The Living Cationic Polymerization of Isobutene.

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Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

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SUMMARY

The polymerization of isobutene initiated by 1-chloro-1-phenylethane has been investigated, and molecular weight studies conducted using size exclusion chromatography. Polymerizations carried out in a 40/60 (v/v) mixture of dichloromethane /cyclohexane, using titanium (IV) chloride as a catalyst in the presence of pyridine at -30 °C were found to be controlled and living. The number average molecular weights of the polymers increased linearly with monomer conversion, and the molecular weight distributions were between 1.15 and 1.20. Efficiencies of initiation were between 80 and 100%, and evidence was found to suggest that backbiting to the initiator had occurred, resulting in the formation of cyclic oligomers during the early stages of polymerization.

The kinetics of polymerization can be explained in terms of active species in equilibrium with dormant species. The effects of temperature and dielectric constant on this equilibrium were studied and a model based upon the Fuoss equation was developed.

Pyridine was found to behave as proton trap in the system, and when it was used in excess the rate of polymerization was retarded. By assuming that the catalyst and pyridine formed a one to one complex, it was possible to show that the reaction was second order with respect to the catalyst.

The synthesis of low molecular weight polyisobutenes was studied. When the concentration of initiator was increased relative to that of the isobutene, such that the theoretical degree of polymerization was 20 or less, the rate of initiation was slow compared to propagation. The efficiency of initiation in these polymerizations was typically between 30 and 40 %. Optimal conditions of temperature and catalyst concentration were established, leading to a 60 % efficiency of initiation.

A one-pot synthesis of phenol end-capped polyisobutene was attempted by adding phenol at the end of a living polymerization. Evidence to substantiate the existence of capped polymer chains in the resultant product was inconclusive.

Block copolymerizations of oxetane and isobutene were conducted using 1-chloro-1-phenylethane/$TiCl_4$, but no copolymer or oxetane homopolymer could be isolated.

Keywords: Fuoss equation; Dielectric constant; Titanium (IV) chloride, 1-Chloro-1-phenylethane; Oxetane.

To family and friends,
thanks.

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List of general nomenclature

R_i = rate of initiation
R_p = rate of propagation
R_t = rate of termination
R_{tr} = rate of transfer
E_p = activation energy of propagation
ε = dielectric constant
ΔG_p = Gibbs free energy of polymerization
ΔS_p = entropy of polymerization

k_i = rate constant of initiation
k_p = rate constant of propagation
k_t = rate constant of termination
k_{tr} = rate constant of transfer
E_t = activation energy of termination
I_{eff} = efficiency of initiation
ΔH_p = enthalpy of polymerization
T_c = ceiling temperature of polymerization

K_i = constant of equilibrium in mechanism of initiation
k_{ion} = rate constant of ionisation of the initiator
k_{col} = rate constant of collapse of the initiator
K_p = constant of equilibrium in mechanism of propagation
k_1 = rate constant of ionisation of dormant chain carriers
k_2 = rate constant of colapse of active chain carriers
k_{app} = apparent rate constant of propagation
k_{pobs} = observed rate constant of polymerization

W_p = weight of polymer
$\overline{M}_n$ = number average molecular weight
MWD = molecular weight distribution
$\overline{DP}_{n\infty}$ = degree of polymerization at 100% conversion

[P] = concentration of polymer chains
$\overline{M}_w$ = weight average molecular weight
$\overline{DP}_n$ = average degree of polymerization

IB = isobutene
Pyr = pyridine
cHex = cyclohexane
DiPhE = 1,1-diphenylethane
M = monomer

PIB = polyisobutene
ED = electron donor
DCM = dichloromethane
Tol = toluene

IBVE = isobutylvinyl ether
^{t}BuCl = *tert*-butyl chloride
Hex = hexane
MtX_n = metal catalyst

1-PEC = 1-chloro-1-phenylethane
DtBP = 2,6-di-*t*-butyl pyridine
TMPCl = 2,4,4-trimethyl-2-pentyl chloride
TMPOAc = 2-acetoxy-2,4,4-trimethylpentane
DiCumCl = 1,3-dicumyl chloride
1-PEB = 1-bromo-1-phenylethane
TMPOH = 2,4,4-trimethyl-2-pentol
CumCl = 2-chloro-2-phenyl propane
CumOAc= dicumyl acetate

Chapter 1: Introduction

1.1 General introduction

Synthetic polymers can be classified into groups according to their method of preparation [1]. Those that are produced as a result of the combination of monomers, dimers, and oligomers to form larger macromolecules are termed step growth, or condensation polymers, and their synthesis often involves the release of a small molecule, such as water [2]. Examples of materials formed by this technique are polyesters (e.g. Terylene), polyureas (e.g. Urylon), and polyamides (e.g. Nylon) [3].

Ring-opening polymerization is a method of preparing polymers from strained cyclic molecules [4]. Cyclic ethers, and amines will readily undergo ring-opening reactions in cationic, or anionic conditions. For example, ethylene and propylene oxide are polymerized on a large scale and are important ingredients in adhesives and surface coatings. Another technique that falls into this catagory is ring opening metathesis (ROMP) [5], used for polymerizing strained cyclic alkenes, such as cyclopentene. The process produces linear polymer chains containing unsaturated sites.

Chain-growth, or addition polymers, are formed by the addition of single monomer units onto an active growing chain. The polymerization of vinyls by either, free radical [6], Ziegler-Natta [7], anionic [8], cationic [9], or group transfer [10] techniques are examples of chain-growth processes.

Although not realised at the time, one of the first published examples of an addition polymerization was reported by Watson [11] in Chemical Essays in the early 19th Century. He described the resinification of the oil of turpentine by sulphuric acid. Later in 1839 the glassification of styrene was independently noted by Deville and Simon [12]. The polymerizations of styrene and isobutene by sulphuric acid were respectively reported by Bertholot [13] in 1866 and Burlerov [14] in 1873.

Early findings such as those helped spur the development and growth of the petrochemical industry, the polymers becoming an important source of many industrial engineering plastics [15]. Compared with free radical polymerizations, and even anionic or Ziegler-Natta type systems, cationic polymerizations have a limited industrial scope. However, one of the main applications of carbocationic polymerization is in the rubber industry providing a route to butyl rubber, a polymer obtained by copolymerizing isobutene and isoprene. These products are used in the automotive and construction industries, or more specialised applications, such as additives in oils, fuels and surface coatings. Polyvinyl ethers, also prepared by cationic polymerization, are used as additives in fuels and oils, and as adhesives.

Although, the majority of conventional polymerizations find important commercial applications, the polymers produced tend to have broad molecular weight distributions and in some cases there is limited control of molecular weight. It was the discovery of the living anionic polymerization of styrene by M. Szwarc in 1956 [16] that provided the first method of producing monodisperse polymers with accurate control of molecular weight. For a long time after it was generally believed that the living polymerization of vinyl compounds by propagating cations was unlikely, because of their inherently high reactivities [17], not only towards propagation but to side reactions also. However, the living cationic polymerization of isobutyl vinyl ether was first reported by Higashimura in 1984, and has since been extended to encompass many other monomers. These methods of living polymerization allow precise molecular design and are of particular importance in the production of telechelics [18,19,20]. Telechelic polymers have applications as viscosity modifiers, corrosion inhibitors, seal swellents, detergents, and surfactants. Also of note is the potential for living polymerizations to provide a synthetic route to novel amphiphilic materials [21,22]. Amphiphilic polymers can be used as hydrogels in biomedical applications.

1.2 Conventional carbocationic polymerization

1.2.1 Preface

Cationic polymerizations can be categorised according to the nature of the atom on which the positive charge of the propagating centre resides. Carbocationic refers to those polymerizations in which the active cation is a positively charged carbon atom [11]. Whereas, if the positive charge is located on a hetero atom such as oxygen, sulphur, or nitrogen then the polymerization is referred to as an onium ion polymerization.

1.2.2 Mechanism of carbocationic polymerizations

The mechanism of carbocationic polymerizations can be divided into four main steps, these being, initiation, propagation, termination and transfer [9,11]. The general description given here on is for vinyl monomers of the type $CH_2{=}CR_2$. The two substituent groups, R-, can be identical or different and drawn from various functionalities (e.g. $-CH_3$, -Ph, $-OCH_2CH(CH_3)_2$). The monomers used in cationic polymerization are discussed in more detail in section 1.2.5.

1.2.2a Initiation

The first step in the process, initiation, involves more than one reaction but results in the generation of a carbocationic species. Suitable initiators are either strongly acidic materials, such as triflic or perchloric acid, or a Lewis acid catalyst in conjunction with a suitable base (see section 1.2.4 for further details). The electrophile ($\overset{+}{E}$) generated from these acids then proceeds to attack the double bond of a vinyl monomer to generate a carbocation, initiating the polymerization (figure 1.1).

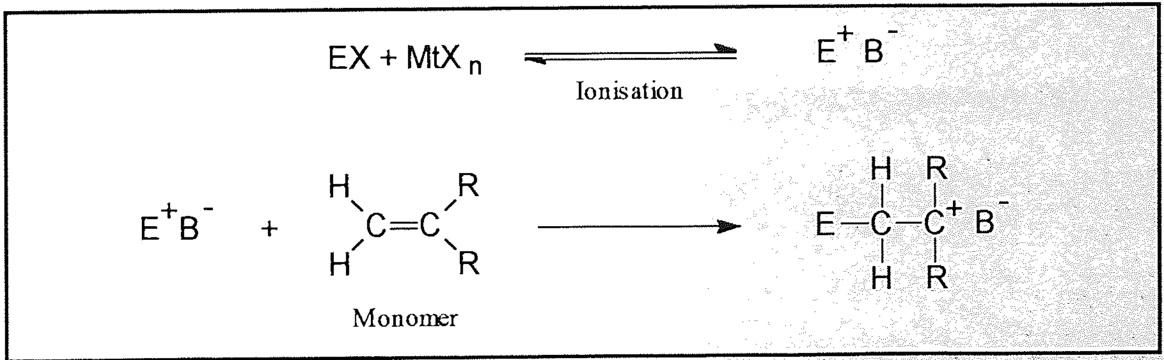


Figure 1.1. General Lewis acid initiation. Where; R = alkyl, alkoxy or aromatic; B^- = counteranion, $^-MtX_{n+1}$

1.2.2b Propagation

Propagation or chain growth occurs by the repeated insertion of monomer between the propagating carbocationic chain end and the counter ion (figure 1.2). The addition of monomer in propagation reactions normally occurs in a head to tail manner, such that the more stable of the possible cations is maintained. However, this step occurs in competition with transfer and termination steps, as outlined in sections 1.2.2c and 1.2.2d respectively.

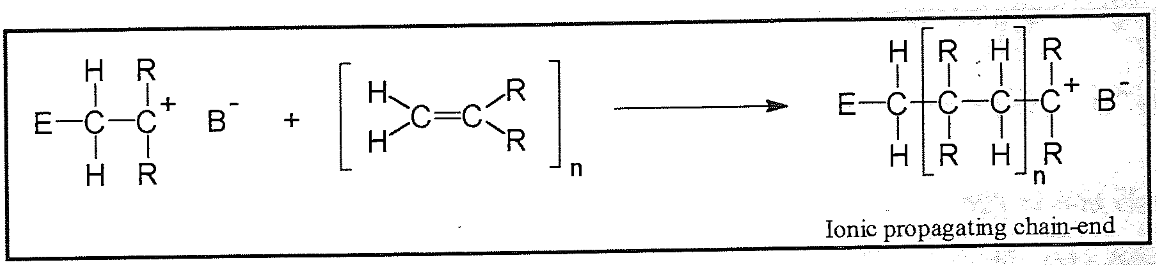


Figure 1.2. Propagation.

The nature of the propagating end is dependent on the solvent, temperature, monomer and counterion. Polar solvents, high temperatures and stable counter ions favour a more dissociated form of the chain end.

Propagation reactions can be complicated in some cases by isomerisation of the propagating cation to a more stable structure [23,24]. This normally involves the intramolecular Wagner-Meerwein shift of a hydride or methide group, figure 1.3. The degree of isomerisation occurring will depend upon the relative stabilities of the isomeric cations and the relative rates of propagation, transfer, termination and rearrangement. Monomers such as isobutene, N-vinylcarbazole, styrene and vinyl ethers polymerize without rearrangement, since there is no route to a more stable cation.

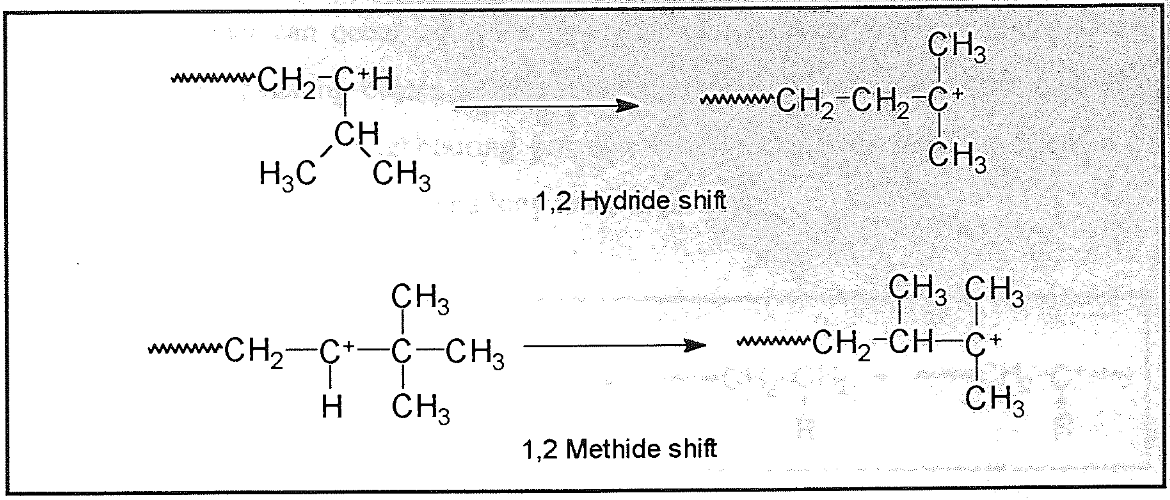


Figure 1.3. Isomerisation of the propagating cation.

1.2.2c Transfer

A transfer reaction may be defined as a reaction that terminates the growth of one chain but initiates the growth of another. A number of different transfer processes may occur [25,26], transfer to monomer (the main chain breaking process), transfer to polymer and transfer to counter ion.

Transfer to monomer is a bimolecular process that leads to an unsaturated terminal group. The β-hydrogen atoms of the carbocation possess a partial positive charge because of hyperconjugation. This renders the carbocation susceptible to attack by a nucleophilic species, such as the monomer, in a way that leads to abstraction of the proton from the chain end (figure 1.4).

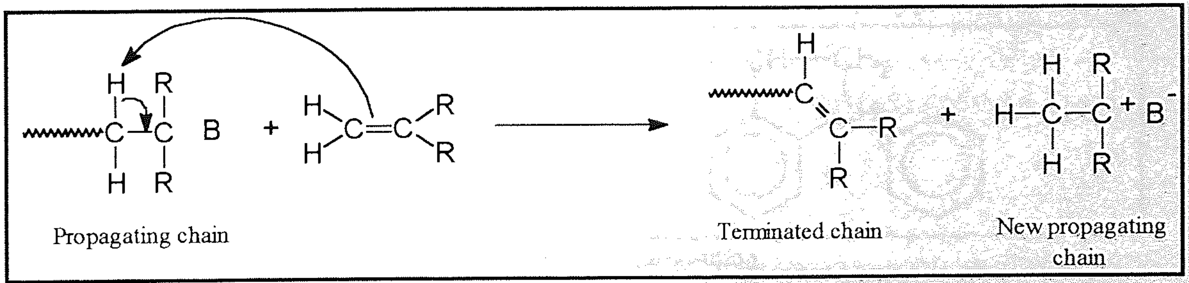


Figure 1.4. Transfer to monomer.

As a consequence of this type of transfer reaction the chain is terminated by a carbon-carbon double bond, and the propagation of a new chain is initiated. The presence of such reactions leads to a reduction, or indeed control, of the molecular weight [51].

Transfer to polymer can occur by either, the shift of a hydride ion from the polymer backbone to a propagating centre or electrophilic aromatic substitution. The shift of a hydride ion between two neighbouring polymer chains is demonstrated in figure 1.5, resulting in a saturated end group and long chain branching.

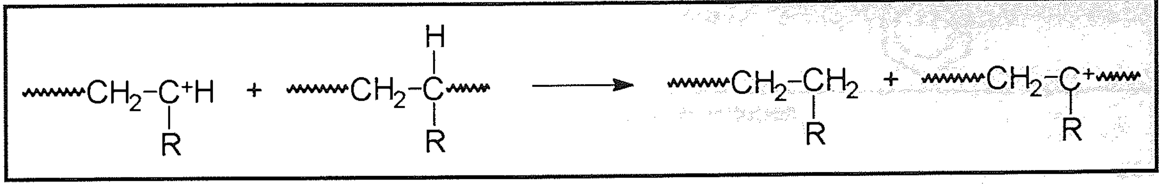


Figure 1.5. Intermolecular transfer to polymer by hydride shift.

A hydride ion can also shift intramolecularly, achieved by the polymer chain folding back upon itself, typically in a 6-membered chair conformation. The results is the creation of a short chain branch. (figure 1.6).

