# STUDIES OF THE CATIONIC POLYMERISATION OF VINYLIC AND ENERGETIC CYCLIC ETHER MONOMERS

HEMANT DESAI

A thesis submitted for the degree of

Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

June 1995

**The University of Aston in Birmingham**

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## SUMMARY

The cationic polymerisation of various monomers, including cyclic ethers bearing energetic nitrate ester ($-ONO_2$) groups, substituted styrenes and isobutylene has been investigated. The main reaction studied has been the ring-opening polymerisation of 3-(nitratomethyl)-3-methyl oxetane (NIMMO) using the alcohol/$BF_3.OEt_2$ binary initiator system. A series of di-, tri- and tetrafunctional telechelic polymers has been synthesised. In order to optimise the system, achieve controlled molecular weight polymers and understand the mechanism of polymerisation the effects of certain parameters on the molecular weight distribution, as determined by Size Exclusion Chromatography, have been examined. This shows the molecular weight achieved depends on a combination of factors including -OH concentration, addition rate of monomer and, most importantly, temperature. A lower temperature and OH concentration tends to produce higher molecular weight, whereas, slower addition rates of monomer, either have no significant effect or produce a lower molecular weight polymer. These factors were used to increase the formation of a cyclic oligomer, by a side reaction, and suggest, that the polymerisation of NIMMO is complicated with end-biting and back biting reactions, along with other transfer/termination processes. These observations appear to fit the model of an active-chain end mechanism. Another cyclic monomer, glycidyl nitrate (GLYN), has been polymerised by the activated monomer mechanism. Various other monomers have been used to end-cap the polymer chains to produce hydroxy ends which are expected to form more stable urethane links, than the glycidyl nitrate ends, when cured with isocyanates. A novel monomer, butadiene oxide dinitrate (BODN), has been prepared and its homopolymerisation and copolymerisation with GLYN studied.

In concurrent work the carbocationic polymerisations of isobutylene or substituted styrenes have been studied. Materials with narrow molecular weight distributions have been prepared using the diphenyl phosphate/$BCl_3$ initiator.

These systems and monomers are expected to be used in the synthesis of thermoplastic elastomers.

Key words: Cationic polymerisation; Energetic cyclic ether monomers; Nitrato or nitrate ester groups; Linear and cyclic oligoethers; polyethers; vinylic monomers.

To my parents and family.

# ACKNOWLEDGEMENTS

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| | |
|---|---|
| ACE | Active chain end. |
| AMI | All monomer in. |
| AMM | Activated monomer mechanism. |
| AMMO | 3,3-(azidomethyl) methyl oxetane. |
| BAMO | 3,3-bis(azidomethyl) oxetane |
| BCMO | 3,3-bis(chloromethyl) oxetane. |
| BNMO | 3,3-bis(nitratomethyl) oxetane. |
| BODN | Butadiene oxide dinitrate. |
| DCM | Dichloromethane. |
| DMF | Dimethyl formamide. |
| DMSO | Dimethyl sulphoxide. |
| DPP | Diphenyl phosphate |
| DRA | Defence Research Agency. |
| DSC | Differential scanning calorimetry. |
| GLYN | Glycidyl nitrate. |
| HIMMO | 3,3-(hydroxymethyl) methyl oxetane. |
| HPLC | High pressure liquid chromatography. |
| IB | Isobutylene. |
| ICI | Imperial Chemical Industries. |
| IMA | Incremental monomer addition. |
| IR | Infra-red spectroscopy. |
| MOD | Ministry of Defence. |
| MS | Mass Spectroscopy. |
| MWD | Molecular weight distribution. |
| NHTPB | Nitrated hydroxy-terminated polybutadiene. |
| NIMMO | 3,3-(nitratomethyl) methyl oxetane. |
| NMR | Nuclear magnetic resonance spectroscopy. |
| PIB | Polyisobutylene. |

| | |
|---|---|
| POWA | Poly(oxetanes) Waltham Abbey. |
| RARDE | Royal Armament Research and Development Establishment. |
| SEC | Size exclusion chromatography. |
| SNPE | Societe Nationale de Poudres et explosif. |
| THF | Tetrahydrofuran. |

# CHAPTER 1.

# INTRODUCTION.

# 1.    INTRODUCTION.

## 1.1    Aims.

For many years the Royal Armament Research and Development Establishment (RARDE), who are now known as the Defence Research Agency (DRA), have had an interest in the synthesis of terminally functional (telechelic) elastomers possessing low glass transition temperatures for use as propellant or explosive binders. In the past, interest has centred on hydroxyl terminated polybutadienes, but over the last few years investigations on alternative systems have commenced.

This report studies the synthesis of novel polyethers and polyisobutylenes for use as alternative low temperature elastomers. Emphasis has been placed on fundamental studies of the polymerisation mechanism, in an attempt to achieve optimised products.

In this chapter the various mechanisms of preparing macromolecules are reviewed, followed by a brief description of the area of energetic materials, with particular attention paid to the field of energetic binders.

## 1.2    Terminology.

Polymerisation reactions may be divided broadly into two classes: step (or condensation) and chain growth depending on the nature of the kinetics of the processes and the final molecular weight distribution (MWD) of the polymer. A step growth[1] polymerisation usually involves reactions between monomer and monomer, oligomer and oligomer, and macromolecule and macromolecule in a series of successive steps. Chain growth polymerisations on the other hand involve propagation where the monomer adds to the growing macromolecule. Step growth polymerisation will not be discussed in detail, except briefly in section 3 where the AMM may be regarded as a special case, because the systems studied here proceed mainly by chain growth.

Addition polymerisation, unlike step growth, has at least three distinctly defined reaction stages; initiation, propagation and termination. These are well studied, for example, for free-radical reactions[2] where although the initiation may involve the use of a radical-ion or a free radical, the propagation involves a radical usually carried on the growing polymer chain. Termination occurs predominantly by combination of two active centres or by disproportionation i.e. loss of a free radical species.

Systems using coordinate catalysts such as transition metals also exhibit defined stages. However, the initiation stage contains a centre around which both the incoming monomer and growing polymer may be bonded during the propagation. Termination is more complicated but debonding of polymer, monomer or another ligand may destroy the active centre. Termination may also be induced by reaction with other impurities. Examples of coordinative systems include Ziegler-Natta[3], metathesis[4,5], metal porphyrin and more recently group-transfer polymerisation[6] (GTP), although there is some dispute about the latter method. The reaction systems are called "living" when transfer and termination processes are absent, thereby supply of fresh monomer to a reaction vessel leads to a proportional increase in molecular weight of the polymer. This allows synthesis of narrow (if rate of initiation is faster than rate of propagation) and controlled molecular weight distributions. These are desirable because the final properties of a polymer do not just depend on the chemical structure but also on the MWD. Moreover, the absence of termination means that further chemistry is possible allowing novel architectures e.g. block copolymers, star and functional polymers. However, the majority of reactions in all of these systems are not living and their MWDs are determined by the relative rates of initiation, propagation and termination. These reactions are often grouped together and referred to as kinetic chain process.

Some of the best examples of living systems are found in the area of ionic, in particular anionic[7], polymerisation. Ionic polymerisation is a broad class of reactions where an ion or a polarisation forms the reactive end of a growing macromolecule. In the case of anionic or carbanionic systems the chain bears a negative charge, usually with an alkali

or alkali-earth metal counter-ion, while in the case of the cationic systems the chain bears a positive charge. These are the two main sub-divisions of ionic polymerisation but a third sub-division may be included with the emergence of the so-called activated-monomer systems (AMM) where the ionic charge is not carried on the growing chain but on the monomer, hence the term activated monomer. The activated monomer is then regenerated after each propagation step. This will be discussed further in section 3, but from this point onwards emphasis is given to cationic systems which are the subject of this study.

## 1.3    Cationic polymerisation.

Cationic polymerisation consists of two main areas classified according to the nature of the propagating active end; carbocationic and onium ion. If the positive charge or the polarisation is based on a carbon atom then the polymerisation is termed carbocationic. If the positive charge is however based on another atom, usually non-metallic, such as oxygen, sulphur, nitrogen or phosphorus, then it may be referred to as an onium-ion polymerisation. In the latter category the monomers are normally heterocyclic compounds and the polymerisation is by a ring opening process. For example the polymerisation of cyclic ethers proceeds by way of oxonium ions. A third minor category resembling carbocationic polymerisation is sometimes defined where strongly delocalised carbocations polymerise monomers such as aldehydes and acetals, by a pseudo-carbocationic mechanism:

$$\text{\textasciitilde\textasciitilde\textasciitilde} \overset{+}{O} = CH_2 \ + \ H_2C = O \ \longrightarrow \ \text{\textasciitilde\textasciitilde\textasciitilde} O - CH_2\overset{+}{O} = CH_2 \qquad (1.1)$$

$$\text{\textasciitilde\textasciitilde\textasciitilde} OCH_2CH_2\overset{+}{O} = CH_2 \ + \ O\text{[ring]}O$$

$$\longrightarrow \ \text{\textasciitilde\textasciitilde\textasciitilde} CH_2CH_2OCH_2OCH_2CH_2\overset{+}{O} = CH_2 \qquad (1.2)$$

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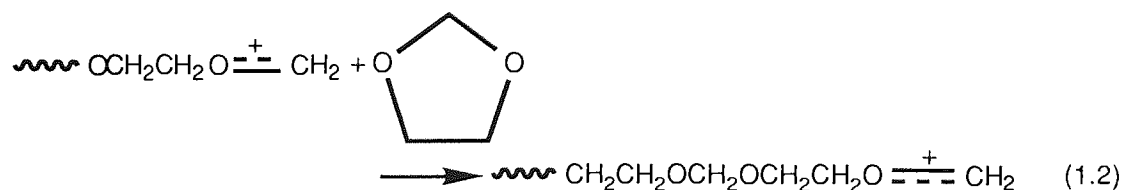
## 1.3.1 Carbocationic systems.

Some of the oldest known examples of synthetic polymerisation processes are carbocationic. In 1789 Bishop Watson[8] described the resinification of oil of turpentine by sulphuric acid. This was followed in the 19th century by the use of metal halides e.g. $BF_3$ as catalysts[9]. It was also around this time two of the monomers which form part of this study were polymerised by cationic processes. In 1866 Berthelot synthesised polystyrene[10] and in 1873 Butlerov[11] polyisobutylene, both polymerisations initiated by sulphuric acid. Since then much research effort has been spent in this area yet the only major industrial application of cationic polymerisation remains that of isobutylene (IB) with metal halide initiation. Nevertheless, many other monomers besides IB and styrene are polymerised by carbocationic systems.

## 1.3.1.1 Carbocationically polymerised monomers and general mechanism.

Before listing some of the monomers it is important to consider the general mechanism by which carbocationic polymerisation proceeds, as shown in scheme 1. The initiating species ($R^+$) may be for example, a proton, a carbenium ion or a metal halide cation. For the initiating species to cationate the monomer, the monomer itself must be susceptible to electrophilic attack. A good example of this type of monomer is the alkenes where the carbon-carbon double bond lends itself to electrophilic attack to form a carbocation. Monomer reactivity is aided, either, if there are electron-repulsive substituents pushing electrons toward the double bond which will stabilise the carbocation or the carbocation may be stabilised by resonance e.g. conjugation with an aromatic ring, a double bond or at least one ether group. Carbocationically polymerised monomers which show some of these features, include ethylene, propylene, isobutylene, styrene, vinyl ethers, butadiene and N-vinylcarbazole.

Cationation:

$R^+$ +  $\longrightarrow$ R—C—C$^+$              (1.3)

Propagation:

 (1.4)

Chain transfer:

 (1.5)
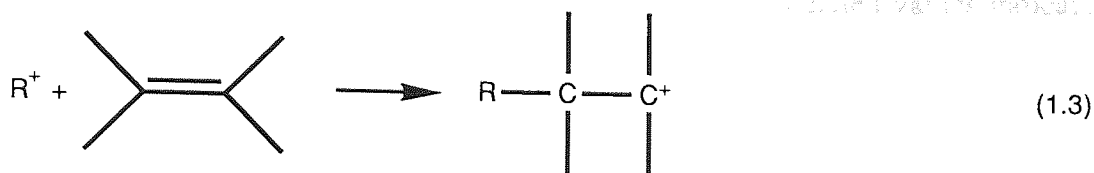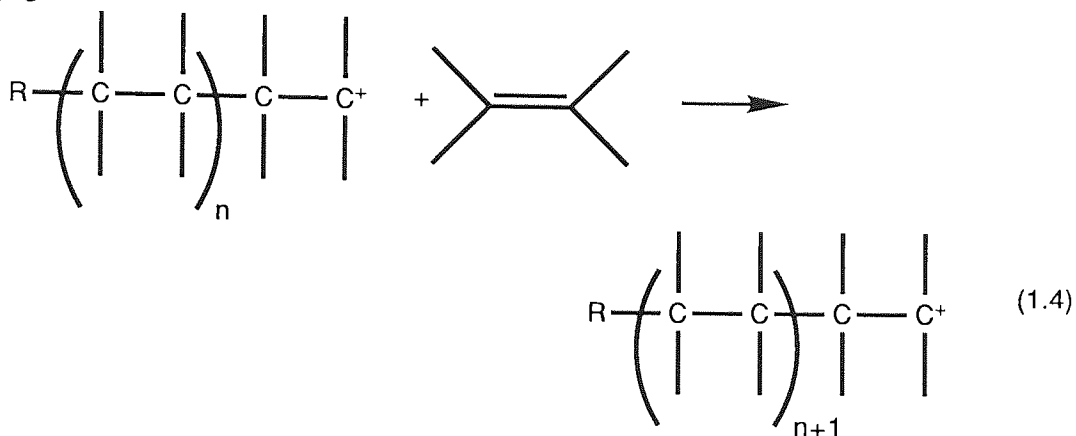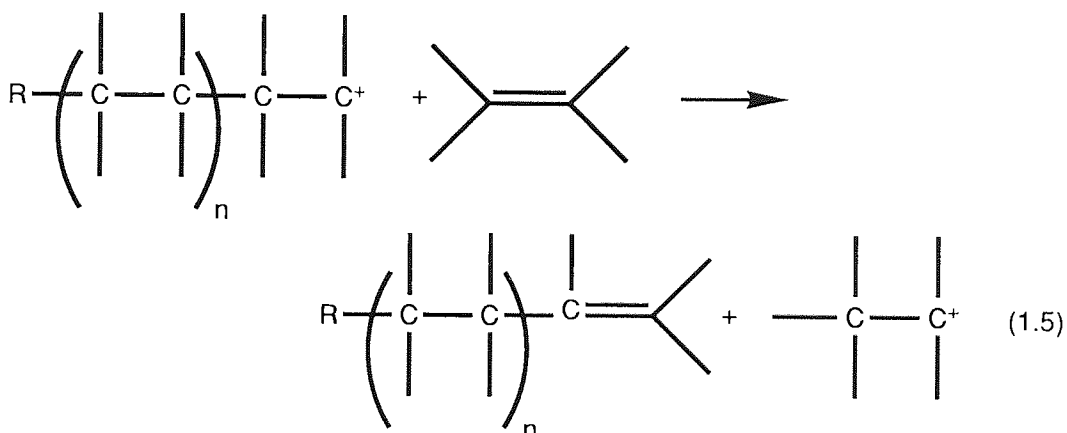
**Scheme 1. A general mechanism of carbocationic polymerisation of an alkene.**

The polymerisability of any monomer is defined in thermodynamic terms by equation 1.6.

$$\Delta G_p = \Delta H_p - T\Delta S_p \qquad (1.6)$$

The free energy of polymerisation ($\Delta G_p$) describes the possibility of the formation of a high polymer and is independent of the reaction mechanism provided the same type of polymer is formed with respect to conformation, tacticity and isomerism of repeating units. For styrene[12] the standard enthalpy ($\Delta H_p$) of polymerisation is -73.1 kJ mol$^{-1}$

and the standard entropy ($\Delta S_p$) is -104 J K$^{-1}$ mol dm$^{-3}$. Calculated values indicate equilibrium monomer concentration[13], $[M]_e$, for the polymerisation is $10^{-7}$ mol dm$^{-3}$, at 0°C. So styrene should polymerise at most usable concentrations. Equation 1.6 also shows that above a certain temperature most polymerisation reactions become unfavourable as the $\Delta S$ term becomes more negative due to a reduction in the total number of molecules in the system upon propagation. This temperature is referred to as the ceiling temperature.

Although a polymerisation reaction may be thermodynamically feasible high polymer will only form from a monomer if a suitable mechanism exists. A sufficiently stable and reactive growing species as well as the absence of groups leading to excessive transfer and termination are the main requirements of such a mechanism. In chain polymerisations, the stable and reactive growing species is largely dependent on the nature of the monomer but it is also significantly dependent on other factors such as temperature, solvent and perhaps most importantly the mode of initiation.

## 1.3.1.2     Initiators for carbocationic polymerisation.

Initiators for carbocationic polymerisation range from simple acids e.g. $H_2SO_4$ to multi-component systems for example 2-chloro-2,4,4-trimethylpentane/$TiCl_4$/ dimethylacetamide/tert-butylpyridine for the polymerisation of chlorostyrene[14] and a survey of the methods of carbocationic initiation is presented in table 1. It is important to note here that $R^+$ is sometimes referred to as the initiator and confusion may occur with catalyst and cocatalyst. In this work, cationogen will be used to describe the species from which $R^+$ originates and the term coinitiator for other species, e.g. Lewis acids, which may be involved in the formation of $R^+$. Other terms will be avoided as far as possible except when the exact nature of the initiation is not known.

The initiation system used governs the nature of polymerisation and hence influences the final architecture of the polymer. Use of di-and tri-functional initiators may give functional telechelic polymers, which in turn may be cured or used in copolymer

formation. The exact features of a system (for a given monomer) are determined by a combination of the initiator, solvent, temperature, time and presence of any additives.

### 1.3.1.3 Solvent.

Carbocationic polymerisations involve propagation reactions in which ions or ion-pairs participate. It is reasonable therefore that in any system involving charged species one of the most important components will be the solvent, for it will affect the type and rates of initiation, propagation, transfer and termination, if any occur, as well as the MWD of the final product. A 'perfect' solvent must be able to dissolve the monomer and polymer over a whole range of molecular weights. Then it must allow high rates of initiation ($R_i$) and propagation ($R_p$) or at least the $R_i$ to be greater than $R_p$ for control of MWD. Moreover, it should not cause transfer or termination while for some applications it should be easily removable from the final polymer. Most solvents are not perfect and the choice of a solvent is often made after a series of trials. One property of a solvent which is often a guide to its nature is the dielectric constant, especially in ionic polymerisations where the polar active centre and the counter-ion need to be stabilised. Solvents of high polarity tend to usually show a high rate of propagation, e.g. isobutyl vinyl ether (IBVE) has a faster $R_p$ in $CH_2Cl_2$ than in n-hexane using $HI/I_2$ system[22] (see scheme 2 below).

$$CH_2 = CH \quad \xrightarrow{HI} \quad HCH_2 - CHI \quad \xrightarrow{I_2} \quad HCH_2 - C^{\delta+} - HI^{\delta-} \cdots I_2$$
$$| \qquad\qquad\qquad | \qquad\qquad\qquad |$$
$$OR \qquad\qquad\qquad OR \qquad\qquad\qquad OR$$

$$HCH_2 - C^{\delta+} - HI^{\delta-} \cdots I_2 \quad \xrightarrow{nCH_2 = CHOR} \quad H - \left( CH_2 - CH \right)_n CH_2 - C^{\delta+} - HI^{\delta-} \cdots I_2$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \qquad\qquad\qquad |$$
$$OR \qquad\qquad\qquad\qquad\qquad\qquad\qquad OR \qquad\qquad OR$$
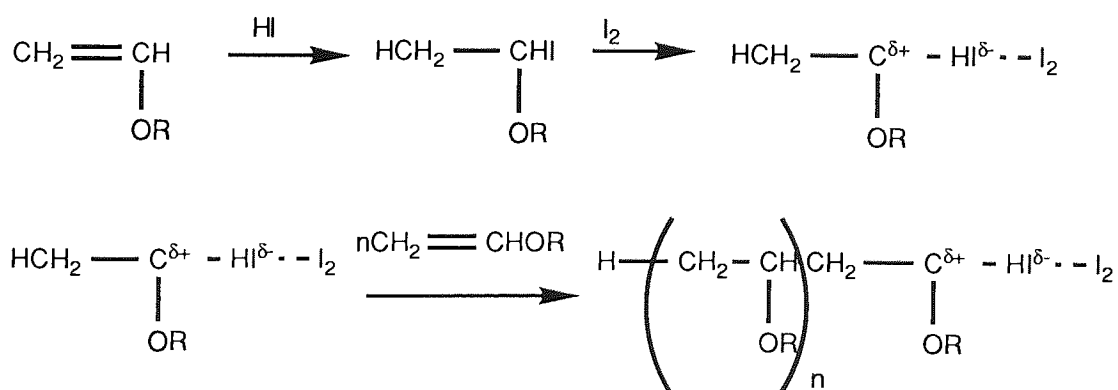
### Scheme 2. Mechanism of IBVE polymerisation from N.M.R. and U.V. spectroscopy studies.

Table 1. A Survey Of Cationic Initiation Methods.

| Method of Initiation | Type of initiators | Source of initiation | Examples | Comments |
|---|---|---|---|---|
| (1). Electrophilic addition to C=C. | → Involving Protonic acids. | → Protonic (Bronsted) acids alone. | → $CF_3SO_3H$, $HClO_4$, $H_2SO_4$, $HCl$, HBF4 Haloacetic acids, Heteropolyacids. | Usually stong acids with stable anions. |
| | | → Activation of weak protonic acids by Friedel-Crafts acids (F-C acids). | → $BF_3$, $AlBr_3$, $TiCl_4$, $SnCl_4$, $BCl_3$, $BBr_3$, $ZnI_2$, Chloroalkyl aluminiums. | |
| | → Initiation by organic cations. | → Stable carbocations. | →Trityl cation, tropylium cation. | Nature of counter-anion can affect rates of initiation and propagation. |
| | | → Carbocations generated in situ. | → Alkyl or aryl halides / F-C acids, t-butyl chlorides / $TiCl_4$, cumyl chloride / $BCl_3$, HI / $ZnI_2$. | |
| | | | →t-butyl chlorides / $AgClO_4$, t-butyl chlorides / $AgBrO_4$, benzyl chloride /$AgIO_4$. | These silver salts can be expensive. |
| | | | →Ester / F-C acids, Ether / F-C acids, $PhCMe_2OMe$ / $BCl_3$, $BF_3.OEt_2$. | Carbocations from esters and ethers. |
| | | | →Acyl or aryl halide and F-C acids to generate oxocarbenium ions. $EtC=OSbF_6$ $PhC=OSbF_6$ acetyl perchlorate. | $RC=OF + SbF_5 \rightarrow RC=O^+SbF_6^-$. |
| | | | →Alkoxy carbenium, dialkoxy carbenium, dioxolenium ions, $Et_3O^+BF_4^-$, $H(OEt)_2C^+BF_4^-$ | |

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Table 1. Cont.

| Method of Initiation | Type of initiators | Source of initiation | Examples | Comments |
|---|---|---|---|---|
| | → Initiation by inorganic Lewis acids. | → Direct initiation. | → $AlEt_3$, $BF_3$ | Mechanism may involve: solvent cocatalysis allylic hydride abstraction self ionisation direct addition. |
| | | → Electrophilic halogens and F-C acids. | → $I_2$ / $ZnI_2$. | |
| (2) Oxidation of the C=C bond. | → Chemical oxidation. | → Single electron transfer. | → High electron affinity Lewis acids, $SbCl_5$, <br><br> $BCl_3$ / $FeCl_3$, <br><br><br><br><br> → Direct oxidation by a stable oxidising cation radical, tri(p-bromophenyl) aminium perchlorate[17], $ArN·^+ClO4^-$ | Proposed reaction for this process[15]: <br> ox + $CH_2$=C< → red + [$CH_2$=C<]·+. <br> 2 [$CH_2$=CH<]·+. → +>CCH₂CH₂CC<+ bicationic dimer. <br><br> Polymerisation of isobutylene. Evidence from spectrophotometric and conductometric studies[16]: <br> $FeCl_3$ + $BCl_3$ → $FeCl_2^+$ + $BCl_4^-$ <br> $FeCl_2^+BCl_4^-$ + $CH_2$=C< → $FeCl_2$ + <br> ·$CH_2$C<+$BCl_4^-$. |

Table 1. Cont.

| Method of Initiation | Type of initiators | Source of initiation | Examples | Comments |
|---|---|---|---|---|
| | | →Charge transfer complexes (CTC) | →CTC with electron acceptors (EA), chloroanil, benzoquinone, tetracyanoethylene, tetranitromethane. | For very nucleophilic monomers of low ionisation potential e.g. N-vinyl carbazole, vinyl ethers: $M + EA \rightarrow CTC \rightarrow \overset{\Delta \text{ or } h\nu}{} CTC^*$ Exciplex $CTC^* \rightarrow$ cation radical $\overset{M}{\rightarrow}$ polymer. |
| | →Physical methods of oxidation. | →Ionising radiation. | → γ-ray radiation | Styrene, THF and IB polymerised in dry conditions. |
| | | | →U.V. radiation, direct short wave U.V., | IB polymerised at temperatures of -115°C to -145°C. |
| | | | photolysis of compounds e.g. diaryl iodonium and diaryl sulphonium. | Vinylic and heterocyclic monomers polymerised[18,19]. |
| | | →Electric Field. | → >5kV p.d. | Styrene polymerised by both cationic and free radical species independently[20]. |
| | | →Electrochemical initiation. | →Direct oxidation of monomers. | Styrene (+1.8V w.r.t. Ag°/Ag+) with Bu$_4$+BF$_4$-: Isoprene and vinyl ethers also polymerised this way. |
| | | | →Electrolytic generation of initiator using supporting electrolyte e.g. BPh$_4$-Na+. | Styrene is polymerised by using LiClO$_4$ as electrolyte in propylene carbonate[21], via HClO$_4$. |

**Table 1. A Survey Of Cationic Initiation Methods.**

The strong interaction of the tri-iodide anion and the propagating species in non-polar solvents suppresses chain transfer and termination while a more polar solvent reduces the interaction because the active centre and the tri-iodide counter-ion are solvated. Although a polar solvent has the effect of increasing Rp it also tends to increase side reactions, so it can be concluded that the stability of the growing carbocation and the nucleophilicity of the counter-anion are important for living cationic polymerisation and are dependent on the solvent used.

Some systems use a combination of solvents for example the polymerisation of isobutylene using cumyl ether/TiCl$_4$ at -80°C uses CHCl$_3$/n-C$_6$H$_{14}$ (40/60 v/v) [23] where the CHCl$_3$ serves to give fast Ri but hexane serves to dissolve high molecular weight polyisobutylene which is insoluble in chloroform.

It is important to point out here that some authors believe that rates of reactions may not vary significantly in different solvents because the free energy of activation for cationation of an alkene is the same for both free and paired cations[24,25]. Yet there is also evidence that solvation of the propagating carbocation can affect Rp; e.g. Stannett studied γ-ray induced polymerisations of ethyl and isopropyl vinyl ethers in various solvents under super-dry conditions [26,27] and found the Rp decreased in the sequence: bulk > C$_6$H$_6$ > Et$_2$O > CH$_2$Cl$_2$ >> MeNO$_2$ implying more polar solvents stabilise the carbocation too much.

### 1.3.1.4  Temperature.

Another factor which affects cationic polymerisations markedly is temperature. In general, reducing the temperature is beneficial as the rates of transfer reactions are also reduced i.e. the activation energy of transfer is higher than that of propagation. High molecular weight (>10$^5$) poly(2-chloroethyl vinyl ether) is attained at -78°C using CF$_3$SO$_3$H in CH$_2$Cl$_2$[30] but not at higher temperatures.

Temperature can also affect stereochemistry of the polymers formed e.g. highly isotactic polyvinylethers are formed at low temperatures in homogeneous

polymerisation but at elevated temperatures there is an increase in random sequences in the backbone.

## 1.3.1.5 Time.

The effect of time on a polymerisation system is important because, in practice, decisions have to be made about how long each phase of the polymerisation should take. In some systems there may need to be a pre-mixing time of cationogen and Lewis acid. In another instance, the polymerisation may need to be quenched after a specified time, if all the monomer is added at the beginning of a polymerisation ('All Monomer In'). Recently the development of quasi-living systems[31] by Kennedy has introduced another facet of the function of time. In these systems monomer is added continuously over a number of hours or even days in order to keep the [M] just above the $[M]_e$, to reduce side reactions. These types of systems are distinctly different from living systems where monomer aliquots may also be added incrementally. The effect of time on a system is foremostly dependent on the nature of the mechanism but alteration of other conditions usually requires adjustments of time. This demonstrates the inter-dependence of all the factors discussed in this section including temperature, solvent and additives.

## 1.3.1.6 Additives.

Additives may be used to change the nature of the polymerisation or to incorporate a compound which has benefits in the final application but does not take part in the polymerisation e.g. a stabiliser to avoid degradation. In the former case electron pair donors[32] e.g. dimethyl acetamide, DMSO, dioxolane and proton traps[33] such as hindered pyridines have been used to impart livingness to polymerisation systems. The electron pair donors work by increasing the stability of the carbocation while the proton traps reduce the effect of adventitious impurities particularly water.

## 1.3.2 Cationic Ring-Opening polymerisation.

The principles already discussed for the cationic polymerisation of alkenes also apply, to a large extent, to cationic ring-opening polymerisation. However, there are differences and these are examined below. First, the general mechanism of ring-opening polymerisation is:

Initiation



$$\text{(1.7)}$$
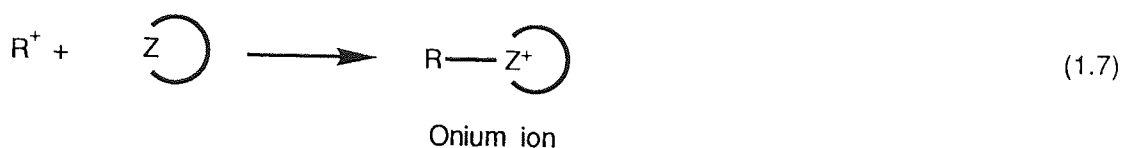
Onium ion

As in carbocationic polymerisation $R^+$ may be a proton donor or a carbenium ion and Z is the heteroatom in the cyclic monomer. Commonly it is an oxygen, nitrogen or sulphur atom.

Propagation This can occur in three different ways (which may also be concurrent).

(a) Activated Chain End Mechanism (ACE).



$$\text{(1.8)}$$
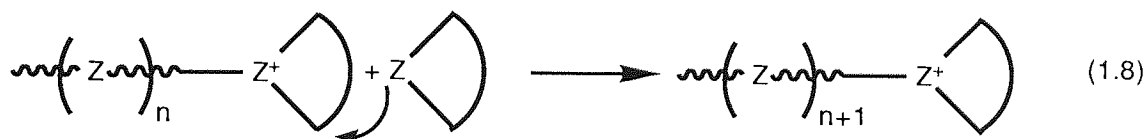
Nucleophilic attack by the monomer molecule on the onium ion.

(b) Activated (protonated in this case) monomer mechanism (AMM).



$$\text{(1.9)}$$
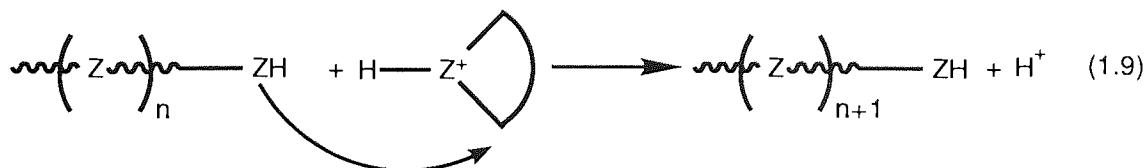
Nucleophilic attack by the chain end on the activated monomer bearing positive charge.

(c) Pseudocationic polymerisation.

$$\sim\!\!\!\leftarrow\!\!\text{Z}\!\!\sim\!\!\!\rightarrow_n\!\!-\!\!\text{Z}^{\delta+}\text{B}^{\delta-} \quad + \quad \text{Z}\!\!\diagup\!\!\!\bigcirc \quad \longrightarrow \quad \sim\!\!\!\leftarrow\!\!\text{Z}\!\!\sim\!\!\!\rightarrow_{n+1}\!\!-\!\!\text{Z}^{\delta+}\text{B}^{\delta-} \quad (1.10)$$
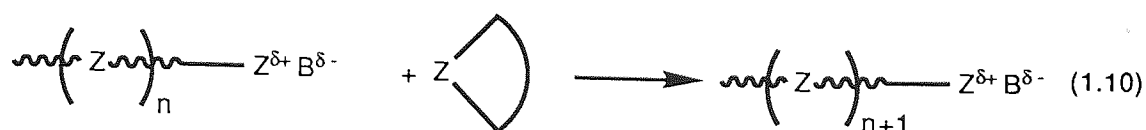
where B is usually a low nucleophilic base (e.g. $ClO_4^-$), as opposed to a non-nucleophilic base (e.g. $PF_6^-$).

Most commercial cationic ring-opening polymers are made by the ACE mechanism.

<u>Termination</u>

(a) For the ACE mechanism these may occur:

     (i)     Reaction with the counter-ion

$$\text{e. g. } R_3O^+ \quad + \quad F\!\!-\!\!BF_3^- \quad \longrightarrow \quad ROR \quad + \quad RF \quad + \quad BF_3 \quad\quad (1.11)$$
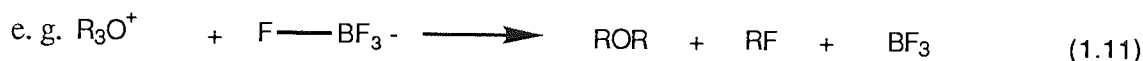
or a stable covalent compound may be formed which may or may not propagate further i.e.

$$\sim\!\!\!\leftarrow\!\!\text{Z}\!\!\sim\!\!\!\rightarrow_n\!\!-\!\!\text{Z}^+\!\!\bigcirc \; X^- \longrightarrow \sim\!\!\!\leftarrow\!\!\text{Z}\!\!\sim\!\!\!\rightarrow_n\!\!-\!\!\text{Z}\!\!-\!\!\smile\!\!-\!\!X \quad (1.12)$$
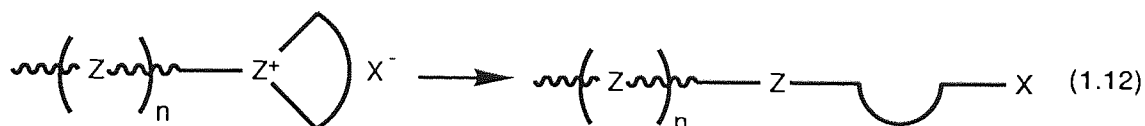
     (ii)     Onium ion reaction with in-chain heteroatom i.e. inter-chain reaction causes formation of non-strained onium ion.

$$\sim\!\!\!\leftarrow\!\!\text{Z}\!\!\sim\!\!\!\rightarrow_n\!\!-\!\!\text{Z}^+\!\!\bigcirc \quad + \quad \text{Z:} \quad \longrightarrow$$

$$\sim\!\!\!\leftarrow\!\!\text{Z}\!\!\sim\!\!\!\rightarrow_n\!\!-\!\!\text{Z}\!\!-\!\!\smile\!\!-\!\!\text{Z}^+ \quad\quad (1.13)$$
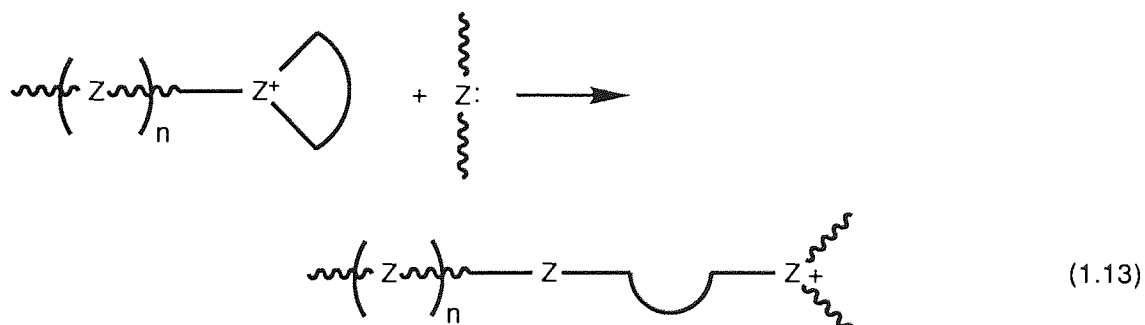
Whereas an intra-chain reaction causes cyclic species to form:

(1.14)



(1.15)
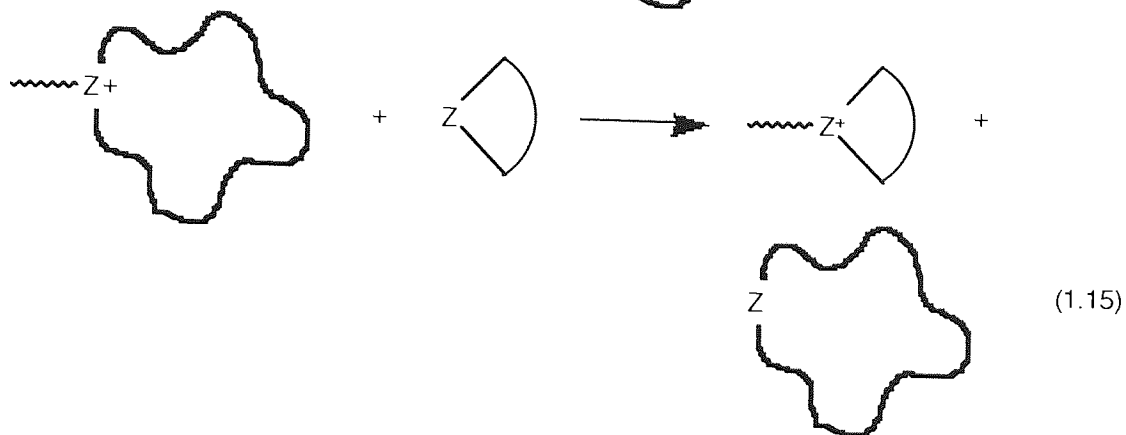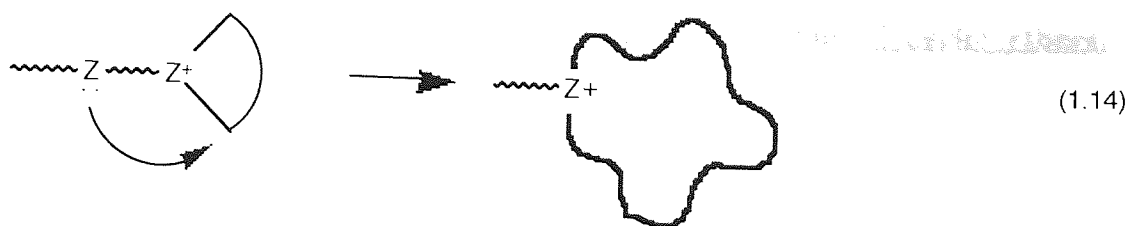
The thermodynamics of the ring-chain equilibria are described by the Jacobson-Stockmayer equation [101]

$$[R_n] = An^{-5/2}$$

(1.16)

where $[R_n]$ is a macrocyclic compound of a number of repeating units n and A is a constant.

    (iii)    Loss of a proton.



+ HX    (1.17)
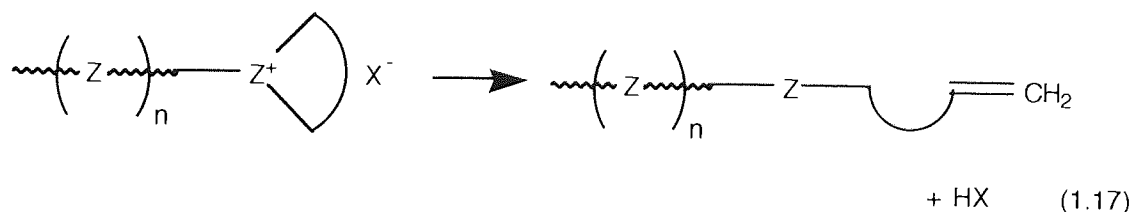
The proton may, of course, initiate another chain.

(b) Activated monomer mechanism.

This mode of propagation in principle, has no termination reactions but in practice the molecular weight obtained tends to a limit because of concentration effects and/or reactions of activated species with impurities.

### 1.3.2.1 Ring-opening oxonium ion polymerisation of cyclic ethers.

Similar to vinylic polymerisations the nature of the monomer, initiator and general reaction conditions determine the kind of final product formed in ring-opening polymerisation (ROP). The type of monomer determines the feasibility of polymerisation and is expressed by the change in free energy of polymerisation ($\Delta G_p$). The reactivity of the monomer is related to kinetics and can be expressed by the rate of polymerisation (or propagation). ROP of heterocyclic compounds depends on the ring-strain and basicity of the heteroatom.

Ring strain depends on the chemical structure, ring size and ring substituents. The exact origin of ring-strain is found in bond angle distortion due to cyclic geometry, bond stretching or compression, repulsion between eclipsed H atoms (conformational strain or bond torsion) and non-bonded interaction between atoms or substituents attached to different parts of the ring (transannular strain, compression of van der waals radii). Ring strain can be measured and is shown in table 2 for various cyclic ethers along with the corresponding enthalpy of polymerisation. The enthalpy of polymerisation shows the importance of ring-strain in determining the polymerisability of the monomer. Hence, oxane does not undergo ROP but oxirane and THF both do, however, oxirane has a lower $[M]_e$ compared to THF.

| Cyclic ether | Ring strain[34] (kJ mol$^{-1}$) | $-\Delta H_{polym.}$[35] (kJ mol$^{-1}$) |
|---|---|---|
| Oxirane | 114 | 94.5 |
| Oxetane | 107 | 81 |
| Oxolane (THF) | 23 | 15 |
| Oxane (pyran) | 5 | ~0 |
| Oxepane[36] | -- | 33.5 |
| Oxocane | 42 | - |

**Table 2. Ring strain and $-\Delta H_p$ for various cyclic ethers.**
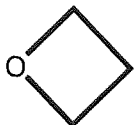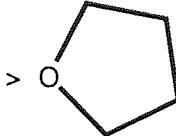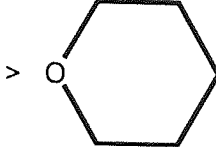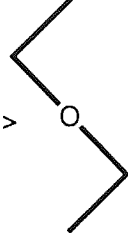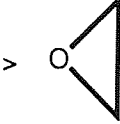
| Cyclic ether | pKa | Reference |
|---|---|---|
| O △ (oxetane) | 2.02 | 37 |
| > O (pentagon) | 2.1 | 37,39 |
| > O (hexagon) | -- | |
| > O (open chain) | 3.59 | 37 |
| > O △ (oxirane) | 3.7 | 38 |

**Table 3.   Basicities of cyclic ethers.**

Nucleophilicity and basicity measure the ability to share the lone pair (or pairs) with an electron acceptor e.g. $R^+$. Basicity of cyclic ethers decreases in the order shown in table 3. Oxetane is more basic than THF due to the lower steric hindrance and also because in THF there is a stronger interaction between the lone electron pair on the oxygen with s-electrons of the C-H bonds. This interaction between the lone pair and s-electrons of the C-H bonds may also explain the low basicity of oxirane. Knowledge of the basicities aids an understanding of transfer and propagation reactions, e.g. the polymer unit in polyTHF is a weaker base than the monomer so it is less likely to take part in nucleophilic substitution type reactions, at the cyclic onium end.

Hence chain transfer is slow and does not affect propagation. In contrast, the basicity of ethylene oxide is lower than that of the monomer unit in polyoxirane so reactions

involving polymer chain become important. Finally, work by Penczek[40] shows that it is the basicity of the monomer which affects reactivity rather than the ring-strain. Substituents may have significant effects on both ring-strain and basicity.

## 1.3.2.2 Initiators and general reaction conditions.

Many of the initiators shown in table 1, are suitable initiators for ROP. The chief requirements of an initiator are that it is a strong electrophile favouring attack on the heteroatom and that it forms a stable counter-ion which will not recombine quickly with the propagating species thereby causing irreversible termination.

The reaction conditions are adjusted so that polymers with high molecular weights are formed. A reasonably polar solvent, such as $CH_2Cl_2$, which facilitates a fast rate of initiation ($R_i$), but which also supports a high molecular weight polymer is chosen. Temperatures below room temperature and down to -78°C are often employed for the polymerisation of cyclic ethers. Flow addition rates of monomers, usually as dilute solutions, are used for the polymerisation of oxiranes because bulk polymerisations are known to lead to explosions. Activated monomer conditions also feature slow addition rates of monomer in order to minimise the competing active chain-end reaction. The effect of reaction conditions will be considered in greater detail in section 3.

## 1.4 Synthesis of copolymers.

There are three major techniques of synthesising copolymers:

i) All monomer in (AMI) method, where two or more monomers are placed in a reaction flask together before initiation. The microstructure of the polymer depends on the relative reactivities of the monomers and the propagating centres. This is usually defined in terms of reactivity ratios: the ratio of the reactivity of the propagating species with its own monomer to the ratio of the propagating species with the other monomer. If the reactivities of the monomers to the propagating centres is approximately equal

then a statistical or random copolymer is formed. When the reactivity ratios are significantly different then compositional drift occurs.

ii) Sequential addition of monomer usually to form block copolymers is a convenient technique but living systems are often necessary. Hence, the range of copolymers prepared by this method is limited.

iii) To increase the diversity of polymers, in particular block copolymers, a class of reactions known as transformation reactions have been used to produce block or graft polymers. The method involves the change of a propagating mechanism, usually a living mechanism, to another by modification of the propagating end. This enables monomers polymerisable by different mechanisms to be incorporated into block copolymers.

iv) To this may be added a fourth method where a macroinitiator or a macromer is used.

## 1.5 Applications.

A wide variety of polymers have been made using cationic techniques but relatively few are produced on a commercial scale. Amongst the most important of these are the productions of polyisobutylene and polyisobutylene-co-isoprene better known as butyl rubber. Indeed, the synthesis of elastomers constitutes a major application of cationically prepared polymers.

Recently, there has been considerable interest in thermoplastic elastomers (TPE), which are block copolymers usually ABA or $(AB)_n$ type, consisting of a hard plastic segment (A) and a soft elastomeric segment (B). The advantages of these types of materials are that they do not require an external curing agent, because the phase separated plastic segments act as physical cross links and the materials may be re-moulded. An eventual aim of this work is to synthesise TPEs which may be used in propellant and explosive compositions as thermally processable binders. At the present time homopolymers

such as polybutadiene are used which have the disadvantage that the composition contains a large amount of explosive component to achieve the required performance. By using binders which have energetic chemical groups the relative amount of the explosive ingredient may be reduced and thus the overall sensitivity (in explosive terms) to an external shock, e.g. bullet penetration, may be decreased. It is thought that an ideal binder for propellant compositions would be a TPE with energetic blocks.

Other applications of cationic polymers include alkali metal carriers through liquid membranes (e.g.polyvinylether-co-polyoxyethylene), polyelectrolytes (polyvinylether with amino pendant groups), epoxy resins in adhesives and engineering polymers such as poly[3,3-bis(chloromethyl)] oxetane (polyBCMO) used in the construction of chemical equipment.

A potentially profitable market for cationically prepared polyethers may be in the biological or pharmaceutical polymers field, where water soluble polymers/gels are being considered as drug delivery and slow drug release materials.

## 1.6    Energetic materials.

Energetic materials are usually classified according to the function they perform. The main functions [56] are as explosives, propellants or pyrotechnics. The term explosive is used in various contexts, but here it will be synonymous with the term 'high explosive' which is defined as a material which can be detonated. High explosives are further divided into materials which detonate easily, primary explosives, and materials which are less easy to detonate, secondary explosives. Hence, for safety reasons a munition is filled predominantly with a secondary explosive and a small amount of primary explosive is used to initiate the main charge. Specifically, high explosives are used to create shock waves, burst, shatter, create airblast, lift and heave. Low explosives, on the other hand, are actually propellants which are materials designed to burn in a controlled fashion. The burning rate law for such materials is:

$$r = BP^\alpha \tag{1.18}$$

where r is the linear burning rate, P is the pressure at the burning surface. B is the burning rate coefficient and is a property of the material, as is $\alpha$ the pressure index, which indicates the nature of the explosive. Most propellants have $\alpha$ equal to or less than one but some materials have values of $\alpha$ greater than 1 and in such cases the rate of burning may exceed the velocity of sound through the material and cause a detonation. Indeed, detonation is defined as the transmission of a shock wave through an explosive material, at a velocity greater than the velocity of sound in the material. This process causes compression and adiabatic heating which liberates energy by exothermic decomposition of the explosive, until detonation occurs. The velocity of the shock wave in solid or liquid explosions is between 1800 and 9000 $ms^{-1}$, an order of magnitude higher than that of a burning process in a propellant. Propellants are commonly used to propel projectiles and rockets, start internal combustion engines, pressurise other piston devices and rotate turbines or gyroscopes.

The third class of energetic materials is known as pyrotechnic. These are mixtures of oxidising and reducing solids, capable of self-sustained combustion at rates which depend on the composition. They are designed to supplement or simulate effects produced by conventional explosives e.g. ignite propellants and produce delays, heat, smoke, light and noise.

In general, energetic materials contain chemical groups which are able to liberate a lot of heat and/or gaseous products. Groups such as $C-NO_2$, $C-ONO_2$, $N-NO_2$ and $C-N_3$ are the main sources of power in energetic ingredients. Usually, these groups are oxidising agents used in conjunction with the rest of the formulation which acts as the fuel. A combination of compounds containing these ingredients is used to achieve a given objective. For instance, initiators or primary explosives are compounds such as lead styphnate (I) or lead 2,4-dinitroresorcinate (II). Secondary high explosives are materials such as RDX (III) and HMX (IV), which are solid, crystalline compounds with high melting points, 204 °C and 278 °C, respectively.
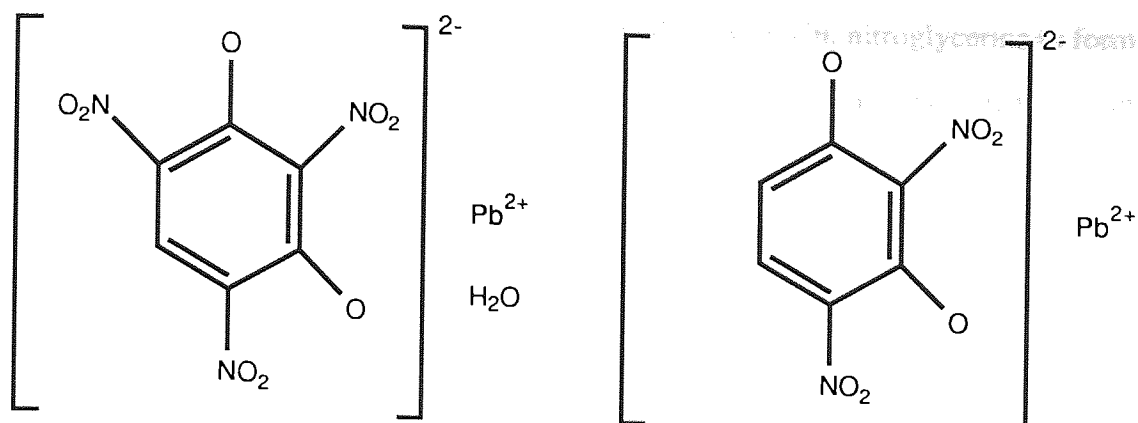
(I)



(II)
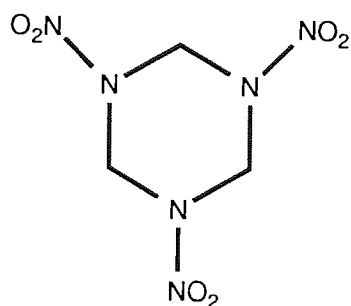


(III)
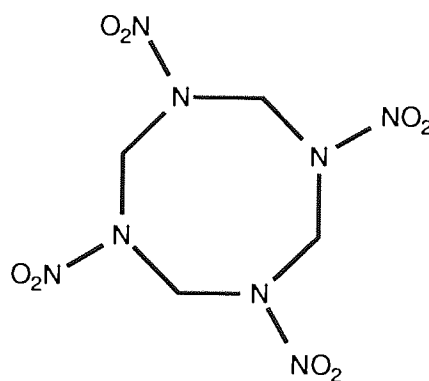


(IV)

High explosives are often desensitised by mixing with wax, liquids (such as trinitro toluene) or polymers. The polymers may be non-energetic e.g. hydroxy terminated polybutadiene (HTPB) or energetic. One of the earliest examples of an energetic polymer is in fact a polyether, nitrocellulose. This is prepared by the action of mixed nitric and sulphuric acids on cellulose. The repeat unit of this polymer is:
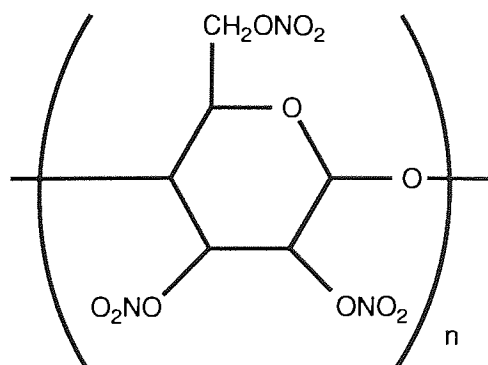
This polymer is a white, fibrous solid and is usually mixed with nitroglycerine to form a gelatinous composition known as double base propellant. However, it is not an elastomer and as modern munitions and rockets are often used in polar conditions or in space where temperatures are low, good elastomeric properties coupled with a glass transition temperature below -50 °C are prerequisites. To meet these requirements recent energetic binders have been designed to have as low a Tg as possible, although as yet, an unplasticised polymer with an inherently low Tg (< -50 °C) has not been produced. The closest a material has come to meeting these requirements is glycidyl azide polymer (GAP) which is reported [57] to have a Tg of -45 °C. The repeat unit of GAP is:
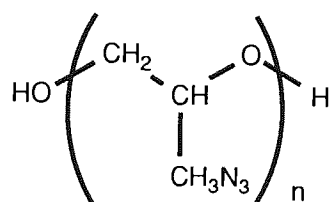


This compound is the main commercial competitor of the two polymers which are the main subject of this report, namely, poly(3-nitratomethyl)-3-methyl oxetane (V), variously known as polyNIMMO, polyNMMO or POWA 1 and poly(glycidyl nitrate) (VI) a material similar to GAP except that the energy is stored in the form of nitrate ester groups (-ONO2) rather than azido groups (-N3).
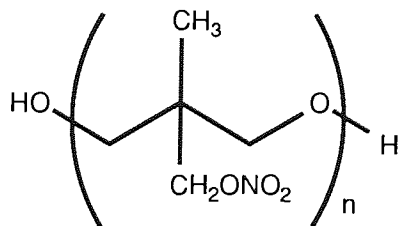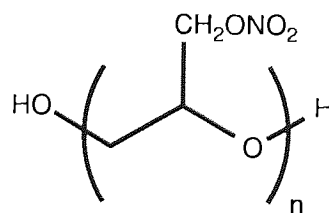


(V)                                         (VI)

Other energetic polymers such as polyvinyl nitrate (VII) and polynitroaromatics e.g. polynitrostyrenes (VIII) have been prepared but are not commercially important.
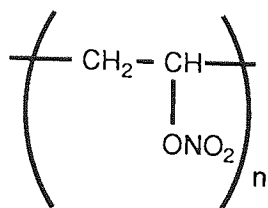
(VII)
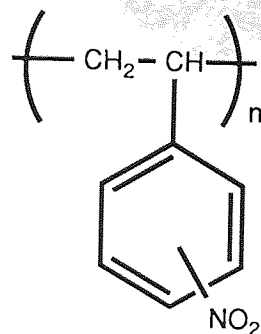


(VIII)

Besides these a group of macromolecules, called Gilligan polymers[66], energetic acrylate[67] and polyurethanes[68] have been made. Gilligan polymers as the name suggests were developed by Gilligan at Naval Surface Weapons Centre at White Oak in the United States. They are prepared by a step-growth process from monomers with pendent nitro and/or fluoro moieties. See Scheme 3.

Energetic acrylates and methacrylates[67] have been reported since 1950. Recently French workers at Societe Nationale de Poudres et Explosif (SNPE) have polymerised monomer XV by free radical techniques to give a resinous material.
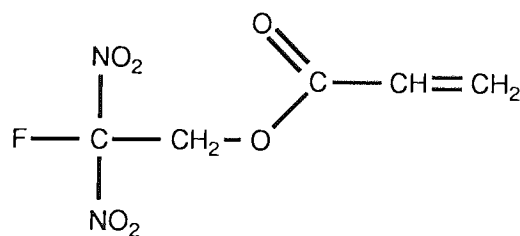


(XV)

Energetic polyurethanes have been investigated, both using energetic diol and/or energetic isocyanates[68]. An example of the latter is XVI.



(XVI)

43

H₃C ... NO₂ ... NO₂ ... CH₂—O ... O ... CH₂—O—CH₂—CH₂OH (structures)

**(IX)**

**(X)**

H₃CC(NO₂)₂CH₂O ... OCH₂C(NO₂)₂CH₃

HOCH₂C(NO₂)₂CH₂O ... O—CH₂C(NO₂)₂CH₂O ... OCH₂C(NO₂)₂CH₂O

**(XI)**
Gilligan polymer 2

$\left( \text{F}\!-\!\!-\text{C(NO}_2)_2\text{CH}_2\text{O} \right)_2$

**(XII)**

$+$

$\left( \text{HOCH}_2\!-\!\!-\text{C(NO}_2)_2\text{CH}_2\text{O} \right)_2$

**(XIII)**

FC(NO₂)₂CH₂O ... OCH₂C(NO₂)₂F

HOCH₂C(NO₂)₂CH₂OCH₂OCH₂OCH₂C(NO₂)₂CH₂O ... OCH₂C(NO₂)₂CH₂OCH₂OCH₂C(NO₂)₂CH₂O

**(XIV)**
Gilligan polymer 3
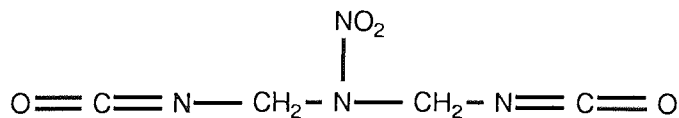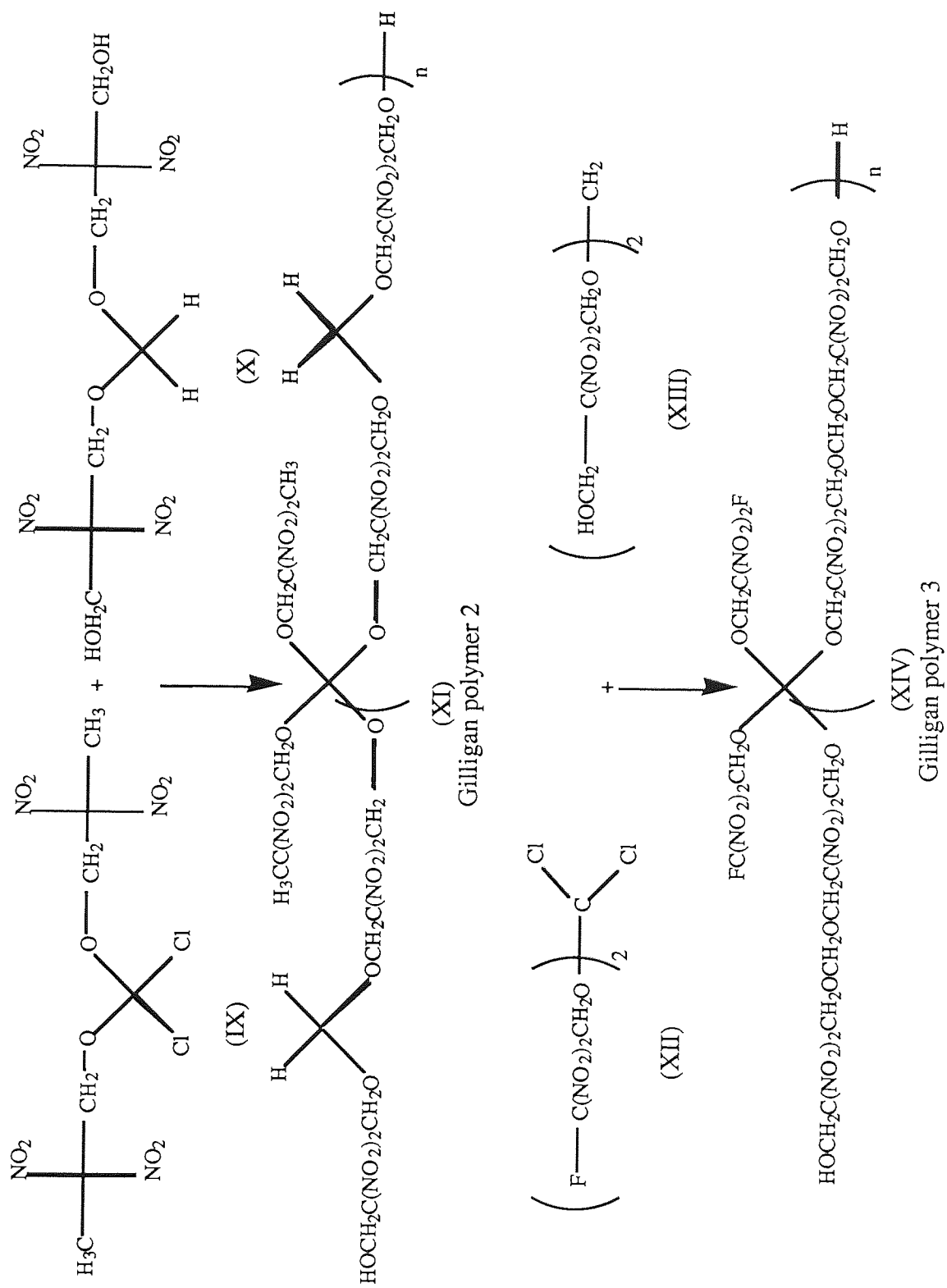
**Scheme 3. Syntheses of Gilligan polymers by step-growth propagation.**

44

## 1.6.1 Energetic polymer (binder) synthesis.

There are two basic approaches to the synthesis of energetic polymers. The first consists of modifying an existing inert polymer and the second of polymerising energetically substituted monomers. GAP is normally prepared by the former method from polyepichlorohydrin (PECH):

$$\left(\!\!-CH_2-CH-O-\!\!\right)_n \quad \xrightarrow[\text{NaN}_3]{\text{DMF}} \quad \left(\!\!-CH_2-CH-O-\!\!\right)_n \tag{1.19}$$

with $CH_2Cl$ on the left (PECH) and $CH_2N_3$ on the right.

PECH
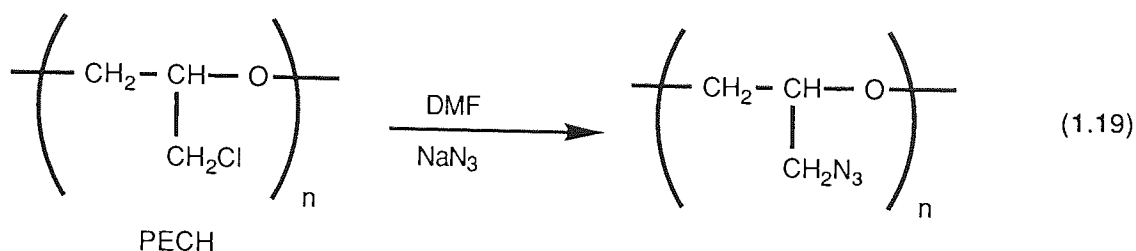
However, analogous azido oxetane monomers[58] synthesised from oxetane derivatives have been polymerised by ring opening polymerisation techniques. See equations 1.20 to 1.23.



$$\tag{1.20}$$



$$\tag{1.21}$$



$$\xrightarrow[\text{Alcohol}]{\text{BF}_3\text{OEt}_2} \quad \left(\!\!-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\!\!\right)_n \tag{1.22}$$

$$\text{(structure)} \xrightarrow[\text{Alcohol}]{\text{BF}_3\text{OEt}_2} \text{(polymer structure)} \qquad (1.23)$$
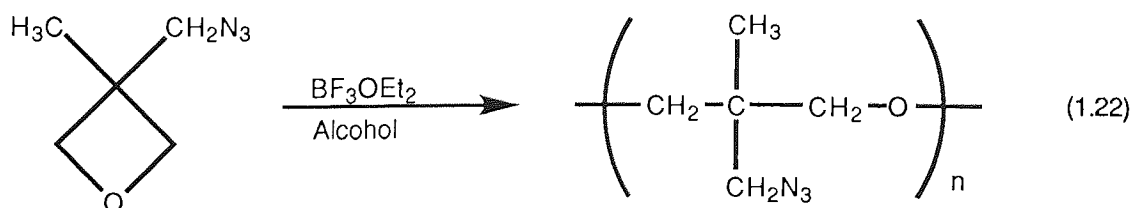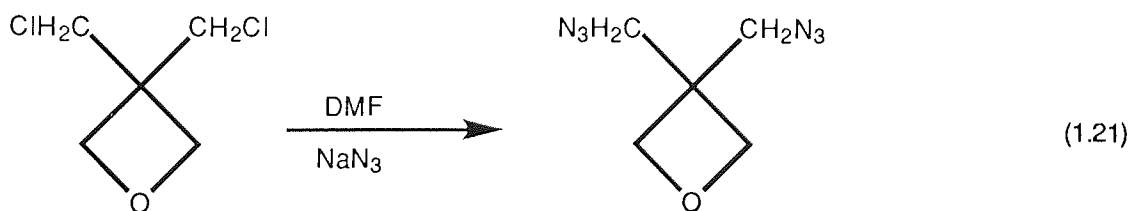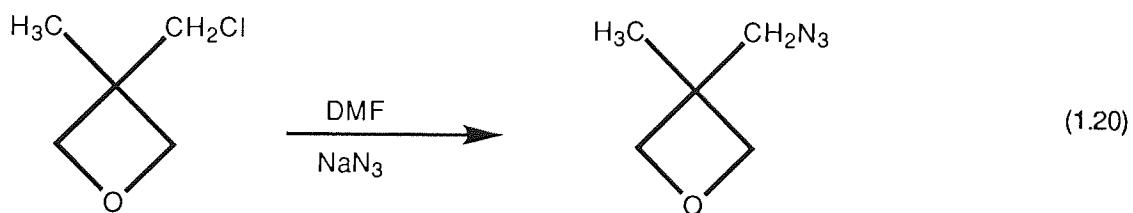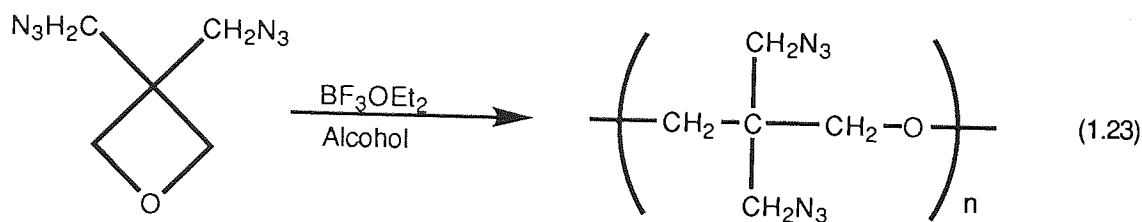
The synthesis of nitrate ester polymers depends on the nitration of suitable functional groups, either on the monomer or the polymer, by reagents such as acetyl nitrate, mixed acid (concentrated $HNO_3$ and concentrated $H_2SO_4$) and dinitrogen pentoxide ($N_2O_5$). Dinitrogen pentoxide has been the key to the energetic binder programme conducted at the Defence Research Agency (DRA). It is a mild nitrating agent which allows modification of polymers such as polystyrene to poly(nitrostyrene) without degradation of the chains [59] and with few side reactions; the main waste product, being $HNO_3$, is easily removed by neutralisation.

