifts of $^1$HNMR spectra obtained when BF$_3$OEt$_2$ reacted with various ratios of ethanol**

a) 1:1 BF$_3$: OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|---|---|---|---|
| CH$_2$ | quartet | 3.501-3.627 | 43.19 |
| CH$_3$ | triplet | 1.105-1.152 | 61.71 |
| *<br>CH$_2$ | quartet | 3.867-3.938 | 15.99 |
| CH$_3$ | triplet | 1.198-1.246 | 26.15 |
| O$^+$H | singlet | 10.667 | 14.10 |

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Assignments according to reaction scheme:

$$BF_3OEt_2 + CH_3CH_2OH \rightleftharpoons F_3B^- \leftarrow {}^+OH\text{-}\overset{*}{C}H_2CH_3 + O\text{-}(CH_2CH_3)_2$$

b) 1:2 BF₃:OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|---|---|---|---|
| CH₂ | quartet | 3.412-3.459 | 57.50 |
| CH₃ | triplet | 1.045-1.098 | 87.00 |
| C̲H̲₂ | quartet | 3.671-3.690 | 20.51 |
| *CH₂ | quartet | 3.690-3.862 | 25.10 |
| 'CH₃ | triplet | 1.107-1.323 | 55.91 |
| O⁺H₂ | singlet | 9.045 | 32.00 |

Assignments according to reaction scheme:

$$BF_3OEt_2 + 2\,CH_3CH_2OH \rightleftharpoons F_3B^- \leftarrow O\text{-}\overset{*}{C}H_2{'}CH_3 + H_2O^+\text{-}\underline{CH_2}{'}CH_3$$

$$+ O\text{-}(CH_2CH_3)_2$$

$$\uparrow\downarrow$$

$$O\text{-}(CH_2CH_3)_2 + F_3B^- \leftarrow {}^+OH\text{-}\overset{*}{C}H_2{'}CH_3 + {'}CH_3\underline{CH_2}OH$$

c) 1:3 BF$_3$:OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|---|---|---|---|
| CH$_2$ | quartet | 3.290-3.381 | 31.05 |
| CH$_3$ | triplet | 0.9721-1.032 | 124.3 |
| *CH$_2$ | quartet | 3.352-3.355 | 32.12 |
| C$\underline{H_2}$ | quartet | 3.7801 | 10.57 |
| O$^+$H$_2$ | singlet | 9.031 | 32.07 |

Assignments according to the reaction scheme:

$$BF_3OEt_2 \; + \; 3 \; CH_3CH_2OH \; \rightleftharpoons \; F_3B \leftarrow O\text{-}\overset{*}{C}H_2CH_3 \; + \; H_2O^+\text{-}\underline{C}H_2CH_3$$

$$+ \; O\text{-}(CH_2CH_3)_2 \quad + \; CH_3CH_2OH$$

$$\rightleftharpoons \quad 2 \; CH_3CH_2OH \; + \; F_3B \leftarrow O^+H\text{-}\overset{*}{C}H_2CH_3 \; + \; O\text{-}(CH_2CH_3)_2$$

The ether in these reactions appear to be free as the chemical shift of the methylene groups have changed from approximately 3.6 to 3.4 ppm. In all cases acidic protons have been produced which are involved in the equilibrium reactions of the type shown in table 3.8. These protons are responsible for the formation of an active centre with oxetane. The structures of the complexes shown in table 3.8 satisfy the ^{1}H NMR data and more significantly they are of the type described in the mechanism of polymerization described in section 3.1.7. Furthermore these results may also indicate why a 1:1 BF$_3$:OH ratio gives the maximum rate of polymerization because it can be observed the proton generated may be exchanged with the excess hydroxyl as shown by the equilibrium reactions. This reduces the number of active centres produced with oxetane and slows the rate of polymerization. (The free ether is a very weak base and is unlikely to be involved in equilibrium reactions).

## Table 3.9. Shows the chemical shifts of $^1H$ NMR spectra obtained when $BF_3OEt_2$ reacted with various ratios of ethanediol

a) 1:1 $BF_3$:OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|---|---|---|---|
| 'CH$_2$, CH$_2$ | quartet | 3.499-3.578 | 52.57 |
| 'CH$_3$, CH$_3$ | triplet | 1.053-1.1502 | 79.17 |
| *CH$_2$ | singlet | 3.37835 | 24.48 |
| O$^+$H$_2$ | singlet | 9.1742 | 39.72 |

Assignments according to reaction scheme:

$$2BF_3OEt_2 + HO\text{-}CH_2\text{-}CH_2OH \rightleftharpoons HO\text{-}CH_2\text{-}CH_2\text{-}^+OH$$
$$\Big| \quad BF_3^-$$

$$\updownarrow$$

$$HO^+\text{-}CH_2\text{-}CH_2\text{-}OH$$
$$\Big| \quad BF_3^-$$

$$\xrightarrow{\hspace{1cm}}$$

$$\overset{*}{C}H_2\text{-}\overset{*}{C}H_2$$
$$H\text{—}O \qquad O\text{—}H \xrightarrow{\hspace{1cm}} F_3B\text{-}O\text{-}(CH_2CH_3)_2$$
$$+ \quad BF_3^-$$

$$+$$

$$O\text{-}('CH_2'CH_3)_2$$

$$\updownarrow$$

$$F_3B\text{-}O\text{-}('CH_2'CH_3)_2$$

$$+$$

$$O\text{-}(CH_2CH_3)_2$$

b) 1:2 BF$_3$:OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|---|---|---|---|
| CH$_2$ | quartet | 3.499-3.560 | 40.43 |
| CH$_3$ | triplet | 1.107-1.165 | 60.70 |
| *CH$_2$ | singlet | 3.622-3.902 | 36.00 |
| O$^+$H | singlet | 10.159 | 17.09 |

Assignments according to reaction scheme

$$BF_3OEt_2 \; + \; HO\text{-}CH_2\text{-}CH_2OH \; \underset{\longleftarrow}{\longrightarrow} \; HO\text{-}CH_2\text{-}CH_2\text{-}^+OH$$
$$\underset{BF_3^-}{|}$$

$$HO^+\text{-}CH_2\text{-}CH_2\text{-}OH$$
$$\underset{BF_3^-}{|}$$



$$\longrightarrow \quad H\!-\!O \qquad O\!-\!H \quad + \; O\text{-}(CH_2CH_3)_2$$

c) 1:3 BF$_3$:OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|---|---|---|---|
| CH$_2$ | quartet | 3.482-3.898 | 26 |
| CH$_3$ | triplet | 1.109-1.170 | 33.50 |
| *CH$_2$ | singlet | 3.692-3.412 | 144.90 |
| CH$_2$ | - | - | - |
| OH$^+$ | singlet | 10.428 | 111.40 |

Assignments according to reaction scheme

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$$BF_3OEt_2 \; + \; 11/2 \; HO\text{-}CH_2\text{-}CH_2OH \; \rightleftharpoons$$

$$
H\!-\!O \overset{\overset{\displaystyle \overset{*}{C}H_2\text{-}\overset{*}{C}H_2}{\diagup \qquad \diagdown}}{\underset{\underset{\displaystyle BF_3^-}{+}}{\diagdown \qquad \diagup}} O\!-\!H
$$

$$+ \; O\text{-}(CH_2CH_3)_2 \; + \; 1/2 \; HO\text{-}\underline{C}H_2\text{-}\underline{C}H_2OH$$

The possible reaction schemes illustrated in table 3.9 satisfy the ^{1}H NMR data obtained. The associated structures also correlate with those described in section 3.1.7 and therefore it might be concluded that those complexes are generated during the initiation of the polymerization of oxetane. The most significant feature of these results is that it seems reasonable to suggest that the structure produced is cyclic in which the oxygen atoms share a positive charge - this was also suggested in section 3.1.7. These results give an explanation of the fact that a 1:1 $BF_3$:OH ratio gave the maximum rate of polymerization. It can be seen from the chemical shifts that in all cases free diethylether is produced which in the 1:1 $BF_3$:OH reaction is able to participate in the equilibrium reactions shown in table 3.9. However when the 1:2 and 1:3 $BF_3$:OH reactions are considered, the free ether produced is not involved in any equilibrium reactions and therefore even though is a weak base it could still be able to accept protons which would reduce the number of active centres produced with oxetane. Finally with the 1:3 reaction there is also free ethanediol which is likely to complex with any protons produced which again would result in reducing the number of active centres.

a) 1:1 BF$_3$:OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|-------|------|---------------------|------|
| CH$_2$ | quartet | 3.469-3.359 | 44.91 |
| CH$_3$ | triplet | 1.069-1.499 | 66.29 |
| O$^+$H | singlet | 9.330 | 11.45 |

Assignments are made according to the free ether and the acidic protons.

$$3\ BF_3OEt_2\ +\ HO\text{-}CH_2\text{-}CHOH\text{-}CH_2OH \rightleftharpoons$$



$$+\ O\text{-}(CH_2CH_3)_2\ +\ 2BF_3OEt_2$$

ether molecule exchanging with one BF$_3$ molecule

b) 1:2 BF$_3$:OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|-------|------|---------------------|------|
| CH$_2$ | quartet | 3.661-3.868 | 70.1 |
| *CH$_2$ | broad | 4.009-4.093 | 55.21 |
| CH$_3$ | triplet | 1.228-1.332 | 150.92 |
| OH (bonded) | singlet | 2.177 | 12.04 |
| O$^+$H | singlet | 9.088 | 30.93 |

Assignments are made according to $CH_2$(broad), OH(bonded), $OH^+$(acidic) and the ether protons.

$$3/2\ BF_3OEt_2\ +\ HO\text{-}CH_2\text{-}CHOH\text{-}CH_2OH\ \rightleftharpoons$$

HO-$CH_2$CH-$CH_2$ *

H—O        O—H

$BF_3^-$ (+)

$$+\ O\text{-}(CH_2CH_3)_2\ +\ 1/2\ BF_3OEt_2$$

ether exchange limited in this case

c) 1:3 BF$_3$:OH

| GROUP | TYPE | CHEMICAL SHIFTS/PPM | AREA |
|-------|------|---------------------|------|
| CH$_2$ | quartet | 3.399-3.467 | 49.8 |
| CH$_3$ | triplet | 1.132-1.138 | 73.0 |
| O$^+$H | don't appear | | |
| OH | don't appear | | |

Data only shows the presence of free ether.

$$BF_3OEt_2 \; + \; HO\text{-}CH_2\text{-}CHOH\text{-}CH_2OH \; \rightleftharpoons$$



$$+$$

$$O\text{-}(CH_2CH_3)_2$$

The explanation for the complexes shown in table 3.10 is similar to that described when BF$_3$OEt$_2$ reacted with ethanediol. The spectra have become more complicated and for this reason it might be useful to carry out these reactions using 2D $^1$H NMR COSY system to distinguish all the hydrogens. However the significant feature of these results is that there is some evidence which supports the cyclic complex similar to that described in section 3.1.7 and for the BF$_3$OEt$_2$/ethanediol complex. Evidence from the chemical shifts indicate that free ether is produced which may account for the BF$_3$:OH 1:1 complex being the most active as explained for the results obtained in table 3.9.

It must be noted that even though this study has thrown some light to support the kinetics and mechanisms discussed in this chapter, further work is necessary to provide more evidence of the nature of the complexes which give rise to the active centres on addition of oxetane.

## 3.2. Copolymerization studies of oxetane and THF

### Introduction

Cationic initiation has been used to copolymerize cyclic ethers. Reports published have been concerned with the kinetics of the reaction, the reactivity ratios of the monomers and the molecular weights of the copolymers[201-206]. In general, the basicity and ring strain are the main factors that govern the reactivity of cyclic ethers.

The kinetics of the cationic copolymerization of cyclic ethers is described by the Mayo-Lewis equation. The copolymerization of two monomers $M_1$ and $M_2$ is generally described in terms of four propagating steps,

$$\sim\sim\sim M_1^+ + M_1 \xrightarrow{k_{11}} \sim\sim\sim M_1^+$$

$$\sim\sim\sim M_1^+ + M_2 \xrightarrow{k_{12}} \sim\sim\sim M_2^+$$

$$\sim\sim\sim M_2^+ + M_2 \xrightarrow{k_{22}} \sim\sim\sim M_2^+$$

$$\sim\sim\sim M_2^+ + M_1 \xrightarrow{k_{21}} \sim\sim\sim M_1^+$$

where $k_{11}$ and $k_{22}$ are the rate constants for the self-propagating reactions and $k_{12}$ and $k_{21}$ the corresponding cross-propagation rate constants.

Under steady state conditions, and assuming that the active centre reactivity is independent of chain length and depends only on the nature of the terminal unit, the reactivity ratios can be defined as

$$r_1 = \frac{k_{11}}{k_{12}} \quad , \quad r_2 = \frac{k_{22}}{k_{21}}$$

and the composition of the copolymer by the equation

$$\frac{M_1}{M_2} = \frac{r_1[M_1]/[M_2] + 1}{r_2 + [M_1]/[M_2]} \cdot \frac{[M_1]}{[M_2]}$$

where

$M_1$ = Copolymer composition of monomer $M_1$.

$M_2$ = Copolymer composition of monomer $M_2$.

$r_1$ = reactivity ratio of monomer 1

$r_2$ = reactivity ratio of monomer 2

The quantities $r_1$ and $r_2$ are the relative reactivity ratios defined more generally as the ratio of the reactivity of the propagating species with its own monomer to the reactivity of the propagating species with the co-monomer. Thus the composition of the copolymer is determined by the reactivity ratios.

Depending upon the various values of $r_1$ and $r_2$ the following copolymers result

| | | |
|---|---|---|
| $r_1 = r_2 = 1$ | : | Ideal statistical copolymer |
| $r_1 = r_2 = 0$ | : | Alternating copolymer |
| $r_1 > 1, r_2 < 1$ | : | Copolymer richer than the feed |
| $r_1 < 1, r_2 > 1$ | | in one monomer |
| $r_1 > 1, r_2 > 1$ | : | Block copolymers. |

### 3.2.1.  Studies involving the copolymerization of oxetane and THF

The catalyst system used for this study was $BF_3OEt_2$/ethanol. This system, although successfully used in the polymerization of oxetane was found to be inactive towards the homopolymerization of THF. A series of experiments was carried out in which the ratio of the concentrations of the comonomers i.e. THF and oxetane was varied, using a 1:1 molar ratio of $BF_3OEt_2$ and ethanol as catalyst. The description of a typical experiment is given in chapter 2, section 2.6.2. After 24 hours the polymer produced was isolated by the following method.

Excess methanol was added to the polymerization reaction and evacuated in a vacuum oven. THF was then used to dissolve the residue such that a saturated solution was produced and this solution was then added to an excess of distilled water in which the purified polymer precipitated. The polymer was then dried in the vacuum oven for a further 24 hours.

Products were analysed by size exclusion chromatography, $^1$H NMR and $^{13}$C NMR. The NMR spectra are shown in appendix 2.

Major Peaks $^1$H NMR (CDCl$_3$) δ 1.76-1.84 (m, 2H, -O-CH$_2$-$\underline{CH_2}$-CH$_2$-O-)

1.51-1.65 (m, 4H, -O-CH$_2$-$\underline{CH_2}$-$\underline{CH_2}$-CH$_2$-O-)

3.40-3.54 (t, 2H, -O-$\underline{CH_2}$-CH$_2$-CH$_2$-O-)

3.34-3.42 (t, 4H, -O-$\underline{CH_2}$-CH$_2$-CH$_2$-CH$_2$-O-)

Major Peaks $^{13}$C NMR (CDCl$_3$) δ 30.1-30.2 (m, 2H, -O-CH$_2$-$\underline{CH_2}$-CH$_2$-O-)

26.2-26.4 (m, 4H, -O-CH$_2$-$\underline{CH_2}$-$\underline{CH_2}$-CH$_2$-O-)

67.6-67.9 (t, 2H, -O-CH$_2$-CH$_2$-$\underline{CH_2}$-O-)

70.9-71.2 (t, 4H, -O-$\underline{CH_2}$-CH$_2$-CH$_2$-$\underline{CH_2}$-O-)

The ratios of the areas under the peaks at 1.76 and 3.42ppm can be used to determine the composition of the copolymers. The dependence of the composition of the copolymer on the ratio of the monomer in the feed is as shown in table 3.11.

**Table 3.11. Copolymerization of oxetane and THF. Dependence of copolymer composition on monomer feed ratio**

| Monomer Ratios THF : Oxetane | Copolymer Composition THF : Oxetane |
|---|---|
| 4.00 : 1.00 | 1.08 : 1.00 |
| 2.03 : 1.00 | 0.86 : 1.00 |
| 0.93 : 1.00 | 0.45 : 1.00 |
| 0.50 : 1.00 | 0.35 : 1.00 |

Using the data shown in table 3.11, the reactivity ratios were calculated as

$$r_{THF} = 0.14 \pm 0.09$$

$$r_{OXT} = 1.20 \pm 0.30$$

The values indicates that oxetane has much higher reactivity than THF and this can be explained by the fact that oxetane has a higher ring strain and higher basicity than THF.