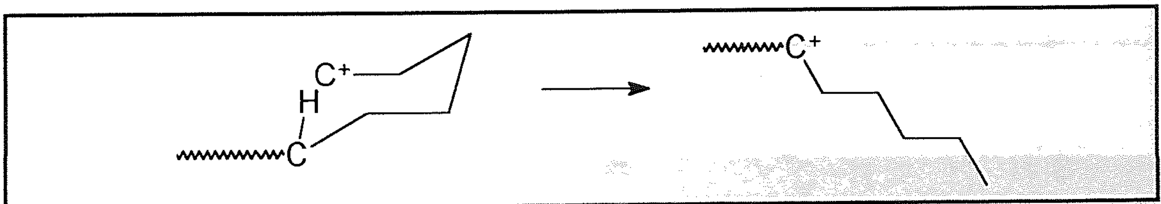


Figure 1.6. Intramolecular hydride shift (polymer backbone shown only).

Intramolecular transfer to polymer can also be achieved by a backbiting reaction to an aromatic substituent, which can yield cyclic terminal structures (figure 1.7). The generated proton can then continue to initiate the growth of a new chain.

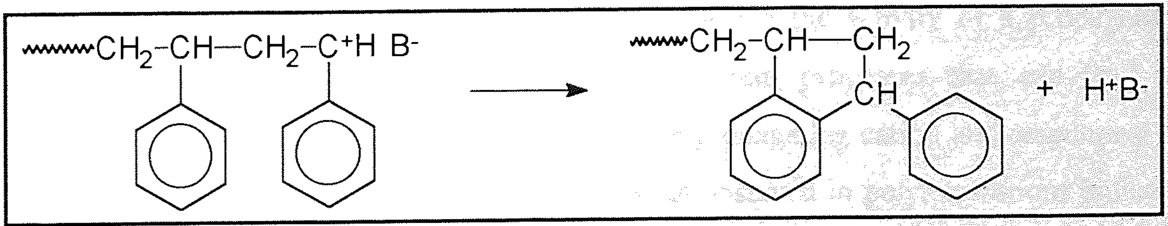


Figure 1.7. Intramolecular transfer to polymer by aromatic substitution.

A propagating centre may also electrophilicilly attack the aromatic substituent on a neighbouring chain, in an intermolecular mechanism (figure 1.8). Transfer by an intermolecular substitution process again provides a route to chain branching.

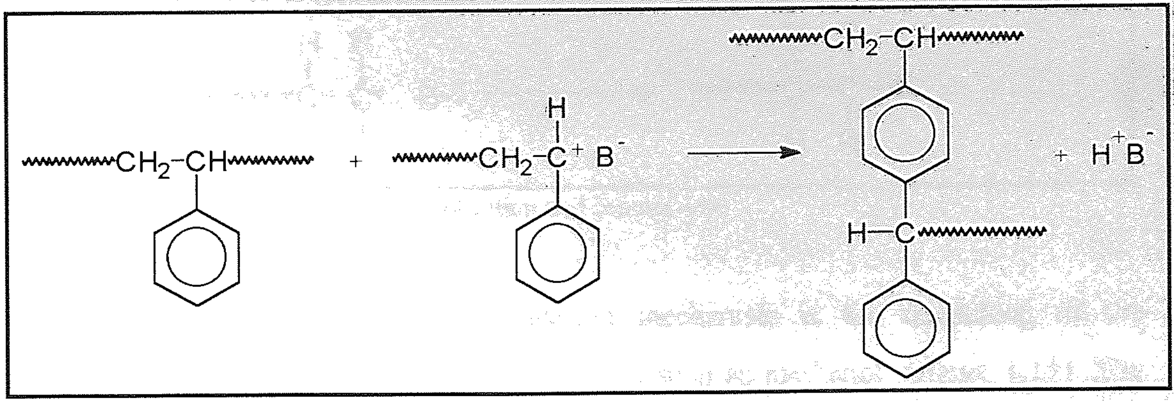


Figure 1.8. Intermolecular transfer to polymer by aromatic substitution.

Transfer to counter ion, figure 1.9, is difficult to distinguish from transfer to monomer. Transfer takes place by rearrangement of the propagating centre to reform the original catalyst/cocatalyst complex [27] with the terminated chain possessing an unsaturated functionality. The regenerated initiator complex can continue to react, initiating the growth a second chain.

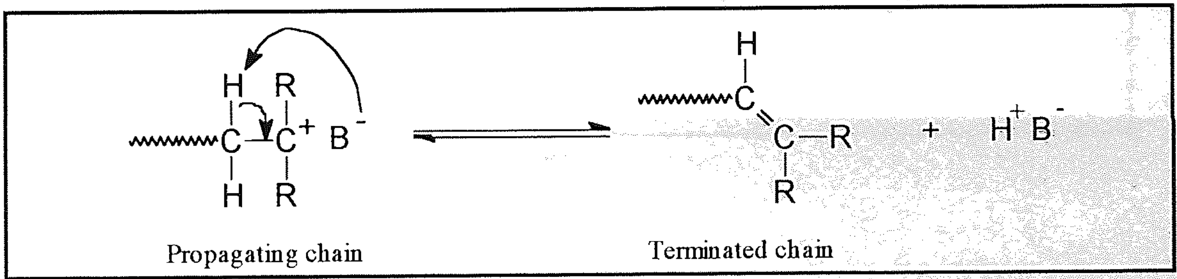


Figure 1.9. Transfer to counter ion.

1.2.2d Termination

A termination reaction may be defined as one in which the activity of a propagating centre is destroyed. There are a number of different processes that can lead to termination. The simplest is the combination of the propagating cation and counterion to form a covalent species (figure 1.10). This is often observed in polymerizations initiated by protic acids, and plays an important part in living polymerization systems, section 1.3.2. The rate of such termination reactions depends on the stability/basicity of the counter-ion.

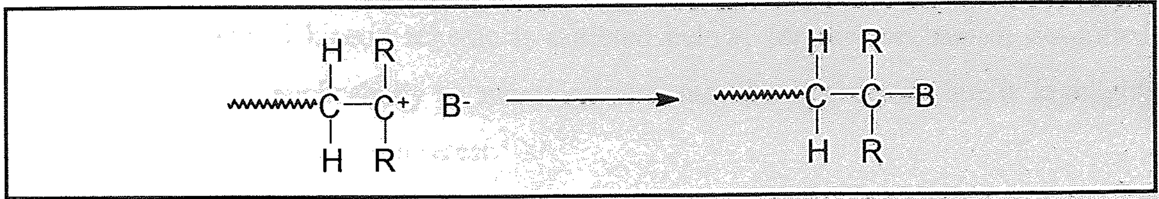


Figure 1.10. Termination by combination of cation and counter-ion.

A second commonly encountered termination mechanism is the quenching of the propagating chain by the addition of a nucleophile such as methanol (figure 1.11). The nucleophile will add to the propagating cation and/or destroy its associated catalyst. Once the catalyst is destroyed re-initiation cannot occur. The quenching agent can be present in the form of undesirable impurities, such as water, or alternatively it may be added deliberately to stop the polymerization after a desired length of time.

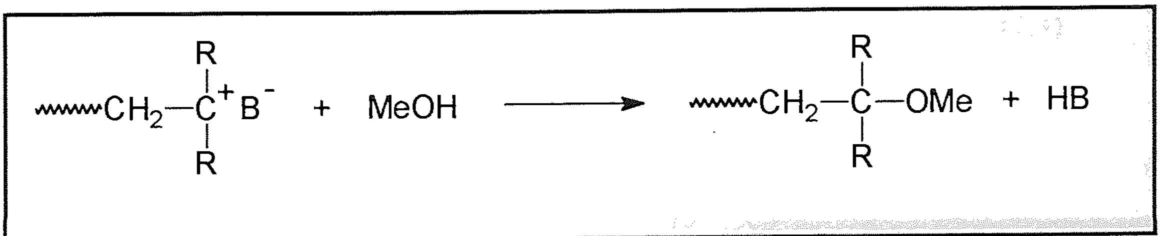


Figure 1.11. Termination by quenching with methanol.

1.2.3 Kinetics of conventional polymerizations

Derivation of a simple kinetic scheme, that is of general validity in carbocationic polymerization, has proved to be almost impossible. A number of complicating factors present difficulties that are indomitable [11]. It is often assumed that a single active species is responsible for propagation, whereas evidence suggests the presence of a multiplicity of active species, ion-pairs, solvated-ion, aggregates, etc. The validity of stationary state assumptions has been questioned [28,29] and for the most part found to be either false or unsubstantiated. Other areas of concern are generated by an incomplete knowledge of the true mechanistic pathways and assumptions of reaction orders without direct confirmation.

However, a general kinetic scheme is outlined below, for the mechanism described in section 1.2.2. Its applicability to many systems may be questioned but it highlights a number of characteristics of interest.

To formulate the scheme it has been assumed that initiation is a second order process, the rate of which, R_i, is given by expression (1.1). Propagation is also simplified, assuming that there is a single propagating species and that the rate, R_p, has a second order dependency, given by expression (1.2). Termination is considered to be a first order process, involving the recombination of the active-centre and co-catalyst fragment. The rate of termination, R_t, is given by (1.3).

$$R_i = k_i[EX][M] \quad (1.1) \qquad R_p = k_p\left[P_n^+\right][M] \quad (1.2) \qquad R_t = k_t\left[P_n^+\right] \quad (1.3)$$

where;

k_i = rate constant of initiation,
k_p = rate constant of propagation,
k_t = rate constant of termination,
$[M]$ = concentration of monomer,
$\left[P_n^+\right]$ = concentration of active propagating species,
$\left[E^+B^-\right]$ = concentration of activated initiator complex,
$[EX]$ = concentration of the initiator,
$\left[MtX_n\right]$ = concentration of the catalyst,
$[I]$ = concentration of initiator.

The concentration of the active initiator species ($[E^+B^-]$) will be dependent on an ionisation equilibrium in solution (figure 1.1). The equilibrium constant, K_i, of the ionisation equilibrium is given by:

$$K_i = \frac{\left[E^+B^-\right]}{[EX]\left[MtX_n\right]} \qquad (1.4)$$

($B^- = MtX_{n+1}^-$)

If a steady state is attained in the concentration of propagating species, then:

$$\frac{d\left[P_n^+\right]}{dt} = R_i - R_t = 0 \tag{1.5}$$

Substituting (1.1) & (1.3) into (1.5) and rearranging the equation leads to:

$$\left[P_n^+\right] = \frac{k_i}{k_t}\left[E^+B^-\right][M] \tag{1.6}$$

Rearrangement and substitution of (1.4) into (1.6) gives:

$$\left[P_n^+\right] = K_i \frac{k_i}{k_t}[EX][MtX_n][M] \tag{1.7}$$

The rate of polymerization can be defined as the rate of monomer consumption and approximated to the rate of propagation:

$$R_p = \frac{-d[M]}{dt} = k_p\left[P_n^+\right][M] \tag{1.8}$$

Substitution of (1.7) into (1.8) gives:

$$R_p = \frac{k_p k_i}{k_t} K_i [EX][MtX_n][M]^2 \tag{1.9}$$

Furthermore, in the presence of unimolecular termination and in the absence of transfer, the degree of polymerization, $\overline{DP}_n$, is given by:

$$\overline{DP}_n = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p\left[P_n^+\right][M]}{k_t\left[P_n^+\right]} = \frac{k_p}{k_t}[M] \tag{1.10}$$

If the rate constants are expressed in the Arrhenius form, then:

$$\overline{DP}_n = \frac{A_p}{A_t} e^{-\left(E_p - E_t/RT\right)}[M] \tag{1.11}$$

where;

E_p and E_t are the activation energies of propagation and termination respectively,

A_p and A_t are the respective Arrehenius pre-exponential factors,

and T is the temperature of polymerization.

Equation (1.11) demonstrates that the degree of polymerization is dependent on the reaction temperature (by difference in activation energies) and the concentration of monomer. It is independent of the concentration of propagating sites.

The treatment described above ignores the effects of transfer reactions, in particular transfer to monomer, on the chain length of the polymer. If such reactions are taken into consideration then, provided that re-initiation of the polymerization is rapid, the rate of polymerization is unaffected by the presence of transfer to transfer agent (C) because the total concentration of propagating species is unaffected by such transfer reactions. However a significant change in polymer chain length will be observed. The magnitude of this effect depends on the rate constant for transfer to C_i and in this case:

$$\overline{DP}_n = \frac{k_p[M]}{k_t + \sum_i k_{tr,i}[C_i]} \qquad (1.12)$$

When transfer takes place solely to monomer and dominates over termination then:

$$\overline{DP}_n = \frac{A_p}{A_{tr}} e^{-(E_p - E_{tr}/RT)} \qquad (1.13)$$

1.2.4 Cationic initiators

There are four main classifications of initiator utilised in carbocationic polymerizations, Bronsted (protic) acids, carbenium ion salts, physical methods and Lewis acid systems.

1.2.4a Protic acid initiators

As already described in the introduction, this method of initiation was amongst the first employed to promote polymerizations of vinyl monomers. The proton from the Bronsted acid adds across the carbon-carbon double bond of the monomer generating a carbocation.

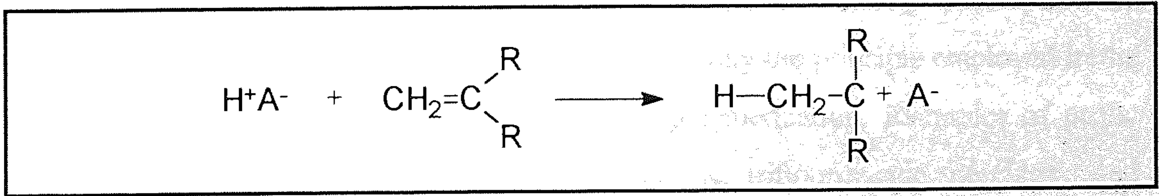


Figure 1.12. Cationation by a protic acid (H^+A^-) .

Propagation will take place by addition of the monomer to the species produced during the initiation reaction. Thus:

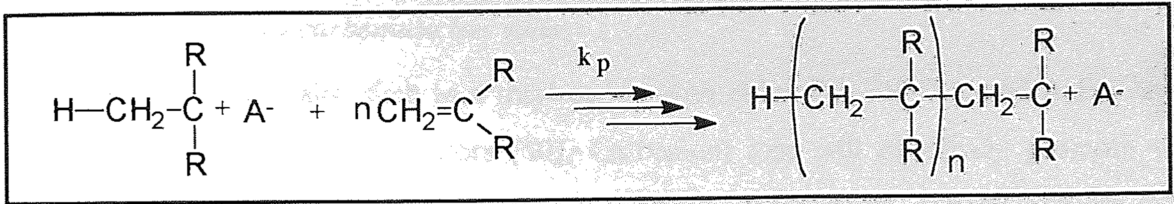


Figure 1.13. Propagation.

However, in competition with propagation will be the reaction of the ions to form a covalent bond between the carbon atom and the anionic species, figure 1.14.

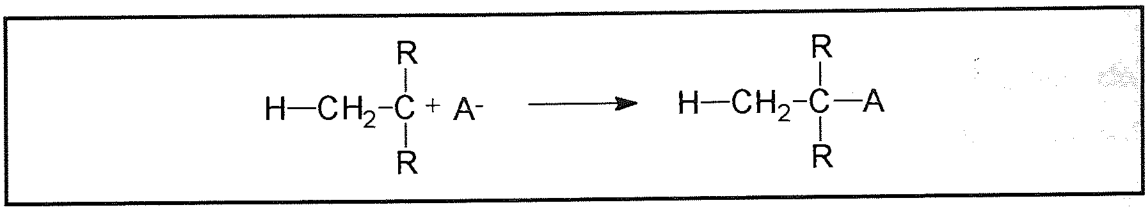


Figure 1.14. Termination.

The probability that this reaction will take place is now dictated principally by the structure of the anion. If that anion is derived from a relatively weak acid it is normally considered to be a strong nucleophile and so such termination reactions take place instantaneously on addition of the acid to the monomer. If, on the other hand, the reaction produces a gegen-ion that is the conjugate base of a strong acid, and hence a weak nucleophile, termination reactions such as those above are relatively slow and consequently propagation can compete effectively. The difference in behaviour of hydrogen chloride acid and sulfuric acid towards isobutene may be explained in this way. Hydrogen chloride reacts with isobutene to form exclusively t-butyl chloride because the chloride ion is a strong nucleophile, whereas on addition of sulfuric acid to isobutene dimers and trimers of the monomer are formed [15]. Such termination reactions may also proceed if the counter anion decomposes readily to form a strong nucleophile, or prevented by forming a stable anion. The latter is effectively the principle employed in the use of Lewis acid systems as catalysts in cationic polymerization. Examples of protic acids found to be effective initiators are, trichloroacetic, triflouroacetic, perchloric and phosphoric acids.

1.2.4b Initiation by carbenium ion salts

Stable carbocation salts, such as a trityl cation with either PF_6^-, $SbCl_6^-$, and AsF_6^-, have been found to be useful initiators [30]. Carbenium ions will effectively promote the polymerization of styrene, N-vinylcarbazole, and alkyl vinyl ethers. The use of these salts allows the ion-generation step to be eliminated from the mechanism making them invaluable in some kinetic studies. However, owing to their high stability they have not been effectively employed to polymerize aliphatic olefins.

1.2.4c Physical initiation methods

Methods of physical initiation include high energy irradiation (γ-rays) [31], high electric field [32], electroinitiation [33], and photoinitiation [34,35]. Further discussion will be given to photoinitiation only.

Diaryliodonium salts have been found to be effective photoinitiators of olefins, figure 1.15.