### 1.6.1.1    Preparation of dinitrogen pentoxide.

The empirical formula of dinitrogen pentoxide is $N_2O_5$ and it is often depicted as:

(XVII)
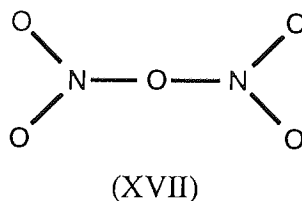
However, its structure depends on the polarity of the solvent medium. Hence, in $HNO_3$ it has a high degree of dissociation[60] into the nitronium ion, $NO_2^+$, the main agent of nitration, and the $NO_3^-$ ion. In relatively low polarity solvents e.g. $CH_2Cl_2$, a low $NO_2^+$ ion concentration is found. Although $N_2O_5$ was first prepared[61] in 1849 it was largely neglected because of the difficulties in preparing it in a pure form and its poor thermal stability which made it difficult to store. These difficulties have been overcome and there are two main routes used to prepare[62] $N_2O_5$. The first process involves the electrolysis[63] of $HNO_3$ in the presence of $N_2O_4$ (equation 1.24), effectively the dehydration of nitric acid.

$$2 \text{ HNO}_3 \xrightarrow[\text{2e}]{\text{N}_2\text{O}_4} \text{N}_2\text{O}_5 \quad \vdots \quad + \text{ H}_2\text{O} \qquad (1.24)$$

Cell Membrane
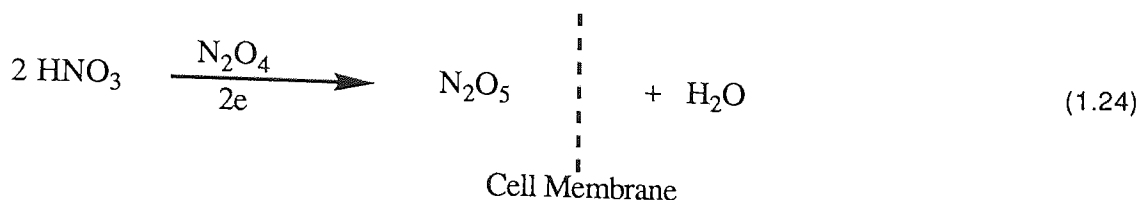
This produces a 15-20% (w/v) solution in anhydrous nitric acid. The second route is the ozonation[64] of $\text{N}_2\text{O}_4$, a gas phase reaction (equation 1.25), which produces $\text{N}_2\text{O}_5$, trapped in the solid form at card-ice/acetone temperatures. The $\text{N}_2\text{O}_5$ is then stored at a temperature of -60 °C in large freezers, it is removed and dissolved in the required solvent prior to use. It is noteworthy that dissolution in $\text{CH}_2\text{Cl}_2$ is an endothermic process, so care should be taken to avoid moisture contamination.

$$\text{N}_2\text{O}_4 \text{ (g)} + \text{O}_3 \text{ (g)} \xrightarrow{+20°\text{C}} \text{N}_2\text{O}_5 \text{ (g)} + \text{O}_2 \text{ (g)} \xrightarrow{-78°\text{C}} \text{N}_2\text{O}_5 \text{ (s)} \qquad (1.25)$$
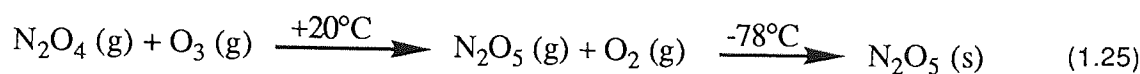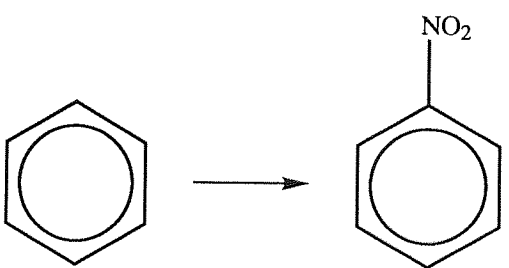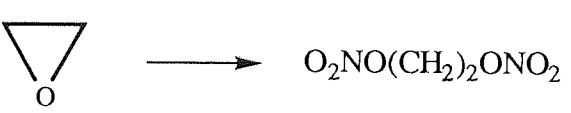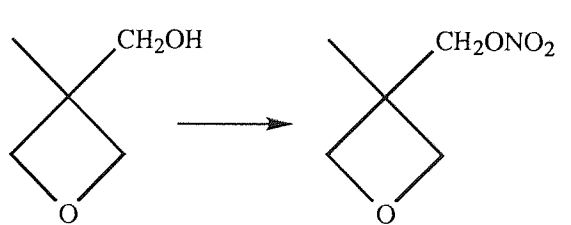
## 1.6.1.2    Nitrations using N$_2$O$_5$.

A summary of $\text{N}_2\text{O}_5$ nitrations is shown in table 4, courtesy of Millar[62]. Millar and Paul have used $\text{N}_2\text{O}_5/\text{CH}_2\text{Cl}_2$ systems to prepare monomers such as glycidyl nitrate (GLYN) and 3-(nitratomethyl)-3-methyl oxetane (NIMMO). NIMMO is made from 3-(hydroxymethyl)-3-methyl oxetane, as shown by the last example in table 4, by either batch or 'flow nitration' process.

The batch process involves the addition of $\text{N}_2\text{O}_5/\text{CH}_2\text{Cl}_2$ from a jacketed dropping funnel, fixed with a $\text{CaCl}_2$ guard tube and kept at a temperature of -20 °C, to a jacketed reaction vessel containing 3-(hydroxymethyl)-3-methyl oxetane in $\text{CH}_2\text{Cl}_2$. The jacket fluid is circulated at a temperature of -30 °C and the $\text{N}_2\text{O}_5$ added, dropwise, at a rate such that the reaction mixture does not rise above -15 °C. This prevents the competing ring-opening reaction.

$$
\text{(XVII structure)} \xrightarrow[> -15°C]{N_2O_5 \ /CH_2Cl_2} \quad O_2NOH_2C-\underset{\underset{CH_2ONO_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2ONO_2 \qquad (1.26)
$$

Metriol trinitrate
(XVIII)
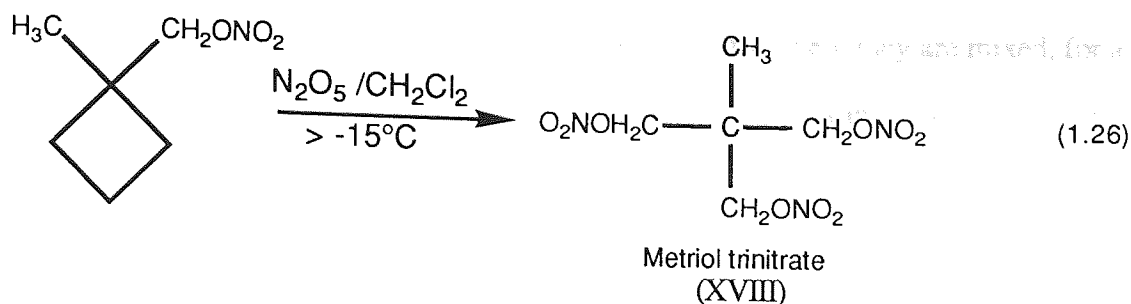
The drawback of the batch process is that the $HNO_3$ produced during the nitration of the hydroxyl group remains and the amount builds up in the reaction vessel, leading to potential increases in side-reactions such as ring-opening.

| Reaction Type | Conditions | Examples | Product Name |
|---|---|---|---|
| Aromatic Nitration | A/O |  | (C-) nitro compound |
| Nitrolysis | A(O) | $R_2NCOCH_3 \longrightarrow R_2N\text{-}NO_2$ | Nitramine |
| Ring Cleavage | O |  $\longrightarrow O_2NO(CH_2)_2ONO_2$ | Nitrate ester or nitramine-nitrate |
| Selective Nitration | O |  | Nitrate ester derivative of strained ring compound. |

A = Nitric acid system.
O = Organic solvent system.

**Table 4.   Summary of $N_2O_5$ Nitrations.**

To overcome this, whilst facilitating the control of the exotherm, a flow reaction technique was developed by Paul[65]. In this system two streams of $N_2O_5$ in $CH_2Cl_2$

and monomer in $CH_2Cl_2$ are passed into a tube or chamber where they are mixed, for a short time (< 1 minute), then immediately dropped into a separating vessel containing aqueous $NaHCO_3$ solution, which neutralises $HNO_3$. The aqueous and organic layers are separated. The organic fraction is dried over anhydrous $CaCl_2$ and assayed by gas liquid chromatography. The inherent safety and convenience of the flow nitration system has been a major factor in enabling the DRA to scale-up and commercially exploit nitrate ester energetic binders. This is especially true in the synthesis of glycidyl nitrate from glycidol (1.27), where the high ring strain added to the exothermic nitration of the hydroxyl could lead to an uncontrolled reaction.



$$\text{(1.27)}$$
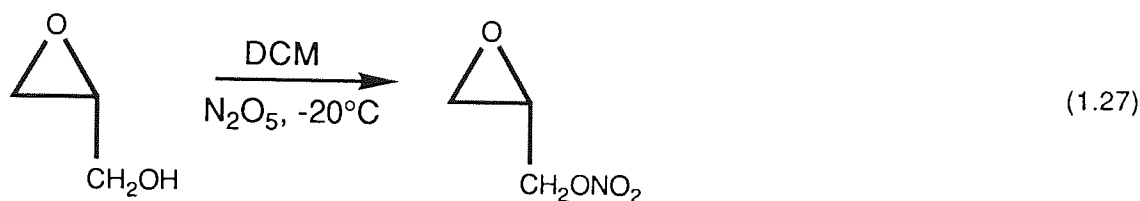
The monomer prepared thus was polymerised, the study of which is the subject of this thesis.

### 1.6.1.3 Synthesis of nitrate ester polymers.

As has already been described in section 1.6.1 there are two basic strategies to make energetic polymers, namely by modifying an existing polymer or by polymerising an energetic monomer. An example of the first approach is the synthesis of nitrated hydroxy terminated polybutadiene[69] (NHTPB) as shown in scheme 4.

The degree of epoxidation and hence nitration may be controlled allowing a range of NHTPBs with differing properties to be prepared. The viscosity of the polymer depends on the molecular weight and structure of the starting material. NHTPB with 10% of the double bonds nitrated gives a Tg of -58 °C and with 20% nitration a Tg of -22 °C. This shows that the presence of $-ONO_2$ groups on the polymer backbone increases the Tg. Indeed, this is a feature of most energetic groups primarily because of their bulkiness.

$$HO-(CH_2-CH=CH-CH_2)_n-OH$$

CH₂Cl₂ — $CH_2Cl_2$

$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-H$$

$$HO-(CH_2-CH=CH-CH_2)_m-(CH_2-\overset{O}{\overset{/\backslash}{CH-CH}}-CH_2)_{n-m}-OH$$

$CH_2Cl_2$   $N_2O_5$

$$HO-(CH_2-CH=CH-CH_2)_m-(CH_2-CH-\overset{ONO_2}{\overset{|}{CH}}-CH_2)_{n-m}-OH$$
$$\underset{ONO_2}{|}$$
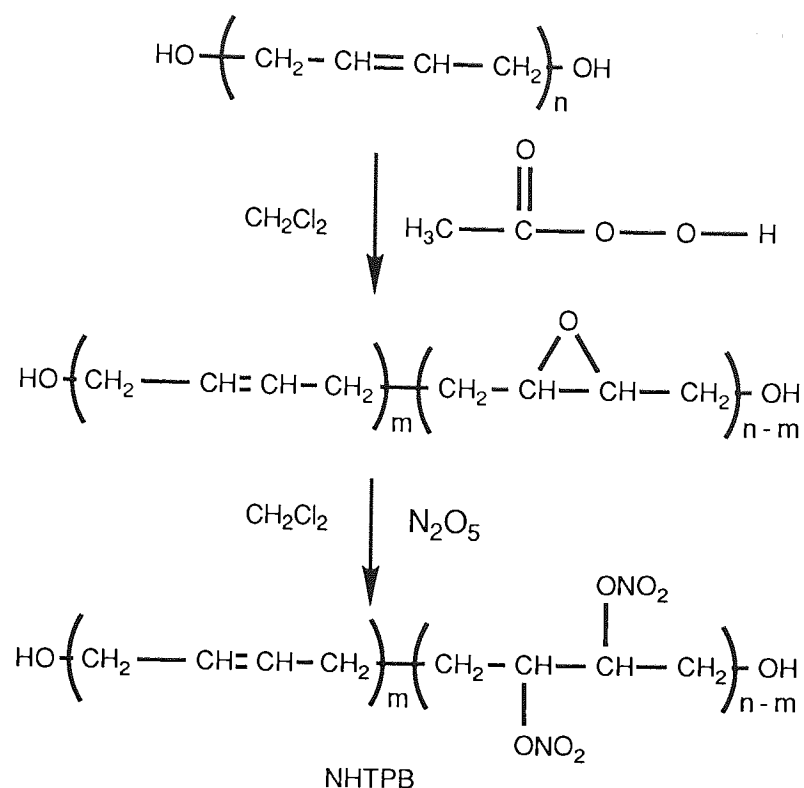
NHTPB

## Scheme 4. Modification of hydroxy-terminated polybutadiene to make NHTPB.

Although some work has been done polymerisation of energetic nitrate ester monomer has received little attention because of the difficulty in obtaining pure monomers, the possibility of an explosive event resulting from the large exotherm associated with the polymerisation decomposing the nitrate ester and difficulty in controlling the polymerisation products. Among the first nitrate ester monomers polymerised were glycidyl nitrate and NIMMO. These monomers were prepared by nitration using acetyl nitrate, a reagent which was relatively hazardous and which had to be removed by distillation to obtain reasonably pure monomer. The polymerisation techniques used by the previous workers were 'all monomer-in' cationic systems based on alcohol/$BF_3$.$OEt_2$. These systems polymerised both monomers but it was particularly difficult to prepare polymers in the molecular weight range of 2000-5000 either uncontaminated with large amounts of cyclic species or very high molecular weight linear species and in reasonable conversion for ease of mixing with the filler. Defence

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Research Agency research improved the synthesis of both monomers with the aid of $N_2O_5$ (which does not have to be removed by distillation) and polymerisations, allowing commercial exploitation. This polymerisation research with emphasis on safety aspects, particularly control of exotherm, is described below.

### 1.6.1.4 Safety and theoretical calculation of enthalpy of explosion.

Many chemical reactions are potentially hazardous but polymerisation reactions with large exotherms and especially such reactions with energetic groups have to be treated with particular caution. The exotherm of the reaction has to be controlled so that the temperature does not rise sufficiently to decompose the energetic group. The decomposition of the nitrate ester group occurs at 170 °C and so it is important that the maximum reaction temperature does not approach this. However, it does not necessarily follow that a composition with high energy, measured by the enthalpy of explosion ($\Delta H_{exp}$), is inherently more hazardous or, more precisely, sensitive. Other factors such as onset of decomposition and chemical compatibility can affect sensitivity. Nevertheless, a knowledge of the energy of the material can aid design of compositions and indicate the safety precautions which should be taken. A method for calculating ($\Delta H_{exp}$) follows.

The enthalpy, or heat, of explosion is the heat of reaction leading to the formation of the explosion products from the solid compound. This is distinct from the heat of combustion ($Q_c^\circ$), which is the heat of formation of the products of combustion from the solid compound. The data from heats of combustion (experimental) can be used to calculate heats of formation of the various products. Hence, for an energetic substance, with a formula $C_\alpha H_\beta N_\delta O_\gamma$,

$$Q_x = \Sigma Qf^{st}(x) - Qf^\circ \tag{1.28}$$

where $\Sigma Qf^{st}(x)$ is the sum of the heats of formation of the various explosion products from the elements in their standard states and $Qf^\circ$ is the heat of formation of the compound from its constituent elements in their standard states.

Similarly, for the heat of combustion

$$Q_c = \Sigma Qf^\circ(c) - Qf^\circ \qquad (1.29)$$

where $\Sigma Qf^\circ(c)$ is the sum of the heats of formation of combustion products from the constituent elements in their standard states.

If combustion data is not available then $Qf^\circ$ can be calculated by the relation

$$Qf^\circ = Qf^a_{(g)} - \Sigma Q^a_{st}(E) - L_v - L_f \qquad (1.30)$$

where $Qf^a_{(g)}$ is the formation of the compound, in the gas-phase, from the free ground-state atoms of its constituent elements. $\Sigma Q^a_{st}(E)$ is the sum of the heats of formation of the individual constituent elements in their standard states (C as graphite) from the free atoms in their ground-states. $L_v$ and $L_f$ are the latent heats of fusion and vaporisation, respectively, of the compound.

However, equation 1.30 can be simplified as the heat of formation of the gaseous compound from the elements in their standard states; $Qf^{st}_{(g)}$ is given by

$$Qf^{st}_{(g)} = Qf^a_{(g)} - \Sigma Q^a_{st}(E) \qquad (1.31)$$

Substituting equation 1.31 into equation 1.30 gives

$$Qf^\circ = Qf^{st}_{(g)} - L_v - L_f \qquad (1.32)$$

$Qf^{st}_{(g)}$ can be calculated for a given compound from its molecular formula i.e. summation of the bond energies.

$$Qf^{st}_{(g)} = \Sigma Q^{st}(b) + Q_R + Q^{st}(X-NO_2) \qquad (1.33)$$

where $\Sigma Q^{st}(b)$ is the sum of the bond energies. $Q_R$ is a correction for resonance stabilisation and $Q^{st}(X-NO_2)$ is the energy of the energetic group. In the case of polyGLYN, X is the oxygen atom of the nitrate ester moiety. The difficulty with equation 1.32 is that for new energetic materials values of $L_v$ and $L_f$ are not often

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known. In such instances they are estimated by using values of analogous materials. This is not a serious drawback to the calculation because the sum of these terms is much less than the magnitude of the $Qf^{st}_{(g)}$. The sum of $Lv$ and $Lf$ is estimated to be between -12 kcal/mol and -18 kcal/mol depending on the molecular weight of the polymer for the POWA series of nitrate ester materials. (NB. Thermochemical convention for explosive calculations is that endothermic changes are treated as negative and exothermic changes as positive). For polyGLYN $Qf^{\circ}$ is calculated as 61.3 kcal/mol.

Returning to equation 1.28, the $\sum Qf^{st}(x)$ term is more difficult to calculate mainly because the products of explosion vary. For example, the oxygen atoms may be distributed as $CO_2$, $CO$, $H_2O$ and $O_2$. This problem was addressed by Kistiakowsky and Wilson[70] who applied thermodynamic and kinetic data to a system '..a time, shortly after detonation, after most of the external work has been done but while the gases are still hot.' They drew up a set of rules to predict the distribution of the products known as the Kistiakowsky and Wilson (K-W) rules:

(1)     Permissible products: only the following molecules (and no free atoms) can appear in the explosion products:

$C_{amorph}$, $CO$, $CO_2$, $H_2$, $H_2O$, $O_2$, $N_2$.
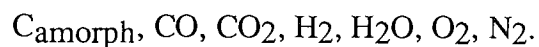
(2)     Distribution of oxygen:

(a)     The C is first oxidised to CO.

(b)     Any residual oxygen then oxidises the H to $H_2O$.

(c)     Any residual oxygen then oxidises the CO to $CO_2$.

(d)     Any residual oxygen then separates as $O_2$.

As the empirical formula of polyGLYN is $C_3H_5NO_4$ and applying the K-W rules the products of explosion are

$$C_3H_5NO_4 = 3CO_{(g)} + H_2O_{(g)} + 3/2H_{2(g)} + 1/2N_{2(g)} \qquad (1.34)$$
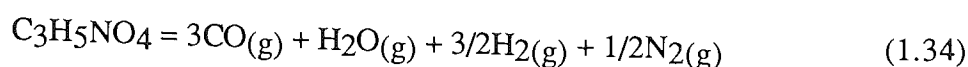
the $\Sigma Qf^{st}(x) = (3 \times 26.39) + 57.8 = 136.97$ kcal/mol.

Using equation 8 the $Q_x = 75.7$ kcal/mol

$$Q_x = 316.7 \text{ kJ/mol}$$

$$Q_x = 2661 \text{ kJ/kg.}$$

This is the figure which indicates the energy of a compound. Comparison of this figure with those calculated for polyNIMMO, 818 kJ/kg, and for glycidyl azide polymer (GAP) 2500 kJ/kg, shows that polyGLYN is expected to be significantly more energetic than polyNIMMO and marginally more so than GAP. Of course, it must be remembered that the calculated value may differ from experimental results and this may be because the theoretical energy of the binder is not fully released during an explosion as well as due to the errors in the experiments or inaccuracies in the assumptions made in the calculations. Nevertheless, $Q_x$ is an important value in assessing the energy and, indirectly, the safety of energetic materials.

## 1.7    Scope of this work.

This work is concerned with the synthesis of energetic materials: monomers, oligomers/plasticisers and polymers based on the nitrate ester moiety as well as vinylic monomers with the ultimate objective of preparing TPEs.

This research forms the basis of this thesis and involves the cationic ring-opening of the cyclic ether: 3-nitratomethyl-3-methyl oxetans (NIMMO). Firstly, the factors affecting the polymerisation such as rate of addition of monomer, OH concentration, ratio of OH:$BF_3.OEt_2$, temperature and the progress of a single reaction as determined by size exclusion chromatography (S.E.C.), are investigated for the alcohol/$BF_3.OEt_2$ initiator

system. Secondly, the polymerisation of NIMMO by activated monomer mechanism is undertaken. The resulting oligomer is end-nitrated with $N_2O_5$ to make a compound which may be a plasticiser. Thirdly, a study of the synthesis and extraction of the main cyclic species is carried out.

The preparation of polyGLYN and methods of converting the secondary hydroxyl end groups to primary hydroxyl groups to improve the curing behaviour with isocyanates. This is tried using both AM and ACE mechanisms using monomers such as oxetanes, oxiranes and NIMMO.

Selective ring-opening of only one epoxide group of butadiene diepoxide using $N_2O_5$ to make BODN followed by polymerisation with AM and ACE mechanisms.

This is carried out with $HBF_4$/butandiol system in $CH_2Cl_2$ to examine whether four membered cyclic ethers are polymerised by AMM conditions.

To synthesise controlled molecular weight polyisobutylene, polystyrene and poly $\alpha$-methyl styrene using $BCl_3$/ester and $BCl_3$/diphenyl phosphate initiator systems. These are studied with a view to sequentially polymerise them to form thermoplastic elastomers.

# CHAPTER 2.

# EXPERIMENTAL.

## 2. EXPERIMENTAL.

The conditions chosen for these studies were governed by the requirements of the given cationic system, which are usually carried out under quite pure conditions to minimise side reactions, and the need for convenience as well as frugality to aid industrial scale-up.

All the glassware was oven dried at 120 °C and purged with dry nitrogen or argon before use. Extra precautions, e.g. vacuum drying, are stated in the procedures when used. Unstabilised dichloromethane (Romil), the main chosen solvent and toluene were distilled from $CaH_2$. The purification and purchase of other solvents and reagents is detailed in the appropriate sections below. All reactions were carried out under an inert atmosphere. Particular care was taken during the handling of energetic monomers and polymers, e.g. teflon sleeves were used on flask necks to avoid frictional discharges which might cause explosion of the energetic compounds.

## 2.1 Synthesis of materials based on 3,3-(nitratomethyl) methyl oxetane (NIMMO).

## 2.1.1 General method for the investigation of factors affecting the polymerisation of NIMMO.

A typical experiment was set up as shown in the diagram below (figure 2.1). Prior to polymerisation the reaction vessel was dried in an oven set at 120°C. The vessel was cooled by purging with dry white spot nitrogen and a magnetic flea placed inside. Temperature control inside the reaction vessel was achieved by using a Haake circulator bath, which pumped a mixture of 1,2-ethandiol/water at the desired temperature through the jacket of the vessel.
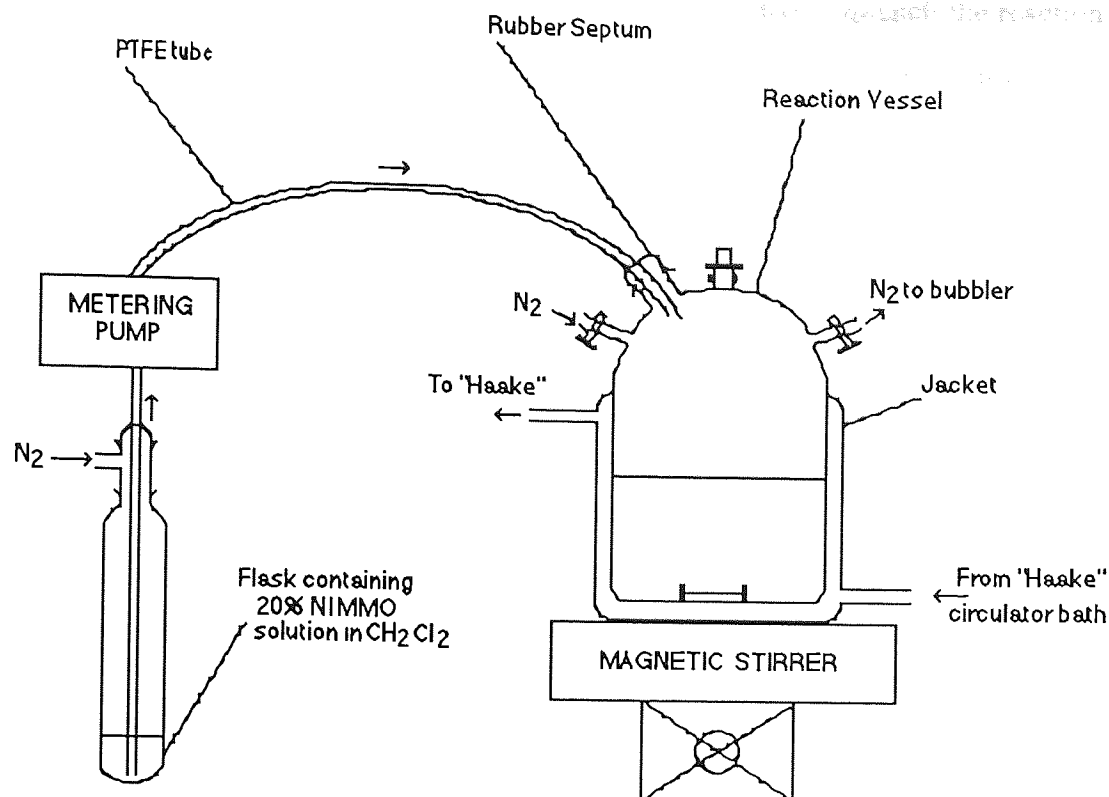
**Figure 2.1. Arrangement of apparatus for the polymerisation of 3,3-(nitratomethyl) methyl oxetane (NIMMO).**

The cationogen (e.g. butandiol, $6.8 \times 10^{-3}$ mol) was weighed into the flask, followed by injection of the required amount, by weight, of the Lewis acid, boron trifluoride etherate (Aldrich, used as received). The mixture was allowed to stir for an hour. The amount of NIMMO solution (20 % w/v, prepared in-house) to be added was calculated using the following equation:

$$\text{moles of NIMMO} = DP \times \text{moles of Initiator.} \tag{2.1}$$

where DP is the degree of polymerisation.

The value of DP is selected and is only expected if the polymerisation is living i.e. no transfer or termination occurs. The required volume of NIMMO solution was pumped into the reaction vessel using a Gilson metering pump at pre-defined rates and for varying periods. When addition of NIMMO was complete, the reaction mixture was

stirred for a further four hours. Water or brine was then used to quench the reaction and the contents of the flask were poured into a large beaker (2L) containing about 200 cm$^3$ of a 5% solution of sodium hydrogen carbonate for neutralisation. The mixture was separated and the lower organic/$CH_2Cl_2$ layer collected in a weighed 250 cm$^3$ round bottom flask. Some samples were dried over anhydrous calcium chloride prior to evaporation of $CH_2Cl_2$ on a "rotavap". The polyNIMMO produced was further dried in a vacuum oven at 100°C for at least 48 h and characterised by size exclusion chromatography (S.E.C.) and N.M.R.

## 2.1.2 Synthesis of linear α,ω-hydroxytelechelic polyNIMMO of low molecular weight by the activated monomer mechanism.

The synthesis of linear, low molecular weight polyNIMMO was carried out in oven dried (120°C) glassware and under an inert, dry $N_2$ atmosphere. NIMMO monomer was distilled at 70°C and 80°C at 2-5 mm Hg. 10g (0.068 mol) of the monomer was made up to a 5% (w/v) solution in distilled $CH_2Cl_2$. 1,4-butandiol (0.39g, 4.33x10$^{-3}$ mol) was added to a 250 cm$^3$ jacketed vessel, kept at a temperature of 17°C, followed by of tetrafluoroboric acid in diethyl ether (0.12g, 6.30x10$^{-4}$ mol). The molar ratio of OH:H$^+$ was 14:1. The monomer solution was added over 16 h and the reaction mixture stirred for a further 4 h. The reaction was quenched with water and neutralised using 5% aqueous $NaHCO_3$. The mixture was separated, the organic layer removed and the $CH_2Cl_2$ evaporated to leave the polymer. The yield of polyNIMMO was 9.51g (92%). The polymer was characterised by S.E.C, I. R. and N.M.R.

## 2.1.2.1 Synthesis of linear, short chain end-nitrated polyNIMMO (LNMOPLAS).

The synthesis of linear, low molecular weight polyNIMMO is described in section 2.1.2. The polymer was first dried in a vacuum oven (20°C for 3 weeks). To a sample of linear polyNIMMO in dichloromethane (0.476g in 11 cm$^3$, 0.50 x 10$^{-3}$

mol) at -21°C was added rapidly a solution of $N_2O_5$ in dichloromethane ((0.18g in 6.5 cm$^3$, 1.7 x 10$^{-3}$ mol). The temperature of the solution was observed to rise to -13°C which was reduced to -20°C by further over 5 minutes. The solution was allowed to warm to 0°C before the mixture was poured into 100 cm$^3$ of 10% aqueous potassium carbonate solution and agitated to ensure thorough mixing. The dichloromethane phase was separated, washed with water (20 cm$^3$) and dried over magnesium sulphate. The dichloromethane was removed by vacuum distillation and the sample dried in vacuo for approximately 2 h, yield 0.39g.

## 2.1.3 Synthesis and extraction of cyclic oligomers of NIMMO.

All glassware was oven dried and the reactions conducted under an inert argon atmosphere. 50 cm$^3$ of undistilled, unstabilised $CH_2Cl_2$ purchased from Romil was placed inside a 500 cm$^3$, 3-necked round bottom flask equipped with a double surface condenser and a magnetic flea . HBF$_4$.OEt$_2$ (3.95g, 0.02 mol) was added to the flask. 50 cm$^3$ of a 20% (w/v) NIMMO solution in $CH_2Cl_2$ was added to another 2 litre, single neck round bottom flask and diluted with 400 cm$^3$ of Romil $CH_2Cl_2$. This solution was then added to the reaction flask using a Gilson 303, H.P.L.C. pump over 16 hours, at room temperature, a further 4 h was allowed for stirring. The final concentration of NIMMO in solution was targeted to be 2% (w/v). When the reaction was complete the mixture was poured into a beaker containing 500 cm$^3$ of water, stirred and then neutralised by addition of 250 cm$^3$ of 5% (w/v) $NaHCO_3$ solution. The organic layer was separated and collected. $CH_2Cl_2$ was evaporated to leave a mixture of predominantly cyclic species which were characterised by S.E.C. The mixture was added dropwise to a large beaker containing 2 litres of rapidly stirring hexane. This was allowed to stand for at least 3 hours and the hexane decanted into a pear shaped flask. After evaporation of the hexane the yield of the cyclic species was 3g (33%). The cyclic species were characterised by S.E.C, N.M.R. and M.S.

## 2.2 Procedures for materials based on Glycidyl nitrate (GLYN).

These include the polymerisation and modification of GLYN by end-capping and block-capping.

### 2.2.1 Activated monomer (AM) polymerisation of GLYN.

The experiments were set up as shown in figure 2.1. The reaction vessel was connected to a cooling circulator (Haake), and charged with 1,4-butandiol (0.64g, $7.1 \times 10^{-3}$ mol). The vessel was then cooled under nitrogen to 0°C and a catalytic amount of tetrafluoroboric acid etherate (0.22g, $1.33 \times 10^{-3}$ mol) was added. The ratio of $OH:H^+$ sought was 10:1. A 25% w/v GLYN solution in dichloromethane (25g, 0.21 mol) was pumped in at a constant flow rate of 0.104 $cm^3$ $min^{-1}$ over a period of 16 h. After the addition was completed a further 4 hours stirring time was allowed before the reaction was terminated by the addition of an excess of aqueous sodium hydrogen carbonate. Stirring was continued until no further gas evolution was noted, whereupon the lower organic layer was separated from the upper aqueous phase, the $CH_2Cl_2$ evaporated and the polymer precipitated into excess methanol. The polymer was isolated, redissolved in dichloromethane (approx. 100 $cm^3$) dried over calcium chloride and the $CH_2Cl_2$ evaporated . The resultant polymer was dried in a vacuum oven at 60°C for 72 h and was characterised by S.E.C. and N.M.R. The yield was 21g (77%).

### 2.2.2 End-capping by AM mechanism.

Attempts were made to end-cap the polymer, prepared as described in section 2.2.1, by sequentially adding a second monomer. Approximately 2 to 8 mol excess (relative to the OH group) of the monomer was added. The monomers used were oxetane, tetrahydrofuran, glycidol, 3,3-(hydroxymethyl) methyl oxetane and 3,3-(nitratomethyl) methyl oxetane.

### 2.2.3 Block-capping by active chain-end method.

PolyGLYN was prepared by the basic method described in section 2.2.1 except that glycerol was used instead of butandiol and that after monomer addition was complete a 9-fold excess of $BF_3.OEt_2$ (relative to glycerol) was added. This was followed by the incremental addition of 24 mol excess (relative to glycerol) of 20% w/v NIMMO solution in dichloromethane. A further 4 h stirring time was allowed after the NIMMO was added before the reaction was neutralised by pouring into a beaker containing excess aqueous sodium hydrogen carbonate. The mixture was separated and the dichloromethane evaporated. The polymer was examined by S.E.C. and N.M.R.

### 2.3 Synthesis and polymerisation of butadiene oxide dinitrate (BODN).

### 2.3.1 Synthesis of BODN.

The apparatus used consisted of a three necked round bottom flask equipped with a thermometer, a pressure equalising dropping funnel and a condenser with a gas outlet at the top connected to a silicone oil bubbler. The dropping funnel was connected to a dry nitrogen source and a rubber septum with a capillary tube or a dropping pipette passing through it was placed on one of the necks of the flask. This was done to remove acidic vapours from the flask. In the absence of a nitrogen flow the product was contaminated with oligomer and the funnel became blocked with cross-linked diepoxide. In the apparatus a mixture of dinitrogen pentoxide (57g, 0.53 mol) and dichloromethane (200 cm$^3$) was stirred at -10 °C. A solution of butadiene oxide (1,3-diepoxybutane, 25g, 0.29 mol) in dichloromethane (25 cm$^3$) was added dropwise over 1h. The temperature was allowed to rise to 20 °C and the mixture stirred for a further 2h before it was poured into saturated sodium bicarbonate solution (400 cm$^3$). After stirring this mixture for 20 minutes, the organic phase was separated washed with water (200 cm$^3$), dried over magnesium sulphate and filtered. The crude product, a yellow oil, could be obtained by evaporation of the solvent but purified product was

product was obtained by first filtering the solution through a bed of activated neutral alumina (40g). The product was analysed by N.M.R and S.E.C.

## 2.3.2   Polymerisation of BODN.

The general methods were similar to those used for NIMMO and GLYN. Active chain -end polymerisations were carried out using the $HBF_4$ and $Et_3OBF_4$ systems and AMM polymerisation was attempted using $HBF_4$/butandiol system in dichloromethane, at 0°C with the monomer added as a 20% w/v solution over 16 h.

## 2.3.3   Copolymerisation of BODN and GLYN.

The activated monomer method as described in section 2.2.1 was used as a basis for the copolymerisation. A 20 % w/v mixture of the two monomers in $CH_2Cl_2$ with a mol ratio of 3.4:1, GLYN (18.75 g, 0.1575 mol) and BODN (9.01 g, 0.046 mol) respectively, was made up. This was added over 8 h to a mixture of 1,4-butandiol (0.25 g, 2.78 x $10^{-3}$ mol) and $HBF_4.OEt_2$ (0.06 g, 3.70 x $10^{-4}$ mol). The ratio of $OH:H^+$ was therefore 11:1, respectively. The reaction was carried out at a temperature of +17 °C.

## 2.4   Procedure for synthesis of polyoxetane by activated monomer mechanism (AMM).

An oven dried 100 $cm^3$, 2-necked jacketed vessel with a magnetic stirrer bar was cooled by passing nitrogen through it. The vessel was then connected to a Haake temperature controller and further cooled to 10°C. The flask was charged with 1,4-butandiol (0.0207 mol) and tetrafluoroboric acid (1.279 x $10^{-3}$ mol), by syringe, to give an overall [-OH] :[$HBF_4$] mol ratio of 32:1. The mixture was stirred for 15 minutes before a 35% solution of oxetane in $CH_2Cl_2$ (w/v) was pumped in at a rate of 0.069 $cm^3$ $min^{-1}$ for 24 hours. Therefore, a total of 35g (0.60 mol) of oxetane was added to the vessel. A further 2 hours of stirring was allowed before the reaction was stopped by pouring the reaction mixture into 200 $cm^3$ of 5% aqueous $NaHCO_3$

solution. The mixture was separated and the $CH_2Cl_2$ evaporated to leave a colourless viscous liquid. This was analysed by size exclusion chromatography and N.M.R.

## 2.5    Synthesis of vinylic polymers.

### 2.5.1    Procedure for the preparation of polyisobutylene.

Isobutylene (I.B.) gas was condensed into a 100 $cm^3$ graduated vessel fitted with a 'rotaflo' tap and a B19 joint, at liquid nitrogen temperature using a vacuum line. The collected gas was bubbled from the graduated vessel into a 3-necked, 500 $cm^3$, round bottomed reaction flask containing 200 $cm^3$ of solvent, a magnetic stirrer bar and fitted with a rubber septum as well as a Dreschel head, through which nitrogen was passed. The graduated vessel containing the isobutylene was allowed to warm up by placing it in an isopropanol-water bath kept at -7°C, the volume of I.B. added was noted. Typically, $3.13 \times 10^{-4}$. mol of I.B. was added and then 0.028 mol of cationogen was added to give an expected molecular weight of 5200. The reaction flask was cooled to a temperature of -30 °C to -40 °C before a ten mole excess of $BCl_3$ solution, with respect to the cationogen, was injected into the flask to initiate the reaction. The reaction mixture was stirred for 2 hours before an excess of methanol was added to terminate the reaction. At this stage white HCl fumes were observed. The reaction mixture was neutralised by pouring into 500 $cm^3$ of aqueous 10% $NaHCO_3$. The organic layer was then separated and evaporated to leave a colourless viscous liquid.

### 2.5.2    Procedures for the preparation of poly(styrenes).

Procedures similar to the synthesis of polyisobutylene (section 2.5.1) were employed for the syntheses of poly(styrenes) except that the monomers were injected into the reaction flasks.
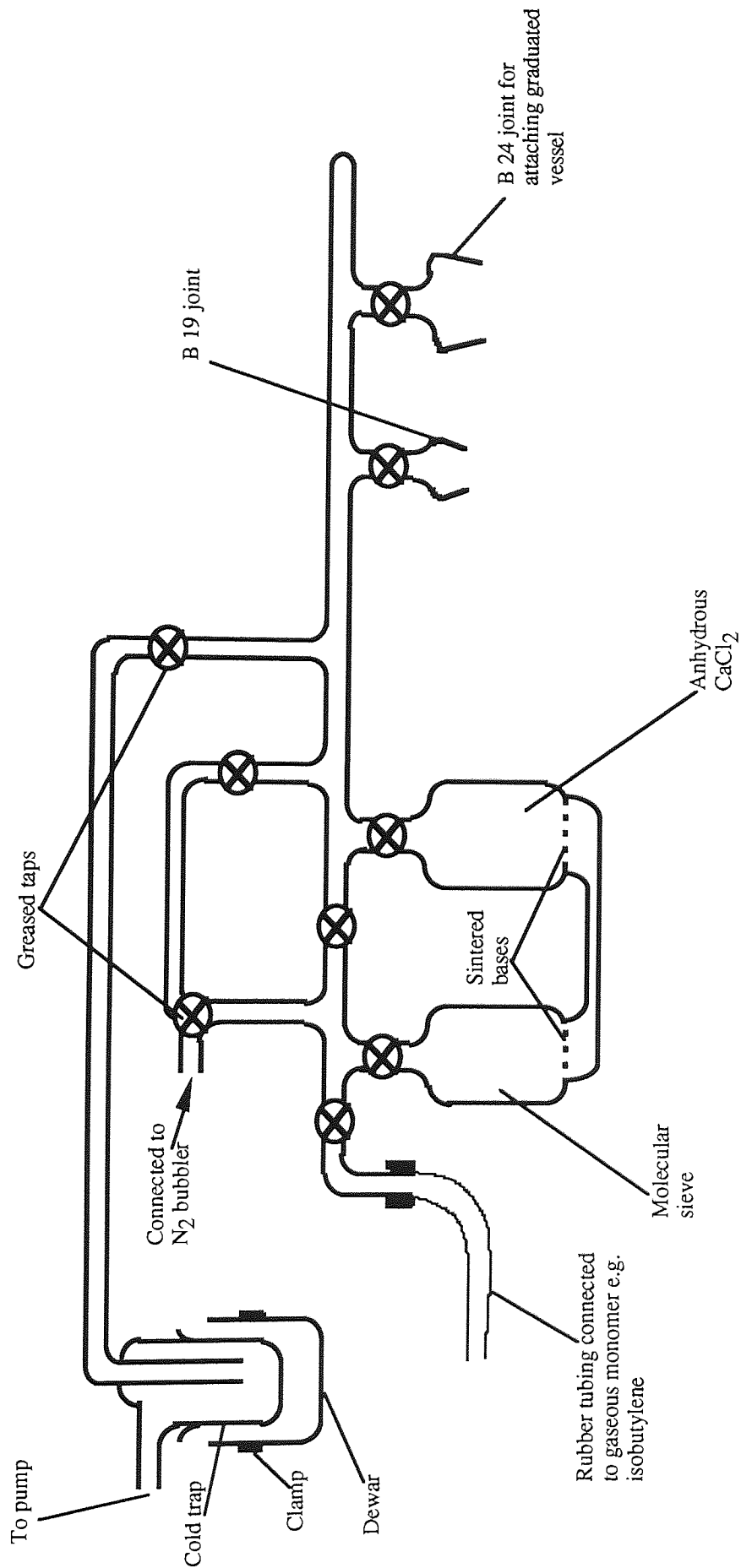
**Figure 2.2.** Schematic diagram of a vacuum line to collect and dry volatile monomers.

To pump

Cold trap

Clamp

Dewar

Connected to N$_2$ bubbler

Greased taps

B 19 joint

B 24 joint for attaching graduated vessel

Anhydrous CaCl$_2$

Sintered bases

Molecular sieve

Rubber tubing connected to gaseous monomer e.g. isobutylene

## 2.6     Characterisation of the Polymers.

This includes structure determination by techniques such as N.M.R., I.R., M.S. and elemental analysis, which will not be detailed here because they are well known and play a relatively minor role in this study.  Size exclusion chromatography (S.E.C.), to determine the molecular weight distribution of the polymer, however, forms a major part of this study and is detailed here.  In addition to S.E.C., differential scanning calorimetry (D.S.C.) is described because the thermal properties of the materials prepared will affect whether the materials are finally used or not.

### 2.6.1    Size Exclusion Chromatography.

Figure 2.3 shows a schematic diagram of a size exclusion chromatograph.  S.E.C. determines the molecular weight distribution (MWD) by separating the polymer sample into fractions according to their molecular size (or more accurately hydrodynamic volume).  This is achieved by a sieving process inside the columns which contain packed spheres of a non-ionic stationary  phase (cross linked polystyrene) whose pore size distribution is controlled.  Polymer molecules of larger size cannot enter these pores as easily as smaller molecules, and are hence eluted rapidly. The smaller molecules enter the pores which hinders their progress through the column and are eluted more slowly.  The polymer solution constitutes the mobile phase and the solvents should have similar polarities to the stationary phase to prevent partitioning of the polymer between the two phases by adsorption.

In this study two separate systems were used insofar as they had different detector systems and algorithms to calculate the various molecular weight parameters. Initially, a Waters system with four Polymer Laboratories 10 $\mu$m columns of $10^5$, $10^4$, $10^3$ and $10^2$ Å arranged in series with a refractive index (R.I.) and U.V. detectors were used.  The system was later changed to 'Viscotek' which included a viscometric detector, although the columns and the mobile phase, THF, were kept the

same. The theory of calibration of S.E.C. systems depends on the columns and detectors. A brief outline is as follows [71,72]:

The classical S.E.C. calibration curve is obtained by plotting the elution volume for standard narrow molecular weight distribution polymers versus the logarithm of peak molecular weight, according to equation 2.2

$$\text{Log } M = a - bV \tag{2.2}$$

where log M is the peak molecular weight of the sample, V is the elution volume, while a and b are constants. This type of calibration curve is referred to as Type 1 by Cheung [71]. Where a differential viscometer detector is available a Type II calibration curve may be obtained. This correlates the logarithm of the intrinsic viscosity of polymer standards versus elution volume (also known as retention volume). The intrinsic viscosity is obtained using equation 2.3

$$[\eta] = \frac{\sum_{i=1}^{n_{dv}} \eta_{sp,i} \, \Delta v}{m} \tag{2.3}$$

where $[\eta]$ is the whole polymer intrinsic viscosity, $\eta_{sp,i}$, the local specific viscosity at elution volume, $v_i$, $n_{dv}$ is the number of data points on viscometer chromatogram, m is the mass of polymer injected and $\Delta v$ is the constant retention volume increment.

A more sophisticated calibration curve is obtained by plotting the logarithm of the size parameter, $J_i$, versus the peak elution volume. The size parameter is the product of the molecular weight (from Type 1 calibration) and the intrinsic viscosity (from type II calibration) at each elution volume. This is known as the Universal calibration curve or Type III curve. This is the curve incorporated in the Viscotek system.
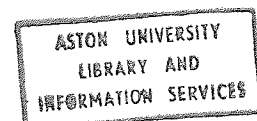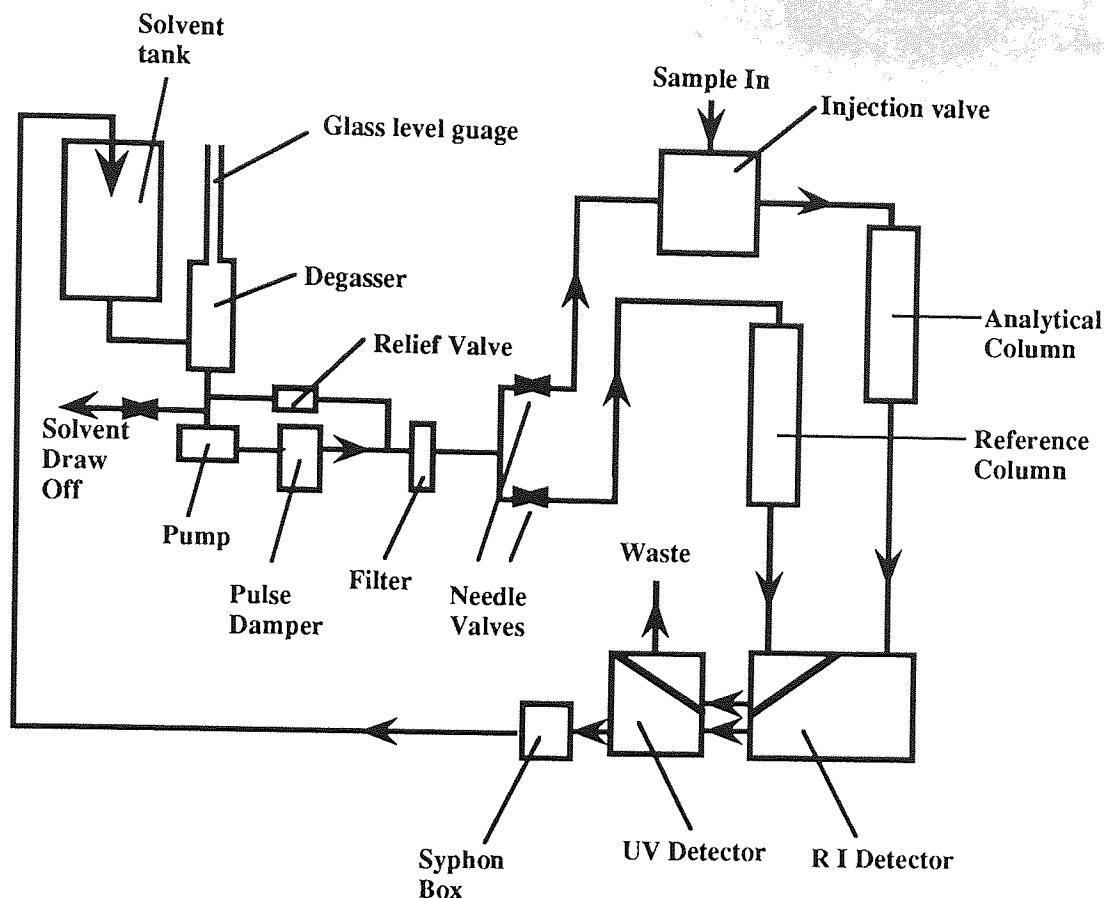
**Figure 2.3. Schematic diagram of a Size Exclusion Chromatography instrument.**

Cheung also identifies Types IV and V calibration curves. Type IV is the correlation of the logarithm of the local intrinsic viscosity ($[\eta]_i$) versus elution volume. The local intrinsic viscosity is the intrinsic viscosity at each elution volume and is given by equation 2.4

$$[\eta]_i = \frac{\eta_{sp,i}}{c_i} \qquad (2.4)$$

where $c_i$ is the concentration at elution volume, $v_i$. $c_i$ is obtained from the R.I. detector. By combing Type IV and Type III calibration curves equation 2.5 can be derived to give a Type V curve.

$$\log M_i = \log J_i - \log [\eta]_i \qquad (2.5)$$

These calibration curves can be used to give information on molecular weight averages, molecular weight distribution and Mark-Houwink parameters. In this study

only Type 1 calibration curves based on polystyrene standards have been utilised where vinylic polymers are considered, and polyTHF standards, where cyclic ether polymers are investigated.

The calculation of molecular weight averages i.e. number average molecular weight (Mn), weight average molecular weight Mw) and z-average molecular weight (Mz) is carried out by applying a calibration curve to the S.E.C. trace from the detector. The type 1 curve can be used with the R.I. trace to give values for $M_i$. This figure, $M_i$, is the molecular weight at elution volume, $v_i$, and when multiplied by the number of molecules ($N_i$) gives $W_i$, the weight of polymer at elution volume $v_i$. Hence, the height of the trace ($h_i$) is proportional to the concentration of polymer:

$$h_i \propto W_i \tag{2.6}$$

so

$$\Sigma\, h_i \propto \Sigma\, W_i \tag{2.7}$$

for the entire S.E.C. trace. However, as

$$W_i = N_i\, M_i \tag{2.8}$$

then

$$h_i = N_i\, M_i \tag{2.9}$$

and this can be substituted, after rearrangement into the definition of number-average molecular weight:

$$Mn = \frac{\Sigma\, N_i\, M_i}{\Sigma\, N_i} \qquad = \frac{\Sigma\, W_i}{\Sigma\, (W_i / N_i)} \tag{2.10}$$

to give

$$Mn = \frac{\Sigma\, h_i}{\Sigma\, (\, h_i / M_i\, )} \qquad\qquad (2.11)$$

Similarly, the definition of weight average molecular weight and Mz is:

$$Mw = \frac{\Sigma\, N_i\, M_i^{\,2}}{\Sigma\, N_i\, M_i} \quad = \frac{\Sigma\, W_i\, M_i}{\Sigma\, W_i} \qquad\qquad (2.12)$$

$$Mz = \frac{\Sigma\, N_i\, M_i^{\,3}}{\Sigma\, N_i\, M_i^{\,2}} \qquad\qquad (2.13)$$

The calculation of Mn, Mw and Mz for a polymer, or at least Mn and Mw, is necessary because, usually, no one average fully describes the S.E.C. trace. For instance the dispersity (D) provides a measure of the breadth of molecular weight distribution i.e.

$$D = \frac{Mw}{Mn} \qquad\qquad (2.14)$$

For polymers made by ideal or living systems this figure should be 1.0 but is usually between 1.0 and 1.1 due to experimental errors.

More accurate information about molecular weight distribution is obtained by plotting weight fraction of polymer versus $\log M_i$. But in this study, as weight fraction is proportional to height of S.E.C. trace, from the R.I. detector, and $\log M_i$ is related to $v_i$ by calibration curve of Type 1, the S.E.C. traces obtained were assumed to, approximately, indicate the molecular weight distributions of samples tested.

Mark Houwink parameters were not determined in this study although equation 2.2 is a modified form of the Mark-Houwink equation. The Mark-Houwink equation is:

$$[\eta] = k\, M^a \qquad\qquad (2.15)$$

where k and a are Mark-Houwink constants. These are usually determined by plotting log [η] versus log M for a series of fractions (preferably monodisperse) for a particular polymer, solvent and temperature. The Mark-Houwink equation used with a Type V calibration curve can be useful for determining more accurately molecular weights for branched or star polymers as the size parameter is more representative of these systems.

Overall, all S.E.C. traces shown and molecular weight data quoted have been based on R.I. detector and Type 1 classical calibration curve. S.E.C. has been the main method of characterising the molecular weight distributions of the polymers prepared, although for some samples these were compared with results obtained from N.M.R. in order to check the validity of calibration.

Unfortunately, there seemed to be a discrepancy in the values generated by the two systems used i.e. Waters and Viskotek and it is not clear if this was due to the poor calibration of the Viskotek's detectors or the algorithms used. To avoid this discrepancy all S.E.C. results are based on the refractive index traces. Even so Viskotek R.I. figures were at odds with Waters R.I. figures based on the same calibration methods. Hence, for Viskotek traces molecular weight data is not shown, instead traces are compared using elution volume and peak heights or areas.

## 2.6.2   Nuclear magnetic resonance spectroscopy.

A Bruker, MSL-300FT N.M.R. spectrometer, at ambient temperature (~22°C) was used to obtain $^1$H spectra at 300.13 MHz and $^{13}$C spectra at 75.46 MHz. All samples were recorded as solutions in $CDCl_3$, with tetramethylsilane as internal reference, at a concentration of about 3% for $^1$H and 15% for $^{13}$C measurements. For the $^1$H spectra, 16 scans were recorded with a delay between pulses of 5.0s. For broadband decoupled $^{13}$C spectra, typically 5000 scans were accumulated, with a delay between pulses of 3.0s. For semiquantitative runs, a gated decoupling pulse sequence was used to suppress the nuclear Overhauser enhancement, with a pulse delay of 5.0s.

### 2.6.3   Differential scanning calorimetry (D.S.C.)

The other widely used instrument of characterisation was the D.S.C. (Polymer Labs D.S.C. 700)  This was important because a requirement of the polymers was that they should have sub-ambient glass transition temperatures (Tg).  The D.S.C. provides this information plus details about the polymers thermal behaviour.  The instrument was calibrated with mercury for sub-ambient use.

### 2.6.4   Fourier transform infra red spectroscopy.

The infra-red (I.R.) spectra were acquired as liquid films between KBr discs on a Nicolet 710 F.T-I.R. spectrophotometer at 4 cm$^{-1}$ resolution.

The results of all these studies are discussed in the following sections.

# CHAPTER 3

# RESULTS AND DISCUSSION: CYCLIC ETHERS.

# 3. RESULTS AND DISCUSSION: CYCLIC ETHERS.

For convenience these two areas are grouped together although there is overlap between items discussed in various sub-sections of this chapter. An attempt to examine these overlaps is made near the end of the relevant section.

## 3.1 Materials based on NIMMO.

The object of this work is to attain control over the polymerisation of NIMMO via a thorough understanding of the system, so that NIMMO species ranging from linear oligomer, cyclic oligomer, telechelic polymer and high molecular weight polyNIMMO can be prepared.

## 3.1.1 Results and discussion of the factors affecting the polymerisation of NIMMO.

The main sources of error in the experiments were from variable purity of NIMMO monomer, the possible use of moisture contaminated $BF_3.OEt_2$, alcohol and glassware. Errors in concentration of monomer entering the reaction vessel through the pump arose because the $N_2$ used to maintain an inert atmosphere tended to stream off the solvent. A minor error may be due to the formation of metal-$BF_3OH$ salts, due to attack of $BF_3.OEt_2$ on the syringe needle, which cause formation of oligomer[49].

The results of the NIMMO polymerisations show that in all the experiments where polymerisation occurred, peaks due to molecular weight of ~3000-6000, an oligomer and unreacted NIMMO monomer are observed (see figure 3.1). The N.M.R spectra of the polymer are shown in figures 3.2 and 3.3. An I.R. spectrum of polyNIMMO prepared by the typical method is shown in appendix. Similar observations have been made by Manser[50] for polymerisation of NIMMO and other oxygen heterocycles by Hammond et al[51], using $BF_3.OEt_2$/alcohol systems. Although high molecular weights are difficult to achieve using $BF_3.OEt_2$/alcohol, the system has the advantage of easily producing $\alpha,\omega$-hydroxy telechelic polymers which may be cured with isocyanates,

Figure 3.1    Typical SEC trace of polyNIMMO initiated with 1,4-Butandiol/
BF$_3$.OEt$_2$ and monomer addition over 16 hours followed by
4 hours stirring at 0°C
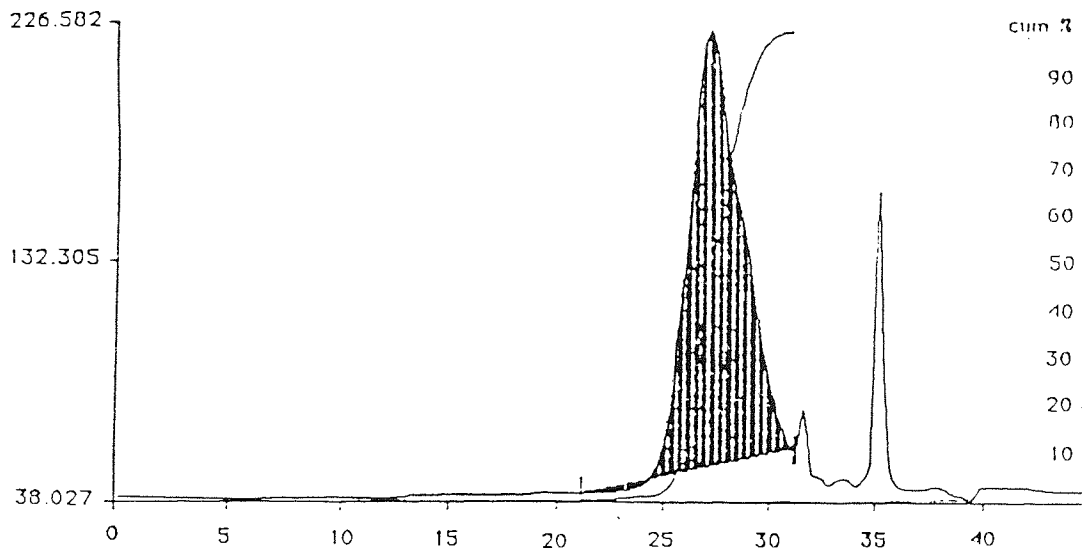


Figure 3.12    SEC trace of polyNIMMO with monomer addition over 4 hours,
followed by 2 hours of stirring at 0°C and 2 hours stirring at 30°C
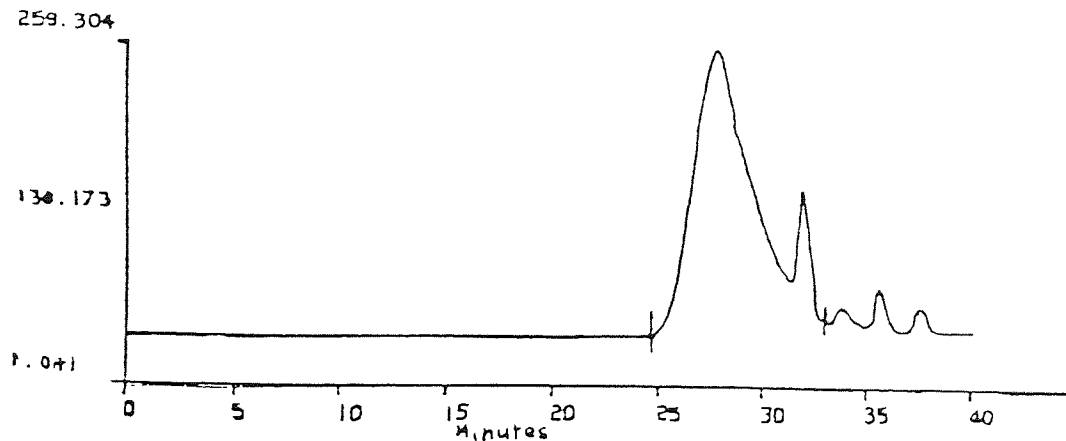


Mp (Peak molecular weight) = 3500          Mw (Weight average)     = 4000
Dispersity = 1.7                           Mn (Number average ) = 2100
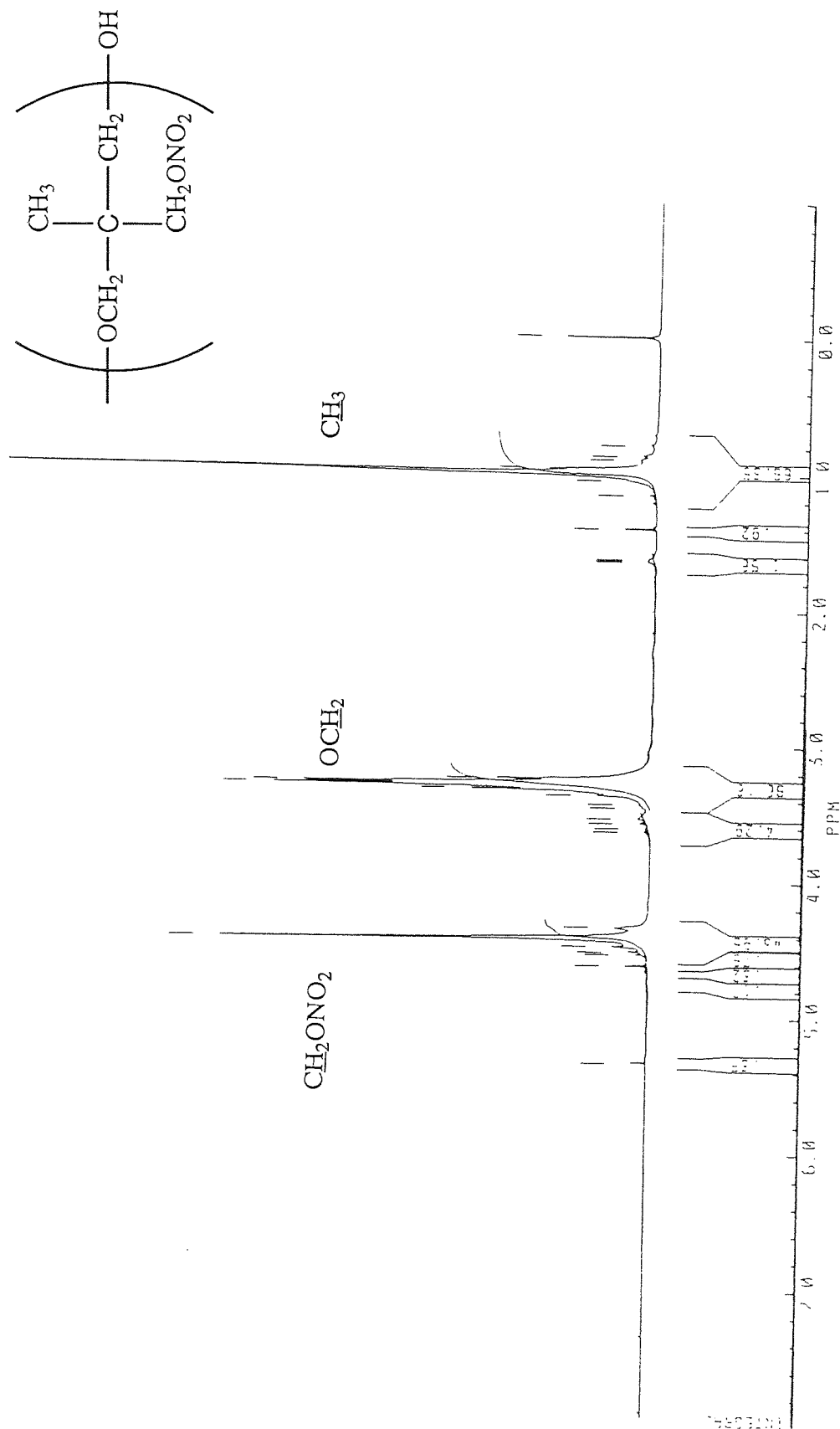
Figure 3.2    Typical $^1$H NMR spectrum of polyNIMMO
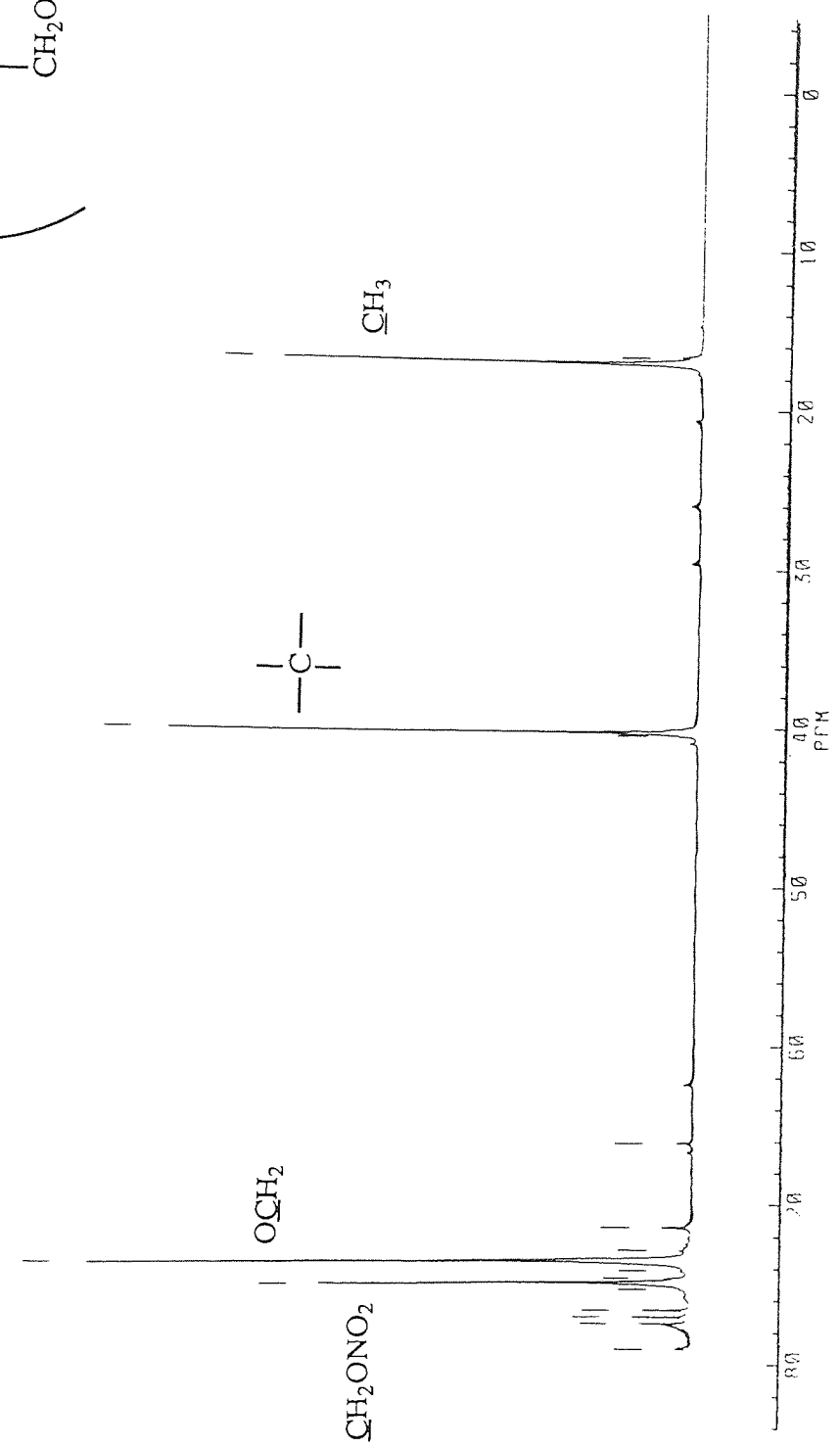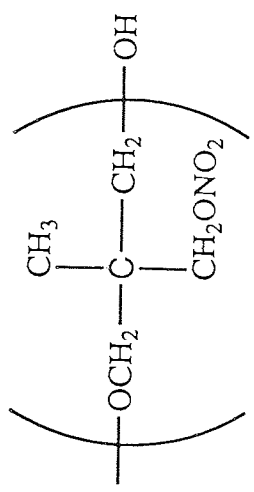
Figure 3.3    Typical $^{13}C$ NMR spectrum of polyNIMMO

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making them suitable for use as binders. However, higher molecular weight polymers are desirable and it was hoped that these investigations would help to achieve this as well as enable optimisation of the system for scale-up purposes. The effects of:

i) alcohol used as cationogen

ii) cationogen:coinitiator mol ratio

iii) temperature

iv) time

v) monomer:cationogen ratio

vi) electron pair donors

were investigated particularly with reference to the molecular weight distribution as determined by S.E.C. The typical method of polymerisation was used unless stated i.e. 1:1 ratio of OH groups to $BF_3.OEt_2$, monomer (20% w/v in $CH_2Cl_2$) addition over 16 hours, followed by 4 hours of stirring and a reaction temperature of 0 °C. As the stoichiometry of the OH:$BF_3.OEt_2$ ratio is not >5:1, respectively, these are not AMM conditions. Hence, although incremental monomer addition technique is utilised the mechanism of polymerisation is predominantly ACE.