The oxymethylene resonances in the $^{13}C$ spectra appear as doublets for both oxetane and THF, as shown diagramatically in figure 3.13. These peaks are unsymmetrical and the structures may be explained in terms of the arrangements of the co-monomer units in the polymer chain. The four combinations shown below show in detail the environment of the -O-CH$_2$- carbons as two sets of doublets. This suggests that these copolymers are not block copolymers but are random copolymers.



**Figure 3.13.** $^{13}C$ NMR of the copolymer oxetane and THF showing oxymethylenes peaks appearing as doublets

With reference to figure 3.13 the peaks can be assigned as;

A$_i$  -O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-$\underline{CH_2}$-CH$_2$-CH$_2$-O-

A$_{ii}$  -O-CH$_2$-CH$_2$-CH$_2$-O-$\underline{CH_2}$-CH$_2$-CH$_2$-O-

B$_{ii}$  -O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-$\underline{CH_2}$-CH$_2$-CH$_2$-CH$_2$-O-

B$_i$  -O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-$\underline{CH_2}$-CH$_2$-CH$_2$-O-

## 3.2.2.   S.E.C studies of the copolymers of oxetane and THF

Figure 3.14 shows a typical size exclusion chromatograph of the copolymer of oxetane and THF.   The overall shape of the chromatograph is similar to that shown in figure 3.3 of poly(oxetane), however and more significantly no oligomer peaks are observed with the copolymer.   The absence of the oligomers has to be due to the incorporation of the THF molecules into the polymer back-bone which disrupts the stereoregularity for stable trimers and tetramers to be produced.

Figure 3.14: An example of a typical sec curve for the copolymer of oxetane and THF

Finally the $M_n$ values of the copolymers were analysed and are shown in table 3.12 below:

### Table 3.12. Dependence of $M_n$ on the ratio of THF:oxetane.

| Monomer Ratios THF : Oxetane | $M_n$/g mol$^{-1}$ (poly {THF}equivalents) |
|---|---|
| 4.00 : 1.00 | 4420 |
| 2.03 : 1.00 | 4659 |
| 0.93 : 1.00 | 5156 |
| 0.50 : 1.00 | 6230 |

The results show that increasing the concentration of THF in the feed decreases the $M_n$ of the copolymer. This is probably because a terminal THF molecule on the polymer chain increases with increasing THF concentration and is more likely to be susceptible to termination and chain transfer reactions compared with an oxetane terminal unit.

# CHAPTER 4
## RING OPENING POLYMERIZATION OF CYCLIC ETHERS USING PORPHINATO-ALUMINIUM CHLORIDE CATALYST

### 4.1. Introduction

The three membered cyclic ethers such as ethylene oxide, propylene oxide, cyclopentene oxide, cyclohexene oxide and styrene oxide have been successfully polymerized using the coordinated anionic catalyst, porphinato-aluminium chloride [(TPP)AlCl][172-173]. Higher cyclic ethers such as oxetane and THF have only been polymerized using cationic intiators. It was therefore decided that an investigation on the effect of this catalyst on the polymerization of oxetane would be desirable. The study of the polymerization examined whether the system gives rise to a polymerization living in nature. The kinetics of this polymerization were studied by dilatometry. Monomers such as 3,3-dimethyloxetane, 3-methyl-3-hydroxymethyl-oxetane, 3-methyl-3-nitrato-methyloxetane and THF have also been investigated for their polymerizability by this catalyst. The effect of the stereochemistry on the mode of ring-opening was examined using cyclopentene and cyclohexene oxides.

### 4.2. The ring-opening polymerization of oxetane using porphinato-aluminium chloride

#### 4.2.1. Experimental and results

The polymerization was carried out as described in section 2.6.3. During the course of this polymerization samples of the polymerizing solution were extracted and added to methanol. The volatile materials were then removed by evaporation under vacuum. The polymer was finally dried under vacuum at room temperature. Samples were taken from the polymerization at a range of times between 10 and 97 hours. The yields of the materials were recorded and the products were analysed by size exclusion chromatography and NMR. The size exclusion chromatography columns were calibrated using poly(tetrahydrofuran) standards as being the closest in structure to the polymer, poly(oxetane) and values of $M_n$ and $M_w$ are quoted on this basis.

When the polymerization of oxetane was carried out as described above, the catalyst formed an intense blue/mauve solution, which did not change when the monomer was added to the reaction. The reaction was carried out at 55°C and when the samples taken from the polymerization were separated and dried it was found that polymeric material had formed. The yields of polymer, determined gravimetrically were plotted as a function of the reaction time and the curve obtained is shown in figure 4.1.



**Figure 4.1:Polymerization of oxetane with tetraphenyl porphinato-aluminium**

In a study of the changes that occur in the number average molecular weight ($M_n$) with conversion, a linear increase in $M_n$ was observed, as shown in figure 4.1 (a). A significant feature of living polymerizations is that the number average degree of polymerization increases with conversion of monomers to polymer and this would appear to be the explanation of the behaviour shown for the polymerization of oxetane.

**Figure 4.1(a) : Dependence of the number average molecular weight and polydispersity on conversion in the polymerization of oxetane.**

The results of the above plot is shown in table 4.1 below:

**Table 4.1. Results showing the relationship of % conversion on $M_n$**

| % conversion of monomer to polymer | $M_n$/g mol$^{-1}$ Poly THF | $M_w/M_n$ |
|---|---|---|
| 22 | 6660 | 1.14 |
| 29 | 7800 | 1.10 |
| 34 | 9670 | 1.13 |
| 37 | 10130 | 1.16 |
| 42 | 10500 | 1.16 |

Temperature = 55°C. [oxetane] = 7.23 mol dm$^{-3}$; [cat] = 0.018 mol dm$^{-3}$; solvent = $CH_2Cl_2$

The polymer produced has a narrow molecular weight distribution as shown in table 4.1 which indicates that the polymerization is not susceptible to transfer reactions since this would lead to broadening of the molecular weight distribution. This is rather surprising since cationic ring-opening polymerization of cyclic ethers leads to intramolecular reactions i.e. back-biting but in

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this case the in-chain ethereal oxygen atom is unable to form a complex with the propagation centre.

The different basicities of the cyclic and linear ethereal oxygen atoms may be the explanation for this effect or, the steric requirements of the active centre will allow the cyclic ether to approach the active centre but not the linear ether. The basicity factor is considered significant because as the conversion of monomer to polymer proceeds the effective relative concentration of linear to cyclic ethereal oxygen increases and hence at higher conversions the probability that transfer reaction could occur must increase if the steric factor has no influence. If the steric factor is concerned then the extent of conversion would have no influence on the relative abilities of the ethereal oxygen atoms to compete for the active centre.

Efficiency of initiation: The standards used for the calibraton of the size exclusion chromatography are not identical to the polymer under analysis, therefore meaningful estimates of the degrees of polymerization and their predicted values cannot be made. However a reasonable comparison can be made to indicate whether it is likely the efficency of initiation approaches 100%. The efficiency of a living system can be calculated using the following equation:

$$\text{Efficiency} = \frac{\text{MWT. OF OXETANE X [MONOMER]}_0 \text{ x \%conv}}{\text{[INITIATOR] x } M_n}$$

If an error $\pm$ 10% is considered, associated with the % conversion then within limits of experimental accuracy, it can be seen that the aluminium porphyrin initiator system is close to 100% efficient for the polymerization of oxetane (table 4.2). The results compare well with those published by other workers[172] which, when used to estimate efficiencies of initiation, in some cases yield of around 150%.

**Table 4.2.  Dependence of catalyst efficiency on % conversion of monomer**

| % conversion | % efficiency of catalyst |
|---|---|
| 22±2 | 78±8 |
| 29±3 | 87±8 |
| 34±3 | 82±8 |
| 37±4 | 85±9 |
| 42±4 | 93±9 |

## 4.2.2.  Nuclear magnetic resonance studies

In order better to understand the mechanism of polymerizaton of oxetane, the polymer obtained was analysed by $^1$H and $^{13}$C NMR spectroscopy.  The $^1$H spectrum, figure 4.2 showed the presence of two major peaks, one centred around 1.76ppm and another around 3.41ppm, with minor peaks in the region of 7.7-9.0ppm.  The peak around 1.76ppm is obviously caused by the presence of the central methylene group ($CH_2CH_2CH_2$) and that at 3.41ppm by the ethereal methylene groups ($CH_2O$) of a monomr unit in the polymer.  Confirmation of this is also obtained from the fact that the ratio of the areas under these peaks is 1:2.  The splitting associated with the peak at 1.76ppm is consistent with two adjacent $CH_2$ groups and that at 3.41ppm, a triplet, the splitting associated with one adjacent $CH_2$ group.  The peaks in the region of 7.7-9.0ppm are attributed to the presence of the aromatic porphinato end-group in the polymer and are of much weaker intensity.  The fine structure and relative peak areas are not so easily defined for the peaks in this region and estimation of the number average degree of polymerization using the relative intensities of peaks in this region with those at 1.76ppm are is inaccurate.

The $^{13}$C NMR spectrum, figure 4.3, however gives more information about the nature of the end-groups present in the polymer.  The DEPT $^{13}$C NMR spectrum of the polymer shows two major peaks, E at 29.92 ppm and D at 67.96ppm, and since both are negative peaks, they are either methylene or quaternary carbons atoms.  Again these peaks are associated with the methylene groups D and E of the polymer chain.  When the spectrum is viewed in greater

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detail after a large numbers of scans, the $^{13}$C spectrum shows considerable detail in the region 30-70ppm. Peaks in this region can be assigned to the end groups associated with the propagating site in the catalyst and the end group leaving the chlorine atom, derived from the catalyst species. It is proposed that the peaks are assigned in accordance with the description in figure 4.3. In view of the nature of this evidence, it would appear that the polymerization is consistent with the porphinato compound acting as a catalyst for this polymerization of oxetane.

It seems likely that the polymerization of cyclic ethers by aluminium porphine type catalysts is a co-ordinated anionic polymerization in which the first step is co-ordination of the monomer to the aluminium atom in the catalyst. This co-ordination step is then followed by anionic attack by the polymeric alkoxide group on the α-carbon atom of the coordinated cyclic ether, such attack being facilitated by the complex formation with the aluminium atom. In view of the fact that the polymerization of oxetane is not normally initiated by an anionic mechanism, an important step in the polymerization reaction must be the coordination of the monomer to the active site in the catalyst, the aluminium atom, followed by anionic attack on the coordinated and consequently electron deficient monomer.


The slower rate of polymerization of oxetane compared with oxirane[172] may be explained if the polymerization of cyclic ethers proceeds by such a coordinated anionic mechanism, the mechanism proposed by Inoue. The first step in the polymerization involves the formation of a coordinated complex between the aluminium atom of the catalyst at the empty sp$^3$ and a lone pair of electrons of the oxygen atom. The formation of this type of complex ensures a positive charge on the oxygen atom and consequently the alkoxide group may attack the α-carbon atom of the complex. The significant difference in rate of polymerization between oxetane and oxirane may be attributed to the following factors:

(i) the equilibrium constant for the formation of the complex with oxetane may be much lower than that for the formation of the corresponding complex with oxirane, or

(ii) which would be a consequence of (i), the charge density on the α-carbon atom of oxetane is considerably less than that on the α-carbon atom of oxirane, in which case the nucleophilic attack by the alkoxide ion in the propagation step would be less favourable.

Figure 4.2: $^1$H NMR of poly(oxetane) initiated by
(TPP)AlCl catalyst

Chemical shift / ppm

$$Al-O-CH_2-CH_2-CH_2-[-O-CH_2-CH_2-CH_2-]-O-CH_2-CH_2-CH_2-CH_2Cl$$

with labels A, B, C (above first three $CH_2$), D, E, D (above repeat unit $CH_2$ groups), F, G, H (above final three $CH_2$ groups)

Figure 4.3: $^{13}C$ NMR of poly(oxetane) initiated by (TPP)AlCl catalyst

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## 4.3. The use of [(TPP)AlCl] catalyst for the polymerization of substituted oxetanes and THF

The catalyst [(TPP)AlCl] was used in the attempted polymerization of the following monomers, 3,3-dimethyloxetane, 3-hydroxymethyl-oxetane, 3-methyl-3-nitrato-methyl-oxetane and THF. The procedure followed is described in section 2.6.3.

### 4.3.1. 3,3-dimethyl-oxetane (DMO)

The procedure for the polymerization of DMO is described section 2.6.3 and the temperature of the polymerization was 60°C. After 48 hours a sample of the solution was removed and added to methanol. On removing the volatile materials no polymer resulted. The experiment was continued for a further 48 hours and still no polymer was formed. Colours were those associated with the active centre. The possible reasons why the polymerization failed could be

(i) steric hindrance by the methyl groups which prevent the molecule attacking the Al-Cl centre

(ii) the methyl groups push electrons into the ring thereby reducing the positive charge on the $\alpha$-carbon and preventing ring-opening.

### 4.3.2. 3-Hydroxymethyl-oxetane (HMO)

The experimental procedure is described in section 2.6.3. After 48 hours at 65°C a sample of the reaction solution was extracted and added to methanol. The volatile materials were removed by evaporation and it was found that no polymer resulted. The experiment was carried out a further 48 hours at 70°C but still polymerization was unsuccessful.

The possible reasons could be similar to the those given for DMO except there could be an added problem that the oxygen atom present in the side chain could compete with the hetero-atom and destroy the active centre.

Al-Cl ⟶ No polymerization

Me CH$_2$ÖH

O

Al-Cl ⟶ polymerization

O

HOH$_2$C  Me

## 4.3.3. 3-Methyl-3-nitratomethyl-oxetane (NIMMO)

The procedure described for the polymerization is described in section 2.6.3. The polymerization was carried out at 65°C for 48 hours, after which time the solution on addition to methanol, followed by removal of the volatile materials gave an oily residue. The residue was then analysed for the number average molecular weight ($M_n$). The experiment was carried out for a further 120 hours. However it was found that the molecular weight did not change over a long period. The maximum number average molecular weight $M_n$ was 350 which indicates that only oligomer formation took place. The possible reasoons why this should occur are

(i) steric factors

(ii) competition between the side chain oxygen atom and the heteroatom.

The chromatograph (figure 4.3(a)) shows two major peaks- a peak representing the porphyrin and a second peak building from the porphyrin peak which is bimodal in nature, and this is ascribed to the oligomer.

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Figure 4.3 (a): A typical s.e.c curve for the polymerization of NIMMO with (TPP)AlCl catalyst

## 4.3.4. THF

When experiments were carried out in an attempt to polymerize THF using [(TPP)AlCl] catalyst, no polymerization was observed. The main reason for the failure of the polymerization was that

(i) the ring-strain energy of the THF is considerably smaller than oxetane and oxirane

(ii) the basicity of THF is also less than that of oxetane and oxirane and thereby reducing the possibility of the coordinated attack by the 'monomer' to Al-Cl centre.

## 4.4. The study of the kinetics of polymerization of oxetane using [(TPP)AlCl] catalyst

Kinetic measurements involving metalloporphyrins as catalyst have been limited. Inoue et al. [207] have carried out a kinetic analysis of the porphinato aluminium alkoxide/porphinato-aluminium chloride system for the polymerization of δ-valerolacetone. They concluded that a termolecular mechanism involving the participation of two aluminium porphyrin molecules. The use of S.E.C was made in the assessment of the kinetic parameters of the system. It was decided that for this study dilatometry was preferred as a technique for measuring the rate of polymerization.

## 4.4.1. Experimental work

The procedure is described in section 2.6.4 (iii) and reactions were carried out at constant temperature, 39°C. A series of experiments was performed in which the concentration of oxetane was kept constant. Since oxetane was transferred to the dilatometer by distillation, the actual concentrations of oxetane varied slighty, and this is shown in table 4.3. The concentration of the [(TPP)AlCl] catalyst was varied from 0.018 mol dm$^{-3}$ to 0.072 mol dm$^{-3}$. The change in height of the meniscus against time is shown in figure 4.4 for this series.

A similar set of experiments was carried out in which the oxetane concentration was varied from 5.67 to 9.92 mol dm$^{-3}$ and the [(TPP)AlCl] concentration was kept constant. The change in height against time for these experiments is shown in figure 4.5.

From the slopes generated in figures 4.4 and 4.5 the rates of polymerization ($R_p$) were calculated and the results are shown in table 4.3 and 4.4 respectively. Using these tables the orders with respect to the concentration of [(TPP)AlCl] and the concentration of oxetane were determined.