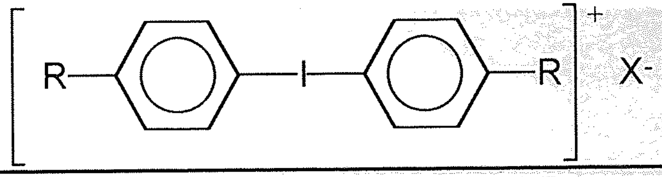
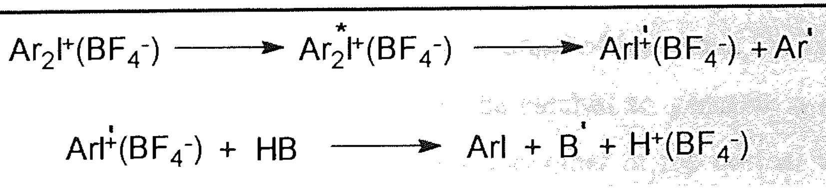


Figure 1.15. Diarylodonium salt; R= H, CH_3, t-C_4H_9; X^- = BF_4^-, PF_6^-, AsF_6^-.

The polymerization is carried out in a polar solvent at 25 °C, and initiated by illumination with a UV light source. This has the effect of exciting the diaryliodonium salt to a higher energy state, which will then decompose into a radical cation, an aryl radical, and a counteranion. Reaction of the radical cation with a protonic compound (HB) forms the initiating species, a strong protic acid (figure 1.16).



$$Ar_2I^+(BF_4^-) \longrightarrow Ar_2\overset{*}{I}^+(BF_4^-) \longrightarrow Ar\dot{I}^+(BF_4^-) + Ar^{\cdot}$$

$$Ar\dot{I}^+(BF_4^-) + HB \longrightarrow ArI + B^{\cdot} + H^+(BF_4^-)$$

Figure 1.16. Mechanism of photoinitiation.

The advantage of photoinitiated polymerizations is that they allow the polymerization process to be spatially directed. Furthermore, the reaction can be activated or deactivated by turning on or off the light source. Such control is useful in the printing and coating industries.

1.2.4d Lewis acid initiation systems

This class of initiation is probably the most commonly used and one of the most important. A Lewis acid is normally used in conjunction with a cocatalyst that acts as the initiator. Some Lewis acids that have been employed are $SnCl_2$, PCl_5, $SbCl_5$ $TiCl_4$, $SnCl_4$, $AlCl_{3-n}R_n$, BCl_3 and BF_3. Under certain conditions some catalysts have been reported to initiate polymerization without the aid of a cocatalyst (initiator). Two mechanisms have been presented to account for the direct initiation of vinyls by Lewis acids alone.

Sigwalt and Olah suggested such initiation involved halometalation [36]. A metalorganic compound is formed by the nucleophilic attack of the monomer on the catalyst. The resultant material may ionise in the presence of excess Lewis acid, to produce a conventional catinogenic species (figure 1.17).

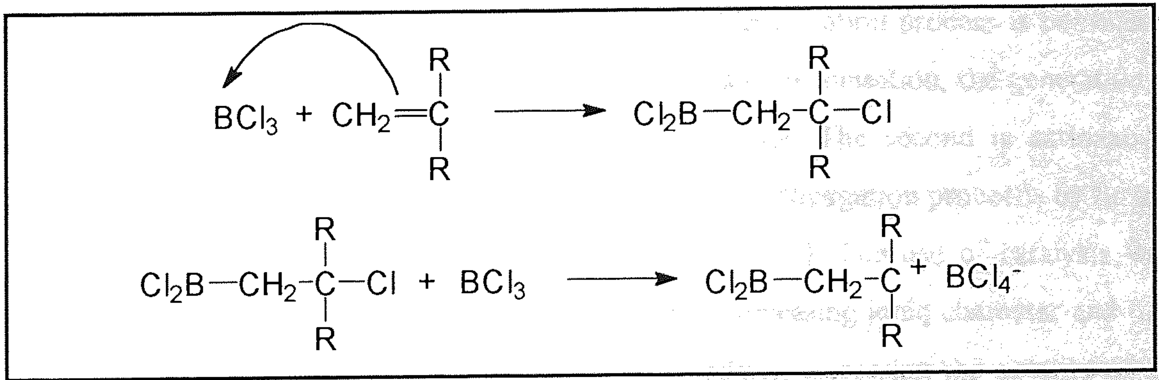


Figure 1.17. Initiation by haloboration.

To explain the unassisted initiation of the polymerization of isobutene by $TiCl_4$, Plesch [36] proposed a mechanism of self-ionisation of the catalyst to generate a cation. The metal cation was then expected to react with the monomer in the normal way (figure 1.18).

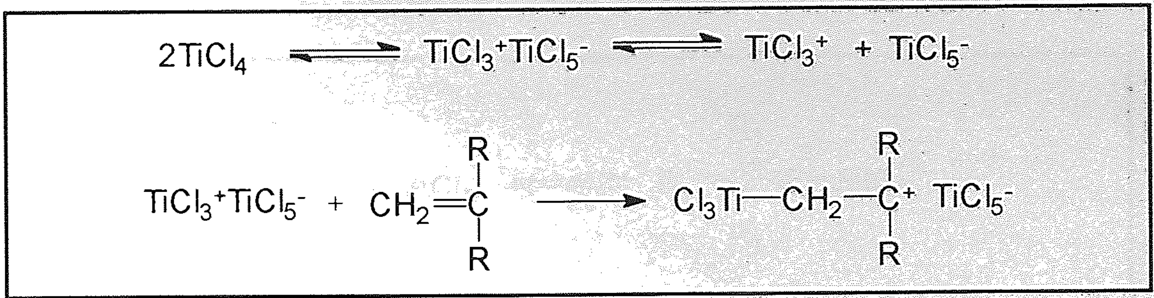


Figure 1.18. Initiation by self-ionisation.

A kinetic study by Faust et al has indicated the mechanism of initiation, at least for the polymerization of isobutene by BCl_3, to be haloboration [37,38], but it may be that each system has to be treated separately and there is no general explanation for such reactions. Apart from these few reported cases, Lewis acids are generally inactive on their own, and require a catinogen, sometimes referred to as the co-catalyst or initiator, to be added. This catinogen reacts with the catalyst to produce the cation and a counterion. Proton donors such as H_2O, ROH and RCOOH will readily initiate the polymerization of high molecular weight polymers in the presence of Lewis acid catalysts, this is largely owing to the high stability of the counterion formed. Important initiators commonly employed are ester, ethers and higher order haloalkanes.

The utilisation of a Lewis acid with a haloalkane produces some of the most rapid and efficient initiating systems for cationic polymerizations, under conditions that are certainly analogous to those found in Friedel-Craft reactions. The initiation process is considered to have two stages, as shown in figure 1.19. The first step is ionisation, the generation of a cation by reaction of the catalyst with the co-catalyst. The second is cationation, addition of the first monomer unit to the ionised species. Propagation proceeds by further monomer insertion between the cation and counterion [39]. The use of catalysts with increasing Lewis acidity will produce complexes with increasing ionic character and thus propagating centres with greater electrophilicity. Similarly, increasing the polarity of the solvent will also support more ionic species, as the charged ions will be better stabilised.

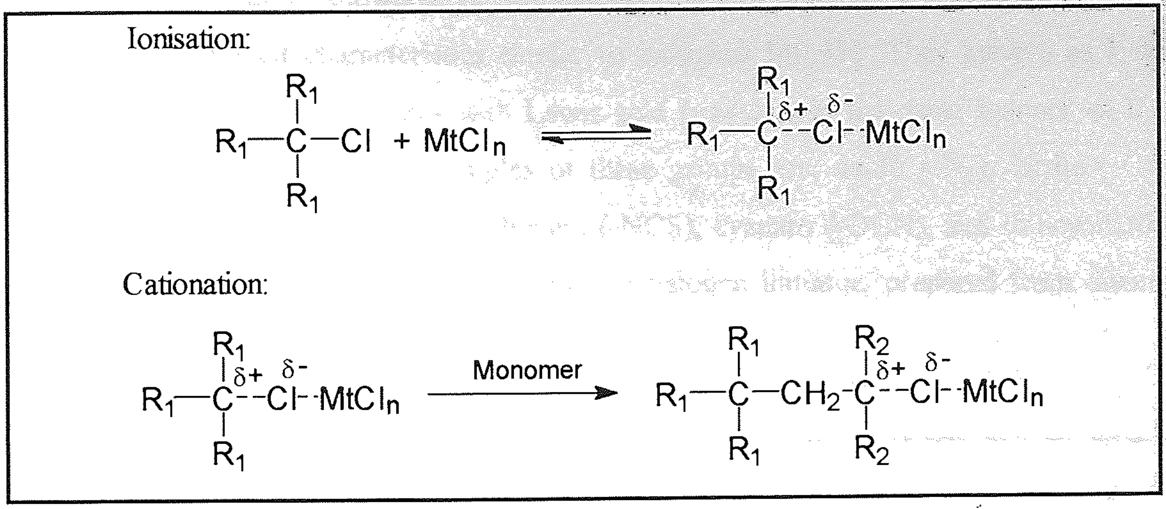
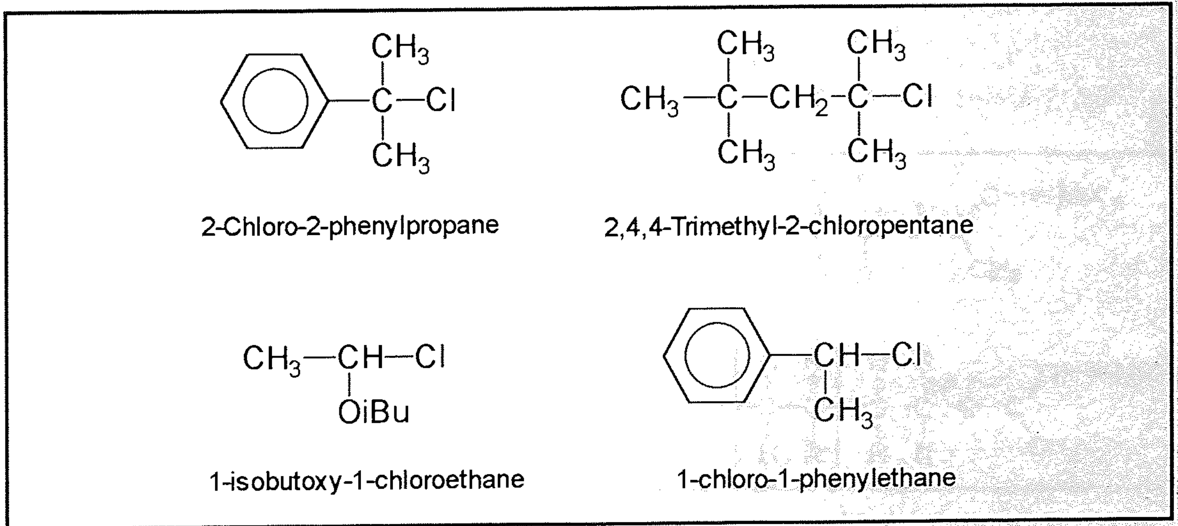


Figure 1.19. Friedel-Craft initiating system.

The stability of the initiating cation compared to that of the propagating centre is important. If the catinogen is significantly more stable than the propagating end, initiation will be slow compared to propagation. Adversely, if the co-catalyst cannot stabilise the generated positive charge adequately then ionisation will be slow and once again slow initiation will be exhibited. For example t-butyl chloride used in conjunction with $SnCl_4$ or $TiCl_4$ is known to be slow at initiating isobutene or styrene polymerizations, whereas 2-chloro-2-phenylpropane is found to be efficient. The phenyl group on this later initiator will stabilise the positive charge by delocalisation around the aromatic ring. Some examples of useful Friedel-Craft initiators are given in figure 1.20.



2-Chloro-2-phenylpropane

2,4,4-Trimethyl-2-chloropentane

1-isobutoxy-1-chloroethane

1-chloro-1-phenylethane

Figure 1.20. Common Friedel-Craft initiators.

The class of initiators known as pseudo halogen initiators contain a functional group, or groups, that exhibit characteristics similar to halogens [40,41]. They behave as Lewis bases that will form complexes with Lewis acid catalysts, in the same manner as their halogen counterparts. Some examples of these groups are; azido (-N_3), nitrile (-CN), carbonylamino (-NCO), thiocarbonylamino (-NCS), cyanato (-OCN), and thiocyanato (-SCN). Figure 1.21. shows a common pseudo halogen initiator, prepared from dicumyl chloride by reaction with sodium azide.

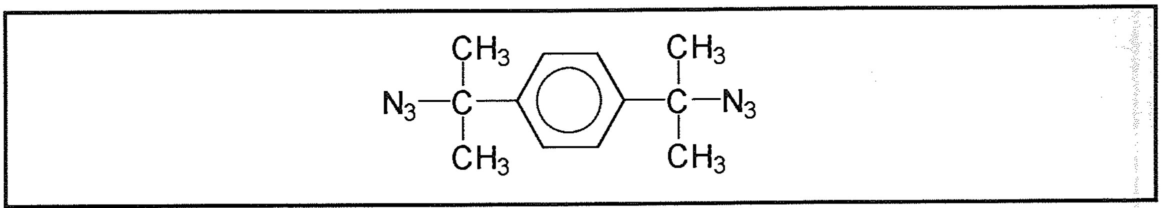


Figure 1.21. Bis(1-azido-1-methylethyl)benzene.

It is recognised that Lewis acids form complexes with ester and ethers, and these complexes have been found to be good initiators in certain systems [42,43]. The electron deficient catalyst will co-ordinate with a lone pair of electrons on the oxygen atom to activate the ester linkage. Propagation then proceeds by insertion of the monomer unit into the activated bond, believed to be an ion-pair [44] (figure 1.22). The degree of ionisation of the ester linkage will depend upon the dielectric permittivity of the solvent system and the strength of the Lewis acid used. The nature of E, in the figure below, will also be of significant importance. The most efficient ester initiators are those in which E has the greatest capability of stabilising a positive charge.

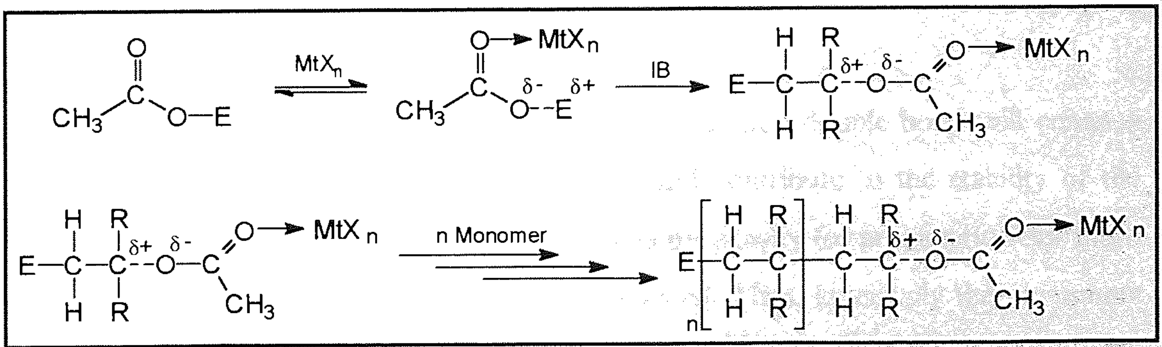
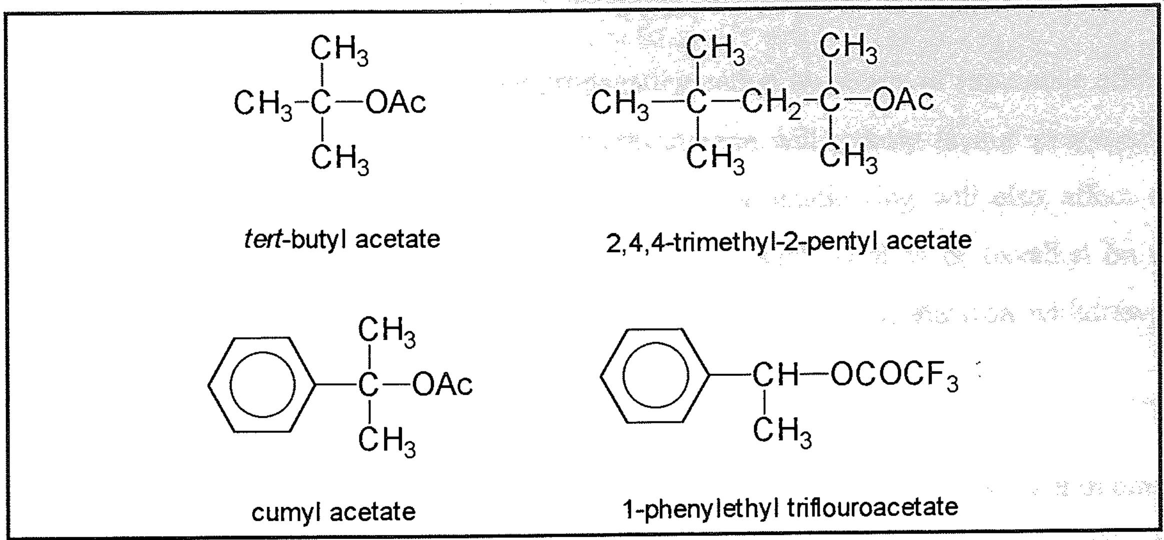


Figure 1.22. Ester initiation.

NMR studies by Higashimura et al have shown that counteranion exchange, between the ester and chlorine, does not occur in the living polymerization of IBVE with $ZnCl_2$ [45].

However, when quenching with an alcohol a chlorine end group is exclusively obtained. Some examples of useful ester initiators are shown in figure 1.23.


tert-butyl acetate

2,4,4-trimethyl-2-pentyl acetate

cumyl acetate

1-phenylethyl triflouroacetate

Figure 1.23. Examples of ester initiators.