### 3.1.1.1    Alcohols as cationogen.

The first factor investigated was the effect of alcohol functionality on the molecular weight. The alcohol functionality is the number of hydroxyl groups per alcohol molecule. Figure 3.4 shows that higher alcohol functionality (desirable because curing is easier) causes a reduction in the molecular weight. This indicates that transfer reactions increase as alcohol concentration rises. Kinetic work carried out by Riat and Amass[52], using ethan-1,2-diol/$BF_3.OEt_2$ and oxetane as monomer, shows that the reaction is first order with respect to monomer and first order with respect to $BF_3.OEt_2$/ethanediol complex i.e.

$$R_p = k_p [BF_3.OEt_2/-(OH)_2] [M] \qquad (3.1)$$

where $k_p$ is a constant and $[BF_3.OEt_2/-(OH)_2]$ is the concentration of what Riat calls "catalyst". Riat postulates that transfer and termination occur i.e.

$$R_t = k_{t1} [p_n*] + k_{tf} [p_n*] [OH] \qquad (3.2)$$

where $k_{t1}$ is a constant due to termination processes involving the growing polymer $p_n*$ and $k_{tf}$ is a constant due to transfer. If these postulates are correct then the polymerisation is kinetically controlled whereby

$$DP = R_p/R_t \qquad (3.3)$$

where DP is the degree of polymerisation. But as

$$[BF_3.OEt_2/-OH] \propto [H^+] \propto [\quad H-O^+\!\diagup\!\!\diagdown \quad] \propto [P_n*]$$
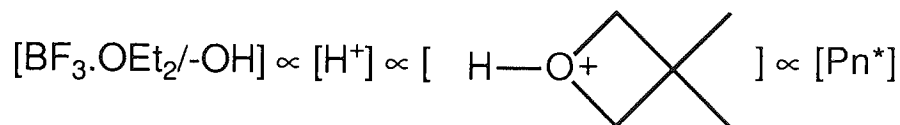
assuming protonic initiation, then combining equations 3.1 and 3.2 gives

$$DP = k_p [M] / (k_{t1} + k_{tf} [OH]) \qquad (3.4)$$

Hence, if $k_{tf} >> k_{t1}$ then DP is proportional to 1/ [OH], so that an increase in alcohol functionality will lead to a decrease in molecular weight (figure 3.4). This fits the results of NIMMO polymerisation qualitatively, but further work is necessary.

### 3.1.1.2    Cationogen : Coinitiator ratio.

The second factor studied was the ratio of cationogen/coinitiator. The influence of hydroxyl concentration on termination is more significant than concentration of $BF_3.OEt_2$. This is shown in figure 3.5 where an excess of $BF_3.OEt_2$ does not affect number average molecular weight (Mn). However, the rate of reaction may vary with a change in the molar ratio of the cationogen to the coinitiator. To verify this kinetic studies need to be undertaken. Nevertheless, this graph may provide a clue to the mechanism of polymerisation because it implies that the initiating species forms as a
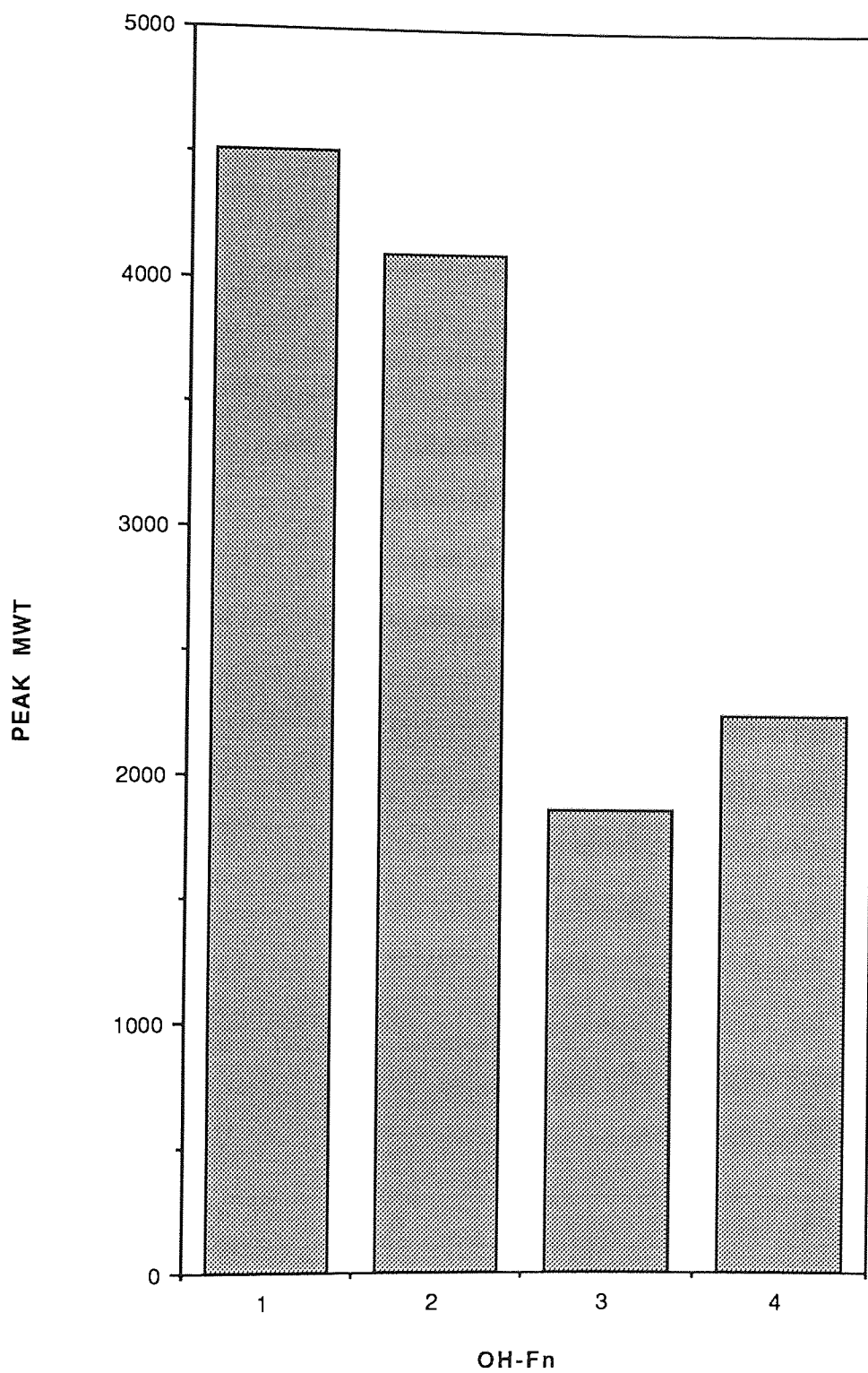
**Figure 3.4. Peak molecular weight versus OH functionality for different alcohol initiators.**
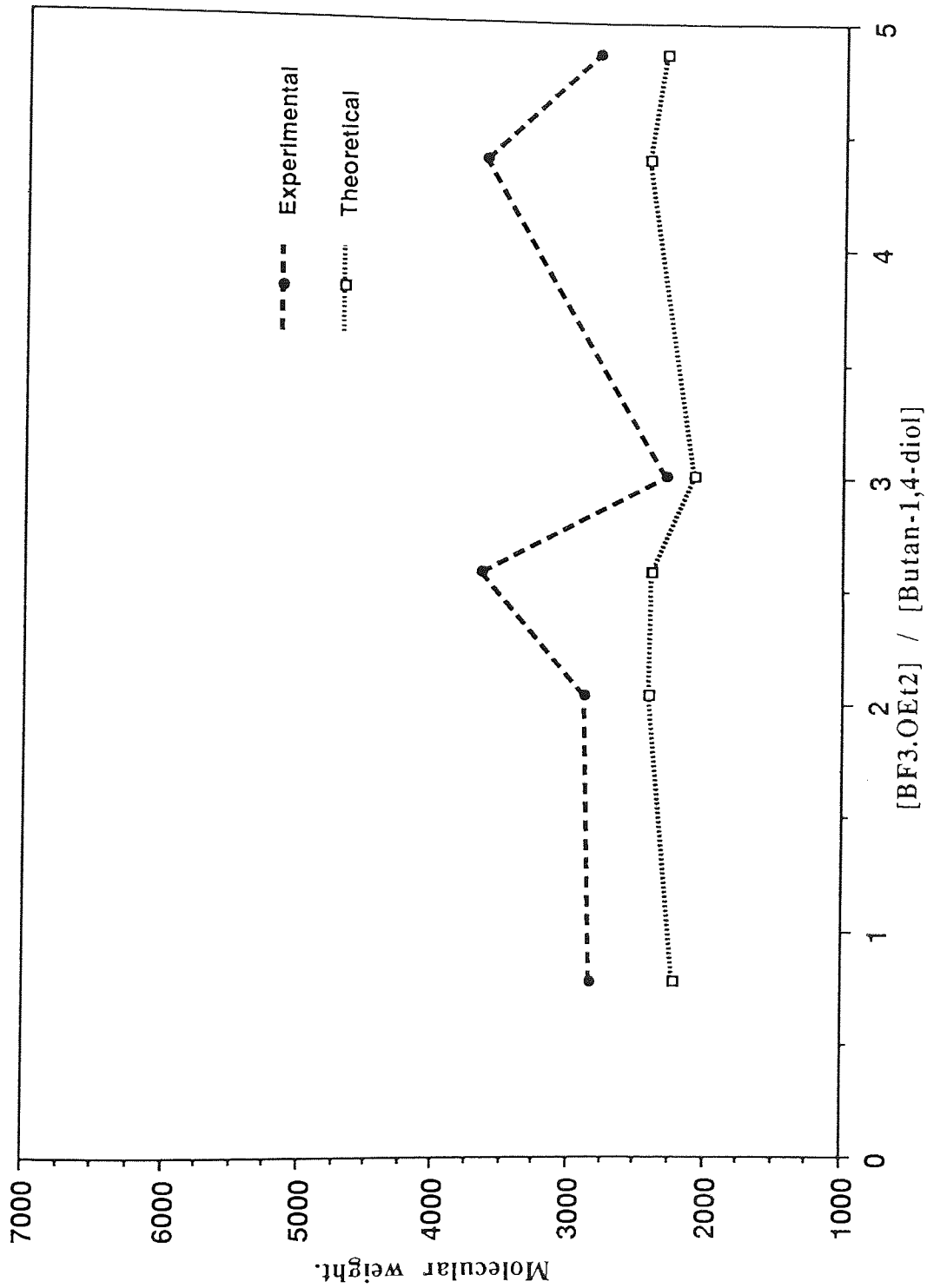
Figure 3.5. Plots of the molecular weights vs cationogen - coinitiator (BF3.OEt2) ratio for the polymerisation of NIMMO at 0°C.

result of an interaction between the $BF_3.OEt_2$ and the OH group. The most likely nature of the initiating species is protonic, so once the $BF_3.OEt_2$ has reacted with the OH groups on the alcohol, an excess of $BF_3.OEt_2$ does not generate more protons. This in turn would cause no increase in Mn as $BF_3.OEt_2$ concentration is raised. Moreover, assuming protonic initiation, an excess of $BF_3.OEt_2$ may be expected to increase transfer reactions because it could react with the terminal OH groups on chains, liberating protons. Yet, as there is no decrease in Mn, the reaction between $BF_3.OEt_2$ and terminal OH groups is probably not significant at the concentrations of $BF_3.OEt_2$ examined.

### 3.1.1.3.    Temperature.

The presence of transfer and/or termination in the polymerisation of NIMMO is confirmed by lowering reaction temperature, which causes the molecular weight to increase, figure 3.6, and is typical of an active-chain end (ACE) type mechanism of polymerisation. Unfortunately, a reduction in temperature also causes the rate of propagation to decrease, so that the overall percentage conversion falls. For optimisation purposes a temperature of 0 °C may provide a balance between high conversion and molecular weight. To achieve high molecular weight polymers, lower temperatures, pure monomer and longer reaction times are necessary.

### 3.1.1.4    Time.

The importance of the relative rates of propagation and transfer is borne out by the effect of time on the polymerisation system. Two aspects of the effect of time were investigated:

(a)    Addition of a given quantity of monomer solution to a pre-mixed $BF_3.OEt_2$/alcohol mixture over 0, 0.5, 1, 2, 4, 16 and 53 hours respectively to see if polymerisation occurred (table 5).

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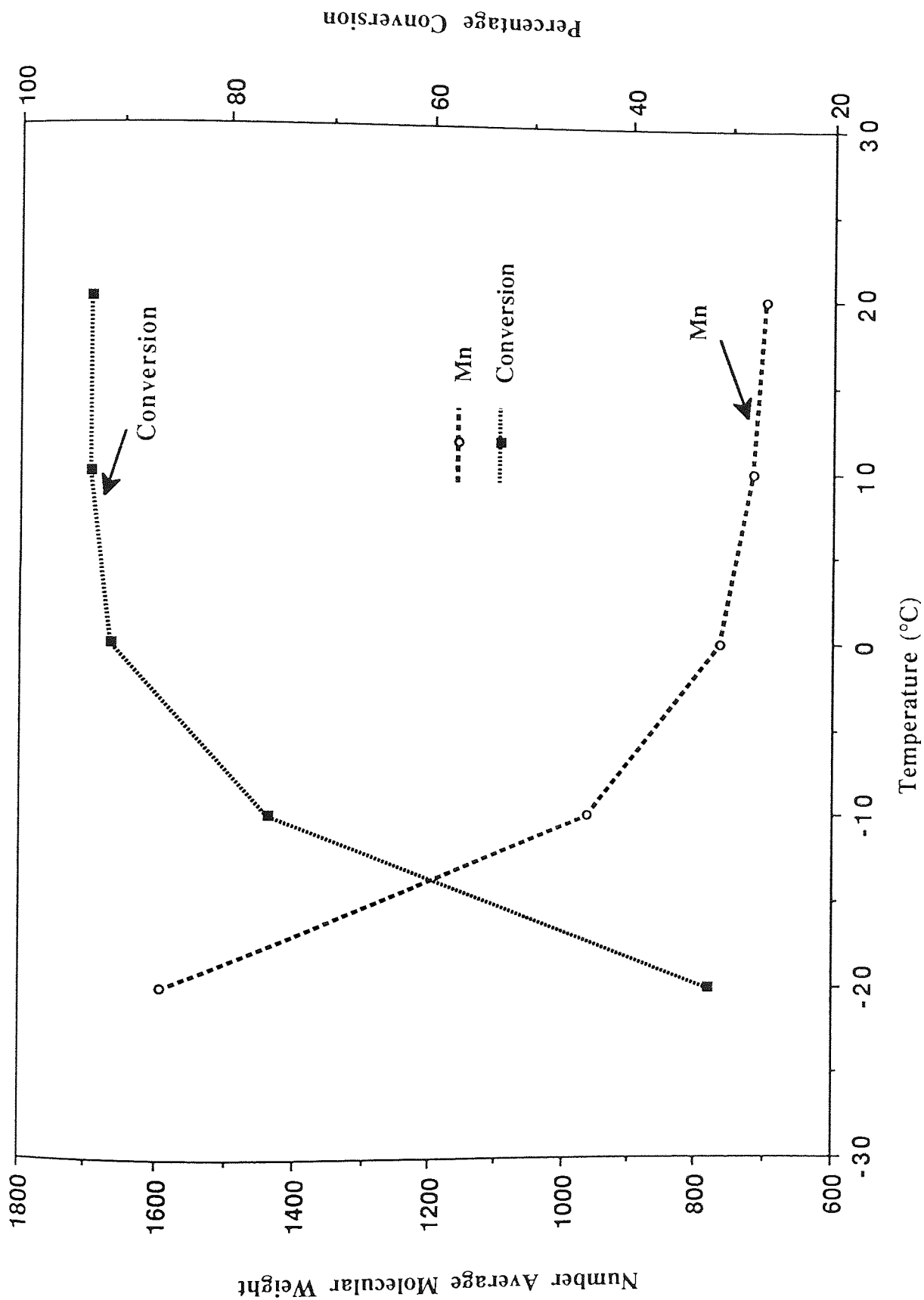
Figure 3.6. Plots showing the effect of temperature on Mn and % conversion for the polymerisation of NIMMO.

| Run Name | Cationogen | OH: coinitiator | Dpe | Temp °C | Addn Time h | Mn | Mp | D | Ht% of Nimmo | Ht% Olig 1 | Ht% Olig 2 | No. Peaks | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HDPN86CR | Glycerol | 3:2 | 45 | 0 | 0+4 | 2150 | 6050 | 2.4 | 92 | 1 | 3 | 4 | Nimmo to initiator |
| HDPN85CR | Glycerol | 3:2 | 41 | 0 | 0+4 | 2650 | 6450 | 2.6 | 51 | 2 | 8 | 4 | Initiator to nimmo |
| HDPN84CR | Glycerol | 3:2 | 49 | 0 | 0.5+4 | 2900 | 5750 | 2.3 | 93 | 1 | 3 | 4 | |
| HDPN83CR | Glycerol | 3:2 | 62 | 0 | 1+4 | 2450 | 4250 | 2.1 | 96 | 1 | 2 | 4 | |
| HDPN82CR | Glycerol | 3:2 | 58 | 0 | 2+4 | 3450 | 8350 | 2.1 | 68 | 1 | 6 | | |
| HDPN81CR | Glycerol | 3:2 | 49 | 0 | 4+4 | 2700 | 7500 | 2.4 | ~20 | - | - | | |
| HDPN70CR | Glycerol | 3:2 | 15 | 0 | 8+4 | 1200 | 1100 | 1.2 | 5 | - | 47 | - | |
| HDPN79CR | Glycerol | 3:2 | 48 | 0 | 16+4 | 2550 | 7200 | 2.3 | ~30 | - | - | | |
| HDPN80CR | Glycerol | 3:2 | 48 | 0 | 53+4 | 2900 | 6900 | 2.2 | ~80 | - | - | | |
| HDPN55CR | Glycerol | 3:2 | 200 | 20 | 140+40 | 1400 | 1000 | 1.5 | 32 | 2 | 32 | 4 | |
| HDPN52CR | Glycerol | 3:2 | 138 | 20 | 0+120 | 1650 | 2750 | 1.6 | 20 | 5 | 22 | 5 | |

The coinitiator is $BF_3OEt_2$ unless stated.
The first figure in the addition time column is the monomer feed time, the second is the stirring time.
Oligomer 1 is the lowest molecular weight compound, and oligomer 2 is the main oligomer peak ($R_t$=32)

Table 5.  The effect of monomer feed and stirring times on MWD.

(b)    For an 8 h addition period of monomer, aliquots of reaction mixture were taken and analysed by S.E.C. (figure 3.9).

Rapid addition of monomer by pouring it into the reaction flask containing the pre-mixed glycerol/$BF_3.OEt_2$ over a few seconds proved to be unsuccessful. A very small amount of polymer is formed (Mp~6000) but a large amount of the monomer is left unreacted (~92%). This is shown in table 5 and figure 3.7. As the period over which the monomer is fed to the reaction vessel is increased, the amount of conversion is improved (i.e. amount of unreacted monomer is lower) with an optimum conversion when the monomer is added over four hours and stirred for four hours (figure 3.7, 4+4h S.E.C. trace). Thereafter, further increase in monomer feed times appears to reduce conversion. In all the chromatograms shown in figure 3.7 it can be seen that the relative quantities of monomer to oligomer ($R_t = 32$ min) and polymer ($R_t = 27$ min) varies, but there is no significant change in the peak molecular weight of the polymer. Why short feed times produce poor conversions is not clear but may be due to complexation of initiating species (protons) with the nitrate esters if the NIMMO is present in excess during the early stages of polymerisation. Or, more likely, due to complexation with impurities in the monomer solution carried through from the nitration stage. Support for the latter notion has become apparent as Aerojet Corporation of USA have prepared polyNIMMO with Mn of 15000 by using vacuum distilled monomer in an AMI polymerisation [74]. An AMI experiment conducted as part of this study (HDPN85CR, table 5, figure 3.8) has a significant amount of unreacted NIMMO and number average molecular weight (2650) is much lower than expected (6000). This suggests that the NIMMO solution used contained some impurities, which was confirmed later by H.P.L.C. work (appendix). However, the nature of the impurities is not known but is thought to contain some nitroform species with $>C(NO_2)_2$ groups.

Long monomer feed times i.e. >16h show an increase in the amount of residual monomer. This may be due to transfer and termination processes becoming enhanced
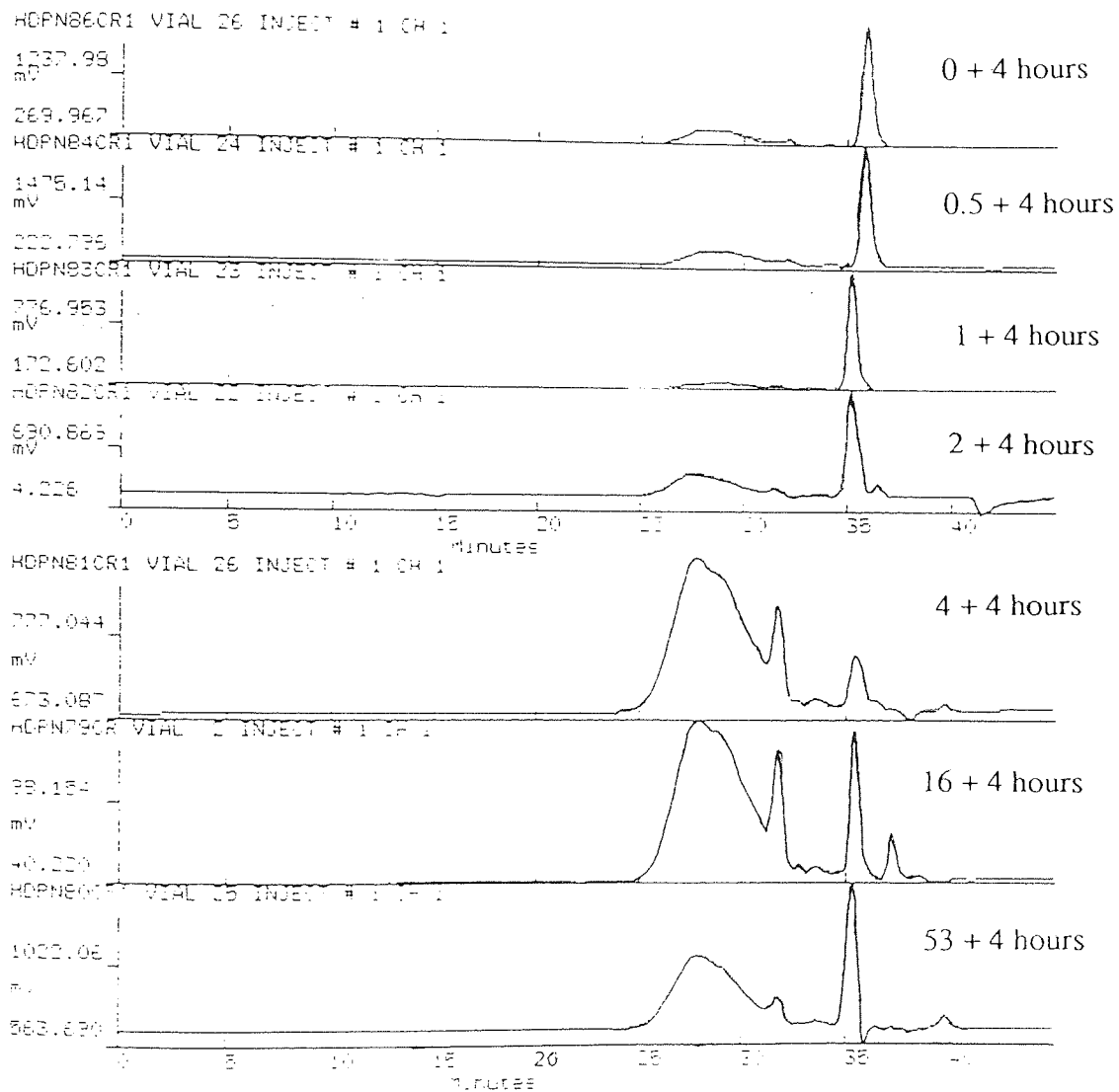
**Figure 3.7** SEC traces of the effect of monomer feed times on MWD
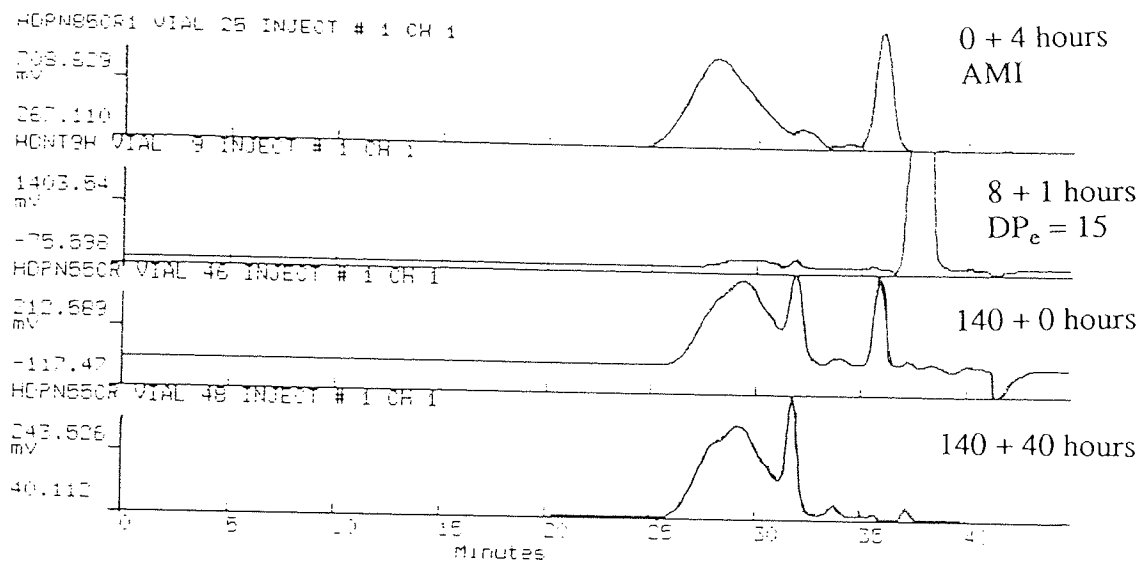
Figure 3.8     <u>Various SEC traces showing the effect of feed and stirring times for NIMMO polymerisations</u>

TIME

Monomer addition started at 0..52 ml/ min.

15 mins.

30 mins

1 hr

2 hrs

3 hrs

4 hrs

5 hrs

6 hrs

7 hrs

8 hrs    Monomer addition stopped after 8 hrs. Reaction stirred for further 2 hrs.

9 hrs

10 hrs   Reaction quenched with water.

High molecular weight

Low molecular weight
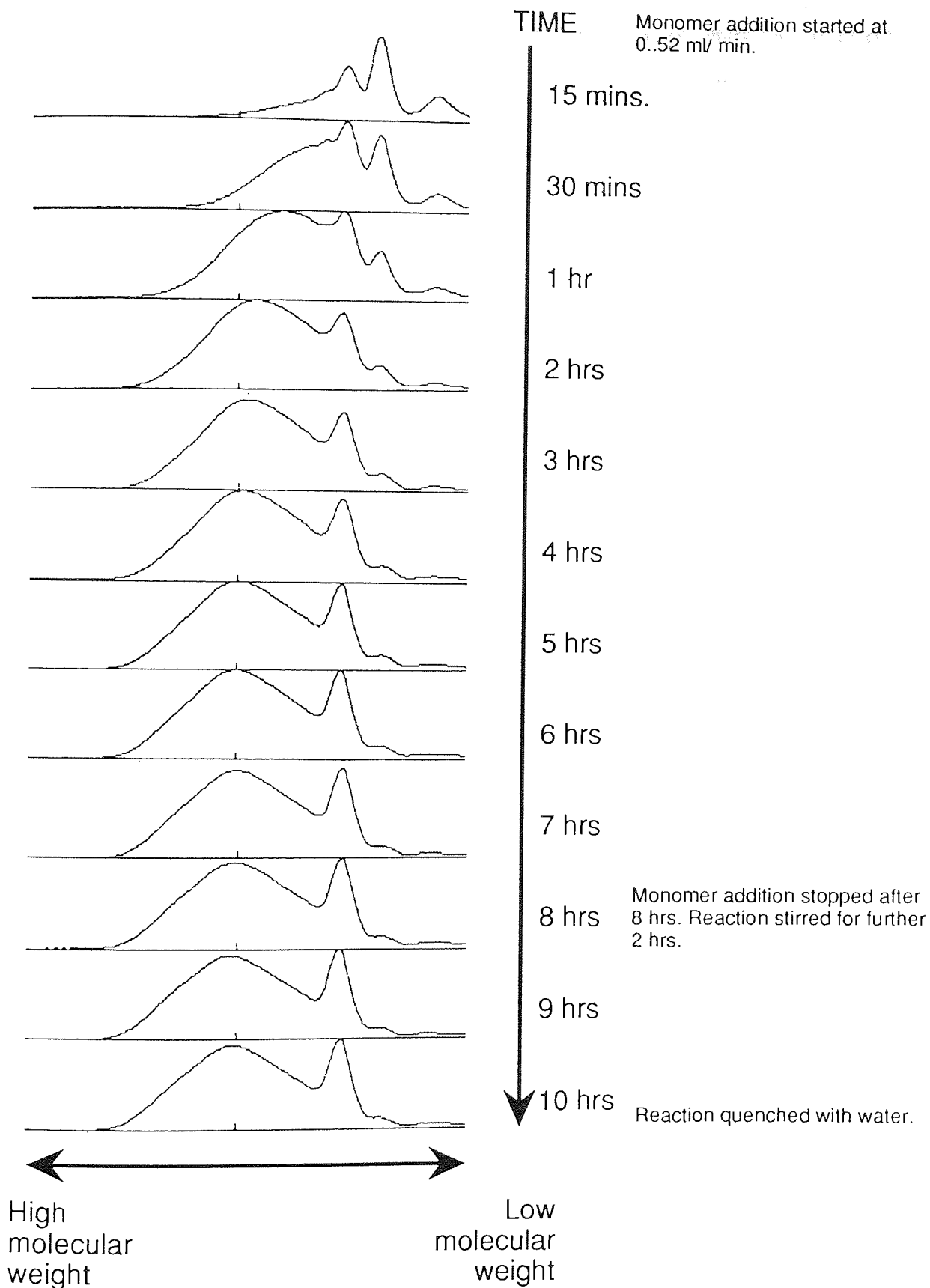
Figure 3.9.  S.E.C. traces with respect to time for a glycerol/BF₃.OEt₂

polymerisation experiment.

over propagation because of the low instantaneous monomer concentration. In effect what may be occurring is that incoming monomer is quickly consumed, allowing the active sites time to react with impurities or undergo other transfer/termination processes before further monomer is introduced. This results in active sites being destroyed over a period of time and monomer added thereafter is consumed very slowly. The last two S.E.C. traces shown in figure 3.8 indicate that after monomer addition is completed (140+0h) the amount of residual monomer may be reduced with prolonged stirring over 40h (i.e. S.E.C. trace 140+40h). This implies that some active sites still remain and that transfer processes probably dominate during the later stages.

Hence, optimum conditions to allow propagation and high conversion are attained when the monomer is fed at such a rate that active sites are not quickly poisoned by impurities in the feed, so that propagation dominates over transfer/termination processes. This seems to be the case with addition over 4h.

Figure 3.9 shows the molecular weight distributions with time for a single experiment. As the monomer is added chain extension occurs in the early stages, up to 4h, but thereafter no significant increase occurs. This may be because the amount of unreacted monomer is higher in the reaction mixture (later stages) causing more transfer to monomer. To test this an experiment where the amount of monomer added decreased with time should be conducted. From the results of figures 3.6 and 3.9 addition of monomer over 4h followed by stirring over 2h, at a temperature of 0 °C and a further 2h stirring at +30 °C may be envisaged to give optimum conditions. The aim of stirring at +30 °C is to reduce amounts of oligomer and, more importantly, unreacted NIMMO by increasing transfer reaction(s) at higher temperatures. Such an experiment (figure 3.12, 4+2+2h, p 75) was carried out and indeed produces polyNIMMO of comparable quality to that achieved by 16h addition and 4h stirring at 0 °C. Transfer reactions such as those shown in scheme 9 are predominantly bimolecular reactions involving the hydroxyl group and the oxonium ion and would be expected to increase with temperature thus liberating protons. These protons would in turn collide more

frequently with monomer to generate new active centres. Hence, the unreacted monomer level could be decreased.

An addition time as short as possible is required to reduce cost on an industrial scale. Another advantage of IMA of around 4h is that the exotherm, associated with the ring-opening of the monomer, is controllable, preventing the risk of the explosive decomposition of the $-ONO_2$ group.

### 3.1.1.5.    Monomer/cationogen ratio.

Theoretically calculated molecular weights, based on monomer:alcohol ratio, are exceeded (see figure 3.5) if the degree of polymerisation expected is around 15 and the alcohol used is butandiol. This is probably due to slow initiation relative to propagation. However, if the degree of polymerisation expected is higher than 15 and the alcohol used is metriol (a tri-hydroxy compound) then molecular weights observed are significantly less than expected (figure 3.10) and suggest the presence of transfer and termination processes. A monomer:cationogen ratio of 44 would be expected to produce a polymer of Mn of 6500. Further evidence for this comes from the plot of dispersity with molecular weight, figure 3.11, where dispersity increases with molecular weight instead of remaining constant which is the case for living systems where $R_i > R_p$. Nevertheless, for use as propellant binders a molecular weight of around 6000 and a dispersity of 2 is acceptable because it allows effective mixing and processing with other ingredients.

### 3.1.1.6    Electron pair donors.

Electron pair donors such as dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF) are known to stabilise propagating centres in cationic vinyl systems[32]. As table 6 shows, polymerisation of NIMMO does not proceed to any significant extent in the presence of large amounts of DMSO or DMF. The most likely reason for this is that the $BF_3.OEt_2$ complexes preferentially with the electron pair donor rather than the alcohol so that cationic species, which initiate polymerisation, are not formed.
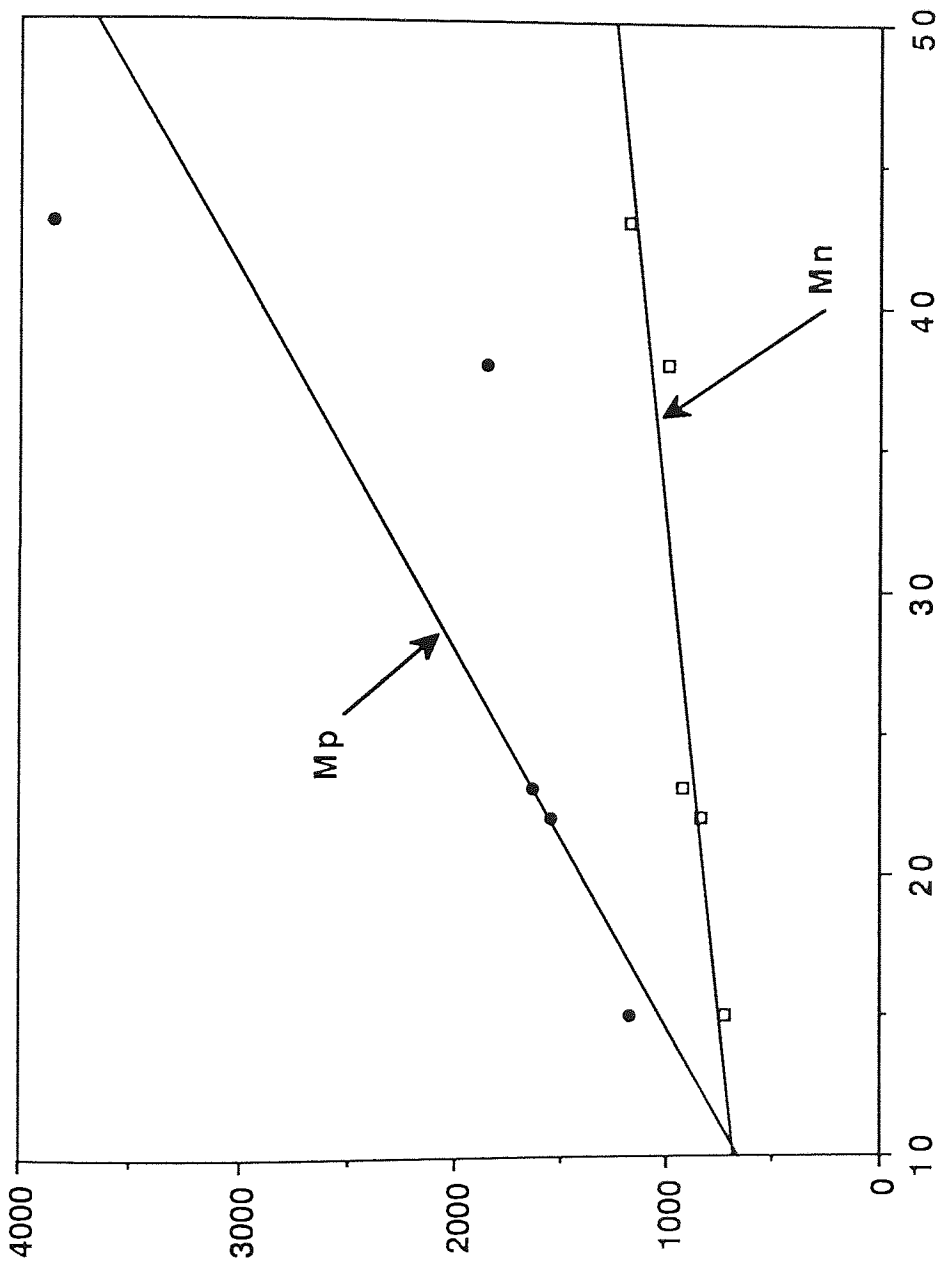
Figure 3.10. Effect of monomer:cationogen ratio on the Mn and peak molecular weight (Mp) for metriol initiated polyNIMMO.
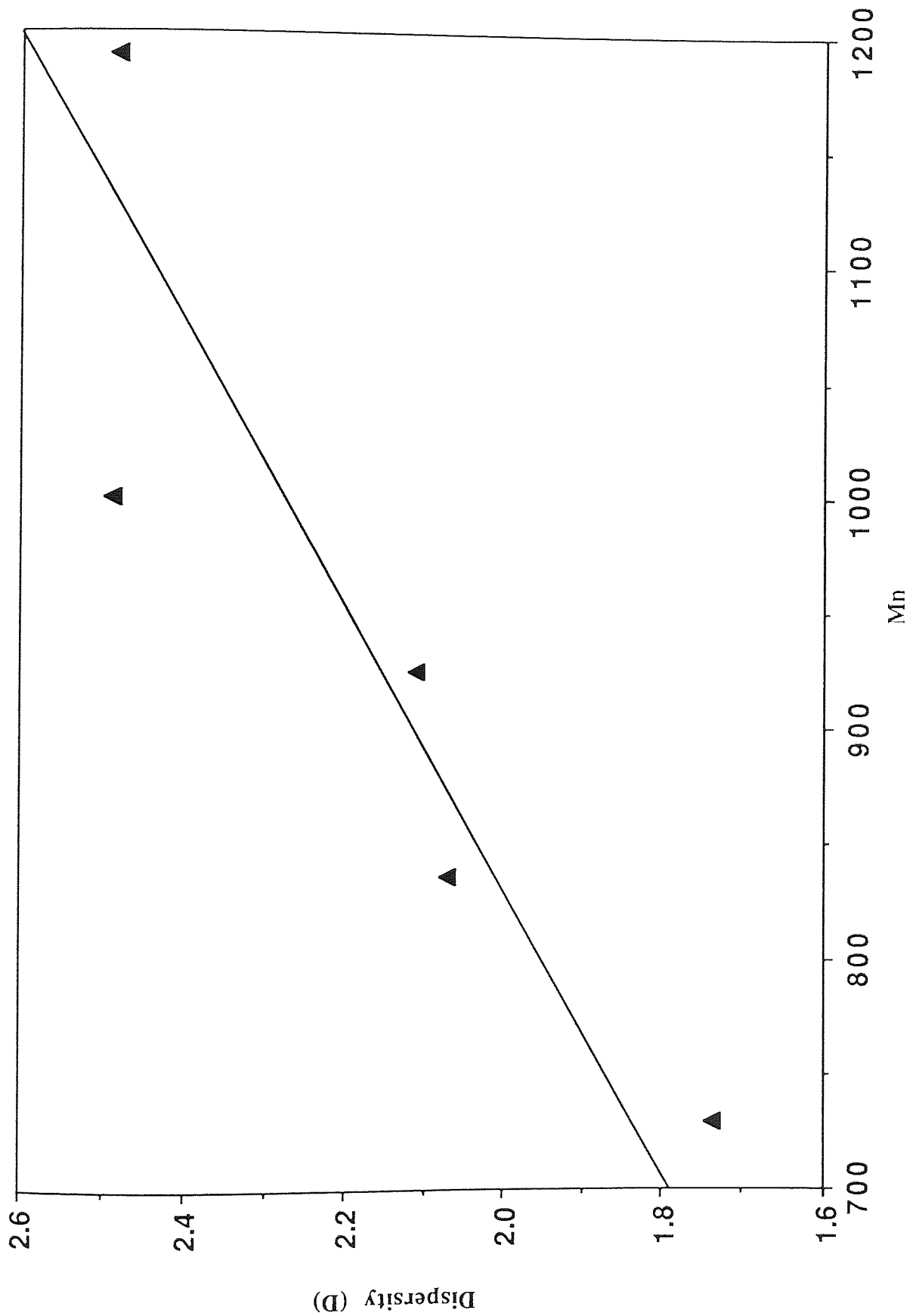
Figure 3.11. Graph showing increase in dispersity (D) with increase in molecular weight.

| Run Name | Cationogen | OH: coinitiator | Dpe | Temp °C | Addn Time | Mn | Mp | D | Ht% Nimmo | Ht% Olig1 | Ht% Olig2 | No. Peaks | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HDPN58CR | Glycerol | 3:2 | 15 | 20 | 8+4 | - | - | - | 98 | 2 | - | 2 | DMSO:OH, 1.7:1 |
| HDPN62CR | Glycerol | 3:2 | 200 | 25 | 16+4 | - | - | - | 90 | - | - | 2 | DMF:OH, 8.0:1 |
| HDPN69CR | Glycerol | 3:4 | 15 | 25 | 16+4 | 2500 | 6650 | 2.1 | 24 | - | 39 | 5 | DMF:OH, 1.0:3 |

The coinitiator is $BF_3OEt_2$ unless stated.
The first figure in the addition time column is the monomer feed time, the second is the stirring time.
Oligomer 1 is the lowest molecular weight compound, and oligomer 2 is the main oligomer peak ($R_t=32$)

Table 6. Effect of electron pair donors on NIMMO poymerisation.

However, in the presence of catalytic amounts of electron pair donor, polymerisation is observed as shown in table 6, figure 3.13. The polydispersity of the polymer obtained under these conditions (figure 3.13) is similar to other NIMMO polymerisations, but where the theoretically expected DP was only 15.

It may be possible, in the presence of correct amount of dimethyl formamide (DMF) and more monomer to obtain higher molecular weight polymers i.e. >6000. The experiment conducted in the presence of dimethyl sulphoxide shows no significant propagation (figure 3.13) but again this may be due to an excess of DMSO relative to initiator complex.

The concept (scheme 5) may be successful with a weak electron pair donor which complexes with the active centre when there is no monomer available (especially when IMA with slow feed rates is desired e.g. to prevent a large exotherm for energetic monomers) but allows propagation in the presence of monomer. A requirement for this balance to be achieved is that the electron pair donor should be less basic than the monomer. Some aliphatic or crown ethers, including cyclic oligomers of the monomer to be polymerised, may also be suitable.

## 3.1.2 Cyclic oligomers of NIMMO

Most of the experiments carried out in the study of NIMMO polymerisation, except the AMM systems, have exhibited significant amounts of oligomers, with a particularly prominent species at a retention time ($R_t$) of 32 minutes. At the beginning of this study it was assumed that this species was the cyclic tetramer. This assumption was based on the work of Goethals[54] who demonstrated that the main oligomeric fraction in the polymerisation of 3,3-dimethyl oxetane by triethyl oxonium tetrafluoroborate is the cyclic tetramer. However, Arimatsu[46] has shown that 3,3-bis(chloromethyl) oxetane (BCMO) produces cyclic trimer as the dominant species when polymerised by $AlEt_3$ as catalyst at 180 °C.
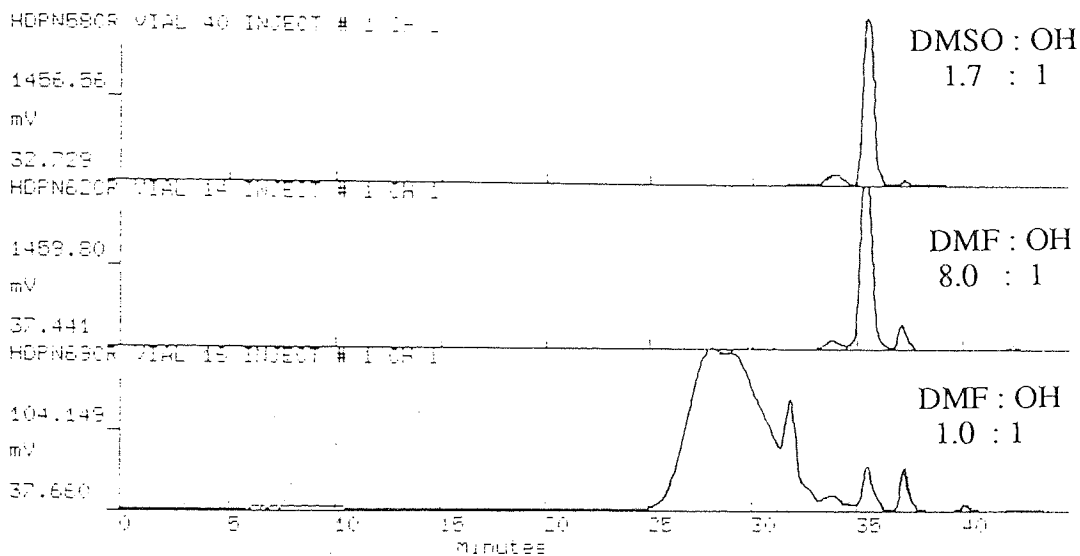
**Figure 3.13** <u>SEC traces showing the effect of electron pair donors on NIMMO polymerisations</u>

Active centres complexed with dimethylformamide

DMF protects cationic centres
from undergoing side reactions
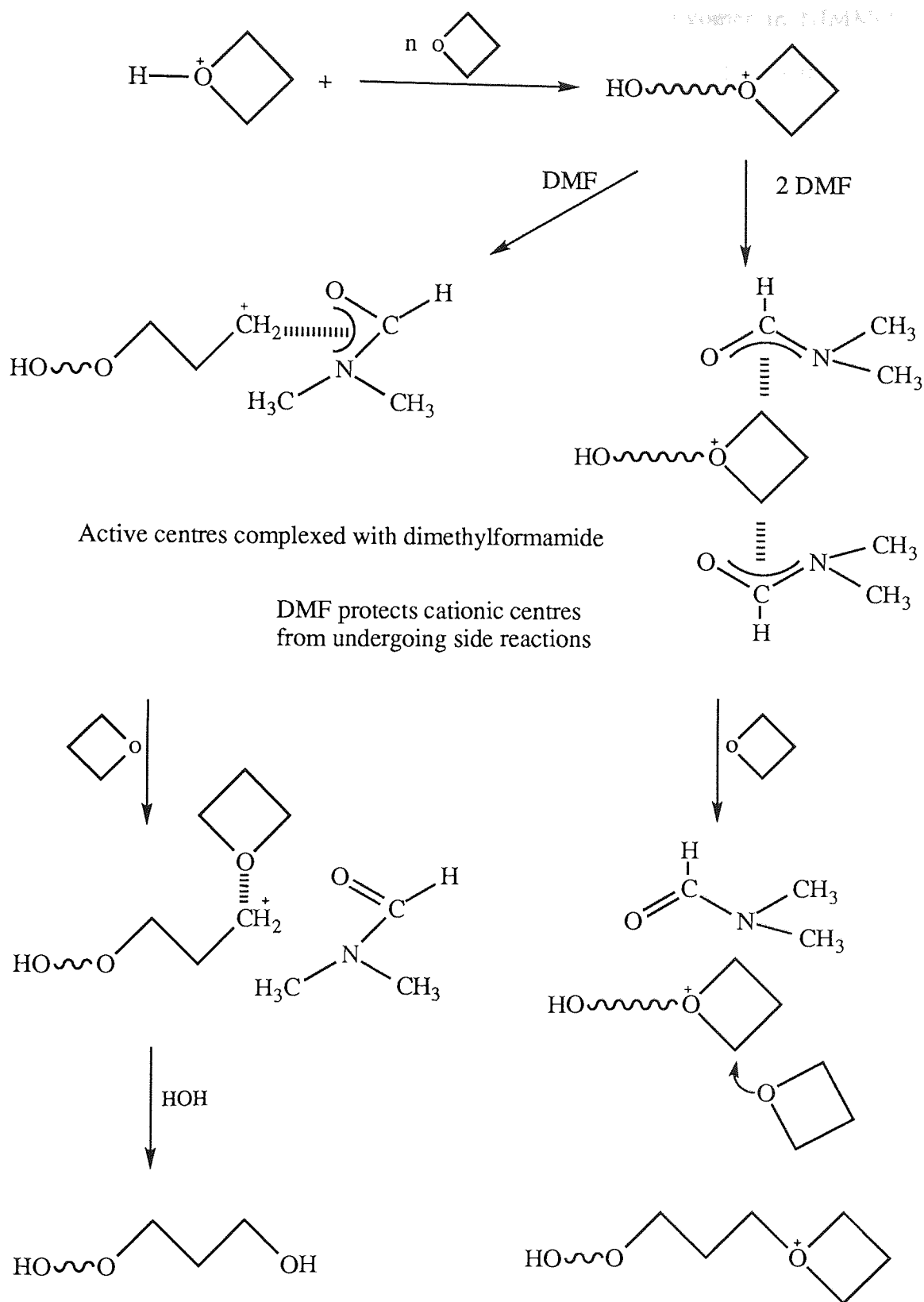
**Scheme 5. Concept of stabilisation of active centres by electron pair donors such as DMF.**

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Hence, in order to ascertain the nature of the principal oligomer in NIMMO polymerisation and to synthesise controlled molecular weight cyclic species, desirable commercially as plasticisers, factors affecting the relative rates of cyclisation and polymerisation ratio were considered and used to design synthetic routes to cyclic oligomers (table 7). Direct separation of oligomers by preparatory S.E.C. and supercritical fluid extraction normally used prove to be time consuming and inefficient.

Slomkowski[55] proposed a general kinetic scheme for the formation of cyclic oligomers, scheme 6, where $L_n$ and $L_{n+m}$ are linear macromolecules, $M_m$ and $M_n$ are cyclic oligomers and $C_n$ and $C_m$ are cyclic oligomers with an active centre. The key feature of this scheme is that cyclisation is expected to occur by an unimolecular or intramolecular end-biting or back-biting process (see also scheme 9). Hence, carrying out the polymerisation at low monomer concentrations would increase the proportion of cyclic species relative to linear polymer (scheme 8).

$$L_n + M_m \underset{k_{b(m)}}{\overset{k_{p(m)}}{\rightleftharpoons}} L_n{+}m \qquad \text{Propagation and depropagation (back-biting)}$$

$$L_n \xrightarrow{k_{e(n)}} C_n \qquad \text{End-biting leading to macrocycles with an active centre on the ring and ring opening}$$

$$C_n + M_m \underset{k_{ex(n)}}{\overset{k_{ex(m)}}{\rightleftharpoons}} M_n + C_m \qquad \text{Exchange}$$
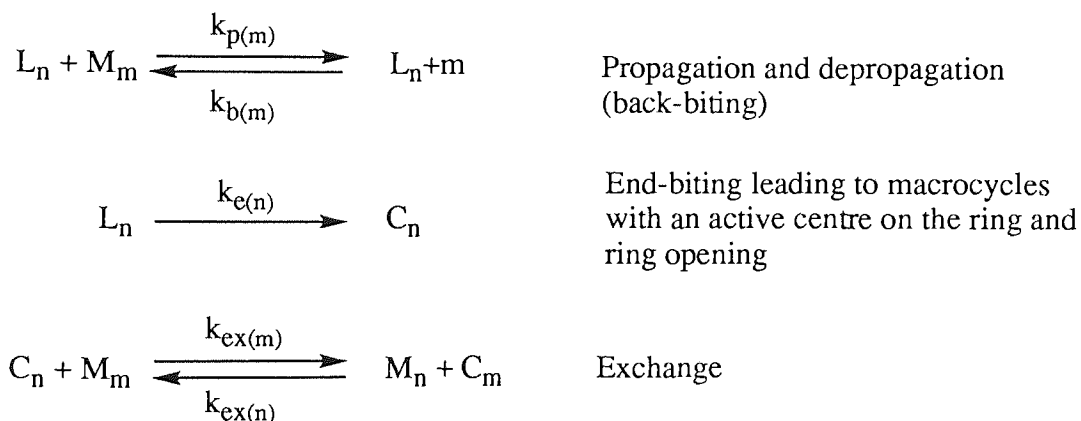
**Scheme 6. Slomkowski's kinetic scheme for the formation of cyclic oligomers.**

An interesting effect of initial monomer concentration on the polymerisation of THF has been reported by Penczek[53] for THF in benzene at 25 °C. This shows that (figure 3.14) a high initial monomer concentration results in a low equilibrium concentration of monomer and raises the suggestion that the oligomer concentration would be similarly affected. Such studies have shown that the $[M]_0$ can also affect formation of polymer relative to oligomer, as shown in figure 3.15.

| Sample | Cationogen | Templating salt | $DP_e$ | Temp °C | Addn Time h | Cationogen: Salt Ratio mol | M (w/v) % | Vol. of DCM in flask Initially. cm³ | Coinitiator | Comment |
|---|---|---|---|---|---|---|---|---|---|---|
| HDN119CR | 1,4-butandiol | - | 15 | 20 | 16+4 | - | 2 | 50 | BF3OEt2 | 1:1, OH:BF3 |
| HDN118CR | 1,4-butandiol | - | 4 | 20 | 16+4 | - | 2 | 50 | BF3OEt2 | 1:1, OH:BF3 |
| HDN111CR | HBF4 | - | 4 | 20 | 16+4 | - | 20 | 20 | - | |
| HDN117CR | HBF4 | - | 4 | 20 | 16+4 | - | 2 | 50 | - | |
| HDN117C1 | HBF4 | - | 4 | 20 | 16+4 | - | 2 | 50 | - | Hexane extraction |
| HDN115CR | Et3OBF4 | - | 4 | 20 | 16+4 | - | 2 | 50 | - | |
| HDN116CR | Et3OBF4 | LiBF4 | 4 | 20 | 16+4 | 1:2 | 2 | 50 | - | |
| HDN108CR | HBF4 | LiBF4 | 4 | 30 | 16+4 | 1:2 | 20 | 20 | - | |
| HDN107CR | HBF4 | LiBF4 | 4 | 20 | 1+1 | 1:2 | 20 | 20 | - | |
| HDN114CR | Et3OBF4 | - | 4 | 20 | 0+4 | - | 2 | - | - | Et3OBF4 added to monomer AMI |
| HDN120CR | HBF4 | LiBF4 | 4 | 20 | 16+4 | 1:2 | 2 | 50 | - | |

The first figure in the addition time column is the monomer feed time, the second is the stirring time.

**Table 7.** Conditions of experiments to enhance formation of cyclic species relative to linear polymer.
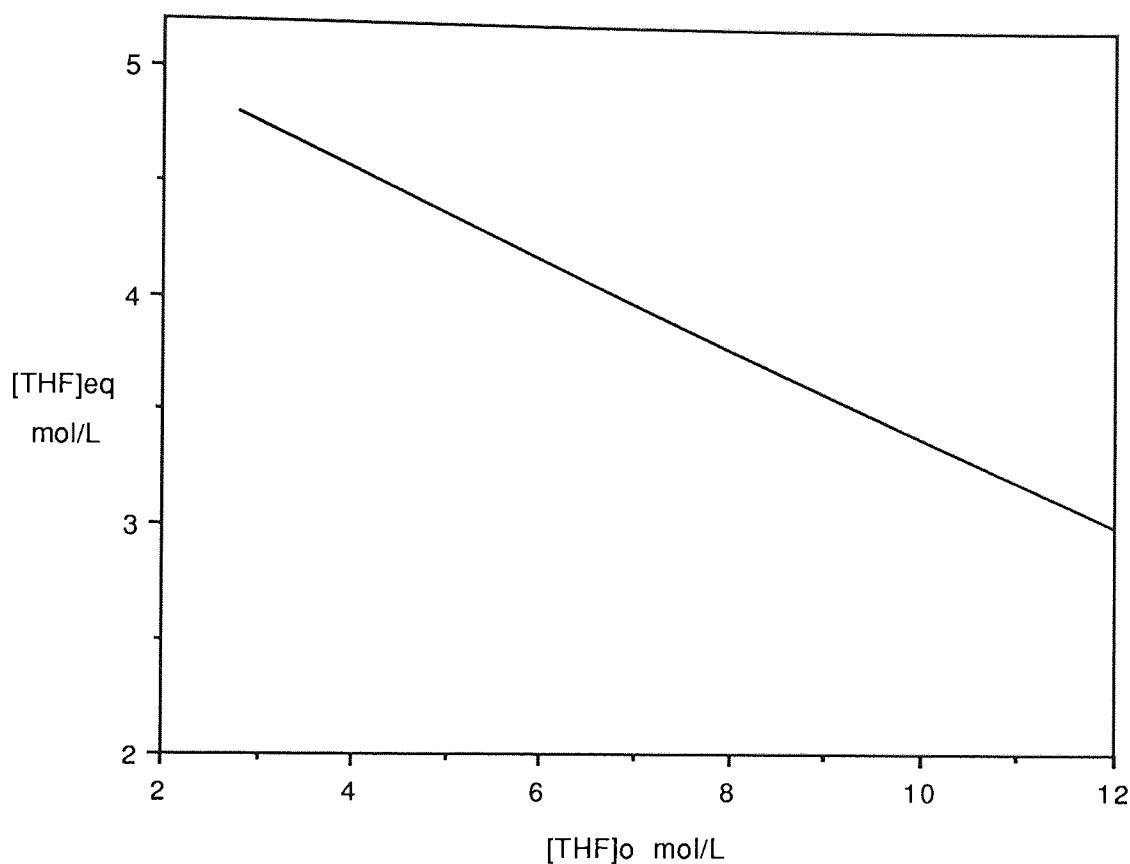
**Figure 3.14.** **Dependence of monomer equilibrium concentration [THF]$_e$ on initial monomer concentration at 25°C in benzene.**

Both these studies show that [M]$_o$ affects oligomer formation but not necessarily cyclic oligomer formation. Experiments were carried out under conditions expected to lead to increased oligomer formation, which were expected to have a similar effect in ACE systems on the formation of cyclic oligomers.

**3.1.2.1** **Effect of dilution of monomer and cationogen:monomer ratio on cyclic oligomer formation.**

An experiment was carried out in which the monomer was added as a 2% (w/v) solution in which the expected DP was 15.
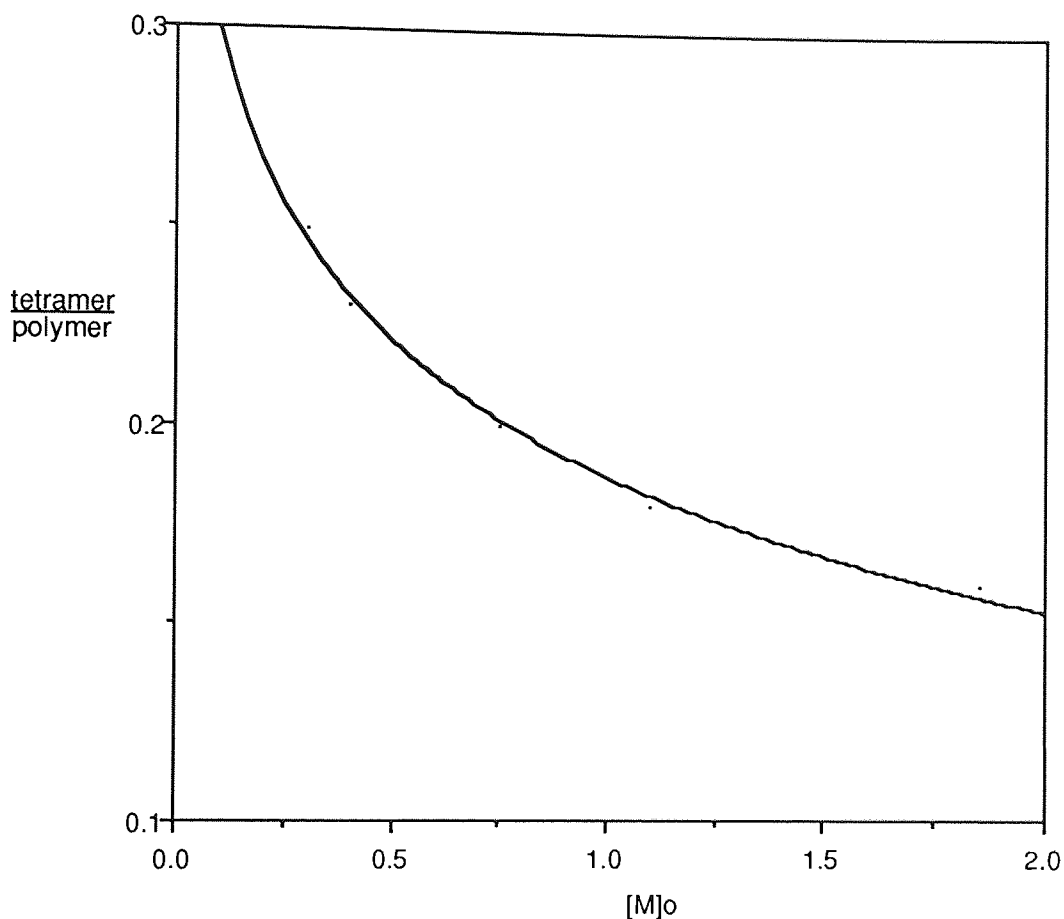
**Figure 3.15 Influence of $[M]_0$ on the tetramer to polymer ratio in the polymerisation of 3,3-dimethyl oxetane[54] with $Et_3O^+BF_4^-$.**

Similar to experiments carried out to produce 3000-6000 molecular weight polymer as shown in figure 3.20, sample POWA 1A. The effect of the dilution is clear in that the oligomer peak at a $R_t$ of 32 minutes is enhanced relative to the higher molecular weight peak at $R_t$ of 28 minutes. A further improvement would be expected if the amount of cationogen was increased so that the expected DP was 4. A comparison of the S.E.C. chromatograms of samples HDN119CR and HDN118CR reflect this, as shown in figure 3.16. In most cases where the monomer was a 20% (w/v) solution the S.E.C. traces show that the higher molecular weight species is more pronounced compared to those in which low concentrations (2%) were used. Samples HDN111CR (20%) and HDN117CR (2%) indicate this as shown in figure 3.17. Work by Dale and
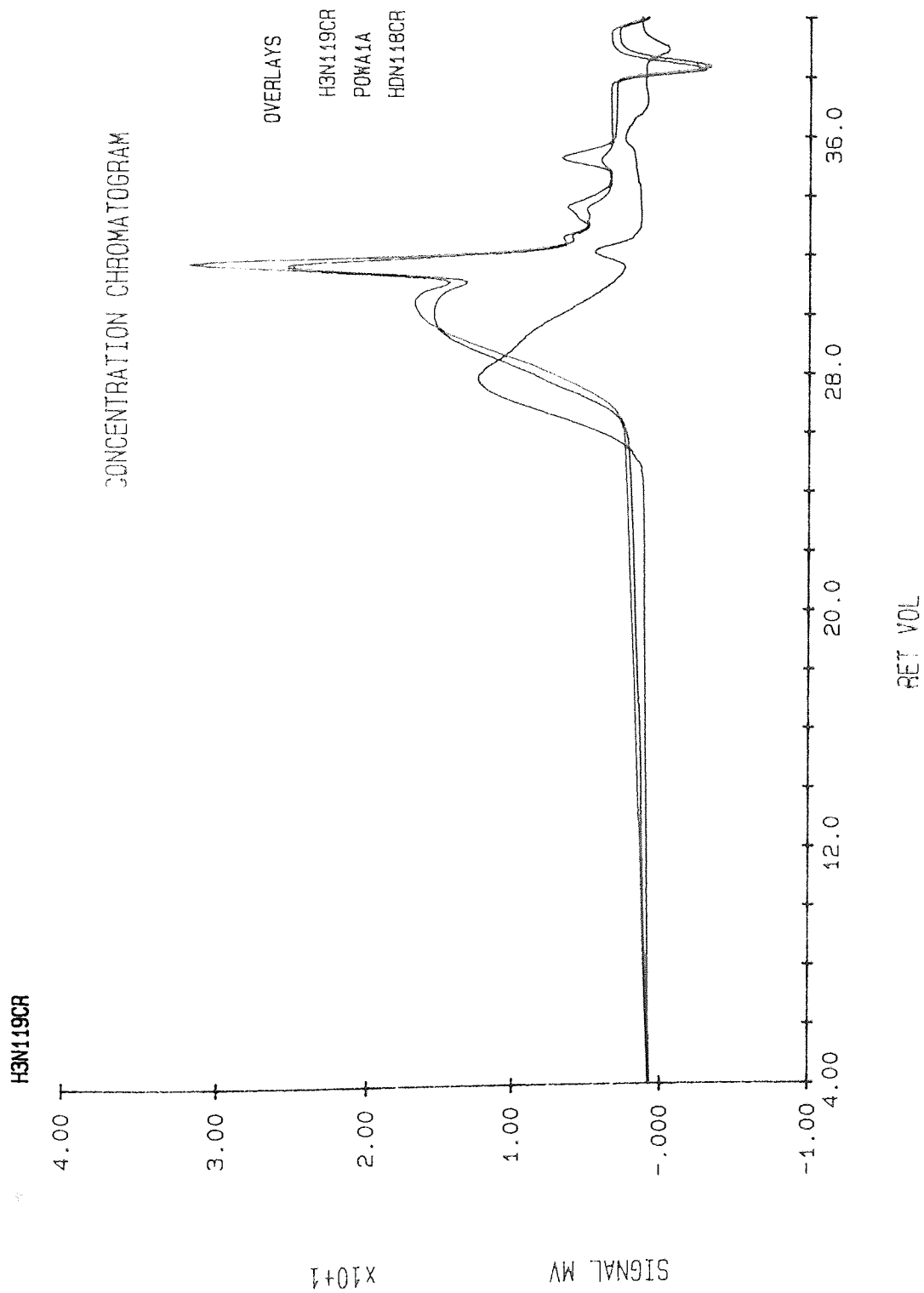
Figure 3.16    Effect of monomer:cationogen ratio on cyclic oligomer formation as shown by samples HDN119CR (DPe = 15) and HDN18CR (DPe = 4)
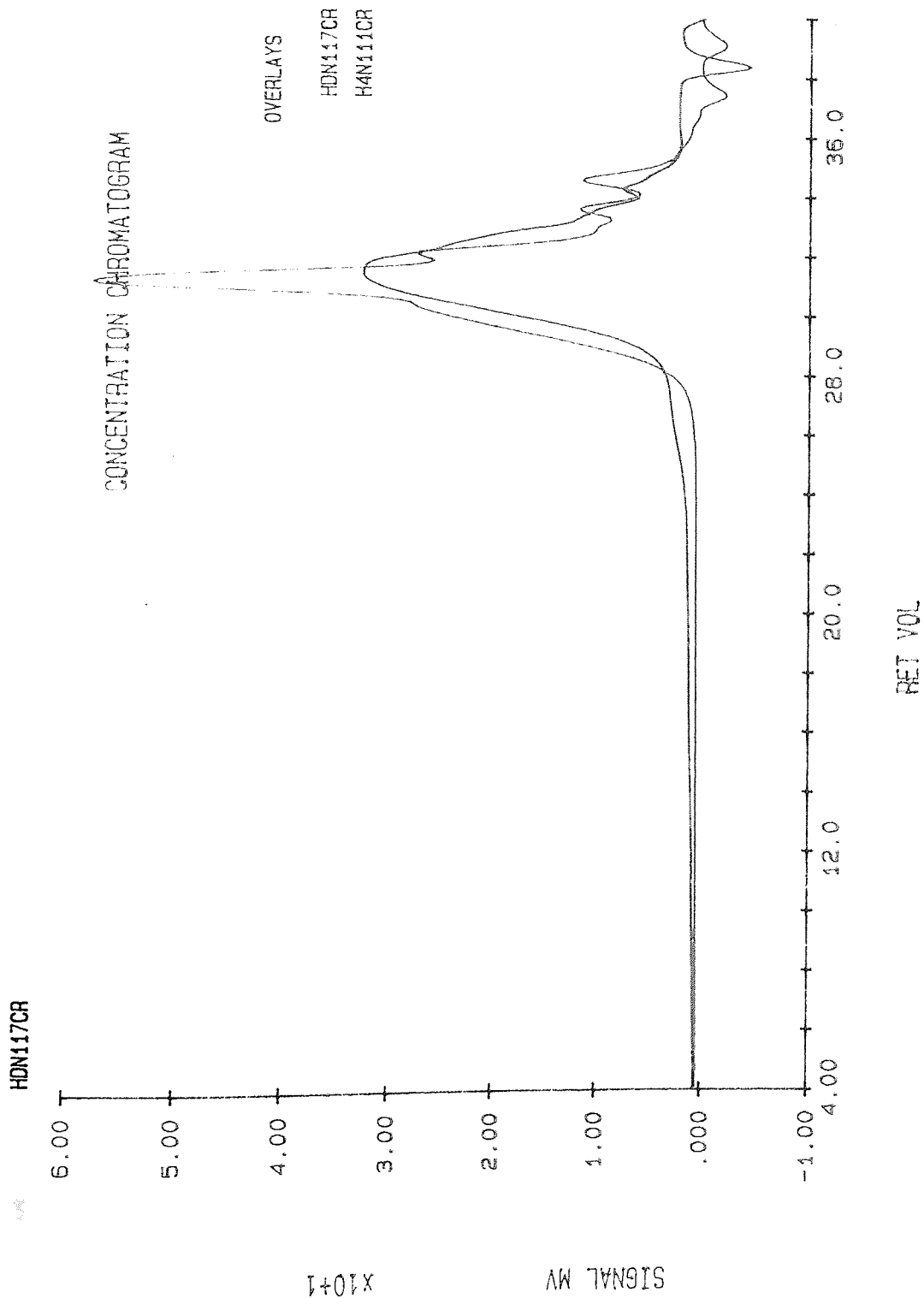
**Figure 3.17** Effect of monomer dilution on cyclic oligomer formation as shown by samples HDN111CR (20% w/v) and HDN117CR (2% w/v)

Fredrikson[77] on various oxetanes using only Lewis acids as initiators confirms that dilution can enhance formation of cyclic oligomers.