## 4.4.2. Dilatometry results



Figure 4.4 : Dependence of meniscus height (cm) against time at constant [oxetane]

**Figure 4.5:Dependence of meniscus height (cm) against time at constant [(TPP)AlCl]**

Figures 4.4 and 4.5 indicate that the meniscus height (cm) against time (hours) shows a linear relationship. Overall the conversions are small in this period. Using the gradients of these slopes the dependence of rate of polymerization on [(TPP)AlCl] and oxetane concentration were determined (table 4.3 and 4.4 respectively).

**Table 4.3. The effect of the [(TPP)AlCl] concentration on $R_p$**

| $\dfrac{[(TPP)AlCl] \times 10^3}{mol\,dm^{-3}}$ | $\dfrac{[Oxetane]}{mol\,dm^{-3}}$ | $\dfrac{R_p \times 10^6}{mol\,dm^{-3}\,s^{-1}}$ | $\dfrac{R_p \times 10^6}{[oxetane]}$ |
|---|---|---|---|
| 18 | 7.23 | 8.45 | 1.17 |
| 25 | 7.18 | 11.95 | 1.66 |
| 36 | 7.16 | 12.81 | 1.80 |
| 48 | 7.22 | 16.59 | 2.30 |
| 54 | 7.14 | 33.75 | 4.73 |
| 72 | 7.25 | 64.51 | 8.90 |

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## Table 4.4.   The effect of the oxetane concentration on $R_p$

| $\dfrac{[(TPP)AlCl] \times 10^6}{mol\ dm^{-3}}$ | $\dfrac{[Oxetane]}{mol\ dm^{-3}}$ | $\dfrac{R_p \times 10^6}{mol\ dm^{-3}\ s^{-1}}$ |
|---|---|---|
| 18 | 5.56 | 3.52 |
| 18 | 6.79 | 4.00 |
| 18 | 9.29 | 5.38 |
| 18 | 13.44 | 7.26 |

### 4.4.3.   Kinetic treatment and calculation of rate constant

The rate of polymerization may be expressed as

$$R_p = \frac{-d[M]}{dt} = k[\{(TPP)AlCl\}]^x\ [oxetane]^y$$

where  k is the rate constant

[oxetane] concentration of oxetane

[{(TPP)AlCl}] concentration of catalyst

x is the order with respect to the catalyst concentration

y is the order with respect to the oxetane concentration

On the basis of the results shown in table 4.3, a linear relationship with an intercept close to the origin was obtained when $R_p$/oxetane was plotted against $[\{(TPP)AlCl\}]^2$. Furthermore a correlation coefficient of 0.950 was obtained. It was concluded that the rate of polymerization is second-order with respect to the concentration of [(TPP)AlCl]. This plot is shown in figure 4.6.

Similarly, if the results in table 4.4 are considered then a linear relationship with an intercept close to the origin is obtained when $R_p$ is plotted against [oxetane]. The correlation coefficient was calculated to be 0.997. This indicates that $R_p$ is first-order with respect to the concentration of oxetane. This plot is shown in figure 4.7.

Figure 4.6: Dependence of Rp on [(TPP)AlCl]



Figure 4.7: Dependence of Rp on [oxetane]

From these plots the rate equation can be expressed in the following way;

$$R_p = \frac{-d[M]}{dt} = k[\{(TPP)AlCl\}]^2 [oxetane]$$

and the values of k determined from these slopes of the lines are $1.6 \times 10^{-3}$ and $1.5 \times 10^{-3}$ ($dm^3$ $mol^{-1})^2$ $s^{-1}$ which are in good agreement and therefore suppport the overall third order kinetics obtained.

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### 4.4.4. Mechanism of the coordination anionic polymerization of oxetane

The rate equation obtained in section 4.4.3 indicates the rate of polymerization is given by

$$R_p = k[\{(TPP)AlCl\}]^2 \, [oxetane]$$

A mechanism should be postulated in which it is believed that two molecules of [(TPP)AlCl] take part simultaneously during chain growth. The rate of polymerization being first order in monomer can be accounted for by a simple propagation step involving one monomer molecule at a time reacting with the catalyst centre i.e.

$$\text{Cat-OP}_n \; + \; \overset{O}{\square} \longrightarrow \text{Cat-OP}_{n+1}$$

These results agree with the kinetic analysis found by Inoue et al. for δ- valerolactone[207]. A mechanism that takes the following form:



During coordination of the monomer the two catalyst molecules are linked by the usual chloride bridging that exists in simple $AlCl_3$ systems. Upon ring-opening the following is considered to occur;

$$\text{Al}-\text{O}-\bigwedge-\text{Cl} \quad + \quad \text{Cl}-\text{Al}$$

$$\Big\updownarrow$$

$$\text{Al}-\text{O}-\bigwedge-\text{Cl}$$
$$\vdots$$
$$\text{Al-Cl}$$

Upon successive additions of the monomer the Al-O-$P_n$ bridging takes place. It must also be noted that the monomer has an equal chance of attacking either Al centre, thereby giving rise to a narrow molecular weight distribution i.e.

$$\begin{array}{ccc} & OP_n\text{-Cl} & \\ Al & \rightleftarrows & Al \\ & OP_n\text{-Cl} & \end{array}$$

However it must also be stressed that further work is required to strengthen further the possibility of this mechanism.

## 4.5. Study of the stereochemistry of the polymerization of cyclopentene and cyclohexene oxides using [(TPP)AlCl] catalyst

### 4.5.1. Introduction

It has been widely accepted that the ring opening step in the [(TPP)AlCl] initiated polymerization of epoxides is an $S_N2$ type reaction that might be expected to give rise to an atactic polymer; monomers such as propylene oxide are an enantiomeric mixture and each enantiomer would appear to be incorporated into the polymer chain in a statistically random manner. It can also be considered that a further source of stereospecificity during the polymerization may arise from the mechanism of opening of the cyclic ether ring itself but this

may not be detectable for the polymerization of a simple monomer such as propylene oxide because rotation may occur about the backbone C-C and C-O bonds between consecutive propagation steps thus masking any stereospecificity in the reaction. The use of chiral catalyst systems may help to distinguish between stereoregularity associated with the coordination step and any inherent in the mode of ring opening but would not give unambiguous information concerning the ring-opening reaction itself. It was decided that the study of the ring-opening polymerization of a bicyclic compound would likely to throw some light on this problem since rotations of the backbone between consecutive steps would be inhibited by the stucture of the polymer.

## 4.5.2. Experimental work

The procedure is described in section 2.6.3., however in this case approximately 15.09g (0.154 mol) of cyclohexene oxide, or 12.94g (0.154 mol) of cyclopentene oxide, were transferred to the reaction flask by distillation under vacuum. On warming to ambient temperature, the polymerization of cyclohexene oxide commenced, however to initiate the polymerization of cyclopentene oxide the reaction vessel was placed in a constant water bath set at 60°C. After 48 hours, the polymers were precipitated by adding to methanol. After evaporation of the volatile materials the structure of the polymer was determined by NMR.

## 4.5.3. Results and discussion

## 4.5.3. (i) Polymerization of cyclohexene oxide

## 4.5.3. (a) The $^1$H NMR of cyclohexene oxide

The NMR spectrum of the monomer cyclohexene oxide was investigated before polymerization; figure 4.8 shows the $^1$H NMR spectrum of the monomer. As expected there are three principal absorbancies in the spectrum but the complexity of the peaks is not as would be expected from a simple inspection of the structure of the molecule. These peaks around 1.8-2.1ppm and 1.2-1.6ppm are associated with the $CH_2$ protons of the cyclohexyl ring a and b respectively. The structure of the peak at 1.2-1.6ppm is, as expected complex, a quintuplet, because of the coupling of the protons with the other adjacent methylene groups of the ring. The absorbance centred around 1.8-2.1 is surprisingly only a triplet, the structure

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normally associated with protons coupled only to a methylene group, such as the methyl group in ethyl iodide. It seems reasonable then to suggest that the methylene group **b** is coupling to the methylene group **a** but not to the methine group **c**. Furthermore the methine proton **c** appears as a singlet and consequently is coupled to no other proton in the molecule. Such information may be interpreted as indicating the conformations of the rings in the molecule. Closer inspection of the absorbancies **a** and **b** reveals them to be two very closely overlapping quintuplets and triplets respectively, indicating that the conformation of the ring is fixed. The two methylene protons **a** are not equivalent, as one is axial and the other equatorial. However the dihedral angles between each of these protons and four protons associated with adjacent methylene groups are such as to favour coupling. If the structure of the methylene group **b** is now considered, a different interpretation is required. The absorbance is two very closely overlapping triplets, one associated with an axial and the other with an equatorial proton. These protons each couple with the two methylene protons, **a**, as would be expected but the protons do not couple with the protons **c**, which suggests that the dihedral angle between these two protons is close to a right angle. Finally, if the dihedral angle between the protons **c** and **b** is close to a right angle, one would not expect the absorbance associated with protons **c** to show any fine structure and, furthermore, the constraints of the ring are such that the protons **c** do not couple with each other either.

Figure 4.8: $^1$H NMR of cyclohexene oxide

## 4.5.3. (b) The $^1$H NMR of poly(cyclohexene oxide)

Polymerization of cyclohexene oxide is rapid when [(TPP)AlCl] is used as catalyst. The polymer obtained on evaporation of the solvent and unconverted monomer was dissolved in deuterated chloroform and the $^1$H NMR spectrum of the material was obtained; this spectrum is shown in figure 4.9. Three principal peaks were obtained, as expected, and these were of the expected intensities, consistent with polymer being poly(cyclohexene oxide). Of particular interest in the analysis of the spectrum is the resonance in the region 3.2-3.6ppm associated with the -CH-O- proton. In the case of the monomer this peak was a singlet so it is evident that the spacial arrangement of these protons had changed during polymerization, because the peak in the polymer appears to be a poorly resolved doublet.

Figure 4.9: ¹H NMR of poly(cyclohexene oxide): (TPP)AlCl catalyst used

In order to establish the nature of the coupling between protons in the polymer a COSY (two dimensional) ^{1}H NMR spectrum was obtained. This is shown in figure 4.10 for poly(cyclohexene oxide) obtained in these studies. The spectrum clearly indicates that there is coupling between the -CH-O- proton and the adjacent -$CH_2$- in the cyclohexyl ring. The next stage in the analysis was therefore to decouple this coupling and to investigate the resulting structure of the -CH-O- resonance. On decoupling of the adjacent methylene protons a broad resonance was obtained that showed evidence of multiplicity and when a Guassian multiplication was applied to the resonance, the structures obtained for the -CH-O- peak is shown in figure 4.11. It is clear that the resonance obtained, after decoupling, is a four line structure. The structure is 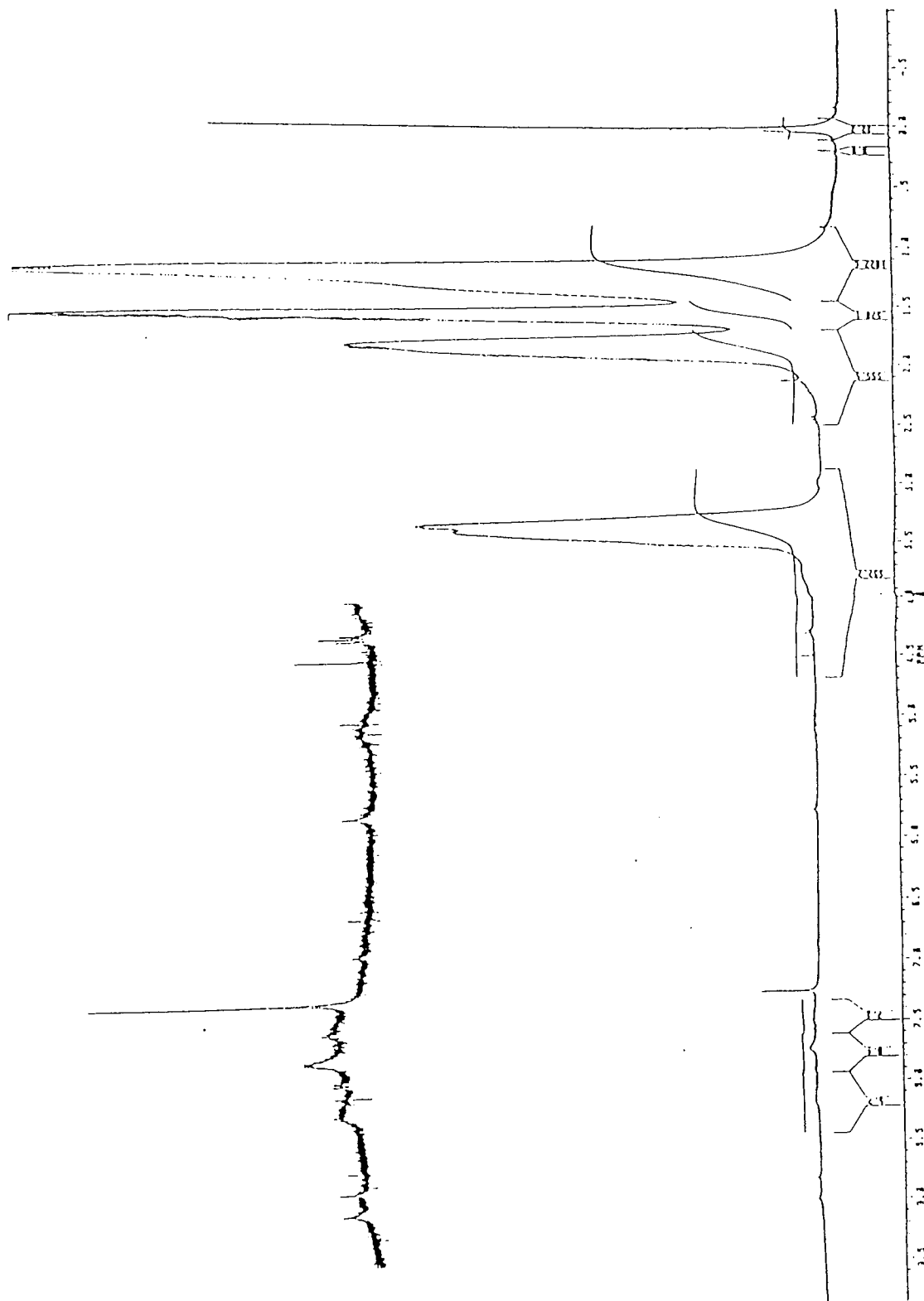interpreted as two doublets, which suggest that the two protons are not equivalent but that each is coupled with the other, because if the protons were equivalent then the peak would be expected to be a simple doublet. If one considers the possible structures of the cyclohexyl ring that could give rise to this ^{1}H NMR the two protons in question could either be *cis* or *trans* to one another as in figure 4.12. If the protons are trans to one another then, since this is a 1,2-disubstituted ring, the two protons are either both axial or both equatorial protons and hence equivalent. However, if the protons are *cis* to one another, then in whichever chair conformation the ring adopts, one proton is axial and the other equatorial. This arrangement of the protons would be in agreement with the observed structure of the ^{1}H NMR. It is not possible to determine whether the resonance in question is a superposition of the spectra due to *cis* and *trans* structures or purely associated with a *cis* disubstituted cyclohexyl ring. It would seem therefore that during polymerization, the propagation step involves a reaction that leads almost exclusively to an intermediate producing a *cis* structure to the polymer.

Figure 4.10: 2-D COSY $^1$H NMR of poly(cyclohexene oxide)

Figure 4.11:   Decoupled spectrum of poly(cyclohexene oxide)

*trans* -poly(cyclohexene oxide)



*cis*-poly(cyclohexene oxide)

## 4.5.3. (c) Mechanism of polymerization of cyclohexene oxide

The polymerization of epoxides using catalysts such as [(TPP)AlCl] has been described by workers such as Inoue as a coordinated anionic polymerization. Although it is known that polymers such as propylene oxide are often stereospecific when polymerized by this type of catalyst, it is possible for such stereospecificity to arise during the propagation step if the monomer is required to coordinate to the aluminium atom in a specific arrangement during each propagation step. Using monomers such as propylene oxide and 2,3-dimethyloxirane it is not possible to distinguish between and $S_N1$ and $S_N2$ type attack when the propagating end attacks the coordinated monomer molecule. The polymerization of cyclohexene oxide shows that the propagation step in [(TPP)AlCl] initiated polymerizations is not only a stereospecific reaction but also that of ring-opening of the epoxide ring occurs in a specific manner , since we have evidence for the formation, almost exclusively, of *cis* 1,2-disubstituted cyclohexane rings.

In order to account for the formation of the *cis* product, particularly since this is derived from a *cis* monomer, the propagating group should be expected to approach the complexed monomer in the same orientation at each propagation step and should also approach on the same face of the monomer as the epoxide ring. This would tend therefore to suggest that the complexed monomer, propagating centre and catalyst site form the kind of complex shown in figure 4.13.