1.2.5 Monomers

Cationically polymerizable monomers are susceptible to propagation reactions involving electrophiles. To generate polymers of high molecular weight the cation formed must be sufficiently stable to sustain propagation and not so reactive as to undergo termination reactions. The solvent, temperature and initiating system employed in a polymerization will greatly influence propagation, but of primary importance is the structure of the monomer unit. Alkenes are the most common of these monomeric compounds and extensive lists can be found in the literature [11]. The reactivity of the propagating cation will depend upon the charge density associated with it.

Electron donating substituents adjacent to the carbon-carbon double bond will enhance the reactivity of that bond to electrophilic attack, and contribute to the stability of the propagating cation. Stabilising the cation reduces its propensity for propagation but more importantly is that transfer and termination are reduced. Thus, kinetically the monomers ethylene, propylene, and isobutylene represent a series of increasing reactivity towards propagation. Ethylene and propylene tend not to form high molecular weight polymer because propagation competes unfavourably with transfer, isomerisation and termination.

Whereas isobutylene possesses two methyl groups with which to stabilise the cation, so propagation can compete favourably with side reactions to form high molecular weight polymer.

Aromatic substituents will stabilise the propagating cation by means of resonance effects. Thus, monomers such as styrene and α-methylstyrene will greatly favour propagation over competing side reactions. Substituents on the aromatic ring will also affect the reactivity of the monomers. Electron donating groups such as alkyl or oxyalkyl on the para position will aid the reactivity of the monomer. Conversely, electron withdrawing groups such as a halogen or nitro will inhibit reactivity.

Some substituents will prevent effective polymerization. Sterically hindered monomers such as 1,1-diphenylethylene have a highly nucleophilic nature but, they will not propagate higher than dimers because the propagating cation is sterically hindered to a second monomer. A commonly encountered problem is the presence of a second nucleophilic site. If the site is more reactive than the double bond the cation may preferentially attack and form a stable or unreactive complex. This explains why acrylates that possess a carbon-carbon double bond and are conjugated with a withdrawing function are not cationically polymerizable.

The potential of a monomer to form a polymer can be thermodynamically evaluated. The ability to polymerize is related to as the free energy of polymerization of the monomer, ΔG_p, and given by the expression:

$$\Delta G_p = \Delta H_p - T\Delta S_p \qquad (1.14)$$

The free energy of polymerization is dependent solely on the monomer and polymer structures, not the mechanism of formation. Exothermically polymerizable monomers have been shown to exhibit a ceiling temperature, T_c, above which the monomer is thermodynamically stable. When T_c is reached ΔG_p changes from a negative to a positive value. Therefore, when $\Delta G_p = 0$ equation 1.14 becomes:

$$T_c = \frac{\Delta H_p}{\Delta S_p} \qquad (1.15)$$

1.3 Living cationic polymerization

1.3.1 Definition of living and controlled polymerizations

The classical definition of a living polymerization, as restated by Szwarc in 1992, is a polymerization in which propagation proceeds in the absence of termination and transfer. Furthermore, once all the monomer has been consumed, the growing chain ends should remain active towards further addition of monomer, for a desired length of time [46].

Recent advances in the understanding of living carbocationic polymerizations have shown the mechanism to involve the reversible formation of an inactive species, which is more correctly defined as reversible termination. This type of mechanism is clearly a contradiction of Szwarc's definition, but the problem has been addressed by Matyjaszewski and Muller [47]. The criterion for a living polymerization is now stated as a chain polymerization without irreversible chain breaking reactions. This notation tolerates the presence of slow initiation and reversible termination, while excluding irreversible termination and transfer because the former allow the polymer chain to increase in length, whereas the latter leads to polymer chains of unchangeable length.

Further treatment was given to the use of the term *controlled*. The definition is given to polymerizations that produce polymers with well-defined topology, functionality and arrangement of comonomers. These polymers should also possess a narrow unimodal molecular weight distribution with the molecular weight determined by the ratio of monomer to initiator. A controlled polymerization may include slow reactions of transfer and termination, but it will not tolerate a rate of initiation which is slower than propagation. A controlled polymer may be living if irreversible termination and transfer are below the detectable limits of current instrumentation.

1.3.2 Mechanism of living carbocationic polymerization systems

1.3.2a The living cationic polymerization of IBVE by HI/I_2.

The first type of polymerization involving a carbocationic species that was recognised as living was the polymerization of IBVE [48]. Initiation was facilitated by a Lewis acid system, consisting of HI and I_2. The first step in the reaction involves H^+ electrophilically attacking the monomer to create an intermediate, CH_3-C^+HOR. The cationic species created does not continue to propagate because the iodide ions in the system have a greater nucleophilicity than the monomer. Therefore, the iodide will add to the cation in preference to the monomer forming a strong covalent bond. The monomer cannot insert into this carbon-iodine bond unless it is activated, in this case by iodine, which behaves as a Lewis acid co-ordinating with the IBVE/HI adduct. The effect of this co-ordination is to polarise and weaken the carbon-iodine bond. Addition of monomer can now occur by insertion into the polarised bond, allowing propagation to take place (figure 1.24) [49].

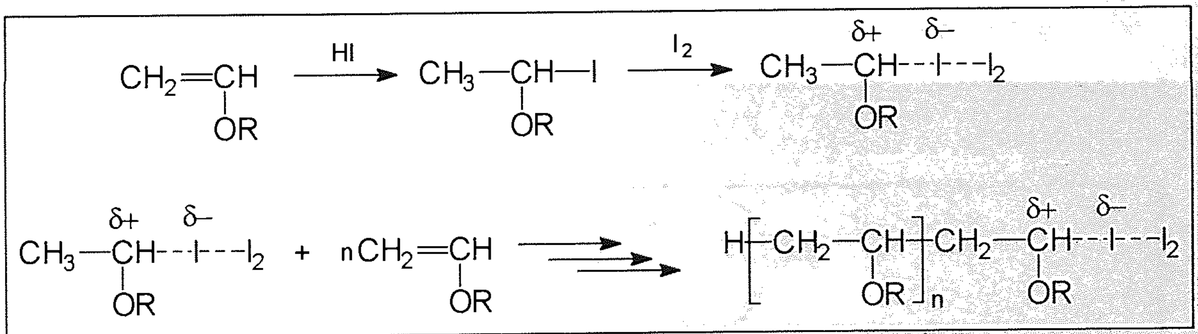


Figure 1.24. Hydrogen iodide/iodine initiating system for the polymerization of IBVE, R = *i*-Butyl.

To produce a polymer possessing a narrow molecular weight distribution the rate of the initiation process must also be considered. If the rate of initiation is slow compared to that of propagation then new chain growth will take place as older chains continue to propagate. The result will be a broadening of the molecular weight distribution as the polymerization proceeds. Therefore, to produce a polymer with a low polydispersity the rate of initiation should be faster, or at least comparable, to that of propagation.

1.3.2b Reversible termination in living cationic polymerization systems.

The above polymerization, and other so-called living polymerizations in general, are believed to involve a propagating species that is either active for only relatively short periods or stable to transfer and termination reactions. Living anionic polymerizations fall into this latter category. The anionic polymerization of styrene, particularly, is known to generate a propagating species that is stable over long periods of time and thus complies to the original definition of a living polymerization described by Szwarc.

In the case of living cationic polymerizations termination and transfer reactions cannot be completely eradicated. To achieve the aim of a living polymerization, the reaction conditions must be manipulated [50] so that the rate of propagation predominates over the rates of termination and transfer. It has already been shown in section 1.2.3 that decreasing the temperature of polymerization will favour propagation, because the rates of termination and transfer reactions are decreased more rapidly than propagation. However, the reduction of temperature alone is not sufficient to induce living characteristics. Termination and transfer reactions are believed to be suppressed in cationic polymerizations because of the existance of a rapid, dynamic equilibrium between relatively short-lived active and long-lived dormant species, figure 1.25 [51]. The active species in the cases of isobutene and styrene polymerizations have been deduced to be ion pairs [52].

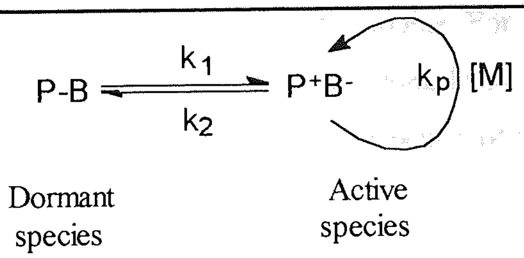


Figure 1.25. Equilibrium between dormant and active chain carriers.

In the above equilibrium the rate constant of ionisation, k_1, is much less than the rate constant of collapse, k_2, so that under equilibrium conditions the concentration of active propagating species remains small in comparison to that of the dormant form [53]. Another consequence is that the transient lifetimes of the cations are short in the active state, such that the mechanism of transfer does not have time to occur but that of propagation does. Therefore, the probability of transfer will be low compared with that of propagation. Transfer and termination are present in these systems, although their rates of reaction are slow, but these reactions can become a limiting factor in synthesising high molecular weight polymer. Matyjaszewski [54,55], studying the living polymerization of styrene estimated that 10% of chains would have transferred if sufficient time elapsed for polymer of 100 000 g mole^{-1} were formed, whereas only 1% will transfer in the preparation of polymer with a molecular weight of 10 000 g mole^{-1}.

1.3.2c The Winstein equilibria and types of active species in solution

The instantaneous concentration and nature of the active species are influenced by a number of factors. In the example of the IBVE polymerization system, if the iodide in the IBVE/HI adduct is exchanged for a halogen of greater nucleophilic character then the active species will be more covalent in nature. Thus, moving down the series of ions of the group 7 periodic elements, Cl^-, Br^-, I^-, represents a decrease in nucleophilicity and therefore an increase in the activity of polymerization. The increased activity occurs because the propagating species becomes more dissociated in nature. As the ions move further apart, the charge density on the chain carriers will rise and the steric hindrance to attacking monomer will be reduced. Therefore, an increasingly reactive chain carrier is produced.

A second method of increasing the concentration, and degree of dissociation of the active species would be to use a stronger Lewis acid than iodine. For example, BF_3OEt_2 would be expected to produce a highly ionic, relatively long-lived, dissociated species that would be highly reactive in the polymerization and beacuse of the nature of its structure prone to transfer reactions.

The polarity of the solvent used in the polymerization will also have a significant effect on the active species. Polar solvents will be able to stabilise the ionic species more readily than non-polar solvents. Thus, the formation of ionised species will be favoured more in polar mediums than non-polar. Further, the proximity of the ions themselves will be altered, as polar solvents will stabilise the charged species better than non-polar.

Therefore, according to the conditions imposed on the polymerization, the gegen-ions associated with the chain carriers can exist in a variety of different states. The possibilities range from inactive covalent forms to highly reactive, fully solvated, free ions. The full series of species attainable is represented in the Winstein ionicity equilibrium, figure 1.26.

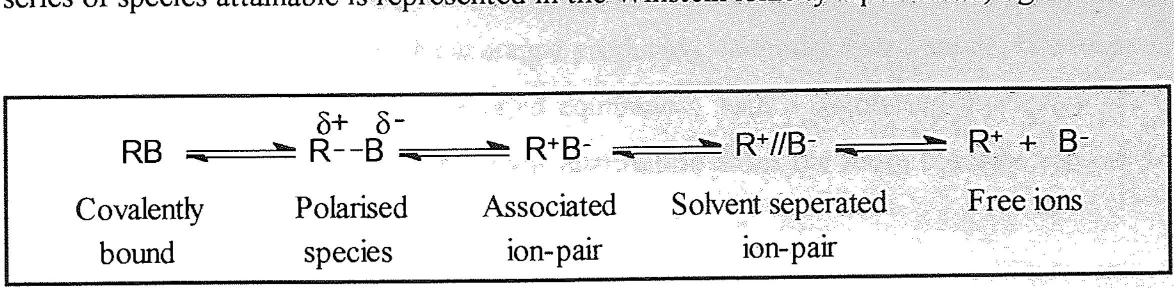


Figure 1.26. Winstein ionicity equilibrium.

To the left of the equilibrium is the covalent species. Moving to the right the species becomes increasingly ionised, progressing through polarised bonds, associated ion-pairs, solvent separated ion-pairs and finally to fully solvated free ions.

There is considerable evidence available to suggest that a variety of propagating species are present in conventional carbocationic polymerizations [56]. Furthermore, these species may be in equilibrium with one another and indeed each may be capable of participating seperately in a propagation reaction with monomer. It is reasonable to suppose however that the propagation rate constants for these reactions will differ considerably, figure 1.27.

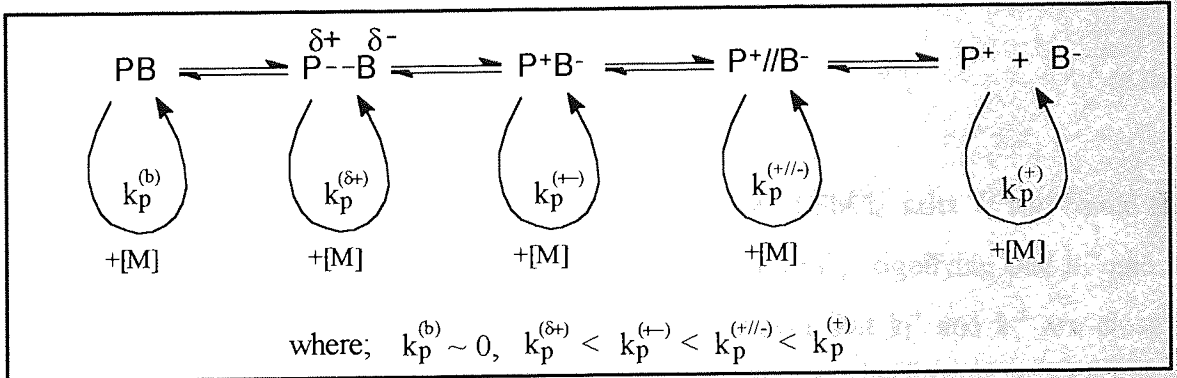


Figure 1.27. Propagation rate constants of ionised species in solution (P = propagating polymer chain).

A further complication arises as to whether the rates of exchange in this multi-stage equilibrium are fast or slow compared with the rate of propagation. If the rates of exchange are slow then polymers with broad, possibly multi-modal molecular weight distributions will be produced. Under slow exchange conditions, the propagating chains will spend prolonged periods in any one state and so it is reasonable to expect that chains in different states will grow at different rates. Control is only gained if the rate of interconversion in the equilibrium is rapid. The contributions from the individual propagating centres will then be averaged producing unimodal distributions. If a relatively dormant chain carrier exists in a rapid equilibrium with a highly reactive chain carrier then, statistically, the molecular weight distribution from the more reactive species will dominate.

1.3.2d The reactivities of charged species in cationic systems.

Studies have shown that free ions and ion pairs have similar reactivities in cationic polymerizations. Higashimura [57] examined the polymerization of styrene in dichloromethane initiated by acetyl perchlorate ($Ac^{+}\,^{-}ClO_4$ in the presence of $n\text{-}Bu_4NCl$ (see section 1.3.3c for common salt effects). Two propagating species, an ion-pair and a free ion were present and the ratio of the weight of the polymers formed from the dissociated species to that formed from the non-dissociated species, was determined experimentally. Using this data, the ratio of the rate constant of propagation by free ions (k_p^{+}) to that of ion pairs ($k_p^{\pm}$) was estimated to be between 10 and 100. Sigwalt [58] used conductance studies to examine the polymerization of p-methoxystyrene initiated by $Ph_3\overset{+}{C}SbCl_6^{-}$ in dichloromethane. The mole fraction of free ions present (γ) was calculated. The rate constant of initiation (k_i) is given by (1.16).

$$k_i = \gamma k_i^{+} + (1-\gamma)k_i^{\pm} \qquad (1.16)$$

The mole fraction of free ions was varied by the addition of $SbCl_6^{-}$ salts. It was found that the rate constant of initiation changed little with variation of γ, signifying that k_i^{+} and $k_i^{\pm}$ are of similar magnitude. Other workers have also shown that k_i^{+} and $k_i^{\pm}$ are close in value. Mayr [59,60] modelled the reaction of carbocations with olefins and kinetically determined the rates to be similar.

The similarity of the reactivity of free ions and ion pairs in carbocationic polymerization has been attributed to the large size of the counterions. The distance between the two ions is relatively large, so that the influence of the counter ion on the propagating centre is reduced. Hence, the reactivity of ion pairs and free ions are similar.

1.3.3 Mediated polymerizations

In the previous section it has been shown that for a living cationic polymerization the lifetime of the propagating species in its active state should be short, and that its lifetime and nature are dependant on the solvent, temperature, and counterion. A number of techniques have been developed to help control the form of these active centres so as to minimise or prevent unwanted termination and transfer reactions.

1.3.3a Common-ion effects

The polymerization of styrene in dichloromethane using 1-phenylethyl chloride as initiator and tin tetrachloride ($SnCl_4$) as catalyst is a conventional polymerization system [61]. The propagating chain carrier spends a large proportion of time in the ionised, or dissociated, state, allowing transfer and termination reactions to occur frequently. The equilibrium concentration of the various species present in a polymerization may be manipulated by the addition of one of the intermediates in an inert form or common ion. In this way the position of equilibrium in the Winstein spectrum in figure 1.27 may be forced to a state where the concentration of chains existing in the covalent form is increased. The addition of excess counterion, B^-, will ensure that this change takes place. If the above polymerization is now conducted in the presence of tetrabutyl ammonium chloride (nBu_4NCl) a living polymerization ensues. Tetrabutyl ammonium chloride provides a source of chloride ions that will co-ordinate with free $SnCl_4$ to form an excess of $SnCl_5^-$ (B^-), driving the equilibrium towards the more covalent species. The life time of the active species is now much shortened, and suppression of transfer and termination reactions takes place [62,63]. The addition of large excesses of salt has been found to suppress the formation of active species to the extent polymerization will not occur.