## 3.1.2.2    Effect of the type of cationogen on cyclic oligomer formation.

It is noteworthy that Dale[78] et al (Scheme 7) did not use a cationogen as an initiator. Instead they propose that the Lewis acid directly coordinates to the monomer causing oligomerisation, where the type of cyclic species formed depends on the activation energy governed by the size of the ring in the transition state. The systems investigated in this study utilise a cationogen and therefore differ from those described above in that no part of the initiator can participate in the cyclic transition state. Dale suggests that if gaseous $BF_3$ was used as an initiator then a fluorine atom may transfer to the oxonium ion. In this case two transition states, (6) and (8) in Scheme 7, are possible. Dale cites the formation of fluorohydrin type species as evidence that this must occur. In the $BF_3.OEt_2$/alcohol systems studied here, fluorohydrin species have not been observed (N.M.R). Indeed, to prevent such a possibility tetrafluoroboric acid ($HBF_4$) or triethyl oxonium tetrafluoroborate ($Et_3^+OBF_4^-$) were chosen, which have the more stable counter-ion, $BF_4^-$.

Moreover, it was thought that these two initiators would indicate the effect of the end-group on cyclisation. For example it would be expected that an electron releasing group would increase the basicity of the end, ether oxygen atom and thereby aid end-biting reaction with the oxonium ion. Alternatively, protonic initiation resulting in an -OH end may be better at allowing end-biting due to the reduction in steric hindrance.

Examination of the S.E.C. traces where protonic (HDN117CR) and ethylonium (HDN115CR) cationogens are used are shown in figure 3.18. This reveals that $Et_3^+OBF_4^-$ forms less of the oligomeric species than $HBF_4$. However, $HBF_4$ also forms more of the species at $R_t$ of 32.4 min. and $R_t$ of 33.8 min., probably corresponding to trimer and dimer, respectively.

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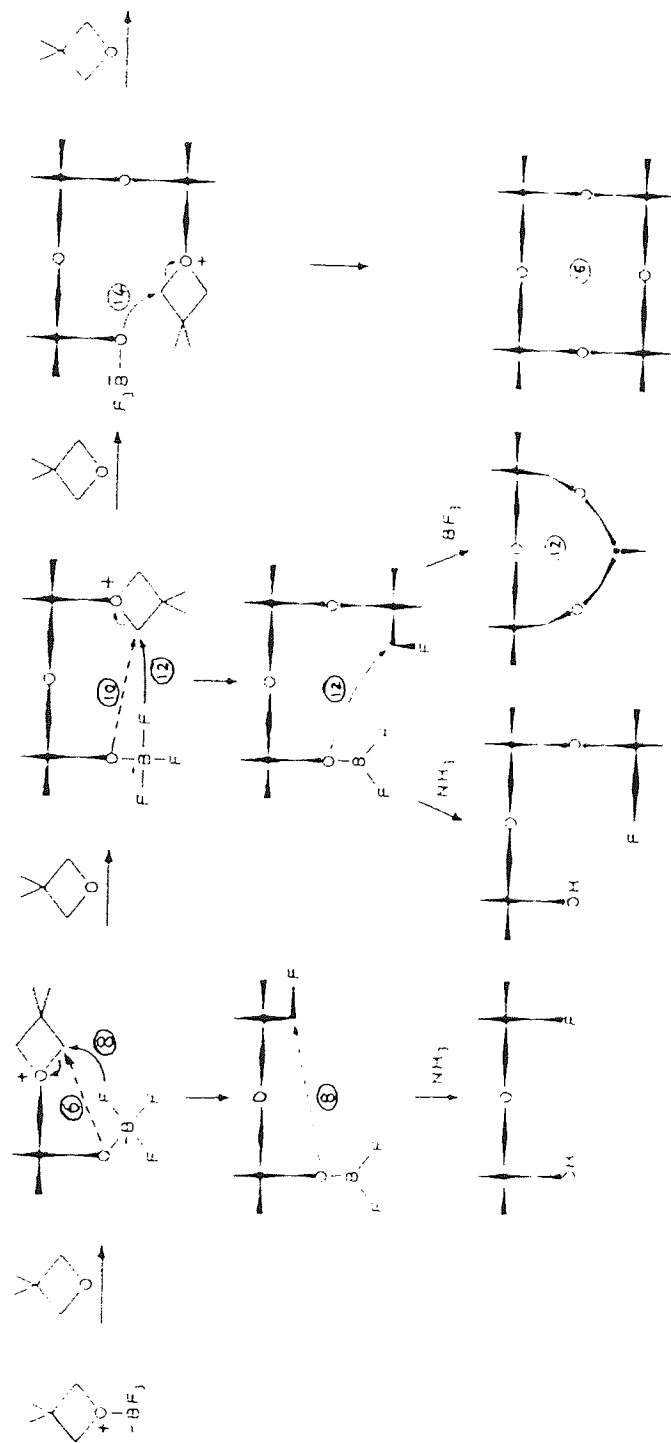
Scheme 7. Dale's reaction scheme for the oligomerisation of 3,3-dimethyl oxetane using BF3 as initiator.

CONCENTRATION CHROMATOGRAM

hdn117cr
hdn116cr
**hdn115cr**
hdn114cr
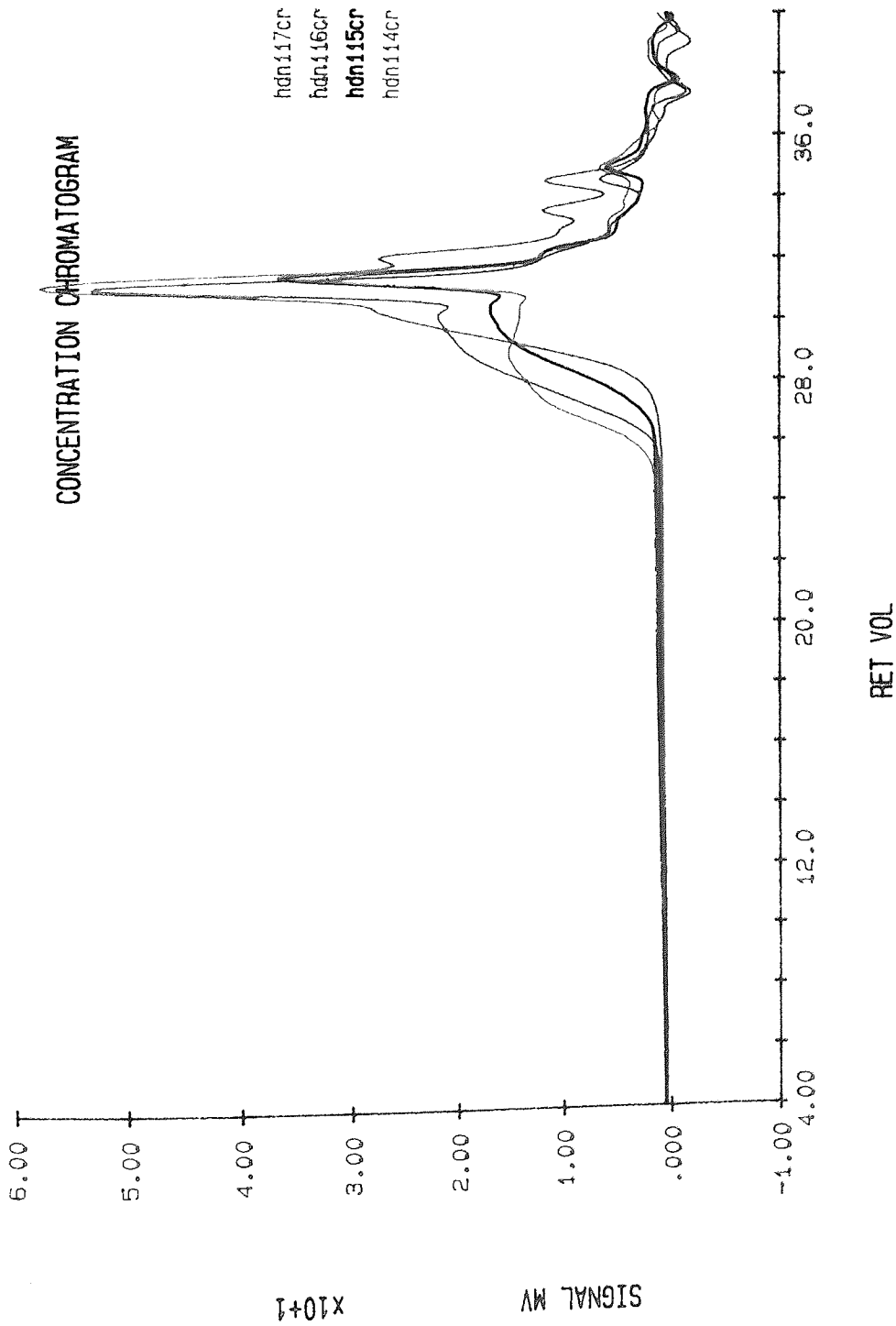
**Figure 3.18    SEC traces of HBF$_4$ (HDN117CR) and Et$_3$OBF$_4$ (HDN115CR) initiated experiments**

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### 3.1.2.3    Metal salts as templates for cyclic oligomer formation.

Based on the work of Dale[49] to use the template effect of metal-$BF_4$ salts in selectively forming oligoethers of ethylene oxide, the effect of $LiBF_4$ on NIMMO oligomers was investigated (figures 3.19 and 3.20). Figure 3.19 shows the results of two parallel experiments: $LiBF_4$ was added to the initiating mixture in one case before monomer addition (HDN116CR), and no $LiBF_4$ salt was present (HDN115CR) in the other. The shapes of the two S.E.C. traces do not display any marked differences, indicating that $LiBF_4$ has not increased the tendency to form a particular oligomer. $LiBF_4$ appeared to be only sparingly soluble in $CH_2Cl_2$ and so a solvent which supports $LiBF_4$ salts and allows polymerisation to be carried out may enable greater control of formation of particular oligomeric species. Careful examination of the two traces may, however, show that some salt has remained in the final product because the HDN116CR trace has marginally shifted to lower elution volume, possibly because complexation with $Li^+$ has increased the hydrodynamic volume of all the products. Sample HDN120CR has a similar S.E.C. trace (figure 3.23) to sample HDN116CR, both containing $LiBF_4$. However, it would be expected that complexation of the salt with the oligomer would decrease the hydrodynamic volume of the oligomer and shift the peak to a higher elution volume. Perhaps the hydrodynamic volume of the uncomplexed oligomer is less than the complexed oligomer because the metal ion in the centre of the cyclic compound 'blows' it up, like air in a balloon. Further work needs to be carried out to establish the effect of salts on elution volumes.

It may be speculated that raising the temperature aids solubility of the salt and sample HDN108CR produced a surprising SEC result where a broader peak with peak $R_t$ of 32 minutes is observed instead of the narrower oligomeric peak usually seen here. This could be because the higher temperature (30 °C) or $LiBF_4$ salt has hindered formation of cyclic species but also prevented propagation to higher molecular weights. However, a more likely reason is that the sample was mistakenly run in THF containing tetrabutyl ammonium fluoride which shifts peaks to higher elution volumes.
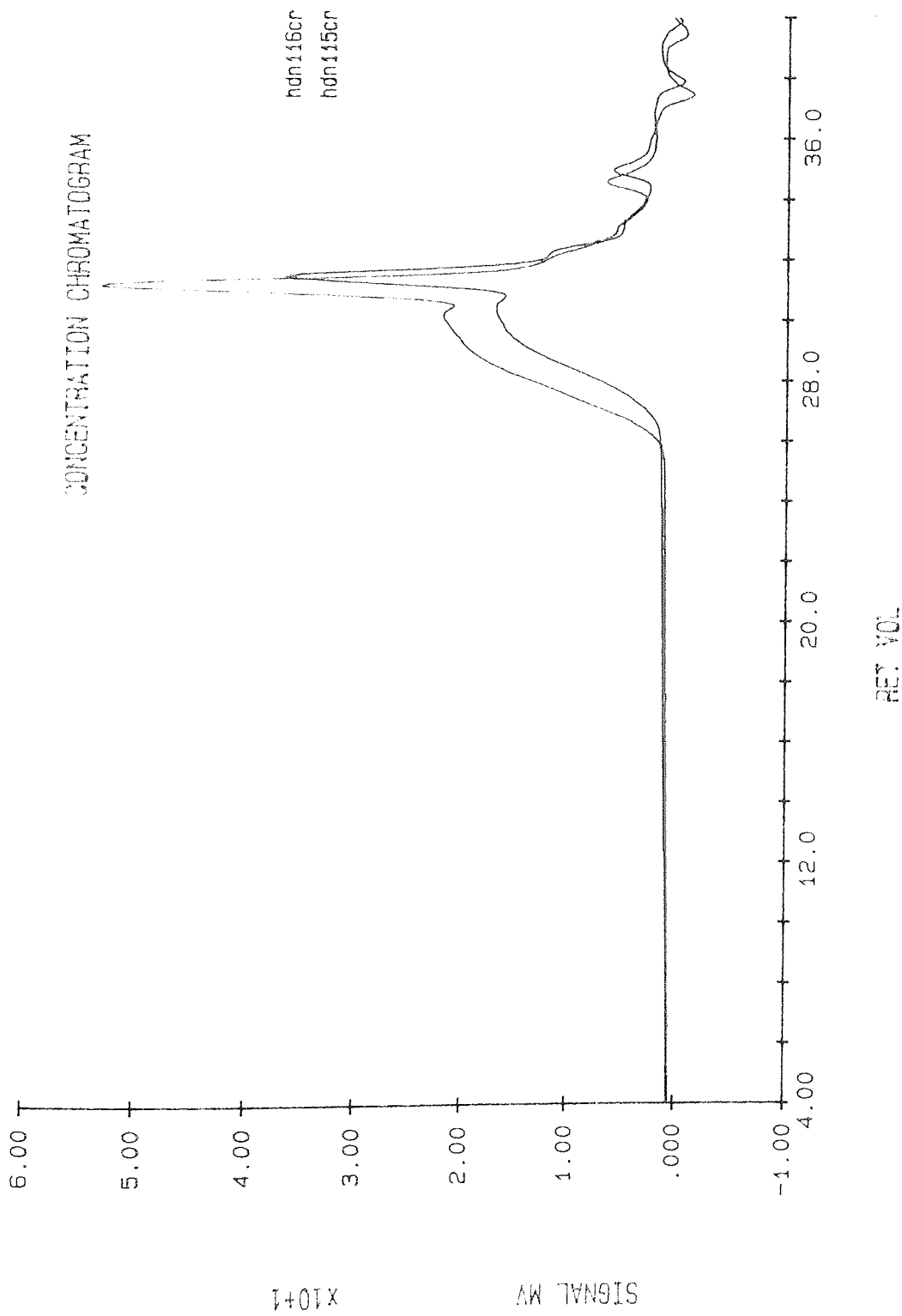
**Figure 3.19**    Effect of LiBF$_4$ (HDN116CR) on MWD and oligomer formation

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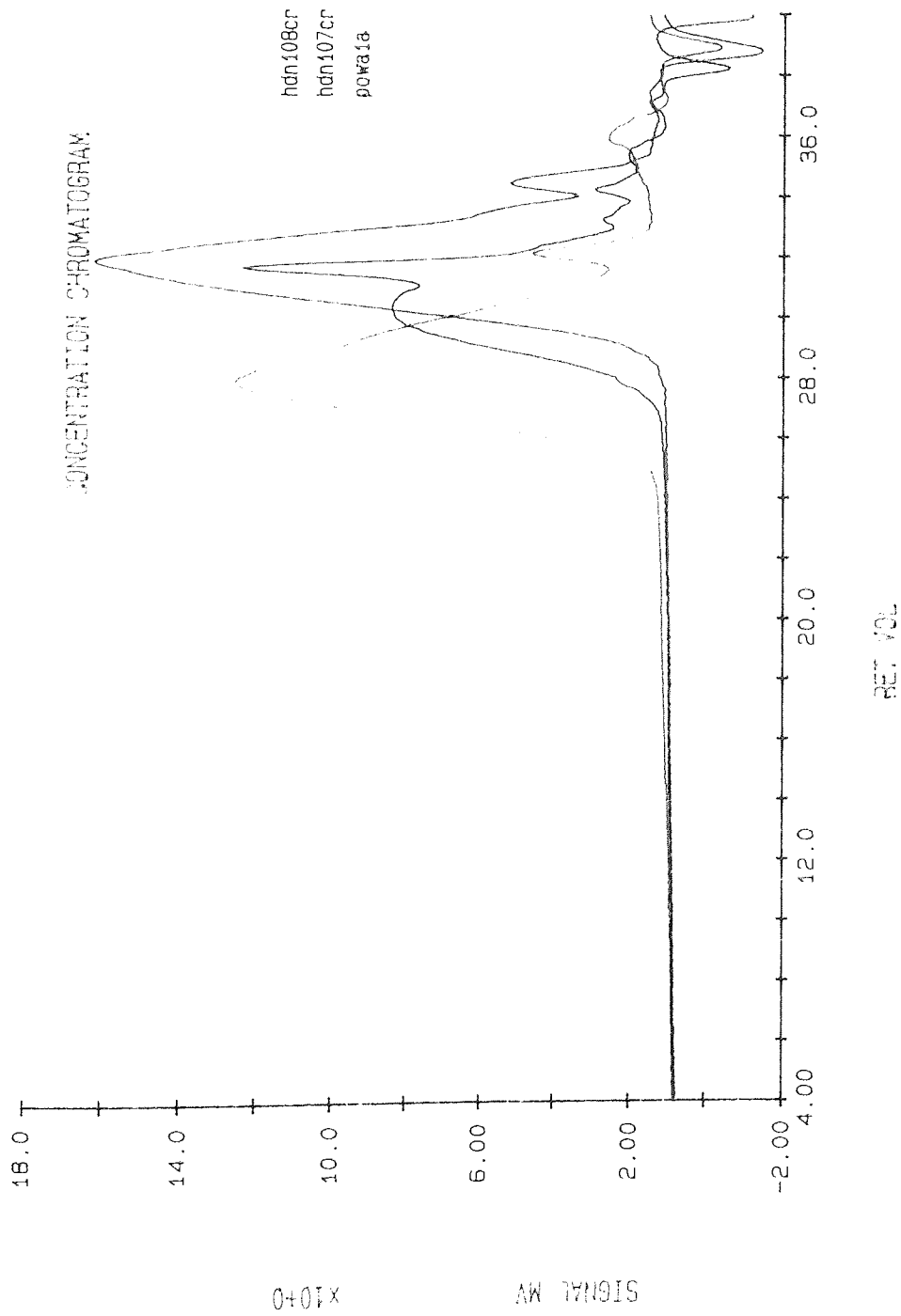
**Figure 3.20** <u>SEC traces of 20% w/v polymerisations with LiBF<sub>4</sub> and without (POWA1A)</u>

### 3.1.2.4    Effect of reaction and monomer addition times on oligomer formation.

The effect of reaction time on cyclic oligomer formation[55] has not been specifically studied but depends on the relative rates of back-biting, end-biting and propagation. Slomkowski[55], predicts (figure 3.21) that systems with fast propagation, slow end-biting and fast back-biting convert monomer first into short linear molecules, then into cycles and later into linear macromolecules. Where n is the number of monomer units in the cyclic species.
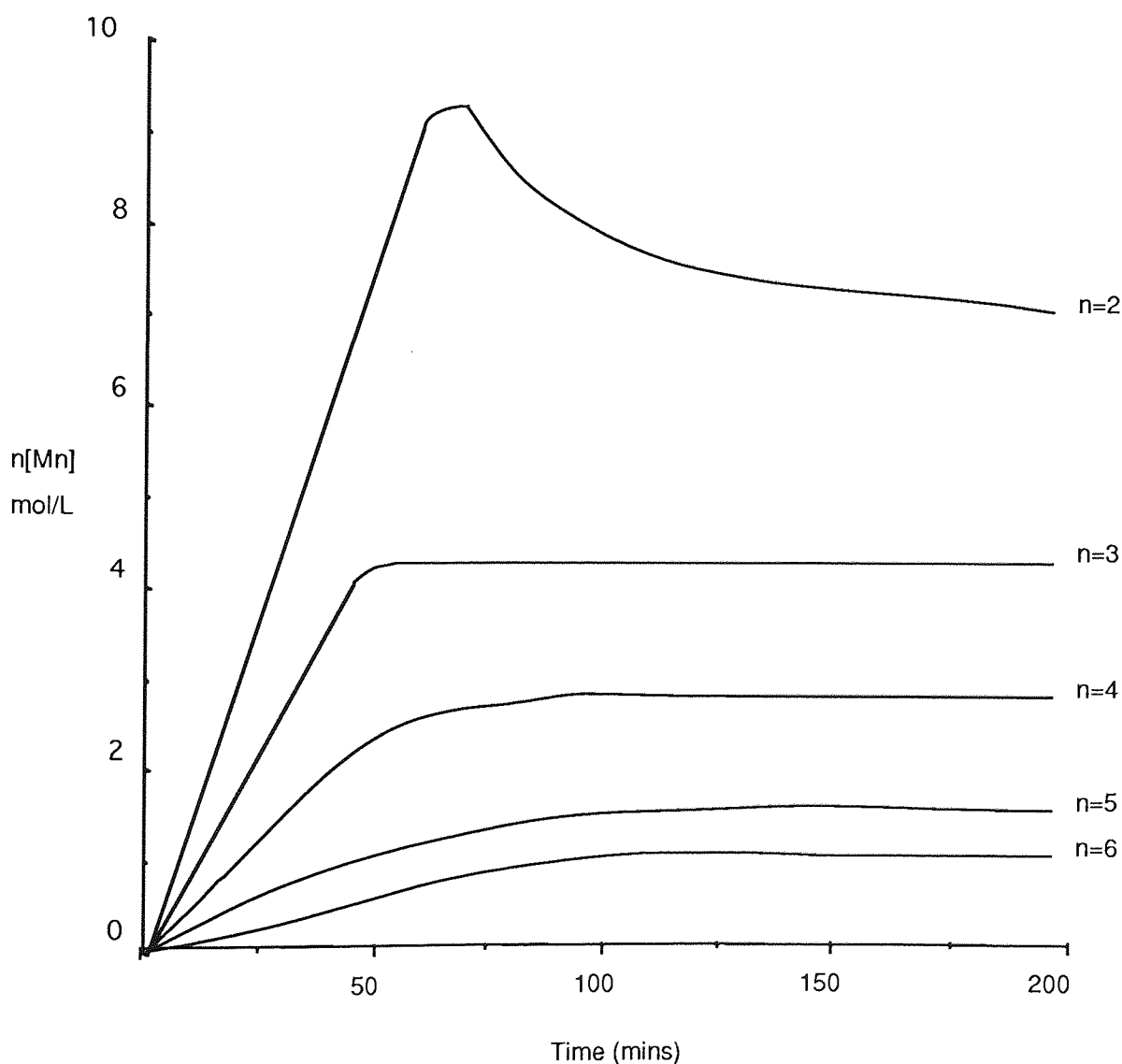


### Figure 3.21. Dependence of the concentrations of cyclic oligomers n[Mn] on time.

In contrast systems with very fast propagation, slow back-biting and no end-biting produce linear macromolecules first and then when nearly all the monomer is consumed some macromolecules are converted to cycles of various sizes. The NIMMO systems under study probably belong to the former class, as figure 3.9 shows cyclisation occurs early and simultaneously with propagation. Even after 15 min. of monomer addition, discrete peaks corresponding to tetramer and probably trimer are visible, along with some higher molecular weight material.

### 3.1.2.5    Separation and characterisation of cyclic species.

Studies of the distribution of cyclic oligomers in NIMMO systems have not included the application of the Jacobson-Stockmayer equation[101]. Such studies require unambiguous identification of all the cyclic oligomers formed. Some progress has been made to establish the nature of the dominant oligomer at $R_t$ of 32 minutes by extracting a mixture of linear polymer, oligomer and cyclic species with n-hexane. Hexane was chosen as the solvent of extraction because it is relatively volatile but also because of its apolar characteristic which should not support hydroxyl groups. Linear species are largely insoluble in hexane but cyclic species are sparingly soluble.

Figure 3.22 shows the S.E.C. of the hexane soluble fraction (HDN117C1), eluting predominantly at $R_t$ of 32 min., with small amounts of other oligomers. Further analysis of this sample by N.M.R. (figures 3.24, 3.25 and 3.26 ) and M.S. indicates that the dominant species is indeed the cyclic tetramer. The N.M.R. shows that NIMMO hydroxyl end-groups from linear oligomer (Lo) were still present but in small amounts compared to the cyclic tetramer peaks (T). The M.S. analysis shows a strong peak at m/e = 589 which is consistent with the molecular ion of the tetramer (MW = 588). The base peak in the spectrum with ionisation at 2.6 V (figure 3.27) is at 86 indicating considerable fragmentation perhaps corresponding to $C_4H_8NO$. A spectrum carried out with ionisation at 1.5 V (figure 3.28) shows a molecular ion at 590 which is also the base peak suggesting less fragmentation has occurred. The slight difference in molecular ion peaks is probably due to an error in calibration.
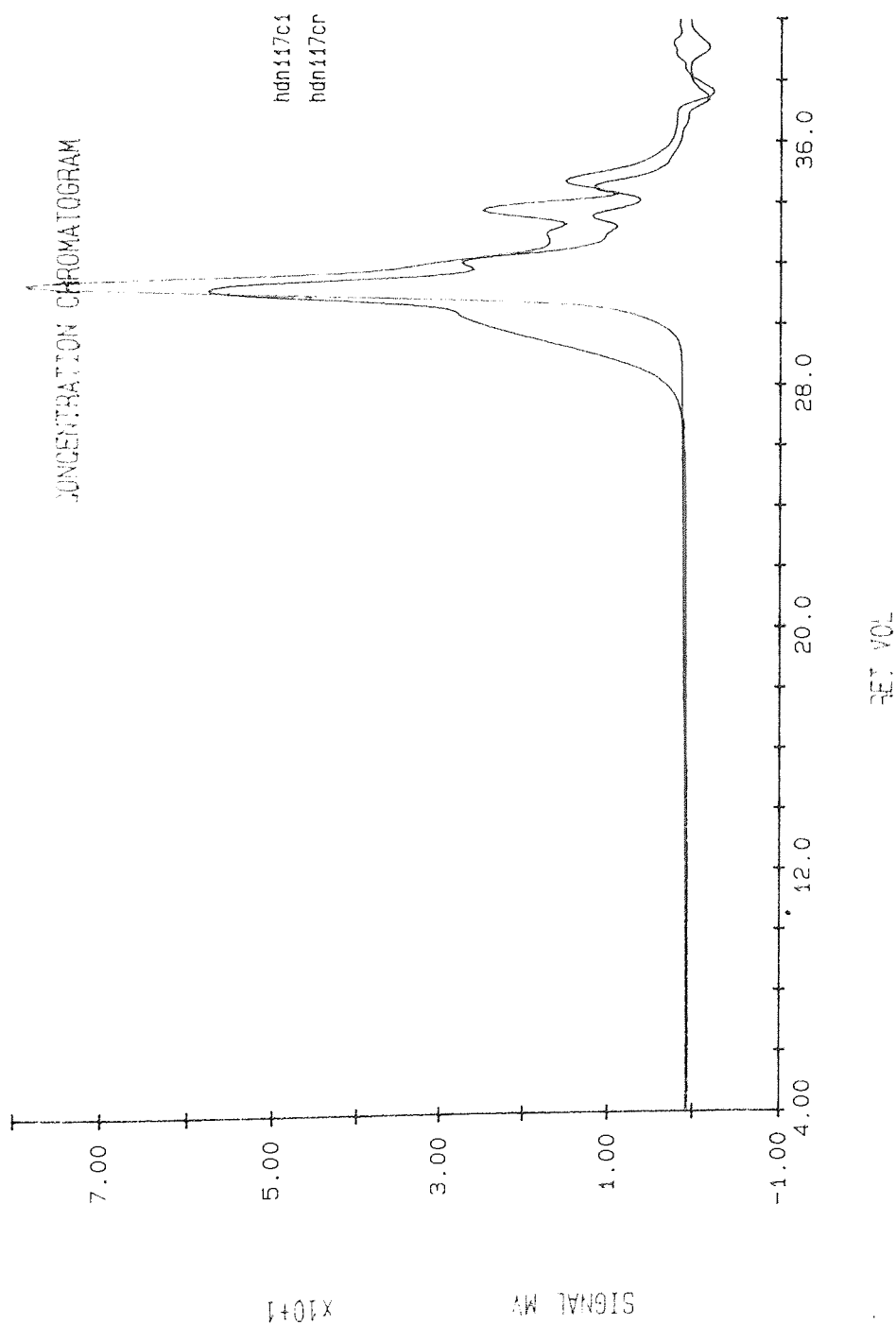
**Figure 3.22** Crude product of oligomerisation reaction (HDN117CR) and hexane soluble fraction (HDN117Cl)

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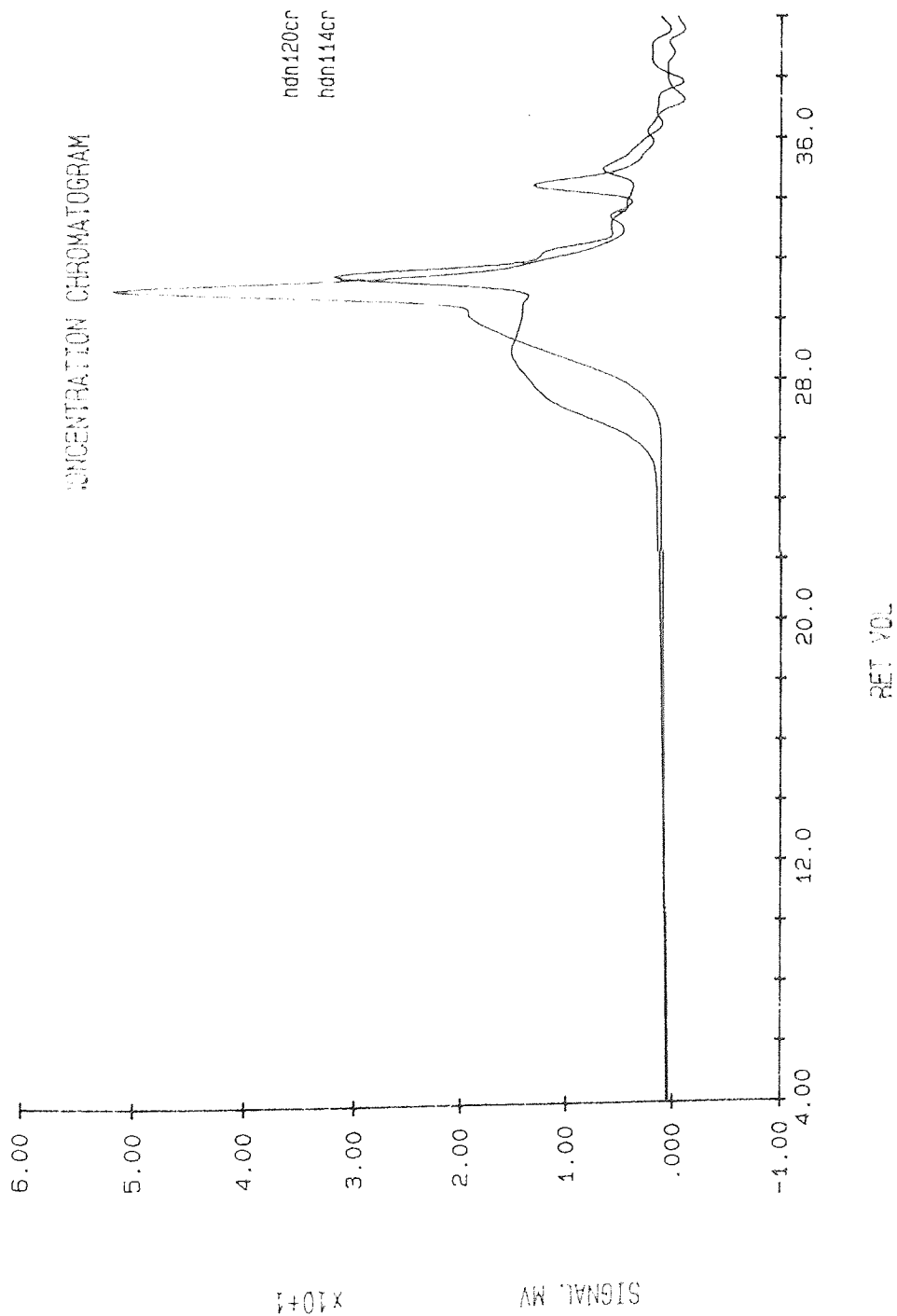
**Figure 3.23    Other SEC chromatograms of oligomerisation experiments**

T = cyclic tetramer

M = monomer

LO = linear oligomer

S = solvent
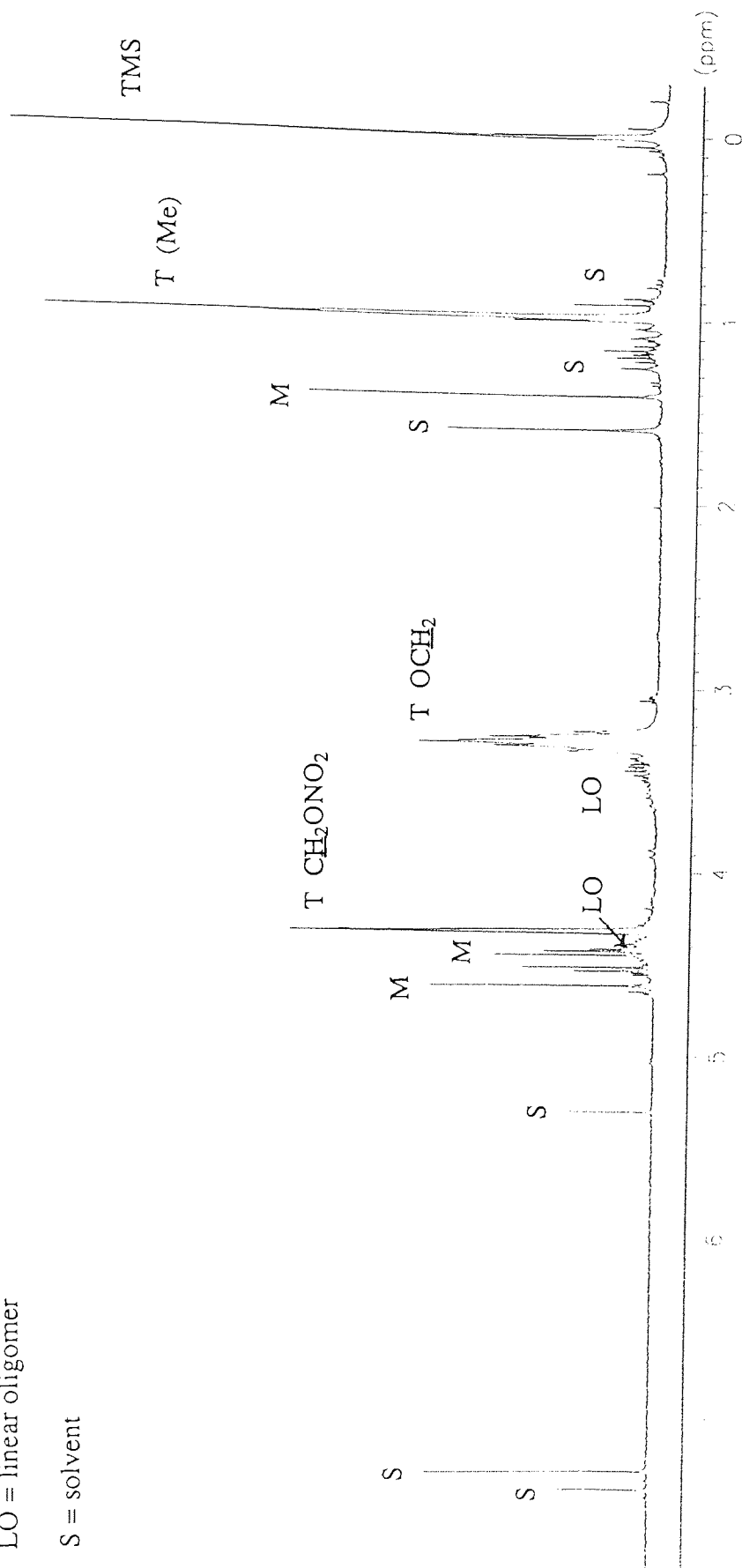


Figure 3.24 $^{1}$H NMR of NIMMO oligomeric species
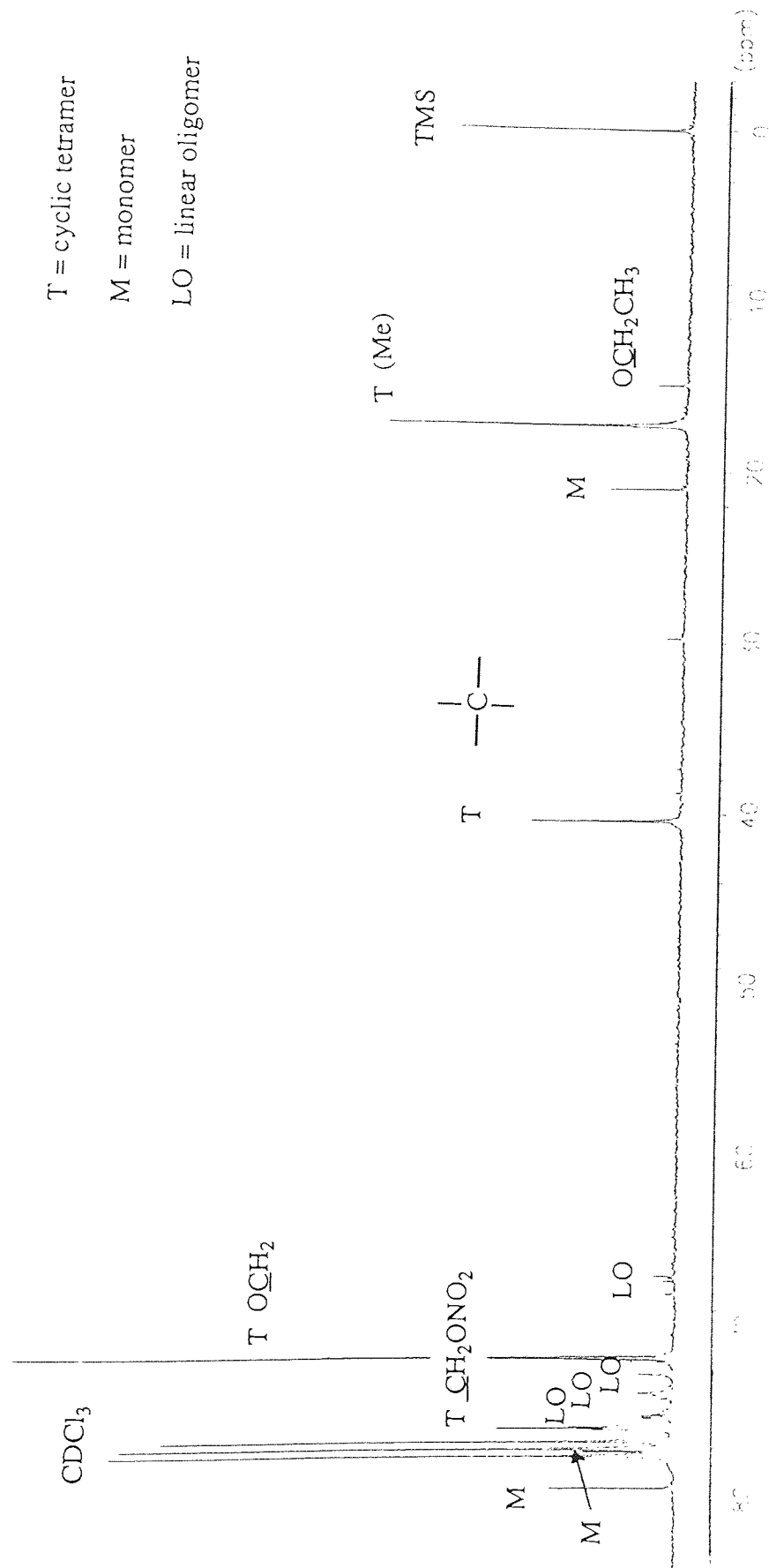
**Figure 3.25** $^{13}C$ NMR of NIMMO oligomeric species
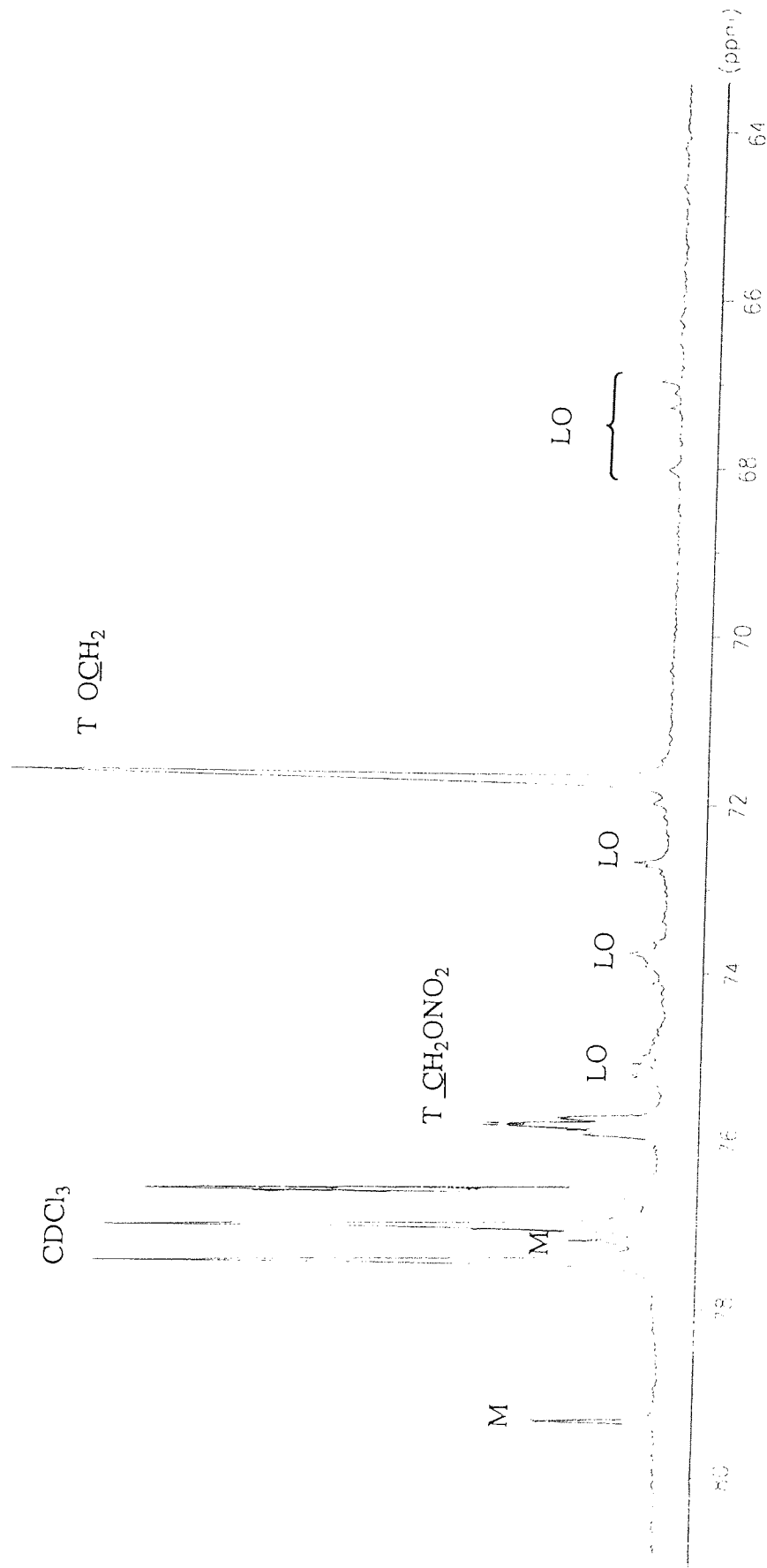
Figure 3.26 Expanded $^{13}C$ NMR of NIMMO oligomeric species
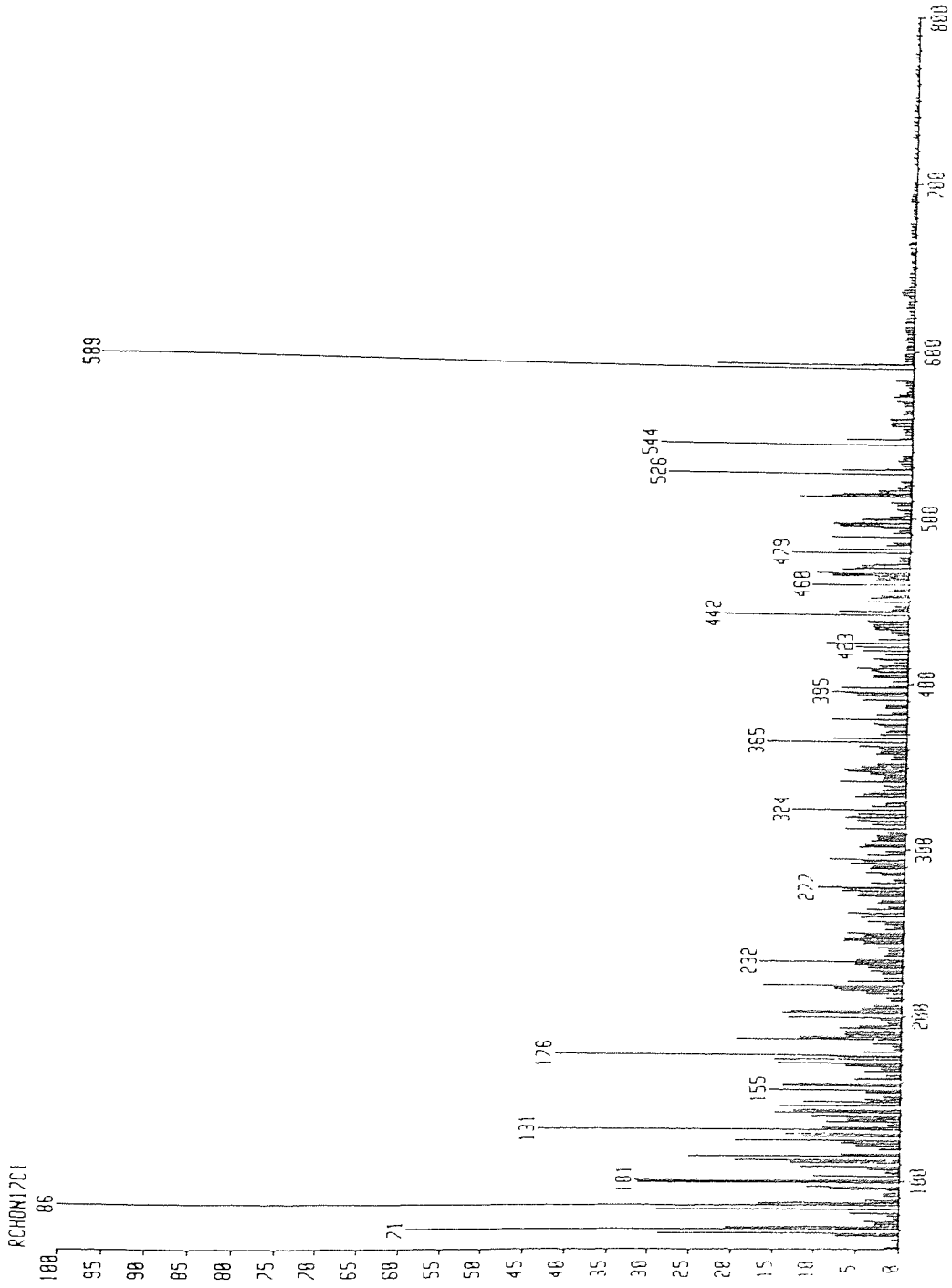
Figure 3.27    Mass spectrum of NMMO oligomeric species (I = 2.6V)
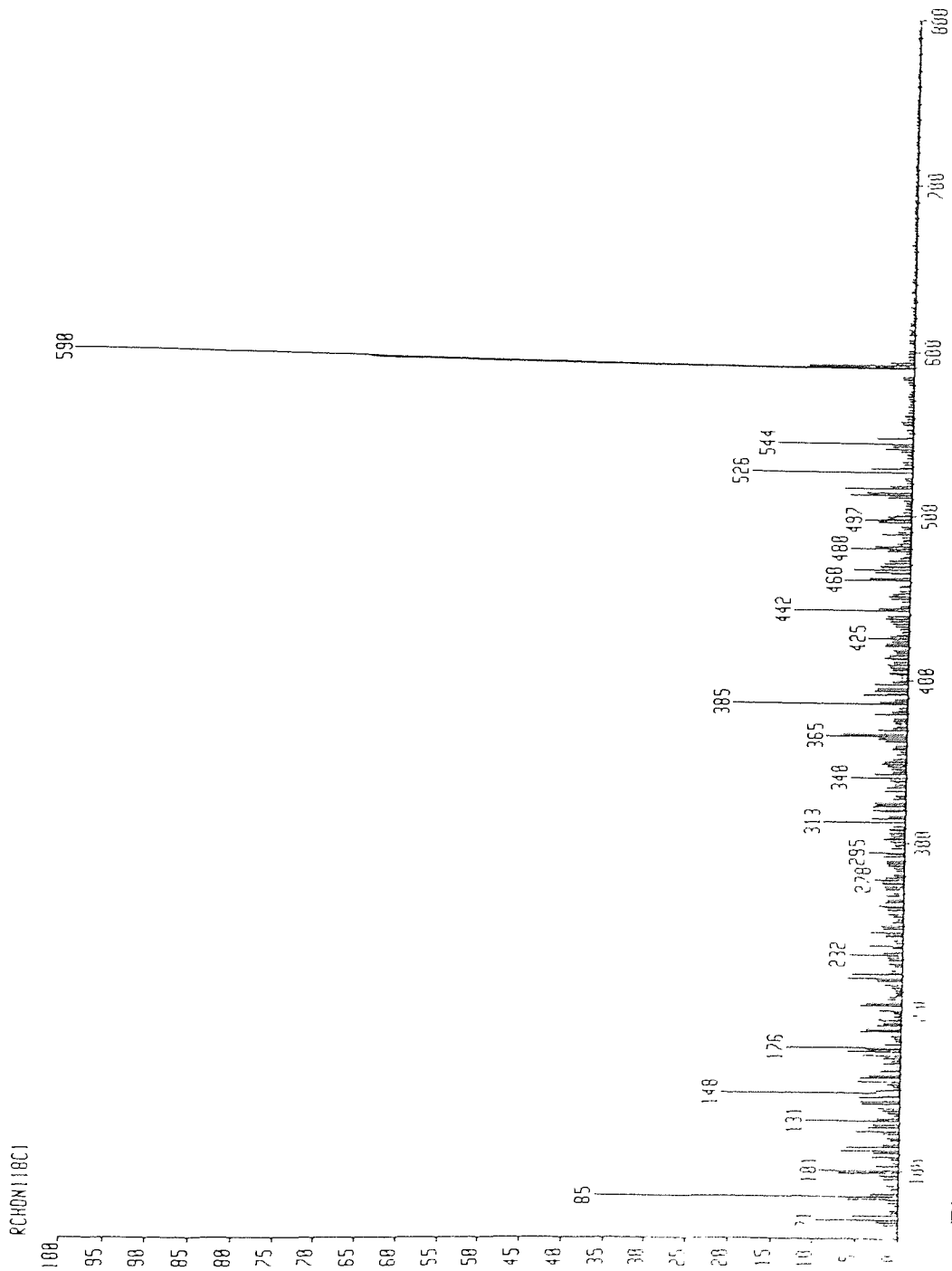
Figure 3.28   Mass spectrum of NIMMO oligomeric species (I = 1.5V)

### 3.1.2.6    Application of cyclic species as plasticiser.

Once the nature of the cyclic species was determined experiments were conducted to examine the potential use of the cyclic oligomer as a plasticiser for polyNIMMO. The dependence of Tg on the weight fraction of oligomer, figure 3.29, shows the plasticising effect of the low molecular weight material. A D.S.C. trace (figure 3.30) of the cyclic material indicates a Tg of -62 °C which is considerably lower than polyNIMMO (POWA1) containing some cyclic species as shown in figure 3.31. The low molecular weight of the oligomer and the lack of H-bonding interactions (due to absence of terminal OH groups) may help to explain this. An increase in the amount of cyclic seems to produce a corresponding reduction in the Tg. This is a possible novel application of cyclic species, especially in the field of energetic materials where plasticisers have usually been molecules which are mixtures of isomers e.g. ethyl nitrobenzenes in compositions with polybutadiene as binder. These plasticisers are of low energy and/or incompatible with the binder, resulting in leaching over the lifetime of the composition, which is supposed to be at least 20 years. This class of compounds, bearing nitrate ester functional groups is expected to be energetic and fully compatible with the new generation of propellant and explosive binders, which includes polyNIMMO and polyGLYN.

### 3.1.3 Overall mechanism of NIMMO polymerisation.

Using the results hitherto discussed an overall mechanism for the polymerisation of NIMMO may be proposed, and this is illustrated as scheme 8.

The reaction of the alcohol with the $BF_3.OEt_2$ produces an initiating mixture; $[Et_2OH]^+$ and $[BF_3OROH]^-$. In this scheme it is deemed that the proton attacks the monomer to form a cyclic oxonium ion because N.M.R. evidence indicates that the final -OH functionality of the polymer is approximately 2, but it is possible that ethyl carbocation may also attack the monomer to give:

$$Et-\overset{+}{O} \diagup\diagdown \quad CH_3 \diagup\diagdown \quad ONO_2$$
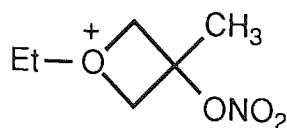
Of course this species can also propagate by the ACE mechanism upon addition of monomer. As the N.M.R. spectra of final polyNIMMO samples are complicated (see figures 3.2 and 3.3) it is difficult to estimate the amount of ethyl ether end groups.

Assuming that protonic initiation occurs under the conditions used in this study, the polymerisation of NIMMO proceeds predominantly by the ACE mechanism. However, if the [OH]>>[M] then it is possible that propagation may occur mainly through an activated monomer mechanism. There is no evidence yet of the magnitude of the contribution of activated monomer reactions to polyNIMMO propagation by IMA but there is evidence that transfer reactions occur between terminal -OH groups and oxonium ion species. The presence of such reactions, which would be expected to increase with temperature, explains why it is possible to reduce the oligomer and unreacted NIMMO content upon stirring at $+30°C$. Besides the reaction of the oxonium ions with OH groups, coupling reactions with the counter-ion formed as a result of $BF_3$ complexation with OH i.e. $-R-OBF_3^-$, is an important reaction, vital for preparation of multifunctional polymers to aid curing. Moreover, the degree of cross-linking affects the 'hardness' of the rubber and some explosive systems require the possibility of generating different degrees of hardness (shore test). N.M.R.[78] evidence suggests that the cationogen plays a major role in the final functionality of the polymer. The use of a trifunctional alcohol, glycerol or metriol, increases the functionality to approximately 2.5, which is probably due to the incorporation of the alcohol into the polymer backbone.
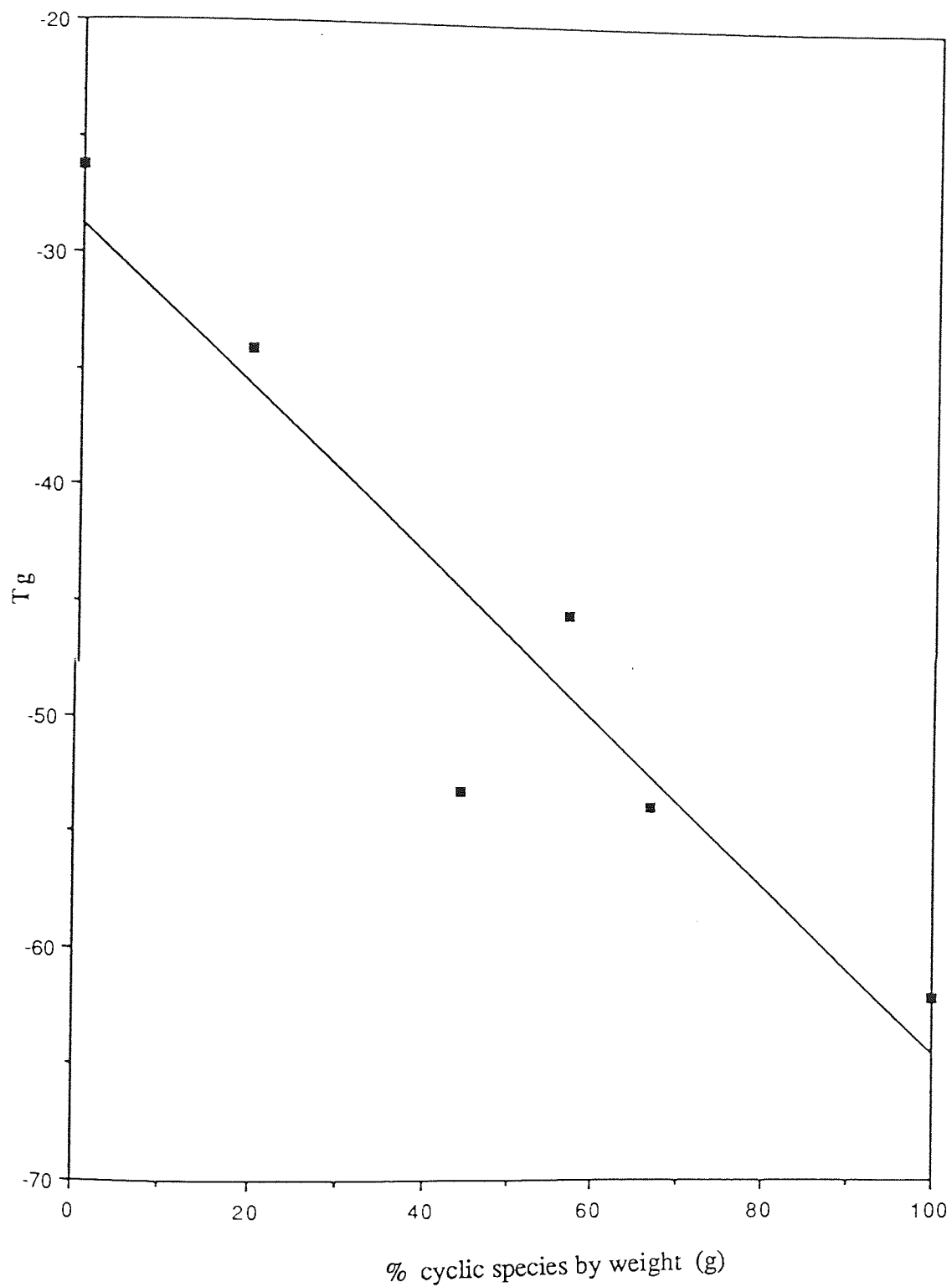
Figure 3.29    Graph showing the relationship between glass transition temperature and the amount of cyclic species added to polyNIMMO

DSC PL

PL Thermal Sciences
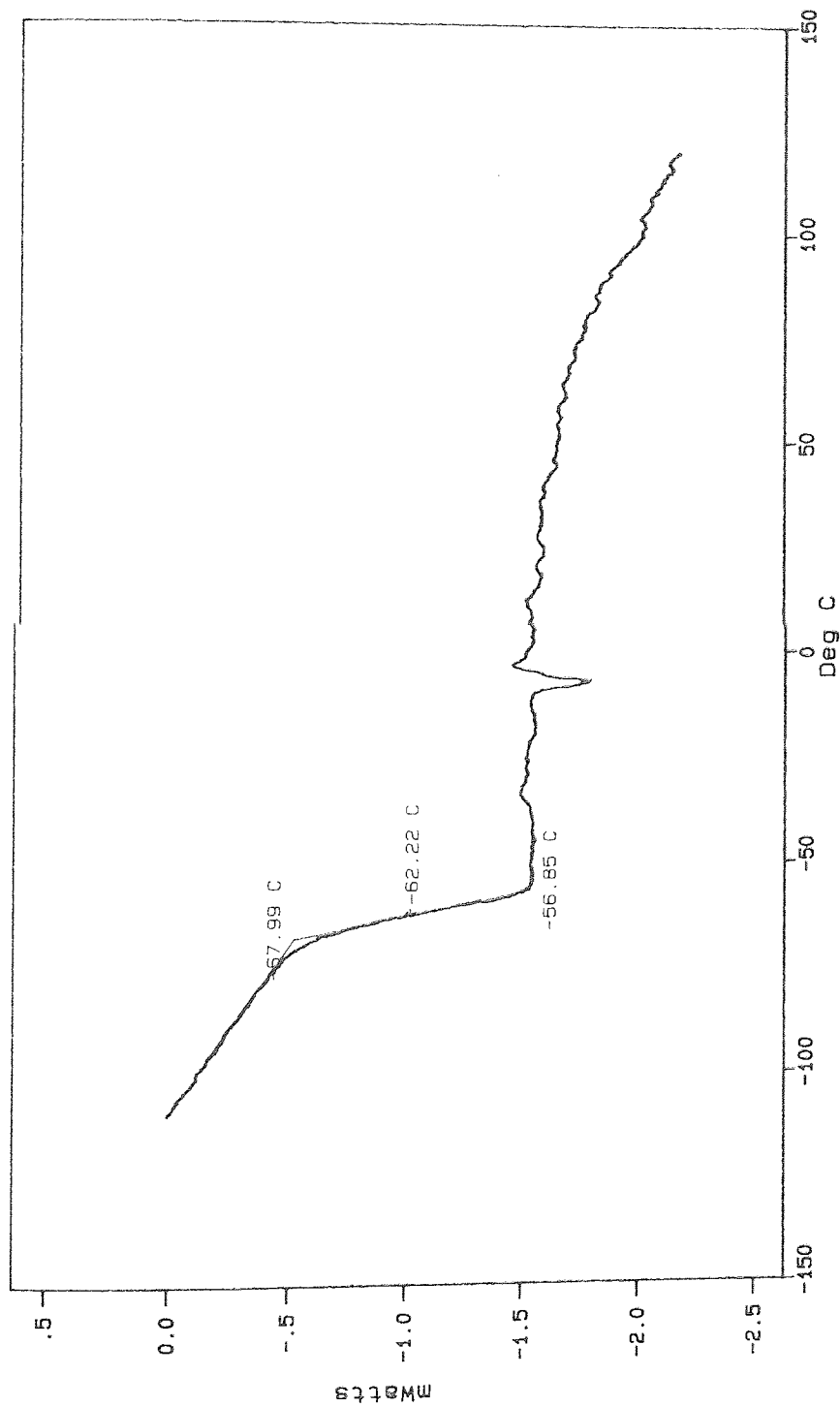
SMPL ID : cyclic



**Figure 3.30  DSC trace of predominantly cyclic material**

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DSC PL
PL Thermal Sciences

SMPL ID : pnmmo
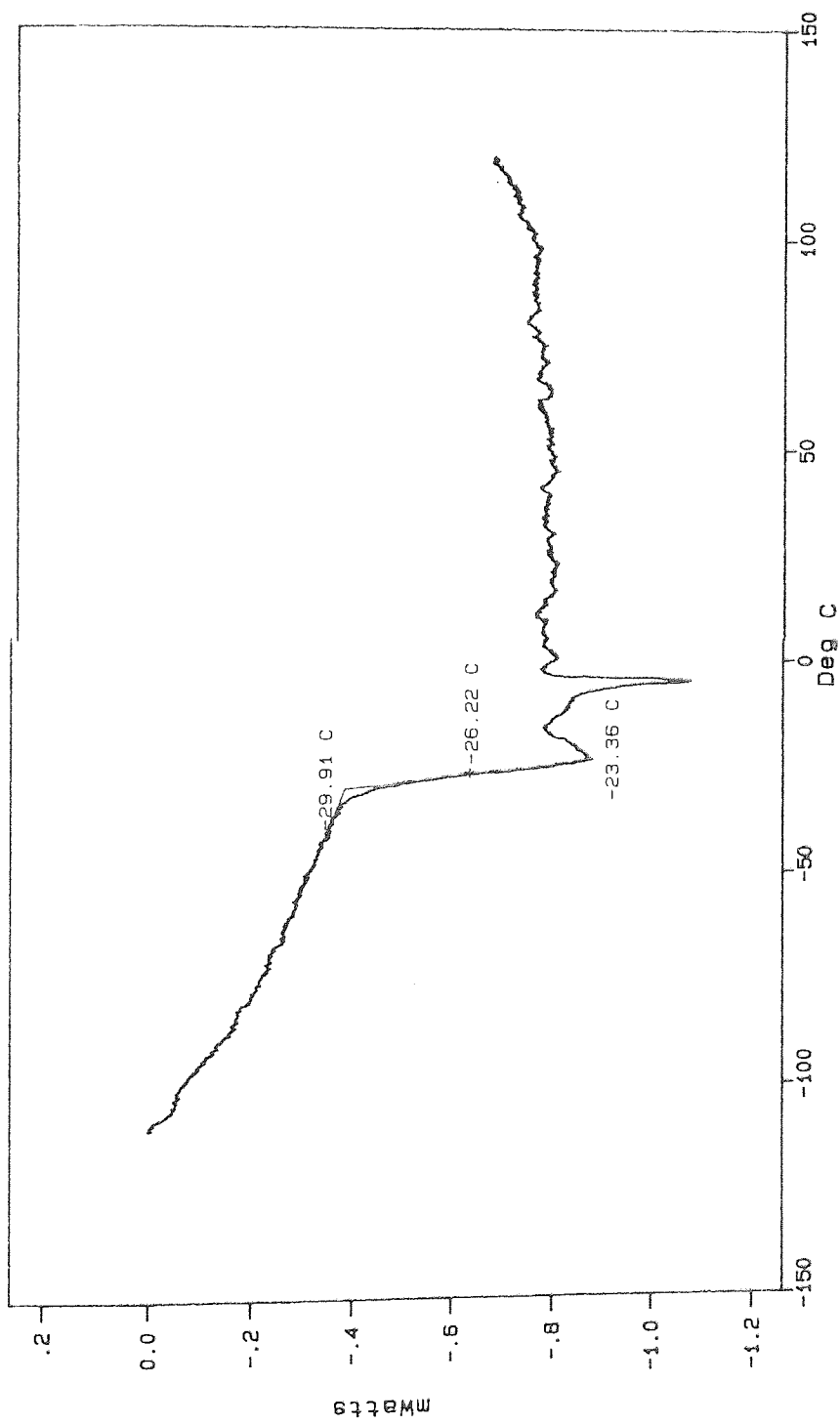
Figure 3.31   DSC trace of standard polyNIMMO (16 + 4 hours) with some cyclic material

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HOROH + BF$_3$.OEt$_2$

Pre-initiation

H$\overset{+}{O}$Et$_2$ + BF$_3\overset{-}{O}$ROH

Initiation
-Et$_2$O

H-$^+$O◇ BF$_3\overset{-}{O}$ROH

[OH]<[M]

HOROH

Propagation

Propagation

ACE

AM

HO⌒⌄$^+$O◇ BF$_3\overset{-}{O}$ROH

HO—R—O⌒⌄OH

Termination

Propagation   H-$^+$O◇

H$\left(\text{O}⌒⌄\right)_n$OH

H$\left(\text{O}⌒⌄\right)_n$O—R—O$\left(⌄⌒\text{O}\right)_m$H
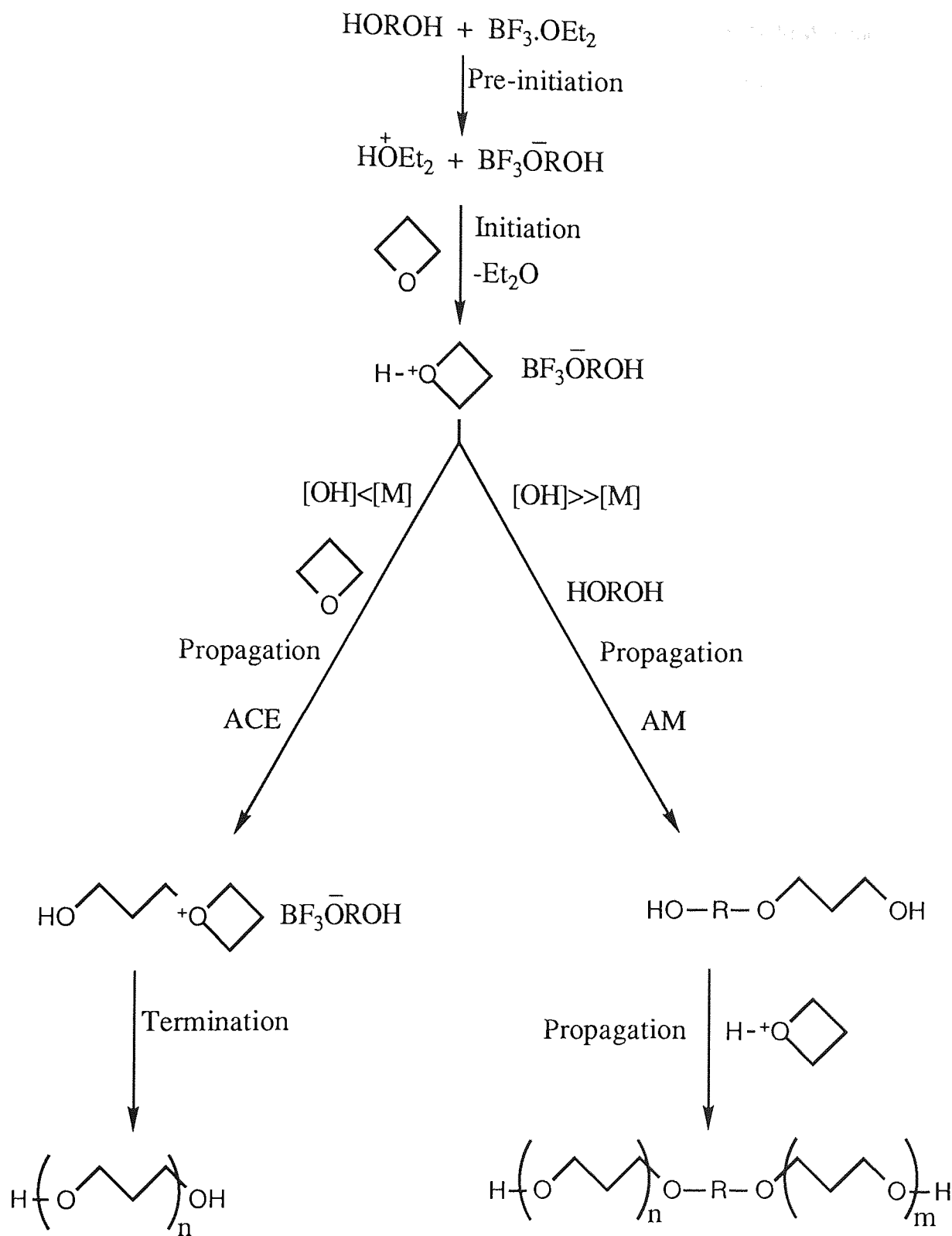
**Scheme 8.   Overall mechanism for the polymerisation of NIMMO.**

The functionality observed is less than 3 because a transferred active centre is likely to produce a difunctional chain. The functionality of the polymer may be further increased if a tetrafunctional alcohol such as pentaerythritol is used. Reaction of the oxonium ion

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with OH groups must occur as indicated by the AMM polymerisation of NIMMO and oxetane as shown in sections 3.1.4 and 3.4. Other transfer and termination processes which may occur are shown in scheme 9. The formation of strainless macrocyclic rings can lead to termination of growing chains.