**Figure 4.13: Mechanism by which the ring-opening polymerization of cyclohexene oxide is thought to occur by [(TPP)AlCl] catalyst**

The mechanism involves a transition state in which a 5-membered 'ring' is adjacent to the 6-membered ring of the cyclohexene. This transition state would lead solely to the retention of the configuration i.e. *cis* 1,2-disubstituted cyclohexene ring.

### 4.5.3. (ii) Polymerization of cyclopentene oxide

### 4.5.3. (d) The $^1$H NMR of cyclopentene oxide

As before, the NMR spectrum of the monomer was investigated before polymerization. The spectrum is shown in figure 4.14. The spectrum seems more complicated than that of cyclohexene oxide but on close analysis it can be seen that there are three principal absorbancies. The peaks around the region 1-2ppm are associated with the CH$_2$ protons of the cyclohexyl ring **a** and **b** respectively. If the areas under these peaks could be determined then they would show that the peaks associated within the 1-2ppm region consist of two quartets and a single quintet. However due to the complexity this is difficult to observe. It seems reasonable therefore to suggest that the methylene group **b** is coupling to the methylene group **a**, but since a single peak for protons **c** at 3.4ppm is shown, group **a** does not couple with group **c**. The fact that **a** does not couple with **c** suggests that the dihedral angle between these two protons is close to a right angle.

Figure 4.14: $^1$H NMR spectrum of cyclopentene oxide

### 4.5.3. (e)  The $^1$H NMR of Poly(cyclopentene oxide)

The spectrum of poly(cyclopentene oxide) is shown in figure 4.15. Three principal absorbancies are indicated. The resonance appearing at 3.8ppm is associated with the -CH-O- protons and is a single peak which suggests that the two C$\underline{H}$O protons are equivalent. Again the neighbouring CH$_2$ protons (**a** protons in monomer) do not have any effect on the C$\underline{H}$O protons. The CH$_2$ protons appear at 1.8-2.0ppm and at 1.4ppm, the reason why two different absorbancies are indicated by these protons is that there is some weak coupling by the C$\underline{H}$O protons as shown by the COSY spectrum in figure 4.16. Finally the CH$_2$-C$\underline{H}_2$-CH$_2$ protons (**b** protons in monomer) are indicated in the region 1.5-1.6ppm and as expected a quintet is observed.

Since the COSY spectrum has indicated coupling between the CH$_2$-C$\underline{H}_2$-CHO protons and C$\underline{H}$O protons a spectrum was then obtained in which this coupling was decoupled to investigate the -CHO resonance. On decoupling, figure 4.17, a single broad peak was obtained which suggests that the two -C$\underline{H}$O protons are equivalent and that their relationship is either *cis* or *trans* in the polymer.

Furthermore the only possible relationship for these hydrogens is *cis* in the structure of cyclopentene oxide, and the work carried out with cyclohexene oxide indicated that there was a retention in the configuration; then on this basis it is also likely that the conformation of these hydrogens is *cis* in the polymer. This then leads towards a mechanism of polymerization similar to that described in section 4.5.3. (c).

Figure 4.15: $^1$H NMR of poly(cyclopentene oxide),

Figure 4.16:  2-D COSY $^1$H NMR of poly(cyclopentene oxide)

Figure 4.17:  Decoupled spectrum of poly(cyclopentene oxide)



3.8    3.7    3.6

PPM

## 4.5.3. (f) Mechanism of polymerization of cyclopentene oxide with [(TPP)AlCl] catalyst

The mechanism is thought to occur in a similar way to that described in section 4.5.3 (c), thus;



**Figure 4.18. Mechanism by which the polymerization of cyclopentene oxide is thought to occur with [(TPP)AlCl] catalyst**

Interestingly, if this mechanism is compared with that of cyclohexene oxide, the transition state in this case involves a 5-membered 'ring' adjacent to another 5-membered ring; whereas with cyclohexene oxide the transition state involved a 5-membered 'ring' adjacent to a 6-membered ring which is much more stable than the latter. This may therefore account for the fact the polymerization of cyclopentene oxide took place at 60°C whilst the cyclohexene oxide polymerization occurred at room temperature.

# CHAPTER 5
## CONCLUSIONS AND FURTHER WORK

### 5.1. Cationic ring-opening polymerization of cyclic ethers
### (a) Kinetic and mechanistic studies

The work presented in this thesis investigated the kinetics and mechanism of the polymerization of oxetane using three different cationic systems, $BF_3OEt_2$/ethanol, $BF_3OEt_2$/ethanediol and $BF_3OEt_2$/propantriol.

An investigation of the molar ratio of $BF_3$:OH which gave the optimum rate was examined using the $BF_3OEt_2$/ethanediol system. It was found that a 1:1 $BF_3$:OH ratio gave the maximum rate of polymerization and consequently it was decided that the determination of the kinetic orders with respect to the concentrations of the catalyst and the monomer were to be carried out using an equal ratio of $BF_3$:OH. It was assumed that the two other systems $BF_3OEt_2$/ethanol and $BF_3OEt_2$/propantriol would give similar results but there is a need to confirm this. Further work carried out on the elucidation of the structure of the catalyst/co-catalyst complexes using $^1H$ NMR indicated that the maximum number of active centres with oxetane would be produced if the $BF_3$:OH ratio was 1:1, this result was common with all three catalyst systems which might suggest that the assumption made above was correct. Kinetic determination of the rate of polymerization of oxetane using the three different catalyst systems was investigated and results can be summarised by the equations shown below:

$$R_p = k_p[BF_3:OH][oxetane]$$

where OH = propantriol and ethanediol

$$R_p = k_p[BF_3:OH]^{1/2}[oxetane]$$

where OH = ethanol.

Thus the overall second order kinetics for the rate of polymerization of oxetane using the catalyst systems $BF_3OEt_2$/ethanediol and $BF_3OEt_2$/propantriol agreed with the work carried out by J.B. Rose[63] when it was observed that the $BF_3/H_2O$ system also gave an overall

second. order kinetics. However with ethanol as co-catalyst an overall 3/2 order kinetics was observed which meant that the mechanism of the polymerization of oxetane was significantly influenced by the type of the co-catalyst used and for the first time the evidence here indicated that there was more than one type of mechanism of polymerization of oxetane to be considered.

To provide further evidence for the kinetic equations, the rate constant (k) was determined from the plots of $R_p$ against [oxetane] and $R_p$ against [catalyst] and it was found that the two rate constant from each plot for all the catalyst systems were close to one another indicating that the rate equations determined were correct. The values of the rate constants were found to be $k_{(diol)} = 2.0$ dm$^3$ mol$^{-1}$s$^{-1}$, $k_{(triol)} = 1.8$ dm$^3$mol$^{-1}$s$^{-1}$ and $k_{(ethanol)} = 0.075$(dm$^3$mol$^{-1}$)$^{1/2}$s$^{-1}$.

In order to explain the difference in the kinetics and the rate constants obtained it was envisaged that the mechanism of polymerizaton of oxetane where the co-catalyst was ethanol was different from ethanediol and propantriol. The mechanism postulated in this thesis suggests that, where ethanol is concerned, a simple adduct with ethanol and BF$_3$ is produced which produces an acidic OH group. The OH group then activates a molecule of oxetane to produce an active centre and the resulting gegenion. However in this case the active centre pair dimerises with another pair. The dimeric species is unable to initiate polymerization but upon breaking the active centre is 'free' for propagation to occur and it is this process that slows the overall rate and is responsible for the 3/2 kinetic order. The formation of the dimer does not occur with ethanediol and propantriol because in this case both co-catalysts contain more than one OH group. A simple adduct with BF$_3$ is formed and the neighbouring OH group is also able to interact with the BF$_3$ to produce a cyclised structure in which two oxygen atoms share a positive charge; the driving force for this originates from the ability to form a 5-membered cyclised structure. Propagation in this case results from the reaction between the oxonium ion and one molecule of oxetane. Since dimerization does not occur the overall rate is faster. Further evidence for these structures was obtained from the ^{1}H NMR studies which showed evidence for a simple adduct with ethanol and BF$_3$OEt$_2$ and the data also supported evidence for the 5-membered cyclised complex when BF$_3$OEt$_2$ was reacted with ethanediol and

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for the 5-membered cyclised complex when $BF_3OEt_2$ was reacted with ethanediol and propantriol. However it must be noted that the $^1H$ NMR studies are still in their preliminary stages and it will be useful if these structures can be examined using low temperature $^1H$ NMR and 2-D COSY system to reveal all the protons present and this might provide a stronger evidence than already obtained. It can be concluded that the NMR evidence is consistent with the mechanism described in this study.

## (b)   Molecular weight studies

The number average molecular weight ($M_n$) of poly(oxetane) was determined using size-exclusion chromatography in which poly(THF) standards were employed. Studies showed that $M_n$ of poly(oxetane) decreased linearly with increasing [OH] at constant $[BF_3OEt_2]$ and that there was no effect on $M_n$ as $[BF_3OEt_2]$ increased at constant [OH]. This indicated that the OH acted as a chain transfer reagent when in excess and termination was very similar to that of the first-order type. The catalyst system used for this study was $BF_3OEt_2$/ethanediol and further work is required to observe whether $BF_3OEt_2$/ethanol and $BF_3OEt_2$/propantriol systems give similar results.

Further work involving molecular weight studies concluded that a linear dependency was observed when $M_n$ was plotted against the [oxetane] at constant [$BF_3$:OH] with all three catalyst systems. Furthermore a linear dependency was also observed when $M_n$ was plotted against the increasing concentration of the $BF_3$:OH 1:1 adduct at constant [oxetane]. It was concluded that the $M_n$ approximately increased in the ratio of 1:2:3 when the catalyst system involved ethanol, ethanediol and propantriol respectively. The reason for this is unknown and more work is required though the answer may be due to the fact that with ethanediol and propantriol there is significant intramolecular H-bonding which may reduce the ability of OH groups to be involved in chain transfer. As with ethanol intermolecular H-bonding is present.

Finally the size exclusion chromatography studies on the poly(oxetanes) showed that the distribution was polymodal and it is likely that both trimers and tetramers were present along with the polymer. However since this work was limited to the polymers further work should

be carried out to separate and characterise the oligomers as this would also give information regarding the mechanism of polymerization.

## (c)   Copolymerization studies

Copolymerization studies of oxetane and THF were also carried out using a 1:1 $BF_3OEt_2$:ethanol system. Initially it was found that the homopolymerization of THF with this system was impossible, but in conjunction with oxetane the copolymerization of THF was successful. Using $^1H$ NMR of the copolymers the composition of each copolymer was determined and it was found that by increasing the THF concentration in the monomer feed ratio the composition of THF increased. Reactivity ratios were calculated using $^1H$ NMR data and it was concluded that $r_{THF} = 0.14\pm0.09$ and $r_{OXT} = 1.20\pm0.30$ which suggests that the oxetane reactivity is approximately 8.5 times greater than that of THF. This can be explained by the fact that oxetane has a higher ring strain and higher basicity than THF and therefore is more prone to ring opening.

The information obtained from $^{13}C$ NMR of the copolymers showed oxymethylene peaks to be doublets which suggested that the oxymethylene groups from both the oxetane and THF molecules had two different environments showing that these copolymers were random copolymers.

$M_n$ was also calculated for the copolymers and results indicated that the $M_n$ decreased if the THF concentration in the monomer feed ratio was increased. This suggests that a polymer chain consisting of a THF terminal unit is more likely to be susceptible to termination and chain transfer reactions compared to that of an oxetane terminal unit. It must be noted that the mechanism of termination is still relatively unknown and therefore further work is required to provide conclusive evidence for this possibility.

The most significant feature of the molecular weight studies was that with the copolymers there was no evidence for the presence of oligomers. Thus the incorporation of THF into the polymer back-bone somehow is able to disrupt the stereoregularity for stable tetramer/trimer

formation. Again this work is in its early stages but it does open up a new area of research, as for example, it would seem reasonable to suggest that the polymer:oligomer ratio could be controlled by amount of THF added, and if so what are the critical concentrations? Finally since back-biting is the predominant mechanism for the formation of oligomers in the homopolymerization of oxetane a suggested further work would involve the use of crown ethers which could stabilise the active chain end which then might prohibit the back-biting mechanism, thereby producing polymers of even higher molecular weight with distributions being narrow, however this is all speculation the work so far has opened up interesting avenues.

## 5.2. The ring-opening polymerization of cyclic ethers using coordinated anionic catalyst

The results show the first recording of a living polymerization of oxetane using coordinated anionic catalyst - porphinato aluminium chloride, [(TPP)AlCl]. Before this it was thought that higher cyclic ethers could only be polymerized cationically. The polymerization showed all the signs of living character which includes a linear dependency of $M_n$ with % conversion and the polydispersity indicating a narrow molecular weight distribution. The efficiency of the catalyst system within experimental errors approached 100% which is another indication that the system is living. Indeed those results compare well with those published by Inoue[172] which estimated the efficiencies of initiation to around 150% when ethylene oxide was used as the monomer.

The kinetics of this polymerization were investigated and the results can be summarised by the equation shown below:

$$R_p = k_p [(TPP)AlCl]^2 [oxetane]$$

i.e. second order in the concentration of the catalyst and first-order in the concentration of the monomer giving overall third order kinetics for the polymerization. Again these results compare well with those obtained by Inoue[207] when a derivative of this catalyst was used to polymerize δ-valerolactone. To support the kinetics, rate constants for the polymerization was calculated from the plots of $R_p$ against [oxetane] at constant [catalyst] and $R_p$ against [catalyst]

at constant [oxetane] and the values obtained were $1.50 \times 10^{-3}$ and $1.60 \times 10^{-3}$ $(dm^3 \, mol^{-1})^2 s^{-1}$ and since these values are close the third order relationship was verified.

The mechanism of the polymerization of oxetane was discussed and it was shown to involve two molecules of [(TPP)AlCl] taking part simultaneously during chain growth, and a single monomer molecule reacting with one active centre.

[(TPP)AlCl] was also used in the attempted polymerization of 3,3-dimethyl-oxetane, 3-hydroxymethyl-oxetane and THF but all were unsuccessful. However 3-methyl-3-nitratomethyl-oxetane (NIMMO) showed signs of oligomer formation. The main reason for the failure of polymerization of the substituted oxetanes could be accounted by the steric factors and competition between the oxygen atoms present in the side chain and the hetero-oxygen trying to compete with the active centre. If the side-chain oxygen atom links with the active centre then polymerization is unsuccessful. The probable reason for oligomer formation with NIMMO is that the nitrato group is able to withdraw electrons from the neighbourly oxygen atoms and therefore favouring competition for hetero-oxygen atom to attack the active centre thereby giving rise to polymerization. Finally THF has a lower ring strain and basicity than oxetane and oxirane so making polymerization with [(TPP)AlCl] even less favourable.

The stereoregularity of the catalyst [(TPP)AlCl] was monitored by the polymerization of cyclopentene oxide and cyclohexene oxide. It was concluded from the study of $^1H$ NMR that relationship of the hydrogens at the point where the ring opens and remains the same as in the polymer compared to that of the monomer. To resolve all the protons, 2D COSY NMR was applied together with the analysis of decoupled spectra. It was suggested that the [(TPP)AlCl] is a stereoregular catalyst. Using these results the possible mechanism involving [(TPP)AlCl] as catalyst was investigated, and it was concluded that neither $S_N1$ or $S_N2$ type of attack is responsible in the mode of ring-opening but a transition state in which bonds are breaking and simultaneously forming; which would result in retaining the original conformations.

There is however a need for further work such as trying to develop living polymers of substituted oxetanes already mentioned. This may be achieved either by using a derivative of the [(TPP)AlCl] as catalyst or by changing the chemistry of the side chain of the monomers such that an attack by the hetero-oxygen atom at the active centre would be more favourable.