Sawamoto [64] has examined the nature of the growing ends in the presence of added salts by in-situ ^{13}C-NMR analysis for the polymerization of IBVE by $SnCl_4$ and nBu_4NCl_4. In the absence of salt NMR spectra clearly show the formation of an electron deficient carbon, attributed to the propagating carbocation. Addition of the salt shifts the signal from that shown for a cation to that expected of a covalent species. These experiments demonstrated the presence of an equilibrium, and that the addition of salt effectively modifies the concentration of the intermediate propagating carbocation.

1.3.3b Electron pair donors

The positive influence of electron pair donors (ED) on cationic polymerizations was first observed by Kennedy, with the development of ester initiator systems for the living cationic polymerization of isobutene [65,66]. It was noted that the addition of 1,1,1-triphenyl acetate ($(C_6H_5)_3COAc$) to a polymerization utilising 2,4,4-trimethyl-2-pentyl acetate (TMPOAc)/BCl_3 as an initiating system substantially reduced the rate of polymerization. Furthermore, the polydispersities obtained were significantly narrow, 1.17 compared with 1.5 for a conventional polymerization. This report has prompted an extensive study and a large number of publications have appeared.

There are three explanations for the effect that EDs have on living carbocationic polymerizations. The first is that they stabilise the carbocation, the second that they co-ordinate with the catalyst reducing its nucleophilicity and finally that they trap protic impurities. The exact role of EDs seems to be dependent on the polymerization system and monomer so that a general theory is inappropriate.

Higashimura et al presented the carbocationic stabilisation theory as explanation for the polymerization of IBVE initiated by $EtAlCl_2$ with IBVE-acetic acid adduct [67,68]. It was found that in the presence of esters, or ethers, the polymerization became living. The conventional system has a much higher rate constant of polymerization than the living system, which was attributed to the propagating carbocations being less active in the later case. The chain carriers shown in figure 1.28 were therefore proposed.

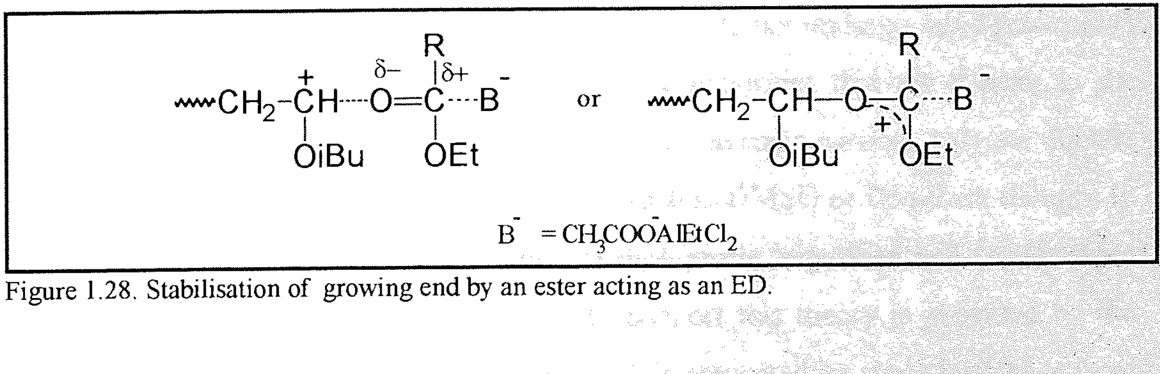


Figure 1.28. Stabilisation of growing end by an ester acting as an ED.

The effects of steric crowding near the carbonyl group of the ester adduct have also been examined [69]. Increasing the bulkiness of the R substituent caused a marked increase in the rate constant of propagation of IBVE. A series of ester adducts, such as those shown in figure 1.28, where R = $-CH_3$, $-C_2H_5$, $-CH(CH_3)_2$, $-C(CH_3)_3$, showed a 10 fold increase in the rate constant of propagation from left to right in this series. Higashimura et al suggested the effect was caused by an increase in steric hindrance, thus weakening the interaction between the growing chain and the carbonyl group of the ester and imposing fewer restrictions on the incoming monomer.

The effects of the basicity of added esters have also been evaluated for the series of compounds $X-C_6H_4-COOC_2H_5$; where X= $-OCH_3$, $-CH_3$, -H, -Cl. All adducts yielded living polymer systems but it was noted that the rate of propagation increased with decreasing basicity. It was suggested that increasingly basic esters would better stabilise the propagating cation and reduce its reactivity.

In all the influence of a large range of ED additives in IBVE polymerizations have been examined, ketones [70], crown ethers [71], cyclic ethers and formals as well as acyclic ethers with oxyethylene units [72]. Experimental evidence suggests the role of these ED's, at least in vinyl ether polymerizations, is to stabilise the propagating cation.

In contrast the evidence collected from polymerizations of isobutene suggests the role of these added EDs to be that of proton trapping. In these polymerizations it is normal to use a mixed solvent system, such as methyl chloride and hexane, to produce a chain carrier of the desired ionicity to promote a living polymerization. Without the addition of EDs to the polymerization of isobutene, by $TMPCl/TiCl_4$, a bimodal molecular weight distribution is produced [73]. A bimodal distribution would suggest the presence of more than one type of propagating centre, and that the centres do not undergo rapid conversion with each other. It is reasoned therefore that protic impurities that are present in the polymerization media initiate the growth of uncontrollable chain carriers, that are distinct from those of the living moieties. Electron donors such as DMSO or DMA are thought to form complexes with the catalyst that will scavenge protic impurities and render them inactive in the polymerization [74]. Evidence to support this theory is provided by the role of 2,6-di-*tert*-butylpyridine (DtBP) [75], which is prevented by steric hindrance from reacting with carbocations or Lewis acids and thus cannot stabilise the propagating cation. It will however support a living polymerization of isobutene. Furthermore, the concentration of the DtBP has no effect on the rate of polymerization. However, other ED such as TEA, DMSO or DMA clearly retard the rate of polymerization with increasing concentration, in which case proton scavenging alone cannot account for all the effects of these additives.

The final influence an ED may have was suggested by Kelen [76] studying the polymerization of isobutene, catalysed by BCl_3 in the presence of DMSO. It was rationalised that the DMSO may complex with the catalyst, reducing its Lewis acidity, and forcing the active species into a more covalent form. Thus, the activity of the cation would be reduced and the rate of propagation retarded.

1.3.3c Control of Lewis acidity

Rather than use mixtures of solvents or additives to control the nature of the propagating end it is possible to regulate the Lewis acidity of the catalyst. Sawamoto et al examined the effect of Lewis acidity in a series of titanium compounds on IBVE polymerizations in dichloromethane [77]. A sequence of isopropoxytitanium chlorides were prepared, of general formula $TiCl_{4-n}(OiPr)_n$. The Lewis acidity of the catalyst reduced with increasing values of n. It was found that $TiCl_4$ and $TiCl_3(OiPr)$ generated rapid polymerizations yielding polymers with broad molecular weight distributions, while no polymer was produced by $Ti(OiPr)_4$. However, when n = 2 or 3 a living polymerization ensued, producing polymers possessing narrow molecular weight distributions. The use of bulky substituents (figure 1.29) has been found to exert steric control, producing polymers with a high degree of isotacticity [78].

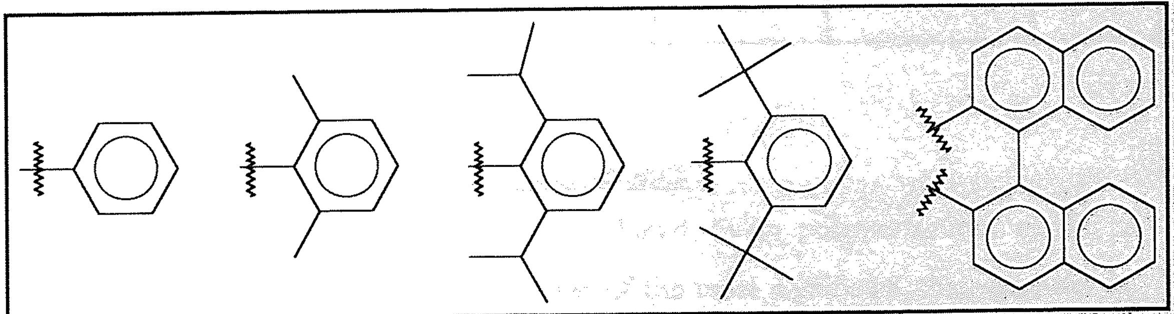


Figure 1.29. Ligands that regulate the Lewis acidity of a catalyst.

1.3.4 Living carbocationic polymerization systems

Utilising the techniques discussed in the preceding sections an extensive range of living cationic polymerization systems have now been developed, for a number of different monomers. In each, the reactivity of the growing cation is carefully controlled by the selection of solvent(s), catalyst, temperature and additives. Table 1.1 gives an example of some of these systems.

Monomer	Initiator System			Additive	Ref.
	Co-catalyst	Catalyst	Solvent		
Isobutene	CuOAc	BCl$_3$	CM	-	[51,81]
	CuCl	BCl$_3$; TiCl$_4$	CM/cHex.	DMSO; DMA	[56]
	DiCuCl	TiCl$_4$	CM/hex.	pyridine	[79,80]
	TMPOH	BCl$_3$	MC	1-methyl-2-pyrrolidinone	[81]
	DiCu Azide	Eth$_2$AlCl	DCM	-	[41]
	t-BuOBenzene	TiCl$_4$	DCM	D^{t}BP	[82]
Styrene	1-PEB	SnCl$_4$	CM	-	[83,84]
	1-PEC	SnCl$_4$	DCM	nBu$_4$NCl	[61]
	TMPCl	TiCl$_4$	DCM/Hex	TEA	[85]
IBVE	HCl	SnCl$_4$	Tol.	nBu$_4$NCl	[45,64]
	CH$_3$COOH	EtAlCl$_2$	Hex.	Esters/ethers	[67]
N-vinylcarbazole	HI	nBu$_4$NI	Tol.	-	[86]

Table 1.1. Living carbocationic polymerization systems.

1.3.5 Features and kinetics of living polymerizations

Since termination and transfer reactions are excluded, living polymerizations exhibit a number of important, exploitable features. One of the most significant characteristics is the ability to control the degree of polymerization. Provided that the rate of initiation is greater than that of propagation all chains may grow at the same rate to produce polymers with narrow molecular weight distributions. The molecular weight distribution will be given by a Poisson distribution:

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + \frac{\overline{M}_n}{\left(\overline{M}_n + 1\right)^2} \tag{1.17}$$

If the initiator molecule is monofunctional, and gives rise to one polymer chain, then the number average degree of polymerization ($\overline{DP}_n$) will equal the ratio of the concentrations of the reacted monomer to the introduced initiator [87] :

$$\overline{DP}_n = \frac{[M]_0 - [M]}{[I]_0} \tag{1.18}$$

Under these conditions the number average molecular mass of the polymer increases linearly with monomer conversion or weight of polymer. Plots of the number average molecular weight against conversion provide a method for testing for the living nature of the polymerization, a linear plot through the origin indicates a living system with the absence of termination and transfer.

It is possible to develop a pseudo-first-order kinetic expression for the living polymerization of isobutene initiated by tertiary halide and Lewis acids [88,89]. Provided initiation is fast the rate of polymerization is given by equation (1.19).

$$R_p = -\frac{d[M]}{dt} = k_p\left[R^+B^-\right][M] = k_{app}[M] \tag{1.19}$$

where;

R_p = rate of polymerization,

k_p = rate constant of propagation,

$[M]$ = concentration of monomer at any time, t,

$[M]_0$ = initial concentration of monomer,

$[R^+B^-]$ = concentration of the active propagating species

$[I]_0$ = initial initiator concentration,

k_{app} = apparent rate constant of propagation, = $k_p[R^+B^-]$.

Equation (1.19) may be integrated to show that for a system with a constant concentration of propagating centres a plot of $\ln([M_0]/[M])$ versus time should produce a linear relationship with the gradient equal to k_{app}. Where k_{app} is dependent on the concentration of the propagating species, as well as k_p. When this method was applied to the kinetics of the polymerization of isobutene utilising *tert*-butyl-dicumyl chloride as an initiator, pyridine as an electron donor, and $TiCl_4$ as the catalyst, the reaction was found to be first order in initiator and monomer, second order in catalyst, and to possess a negative order in pyridine.

An alternative method of elucidating k_{app} has been presented by Endsor [90]. For a living polymerization it has already been shown that the degree of polymerization can be given by:

$$\overline{DP_n} = \frac{[M]_0 - [M]}{[I]_0} \tag{1.20}$$

and applying the pseudo-first order rate equation from (1.19) and rearranging gives:

$$[M] = [M]_0 e^{-k_{app}t} \tag{1.21}$$

Combining (1.20) and (1.21):

$$\overline{DP_n} = \frac{[M]_0\left(1 - e^{-k_{app}t}\right)}{[I]_0} \tag{1.22}$$

At complete conversion the degree of polymerization will be given by:

$$\overline{DP}_{n\infty} = \frac{[M]_0}{[I]_0} \tag{1.23}$$

Substituting equation (1.23) into (1.22) gives:

$$\overline{DP}_n = \overline{DP}_{n\infty}\left(1 - e^{-k_{app}t}\right) \tag{1.24}$$

Re-arranging:

$$1 - \frac{\overline{DP}_n}{\overline{DP}_{n\infty}} = e^{-k_{app}t} \tag{1.25}$$

Taking logs:

$$\ln\left(1-\frac{\overline{DP}_n}{\overline{DP}_{n\infty}}\right)=-k_{app}t \tag{1.26}$$

Re-writing equation (1.26) :

$$\ln\left(\overline{DP}_{n\infty}-\overline{DP}_n\right)=\ln\overline{DP}_{n\infty}-k_{app}t \tag{1.27}$$

The apparent rate constant is found by plotting $\ln\left(\overline{DP}_{n\infty}-\overline{DP}_n\right)$ against time. Care should be exercised in this approach since it should be applied only in the early stages of polymerization. At high conversion large error can become involved since, as $\overline{DP}_n$ approaches $\overline{DP}_{n\infty}$ then $\ln\left(\overline{DP}_{n\infty}-\overline{DP}_n\right)$ approaches $\ln(0)$ which tends towards $-\infty$.

1.4 Applications of living systems

1.4.1 Preface

Living cationic polymerizations provide a useful means for the preparation of polymers that possess controlled molecular weights, well-defined topologies, and quantitatively functionalised chain ends. Control of the molecular weight and topology enables the polymers physical characteristics to be tailored to the end application [19,20]. For example, linear short chain polyisobutenes, or vinyl ethers, that possess a suitable functionality have been found to be useful in the additive's industry as surfactants, corrosion inhibitors and seal swellents. Whereas, similar polymers with a star shape topology (section 1.4.4) are good viscosity and rheology modifiers. The physical characteristics that the star polymer imparts in its application will depend on its molecular weight and the number of arms it possesses. Therefore, the capability of controlling polymer architecture by living polymerization techniques is highly desirable.

1.4.2 Functionalisation of polymer chains

There are two general methods to functionalise a polymer chain end in living polymerizations [91]. The first is to use a functional initiator, which incorporates the functionality in the head, or α-end, of the polymer chain, figure 1.30. However, this method does have some limitations, in that the functionality must not be reactive in the polymerization.

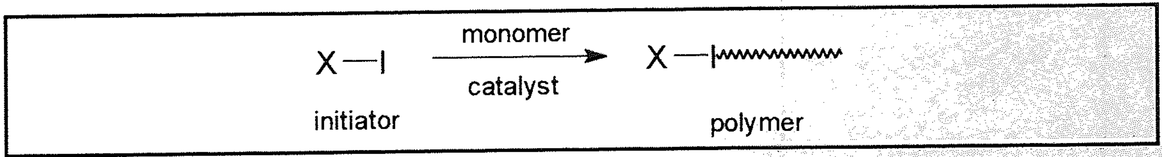


Figure 1.30. Functional head group. X = Functional group; I = initiator.

Given the limitations of the application of such techniques, a number of different functional initiators have been successfully applied in the polymerization of a variety of monomers. Examples of some of these functionalities, and the conditions for their use are described in table 1.2.

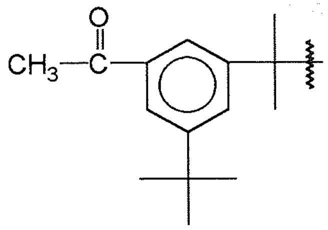
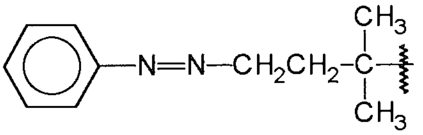
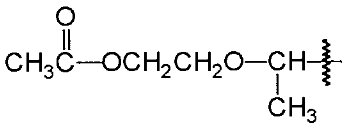
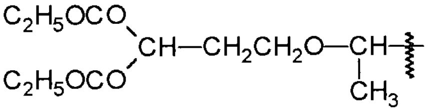
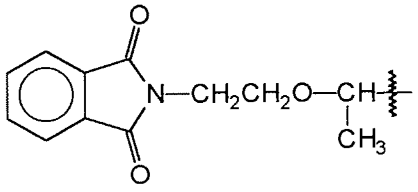
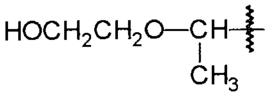
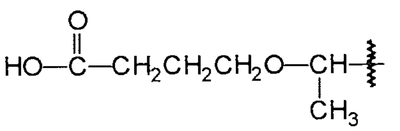
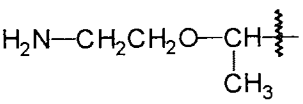
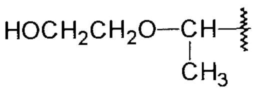
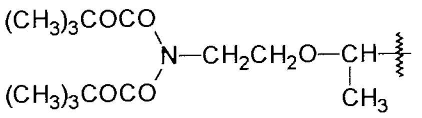
Head Function	Polymer	Polymerization System	Ref.
	PIB	BCl_3/DMA/MeCl	[92]
	PIB	$TiCl_4$	[93]
     	Polystyrene Polyalkoxystyrene	$SnCl_4$/nBu_4NCl/DCM ZnI_2	[94] [95]
 	IBVE	$EthAlCl_2$/hexane	[96]

Table 1.2. Functional initiators.