To date there is no evidence to suggest that the nitrate ester group takes part in transfer or termination processes. However, some form of complexation between the $-ONO_2$ group and the cation, whether protonic or oxonium ion, would be expected and perhaps this plays a role in those systems being dominated by transfer reactions. Evidence for this domination is that high molecular weight polymers (>6000) are difficult to form, both by AMI and IMA techniques. In addition, the experiment in which the reaction was stirred for 40 hours after monomer addition was complete, it was observed that the monomer declined, oligomer increased but there was no propagation to form higher molecular weight material (figure 3.8). Nevertheless, for binder applications this is not a disadvantage, in fact it allows formation of material with the required viscosity for processing and the desired functionality, particularly by IMA which tends to promote transfer reactions. The appendix shows some of the properties of polyNIMMO so far tested.

Finally, polar impurities such as water can cause termination and transfer in ACE systems while in AMM systems they can compete with the alcohol for the protonated monomer.

### 3.1.4 Discussion of Synthesis of linear α,ω-hydroxytelechelic polyNIMMO and α,ω-nitratotelechelic polyNIMMO.

The MWDs of the hydroxy terminated and end-nitrated oligomers of NIMMO were determined by S.E.C. using the Viscotek system. Figures 3.32 and 3.33 show the chromatograms of the two compounds, which are very similar. This indicates that the use of $N_2O_5$ as a nitrating agent does not markedly affect the molecular weight distribution, either through cross-linking or chain scission reactions, unlike other

1. Coupling reactions

1a. HO——R——OH    +    HO⌇O⁺◇ ⟶

HO——R——O⌒⌒⌒O⌇OH    +    H⁺ .

1b. HO⌇OH    +    HO⌇O⁺◇ ⟶

HO⌇O⌒⌒⌒O⌇OH    +    H⁺ .

1c. HO——R——O⁻BF₃    +    HO⌇O⁺◇ ⟶

HO——R——O⌒⌒⌒O⌇OH    +    ' BF₃ '
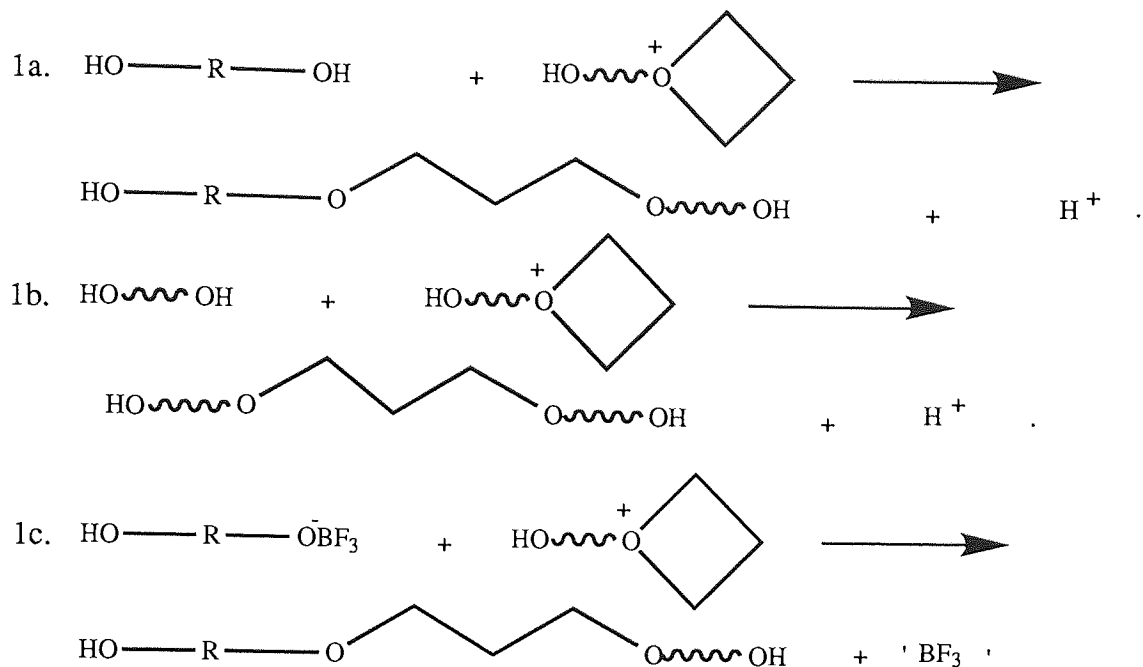
2. Backbiting reactions

2a. HO⌇O⁺◇ ⟶    +    H⁺ .

2b. HO⌇O⌇O⁺◇ ⟶
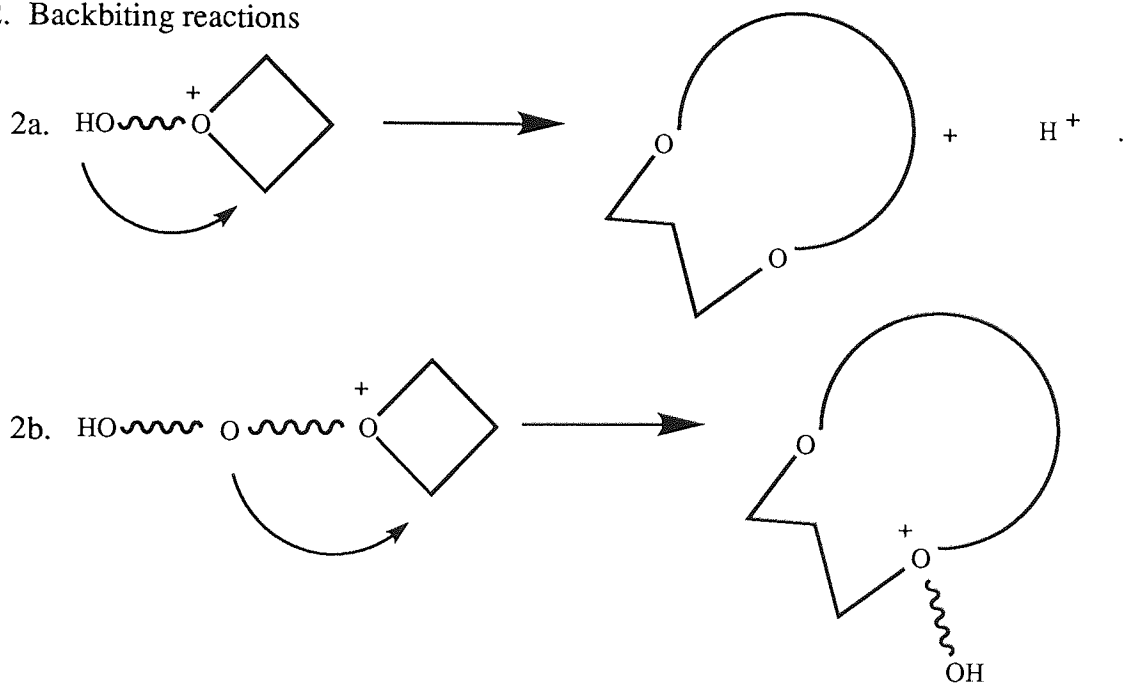
3. Reactions with polar impurities

HO⌇O⁺◇    —HOH→    HO⌇O⌒⌒⌒OH

+    H⁺
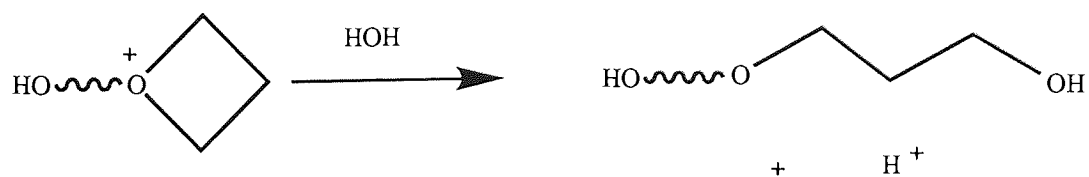
**Scheme 9.** **Transfer and termination processes which may occur in the polymerisation of NIMMO.**

125
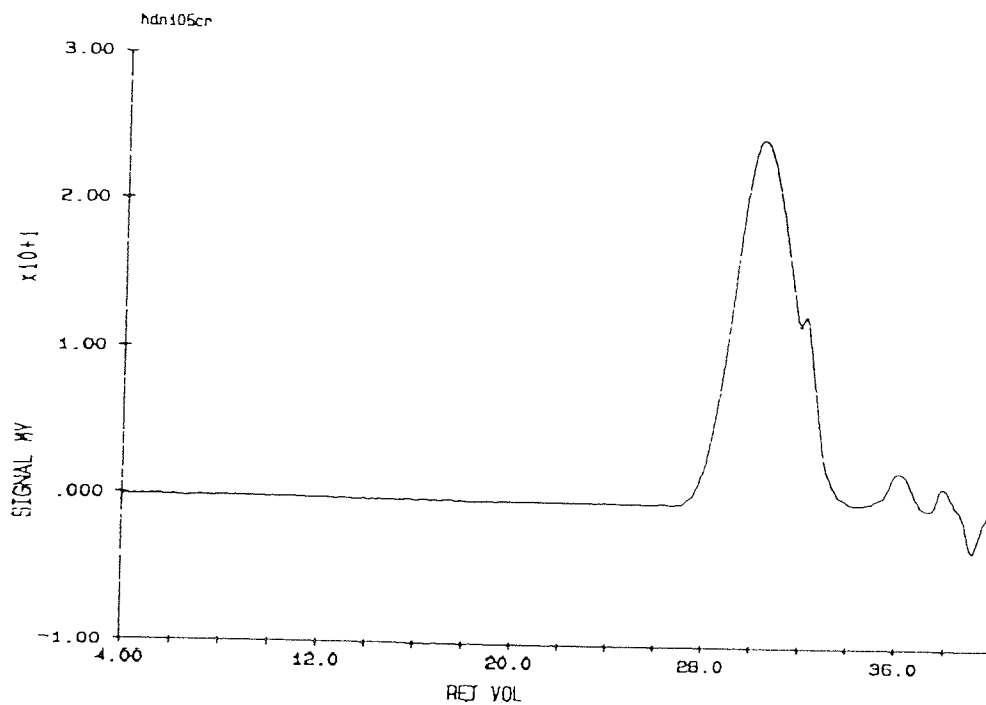
Figure 3.32    SEC trace of hydroxy terminated oligomer of NIMMO
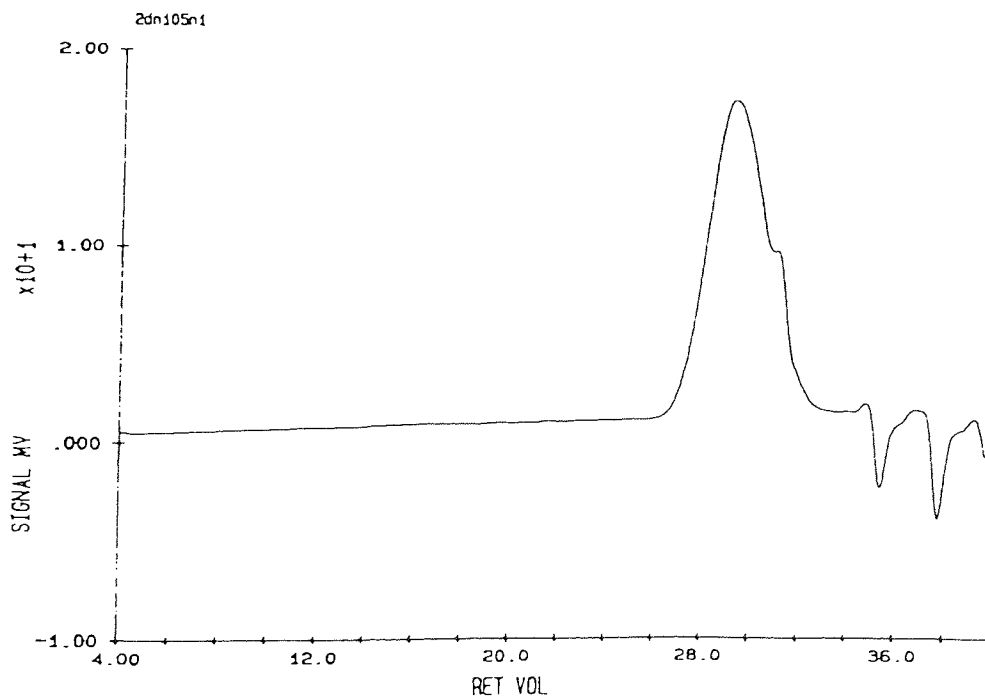


Figure 3.33    SEC trace of nitrato terminated oligomer of NIMMO

nitrating agents with certain polymers[75]. However, a slight increase in molecular weight is observed, which is probably due to the replacement of the hydroxyl proton by the bulkier nitro group. Using the Viskotek system's 'Unical 1' calibration to calculate molecular weights; the number average molecular weight (Mn) of the hydroxyl terminated oligomer of NIMMO was 450, the weight average molecular weight (Mw) was 850 and the dispersity (D) was 1.9. The values of Mn, Mw and D for the corresponding end-nitrated oligomer were calculated as 750, 1450 and 1.9. The dispersities show that the molecular weight distribution has not changed significantly however replacement of two protons from the ends of the linear difunctional oligomer by two $-NO_2$ groups should lead to an increase in molecular weight of only 90. Instead the Mn and Mw values have increased significantly more than 90.

Two explanations may be proposed for this effect. Firstly, the end-nitrated oligomer does not interact as strongly with the size exclusion columns, compared to the hydroxy-terminated oligomer, and is eluted quicker. Secondly, it can be seen that all the peaks of the end-nitrated material, including solvent peaks, have eluted quicker suggesting that there is a slight instrumental error between the two traces. Nevertheless, the compounds prepared, even using the highest Mw value, are less than 10 NIMMO units long indicating that they are oligomers.

This is further confirmed by the $^{13}$C N.M.R. spectrum of the hydroxy-terminated oligomer (figures 3.34 and 3.35) which show the $CH_2OH$ end groups, peaks F in the structure, the in-chain NIMMO $-OCH_2$ (peaks D) and the $-CH_2ONO_2$ peaks (E). From the integral of the $-CH_2OH$ peaks and the in-chain peaks D and E, the value of n in the structure (figure 3.34) is calculated to be 2.7, which gives a value of Mn of about 1180. This should be a reasonably reliable estimate of the molecular weight of the oligomers, and corresponds to about 7.4 NIMMO units including the two at the ends.

The $^{13}$C N.M.R spectra of the NIMMO oligomers also confirm the proposed structures. As indicated on the spectra, all the major peaks can be readily assigned. The absence of peaks at about 30 ppm and 63 ppm (figure 3.34), which would be due
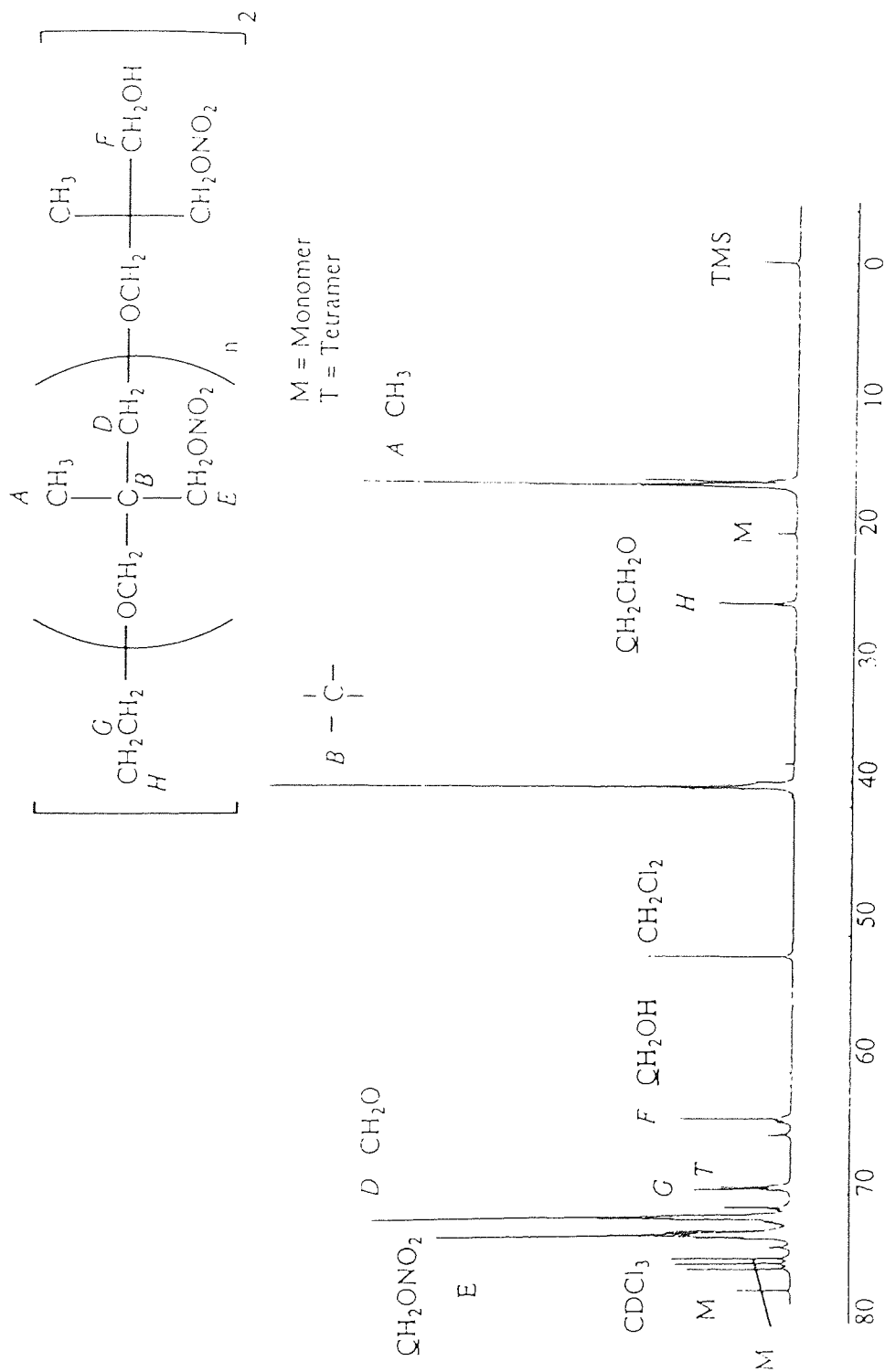
Figure 3.34  $^{13}C$ NMR spectrum of hydroxy terminated NIMMO oligomer
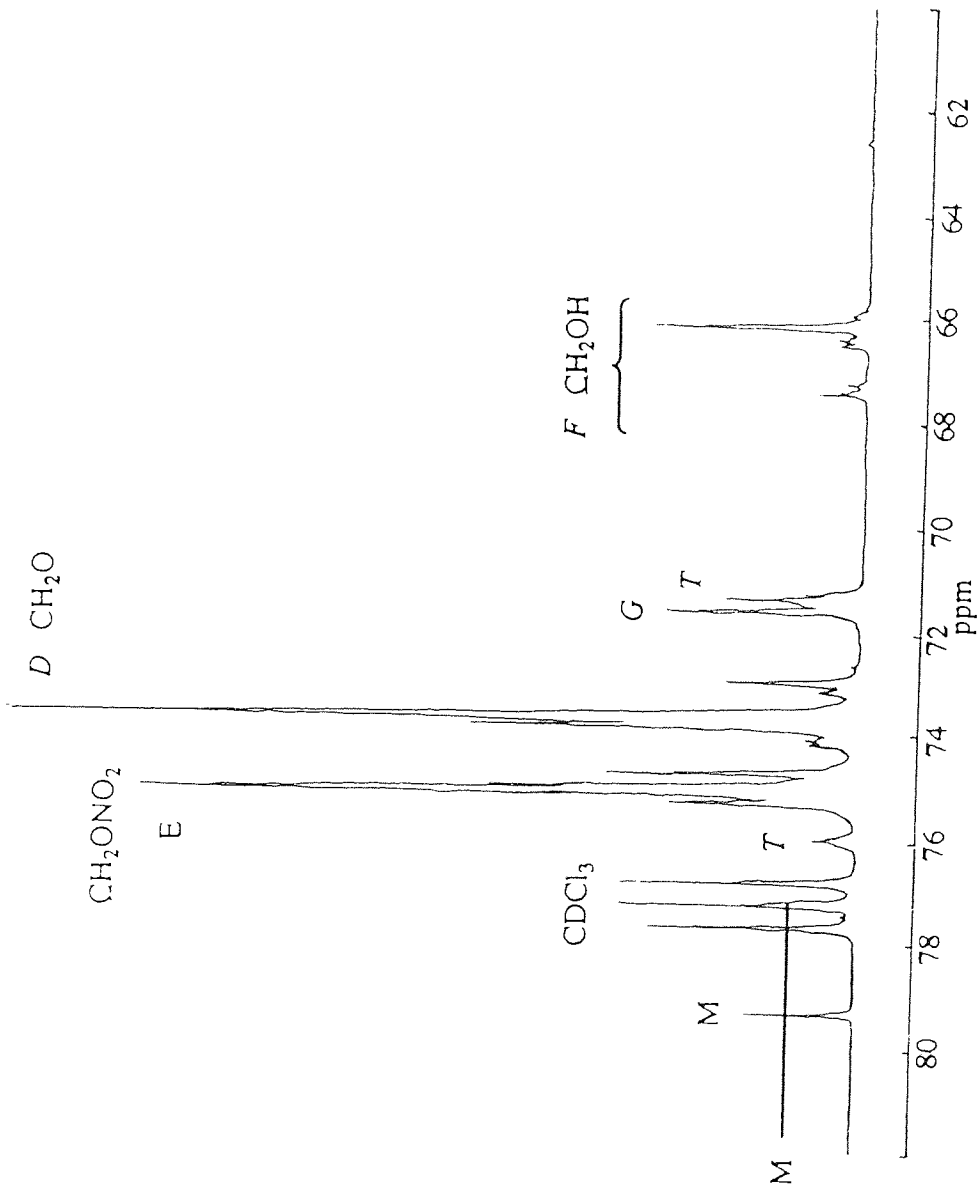
Figure 3.35    Expanded $^{13}C$ NMR spectrum of hydroxy terminated NIMMO oligomer

to 1,4-Butandiol end groups is noteworthy, as polyNIMMO samples prepared by the active chain-end mechanism often show Butandiol end groups. The central -CH$_2$ peaks of the 1,4-Butandiol units (-OCH$_2$CH$_2$CH$_2$CH$_2$O-) appear almost exclusively at about 26 ppm, indicating that they are incorporated into the 'middle' of the chains as -CH$_2$OCH$_2$CH$_2$CH$_2$CH$_2$OCH$_2$ - units rather than as -CH$_2$CH$_2$CH$_2$CH$_2$OH end groups This is characteristic of an activated monomer polymerisation. The samples also show the presence of dichloromethane, monomer and cyclic tetramer.

The corresponding spectra of the end-nitrated oligomer of NIMMO (figures 3.36 and 3.37) are very similar to figures 3.34 and 3.35, as expected. The main difference is that the peaks between 66 and 68 ppm in figures 3.34 and 3.35, which were assigned to the -CH$_2$OH end-groups, have disappeared, indicating their efficient nitration. The end hydroxyl groups are converted to -CH$_2$ONO$_2$ groups and therefore become similar to in chain -CH$_2$ONO$_2$ groups in band E. The fact that bands E and D show several peaks with slightly different chemical shifts, whereas higher molecular weight polyNIMMO shows only one peak for each, is due to the oligomeric nature of the samples.

The infra-red spectrum of the end nitrated NIMMO oligomer (figure 3.39) shows that both the OH bands (3619, 3439 cm$^{-1}$), which are present in the hydroxy terminated oligomer (figure 3.38), have disappeared. This suggests that terminal hydroxy groups have reacted with N$_2$O$_5$ to form nitrato end groups. From the analysis of these compounds the reactions of synthesis are shown in scheme 10.

As the materials are envisaged as plasticisers their thermal properties were studied by D.S.C. The clear, pale yellow liquids show an endothermic transition, glass transition, which is the dominant feature. The hydroxy terminated oligomer (figure 3.40) shows a transition at -33°C while the end-nitrated oligomer (figure 3.41) shows a transition at -39 °C. The lower transition of the end nitrated oligomer may be due to the reduction in hydrogen bonding interactions between the hydroxy groups upon nitration. It should also be noted that the glass transition temperature of a polymer rises with increasing

molecular weight[76] and, indeed, the Tg of linear difunctional polyNIMMO of molecular weight 4000 usually has a transition at about -25 °C. Another feature, probably, leading to a slightly lower Tg for these compounds is the presence of small amounts of cyclic species, which may also be acting as plasticisers.

$$HBF_4 \quad + \quad HOCH_2CH_2CH_2CH_2OH$$
$$(1 \text{ mol}) \qquad\qquad (> 5 \text{ mol excess})$$

Slow, continuous
incremental monomer
addition

$CH_2Cl_2$

Hydroxy terminated oligomer of NIMMO

$N_2O_5 \,/\, CH_2Cl_2$

$+ \; HNO_3$

Nitrato Terminated oligomer of NIMMO

where $x + y \leq 10$
and $R = CH_2ONO_2$
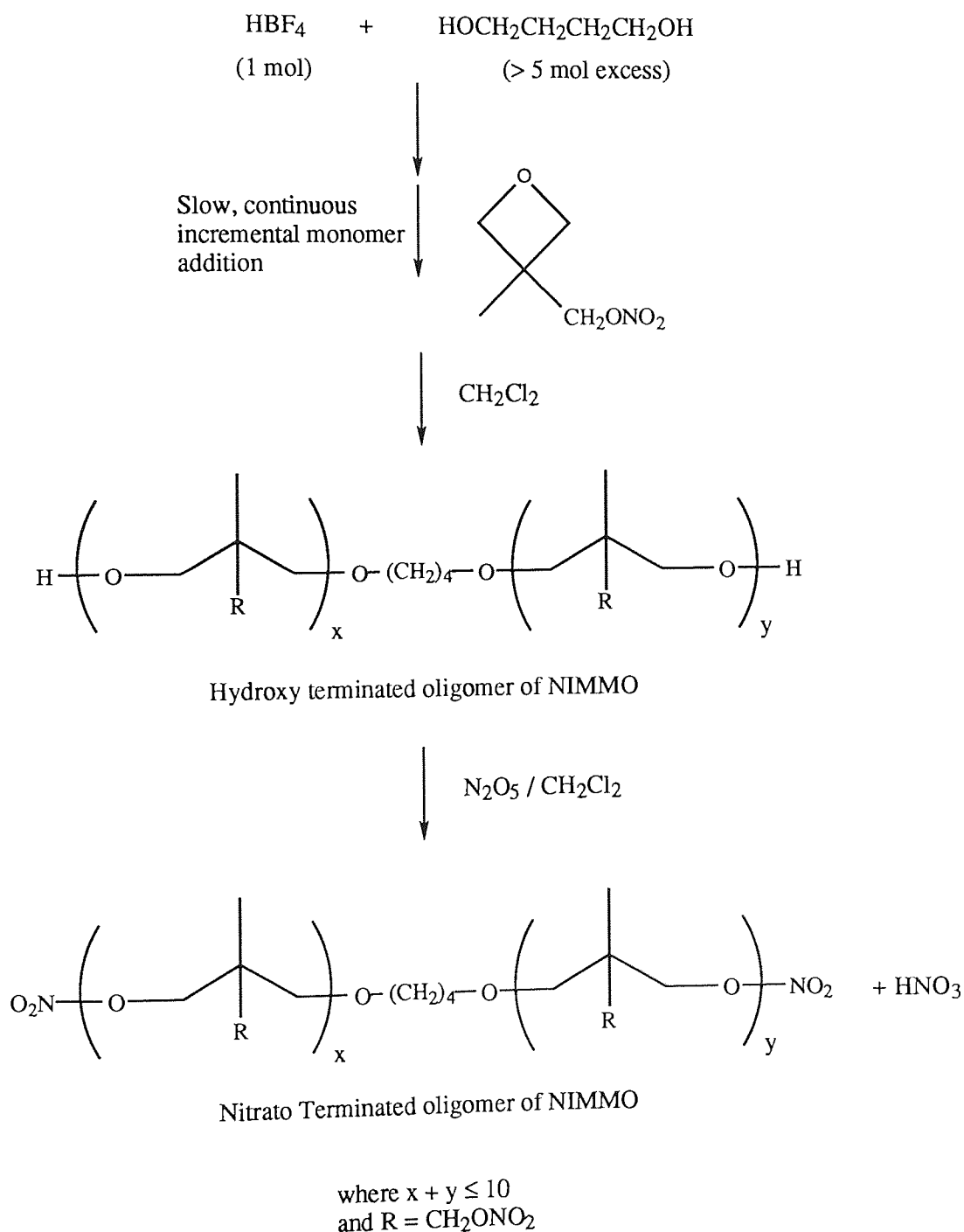
**Scheme 10. The activated monomer synthesis of hydroxy terminated oligomer of NIMMO followed by end-nitration to form the nitrato terminated oligomer.**

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OH peaks should appear here

-OCH$_2$CH$_2$CH$_2$CH$_2$O-

M

M
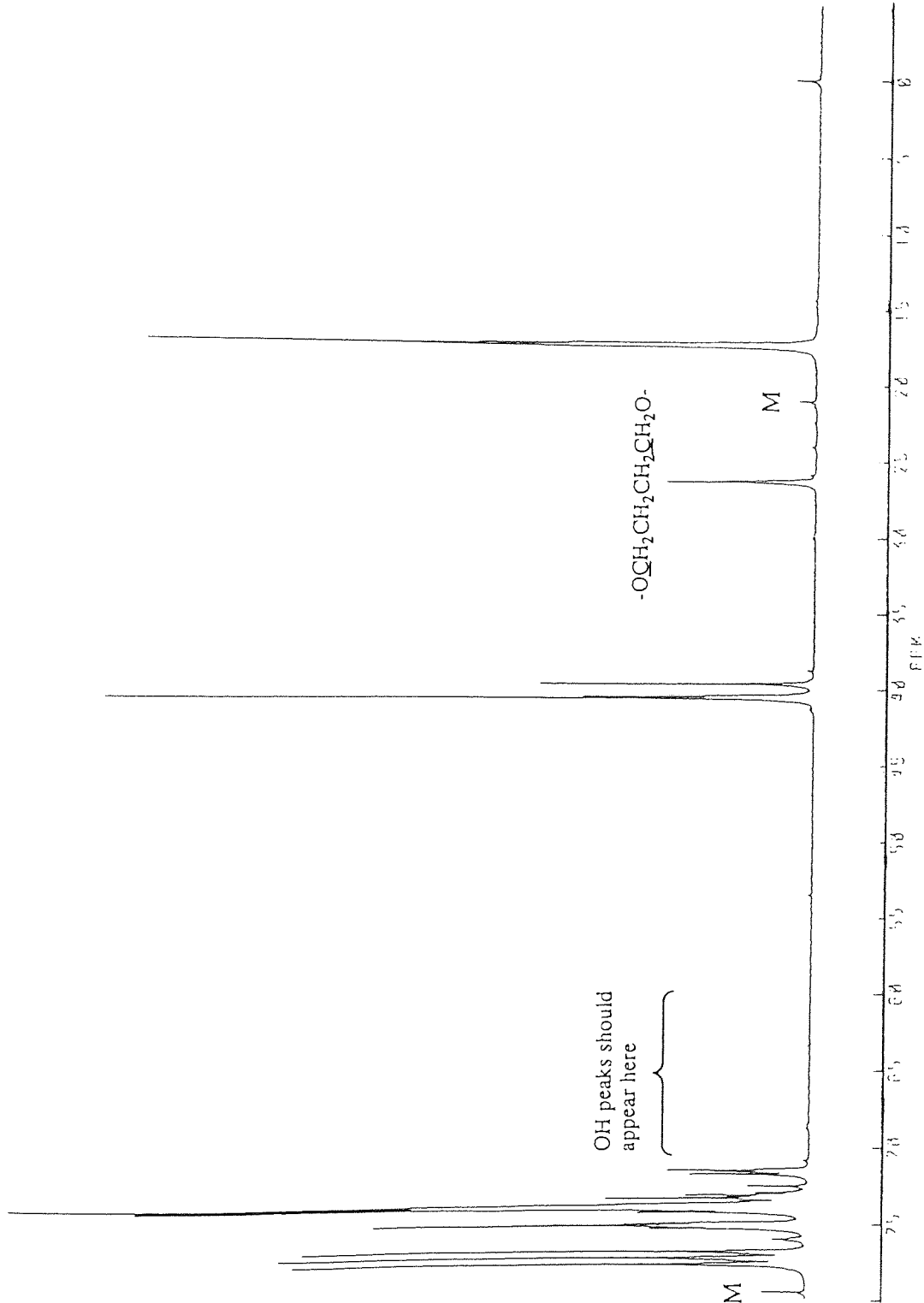
Figure 3.36    $^{13}$C NMR spectrum of nitrato terminated NIMMO oligomer
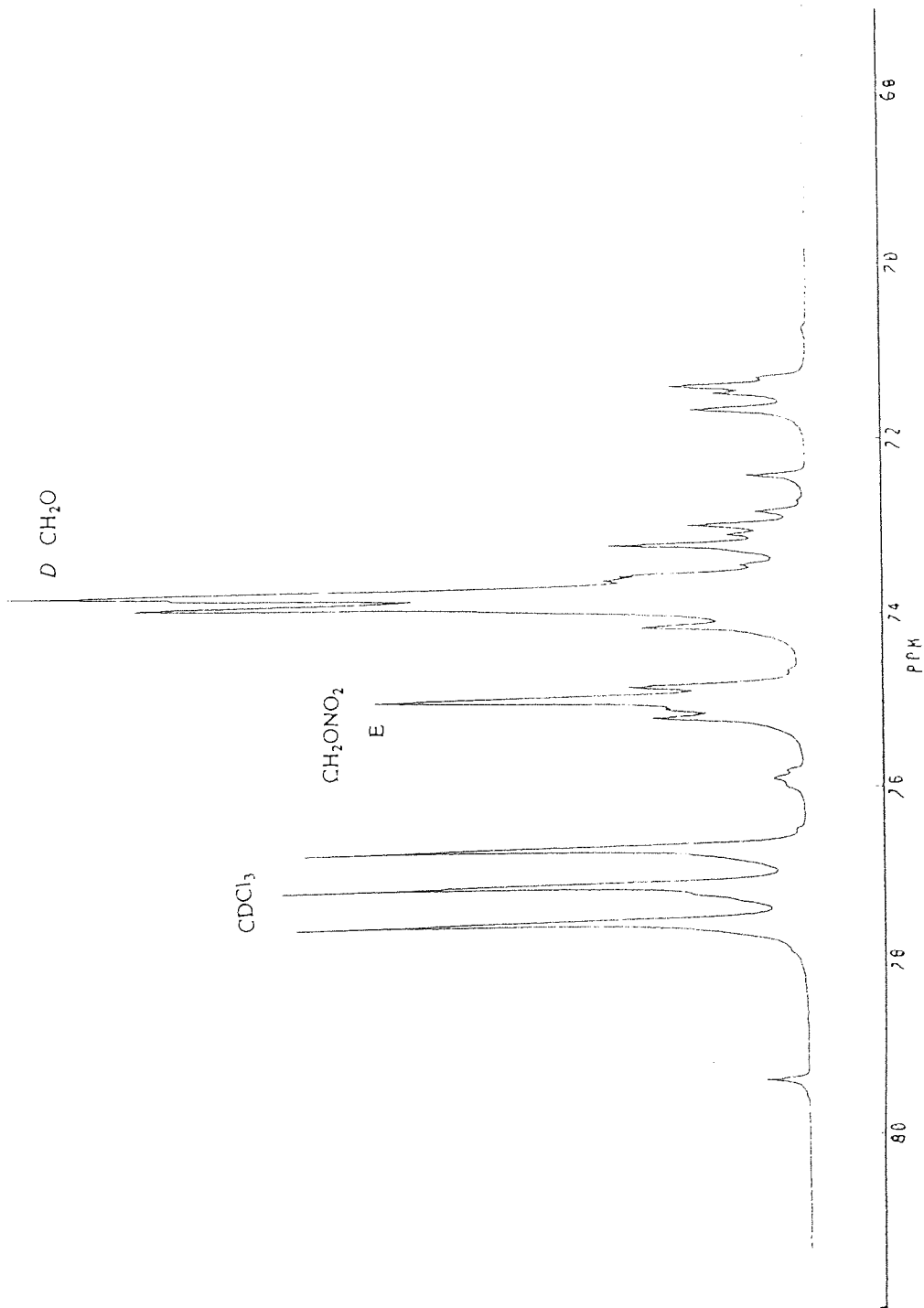
Figure 3.37 Expanded $^{13}C$ NMR spectrum of nitrato terminated NIMMO oligomer

133
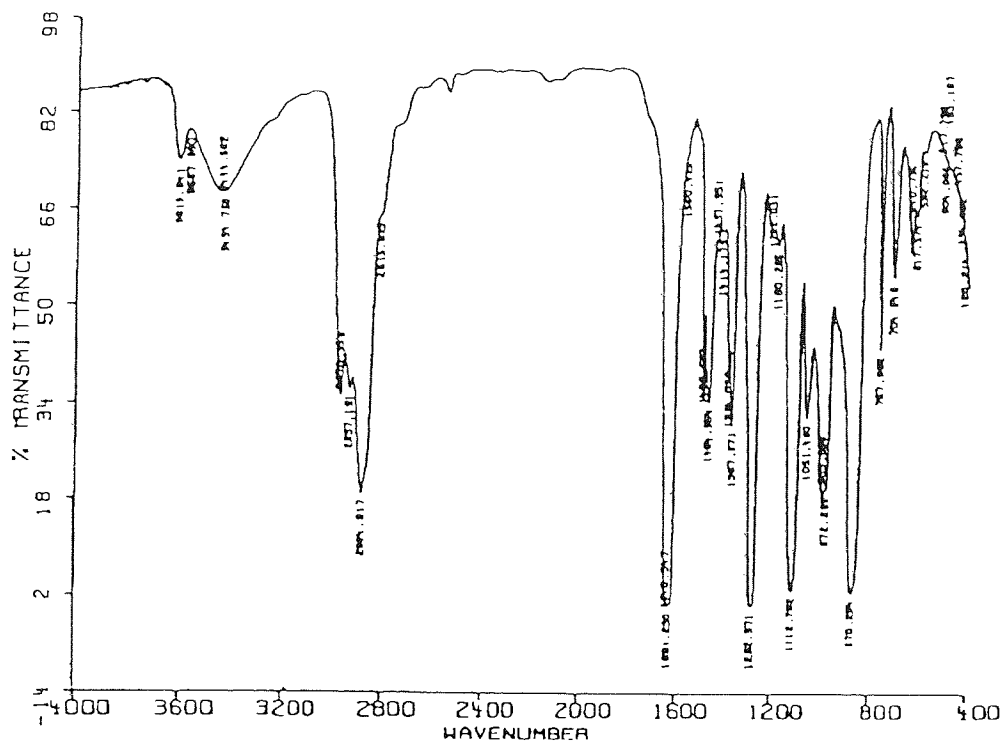
Figure 3.38    Fourier transform I.R. spectrum of hydroxy telechelic oligomer of NIMMO
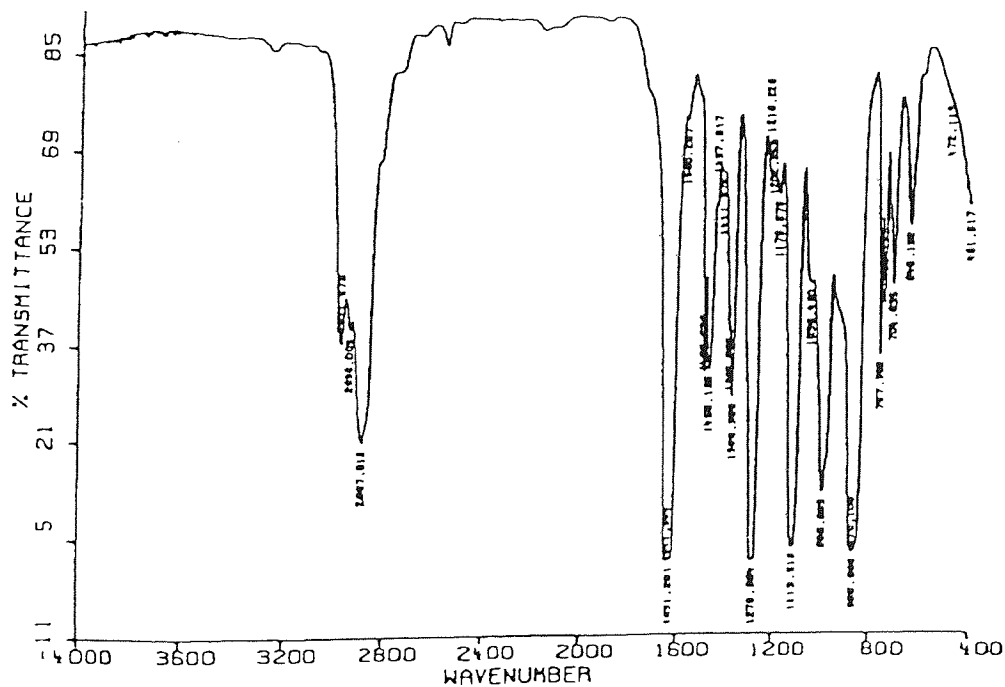


Figure 3.39    Fourier transform I.R. spectrum of nitrato telechelic oligomer of NIMMO

SMPL ID : hdpn105cr
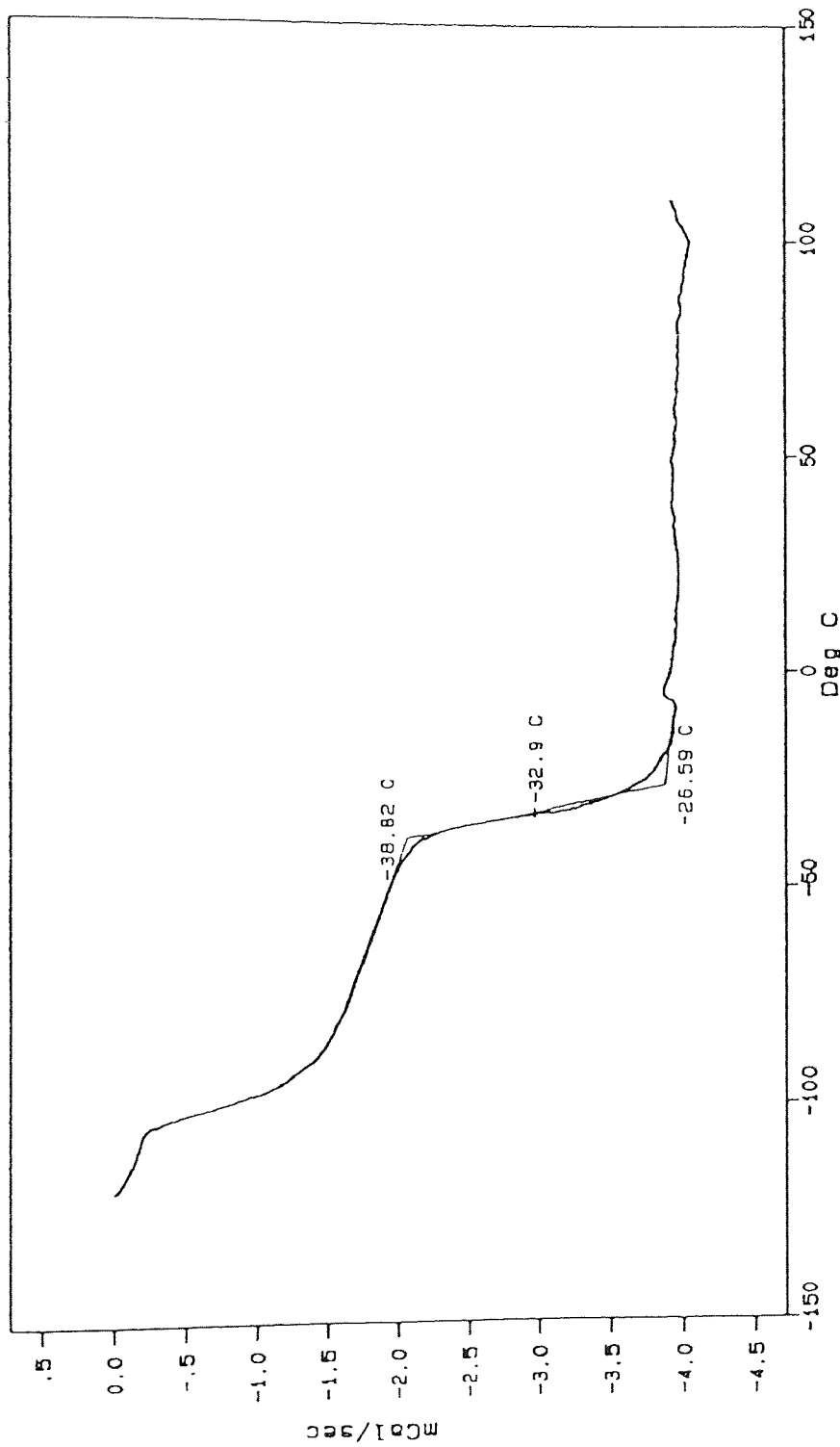


Figure 3.40    DSC trace of hydroxy terminated difunctional oligomer of NIMMO

SMPL ID : 1nimmoplas2
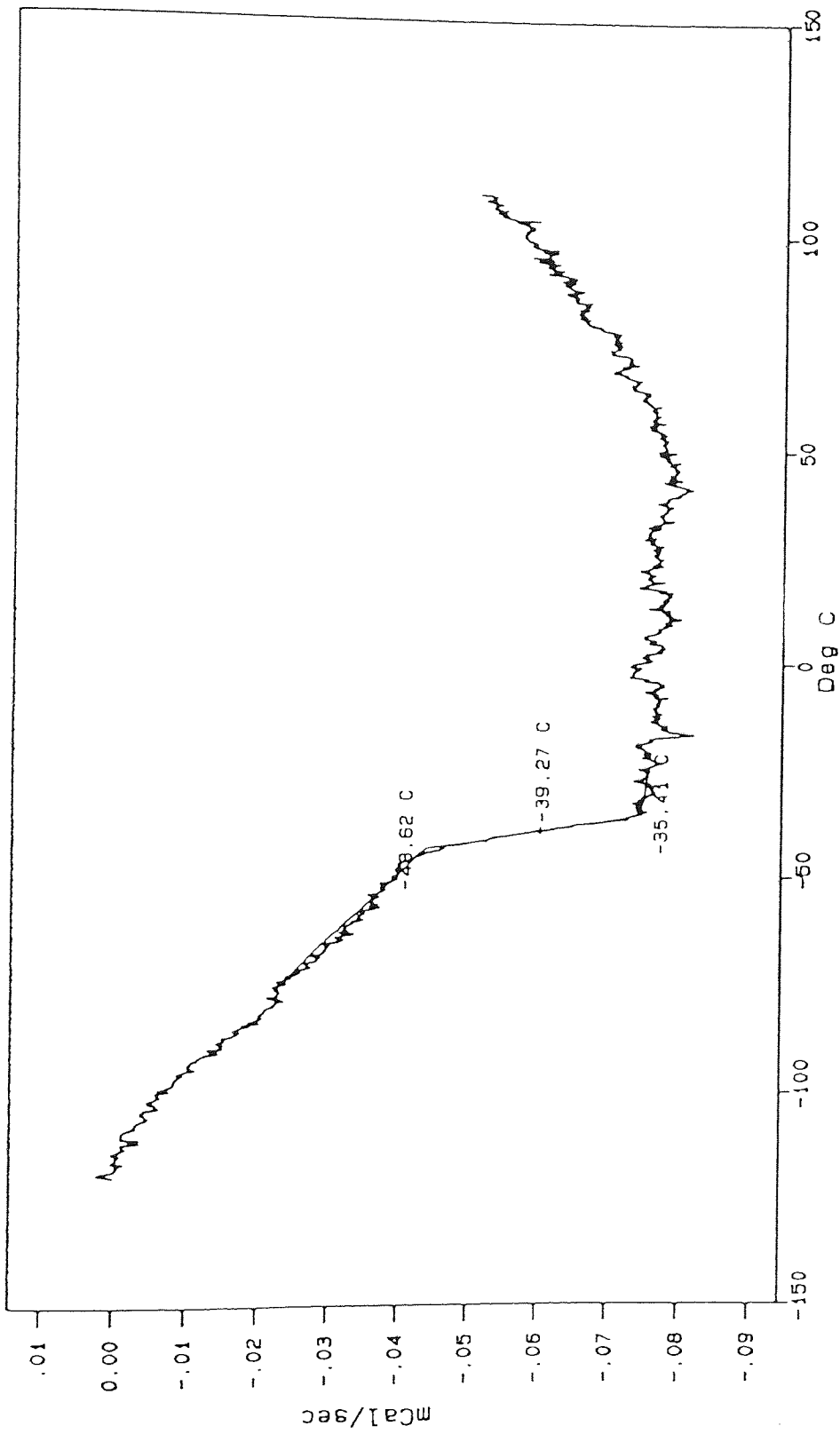


Figure 3.41   DSC trace of end-nitrated difunctional oligomer of NIMMO

## 3.2    Materials based on glycidyl nitrate (GLYN).

The synthesis of polyGLYN by the AMM is discussed followed by attempts to modify the hydroxy ends of the polymer.

### 3.2.1.  PolyGLYN by activated monomer mechanism.

Poly(glycidyl nitrate), which is also known as POWA 3, was analysed by size exclusion chromatography (figure 3.42), to determine its molecular weight distribution, and by N.M.R. (figures. 3.43 and 3.44) and I.R. spectroscopies (figure 3.45) to ascertain its chemical structure.  The thermal behaviour of the polymer is of particular interest and the differential scanning calorimeter results (figure 3.46) give some indication of this.  The chemical structure of the polymer and its relationship with the conditions are discussed because these are very closely tied to the mechanism of polymerisation .

Glycidyl nitrate is polymerised by a cationic technique where the conditions are carefully controlled so that the mechanism of propagation is altered from the conventional 'active chain-end' (ACE), used for cyclic ethers, to an activated monomer[92].  The result of this is an hydroxytelechelic polymer with a narrow molecular weight distribution i.e. almost oligomer and monomer-free product. as shown in figure 3.42.  This is a clear advantage insofar as there would be little unreacted monomer in the final propellant or explosive composition which may cause an increase in sensitivity.  Hence, using this method the small amount of monomer (<4%) is easier to remove and in some cases the monomer level may be low enough so that a purification step is not required.

The S.E.C. trace shows a polymer of number average molecular weight (Mn) of 1300, a weight average molecular weight (Mw) of 2000 and dispersity of 1.5.  These values are Viscotek's 'universal calibration' equivalents.  The dispersity, although close to those observed for 'living' polymerisation systems, which typically have values less
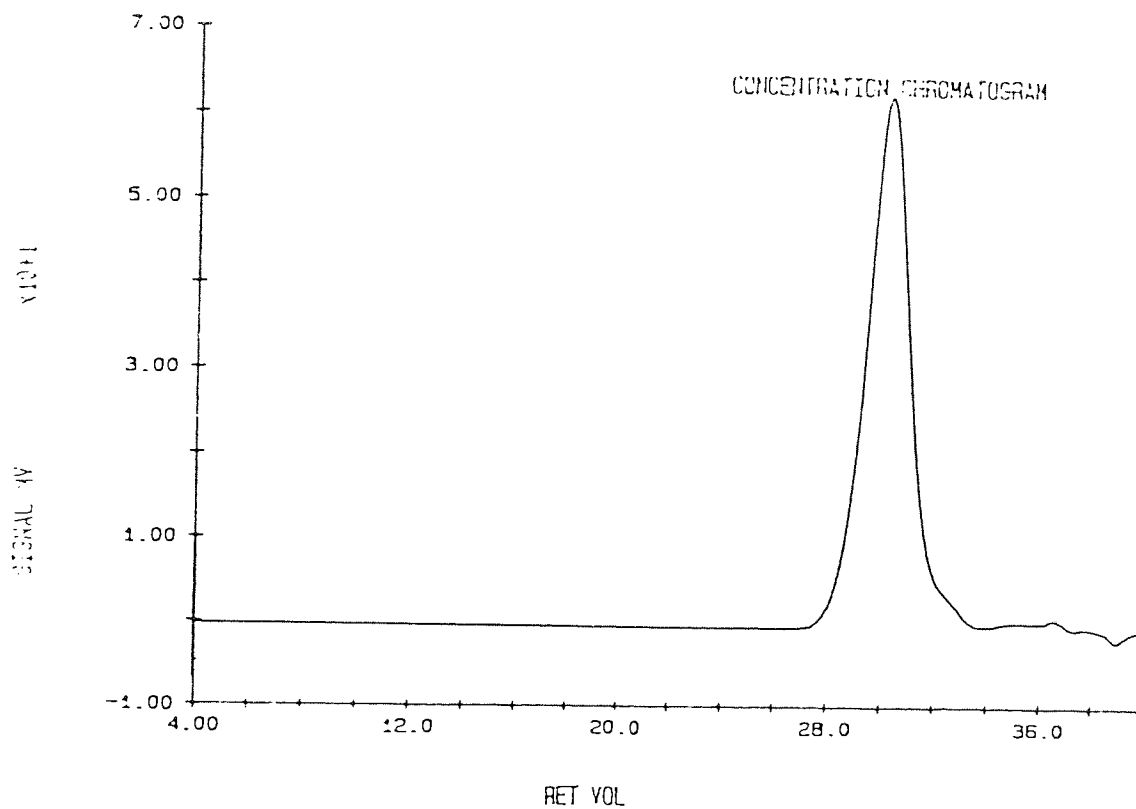
**Figure 3.42** <u>SEC trace of polyGLYN sample free of oligomer and monomer contamination</u>

'Universal Calibration' equivalent molecular weights (as opposed to THF equivalent) for the sample shown above are:

$$M_n = 1300$$
$$M_w = 2000$$
$$D = 1.5$$
$$M_p = 1750$$

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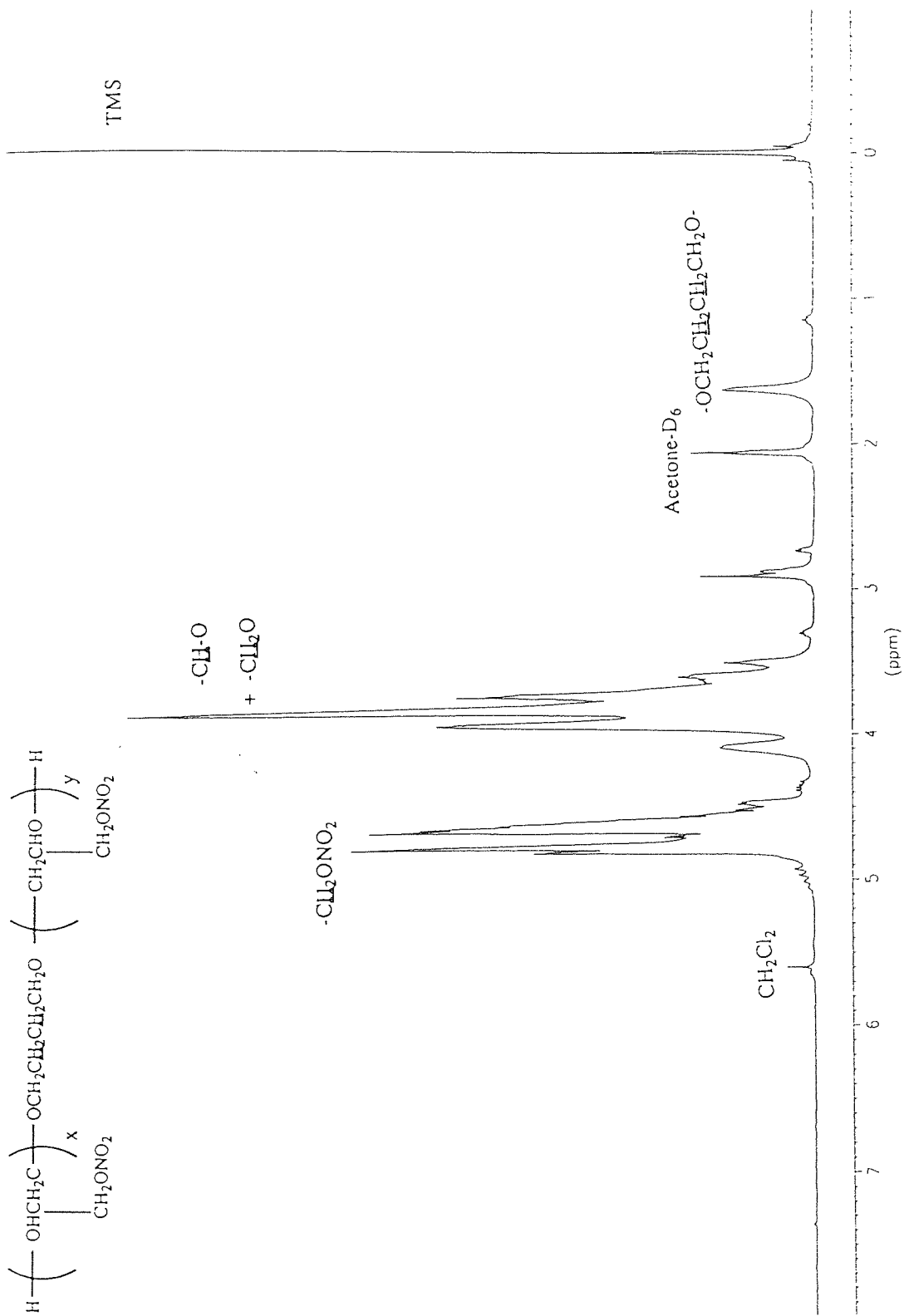
Figure 3.43   $^1$H NMR spectrum of poly(glycidyl nitrate) Batch 3.17
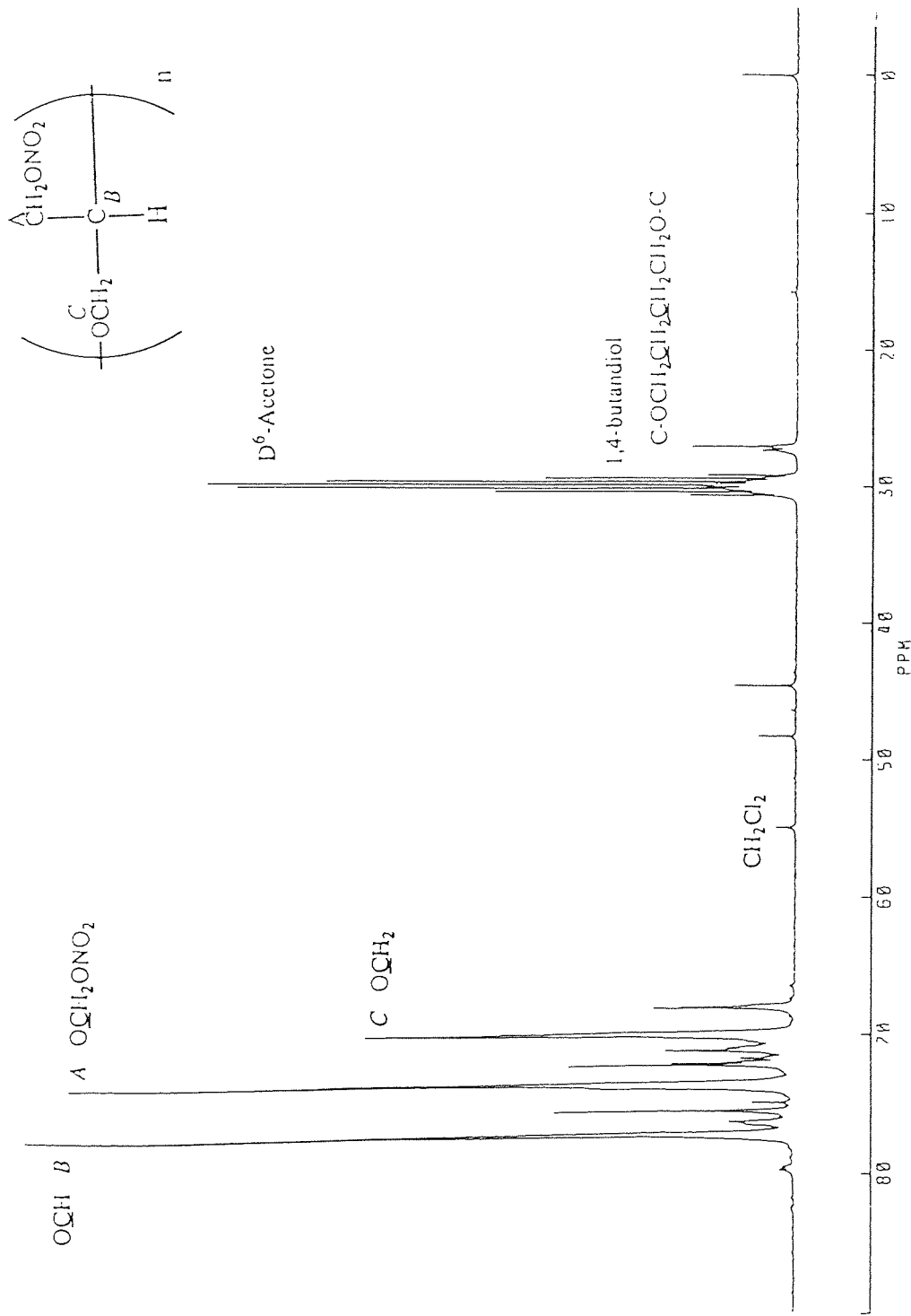
Figure 3.44   $^{13}C$ NMR spectrum of poly(glycidyl nitrate) Batch 3.17
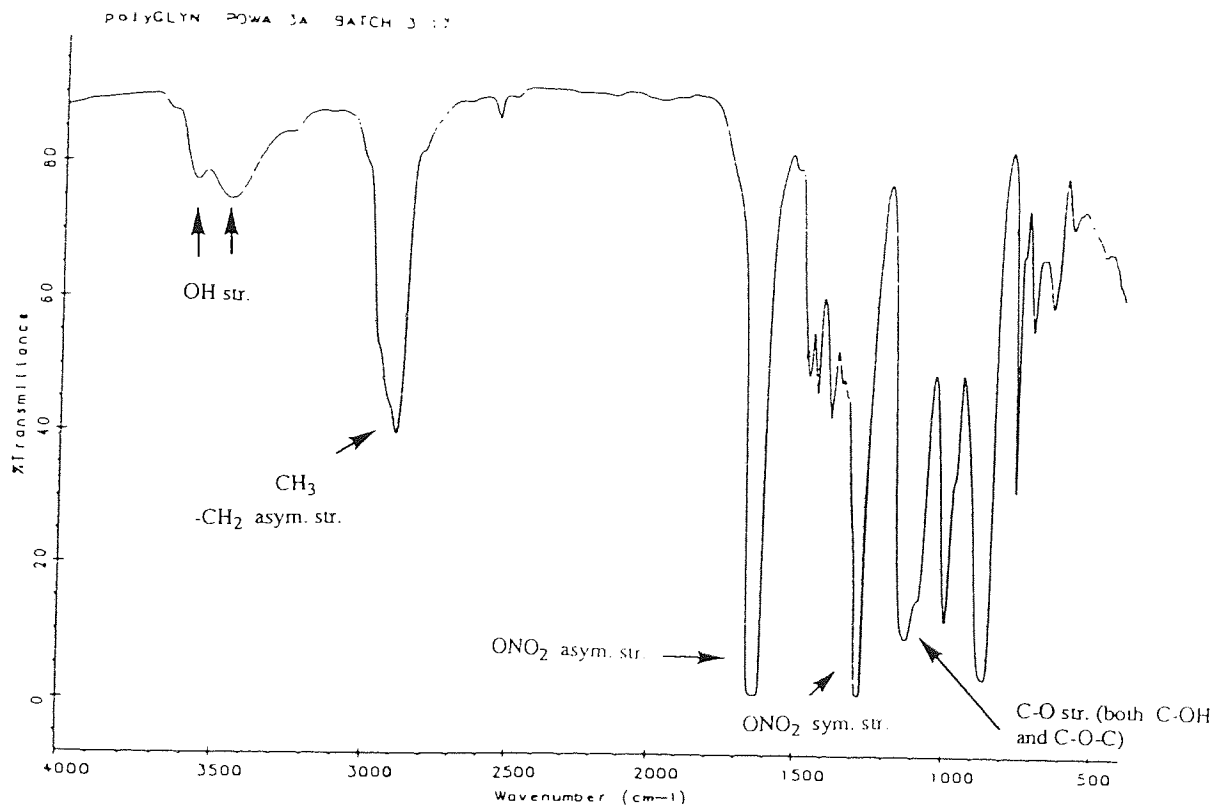
Figure 3.45    Fourier Transform I.R. spectrum of poly(glycidyl nitrate) Batch 3.17

```
DSC  (PL)
STANTON REDCROFT
```

mWatts

0

−6

−68                    Deg C         18

−38.91 C

−35.21 C

−31.9 C
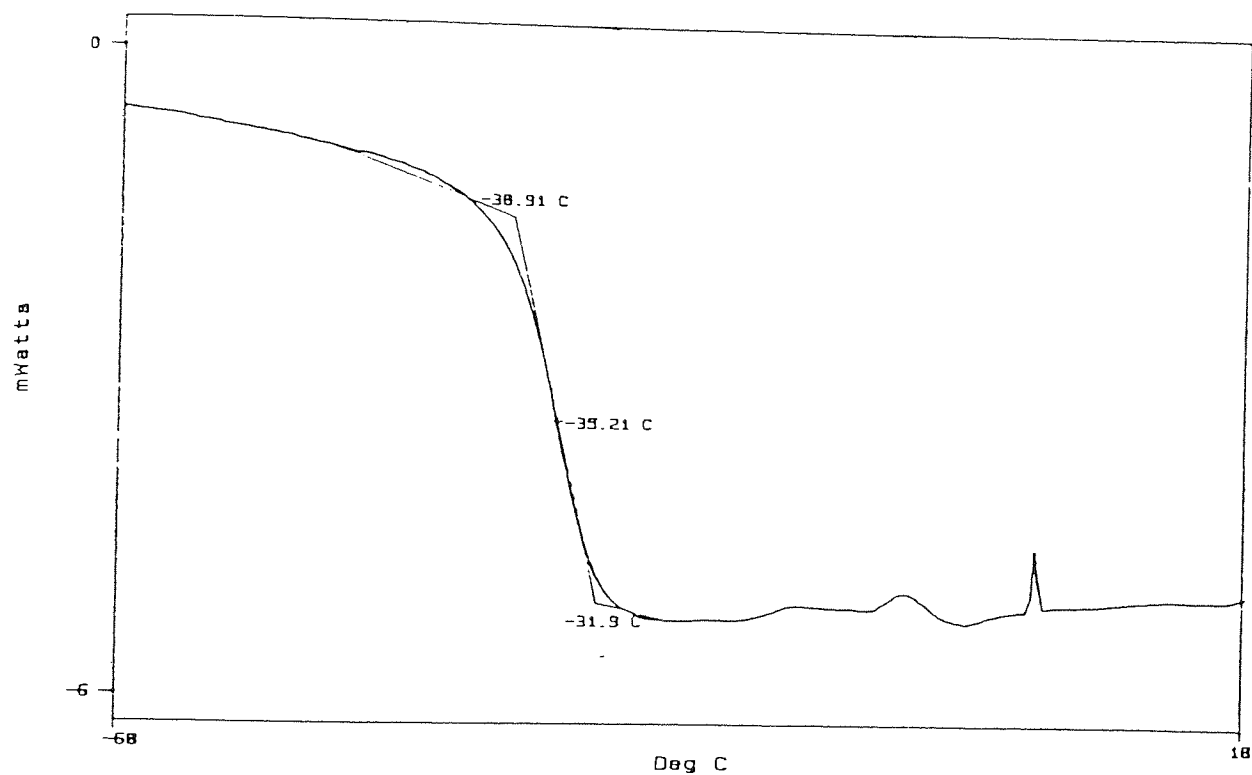
Figure 3.46    DSC trace of poly(glycidyl nitrate) Batch 3.17 showing the glass transition temperature at -35°C

The heating ramp rate was set at 10°C per minute and data points were collected between the temperatures of -120°C to +110°C.

than 1.1, in addition to the fact that the molecular weight observed is less than the expected Mn of 3600, indicates that this is not an example of a living chain growth system with fast propagation. Moreover, due to the pre-mixing of the catalyst with the butandiol and the incremental addition of monomer the system is not a living system with slow initiation. It is, more likely, to be a step growth system where the reaction of the activated monomer with the hydroxyl group and the subsequent elimination of the proton may be regarded as a condensation reaction. However, number average molecular weights of up to 3500 have been achieved.