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# APPENDIX 1

NMR spectra of the $BF_3OEt_2/ROH$ complexes referring to the study described in section 3.1.8.
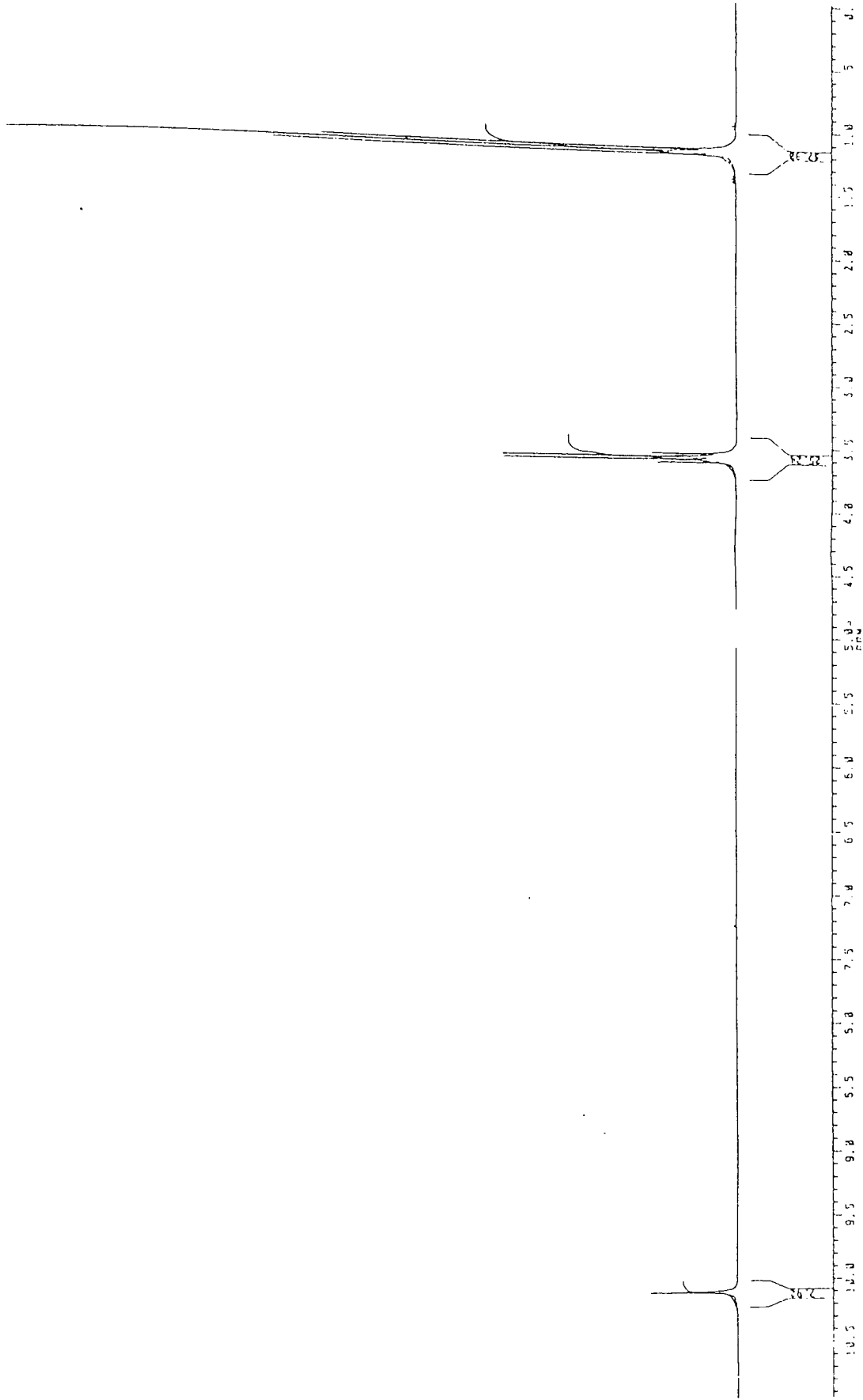
Fig. (1): $^1$H NMR of $BF_3OEt_2$-
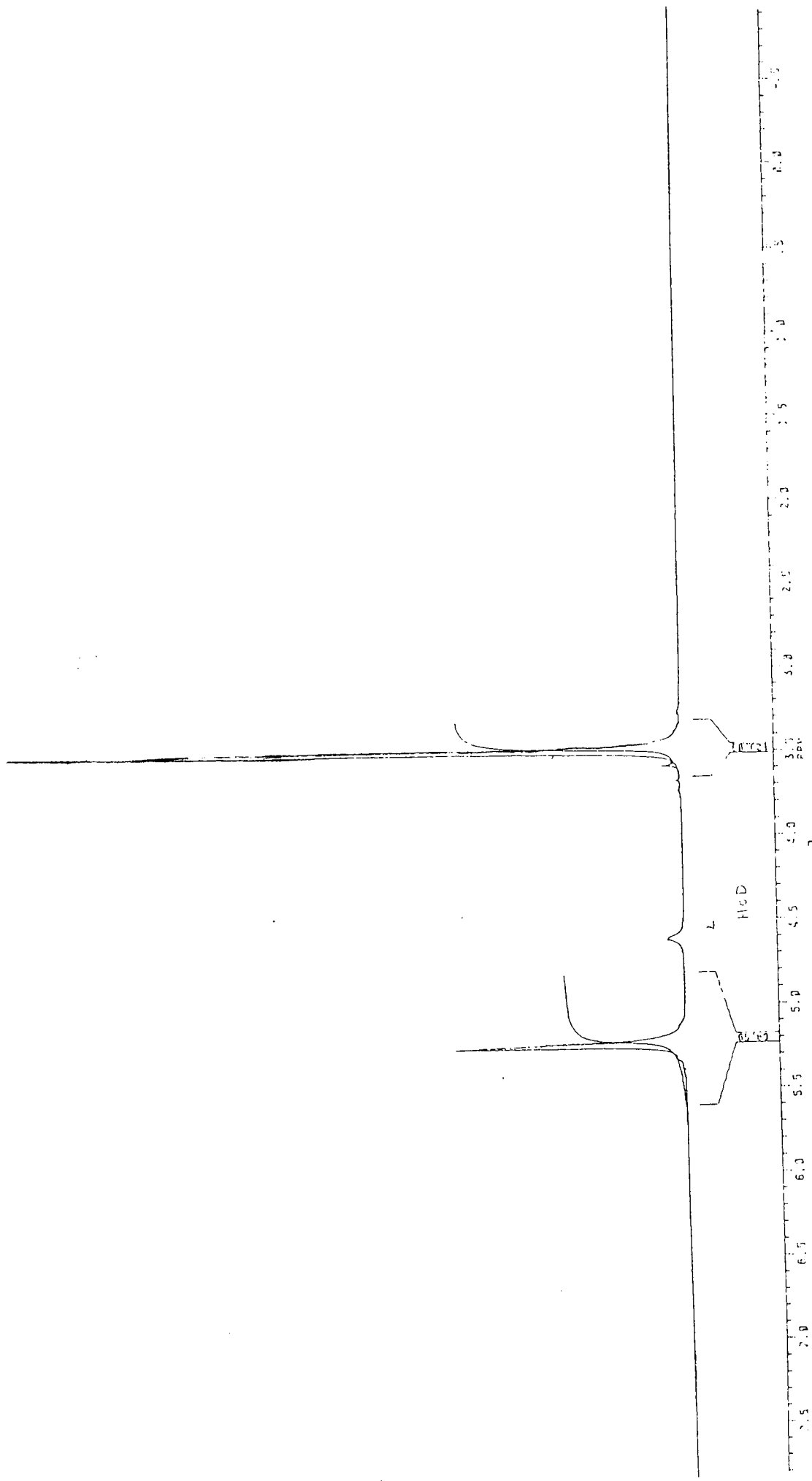
Fig. (2): $^1$H NMR of ethanediol
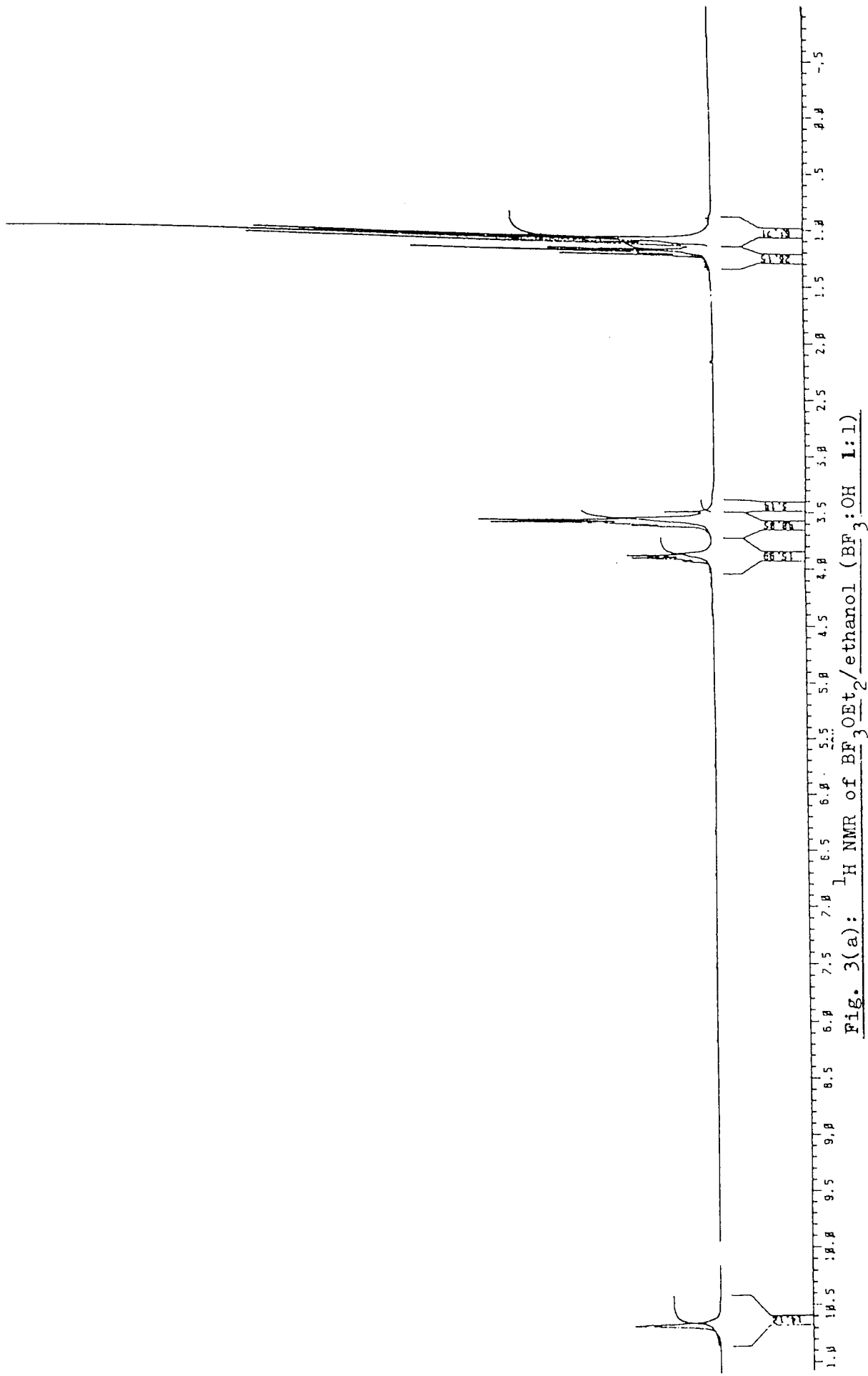
Fig. 3(a): $^1H$ NMR of $BF_3OEt_2$/ethanol ($BF_3:OH$ **1:1**)
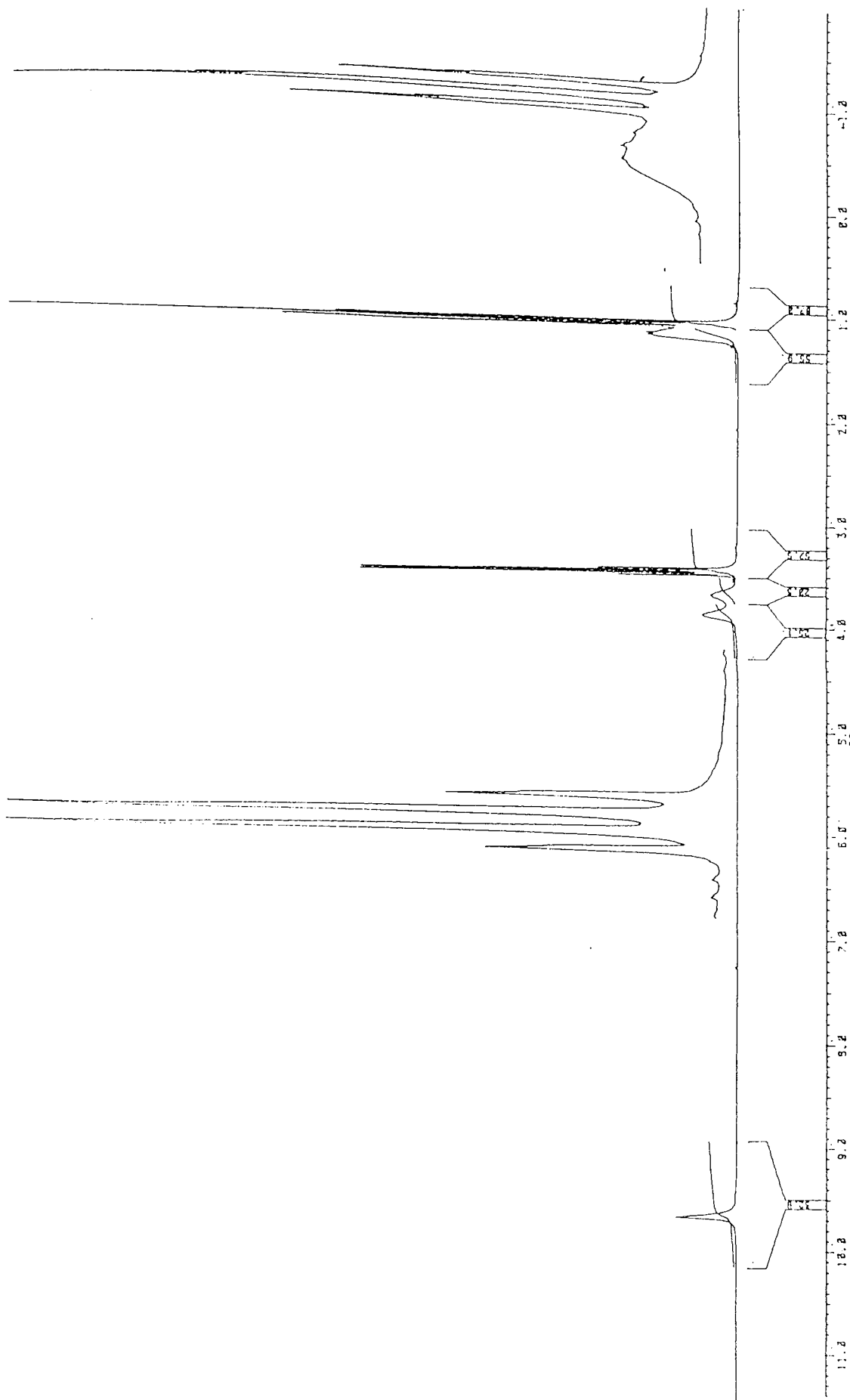
Fig. 3(b): $^1$H NMR of $BF_3OEt_2$/ethanol ($BF_3$:OH 1:2)

Fig. 3(c): $^1H$ NMR of $BF_3OEt_2$/ethanol ($BF_3$:OH 1:3)