An alternative and frequently used method is by quenching the living chain ends with a suitable nucleophile, known as the end-capping method. This process attaches the functional group to the tail or ω-end of the polymer chain, figure 1.31.

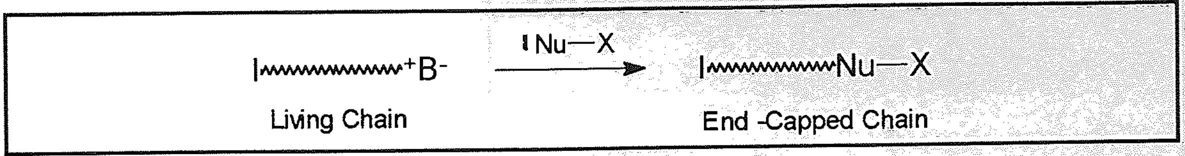


Figure 1.31. End capping with functional nucleophile NuX.

This method again has its limitations. Some living polymer chain ends, particularly those of isobutene, do not readily react with capping reagents. Living chains of vinyl ethers will readily accept malonate ions [97], but isobutene chains will not. An extensive search for suitably reactive nucleophiles for capping polyisobutene chains has mostly been unproductive, as most initiators yield a tertiary chloride end group. The exceptions are reactions involving organosilicon compounds. It has been found that these reagents will quantitatively add to most living cationic chain carriers to produce a variety of functionalities [98,99,100], figure 1.32.

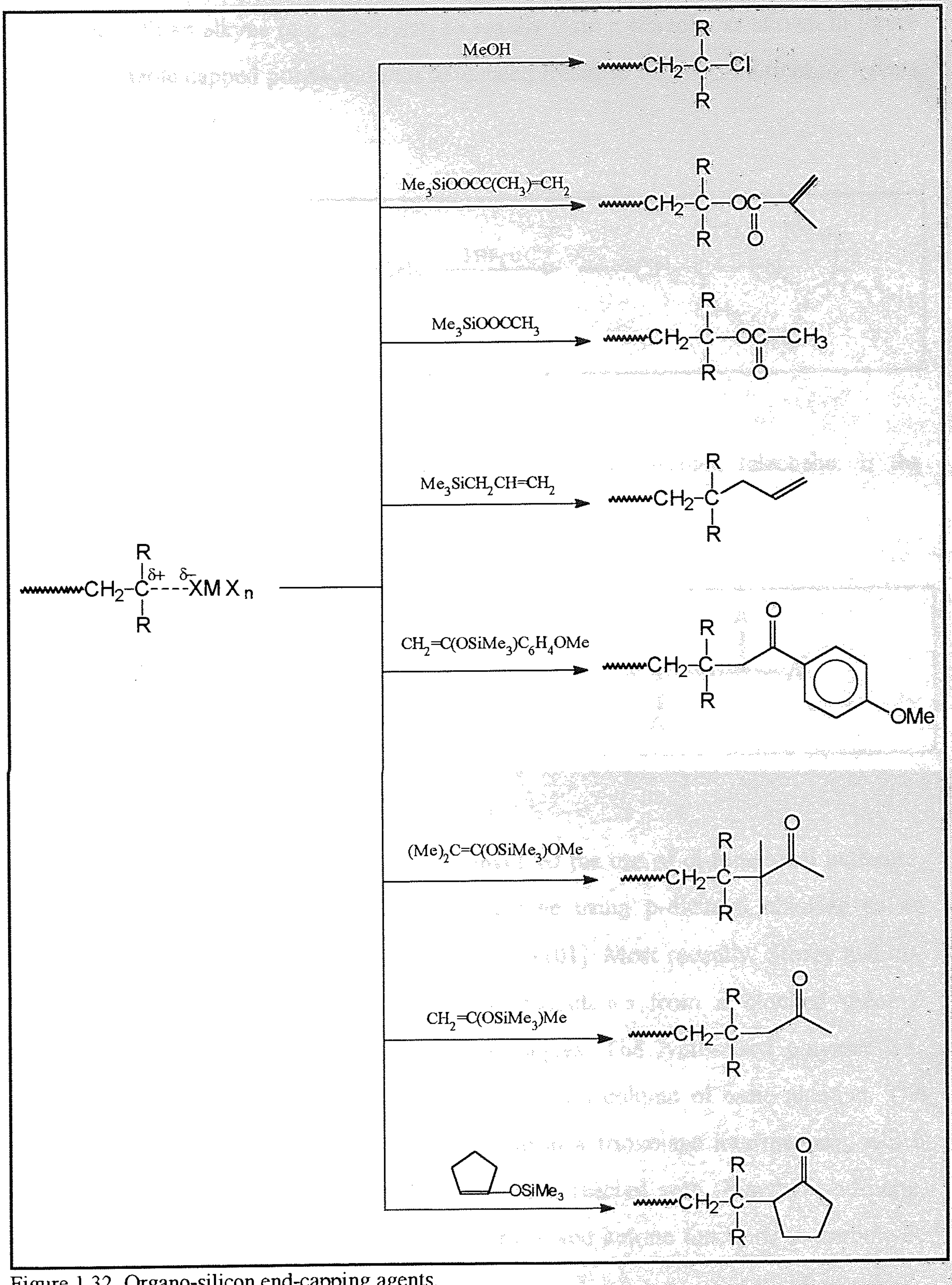


Figure 1.32. Organo-silicon end-capping agents.

Given that living polymer chain ends will undergo only a few reactions, an alternative is a post-polymerization reaction on the "naturally" terminating end group. For example, an azide terminated polyisobutene was prepared by a polymerization reaction initiated by 1-azido-methylethyl benzene/Eth$_2$AlCl in methylchloride. The azide terminated polymer was then reacted with an alkyne (e.g. 2-butyne) to readily form a triazole, as shown in figure 1.33. Such triazole capped polyisobutenes have been found to be good lubricating agents when added to fuels [40].

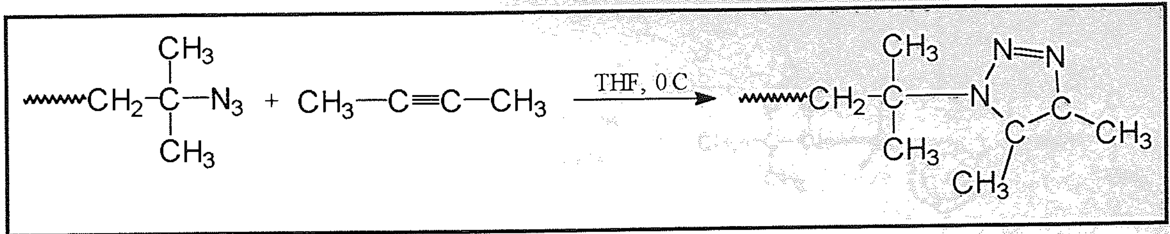


Figure 1.33. Triazole capped polyisobutene.

Polymers that contain two or more functional groups are termed telechelic. If the functions are identical the term homotelechelic is used, figure 1.34.

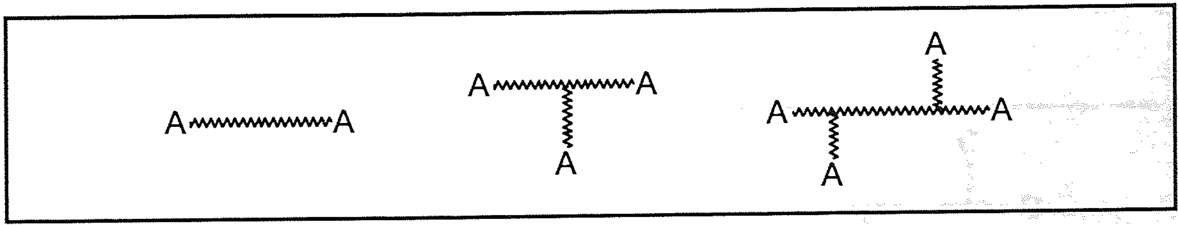


Figure 1.34. Homotelechelic polymers.

Some of the first homotelechelics synthesised involved the use of di-functional initiators. For example, the inifer polymerization of isobutene using p-dicumyl chloride as an initiator yields a α,ω-di(tert-chloro)polyisobutylene [101]. Most recently, Storey and co-worker [102] prepared such di-chlorinated polyisobutenes from a blocked dicumyl initiator using living cationic polymerization techniques. The synthesised polymer was subsequently dehydrochlorinated by passing it through a column of basic alumina. The vinylic product was then treated with ozone to form a trioxolane intermediate, which reduces to a mixture of aldehydes and ketones, when reacted with trimethyl phosphite. The final step involved the oxidation of the aldehyde and ketone functions to carboxylic acid groups, figure 1.35.

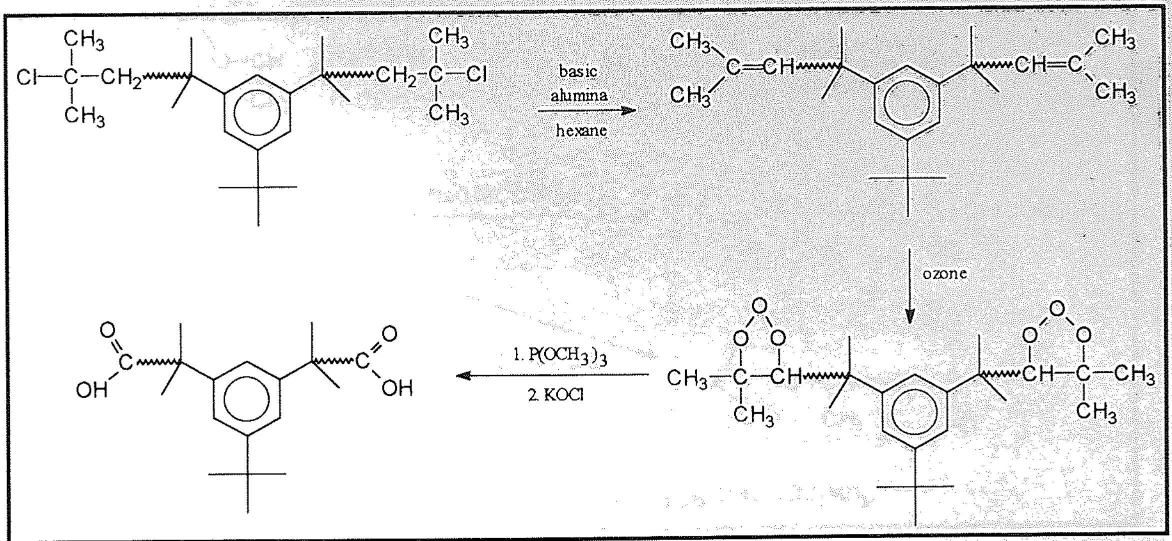


Figure 1.35. Synthesis of homotelechelic carboxylic acid functionalised polyisobutene.

Polymers with dissimilar end-functions are described as heterotelechelic or asymmetric telechelic, figure 1.36.

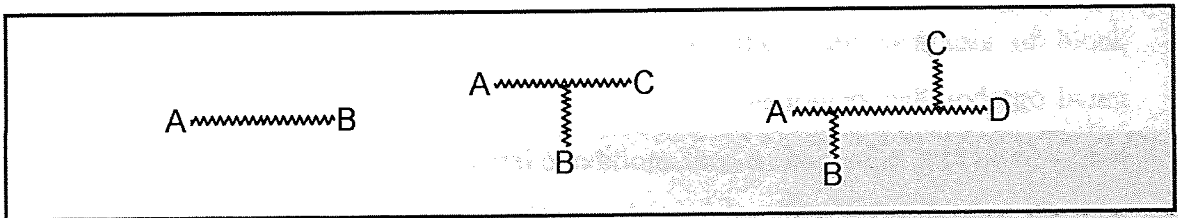


Figure 1.36. Asymmetrical telechelic polymers.

Heterotelechelics are synthesised by combining functional initiator and end capping techniques. A good example of this method would be the work carried out by Higashimura et al on the living cationic polymerization of isobutyl vinyl ether. A range of functional initiators and capping reagents were employed to produce a variety of heterotelechelic polymers. Figure 1.37 shows some examples of these functionalised polymers, in all of the given cases the polymer chains were found to be completely functional.

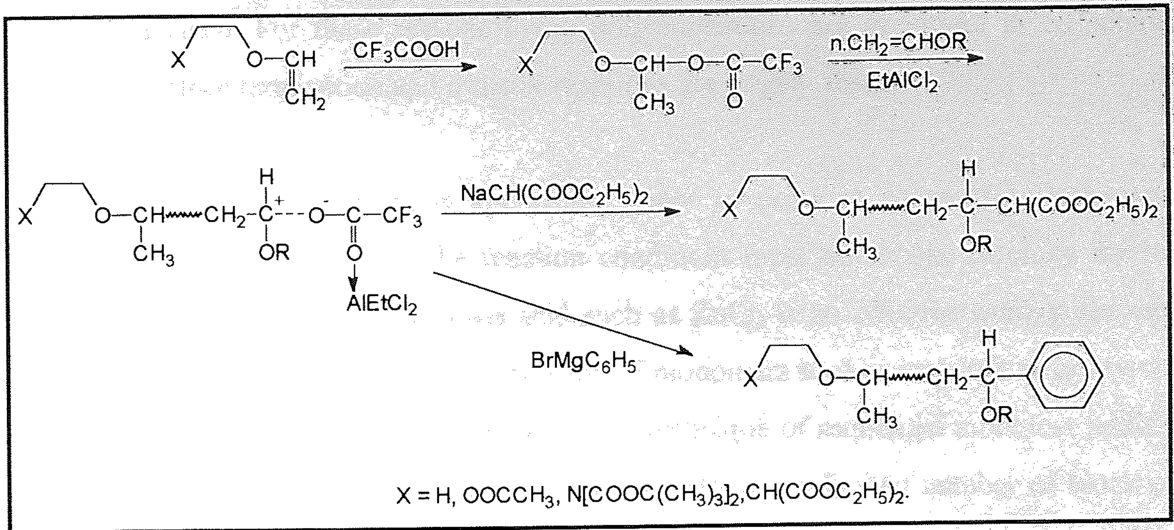


Figure 1.37. Synthesis of heterotelechelic *i*-butyl vinyl ether.

1.4.3 Co-polymers

1.4.3a Sequential monomer addition technique

A number of methods have now been developed for the clean synthesis of block copolymers using living polymerization techniques. If two monomers will undergo living polymerization under identical experimental conditions then a copolymer may be prepared by sequential monomer addition (SMA). This technique involves polymerizing the first monomer to completion and then adding a batch of the second monomer to create a di-block co-polymer. Tri-block co-polymers are prepared in a similar way, except difunctional instead of monofunctional initiators are used, the first monomer occupying the central block.

To avoid the presence of homo-polymer in these materials, the living chain ends of the first monomer must quantitatively initiate the second monomer batch. If the cation formed by the addition of a molecule of the second monomer to the polymer chain end is less stable than the cation produced by the first, then initiation of the second monomer will not be favourable. The purity of the polymer chains produced from the polymerization of the first batch is also important. Polymer chains that have undergone irreversible termination, and those terminated by vinyl groups, will fail to initiate polymerization of the second monomer. Although in the later case, the vinyl group may be incorporated into the polymer architecture as the polymerization proceeds, to create a branched chain. For these reasons living polymerizations are important in co-polymer synthesis, since termination and transfer reactions are largely absent.

The SMA method is limited in application, since in order to successfully polymerize monomer in a living manner the reaction conditions must be chosen carefully for that combination of monomers. A Lewis acid such as $ZnCl_2$ is an effective catalyst for vinyl ethers, but will fail to initiate polymerization of monomers such as isobutylene or styrene. Therefore, a block copolymerization using the technique of sequential monomer addition will not be possible under these conditions. Nevertheless a limited number of block co-polymers have been prepared cationically. Isobutene and styrene, have been copolymerized using dicumyl chloride/$TiCl_4$/pyridine as initiator to produce an elastomeric material [103]. Other examples include; isobutene and isoprene by cumyl acetate/BCl_3 [104], and indene and isobutene by 1,4-bis(2-methoxy-2-propyl)benzene/$TiCl_4$/di-tert-butylpyridine [105].

1.4.3b Step-wise copolymerization technique

When the sequential monomer addition technique is not applicable an alternative option is to carry out the copolymerization in two stages. The first monomer is polymerized as normal and quenched normally to generate a tertiary chloride end group. This polymer is then used as a macroinitiator in a second polymerization system, which allows sequences of second monomer to be prepared. For example, a block copolymer of poly(isobutene-b-styrene) was prepared and isolated in this way. This macromolecule was then utilised as an initiator for an atom transfer radical polymerization (ATRP) of methyl methacrylate, so enabling a tri-block copolymer to be produced [106]. Other procedures have been developed that enable the cross over from cationic to anionic polymerizations [107].