Further evidence of condensation reactions is provided by the N.M.R. spectra, figures 3.43 and 3.44, which show that the butandiol fragment is in the centre of a polyGLYN chain and that the terminal hydroxyl groups are associated with in-chain monomer units. In the case of the polymerisation of NIMMO, by a more conventional active chain-end mechanism, propagation sometimes takes place from one end of chain and the butandiol fragment is then observed at the end of the chains[93]. The mechanism by which the polymerisation of glycidyl nitrate proceeds is believed to be as follows:

$$HO \diagdown R \diagup OH \quad + \quad HBF_4 \quad \longrightarrow \quad HO \diagdown R \diagup \overset{+}{O} \diagup H \quad BF_4^- \qquad (3.5)$$

Excess        Catalytic                H

$$HO \diagdown R \diagup \overset{+}{O} \diagup H \quad BF_4^- \quad + \quad H_2C \overset{}{\diagdown}O\diagup CHCH_2ONO_2 \quad \longrightarrow$$

             H

$$HO \diagdown R \diagup OH \quad + \quad H_2C \overset{}{\diagdown}O\diagup CHCH_2ONO_2 \quad + \quad BF_4^- \qquad (3.6)$$

                                    $\overset{+}{O}$    (A)

                                    H

Activated monomer

$$HO{-}R{-}OH \quad + \quad H_2C{-}CHCH_2ONO_2 \longrightarrow$$

(with epoxide $O{+}{-}H$)

$$HO{-}R{-}O{\frown}{\frown}OH \quad + \quad HBF_4 \qquad (3.7)$$
$$\underset{CH_2ONO_2}{}$$

$$HBF_4 \quad + \quad H_2C{-}CHCH_2ONO_2 \longrightarrow$$

$$H_2C{-}CHCH_2ONO_2 \quad + \quad BF_4^- \qquad (3.8)$$
(with $O{+}{-}H$)

$$HO{-}R{-}O{\frown}{\frown}OH \quad + \quad H_2C{-}CHCH_2ONO_2 \longrightarrow$$
$$\underset{CH_2ONO_2}{} \qquad (O{+}{-}H)$$

$$HO{\frown}{-}O{-}R{-}O{\frown}{\frown}OH \quad + \quad 'H^+ ' \quad (3.9)$$
$$\underset{CH_2ONO_2}{} \qquad \underset{CH_2ONO_2}{}$$

$$HO{\frown}{-}O{-}R{-}O{\frown}{\frown}OH \quad + \quad (x{+}y{-}2)\, H_2C{-}CHCH_2ONO_2$$
$$\underset{CH_2ONO_2}{} \qquad \underset{CH_2ONO_2}{} \qquad (O{+}{-}H)$$

$$\longrightarrow \quad H{-}\left(O{\frown}\right)_x O{-}R{-}O\left(\frown O\right)_y{-}H \qquad (3.10)$$
$$\underset{CH_2ONO_2}{} \qquad \qquad \underset{CH_2ONO_2}{}$$

polyGLYN

This type of polymerisation is known as the activated monomer mechanism (AMM) and takes its name from the protonated monomer, species A, which is regenerated after each successive propagation step. In the conventional ACE type mechanism, species A is also generated but the conditions are such that it reacts further with monomer[94]:

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$$HBF_4 \quad + \quad H_2C\underset{O}{\overset{\diagup\diagdown}{-}}CHCH_2ONO_2 \quad \longrightarrow \quad H_2C\underset{\underset{H}{\overset{|}{O+}}}{\overset{\diagup\diagdown}{-}}CHCH_2ONO_2 \quad BF_4^-$$

$$H_2C\underset{\underset{H}{\overset{|}{+\,O}}}{\overset{\diagup\diagdown}{-}}CHCH_2ONO_2 \quad BF_4^- \quad + \quad n\ H_2C\underset{O}{\overset{\diagup\diagdown}{-}}CHCH_2ONO_2 \quad \longrightarrow$$

$$H\left(O\diagdown\diagup\diagdown\right)_n \overset{CH_2ONO_2}{\underset{}{\overset{+}{O}}}\diagup CH_2ONO_2 \quad BF_4^- \qquad (3.11)$$
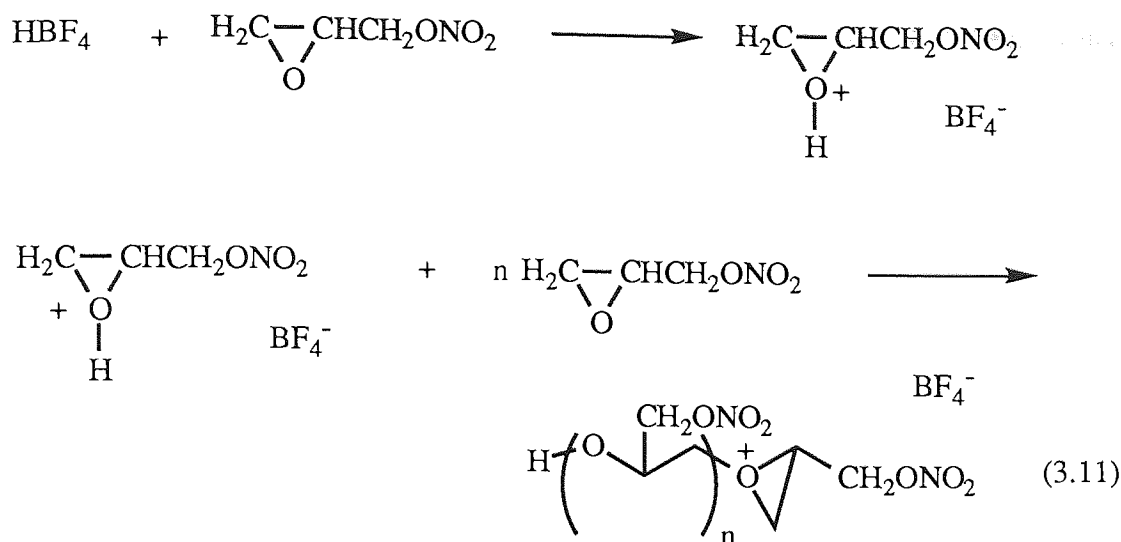
Active chain-end (C)

Under ACE conditions species C can undergo internal back-biting or end-biting reactions to produce cyclic species, react with impurities causing termination and/or react with counter-ion also causing termination or dormancy. In the case of glycidyl nitrate, ACE experiments produced a very low yield of polymer probably due to the aforementioned termination reactions. In addition to this as it is well known that neat oxiranes polymerise explosively by an ACE mechanism and that it is difficult to control molecular weight distributions. This mode of propagation was considered unsuitable for GLYN. Hence, the AMM was developed to polymerise GLYN because it enables control of the exotherm and molecular weight ($\leq 3500$) to produce an $\alpha,\omega$-hydroxytelechelic polymer, free of oligomer contamination. The two key factors in achieving this are the maintenance of at least a ten-fold excess of hydroxyl groups over the protonic acid catalyst, tetrafluoroboric acid, and the slow addition of monomer solution over at period from 16 to 40 hours.

The maintenance of an excess of hydroxyl groups over protonic acid ensures that the protonated monomer reacts with the hydroxyl groups. If the ratio of OH:$H^+$ is near to 1:1 then the probability of the protonated monomer reacting, within a given time interval, with the hydroxyl group is reduced. Consequently, the protonated monomer level builds up to the extent that further incoming monomer reacts with species A by a predominantly ACE mechanism. The slow addition of monomer helps to suppress

ACE type propagation because the monomer is fed in at a rate such that the activated monomer cannot react with unprotonated monomer. In other words the rate of monomer addition has to be less than the rate of monomer protonation and subsequent reaction with an hydroxyl group.

The result of slow monomer addition and an excess of hydroxyl group over the acid catalyst is the formation of linear polyGLYN chains with hydroxyl end groups. The polymers do have disadvantages due to the nature of the monomer and to limitations of the AMM. Firstly, secondary hydroxyl groups are formed predominantly as nucleophilic attack by the oxygen atom of the hydroxyl group of an existing chain occurs on the least hindered carbon of the monomer. Secondly, molecular weights greater than 3500 (Mn) are very difficult to achieve. The reasons for this are probably due to impurities in the monomer feed, alcohol, catalyst and the presence of adventitious moisture in the apparatus. Thirdly, the recovered yield of polymer is around 80%. Clearly, a certain amount of material is lost in the work-up, especially through dissolution of low molecular weight alcohols in water. In addition to this conversion from monomer to polymer/oligomer is ca 95% (by area of unreacted monomer peak from S.E.C.) which necessitates the precipitation stage to reduce monomer level to acceptable quantities for formulations and sale. Work is under progress to improve conversion as well as to reduce unreacted monomer levels so that a precipitation step is not necessary. This should lead to a significant saving in costs and a reduction in the overall price of the binder. Despite these difficulties concerning the AMM, an energetic polymer with variable functionality, molecular weight and, therefore, viscosity suitable for formulations is preparable.

### 3.2.2. End-Capping of PolyGLYN.

The need to end-cap polyGLYN has arisen because workers attempting to cure the polymer using a conventional isocyanate system e.g.

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$$3 \text{ HO}\!\sim\!\!\sim\!\!\sim\!\!\sim\!\text{OH} \quad + \quad 2 \overset{\displaystyle \text{NCO}}{\underset{\displaystyle |}{\text{OCN}\!-\!\!-\!\text{R}\!\sim\!\!\sim\!\text{NCO}}} \longrightarrow$$

$$\sim\!\!\sim\!\text{O}\!-\!\!-\!\overset{\displaystyle O}{\overset{\displaystyle \|}{\text{C}}}\!-\!\!-\!\underset{\displaystyle \underset{\displaystyle H}{|}}{\text{N}}\!-\!\!-\!\text{R}\!-\!\!-\!\underset{\displaystyle \underset{\displaystyle H}{|}}{\overset{\displaystyle \overset{\displaystyle \text{NCO}}{|}}{\text{N}}}\!-\!\!-\!\underset{\displaystyle \underset{\displaystyle O}{\|}}{\text{C}}\!-\!\!-\!\text{O}\!\sim\!\!\sim \qquad (3.12)$$
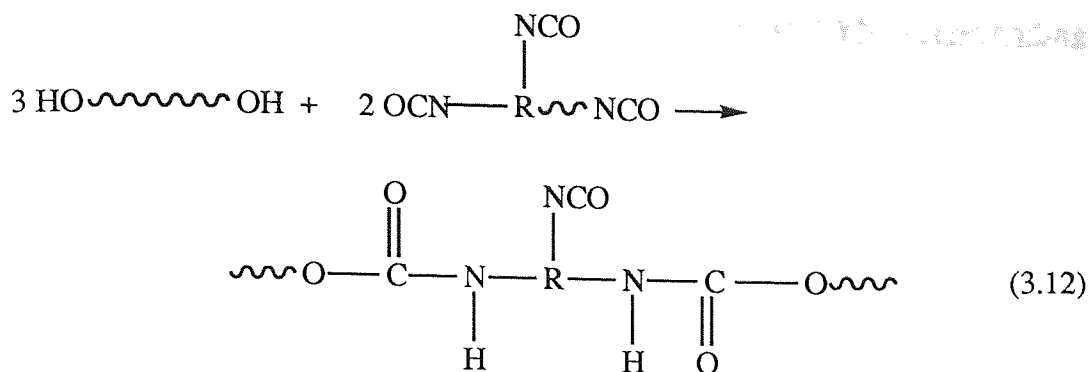
cross-linked rubber.
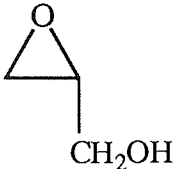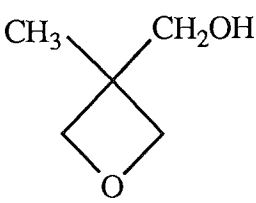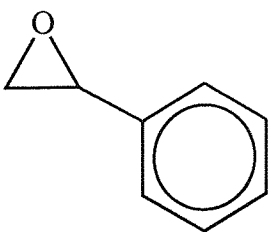
have reported that significant gassing occurs because of the relatively low reactivity of the GLYN ends. Most of the hydroxyl groups are secondary and are also likely to be deactivated by the proximity of the $-ONO_2$ group, which has a negative inductive effect. Owing to this low reactivity, moisture present in the mixture reacts preferentially with the isocyanate causing gassing e.g.

$$H_2O \quad + \quad RNCO \quad \longrightarrow \quad RNH_2 \quad + \quad CO_2 \uparrow \qquad (3.13)$$
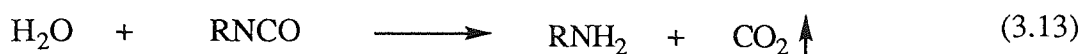
Recent studies of rigorously dried and cured samples of polyGLYN have shown an inherent instability. After storage of about a year at room temperature, the rubber degrades to become a viscous liquid of the same consistency as the initial polymer but further storage does not change the viscosity[102]. The exact nature of the degradation is not known and work is in progress to elucidate this. Nevertheless, as polyNIMMO, a material very similar to polyGLYN, does not show the same behaviour, it has been speculated that the nitrate ester group nearest the urethane link destabilises it, causing degradation. To overcome these problems controlled end-capping, where only 2 to 3 different monomer units are attached to the ends, has been suggested. Initially, it was expected that sequential addition of the second capping monomer in an AM system would enable this.

As the S.E.C. and N.M.R. results indicate, the degree of end-capping achieved is low, although quantitative analysis is difficult. Table 8 shows the end-capping monomers corresponding to the sample name.

**Table 8.** Monomers used to end-cap and block-cap polyGLYN corresponding to sample name and conditions.

| Sample Name | End-Capping Monomer | Polymerisation Type | Comments |
|---|---|---|---|
| POWA 3A | - | AMM | [a]PolyGLYN used as starting material for samples |
| HDGN06CR | Oxetane | AMM | Sequential |
| HDGN09CR | Oxetane | AMM | Repeat experiment |
| SWGN02CR[a] | Glycidol <br><br> $\triangle$ with O and CH$_2$OH | AMM | Low yield 7%, perhaps glycidol helps to solubilise polymer in water, hence lost during work-up. |
| SWGN05C2[a] | 3,3-(hydroxymethyl) methyl oxetane (HIMMO) <br><br> CH$_3$ CH$_2$OH structure with O | AMM | Cross-linked sample, mixture of CH$_2$Cl$_2$ soluble and insoluble fractions. Two peaks one at exclusion limit observed on S.E.C. |
| SWGN09CR[a] | Styrene Oxide <br><br> epoxide with phenyl structure | AMM | OH:H$^+$ ratio, 18:1 mol. Styrene oxide added over 4 hours, 20 % w/v soln. OH:styrene oxide ratio, 1:8 mol. Temperature =17 °C |
| SWGN03CR[a] | NIMMO | AMM | Added over 32 h, 20% w/v soln. |
| SWGN04CR[a] | NIMMO | ACE | BF$_3$.OEt$_2$:OH ratio $\approx$ 3:1 mol |
| HDGN38CR[a] | NIMMO | ACE | Block cap. BF$_3$O.Et$_2$:OH ratio 3:1 mol, OH:NIMMO ratio, 1:3 mol |

S.E.C. traces show that some chain growth occurs for most monomers and that, considering the relatively small amounts of end-capping monomer added, the starting material, POWA 3A, has been modified (figure 3.47). Figure 3.48, sample SWGN02CR, however, indicates that glycidol as an end-capping monomer does not produce any significant chain extension. The N.M.R. spectrum (figure 3.49) seems to confirm this as the GLYN end-group triplet observed at a shift of 67.9 ppm, for POWA 3A, has not been significantly affected. The absence of any other peaks in the 32-68 ppm region suggests that glycidol monomer or ring-opened glycidol i.e. glycerol has not been recovered. The low yield obtained was surprising and perhaps the polymer which had been end-capped had become water-soluble and was lost in the work up.

Similarly, oxetane was considered as a possible end-capping monomer, once it was demonstrated that it can be polymerised by AMM. Unfortunately, although propagation occurs and some oligomers are observed on the S.E.C. chromatogram (figure 3.50, HDGN09CR) the N.M.R, figures 3.51 and 3.52, indicates that the GLYN end-group triplet at 67.9 ppm remains. Therefore, some GLYN end groups have probably been capped but not enough to significantly improve the curing behaviour. The appearance of peaks at 61.6 ppm (figure 3.52) corresponding to the presence of oxetane chain ends, $-OCH_2CH_2\underline{C}H_2OH$, supports this view. However, it is possible that these peaks could be caused by linear oligomer(s) of oxetane. Detailed N.M.R. studies to determine peaks corresponding to dyads needs to be carried out.

Attempted end-capping using NIMMO (figure 3.53, SWGN03CR or SWGN04CR) and styrene oxide (figure 3.54, SWGN09CR) also shows only partial chain extension under AMM conditions. In the case of styrene oxide the S.E.C. shows presence of oligomers as well as unreacted monomer at $R_t$ of 35 minutes. The N.M.R. spectra (figures 3.55, 3.56 and 3.57), of samples suggest that significant capping has not occurred. The decision to use styrene oxide as the end-capping monomer was based on the reasoning that a hindered monomer producing a less reactive secondary
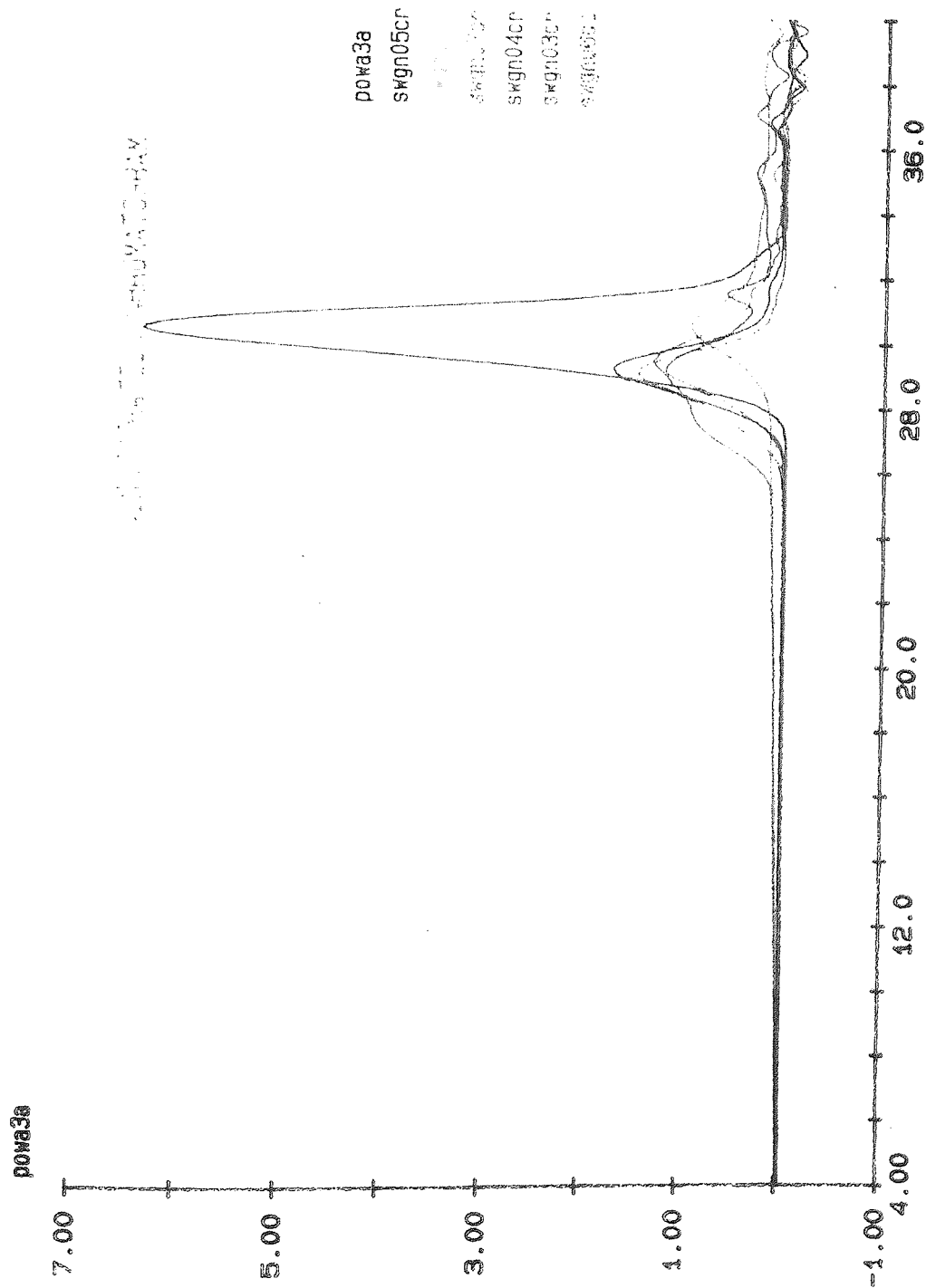
Figure 3.47    SEC traces showing the effect of end-capping procedures on poly(glycidyl nitrate) (POWA3A)
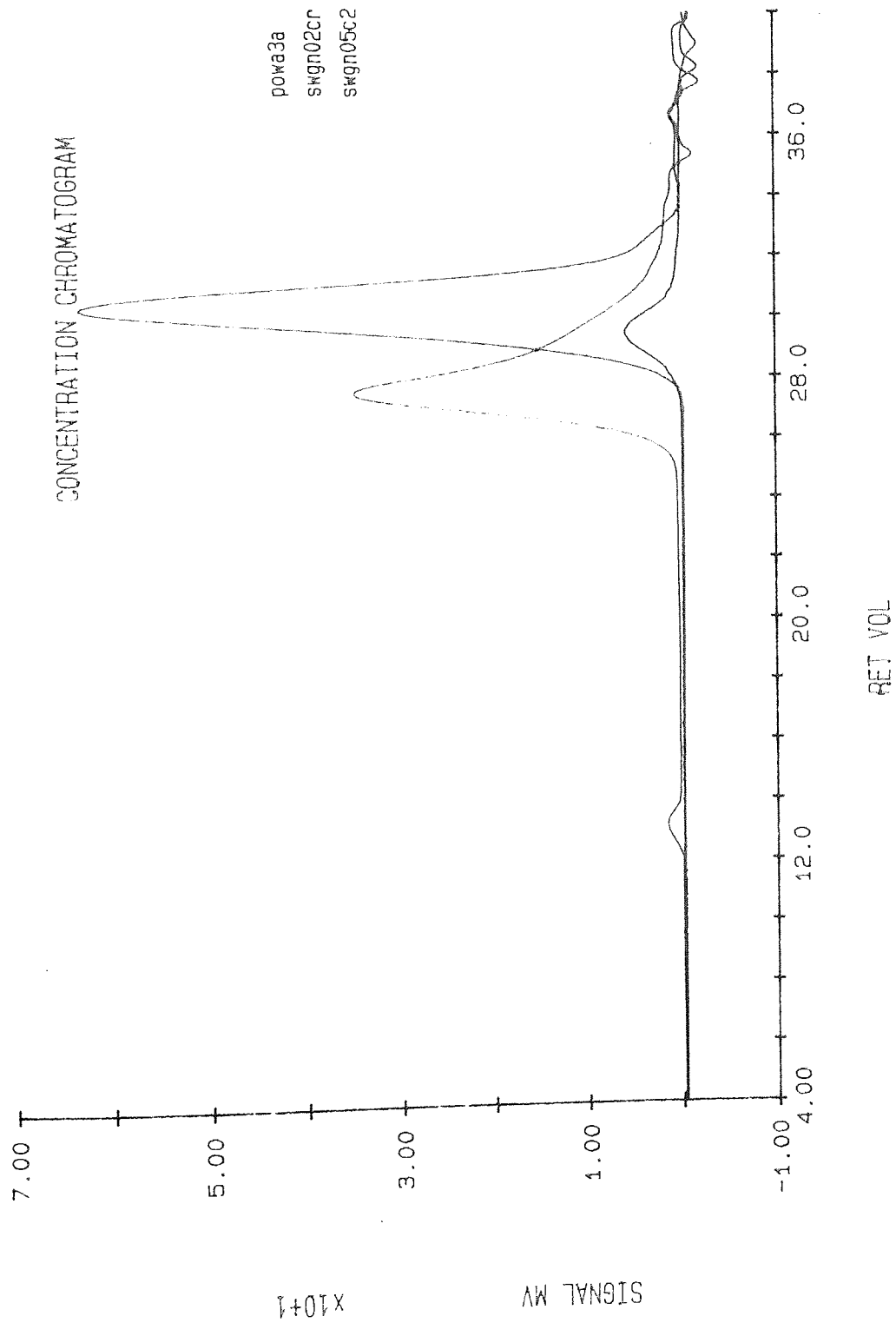
**Figure 3.48** Glycidol (SWGN02CR) and HMMO (SWGN05C2) as end-capping monomers
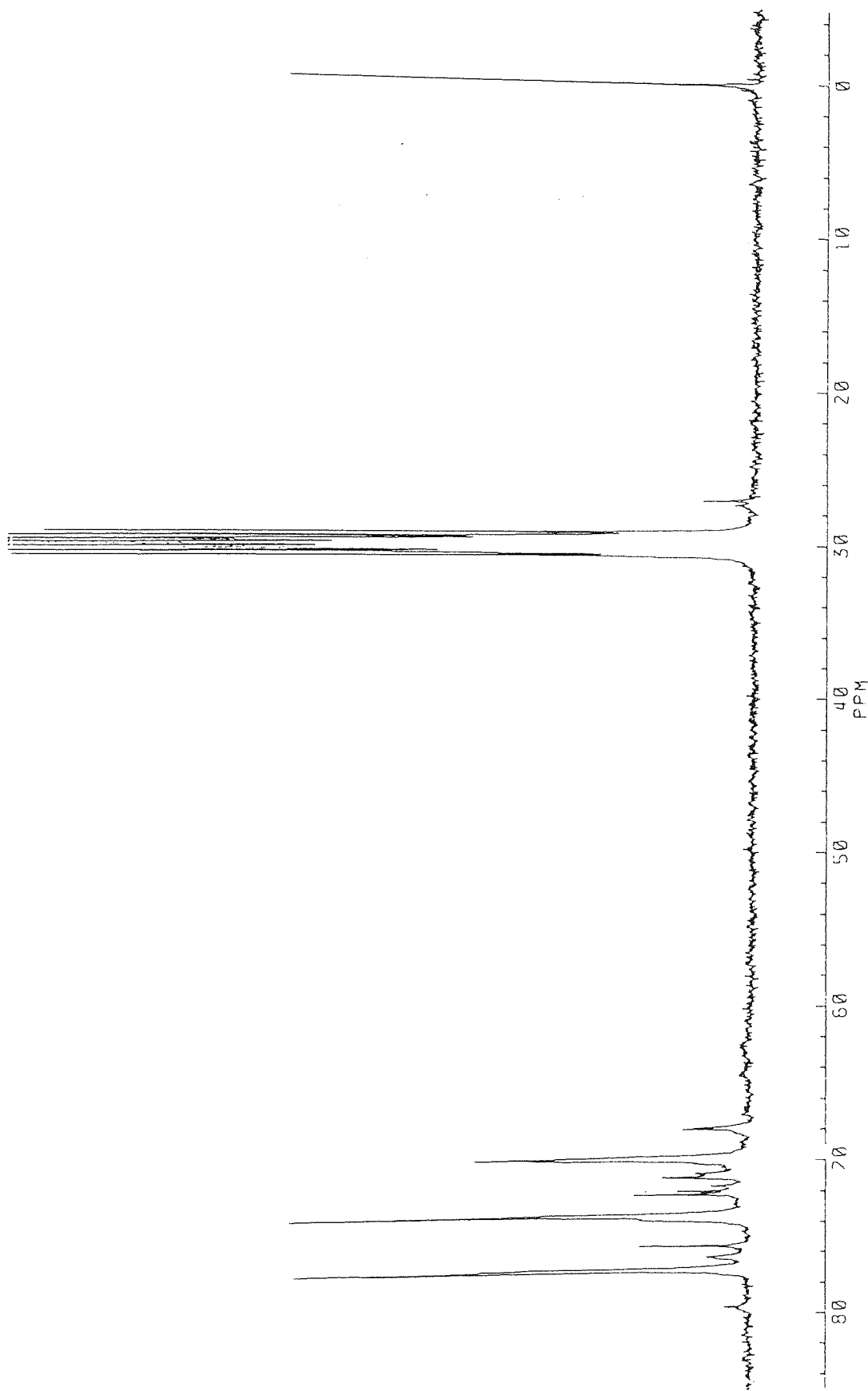
Figure 3.49  $^{13}$C NMR of experiment using glycidol as end-capping monomer for poly(glycidyl nitrate)

(HDGN09CR)
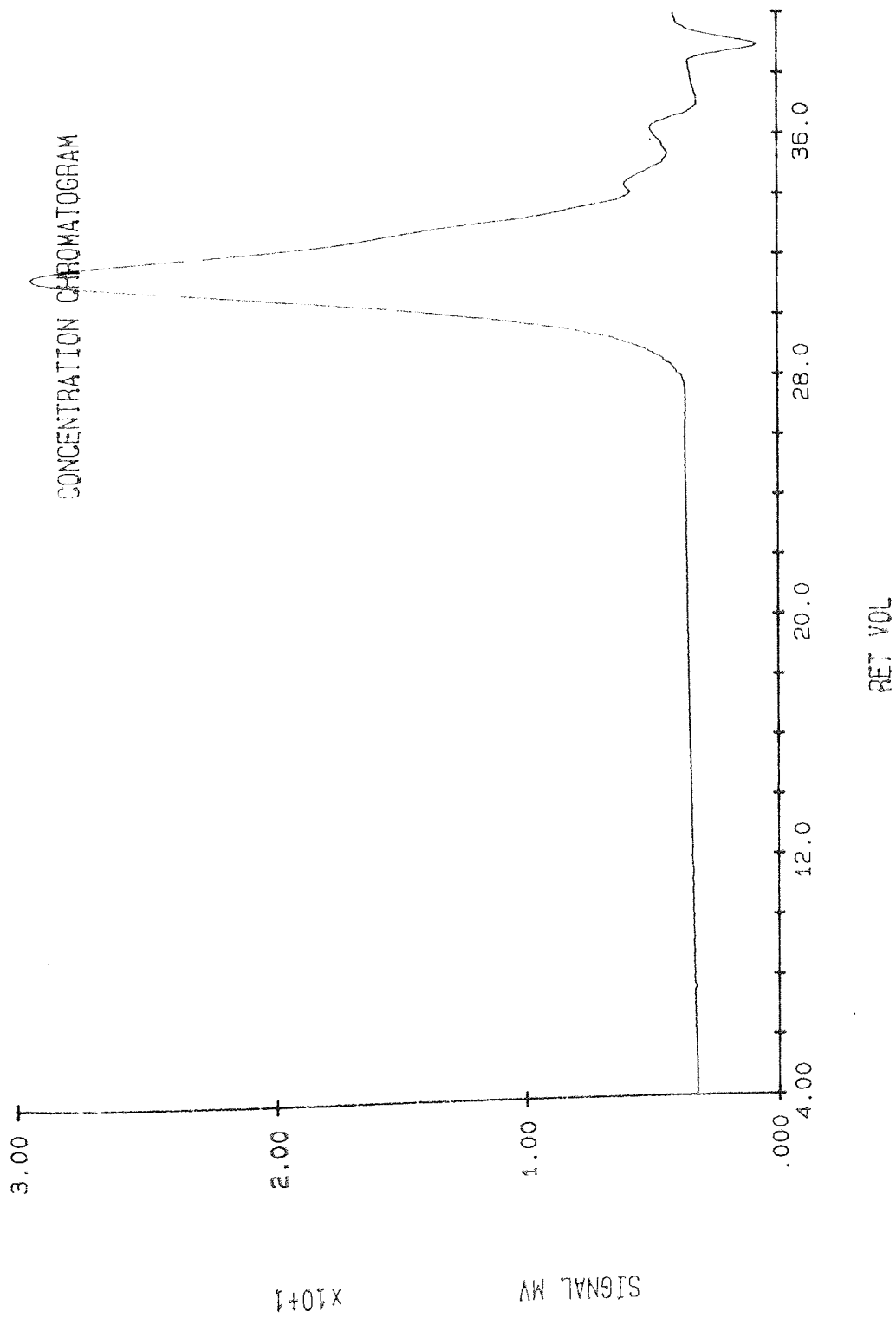


**Figure 3.50** **SEC trace for experiment using oxetane as end-capping monomer for poly(glycidyl nitrate)**
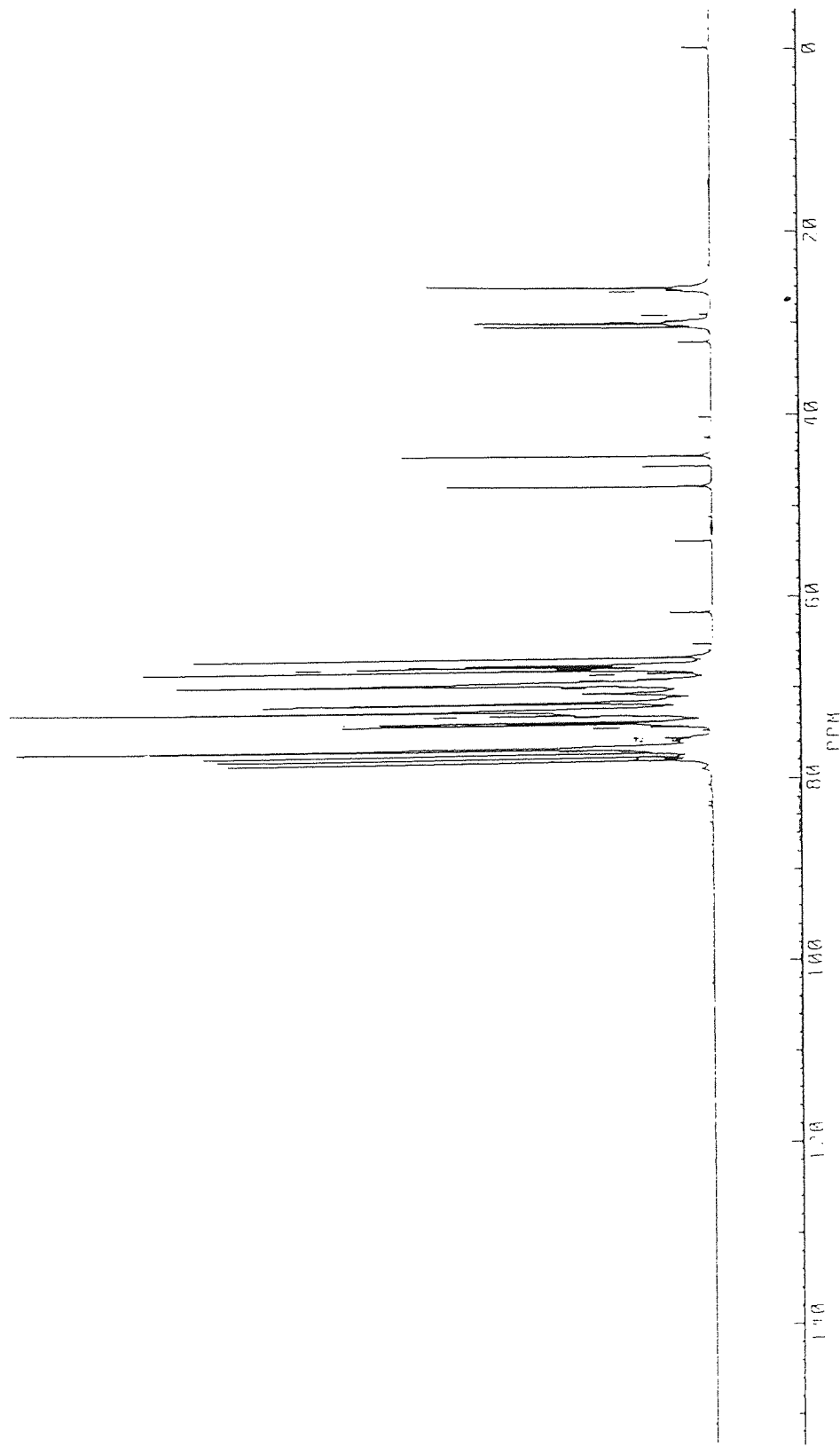
Figure 3.51    $^{13}$C NMR of experiment using oxetane as end-capping monomer for poly(glycidyl nitrate)

154
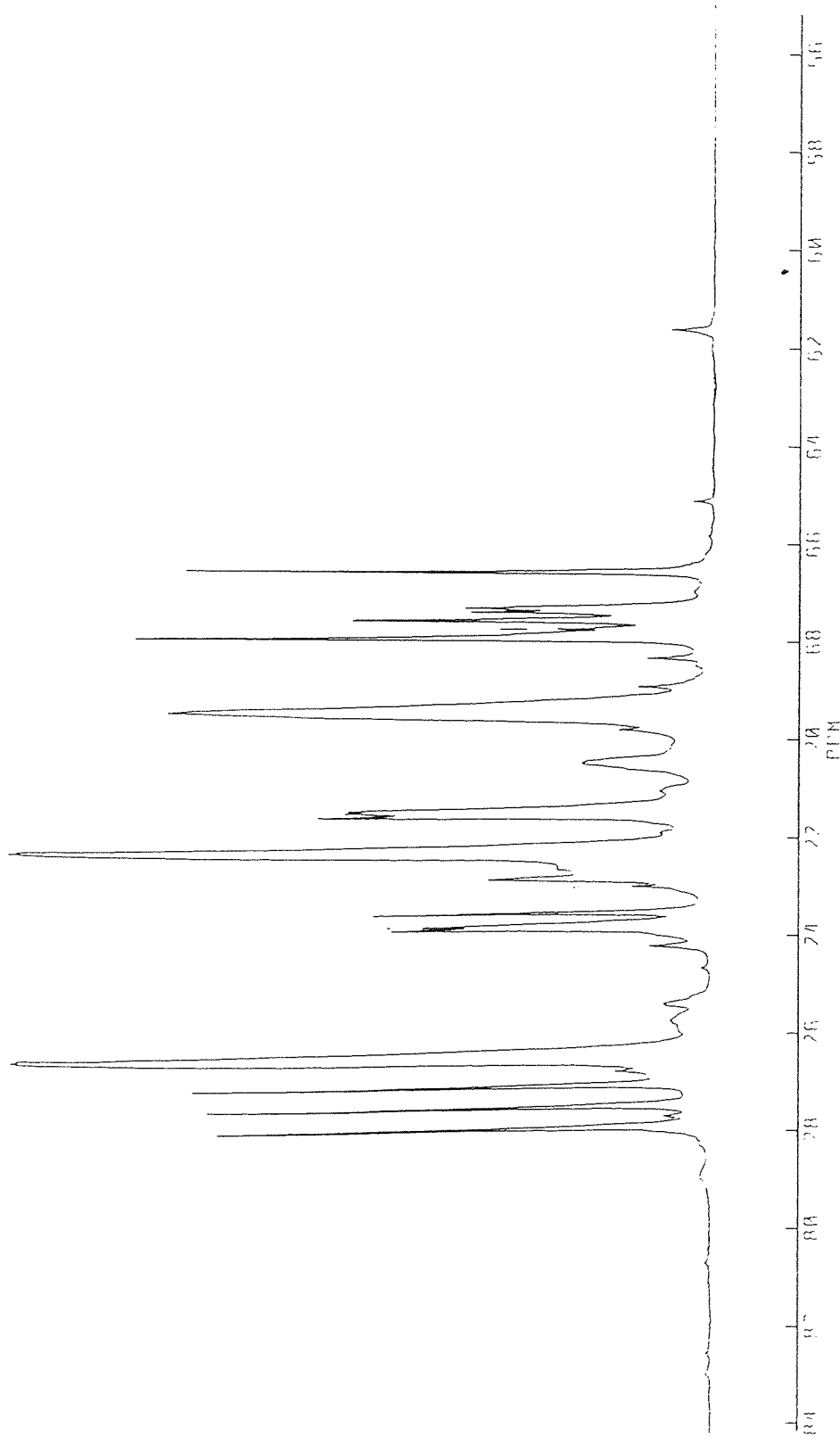
Figure 3.52    Expanded $^{13}$C NMR of experiment using oxetane as end-capping monomer for poly(glycidyl nitrate)
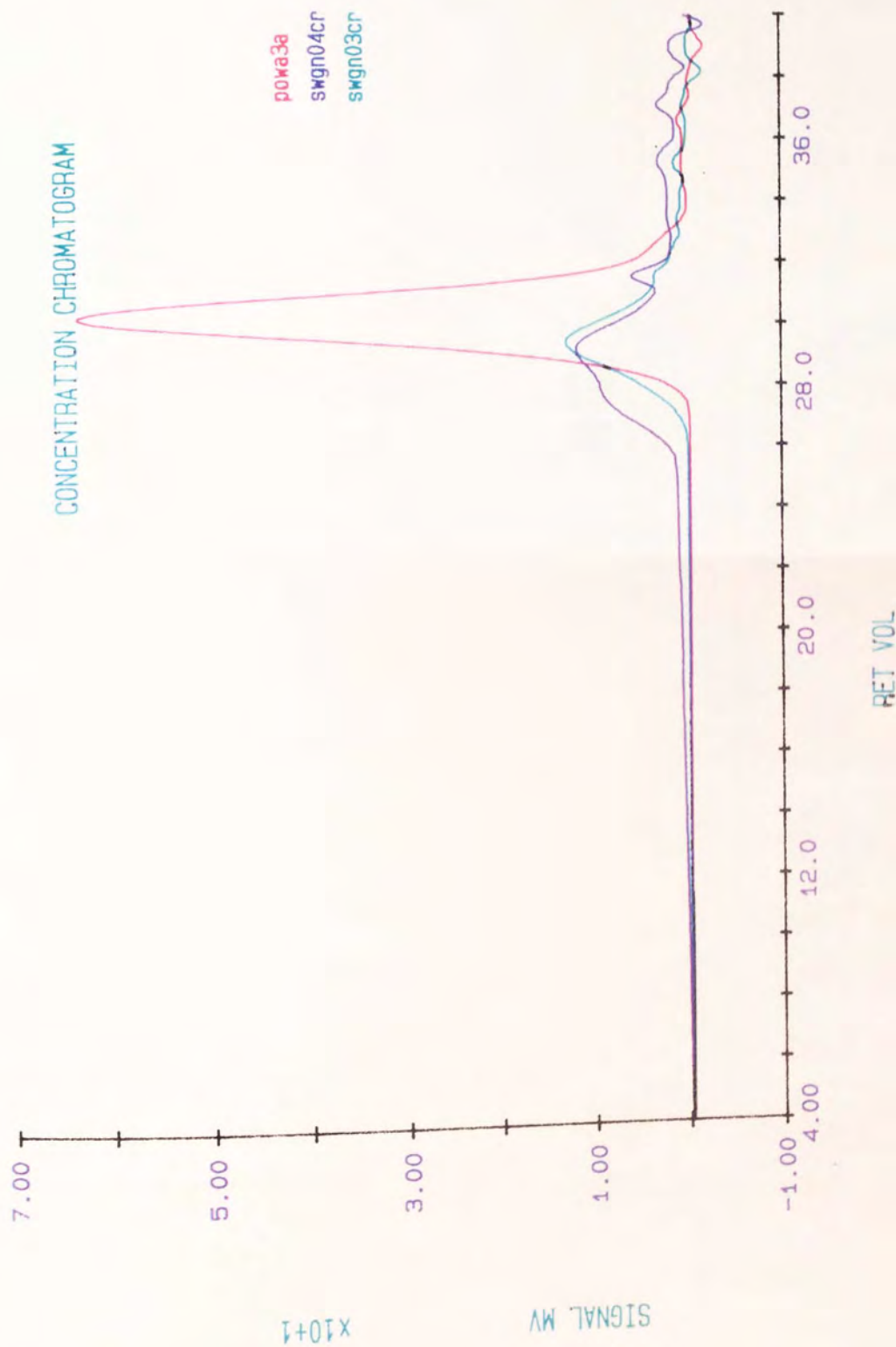
**Figure 3.53** SEC traces of NIMMO as end-capping monomer by AMM (SWGN03CR) and ACE (SWGN04CR)

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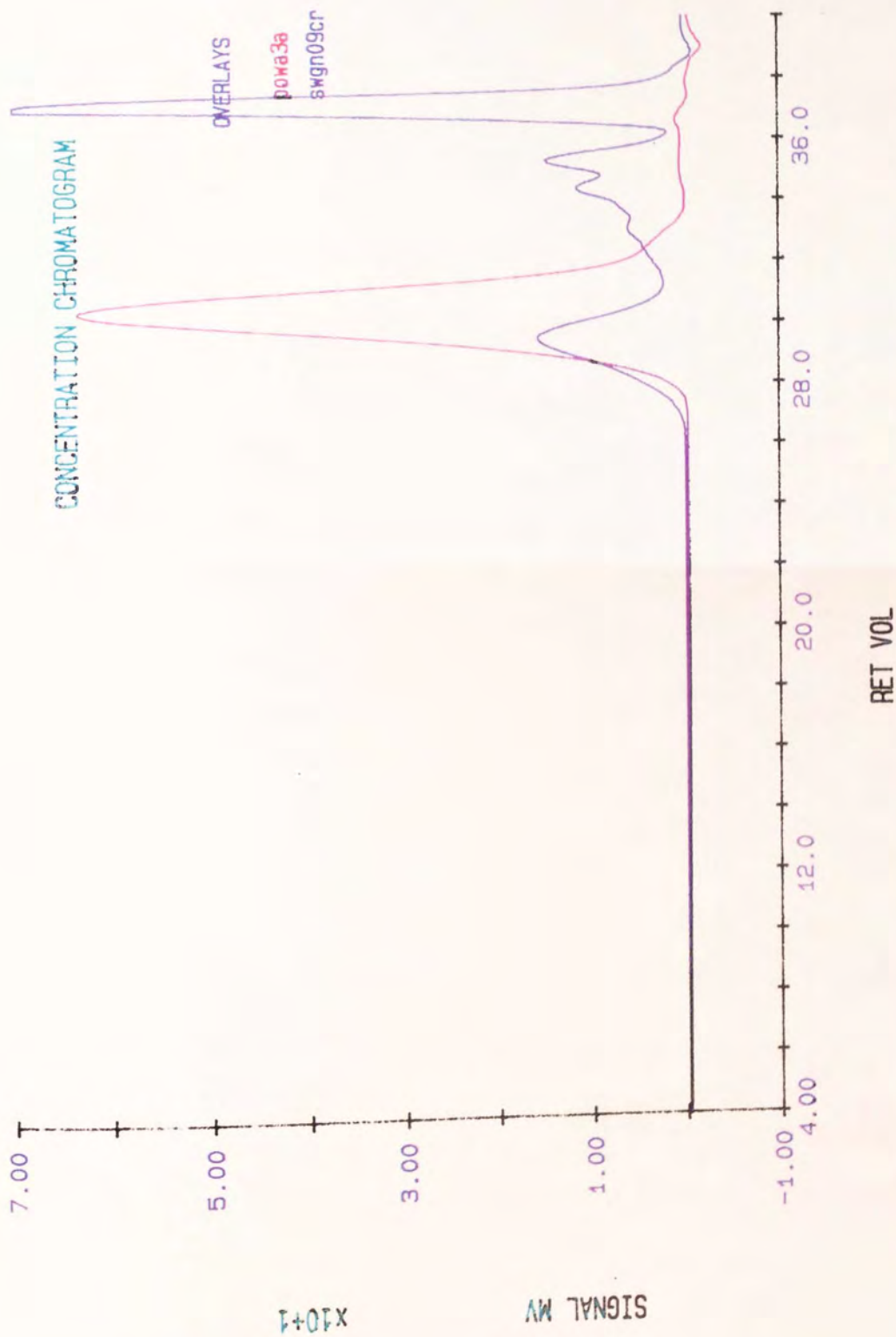
**Figure 3.54** <u>SEC trace of attempted AMM end-capping with styrene oxide (SWGN09CR)</u>

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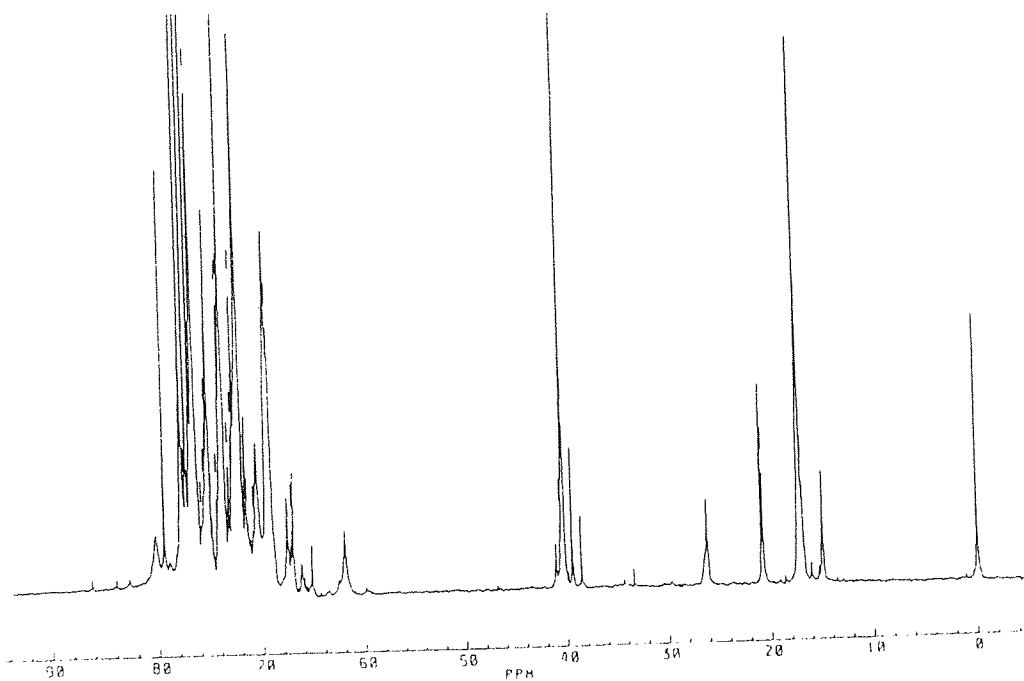
Figure 3.55    $^{13}C$ NMR of NIMMO as end-capping monomer by AMM
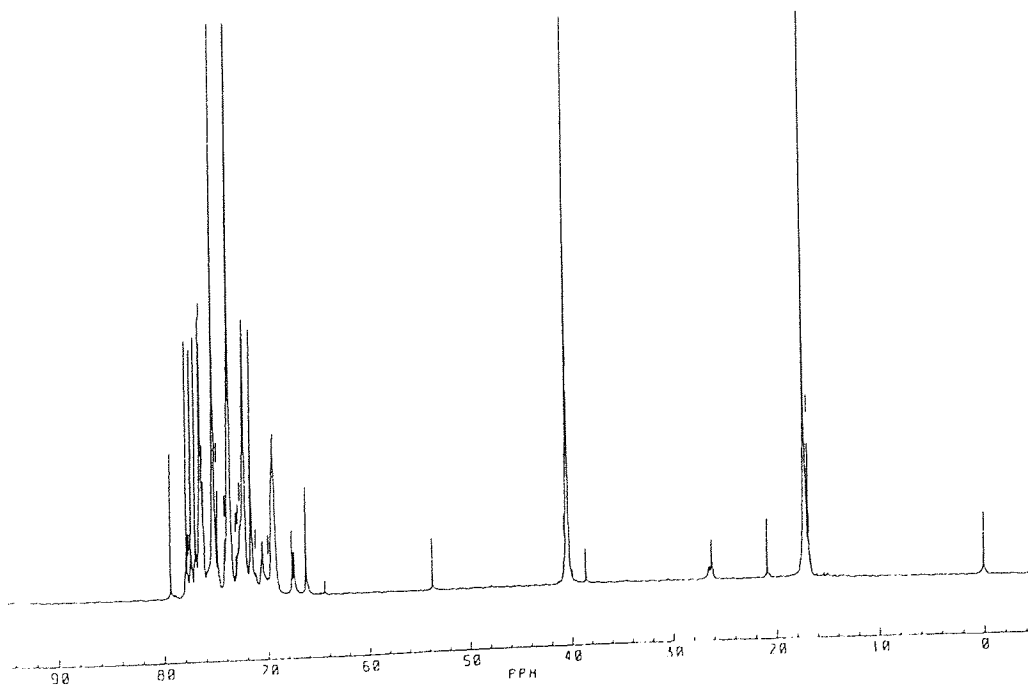


Figure 3.56    $^{13}C$ NMR of NIMMO as end-capping monomer by ACE mechanism

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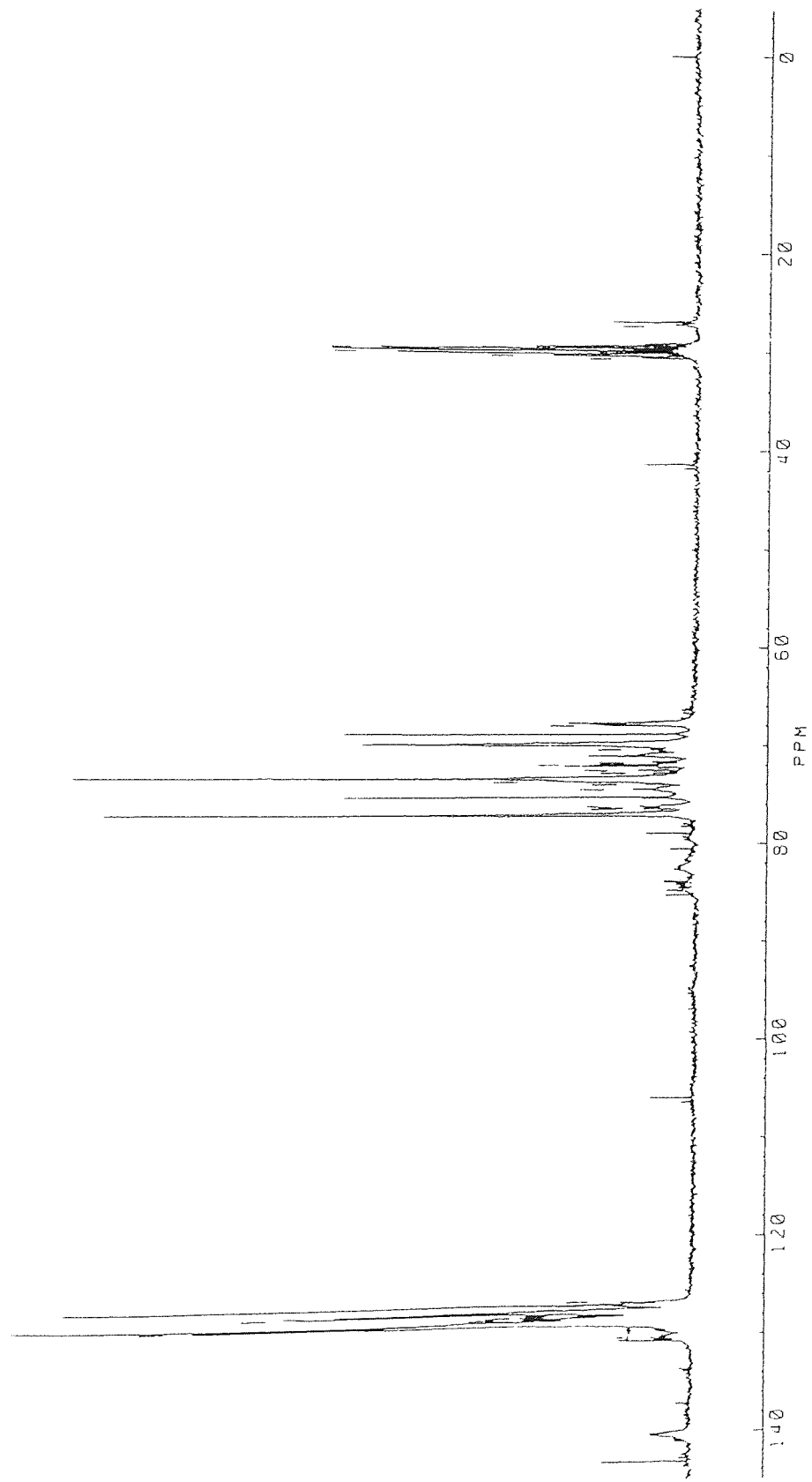
Figure 3.57   $^{13}$C NMR of styrene oxide as end-capping monomer
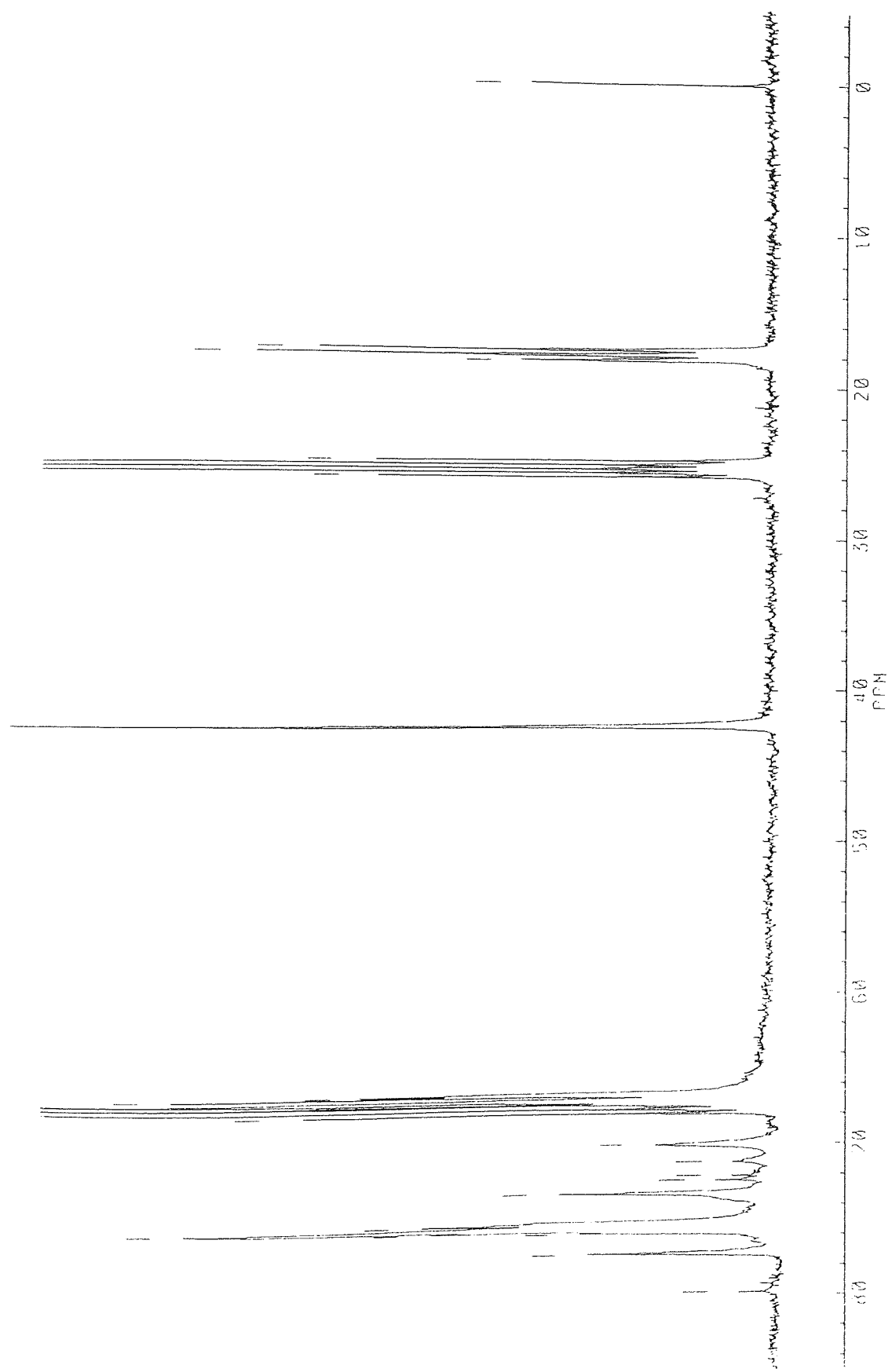
Figure 3.58   $^{13}$C NMR of HMMO as end-capping monomer

hydroxyl group after protonation and propagation would increase the capping efficiency, relative to a monomer which successively generates a primary hydroxyl group. See scheme below.
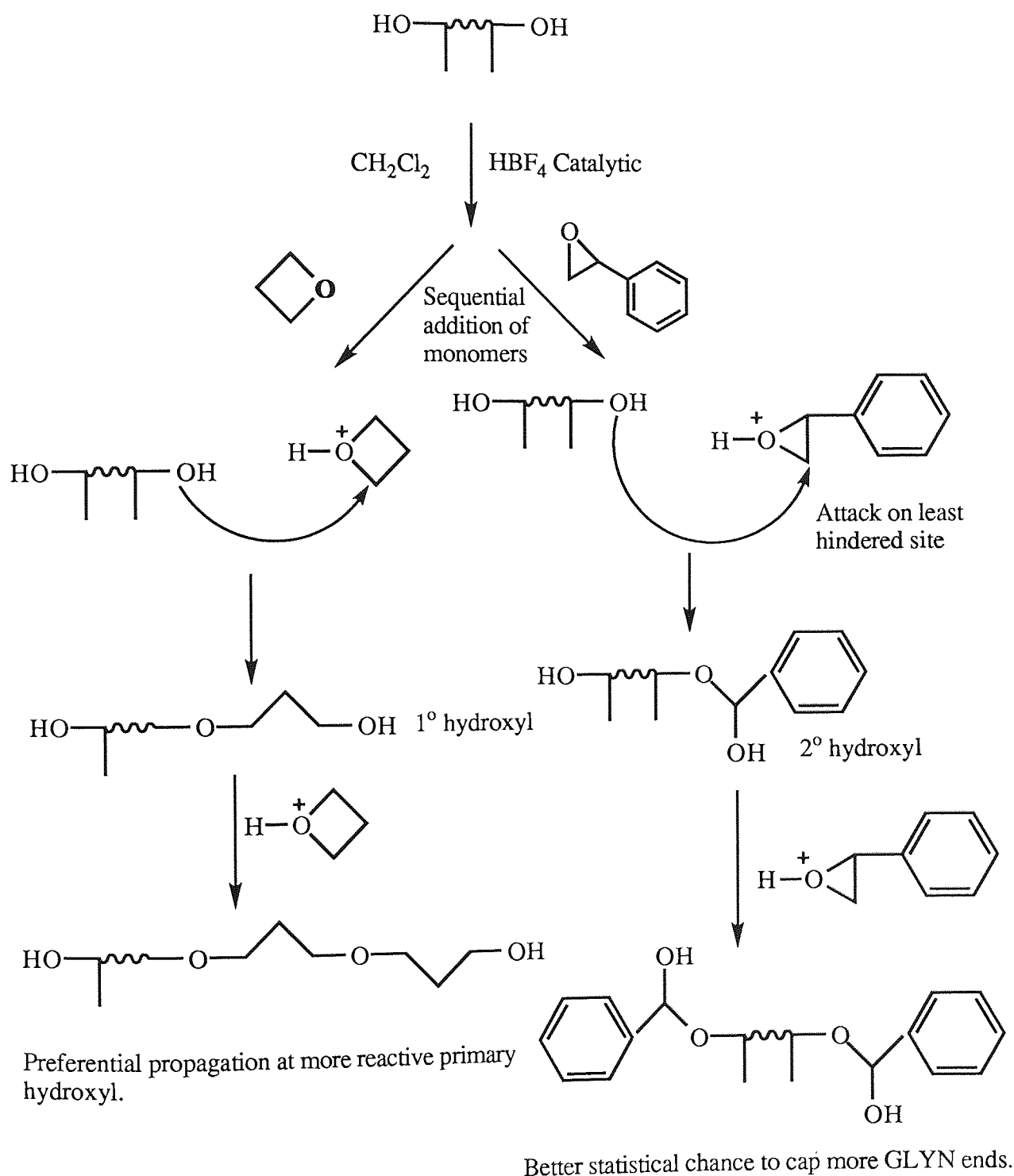


**Scheme 11. Rationale for using styrene oxide as end-capping monomer instead of oxetane by AMM.**

The exact reasons why significant improvement in capping is not achieved with styrene oxide compared to oxetane may be due to a number of factors. Firstly, styrene oxide may not be a sufficiently reactive monomer to proceed by AMM. An experiment to examine this should be carried out by attempting to homopolymerise styrene oxide by AMM. Secondly, although styrene oxide would form terminal secondary hydroxyl groups there is probably still a sufficient difference in reactivity between these and GLYN ends due to the -I effect of the nitrato group. This means that, as for oxetanes, some end-capping occurs but after a point further capping monomer reacts with styrene ends. Thirdly, a characteristic feature of AMM polymerisation is that concentration effects probably prevent propagation to higher molecular weights (i.e. >3500). These concentration effects result from the fact that overall molar concentration of hydroxyl groups, and more importantly protons, diminishes as more monomer, in solvent, is pumped into the reaction vessel. So the chances of a protonated monomer reacting with a hydroxyl group is low and the chances of a monomer unit being protonated is lower still. A way to improve this might be to try further sequential addition of protonic acid catalyst during later stages and/or remove solvent, perhaps by streaming off with a healthy flow of nitrogen gas. If end-capping with styrene oxide had been successful then although curing would have been expected to be slow it would have enabled testing of the hypothesis that the proximity of the nitrate ester group in the cured rubber is somehow responsible for its degradation with time.

The monomer which shows a quite different S.E.C. trace (figure 3.48, SWGN05C2) and N.M.R. spectrum (figure 3.58) is 3,3-(hydroxymethyl) methyl oxetane (HIMMO). Considerable propagation has occurred, relative to the starting material POWA 3A, but two peaks, one at the exclusion limit of the columns, indicating cross-linking and another peak at a $R_t$ of 27 minutes are observed. Vandenberg[82] et al have found that homopolymerisation of HIMMO and 3,3-bis(hydroxymethyl) oxetane can lead to high molecular weight insoluble polymers when polymerised with aluminium alkyl/$H_2O$ initiators. They propose this is a result of branching due to the

(HDGN38CR)



CONCENTRATION CHROMATOGRAM
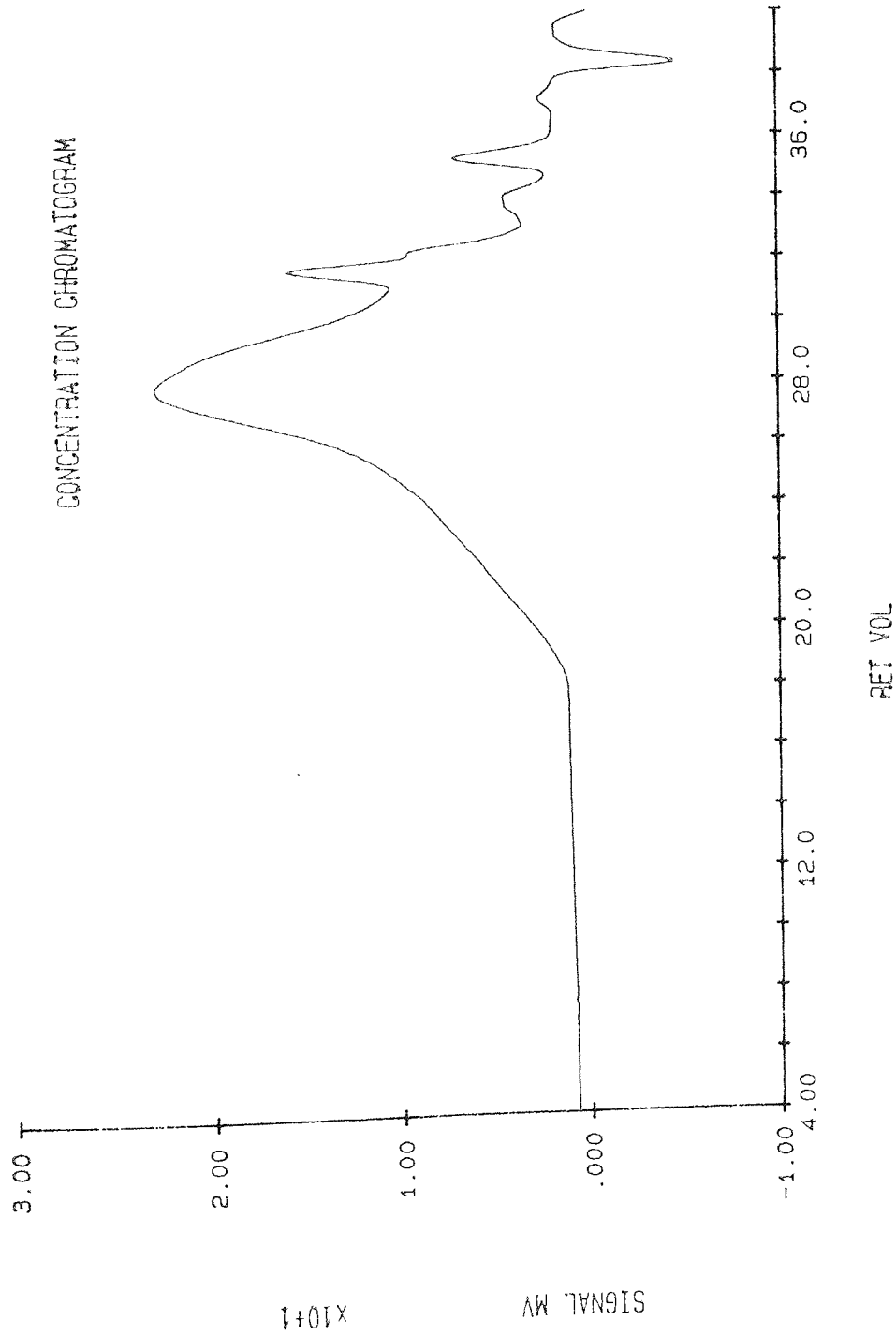
**Figure 3.59** SEC trace of block-capping experiment with NMMO as monomer

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reaction of an oxonium ion with the pendant hydroxymethyl group on a homopolymer or on a monomer as shown in scheme 13. These reactions may be envisaged in the experiment to cap polyGLYN. The material at the exclusion limit is likely to be highly cross-linked homopolyHIMMO. The chain extension of POWA 3A is likely to be due to branching at some GLYN ends as depicted below in scheme 12.