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Fig. 4(a): $^1$H NMR of $BF_3OEt_2$/ethanediol ($BF_3$:OH 1:1)
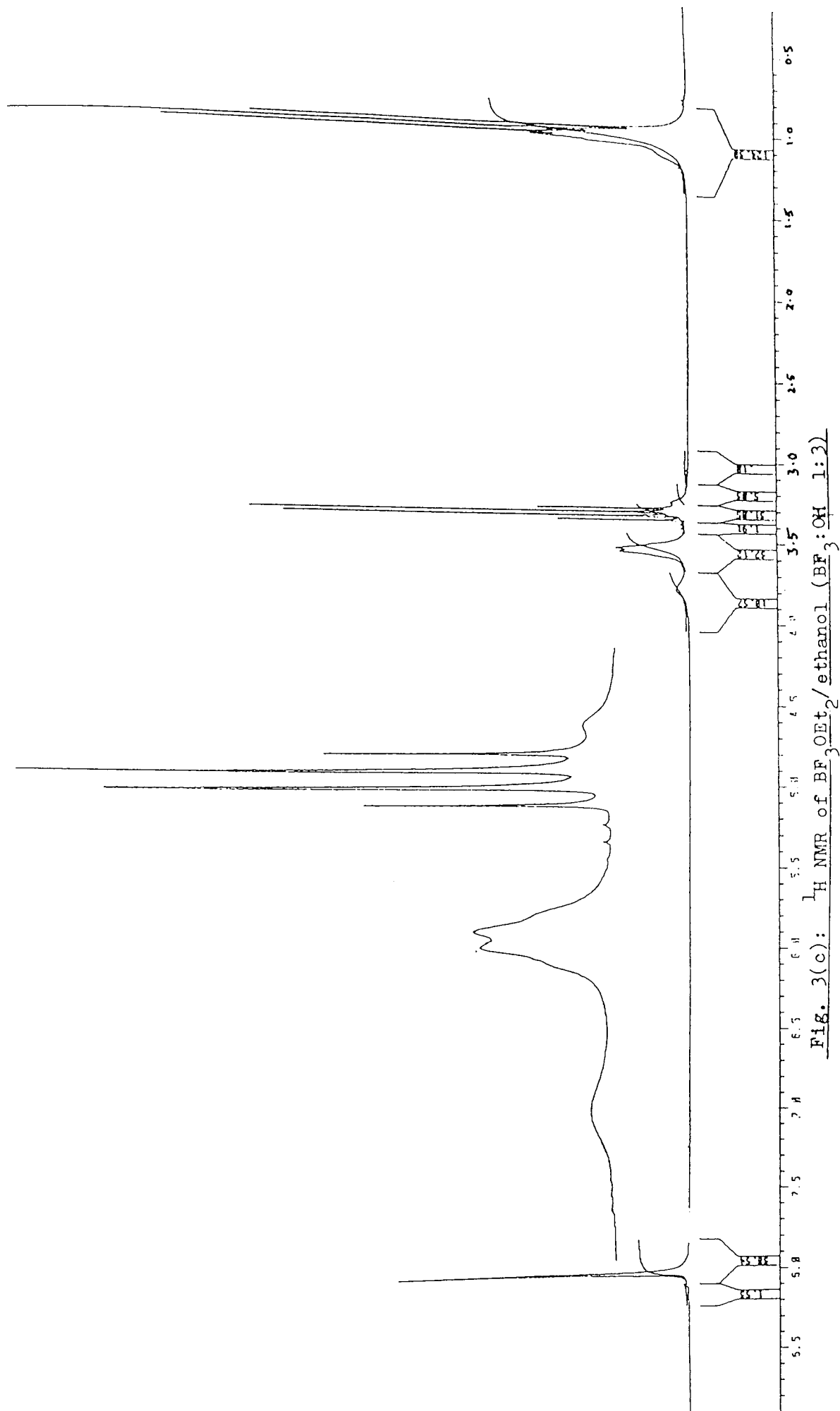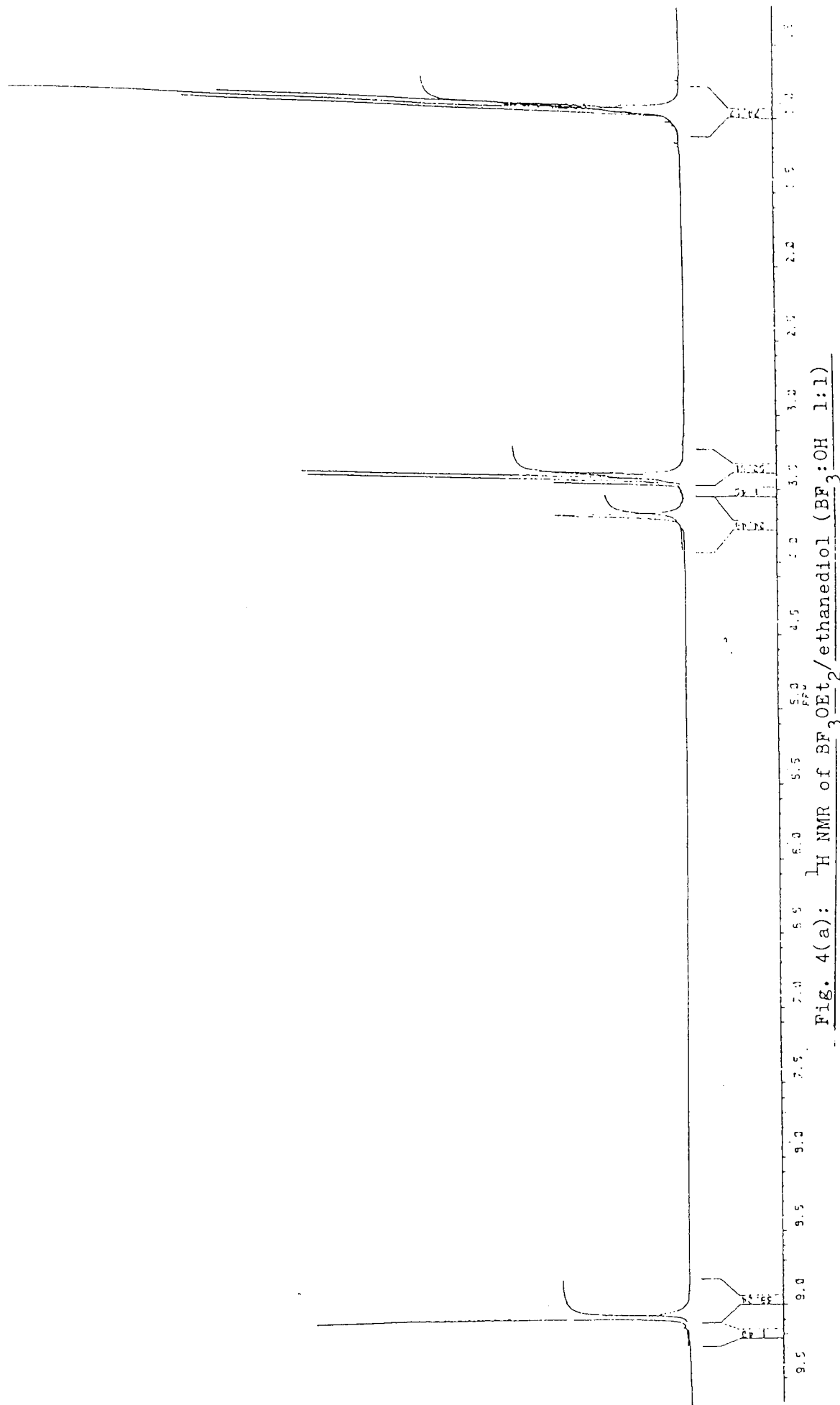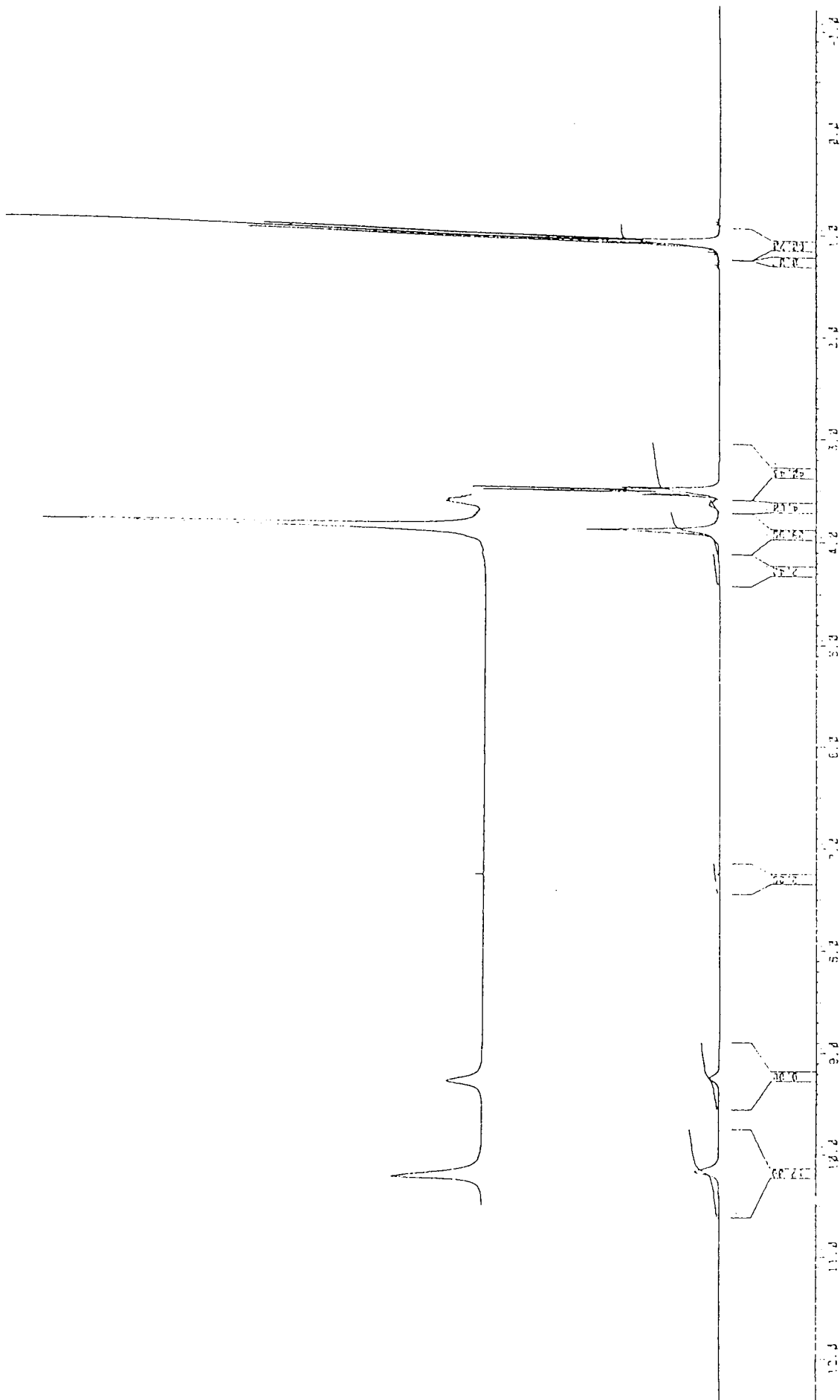
Fig. 4(b): $^1$H NMR of BF$_3$OEt$_2$/ethanediol (BF$_3$:OH 1:2)
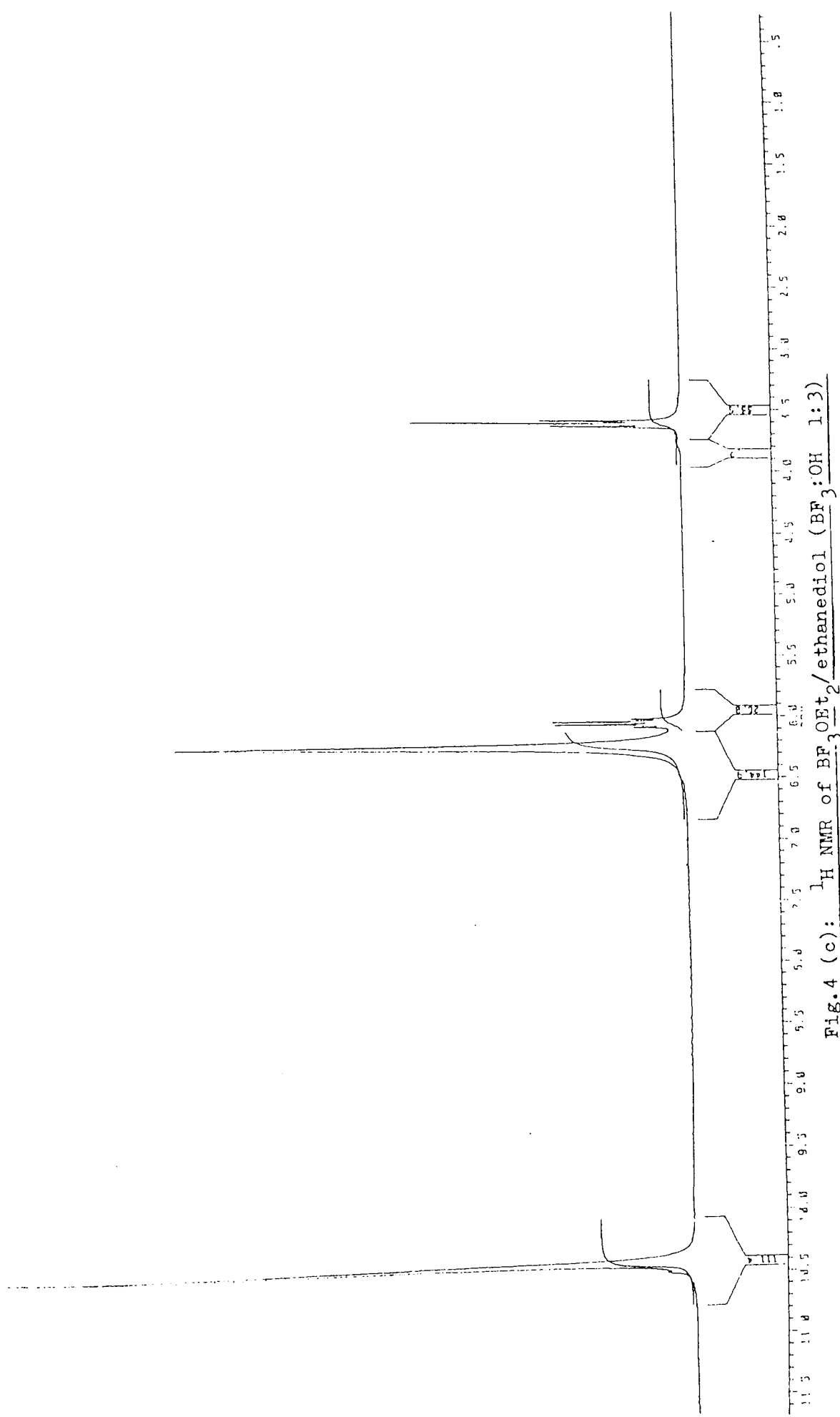
Fig.4 (c): $^1$H NMR of BF$_3$OEt$_2$/ethanediol (BF$_3$:OH 1:3)