One pot synthesis of polymerization incompatible monomers has been achieved with the aid of unpolymerizable monomers such as 1,1-diphenylethylene. For example, a copolymer of isobutene and IBVE has been prepared by Faust et al [108,109]. The isobutene was polymerized by the TMPCl/$TiCl_4$ initiating system. When the polymerization was complete a quantity of DiPhE capping agent was added. The reaction conditions were then modified by the introduction of nBu_4NCl prior to IBVE addition. The result was 100% crossover efficiency.

1.4.4 Star polymers

There are three methods of producing star shaped polymers from living polymerizations. The first involves the use of multifunctional initiators, which will initiate a discreet number of propagating centres that grow out from the central core simultaneously. A second technique involves the use of coupling agents. In this process a number of growing chains are coupled together at the end of the reaction. Lastly cross-linking agents can be employed to link a number of chains together.

1.4.4a Multifunctional initiators

A successful multifunctional initiator must be able to rapidly initiate the growth of several chain branches. To achieve rapid initiation each of the initiation sites must be capable of becoming rapidly active, without significantly influencing the ability of other sites to also become active. Therefore, the multifunctional initiator must be able to support multiple cationic charges simultaneously. If these criteria are not met then slow initiation will occur and the chain branches will not be the same length.

A number of multifunctional initiators have now been successfully employed to produce polymers containing three to eight arms. Figure 1.38 shows a tetrafunctional initiator and figure 1.39 gives some examples of trifunctional initiators [110].

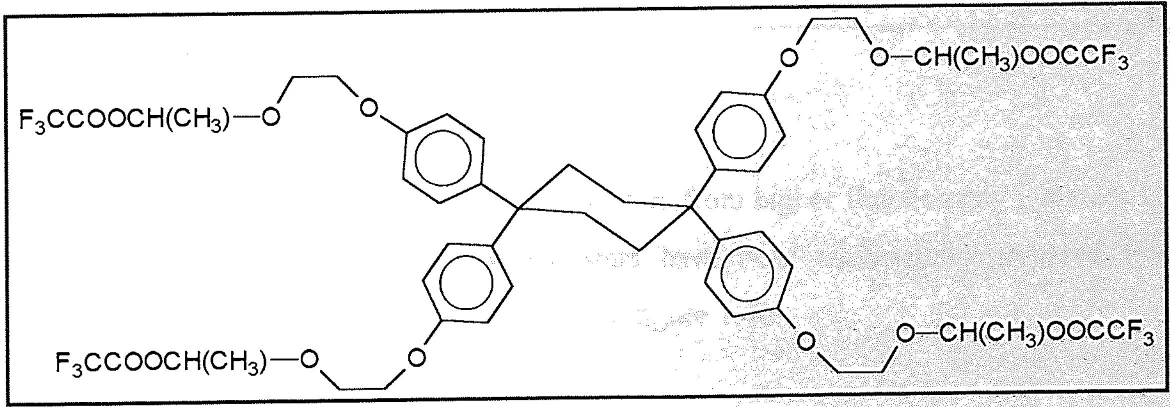


Figure 1.38. Tetrafunctional initiator.

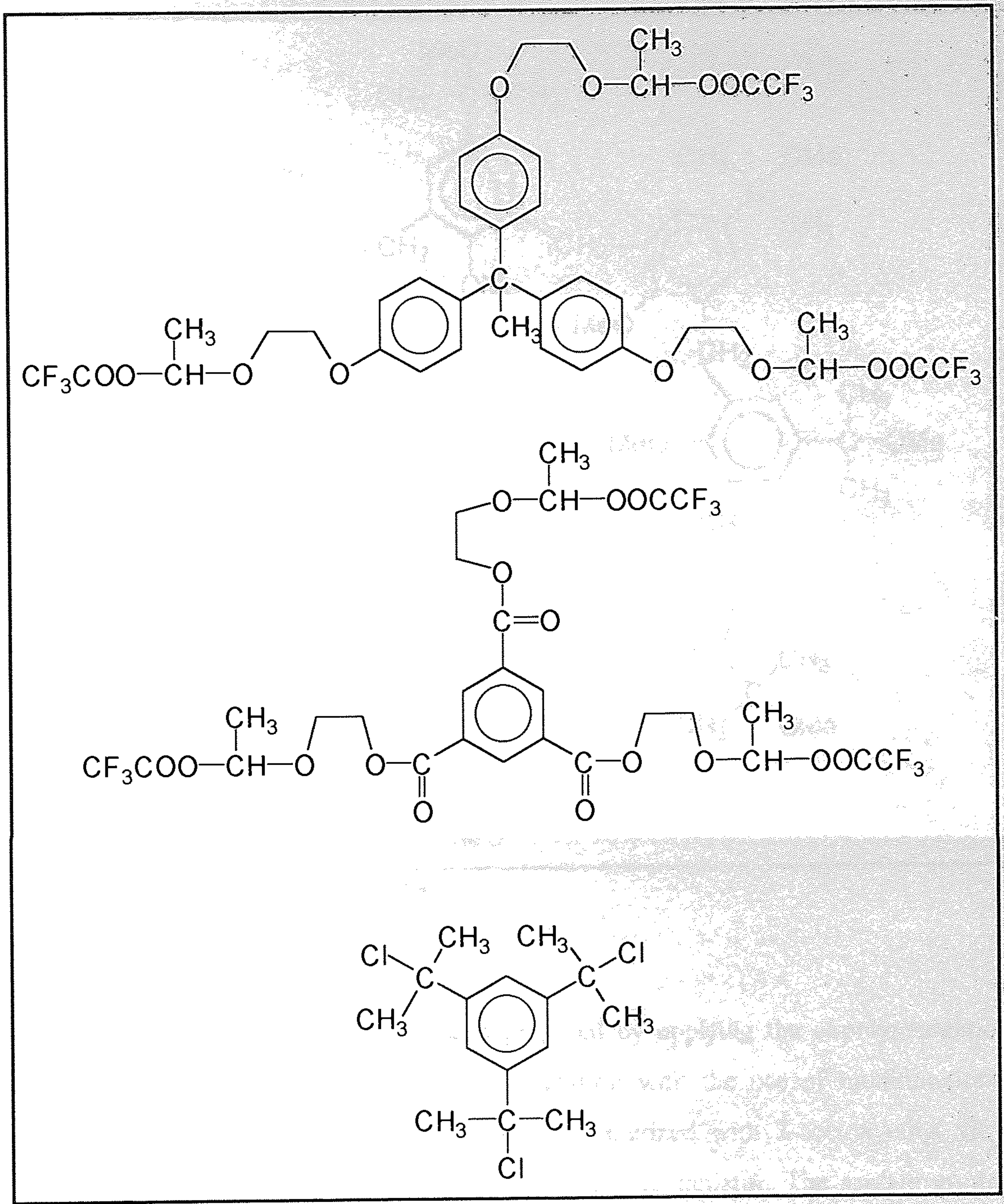


Figure 1.39. Trifunctional initiators.

It is only recently that the polymerization of stars from higher functionality initiators has been achieved. Octa-arm polyisobutene stars have been successfully prepared from calixarene by Kennedy et al [111], as shown in figure 1.40.

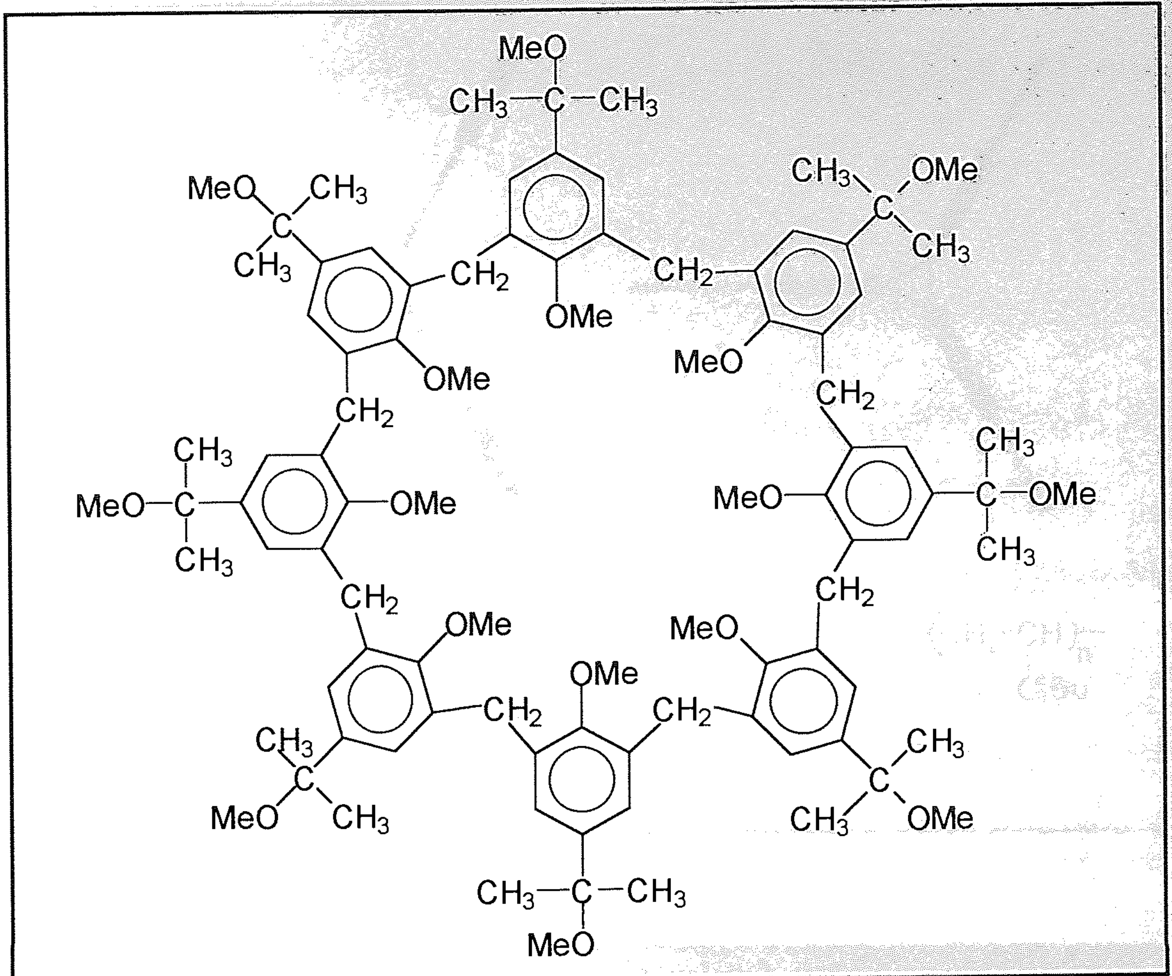


Figure 1.40. Calixarene, an octa-arm initiator.

Amphiphilic tri-armed polymers have been prepared by applying the copolymerization techniques described in section 1.4.3 in combination with the use of multifunctional initiators [21,22,112,113]. IBVE was block copolymerized with 2-acetoxyethyl vinyl ether ($CH_3COOCH_2CH_2O\text{-}CH{=}CH_2$) using a trifunctional initiator. The acetate groups were then hydrolysed to form hydrophilic hydroxyl functional groups. The structure of polymer produced by this method is shown in figure 1.41.

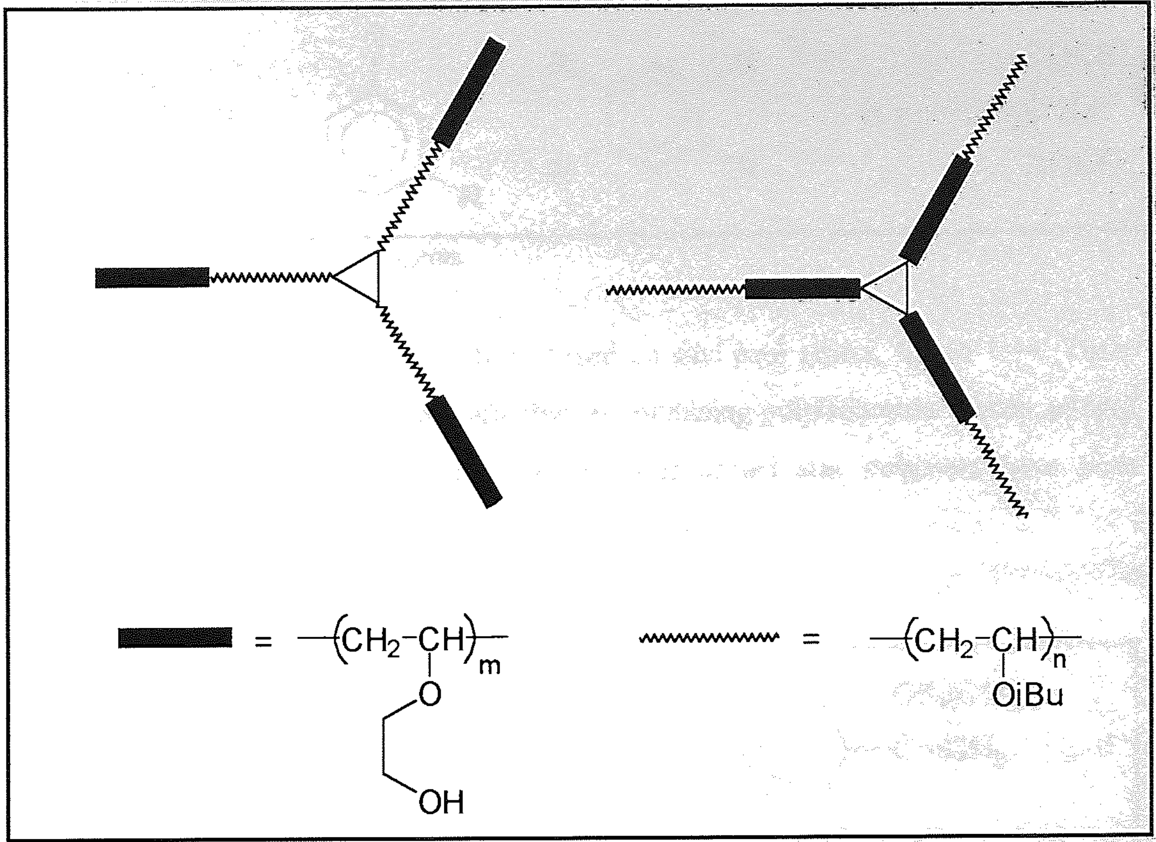


Figure 1.41. Amphiphilic tri-armed block copolymer.

1.4.4b Coupling agents

Multifunctional coupling agents are compounds bearing two or more functional groups that combine with living polymers in a quantitative termination reaction, figure 1.42.

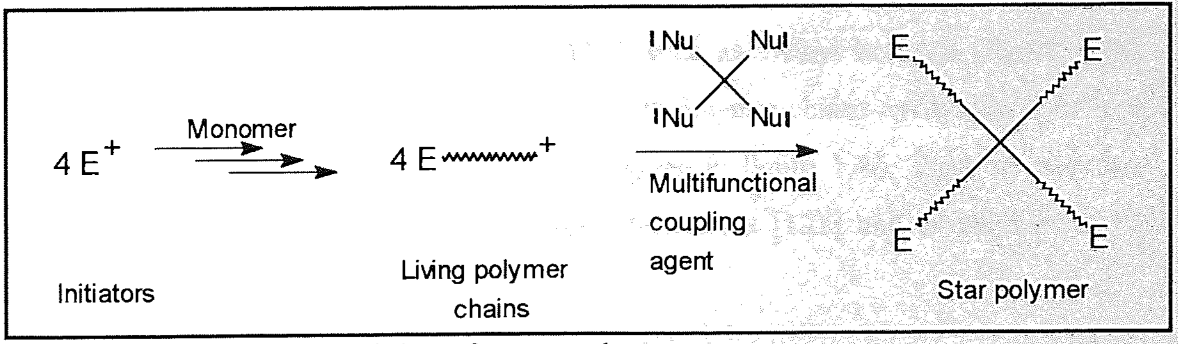


Figure 1.42. Coupling of living chains to form star polymers.

As described in section 1.4.2, sodium malonate anions have been found to be effective terminating agents with living vinyl ether polymerizations. Reagents that possess two or more sodium malonate functionalities have been used to synthesis bi-, tri, and tetra armed star polymers, figure 1.43 [114].

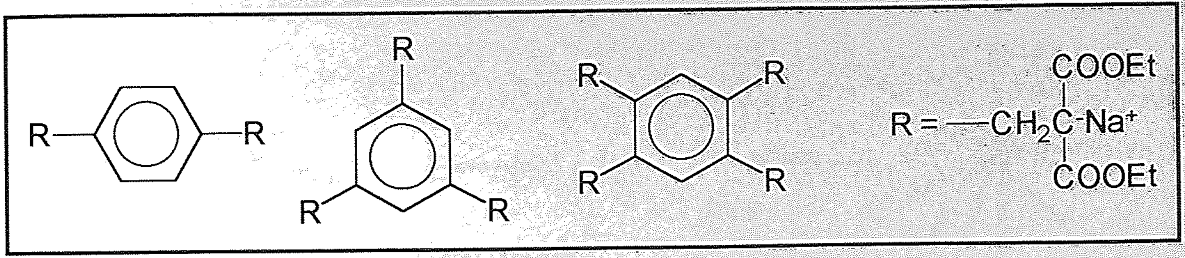


Figure 1.43. Sodiumalonate coupling agents.

Another group of coupling agents is those based on silyl enol ethers, figure 1.44. These are some of the few reagents that are effective at combining polyisobutene chains, as well as polystyrenes and polyvinyl ethers. Two to four armed star polymers have been synthesised successfully [115,116,117,118] by this technique.