Vandenberg has also shown that oxetanes bearing hydroxy methyl groups or hydroxyl groups directly connected to the ring are very reactive e.g. 3-hydroxymethyl oxetane polymerises explosively if neat. Nevertheless, it may be an advantage to use highly reactive monomers producing polyGLYN with some branched primary hydroxyl groups, especially if the material is partially cross-linked. This would mean that to get a good cured rubber only a few further urethane links would be necessary to increase the stability of the rubber. An additional aspect of this type of monomer in AMM conditions is that the effective molar concentration of the hydroxyl groups would be expected to increase, compared to non-hydroxy functionalised monomers and may cause chain extension. Thereby, higher molecular weight polymers should be attainable. However, care will be needed to neutralise the acid in aqueous solutions as the polymer may become water soluble.

### 3.2.3 Block Capping.

For polyGLYN to be commercially successful a requirement to find a cheap, quick solution to the cure problem without sacrificing its most beneficial property, that of energy, is sought. To achieve this quickly it can be expected that using $BF_3.OEt_2$ as the coinitiator and the polyGLYN as the cationogen, would result in better capping as the counter-ion generated is more likely to complex with the oxonium ion. Hence, an excess of $BF_3.OEt_2$ was added to a solution of polyGLYN whereby the ratio of $BF_3.OEt_2$ to hydroxyl was 3:1, respectively, to ensure that all hydroxyl groups were activated so that the side reaction leading to homopolyNIMMO was not significant.
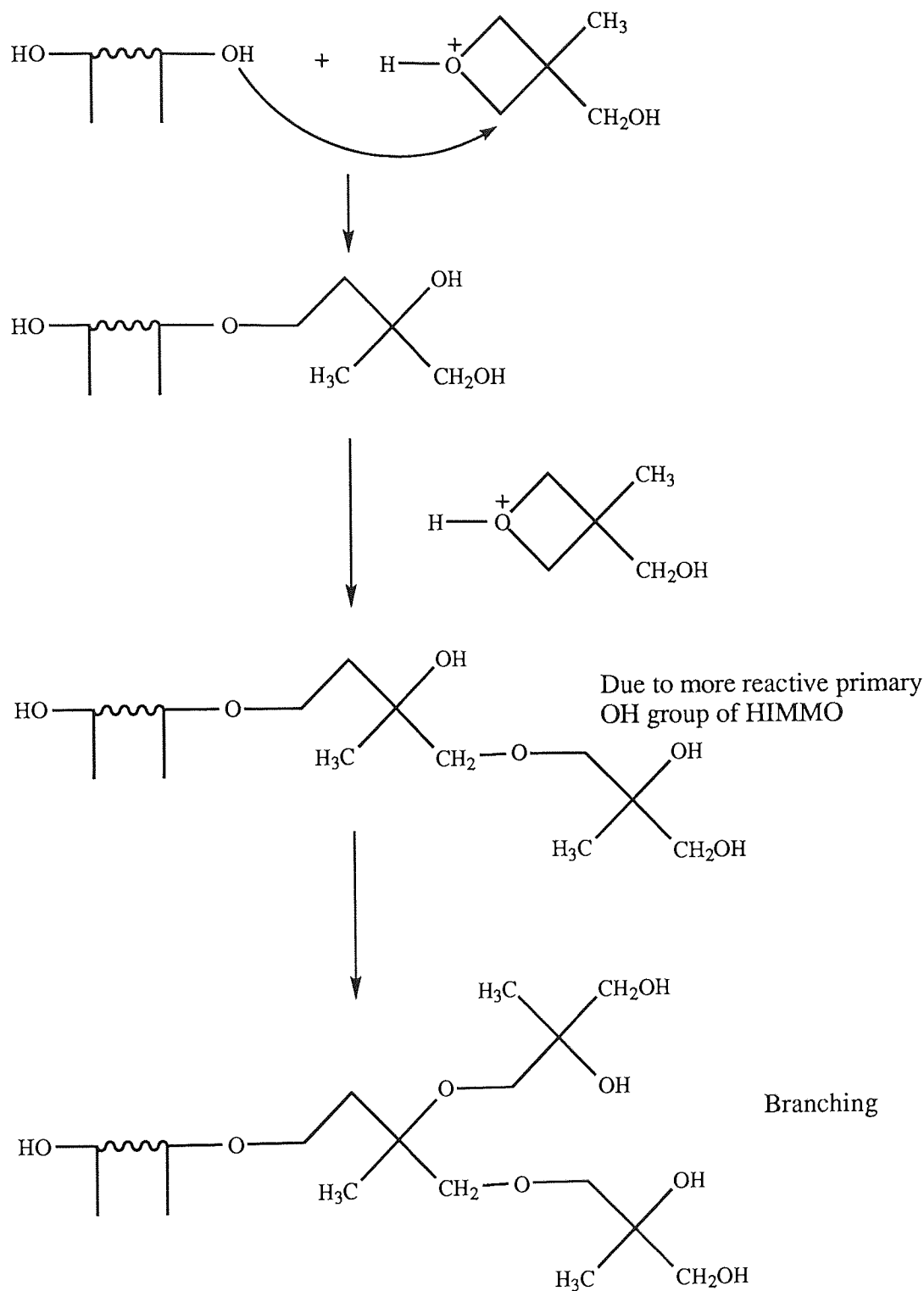
**Scheme 12. Branching due to HIMMO at some GLYN ends under AMM conditions.**

Experiments SWGN04CR and HDGN38CR, shown in table 8 and figures 3.53 and 3.59 indicate that the MWD of the final material is similar to that typically observed for NIMMO polymerisations (figure 3.1).

ACE = Activated Chain End
AM = Activated Monomer

Transfer by polymer

a

b

ACE

AM

Transfer by monomer

c

ACE
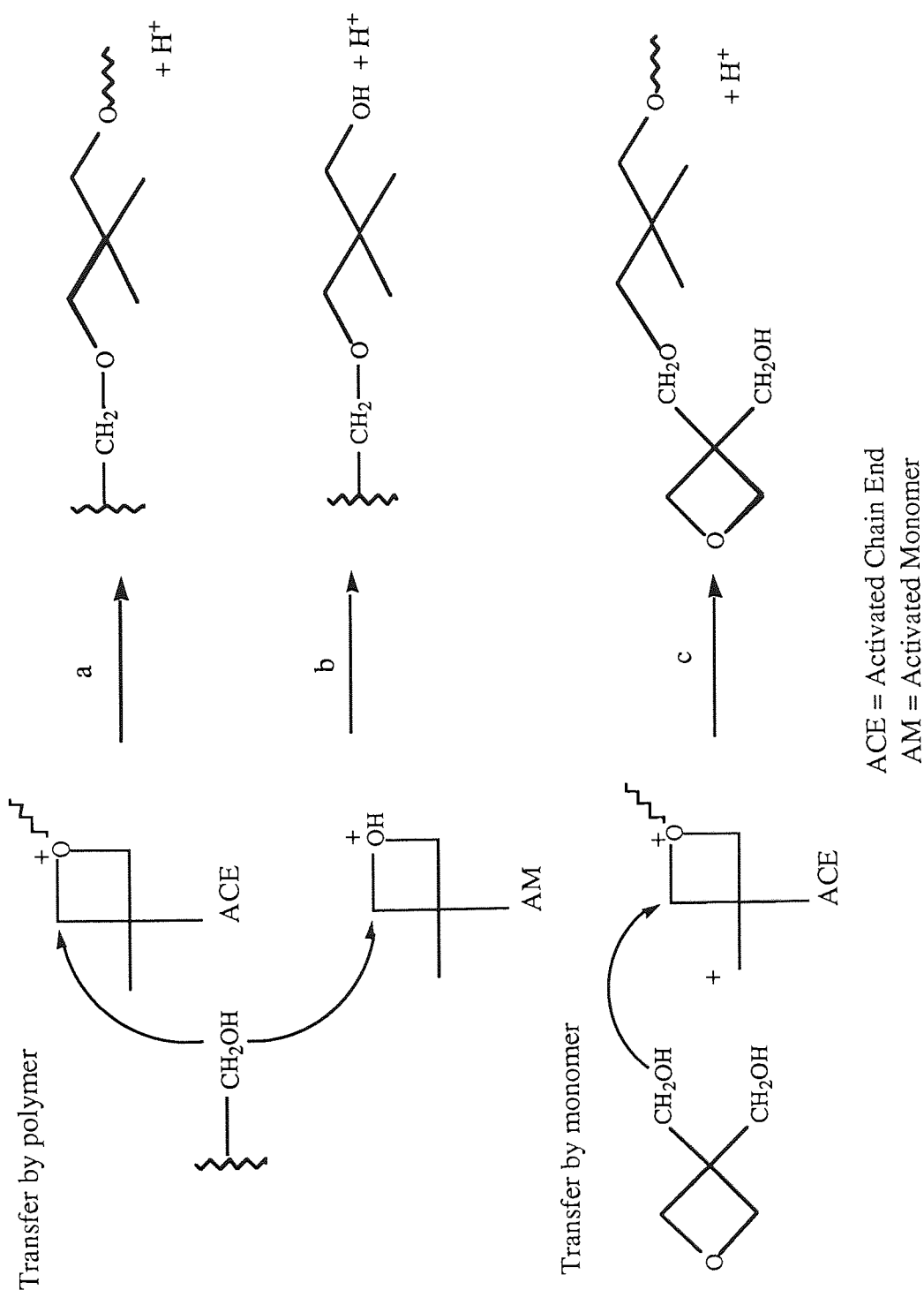
Scheme 13. Vandenberg's proposed transfer reactions leading to branching in hydroxymethyl oxetanes.

Cyclic oligomer is present suggesting that recombination with the counter-ion is inefficient therefore degree of capping is not as high as expected, as shown in scheme 14 and figure 3.60. The $^{13}C$ N.M.R. shows that the OH groups due to GLYN end groups are still present ($\approx$ 69 ppm) and although NIMMO end groups ($\approx$ 67 ppm) are

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also present, the magnitude of the capping has been estimated to be no more than 30 % of the initial GLYN hydroxyl end groups.
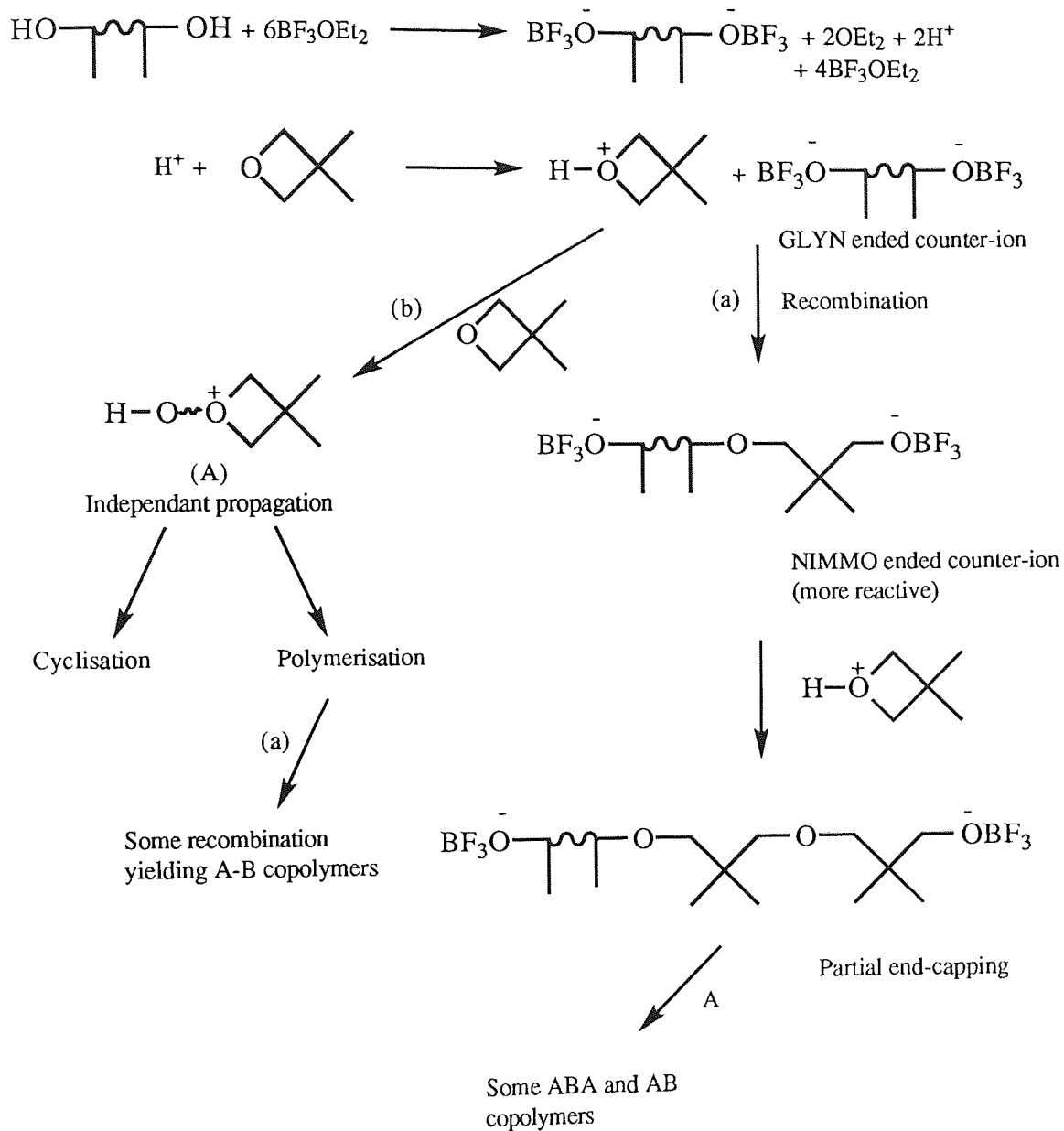


**Scheme 14. Possible reactions in ACE type block-capping systems.**
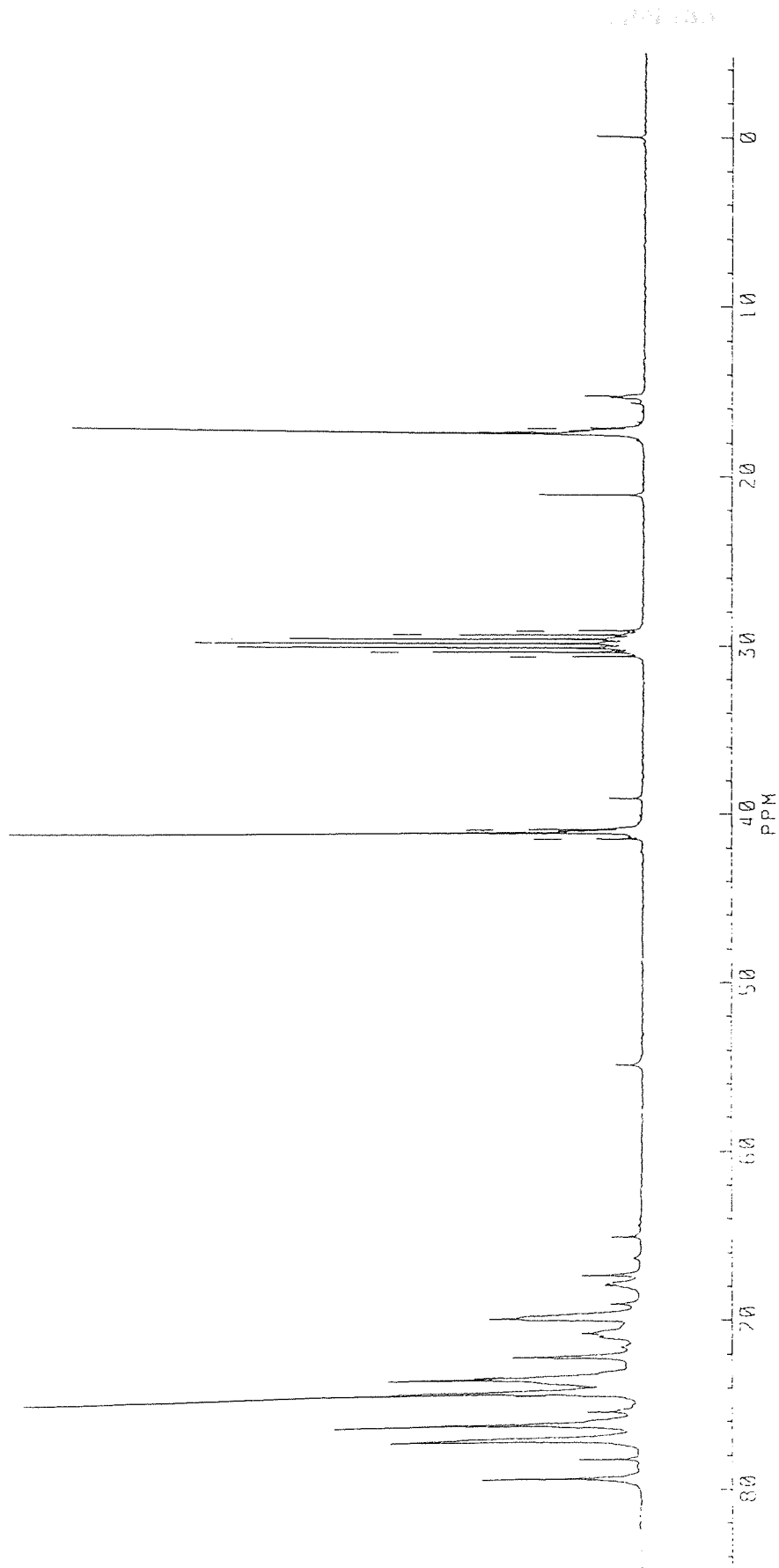
Figure 3.60    $^{13}C$ NMR of block-capping experiment with NMMO as monomer

## 3.3    Results and discussion of Materials based on butadiene oxide dinitrate.

To date one of the most energetic polymers prepared is polyGLYN as shown by the calculations outlined in section 1.6.1.4. However, even more energetic polymers are sought, in particular, to improve the performance of gun and rocket propellants. In order to achieve this a better oxygen balance, i.e. a higher oxygen to carbon ratio, is required. A potential monomer with a higher oxygen balance than GLYN is butadiene oxide dinitrate (BODN).

The equation for the nitration of diepoxybutane to the dinitrate is as follows:



$$\text{(3.14)}$$
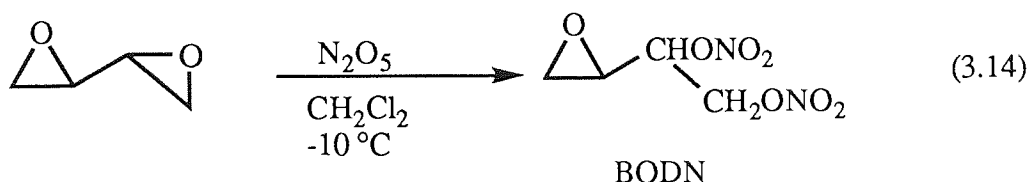
Earlier work to prepare BODN[84] was unsuccessful because the diepoxybutane was used as a dilute solution (5% w/v) in $CH_2Cl_2$, to which the nitrating agent was slowly added. This resulted in cross-linking of the diepoxide with the formation of a very small amount of BODN. The cross-linking is probably due to the very reactive nature of the diepoxide and is initiated by adventitious moisture in the presence of the acidic nitrating agent. In order to improve the procedure the diepoxide was added slowly to a solution of $N_2O_5$ in $CH_2Cl_2$. It was expected that an additional advantage of this procedure would be deactivation by the nitrate ester substituents which would prevent ring-opening of the BODN monomer. Sample HDBNASMO in figure 3.61 demonstrates that formation of higher molecular weight or cross-linked species does not occur if this method is adopted. Some oligomers are formed and elute at retention volumes of 31 $cm^3$, 32 $cm^3$ and 33.5 $cm^3$. However, the main constituent of the mixture is the peak at 34 $cm^3$ which is consistent with the peak corresponding to monomer of the size of BODN. The N.M.R. (figures 3.63 and 3.64) confirms that epoxy groups and nitrate ester moieties are present.

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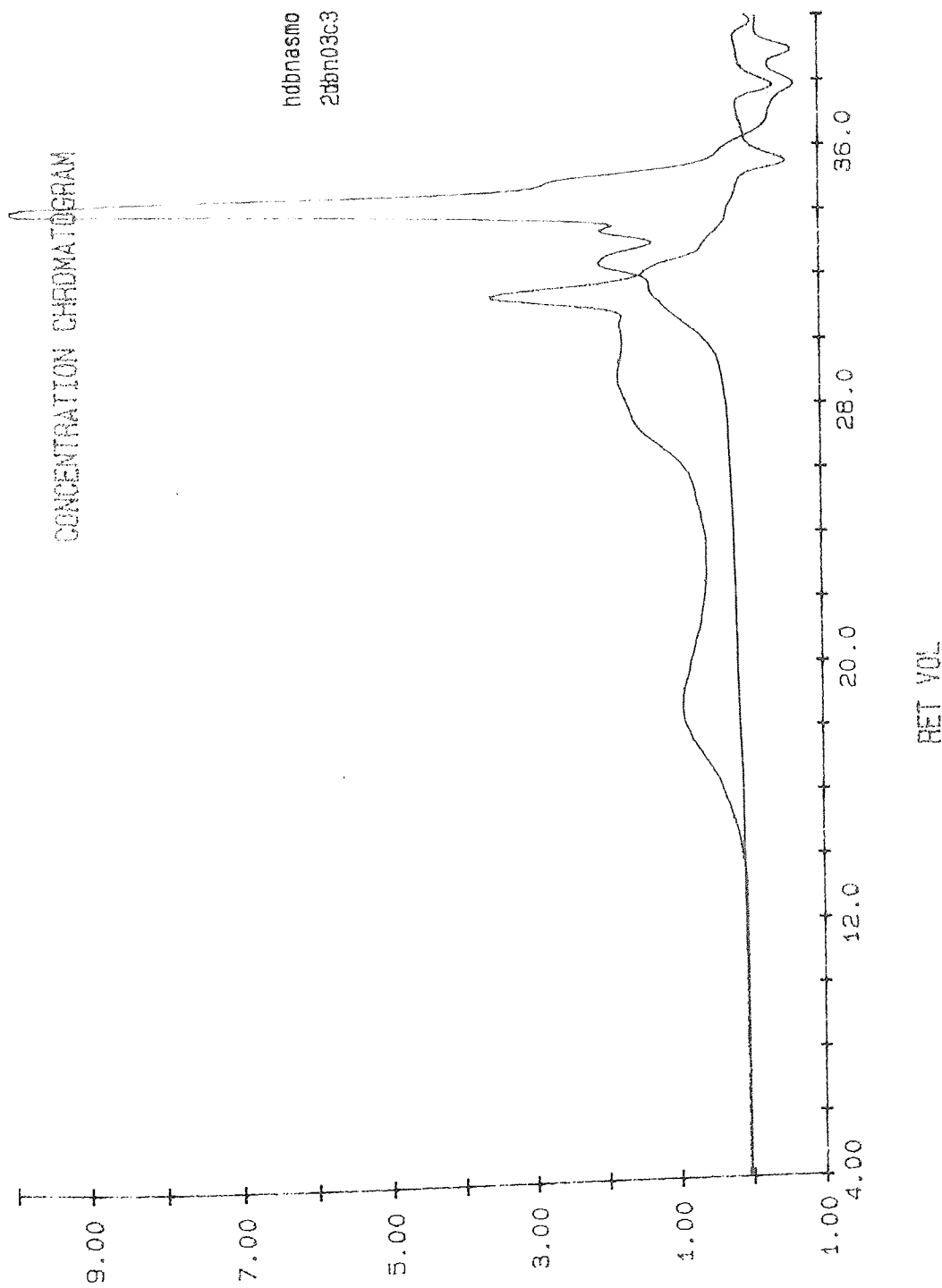
**Figure 3.61** **SEC traces of BODN (HDBNASMO) and Et₃OBF₄ initiated polymer (2DBN03C3)**

CONCENTRATION CHROMATOGRAM

hdbnasmo
hdtp11cr
hdgn03cr

RET VOL
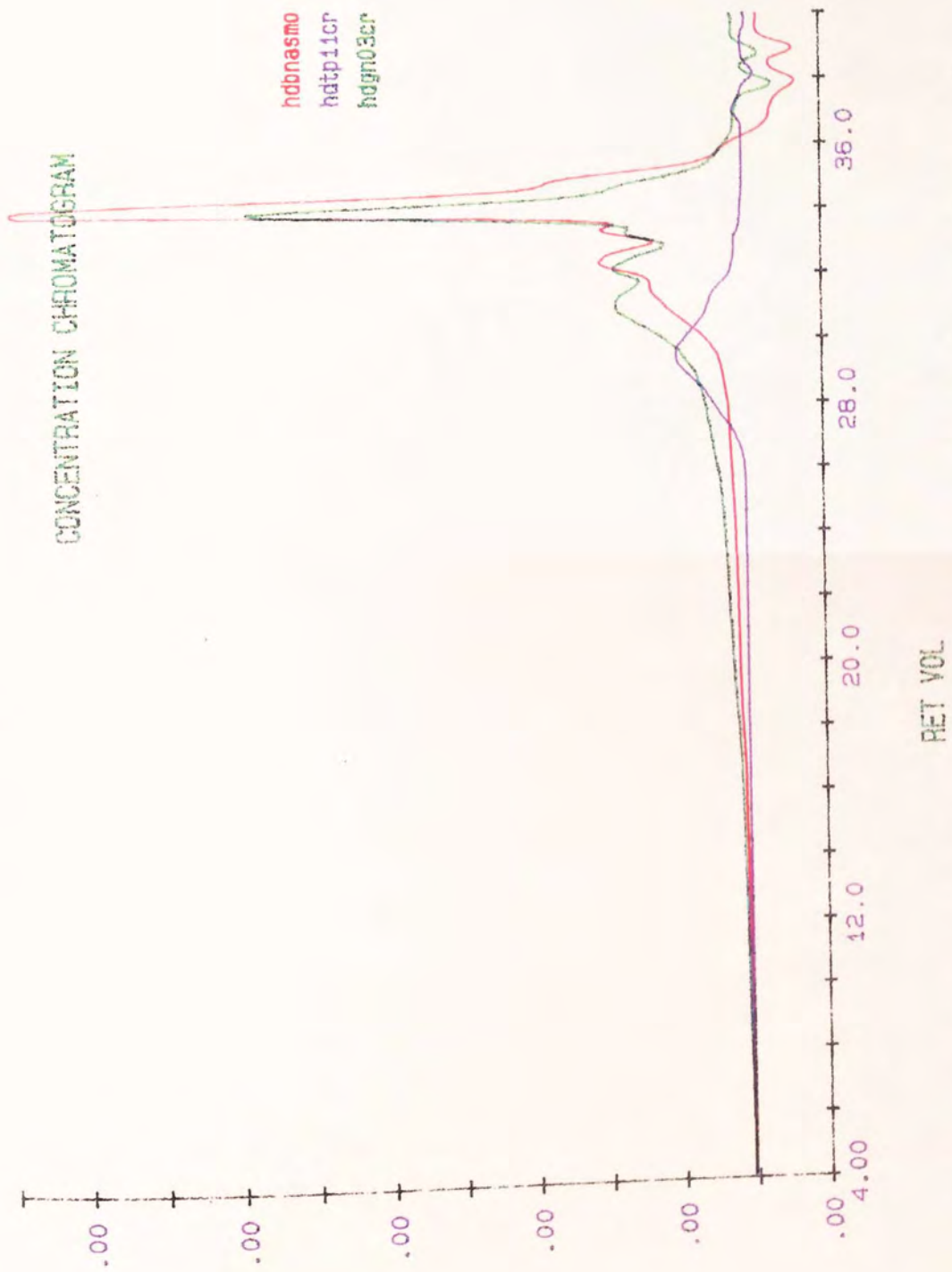
Figure 3.62    SEC traces of HBF$_4$ initiated experiment (HDGN03CR) and copolymer of GLYN/BODN

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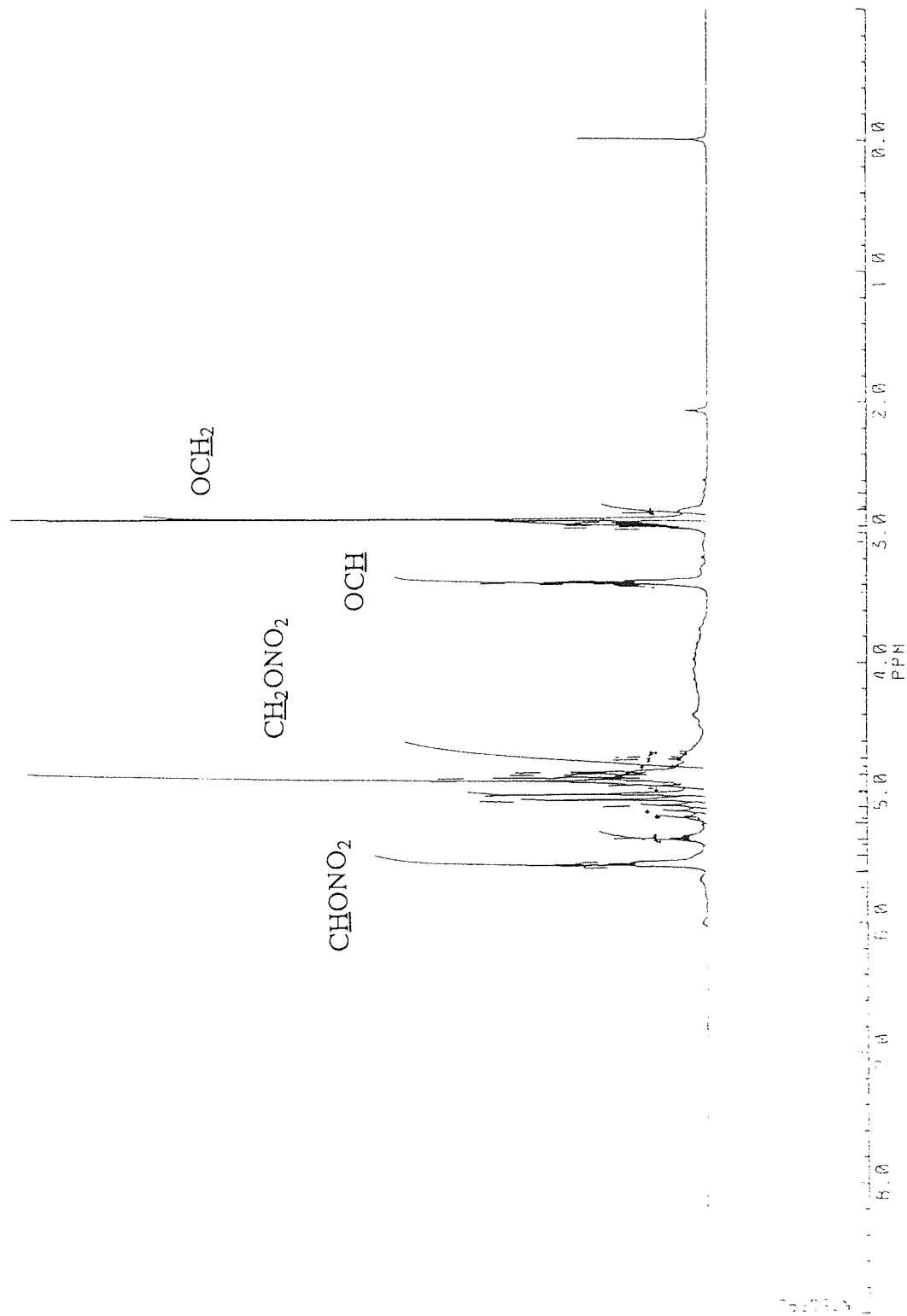
Figure 3.63    $^1$H NMR spectrum of predominantly BODN monomer

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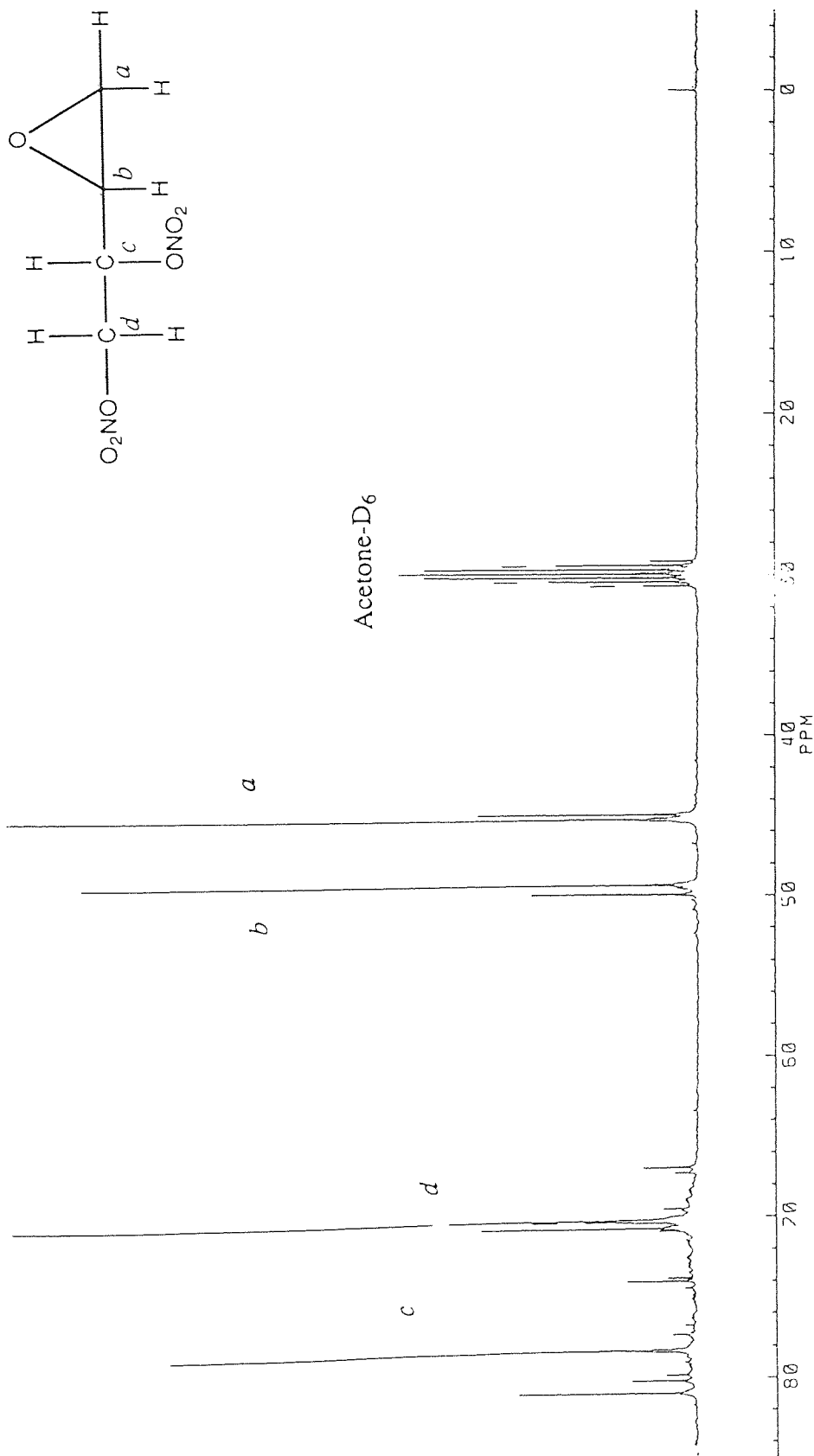
Figure 3.64 $^{13}C$ NMR spectrum of predominantly BODN monomer

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| Sample name | Cationogen | Temp °C | $DP_e$ | Addn. Time h | Comments |
|---|---|---|---|---|---|
| HDBNASMO | - | - | Monomer | - | nitration of diepoxybutane |
| HDGN03CR | $HBF_4$ | 0 | 15 | 16 + 4 | IMA, 20% w/v solution |
| 2DBN03C3 | $Et_3OBF_4$ | +17 | 15 | 0 + 4 | AMI, 5% w/v monomer solution |
| HDTP11CR | AMM Butandiol-$HBF_4$ $H^+$:OH, 1:15 | +17 | 70 | 8+4 | Ratio GLYN:BODN 4:1 mol Mixed monomer feed |

The first figure in the addition time column is the monomer feed time, the second is the stirring time.

**Table 9 . Conditions of experiments with BODN.**

Table 9 shows the conditions of polymerisations of monomer prepared as above. Figure 3.62 shows the S.E.C. of a sample initiated with $HBF_4$ and labelled as HDGN03CR. This indicates that the amount of BODN monomer decreased relative to the oligomer suggesting some propagation occurred but not to the molecular weight expected. It may be that the epoxy oxygen is not sufficiently basic to form a stable oxonium ion to support significant polymerisation. Alternatively, the presence of impurities in the starting mixture may have caused rapid termination. However, as there is some increase in oligomer an experiment where a carbocation is used as an initiator ought to demonstrate whether the monomer is polymerisable.

Hence, an all monomer-in (AMI) experiment, with a 5% w/v monomer solution in $CH_2Cl_2$, at +17 °C, was conducted (figure 3.61, sample 2DBN03C3) and clearly proves that high molecular weight material can be prepared. The S.E.C. trace shows that all the peaks, including the characteristic negative solvent peaks at retention volume of $\approx 38$ $cm^3$ have shifted to lower retention volumes by approximately 2 $cm^3$ possibly due to experimental error (because the solvent system was temporarily

changed to run other samples). Nevertheless the peaks at retention volumes of 18 cm$^3$ and 28 cm$^3$ must be due to macromolecular species. It is partly because of this type of experimental error and partly due to unreasonable data obtained when using the Viskotek system that quantitative analysis of the samples has not been undertaken. Instead, the results are compared qualitatively using retention volumes. Further evidence that high molecular weight polymers are formed comes from the fact that the isolated material does not re-dissolve either in CH$_2$Cl$_2$ or THF. It remains as a yellow, translucent gel.

Once the process is optimised and larger amounts are available it should be interesting to examine tacticity effects of this polymer, as there are two asymmetric centres in the repeat unit:
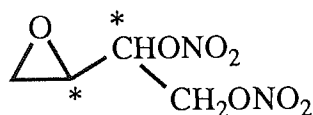


An asymmetric centre also exists in GLYN and the copolymer of GLYN-BODN may also be worth studying in terms of tacticity. Such a polymer with some BODN incorporated into a predominantly GLYN backbone has been prepared (HDTP11CR) by the AMM, although the exact ratio of GLYN:BODN has not yet been determined. The S.E.C. (figure 3.62) shows the molecular weight to be of the same order as homopolyGLYN (figure 3.42, POWA3A) but considerably less than expected (Mn = 8000). Again this is probably due to impurities including moisture but also, in this case, oligomer contamination in the monomer mixture. It is clear that very little of the peak ascribed to BODN monomer (R$_t$ = 34 min.) remains at the end of the reaction. N.M.R. spectrum (figure 3.66) indicates the presence of both GLYN and BODN peaks but it is not entirely clear how much incorporation has occurred. However, a D.S.C. trace of the sample (figure 3.67) suggests that the polymer formed is not homopolyGLYN as the glass transition temperature, -17 °C, is significantly higher than that observed for polyGLYN, -36 °C. Moreover, other secondary
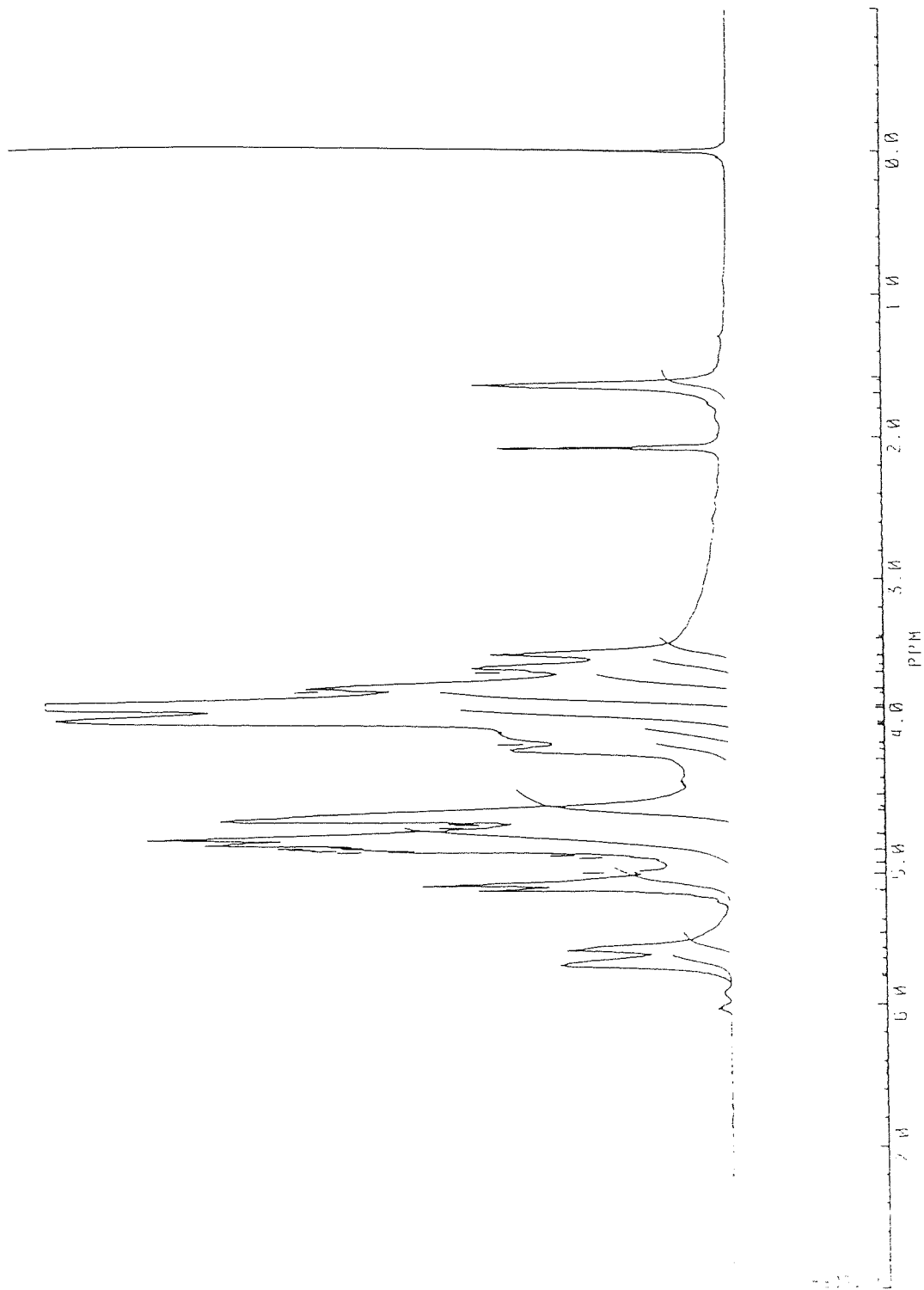
Figure 3.65    $^1$H NMR spectrum of GLYN/BODN copolymer
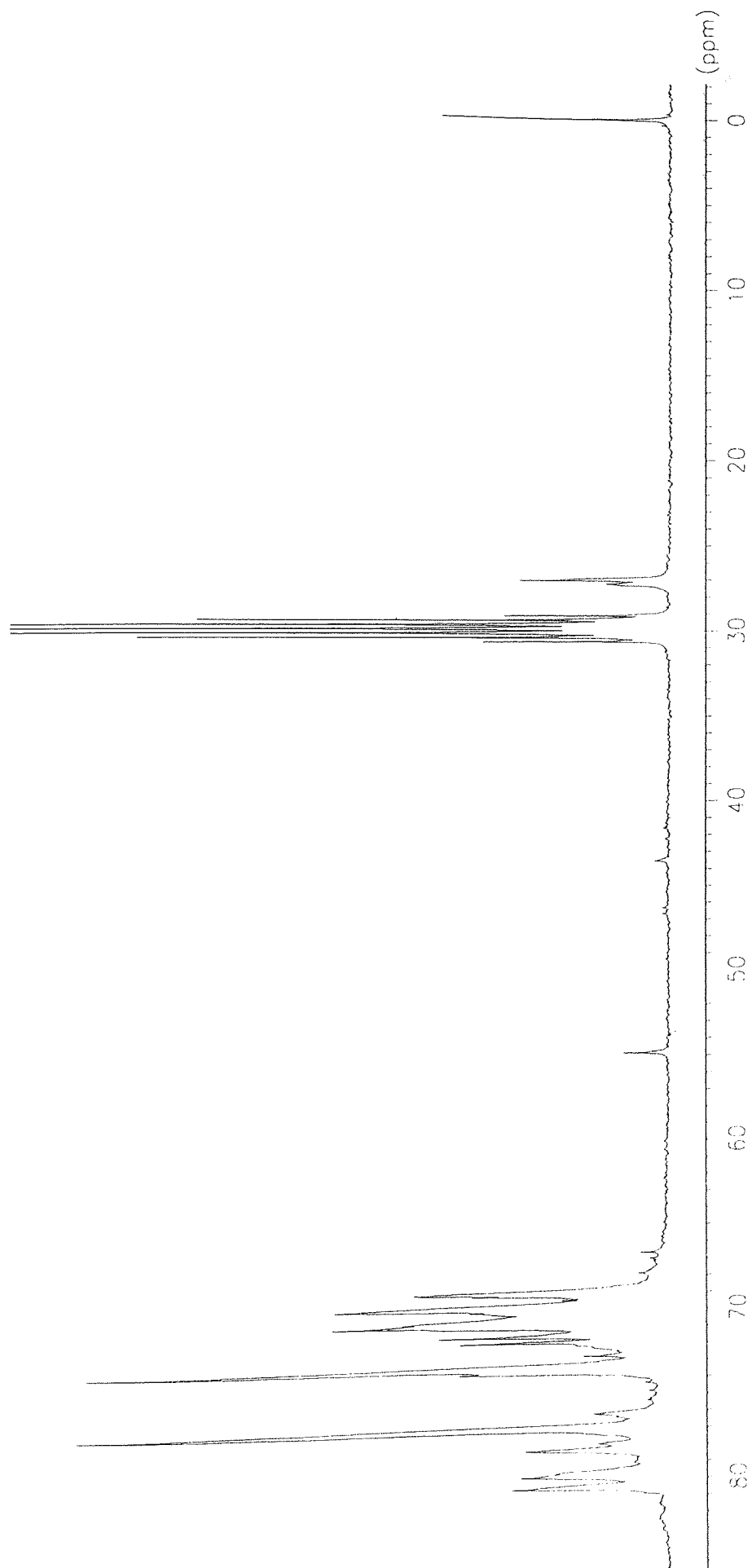
Figure 3.66   $^{13}$C NMR spectrum of GLYN/BODN copolymer

transitions are not observed, indicating that the polymer does not have a block structure.

At this stage BODN based materials are not expected to be widely used in propellant and explosive compositions even though they are to date the most energetic polymers prepared. The reasons for this are that, firstly, the glass transitions are expected to be higher, even for copolymers, because of the bulkier BODN monomers which impede motion of the backbone, as demonstrated by the BODN-GLYN copolymer. To achieve the Ministry of Defence stipulated target Tg of -50 °C will require considerable plasticisation which will in turn lead to formulations with poor mechanical integrity to function as binders. Secondly, there is some evidence[85] that secondary nitrate esters, $-CHONO_2$, are less stable to thermal degradation than primary, $-CH_2ONO_2$, nitrate esters. The mechanism, postulated by Chen is believed to proceed via the unimolecular, homolytic decomposition of the nitrato group into two radicals which then cause scission of the polyether backbone:

$$RONO_2 \longrightarrow RO\bullet + \bullet NO_2 \qquad (3.15)$$
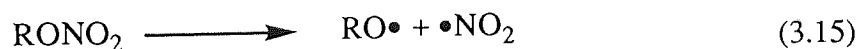
In-house work has indicated that such processes occur for polyNIMMO[86,87] and polyGLYN[88] and are therefore expected for BODN materials. Nitrate ester polymers are often stabilised by the addition of a radical scavenger such as 2-nitrodiphenyl amine, although this increases the lifetime of the composition it does not eradicate the problem and secondary nitrate esters have shorter lifetimes. However, BODN materials may yet find applications where relatively small amounts are required e.g. BODN oligomer may act as a very energetic plasticiser. Alternatively, work is continuing because it may be used in civilian applications, such as in petroleum fuel, where small amounts will help to combust carbonaceous material in automotive engines so improving performance. Some interest has been shown by oil companies in this respect.

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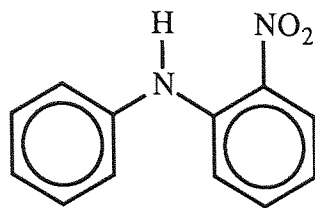
2-Nitrodiphenyl amine radical scavenger

Another reason for the continuation of work on nitrate ester binders is that other energetic functional groups e.g. azido used by industrial competitors for their binders also suffer from the problem of thermal degradation[89]. At the present time nitrate ester polymers discussed here also have promising mechanical properties and meet some requirements postulated by Stacer for an ideal propellant binder[90]. One of these is that the binder must wet the filler[91] so that voids in the final compositions are not observed. The presence of $-ONO_2$ groups seems to aid this with fillers which have the similar nitramine ($>NNO_2$) moiety.
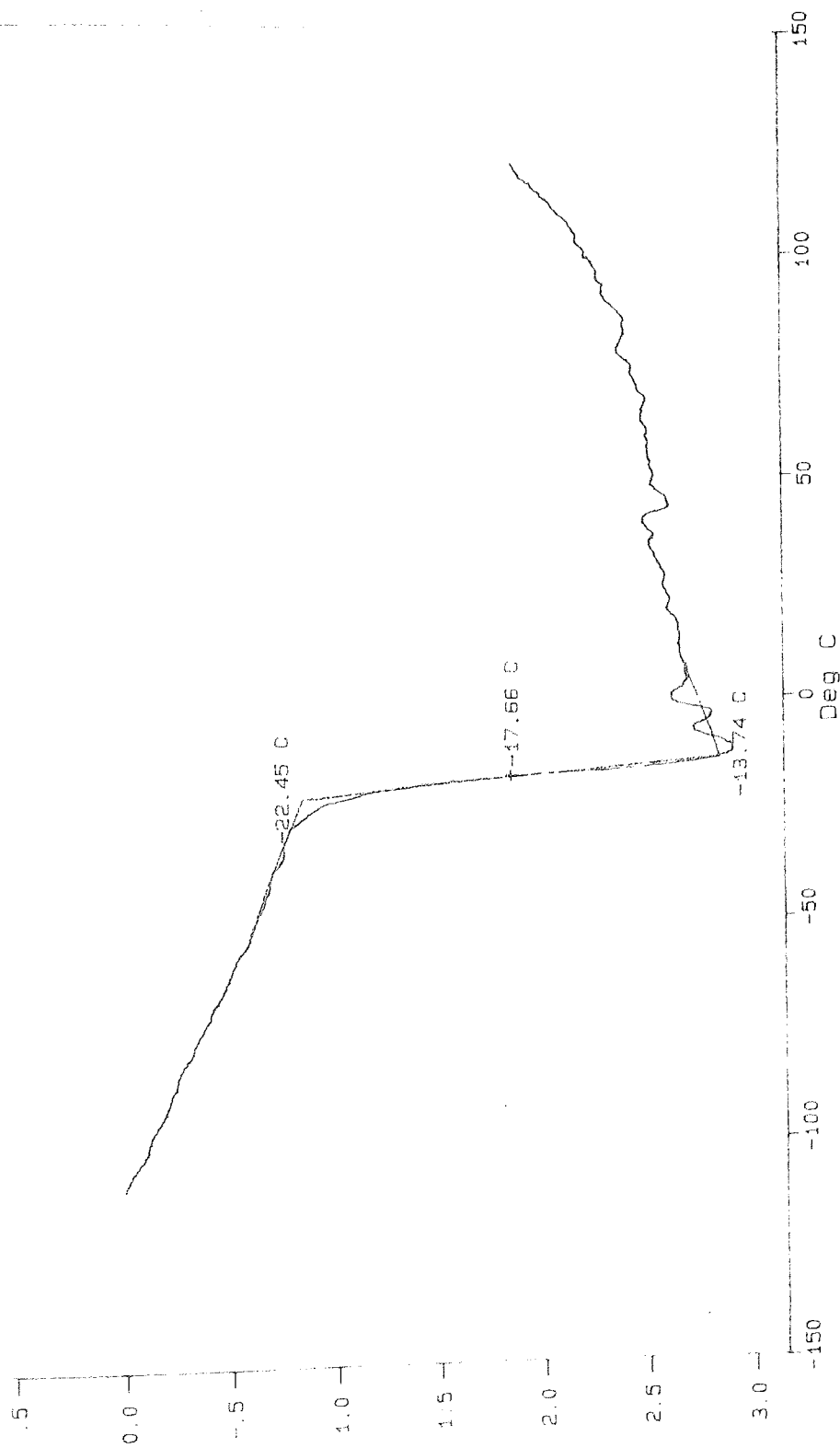
Figure 3.67    DSC trace of GLYN/BODN copolymer

## 3.4 Results and Discussion of polyoxetane prepared by AMM.

Figure 3.68 shows the S.E.C. trace of the polymer prepared by the ring-opening of unsubstituted oxetane. Although a very small amount of oligomer is detected (<2%) it is much less than that usually observed for polymers prepared via the active chain-end (ACE) mechanism. This, allied to the fact that the dispersity of the polymer is less than 1.2, suggests that the dominant mode of propagation is not through the ACE mechanism, although narrow dispersity polymers may be prepared by the ACE mechanism, sub-ambient temperatures as low as -78 °C are normally required and/or living systems. Moreover, the conditions used in this preparation are not suitable for ACE type propagation due to the large excess of hydroxyl concentration, relative to the active cationic species, which hinders 'all monomer in' ACE propagation.

The number average molecular weight (Mn) of the polymer is 1200 and the peak molecular weight is 1300. However, the expected Mn is 1800 assuming that all the monomer is incorporated into a polymer growing from the 1,4-butandiol. That is

$$Mn = [(\text{wt of monomer used}) / (\text{mole of Initiator})] + \text{Mwt of Initiator} \qquad (3.16)$$

This anomaly could be due to a number of factors, for example the presence of hydroxy species in the reaction, particularly, water which is known to initiate AMM polymerisation of oxiranes[79], the evaporation of the monomer during the addition process, insufficient stirring time which may result in the yield of polymer recovered to be about 90 % and inaccuracies in the molecular weight measurements. Further work is in progress to investigate this phenomenon.

N.M.R. spectroscopy was used to establish the overall structure of the polymer, the types of end group present and the way in which the 1,4-butandiol co-initiator was incorporated into the polymer chain. The latter two features are dependent on the polymerisation mechanism and therefore provide useful information about this.

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**Figure 3.68** <u>An SEC refractive index detector trace of a narrow molecular weight</u>
<u>poly(oxetane)</u>
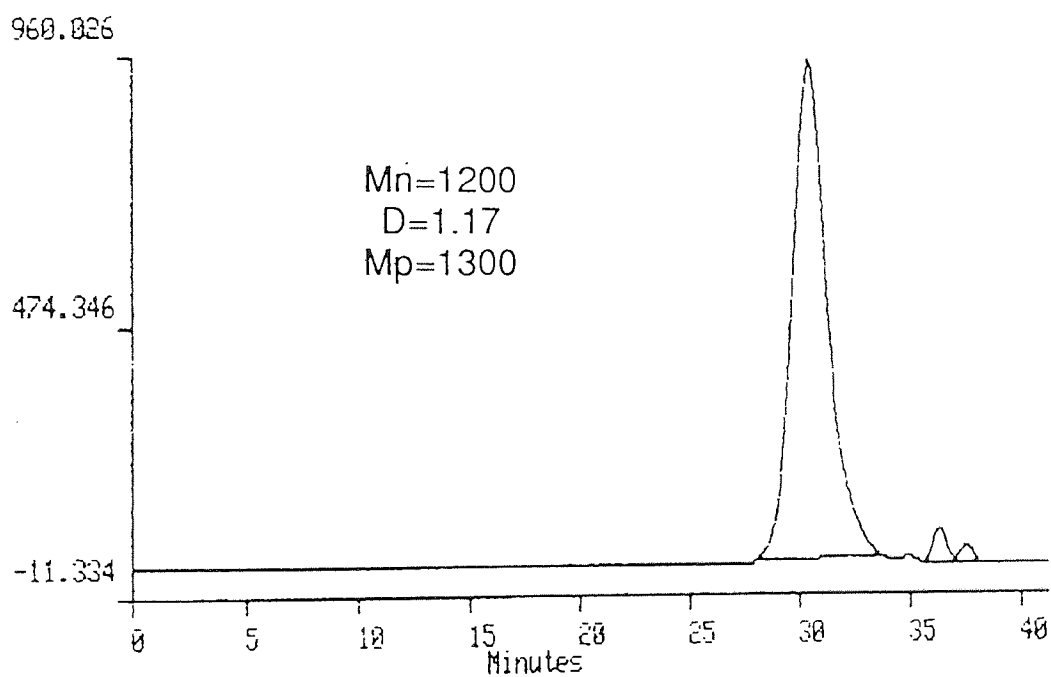


| Peak retention time (Mins) | Area % | Height % |
|---|---|---|
| 30.51 | 95.23 | 90.40 |
| 36.40 | 2.40 | 6.20 |
| 37.63 | 1.14 | 3.25 |

The polymer was identified as linear poly(oxetane) or poly(trimethylene oxide), from its proton (figure 3.69) and $^{13}$C N.M.R. (figure 3.70) spectra. The 300 MHz $^1$H spectrum shows bands at 3.49 ppm (triplet), and 1.81 ppm (pentet), in the ratio 2:1, assigned to the $-OCH_2CH_2CH_2O-$ and $OCH_2CH_2CH_2O-$ groups respectively. The spectrum also shows peaks of equal intensity at 3.41 ppm and 1.61 ppm. These peaks, with the characteristic multiplet lineshape found in polyTHF, are assigned to $-OCH_2CH_2CH_2CH_2O-$ and $-OCH_2CH_2CH_2CH_2O-$ groups respectively, arising from the 1,4-butandiol co-initiator fragments. The symmetry of the resonances indicates that they are present in symmetrical environments (i.e. C-$OCH_2CH_2CH_2CH_2O$-C rather than C-$OCH_2CH_2CH_2CH_2OH$). The observed shifts agree well with literature values for poly(oxetane-co-tetrahydrofuran) copolymers[80].

More structural details were obtained by $^{13}$C N.M.R. spectra at 75.46 MHz. In order to understand the relationships of the end group resonances to those in chain, and the expected positions of the resonances due to the 1,4-butandiol fragments, use is made of the additive nature of $^{13}$C N.M.R. chemical shifts[81]. On the basis of simple additive parameters it is possible to calculate chemical shifts to an accuracy of about 1 ppm. This is often very useful in distinguishing between alternative assignments, particularly when comparing end groups with similar in chain units. The fragments to be considered, together with their calculated chemical shifts[81, p142], are given in table 10.

The main in-chain resonances are observed at 67.7 ppm (relative area A) and 30.1 ppm (relative area B), assigned to the $-OCH_2CH_2CH_2O-$ and $OCH_2CH_2CH_2O-$ groups respectively, in good agreement with the calculated (table 11) and literature values[80]. In addition to the main peaks, the spectrum also shows a number of smaller peaks, with an intensity of about 7% of the main ones. These are assigned to end groups and 1,4-butandiol fragments.

OCH$_2$CH$_2$CH$_2$O
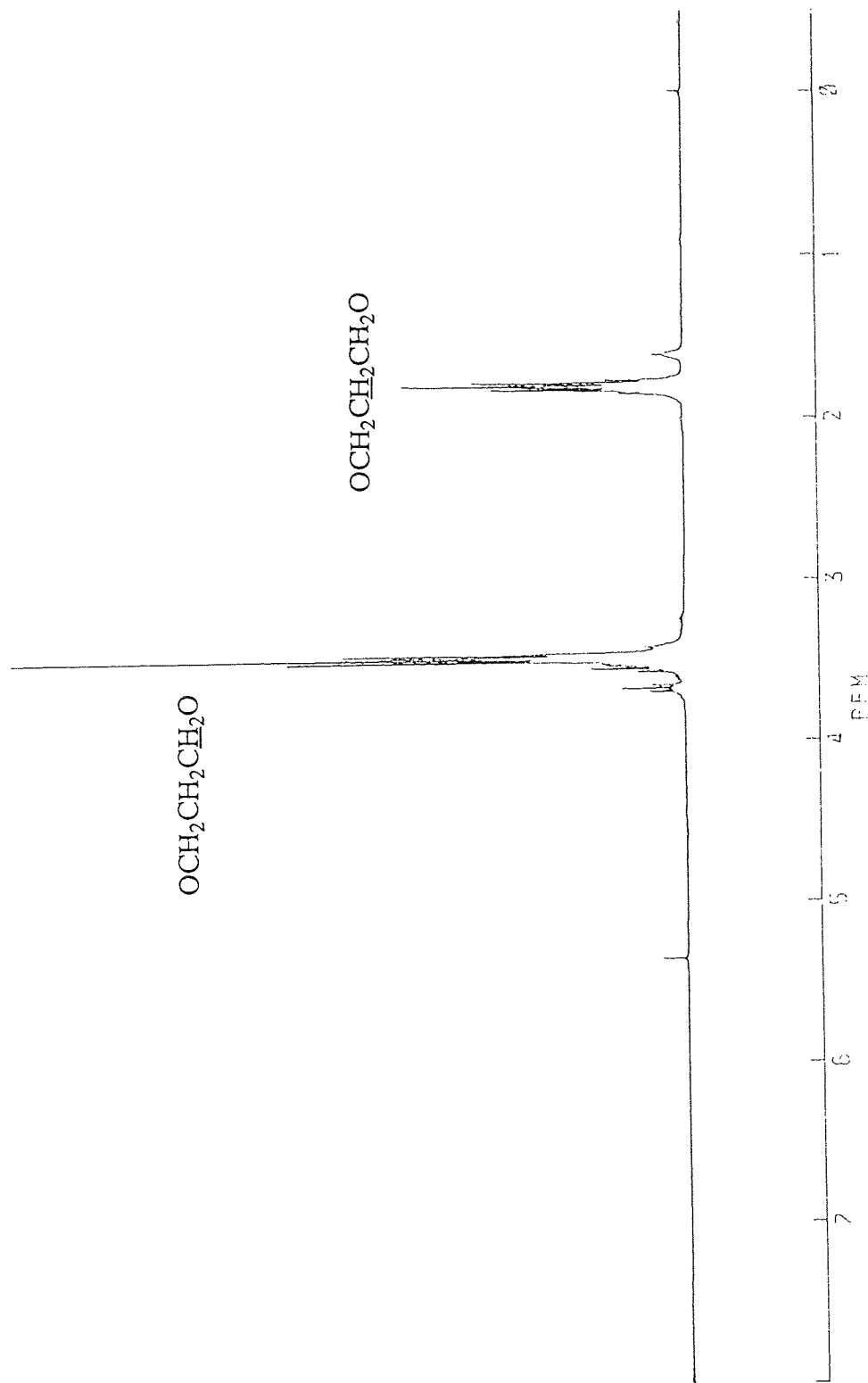
OCH$_2$CH$_2$CH$_2$O

Figure 3.69    300MHz $^1$H NMR spectrum of poly(oxetane)

184
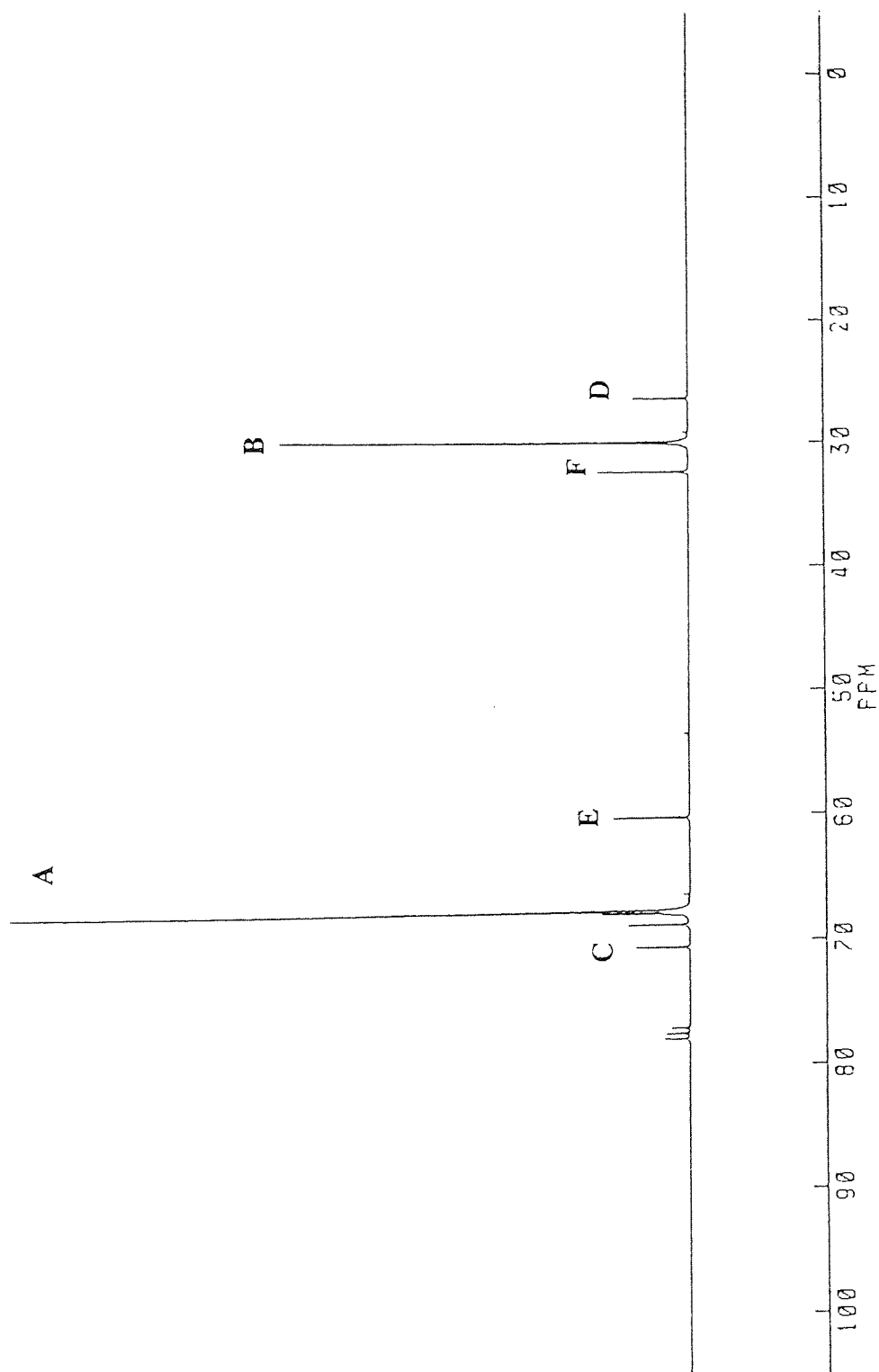
Figure 3.70  $^{13}$C NMR spectrum of poly(oxetane)

| Structure and $^{13}$C Shift (ppm from TMS) | Group |
|---|---|
| -CH$_2$-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-CH$_2$-0<br>B   A<br>31.2  66.9 | I |
| -CH$_2$-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-CH$_2$-0<br>D   C<br>27.3  69.5 | II |
| -CH$_2$-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-CH$_2$-0H<br>F   E<br>33.3  59.6 | III |
| -CH$_2$-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-0H<br>H   G<br>29.8  62.2 | IV |

**Table 10  Calculated $^{13}$C N.M.R. chemical shifts for in-chain and end group polymer structures.  The shifts were calculated using the additive shift parameters given by Stothers[81].**

| Carbon Atom | Calculated Shift (ppm from TMS) | Observed Shift (ppm from TMS) |
|---|---|---|
| A | 66.9 | 67.7 |
| B | 31.2 | 30.1 |
| C | 69.5 | 70.6 |
| D | 27.3 | 26.6 |
| E | 59.6 | 60.3 |
| F | 33.3 | 32.6 |
| G | 62.2 | -a |
| H | 29.8 | -a |

a) not observed

**Table 11.  Comparison of calculated and observed $^{13}$C N.M.R. chemical shifts for the various carbon atoms expected in poly(oxetane) prepared with 1,4-butandiol as co-initiator.**

From the additive scheme, it is clear that the terminal $CH_2OH$ resonances will occur at about 60 ppm. The spectrum shows only one peak in this region, at 60.3 ppm. This is close to the calculated value for the terminal $CH_2OH$ group of an oxetane end group (structure III, table 10). The calculations suggest that a tetramethylene oxide end group, structure IV, should have an appreciably different chemical shift (62.2 ppm), and this resonance has been observed at about 62.5 ppm in a number of polymers[80]. It is concluded therefore that the polymer contains only one type of end group, derived from oxetane, structure III, and that it does not contain end groups derived from 1,4-butandiol, structure IV. This assignment is confirmed by the observation of a peak of a resonance 32.6 ppm, which is assigned, on the basis of the additive shift calculations, to the penultimate carbon atom in an oxetane end group, $OCH_2CH_2CH_2OH$. The fact that this is of equal intensity to the peak at 60.3 ppm is further evidence that there is only one type of $CH_2OH$ end group. The carbon spectrum indicate the presence of fragments derived from the 1,4-butandiol initiator, however, by the presence of peaks of similar intensity to those associated with the end groups at 26.6 and 70.6 ppm. These are assigned to tetramethylene oxide units in a symmetrical in-chain environment, as in structure II.