Fig. 5(a): $^1$H NMR of BF$_3$OEt$_2$/propantriol (BF$_3$:OH 1:1)
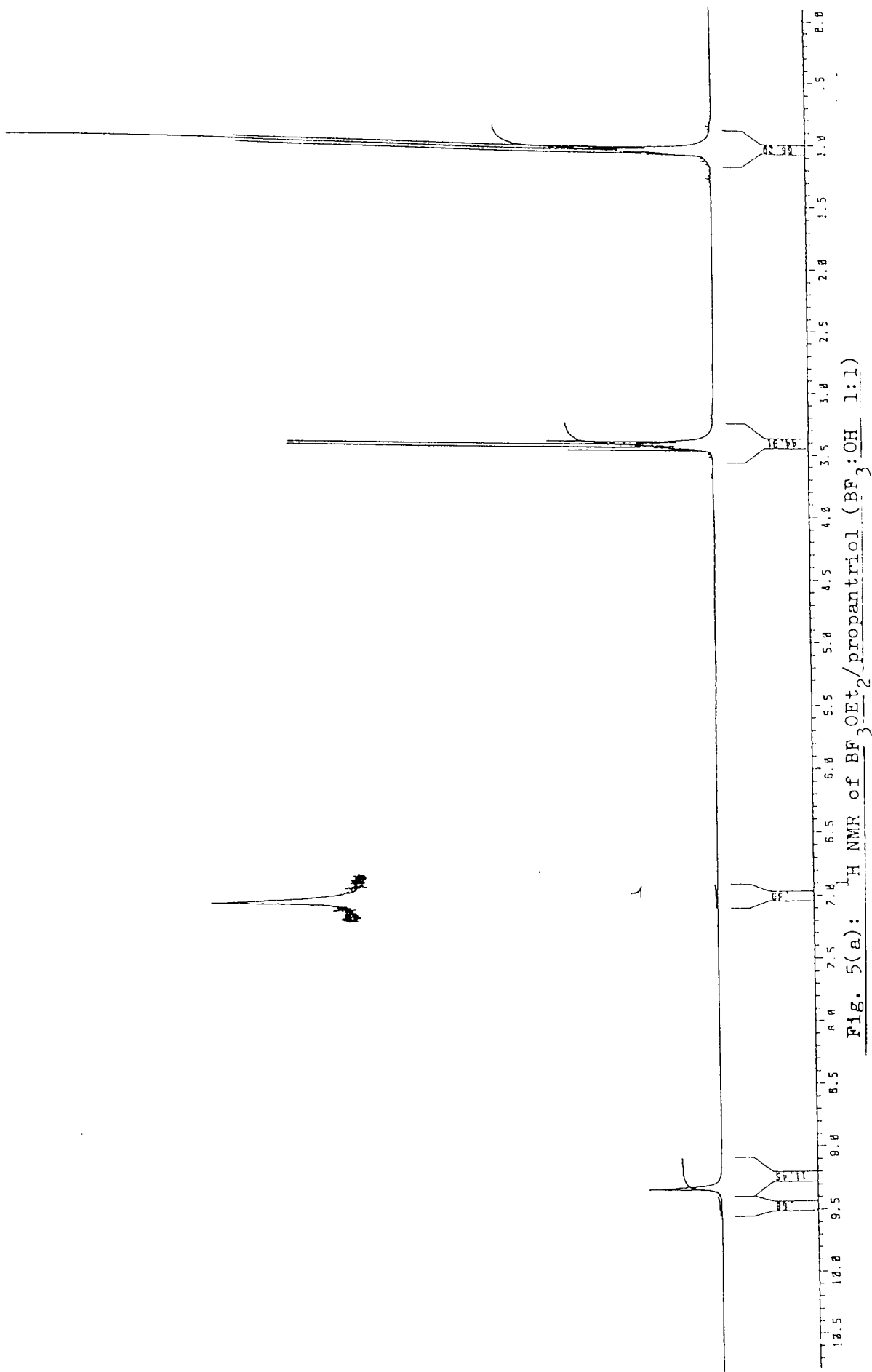
Fig. 5(b): $^1$H NMR of BF$_3$OEt$_2$/propantriol (BF$_3$:OH 1:2)
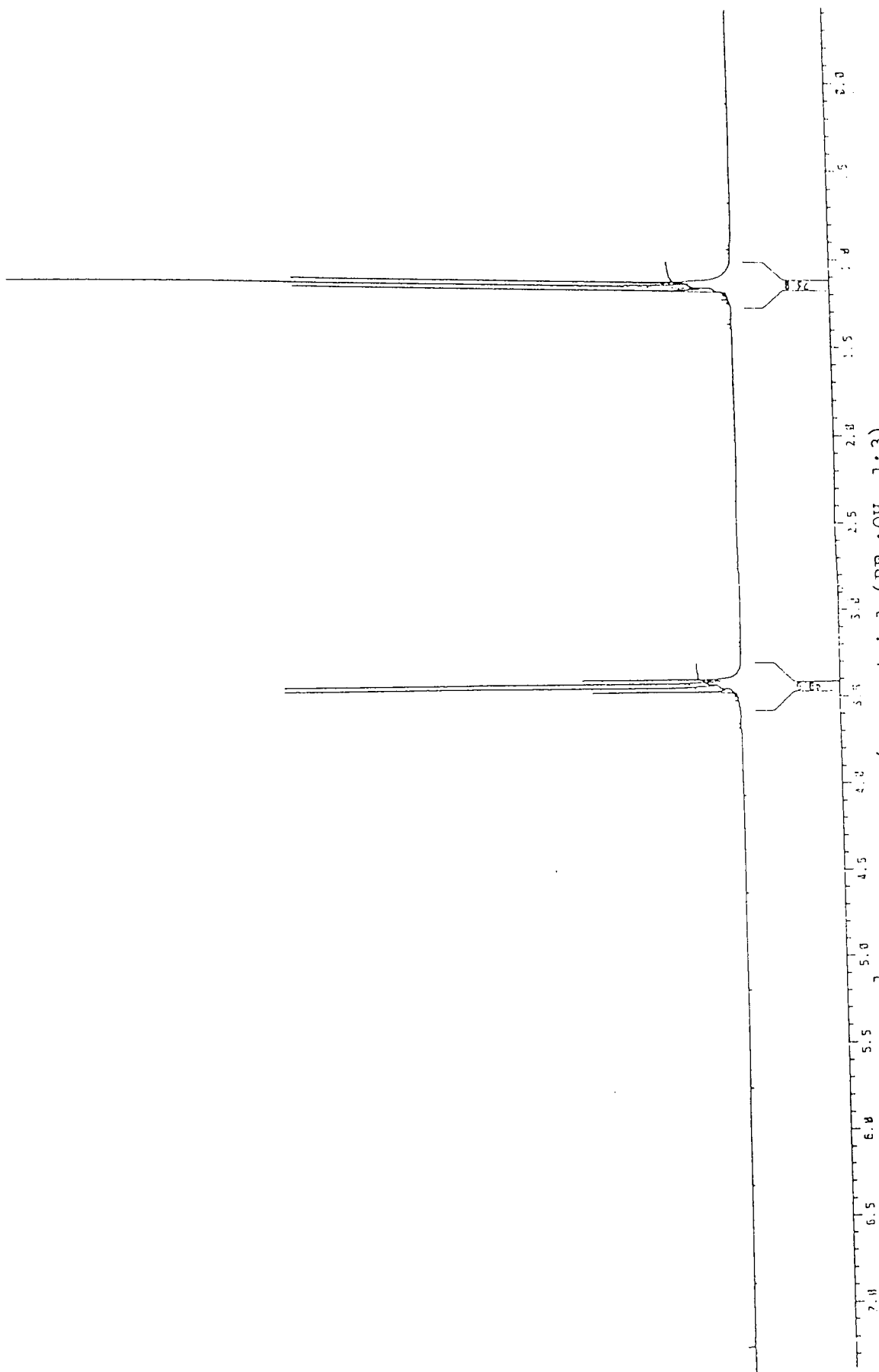
Fig. 5(c): $^1$H NMR of $BF_3OEt_2$/propantriol ($BF_3:OH$ 1:3)

# APPENDIX 2

NMR spectra of the copolymer of oxetane and THF referring to section 3.1.9.

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Fig. 1(a): $^1$H NMR of the copolymer of THF and oxetane;feed ratio 4.00:1.00 respectively.

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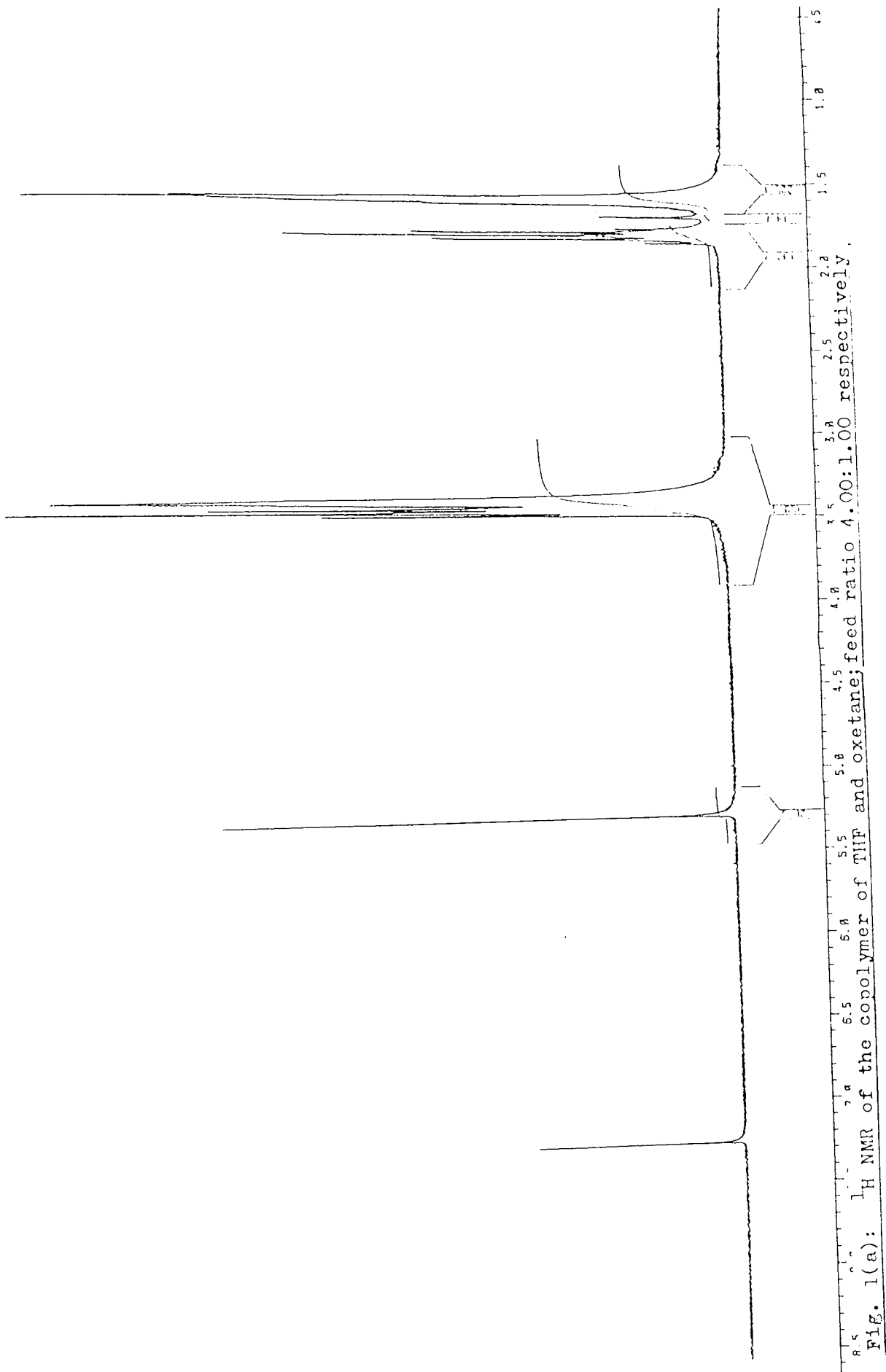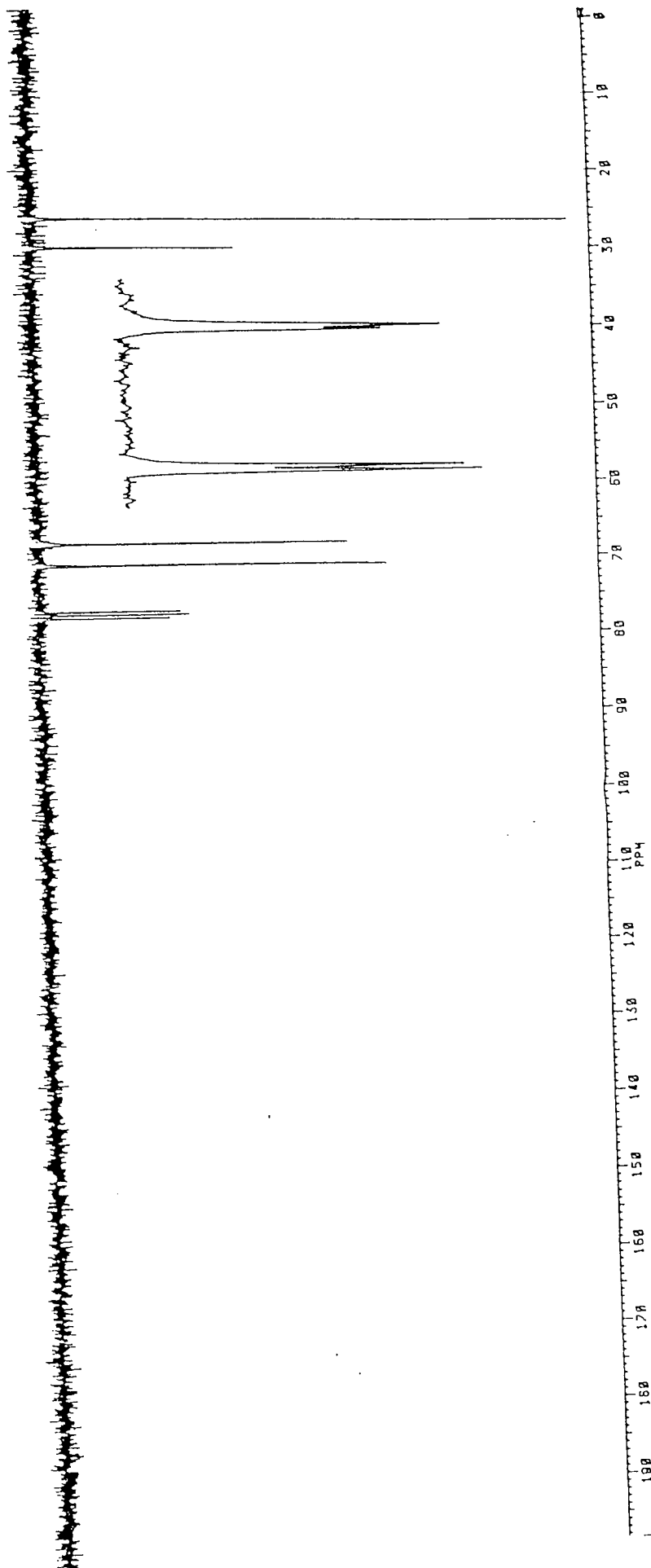
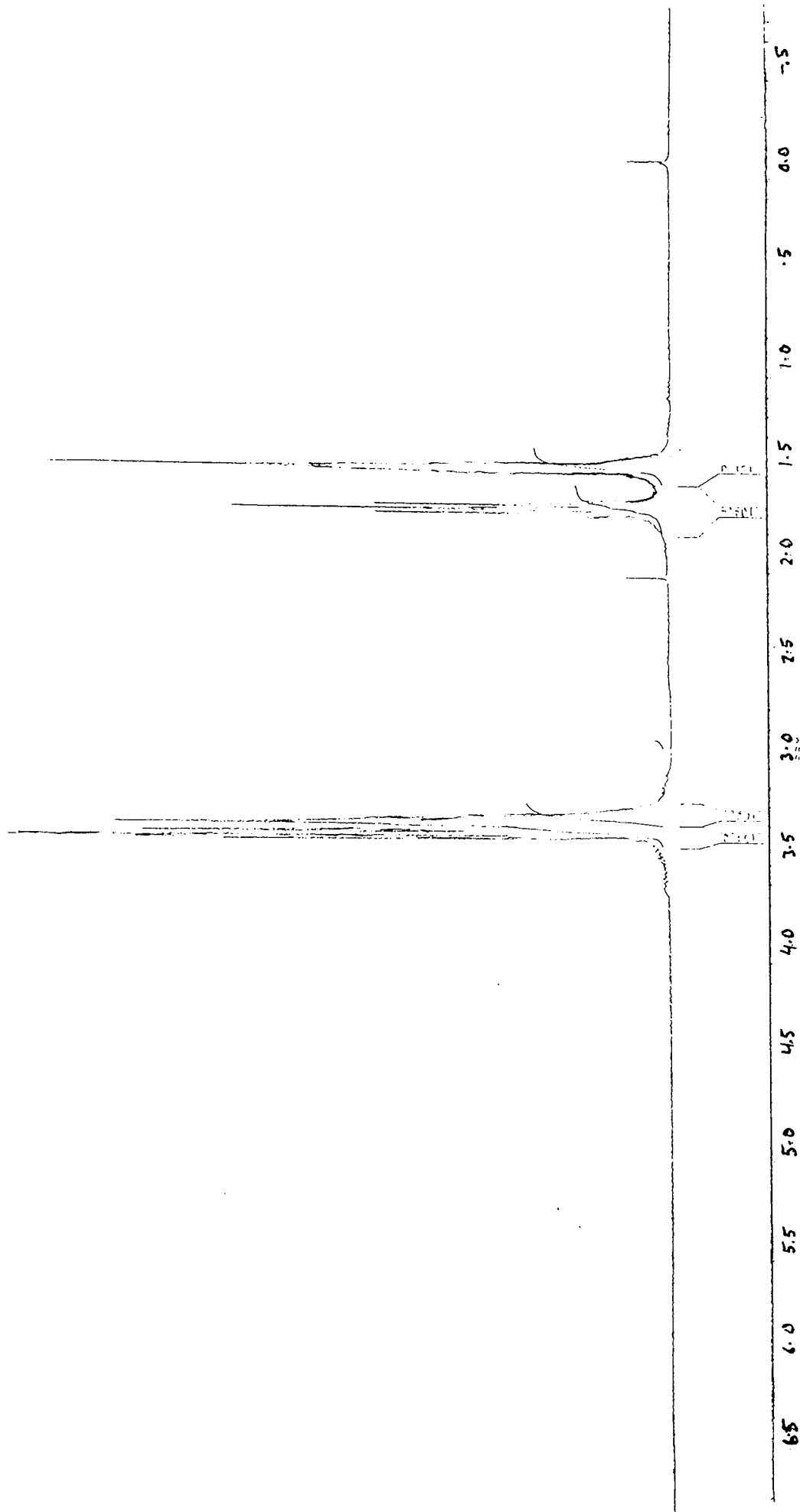Fig. 1(b): $^{13}C$ NMR of the copolymer of THF and oxetane; feed ratio 4.00:1.00 respectively
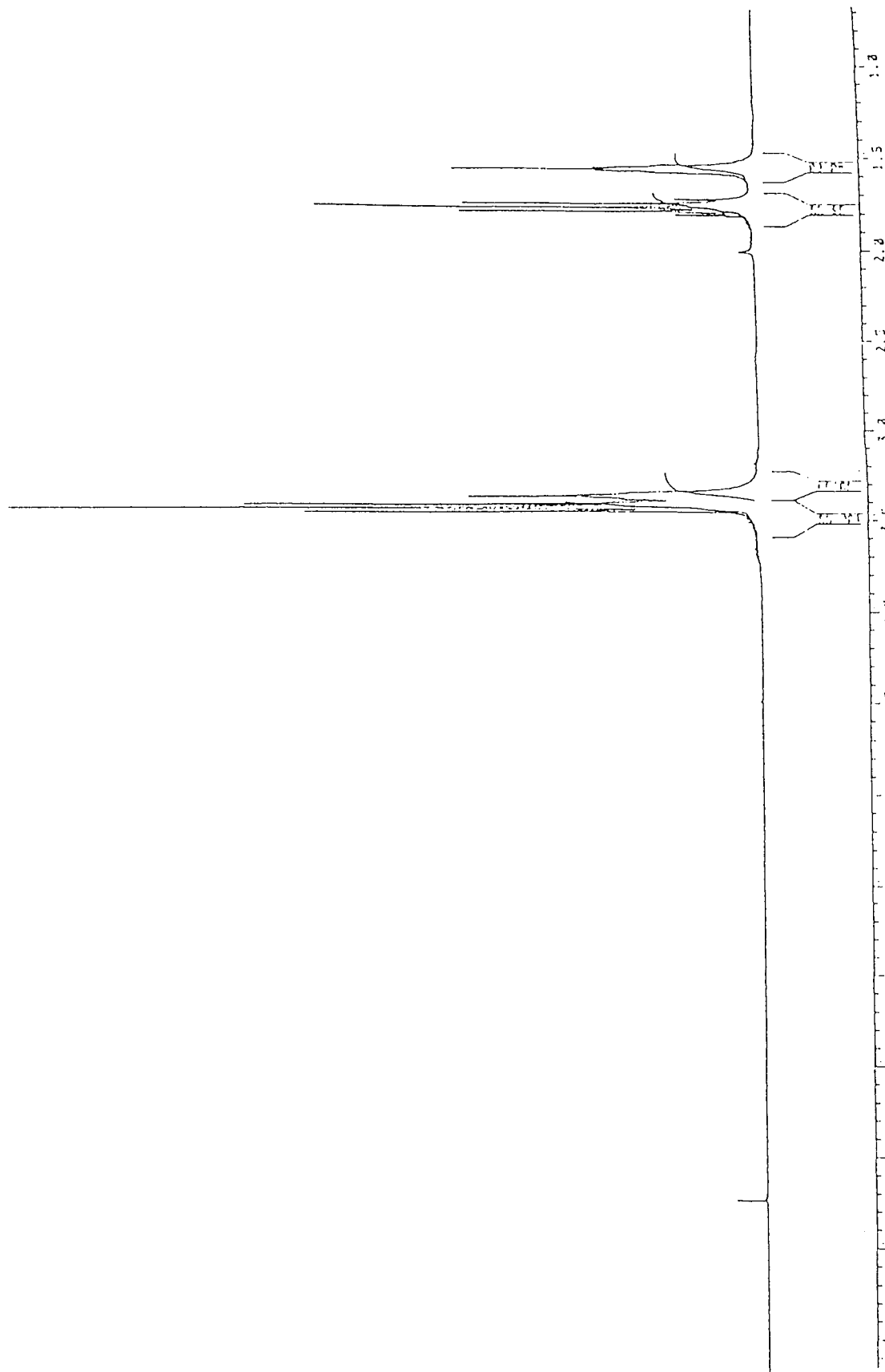
**Fig. 2(a):** $^1$H NMR of the copolymer of THF and oxetane; feed ratio 2.03:1.00 respectively
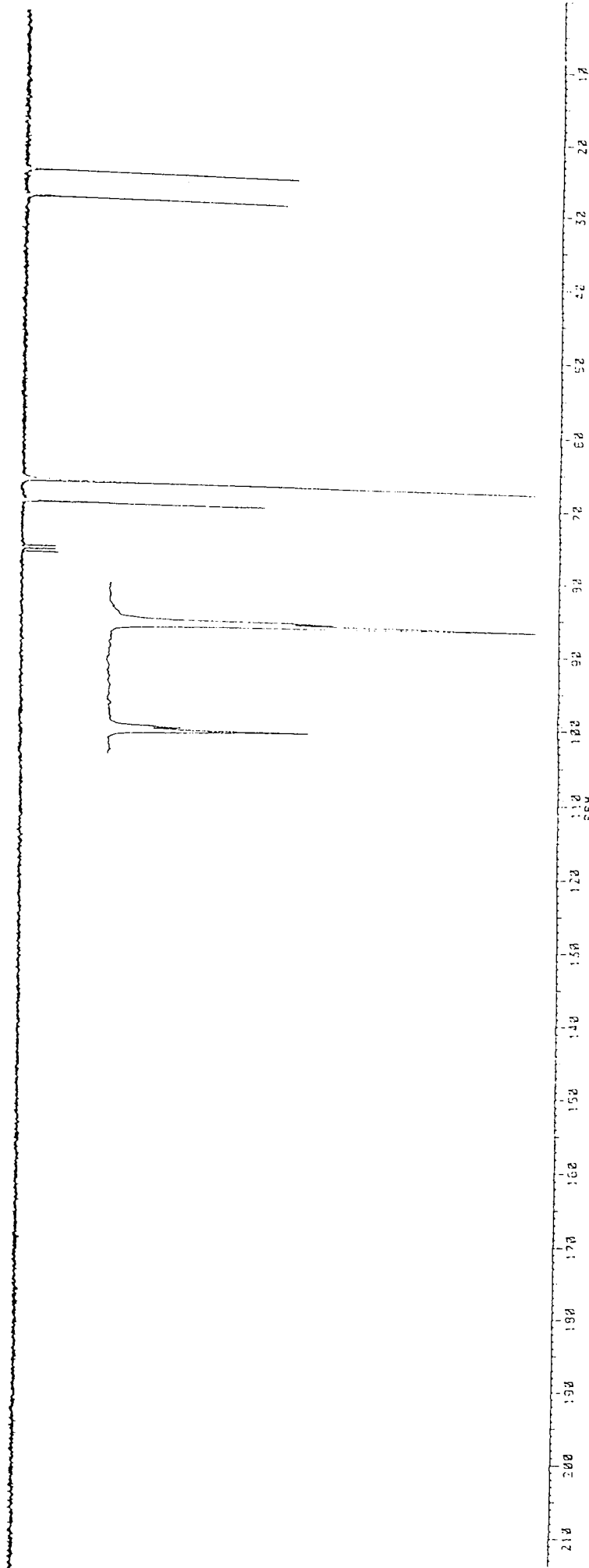
Fig. 2(b):  $^{13}C$  NMR of the copolymer of THF and oxetane; feed ratio 2.03:1.00 respectively

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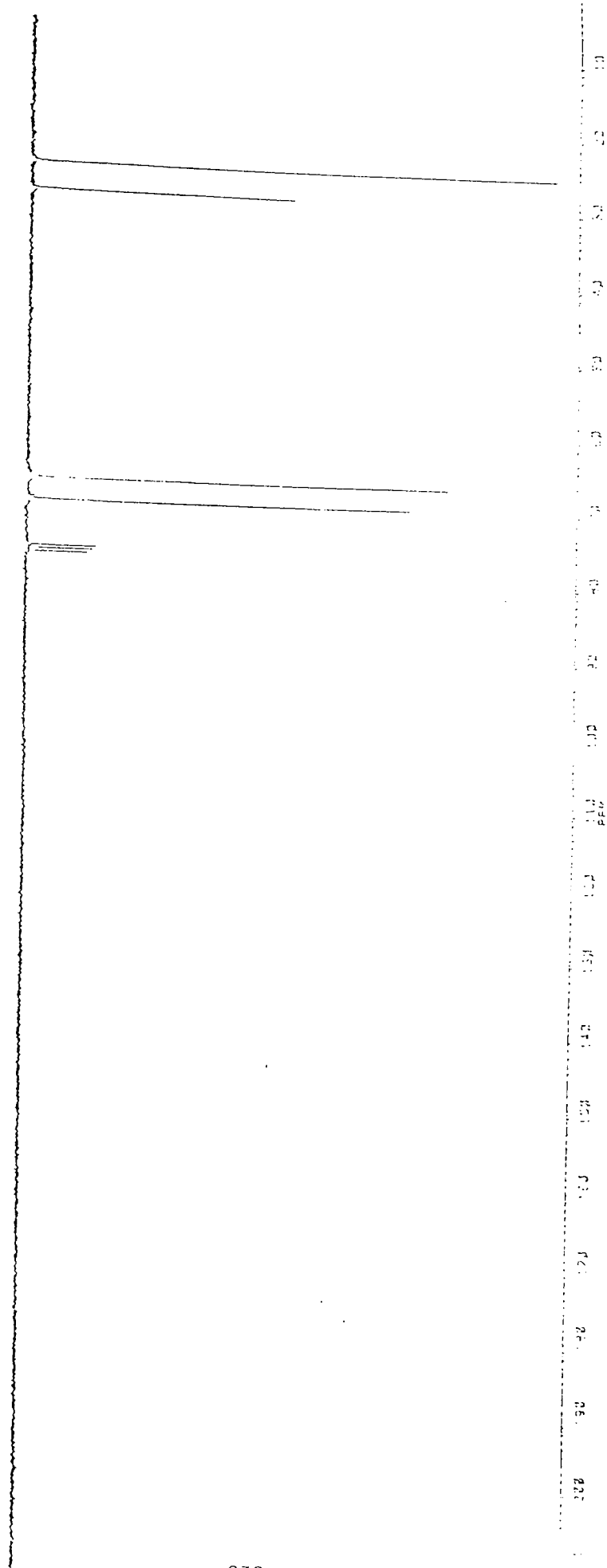Fig. 3(a): $^1$H NMR of the copolymer of THF and oxetane; feed ratio 0.93:1.00 respectively

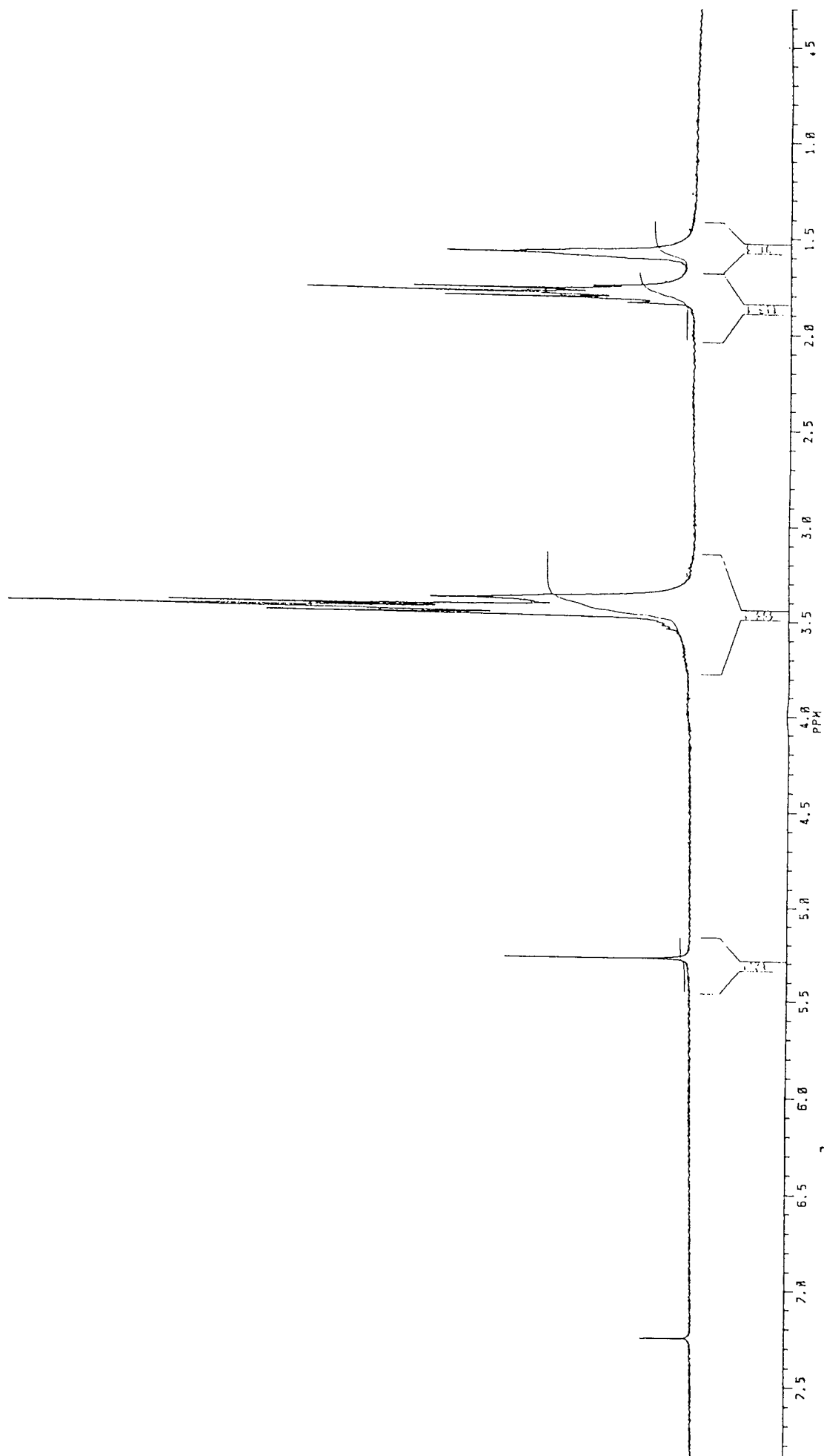Fig. 3(b): $^{13}C$ NMR of the copolymer of THF and oxetane; feed ratio 0.93:1.00 respectively

232

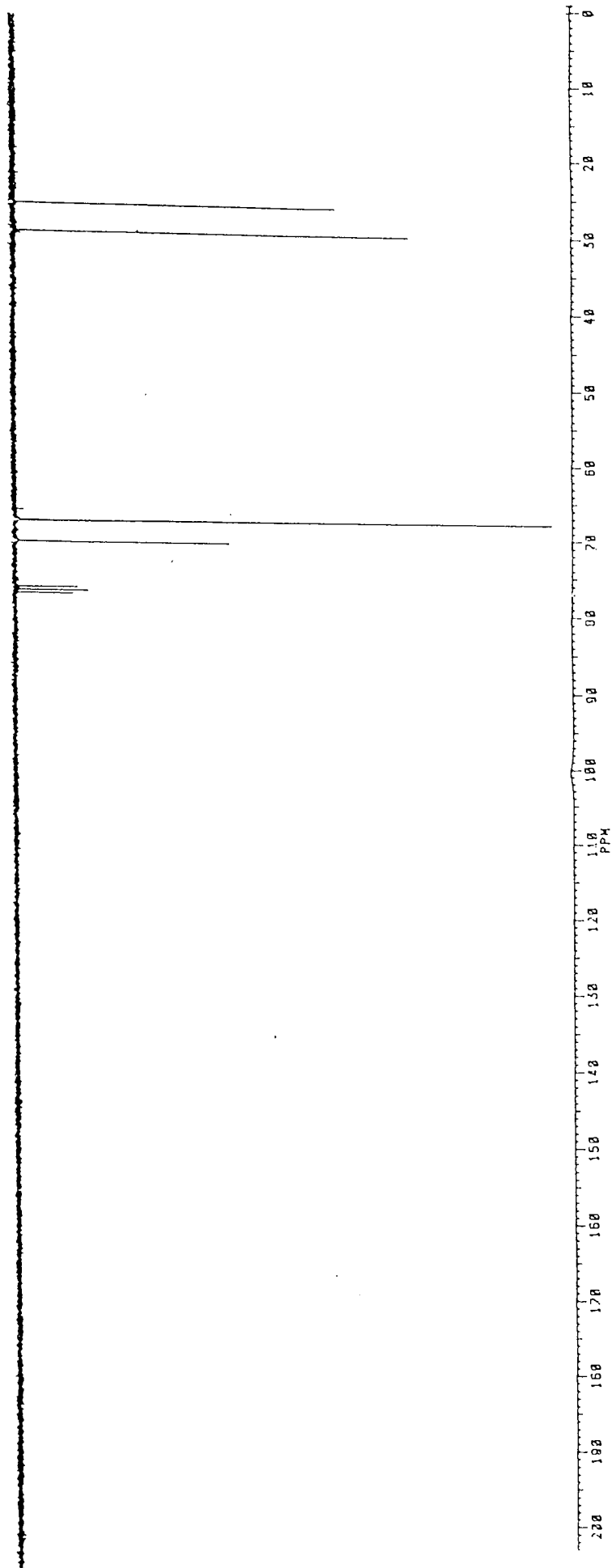Fig. 4(a): $^1$H NMR of the copolymer of THF and oxetane feed ratio 0.5:1.00 respectively

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Fig. 4(b): $^{13}$C NMR of the copolymer of THF and oxetane; feed ratio 0. 5:1.00 respectively