There are, in principle, six types of polymer structure.

$$HO-(CH_2)_3-O-[(CH_2)_3O]_m-(CH_2)_4-O-[(CH_2)_3O]_n-(CH_2)_3-OH$$

TYPE 1

$$HO-(CH_2)_3-O-[(CH_2)_3O]_m-(CH_2)_4-O-[(CH_2)_3O]_n-(CH_2)_4-OH$$

TYPE 2

$$HO-(CH_2)_4-O-[(CH_2)_3O]_m-(CH_2)_4-O-[(CH_2)_3O]_n-(CH_2)_4-OH$$

TYPE 3

$$HO-(CH_2)_3-O-[(CH_2)_3O]_n-(CH_2)_3-OH$$

TYPE 4

$$HO-(CH_2)_3-O-[(CH_2)_3O]_n-(CH_2)_4-OH$$

TYPE 5

$$HO-(CH_2)_4-O-[(CH_2)_3O]_n-(CH_2)_4-OH$$
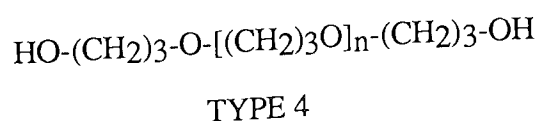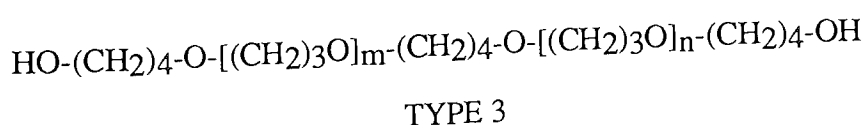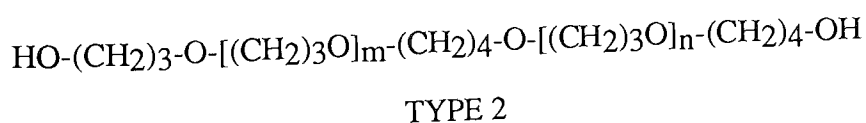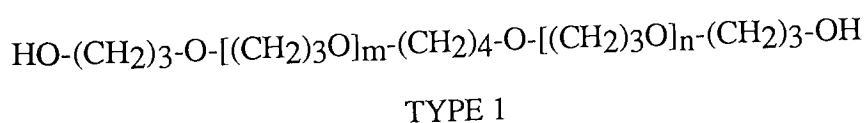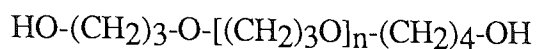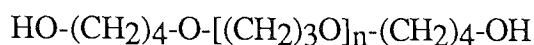
TYPE 6

Type 4, which does not contain fragments derived from the 1,4-butandiol co-initiator, could arise from the presence of small quantities of water in the system or competing ACE propagation and is probably present in small proportions. Of the other structures only type 1 is consistent with the observed $^{13}C$ N.M.R. spectrum, since all the other structures contain tetramethylene oxide end groups. The results presented so far do not prove conclusively that the polymerisation is proceeding via the activated monomer mechanism because the activated monomer oxonium ion species has not been observed directly. The clear differences in end groups and co-initiator incorporation between this polymerisation and others thought to proceed by the active chain end mechanism are consistent with an activated monomer polymerisation mechanism. Certainly, the S.E.C. and N.M.R. results show that the polymerisation method employed in this work produces a polymer which is significantly different from that produced by a more conventional active chain end polymerisation.

From the relative areas of the end group and in-chain resonances, it is possible to estimate the number average molecular weight of the polymer. While accurate quantitative $^{13}C$ measurements require careful consideration of relaxation times and experimental conditions, semi-quantitative measurements were readily made using a gated decoupling pulse sequence to eliminate nuclear Overhauser enhancements, and a pulse delay of 5.0 sec. From the relative areas of the $CH_2OH$ carbons at 60.3 ppm and the in chain $OCH_2$ carbons at 67.7 ppm, a value of Mn 1050 was estimated in reasonable agreement with the value from S.E.C.

## 3.5    A possible alternative to the activated monomer mechanism.

Hitherto, it has been assumed that the activated monomer mechanism as postulated by Penczek and outlined in scheme 10 is correct. Although, the mechanism explains most of the results presented it still leaves certain questions unanswered. These include, why expected molecular weights are rarely achieved as shown by the polymerisation of NIMMO, GLYN and oxetane where monomer is added slowly and the OH:H$^+$ ratio is greater than 5:1. A second question is why the catalytic amount of acid added should not simply complex with the large number of hydroxy groups resulting in little propagation and poor conversion, yet as the S.E.C. traces of polymers prepared show residual monomer levels of less than 10%. Another observation which must be addressed is why more basic cyclic ether monomers such as oxetanes and THF are more difficult to polymerise than the less basic oxiranes. This work shows that oxetane monomers may be ring-opened to form oligomers but to date there are no reports of any propagation of THF. It would be expected that more basic monomers would form the 'activated monomer' readily and therefore should be easier to polymerise. Lastly, the effect of the ring-strain of the monomers should be considered. It appears that the amount of strain determines the ease of polymerisation and the molecular weights attained, the highly strained oxiranes leading to the highest molecular weights.

In order to answer some of these questions an alternative mechanism may be postulated as shown in scheme 15. A substituted oxirane monomer e.g. GLYN or epichlorohydrin is chosen so that the mechanism takes into account the formation of predominantly secondary hydroxyl ends, which are usually observed. The main feature of this alternative mechanism is that an activated monomer species is not formed. Instead, water which should be a good leaving group is displaced in an S$_N$2 type reaction directly by the monomer. In principle any monomer i.e. oxirane, oxetane or THF should be able to do this, however the activation energies and the overall free energies of propagation would be different. Hence, monomers with high

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$HOCH_2CH_2CH_2CH_2\text{-}OH + HBF_4 \xrightleftharpoons{CH_2Cl_2} HO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\overset{+}{O}\overset{H}{\underset{H}{\diagdown}} \quad BF_4^-$

$X = ONO_2$ or Cl etc.

Species D

Slow $S_N2$

Fast

a

b
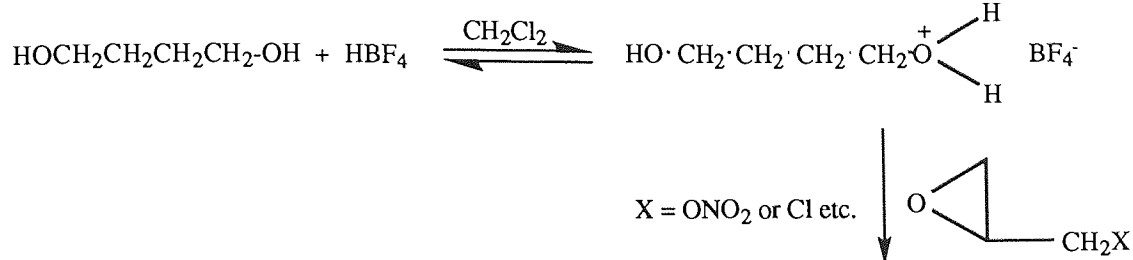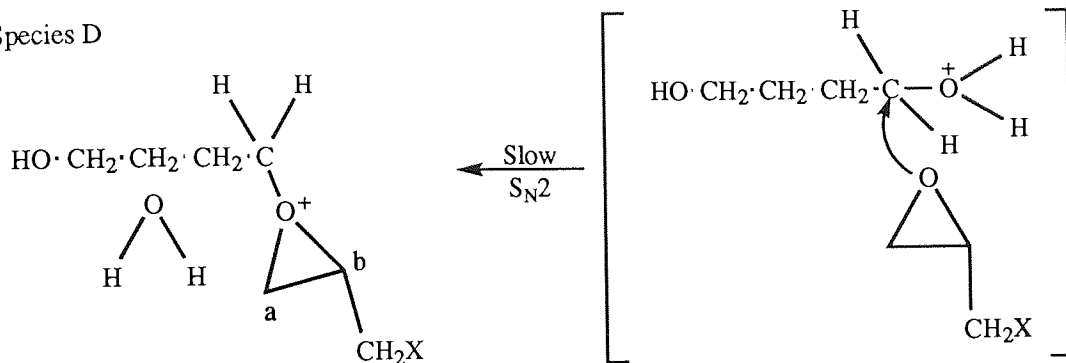
As in $CH_2Cl_2$, $H_2O$ tends towards the more polar oxonium ion
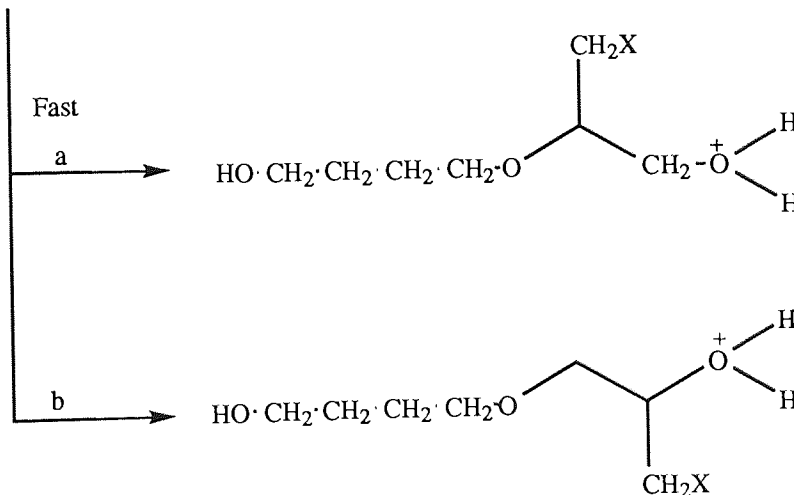
Dominant species because carbon atom b is more electropositive

**Scheme 15. A possible alternative to AMM. (continued overleaf)**

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**Species D**

Fluxionality
of protons
and -I effect
of X

**Species F**

excess H₂O

**Scheme 15. A possible alternative to AMM.**

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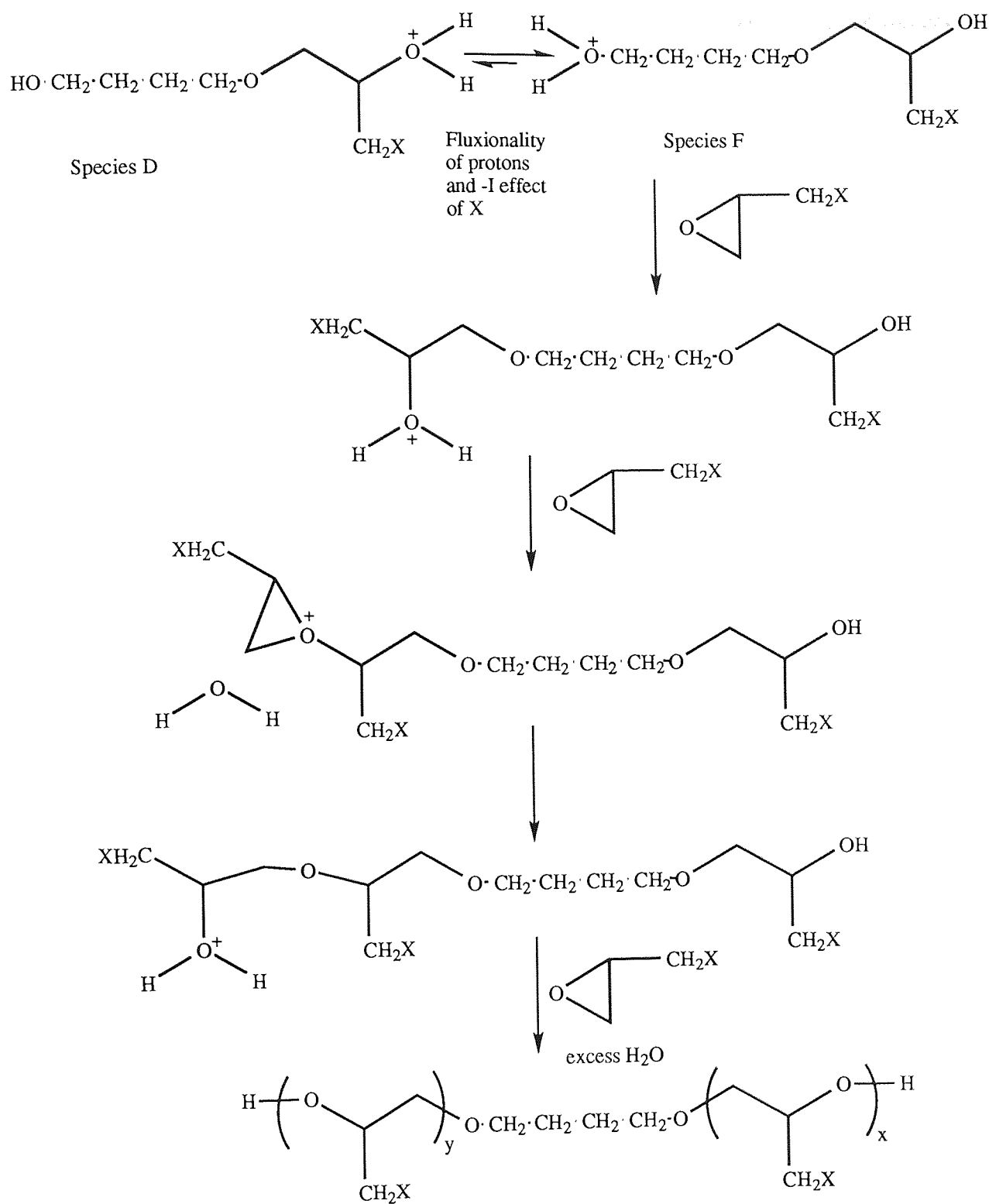
ring strain may compensate for the activation energy of the process, while monomers with low ring-strain would be more difficult to polymerise under conditions of high hydroxyl concentration, low acid concentration and slow monomer addition.

Once, species D is formed, which is the same as an ACE type oxonium ion, then it is able to propagate via the ACE mechanism if sufficient monomer is present. Under low monomer concentration and in $CH_2Cl_2$ the eliminated water molecule is likely to recombine with the oxoniums ion, forming an unstrained oxonium ion, which should be of lower energy.

The attack by the oxygen atom of the water molecule can occur on two possible positions, labelled as carbon atoms a and b. Computer molecular modelling[103] using *ab initio* codes (Gaussian) suggests that carbon atom b is more electropositive, due to the -I effect of the $-ONO_2$ group in GLYN, and this is where the water molecule should attack. This would lead to the formation of secondary hydroxyl groups usually observed.

The observation that the butandiol fragment is usually somewhere in the middle of the chain can be accounted for by the fact that the unstrained oxonium ions proximity to the electron withdrawing group is likely to make its oxygen less basic than the butandiol oxygen, species E, so proton fluxionality will tend to push the equilibrium towards species F. Then as further monomer is added propagation should occur from both ends. If this mechanism is correct then the basicity of the monomer is not the most important factor as long as it is able to displace the $H_2O$ molecule.

This mechanism would also explain why expected molecular weights are not observed. Scheme 16 shows that the eliminated water can act as a competing hydroxyl group for the proton and start a new chain. Another reason for lower molecular weights may be that some form of chain scission is occurring as a competing reaction to propagation. This may be as a result of protons forming unstrained oxonium ions with in-chain ether oxygen atoms, reaction (2) scheme 16,

which may be attacked to displace an alcohol, thus causing chain scission. This would explain the fact that unreacted monomer levels are low yet expected molecular weights are not achieved.

This mechanism would also show narrow molecular weight, telechelic species, relatively free of cyclic oligomers, like the presently accepted AMM. However, considerable further work needs to be carried out to corroborate the steps. The best way to do this would be to carry out an *in-situ* N.M.R experiment monitoring the various species formed throughout the reaction. Unfortunately, due to the continuous pumping of the monomer solution, over 2 to 40 hours, this is practically difficult. A greater understanding of the processes involved may be obtained by molecular modelling of factors such as basicity of monomer, in-chain ether, end-chain hydroxyl groups, the energies of the various species, the free energy and activation energies of the reactions outlined. For instance it may be possible to model whether a cyclic oxonium ion is more stable than a ring-opened carbocation, and so the nature of the active centre may be determined.

1. $HBF_4$ + $\underline{HOH}$ $\longrightarrow$ ...

From $S_N2$
reaction of
monomer
with alcohol

2.

Chain Scission
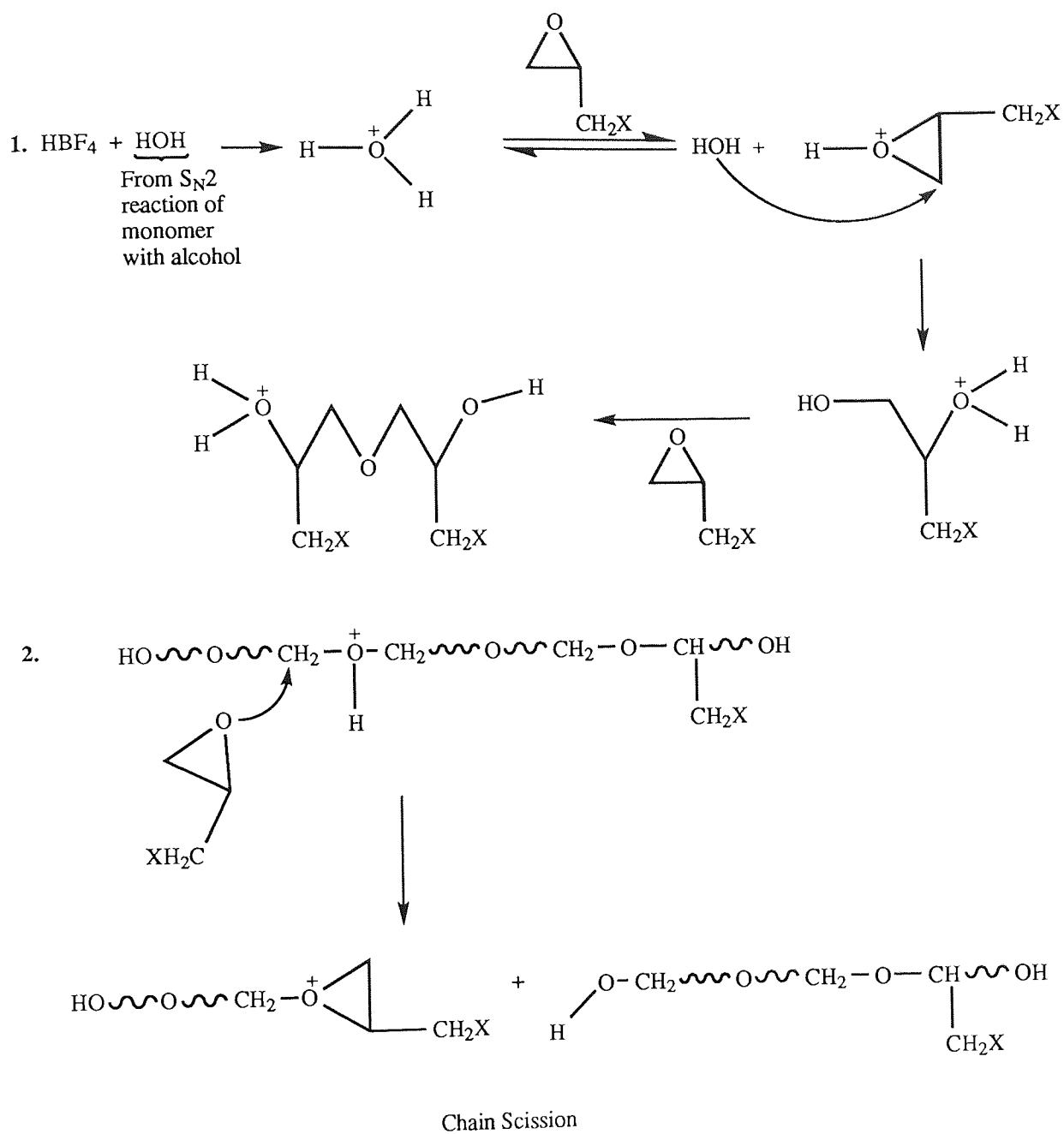
**Scheme 16. Reactions competing with propagation which may lead to molecular weights lower than expected under AMM conditions.**

# CHAPTER 4

# RESULTS AND DISCUSSION: VINYLIC POLYMERISATIONS.

# 4 Results and Discussion of vinylic polymerisations.

Table 12 below shows the reaction conditions S.E.C. (figure 4.1) and N.M.R. (figures 4.2 and 4.3) results for the polymerisations of isobutylene. Polymerisations of α-methyl styrene were also attempted and an example is shown in figure 4.4.

Before the results are fully discussed some of the weaknesses in the experimental procedure should be noted. These include the errors due to the weight and volume measurements of the reagents, especially the volume of isobutylene collected in the graduated vessel. Although care was taken to note the volume of isobutylene at -7°C, at which temperature the density of IB was known, it is possible that the temperature inside the graduated vessel was not -7°C. A second and major source of error in the isobutylene polymerisations was the loss of monomer upon bubbling from the graduated vessel into the reaction flask. An unknown quantity of monomer must have been streamed off along with the $N_2$ from the reaction flask. Partly as a result of this loss and due to the varying amounts of monomer and solvent used, the concentration of the monomer must have differed between reactions. However, it was attempted to keep the concentration of the monomer constant for different experiments.

DPP/BCl3 system gives the narrowest unimodal polyisobutylene (see figure. 4.1) compared to the t-butyl acetate and α-methyl benzyl acetate under the conditions used. There may be a number of reasons why this is so, but before discussing these the mechanism proposed for ester/BCl3 systems[41] should be considered. Scheme 17 below shows an adapted version of Sawamoto's mechanism for the polymerisation of IB by DPP/BCl3 system.

This scheme, involving polarisation of the ester bond or ether in the case of ether/BCl3 systems followed by insertion of the monomer, has also been proposed for other monomers such as isobutylvinyl ethers[41] and styrenes[42].

| Name | Moles of M | Cationogen | Moles of cationogen | Coinitiator | Cationogen:coinitiator ratio | Temp. (°C) | Solvent | Mn expected | Mn observed | Peak molecular weight (Mp) | Dispersity (D) | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HDIB01<br><br>IB=Isobut-ylene | 0.0279 | t-butyl acetate | $3.133 \times 10^{-4}$ | $BCl_3$ | 1:10 | -32 | $CH_2Cl_2$ | 5251 | 6950 | 16300 | 1.405 | Low yield 11 % due to loss of IB through vaporisation. |
| HDIB02 | 0.1374 | " | $1.507 \times 10^{-3}$ | " | " | " | " | 5115 | 11000 | -- | 2.110 | Higher Mn probably due to incomplete initiation. |
| HDIB03 | 0.1117 | " | $1.228 \times 10^{-3}$ | " | " | " | " | 5103 | 7700 | 10000 | 2.983 | Immediate precipitation. White solid observed. 97 % yield. |
| HDIB04 | 0.0670 | " | $6.887 \times 10^{-4}$ | " | " | -40 | " | 5458 | 11600 | 31000 | 1.727 | White precipitate observed. 60% yield. |
| HDIB05 | 0.0614 | " | $8.867 \times 10^{-4}$ | " | " | -35 | " | 3886 | 2500 | 10800 | 1.975 | No precipitate after 16 hours. 30 % yield. |
| HDIB06 | 0.1061 | " | $1.190 \times 10^{-3}$ | " | " | -39 | " | 5002 | 1300 | 9100 | 3.476 | DMSO used to stabilise carbocation and impart 'livingness'. Attempt unsuccessful. |
| HDIB07 | 0.0782 | " | $8.780 \times 10^{-4}$ | " | " | -32 | " | 4995 | -- | -- | -- | DMSO (1 cm$^3$) experiment repeated. No precipitation. No reaction. |
| HDIB08 | 0.1228 | " | $2.840 \times 10^{-3}$ | " | " | -40 | " | 2426 | 1200 | 5000 | 1.551 | DMSO (0.5 cm$^3$) ~10 % yield. |

Table 12.  Results and conditions of the polymerisation of vinylic monomers.

| Name | Moles of M | Cationogen | Moles of cationogen | Coinitiator | Cationogen:coinitiator ratio | Temp. (°C) | Solvent | Mn expected | Mn observed | Peak molecular weight (Mp) | Dispersity (D) | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HDIB09 | 0.0670 | α-methyl benzyl acetate. | $1.130 \times 10^{-3}$ | $BCl_3$ | 1:10 | -50 | $CH_2Cl_2$ | 3314 | 3300 | 12200 | 1.774 | Temperature raised to -20°C for one hour. 35 % yield. |
| HDIB10 | 0.0436 | " | $5.310 \times 10^{-4}$ | " | " | -30 | " | 4606 | -- | -- | -- | DMSO ($0.5cm^3$). No reaction. |
| HDIB11 | 0.0414 | " | $9.290 \times 10^{-4}$ | " | " | -34 | " | 2500 | -- | -- | -- | DMSO ($0.5cm^3$). No reaction. |
| HDIB12 | 0.1340 | " | $2.680 \times 10^{-3}$ | " | " | -20 | Toluene | 2809 | -- | -- | -- | No reaction. Slow or no reaction due to solvent. |
| HDIB13 | 0.1005 | " | $2.780 \times 10^{-3}$ | " | " | -30 | " | 2027 | -- | -- | -- | DMSO ($0.5cm^3$). No reaction. |
| HDIB14 | 0.1340 | Diphenyl phosphate | $1.670 \times 10^{-3}$ | " | " | -28 | $CH_2Cl_2$ | 4490 | 1250 | 4050 | 1.339 | See fig. 4.1 for SEC trace. |
| HDIB15 | 0.1563 | " | $1.750 \times 10^{-3}$ | " | " | -40 | " | 5000 | -- | -- | -- | Suck back into IB flask. No reaction. |
| HDIB16 | 0.1340 | " | $1.500 \times 10^{-3}$ | " | " | -20 | " | 5000 | 1400 | 4200 | 1.222 | Single narrow peak. 70 % yield. |
| HDIB17 | 0.0670 | " | $7.570 \times 10^{-4}$ | " | " | -40 | " | 4963 | -- | | -- | DMSO ($0.5cm^3$) added |

Table 12. cont. Results and conditions of the polymerisation of vinylic monomers.

| Name | Moles of M | Cationogen | Moles of cationogen | Coinitiator | Cationogen:coinitiator ratio | Temp. (°C) | Solvent | Mn expected | Mn observed | Peak molecular weight (Mp) | Dispersity (D) | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HDMeS01 MeS=α-methyl styrene. | 0.0924 | Diphenyl phosphate | $4.260 \times 10^{-3}$ | $BCl_3$ | 1:10 | -30 | Toluene | 2564 | Multi-modal peak. | -- | -- | Exotherm from -30°C to 0°C. 83 % yield. Multi-modal polymer peaks formed but dispersity is very broad. See fig. 4.4. |
| HDMeS02 | 0.0462 | " | $2.150 \times 10^{-3}$ | " | " | -25 | $CH_2Cl_2$ | 2544 | Multi-modal peak. | -- | -- | As HDMeS01 but cloudy solution forms upon termination. 90 % yield. |
| HDMeS03 | 0.04460 | 1,4-butandiol | $2.200 \times 10^{-3}$ | $BF_3 \cdot OEt_2$ | 1 : 2 | 0 | " | 2471 | -- | -- | -- | No reaction. |

Table 12. cont. Results and conditions of the polymerisation of vinylic monomers.

199
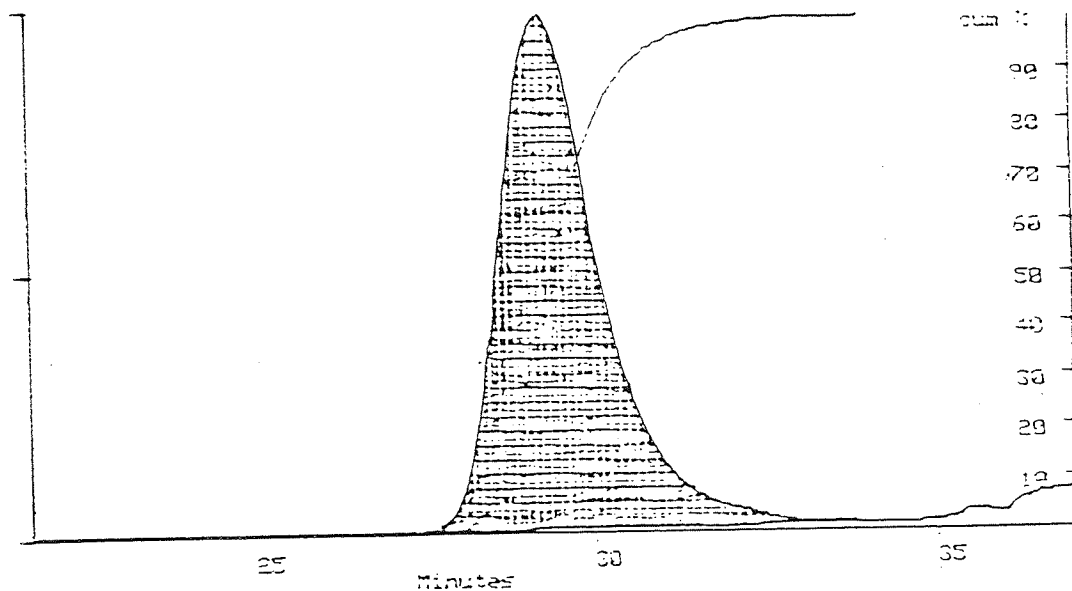
Figure 4.1    SEC trace of polyisobutylene initiated by the diphenyl phosphate/BCl₃ system
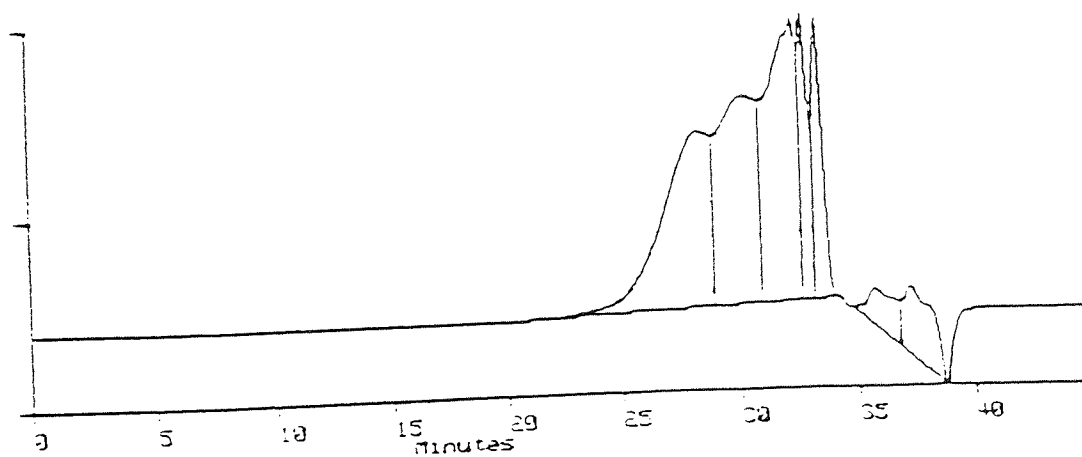


Figure 4.4    SEC trace of poly(α-methylstyrene) pepared by the diphenyl phosphate/BCl₃ system
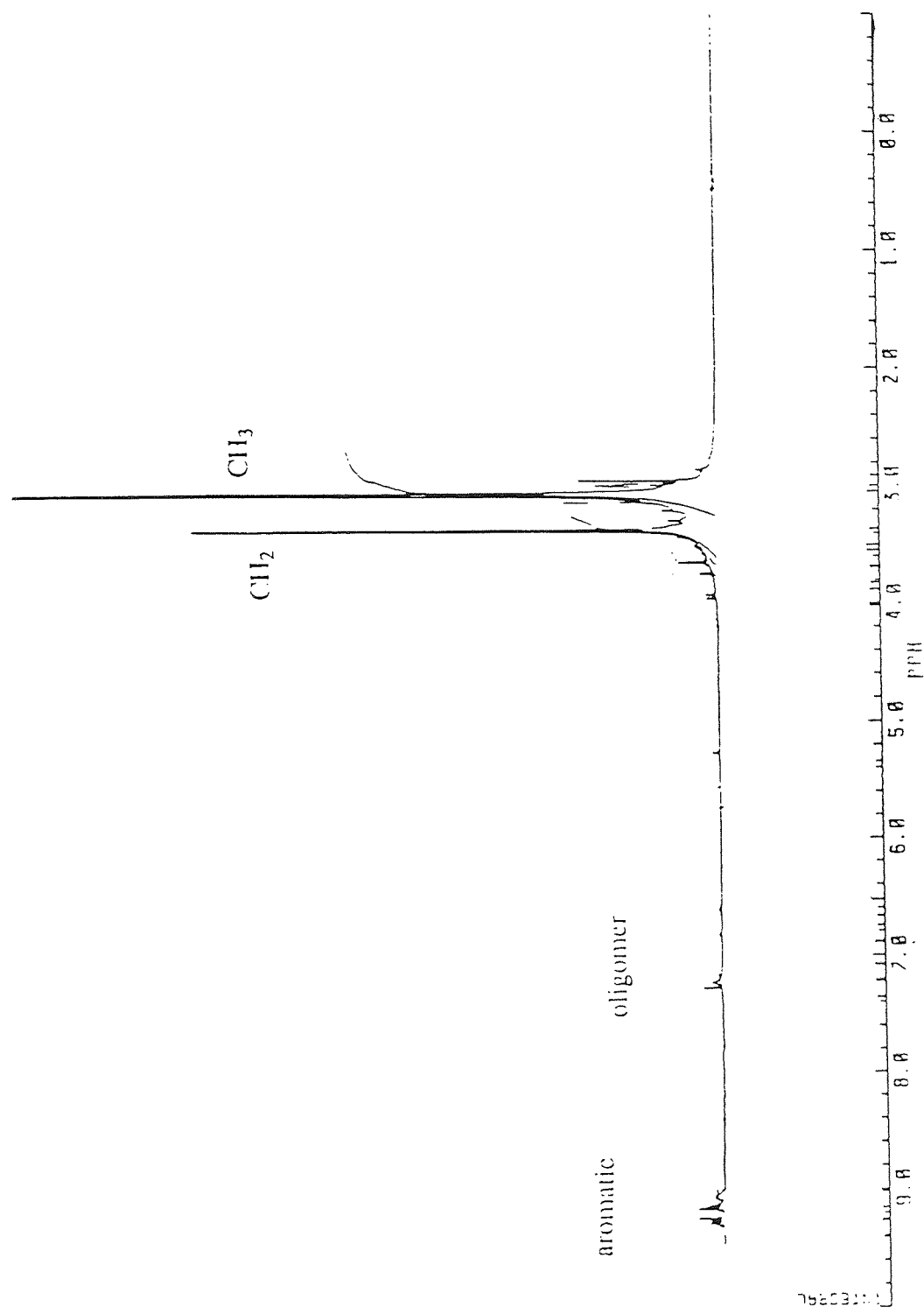
Figure 4.2    $^1H$ NMR spectrum polyisobutylene prepared with diphenyl phosphate/$BCl_3$ system
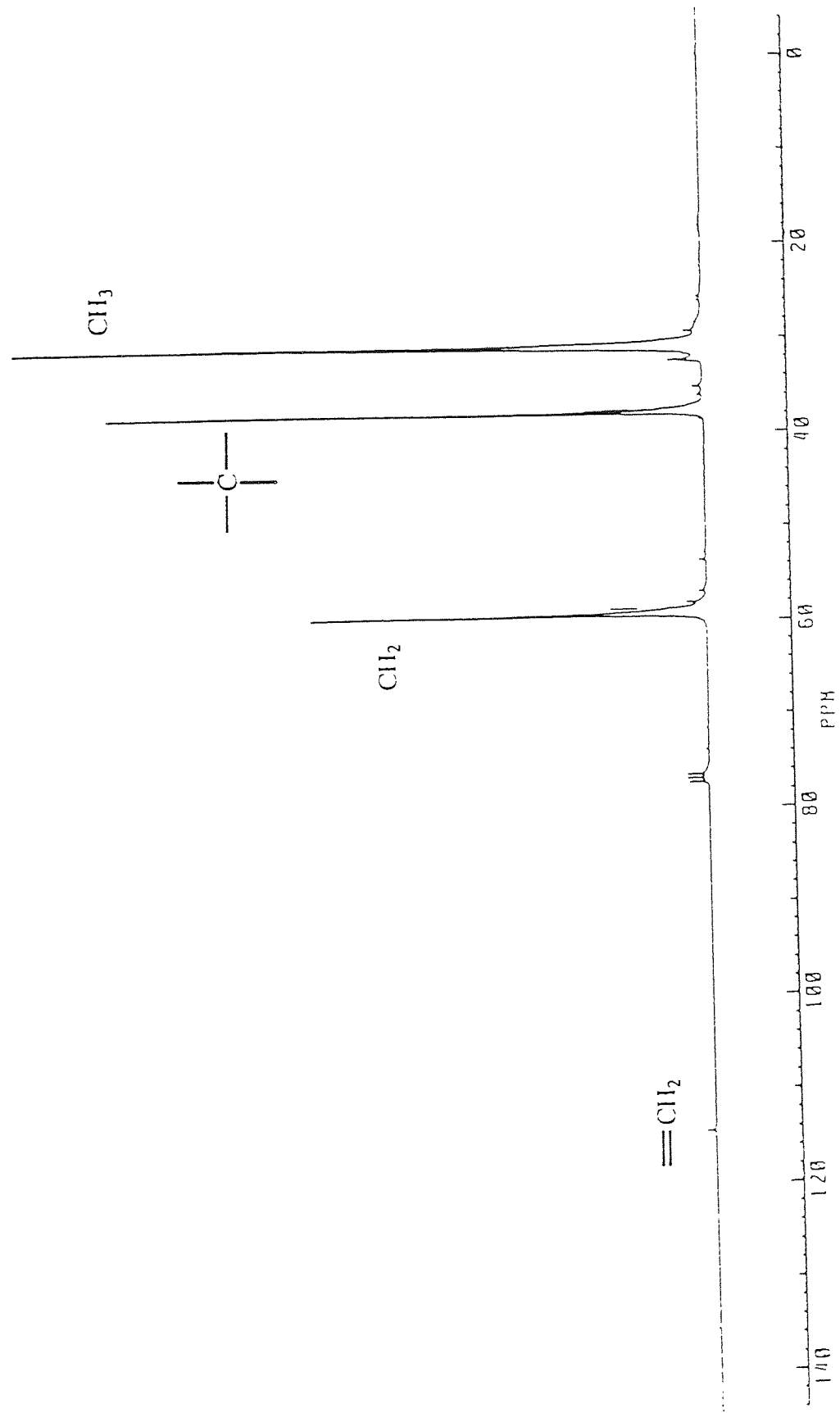
Figure 4.3    $^{13}C$ NMR spectrum of polyisobutylene prepared with diphenyl phosphate/$BCl_3$ system
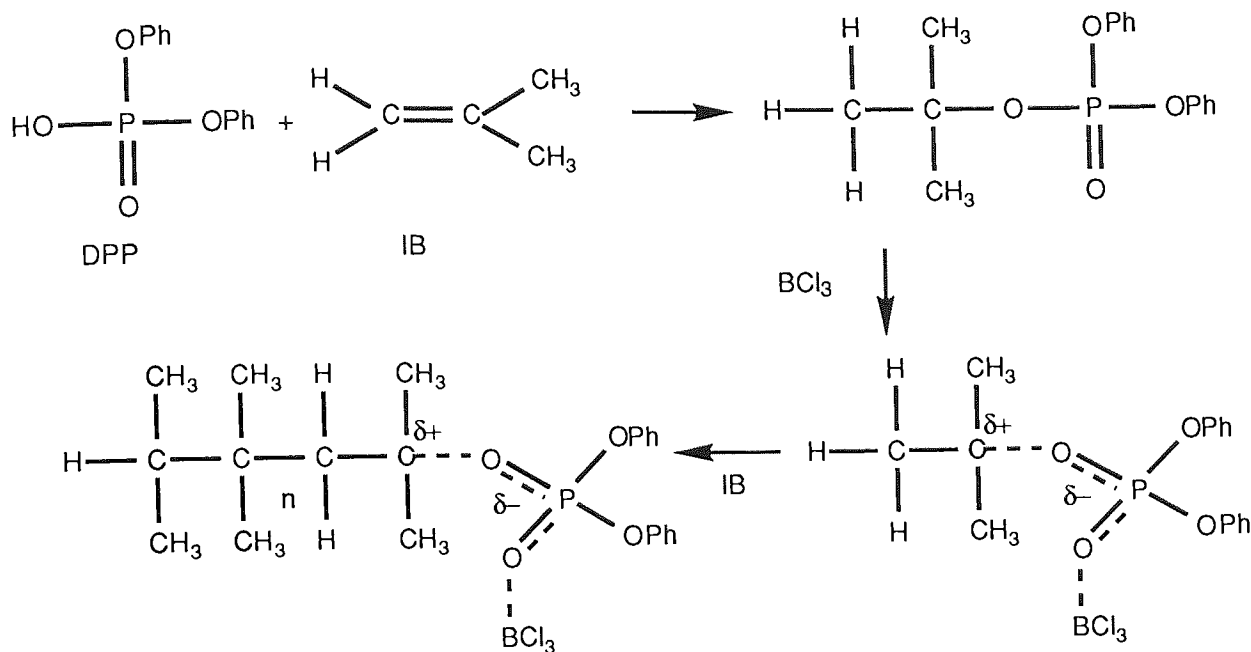
**Scheme 17. Mechanism of the polymerisation of isobutylene by diphenyl phosphate/BCl3 system.**

It is unclear why DPP is better than t-butyl acetate and $\alpha$-methyl benzyl acetate. However, the following factors may individually, or in combination, account for the observed facts. These are :

DPP may reduce the reaction between the growing carbocation and the BCl3:
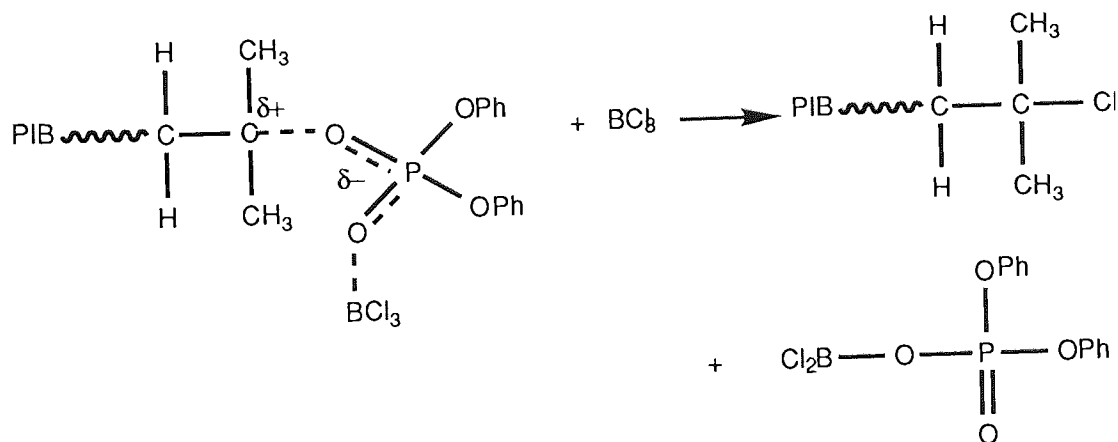


The chlorine terminated PIB may later be initiated and propagate, i.e. lie dormant, or may simply remain terminated depending on the reaction conditions.

The ionicity of the ester as measured by the pK of the corresponding acid indicates that rate of propagation becomes faster with increasing acid strength[43] (Although

other factors may alter this, e.g. resonance stabilisation within the ester molecule). Hence, it would be reasonable to expect the more acidic diphenyl phosphate to have faster Rp than the less ionisable t-butyl acetate and $\alpha$-methyl benzyl acetate.

Electronic effects e.g. resonance would be expected to play a part in the stabilisation of the ion involved. For instance, $\alpha$-methyl benzyl acetate would have been expected to have a higher Rp (so yield higher molecular weight PIB) than t-butyl acetate because of the resonance stabilisation of the counteranion due to the benzyl group. However, this is not the case implying that other non-ionic processes may be occurring. This is corroborated by Fausts[43] work where he observed similar results when using benzoate and cinnamate esters.

Steric hindrance may be a factor but this is not considered likely because DPP has phenyl ether substituents. Another observation which needs some explanation is why the DDP/BCl3 system produces unimodal PIB but multimodal poly $\alpha$-methyl styrene (see figure 4.4). The reasons for this must lie in the differences between the monomers. Despite the presence of the bulky aryl group in $\alpha$-methyl styrene it is one of the most susceptible cationically polymerisable monomers because of electronic effects. However, it is also more likely to undergo transfer and termination leading to oligomerisation and an eventual multimodal S.E.C. trace. It is not clear what the mechanism of transfer is in styrenes but semi-empirical calculations indicate[44] charge is present on the $\beta$-hydrogen atoms which can be attacked by a basic monomer, by the anion, or the solvent leading, respectively, to a protonated monomer (hence a new macromolecule), protonic acid or the protonated solvent. In any case the chain is terminated.

In addition to inter-molecular transfer and termination, intra-molecular reactions via Friedel Crafts alkylation[45] also occur giving rise to indans. Isomerisation, which may be reversible (causing rate reduction) or irreversible (termination) has been observed to occur[46] in $\alpha$-methyl styrene by [1]H N.M.R. and U.V. It is thought that the isomerisation proceeds through two 1,2-hydride shifts or one 1,3-hydride shift.

Due to these more pronounced transfer/termination steps for α-methyl styrenes it is not surprising that a multimodal peak is observed for poly (α-methyl styrene) rather than the PIB.

In these investigations the use of dimethyl sulphoxide (DMSO) as a means to prepare narrow dispersity polymers was prompted by reports written by Kennedy et al.[32,47,48] They claim that electron pair donors convert certain non-living systems to living systems. The role of the electron pair donor is thought to involve stabilisation of the growing carbocation, by forming a complex which, although, reduces the overall Rp also reduces the rate of transfer and termination by hindering recombination of counter-ion and carbocation. However, the results in this report show that polymerisation does not generally occur and when it does (HD1B06) the dispersity is broad. This may be due to the conditions and quality of the DMSO used. That is, the DMSO may have been impure (wet), the concentration of DMSO was unsuitable, the temperature of the reaction was too low or that the DMSO-carbocation complex, in the solvent used, was too strong. If the correct conditions and/or suitable electron pair donor are used then it should be possible to produce controllable, narrow molecular weight vinylic macromolecules.

The polymerisation of 3-nitro styrene using the DPP/BCl3 system, under similar conditions to those of IB polymerisations, proved to be unsuccessful. The observation of a pale yellow solution, upon addition of the initiatory mixture, which becomes colourless when quenched with methanol suggests that a stable charge transfer complex forms. This complex, probably between the nitro group and the initiatory species, probably inhibits the formation of a polymer.

**CHAPTER 5.**

**CONCLUSIONS AND FURTHER WORK.**

# 5.1    Conclusions.

The cationic polymerisations of cyclic ethers and vinylic monomers has been studied. In extensive investigations of the polymerisation of NIMMO by the alcohol/$BF_3.OEt_2$ system it has been found that difunctional, trifunctional or tetrafunctional hydroxy telechelic polyNIMMO can be synthesised. Optimum conditions to produce telechelic polyNIMMO have been developed based on 'incremental monomer addition' because the AMI technique is potentially hazardous due to the risk of a large uncontrollable exotherm. A $BF_3.OEt_2$:OH ratio of 1:1, a reaction temperature of 0 °C, and monomer addition over 4 hours of a 20 % w/v solution of NIMMO in $CH_2Cl_2$, followed by 2 hours of stirring and a further 2 hours of stirring at +30 °C produces hydroxy telechelic polyNIMMO with less than 5% unreacted monomer contamination.

Higher molecular weight polyNIMMO (>6000) can be prepared by lowering the temperature below 0 °C, however there is a decrease in the conversion from monomer to oligomer or polymer.

The main cyclic oligomer found during polymerisation of NIMMO has been purified and characterised. This has been identified as the cyclic tetramer. A procedure for the almost exclusive synthesis of the cyclic species has been developed based on the dilution of the monomer to a 2 % w/v solution in $CH_2Cl_2$, a cationogen ($HBF_4$) to monomer ratio of 1:4, respectively, and IMA over at least 2 hours. The use of $LiBF_4$ as a templating $Li^+$ ion source in order to enhance cyclisation was unsuccessful due to its low solubility in $CH_2Cl_2$. The cyclic species extracted act as miscible and compatible plasticisers for the parent homopolymer.

Linear oligomers of NIMMO have been prepared by the activated monomer mechanism and have been further nitrated to form novel nitrato telechelic oligomers, which are envisaged as highly energetic plasticisers or automobile fuel additives

(oxidisers). However, the AMM did not produce higher molecular weight (>1500) polymers.

AMM polymerisation of GLYN has led to the synthesis of an $\alpha$, $\omega$-hydroxy telechelic polymer which has a higher oxygen to carbon ratio than polyNIMMO and is therefore more energetic in terms of use in propellant compositions. The polymerisation system was $HBF_4$/alcohol, at 0 °C, and the monomer was added as a 20% w/v solution in $CH_2Cl_2$ over 16 hours. This material has a lower glass transition temperature -36 °C, than polyNIMMO, -25 °C. Some of the properties of these materials are shown in the Appendix.

In order to solve the degradation of the isocyanate cured polyGLYN binder, believed to occur through scission of the urethane link, end-capping and block-capping of the prepolymer to produce different hydroxyl groups were attempted. End-capping using less than 3 mol equivalents relative to GLYN hydroxyl groups of the capping monomer was found to be incomplete, especially if the new hydroxyl end was primary, for example when oxetane, HIMMO or NIMMO monomers were used. The N.M.R. evidence shows the presence of unmodified GLYN hydroxyl ends and some new oxetane hydroxyl ends. The use of substituted oxiranes to form less reactive secondary hydroxyl groups upon capping, which would be less likely to form blocks at the end of the prepolymer, was attempted using styrene oxide. Again the degree of capping was low probably due to the formation of blocks and the side reaction leading to homopolymer. Even when 8 mole equivalents of NIMMO relative to prepolymer hydroxyl groups was used the degree of capping, although better, is not greater than 30%.

A novel highly energetic monomer bearing two nitrate ester groups, known as butadiene oxide dinitrate (BODN) has been synthesised from diepoxybutane using $N_2O_5$. The deactivating effect of the nitrato groups has been used to selectively open one ring whilst keeping the second ring intact and under conditions (-10 °C, addition of the diepoxybutane to $N_2O_5$) where the polymerisation or cross-linking of the

diepoxybutane has been prevented. The polymerisability of the monomer has been demonstrated using triethyl oxonium tetrafluoroborate as the cationogen, although control over the system has not been achieved. In addition, a copolymer with GLYN has been prepared.

The activated monomer polymerisation of oxetane (trimethylene oxide) has also been studied. Although the monomer has similar ring-strain but greater basicity than oxirane, it does not polymerise to expected molecular weights.

Cationic polymerisation of isobutylene with t-butyl acetate, $\alpha$-methyl benzyl acetate and diphenyl phosphate as cationogens and $BCl_3$ as coinitiator were studied. The diphenyl phosphate/$BCl_3$ system was the best for preparing telechelic polyisobutylene with narrow molecular weight distributions. This system was also suitable for the polymerisation of $\alpha$-methyl styrene but multi-modal peaks were observed suggesting that transfer/termination reactions were present.

## 5.2    Further work.

Although NIMMO materials ranging from oligomers to high polymers are preparable using monomer with some impurities, further work should be carried out to improve the nitration of HIMMO, perhaps at lower temperatures between -30 °C and -20 °C, so that better quality NIMMO is obtained. An alternative is to distil the crude monomer under vacuum at a temperature less than 80 °C. Examination of the residue by N.M.R, I.R etc. should indicate the nature of the impurities. Once this is known the effect of these impurities on MWD of polymerisations may be carried out by simply adding measured amounts to reactions.

To improve the conversion of higher molecular weight polyNIMMO (>6000) at temperatures below 0 °C, it may be necessary to increase the monomer feed concentration to 40-70 % w/v in $CH_2Cl_2$. This should increase the rate of propagation and as transfer/termination reactions should be slower, higher molecular weight products should be formed.

To reduce transfer/termination reactions at ambient temperatures the use of additives such as DMSO, DMF and dimethyl acetamide should be more carefully investigated, particularly in terms of the amounts added. Whether the ring-opening polymerisation of NIMMO or other strained cyclic ethers proceeds by an ACE mechanism involving a cyclic oxonium ion or a ring-opened carbocation as the active centre should be studied by *in-situ* N.M.R. experiments. If the propagation proceeds via a carbocation then suitable crown ethers may be able to coordinate around the active centre and hinder back-biting reactions to form cyclic oligomers and other transfer/termination reactions. Evidence to support such complexation between ethers and active centres has been found by Amass and Gourderes[105] when polymerising oxetane, using a $BF_3.OEt_2$/alcohol system with veratrole [1,2-dimethoxybenzene, $C_6H_4(OCH_3)_2$], who observed the formation of higher molecular weight polyoxetanes than any prepared without the additive.

Kinetic studies of the polymerisation of NIMMO to determine the orders of reaction relative to alcohol, monomer and $BF_3.OEt_2$ should also be carried out. Comparison of data between NIMMO and other similar monomers e.g. 3,3-dimethyl oxetane may indicate the effect of the nitrato group on the polymerisation.

In the synthesis of cyclic oligomers a different solvent e.g. pyran may help to dissolve the $LiBF_4$ and help cyclisation. Other salts more soluble in DCM may also be investigated e.g. LiCl, or with different metal counter-ions. Further work to see if the presence of these salts in the final polymer has an effect on its retention time on the S.E.C. columns should be carried out.

Methods to make polyGLYN of higher molecular weights (>3000), linear hydroxy telechelic oligomers, linear end-nitrated oligomers and cyclic species need to be found. Work similar to that carried for NIMMO materials should enable the synthesis of these GLYN compounds. The effect of cationogen to monomer ratio, dilution of monomer and temperature of reaction should provide interesting information about the nature of the propagation of GLYN systems.

The end-capping of polyGLYN should be investigated in detail using substituted oxiranes e.g. styrene oxide, propylene oxide and tert-butyl glycidyl ether. The use of more hindered substituents may help to produce a better degree of capping under AMM conditions. Alternatively, to prevent the side reaction of homopolymerisation which occurs when an unsubstituted monomer such as oxetane is used, a less reactive monomer, but which may proceed under AMM conditions, such as THF or hexamethylene oxide should be considered. Hexamethylene oxide, indeed, may be more suitable in that it has more ring-strain than THF and if ring-strain determines whether the monomer proceeds by AMM then it is more likely to cap polyGLYN. To improve capping, raising the amount of $HBF_4$ added so that $OH:H^+$ ratio is approximately 1:1 may help to generate more activated monomer species which would react with the GLYN ends.

Another possibility of improving degree of capping may be to form a reactive end by sequential addition of the capping monomer e.g. oxetane and protect it by using $R_3SiCl$ or $R_3SiBF_4$, followed by further addition of monomer. The protecting group could be selected so that it does not react with the secondary GLYN hydroxyl ends but only with any primary ends formed.

The synthesis of the BODN monomer may be improved by using flow reaction techniques whereby the epoxybutane solution in dichloromethane could be mixed in a reaction chamber or tube for a very short time with a stream of $N_2O_5$ in dichloromethane. This should prevent ring-opening of both epoxide groups and homopolymerisation of diepoxide. This may allow the process to be scaled-up more easily. Control over the homopolymerisation of the monomer has yet to be achieved and various cationogens e.g. triflic anhydride may be suitable. Detailed N.M.R. studies should be carried out to determine the nature of the copolymer with GLYN i.e. is it a statistical or alternate copolymer. Tacticity should also be determined. Obviously, copolymers and terpolymers with NIMMO, GLYN or other cyclic ethers

should provide a range of materials with different properties, particularly, in terms of energy and hydroxyl ends.

The polymerisation of polyoxetane by AMM has raised questions about the exact nature of the mechanism. Evidence is required to support the alternative mechanism, involving the elimination of $H_2O$ molecule in an $S_N2$ type reaction. This may be directly observed by carrying out an *in situ* N.M.R. experiment where the nature of the propagating species may be observed. This should indicate whether the activated monomer species ever forms. However, due to the sequential addition of the monomer and the possible short lifetime of the activated monomer species this could be difficult. Hence, *ab initio* level calculations of the enthalpies of formation of the various postulated species should be undertaken. Moreover, the basicities or nucleophilicities of the monomers, in-chain ether oxygen atoms, end-chain hydroxyl groups should provide clues about the mechanistic processes. In any case, the effect of factors such as reaction temperature and monomer feed concentrations on preparing higher molecular weight polymers should be examined.

The use of mixed solvents ought to be examined in the polymerisation of vinylic monomers, e.g. isobutylene, to support the initiator system and prevent precipitation of the polymer once a certain molecular weight is reached. Solvents such as $CH_2Cl_2/n\text{-}C_6H_{14}$ or $CHCl_3/n\text{-}C_6H_{14}$ may be suitable. The diphenyl phosphate/$BCl_3$ system should be optimised for the polymerisation of $\alpha$-methyl styrene and the polymerisation of other styrenes e.g. methoxy styrenes or styrenes with protected alcohol groups should be investigated. The use of additives e.g. DMSO in vinylic systems to reduce transfer/termination reactions should be continued with a view to obtaining living systems.

If vinylic living systems are developed which may also initiate cyclic ether polymerisations, then block copolymers leading to novel thermoplastic elastomers should be feasible. The synthesis of this type of material has been the long term aim of this research. In the near future block copolymers using cyclic ether hard segments

with monomers such as NIMMO and GLYN as soft segments should be easier to prepare, via sequential polymerisation forming ABA type compounds. As the molecular weights of the polyethers prepared in this report are low, chain extension of these ABA via urethane chemistry should enable $(ABA)_n$ or $(AB)_n$ type architectures.

Although cyclic ether monomers which will form hard blocks are known, e.g. styrene oxide and symmetrically 3,3-substituted bis oxetanes, considerable synthetic effort needs to be devoted to this area so that cheap, energetic monomers may be prepared. It is this area where immediate research should be focused.

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**APPENDIX**
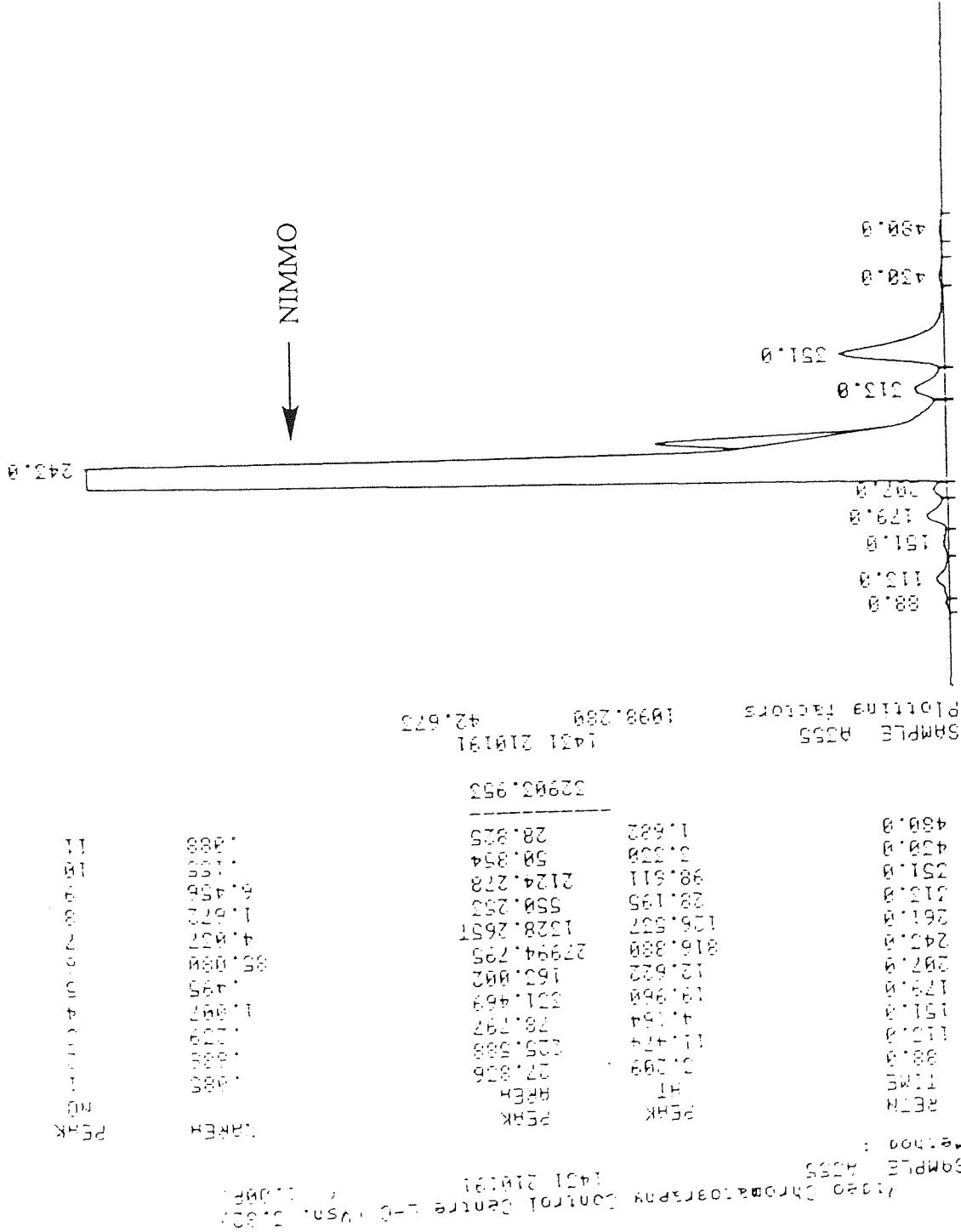
NIMMO

HPLC trace of NIMMO monomer showing presence of other impurities

Fourier transform I.R. spectrum of polyNIMMO
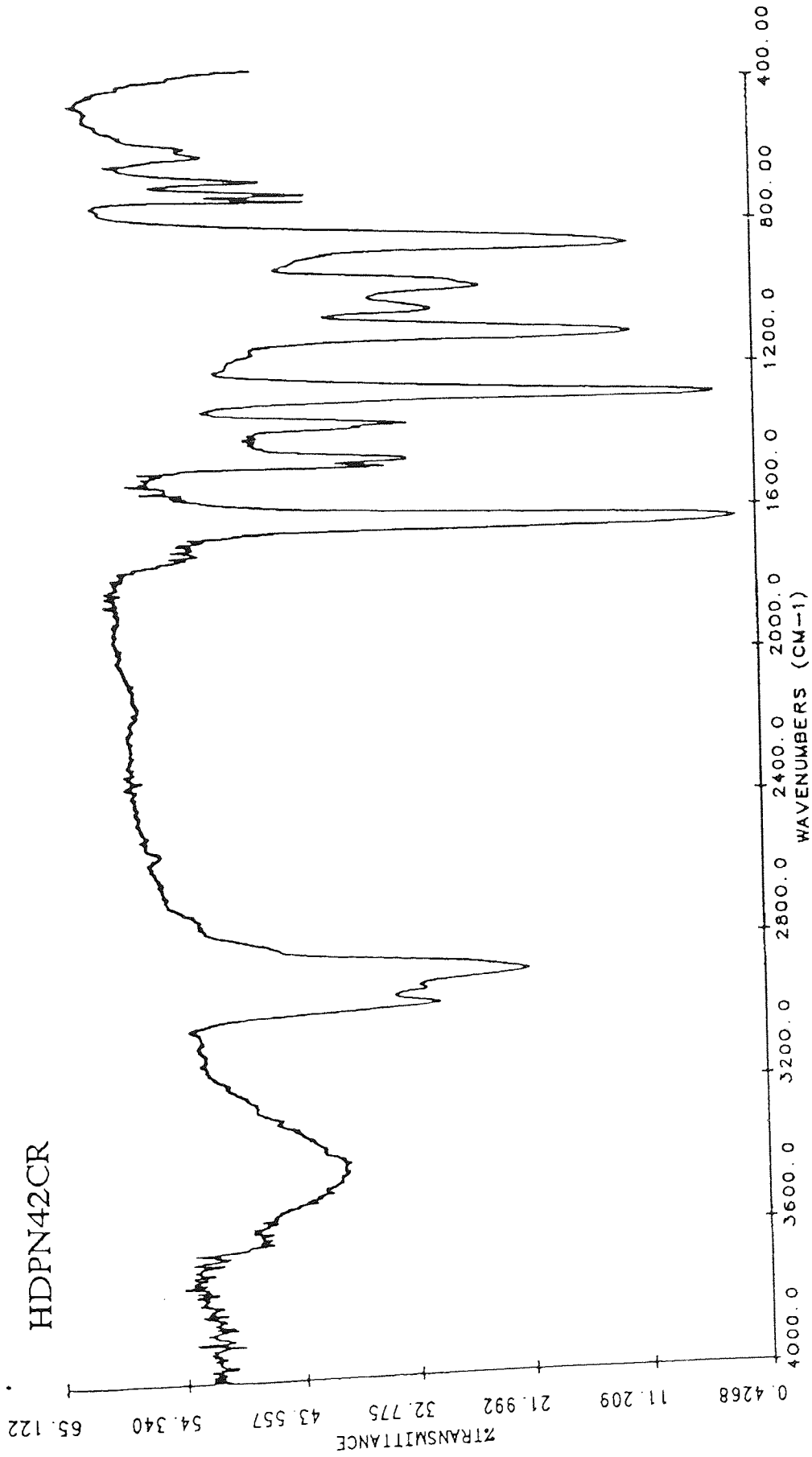
# APPENDIX.

| | |
|---|---|
| Density | 1.26 gcm$^{-3}$. |
| Viscosity | 160 poise @ 60 °C |
| | 1350 poise @ 30 °C |
| Glass transition temperature (Tg) | -25 °C. |
| Onset of decomposition | 170° C |
| Temperature of ignition | 187 °C |
| Exotherm maximum | 229 °C |
| DH$f$ | -309 kJ/kg. |
| UN hazard classification | Class 3 (flammable liquid) |
| Impact (Rotter) Figure of insensitiveness | Out of range. |

**Properties of PolyNIMMO of molecular weight 5000.**

Data Sheet for Poly(GlycidylNitrate)

# POWA 3A

## Provisional Data Sheet

Description

POWA 3A is a homopolymer of glycidyl nitrate (GLYN) possessing terminal secondary hydroxyl groups. This pale yellow energetic liquid polymer can be subsequently crosslinked with multifunctional isocyanates or difunctional isocyanates in conjunction with triol to yield solid rubbery materials. It has potential applications as an highly energetic binder in a wide variety of formulations.

Structure

$$H \left( O\text{-}CH_2\text{-}\underset{\underset{CH_2ONO_2}{|}}{CH} \right)_n OH \qquad n=30$$
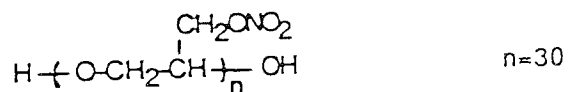
Properties

Molecular weights $M_w = 4400 \qquad M_n = 3000 \qquad M_w/M_n = 1.46$
($M_n$- from nmr end group analysis)
($M_w$- from gpc)

Purity $\geq 99\%$
(NMR, IR, GPC)

Impurities GLYN (0.5%)

Density $1.39 \text{ gcm}^{-3}$

# APPENDIX

Viscosity

46 poise @ 50°C

163 poise @ 30°C

Glass transition
temperature (DSC)

$-35^0C$

Functionality

$\leq 2$

Miscibility

Fully miscible with all commonly used energetic
plasticisers. (For example K10, Metriol trinitrate,
and BDNPA/F have been successfully employed)