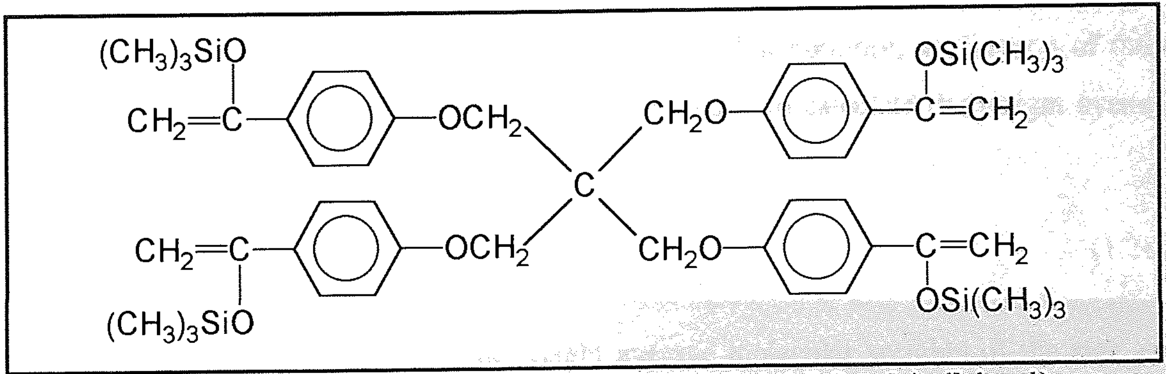


Figure 1.44. Coupling reagent, pentaerythritol tetrakis{p-[1-[(tri-methylsilyl)oxy]vinyl]phenyl}.

1.4.4c Cross-linking agents

Multi-armed stars of higher orders can be synthesised by reaction of the living polymer chain with a difunctional vinyl compound [119], such as divinyl benzene (figure 1.45). This type of reaction produces a micro-gel core with polymer chains emanating outwards. Examples of divinyl compounds employed are given in figure 1.46. Stars of polyvinyl ethers [120], polyisobutene [121], polystyrene derivatives [122] and amphiphilic block copolymers have been prepared [69,123].

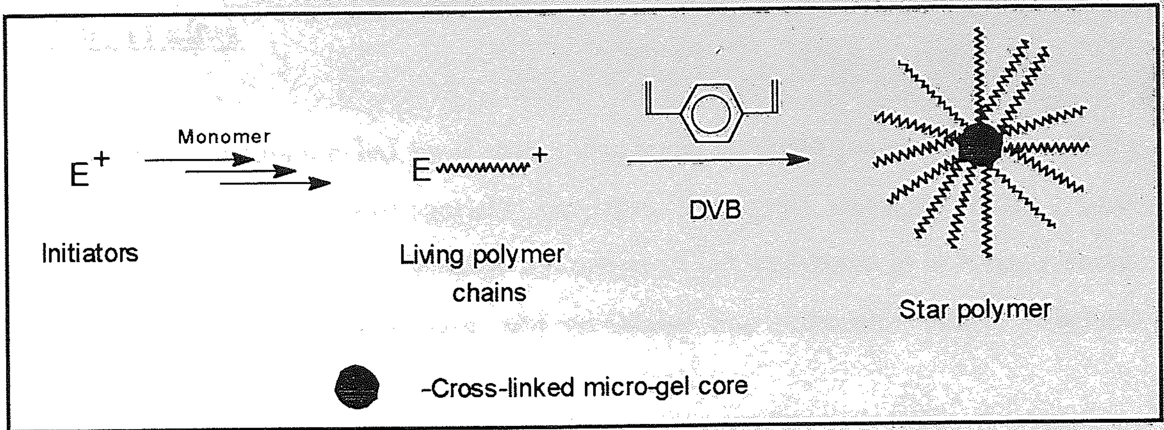


Figure 1.45. Multi-armed star branched polymer synthesis.

The structure and formation of these stars have been studied by viscometry and computer aided deconvolution of multimodal size exclusion chromatography traces. It was found that the micro-gel cores of adjacent stars can couple together, and that the cores themselves will contract over a period of time [124]. Furthermore, application of these techniques has facilitated the derivation of an expression to calculate the weight average number of arms per star macromolecule [125]:

$$\overline{N_w} = \frac{\overline{M}_{w,star}}{\overline{M}_{w,arm} + RM_L} \qquad (1.28)$$

where, $\overline{M}_{w,star}$ and $\overline{M}_{w,arm}$ are the weight average molecular weights of the star and arm respectively, R is the molar ratio of core forming comonomer to monomer, and M_L is the molecular weight of the linking comonomer.

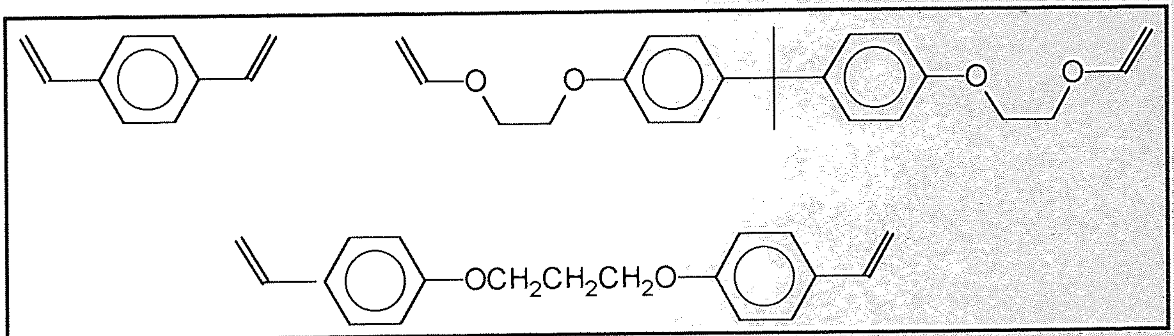


Figure 1.46. Divinyl linking reagents.

These polymers, possessing a star shaped topology, have been found to have a high resistance to shear-enduced thermal degradation, which makes them particularly good candidates for use as viscosity modifiers in oils [126].

1.5 Project aims

In the preceding sections it has been shown that living cationic polymerizations offer a large scope for the synthesis of speciality polymers. The scope and aims of this project are to identify a system that is suitable for polymerizing isobutene in a living manner, study the kinetics of polymerization, and synthesise low molecular weight telechelic materials.

Chapter 2: Experimental

2.1 Vacuum and Schlenk line techniques

The following techniques and apparatus were selected because of the sensitivity of the polymerizations to impurities and the hygroscopic nature of some of the reagents. These techniques allow material to be manipulated either under argon or vacuum, safely secure in the knowledge that the purity of the reagent is preserved.

All glass vessels were cleaned prior to use by soaking in Decon-90, followed by rinsing with acetone and then finally dried in an oven at 240 °C for at least four hours. To minimise the re-absorption of moisture onto the glass, the vessels were evacuated, or put into an inert atmosphere, while still hot.

2.1.1 Vacuum line

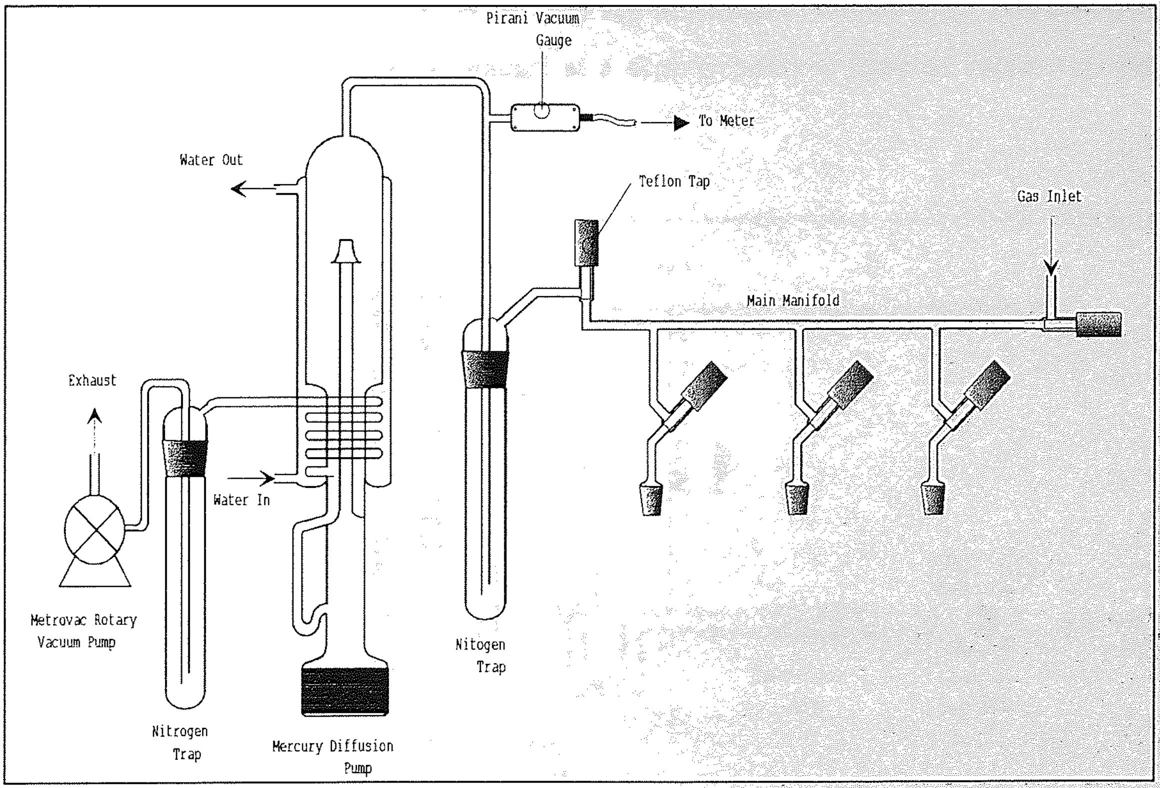


Figure 2.1. High vacuum line.

Figure 2.1 shows a diagram of the vacuum line that was used. The main glass manifold was evacuated by a Metrovac rotary vacuum pump used in conjunction with a mercury diffusion pump, both of which were protected from solvents by liquid nitrogen traps. Reagent flasks were attached to the manifold through B19 ground glass joints, which could be isolated from the manifold by greaseless Teflon taps. The system was capable of achieving pressures of 10^{-3} to 10^{-4} mm Hg, as measured by a Pirani vacuum gauge. Prior to use the glass was flamed with a bunsen, while under vacuum, to remove any moisture adsorbed onto the inside surface.

A gas inlet allowed the introduction of argon into the manifold for manipulation carried out by Schlenk techniques.

2.1.2 Gas handling line

Isobutene has a boiling point of -5.6 °C at atmospheric pressure. In order to handle this monomer on a laboratory scale a gas feed line was developed (figure 2.2). Isobutene was passed through two columns packed with silica-gel (or alterntively BaO) to dry the gas which was fed into the manifold at the gas inlet tap described in section 2.1.1. The bubbler ensured the gas in the line was maintained at a slightly positive pressure relative to the surrounding atmosphere.

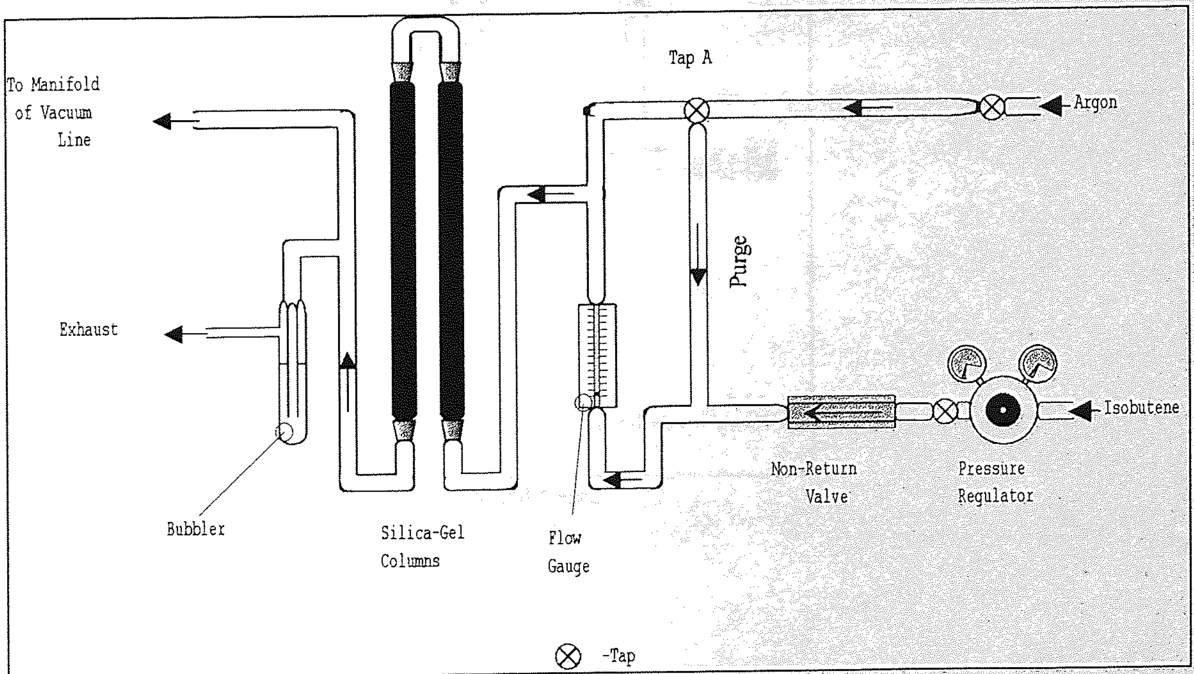


Figure 2.2. Gas handling line.

Tap A could be set in one of three positions, such that:

(1) the argon by passed the flow gauge and could be used to flood the evacuated manifold of the vacuum line,

(2) it was open so as to purge the entire gas handling line with argon,

(3) it was closed for introduction of isobutene into the system.

After use the line was purged with argon, flushing out the monomer.

2.1.3 Degassing

To remove gases dissolved in liquids, a pre-requisite before distillation, a freeze-thaw procedure was used. The liquid to be degassed was contained in a flask, as shown in figure 2.3, and attached to the vacuum line with the tap closed. The contents were frozen using liquid nitrogen and the manifold evacuated. The material was then evacuated by opening the relevant taps. Once the vacuum was established the tap to the solvent flask was closed, and its contents allowed to warm to ambient temperature. As the liquid melted trapped gasses were released. The contents of the vessel were then once again frozen and the procedure repeated until no further gas was released during thawing.

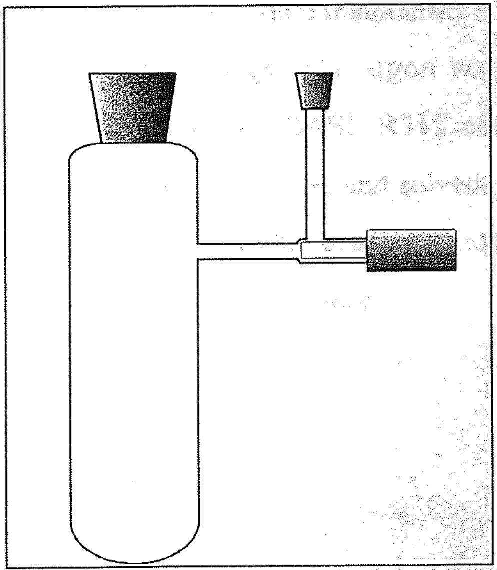


Figure 2.3. Solvent flask.

2.1.4 Vacuum distillation

Trap to trap distillation was used to transfer solvent or monomer from one vessel to another. The vessel containing the de-gassed material was attached to the manifold. A second receiver vessel was also fixed to the line, evacuated and cooled with liquid nitrogen. The manifold was then isolated from the vacuum pumps by closing the appropriate Teflon tap and the taps between the two flasks were opened, allowing the liquid to distil.

2.1.5 Schlenk techniques

The Schlenk technique for handling air sensitive material under argon was used where appropriate. The argon inlet to the vacuum line, figure 2.1, was opened to the evacuated manifold, to which was attached a vessel with a removable joint or tap. When a slight positive pressure was established in the vessel the tap or stopper was removed and the sensitive material was transferred to the vessel, normally by syringe. When the transfer was complete the stopper or tap was replaced and the vessel isolated.

2.2 Glove box

Sensitive materials were stored, and if necessary transferred, under an inert atmosphere within a Halco Engineering Ltd glove box, which maintained a dry argon environment at a positive pressure relative to the surroundings. The argon was continuously re-circulated through three absorbent columns containing, BASF R311 catalyst, 3 Å molecular sieve and activated carbon, to remove oxygen, moisture, and solvent vapours. Access to the box was via a double doored port that could be evacuated, and filled with argon. This minimised contamination with the outside atmosphere.

2.3 Materials and purification

2.3.1 Cyclohexane

Spectrophotometric grade cyclohexane was obtained from Aldrich Chemicals. Prior to use it was dried, and stored, over calcium hydride for a period of 24 hours. The cyclohexane could then be freshly distilled as required.

2.3.2 Dichloromethane

Super purity grade dichloromethane (DCM), 99.9 %, unstablised, was obtained from Romil Chemicals. Vigorous drying precautions were necessary because dichloromethane forms azeotropes with water. The solvent was stored in the dry box and prior to use it was placed in a round bottom flask over calcium hydride for 24 hours. The solvent was then refluxed under argon for 30 minutes in the apparatus shown in figure 2.4. The distillate was collected from a still head at the top of the reflux column; the first 25 ml collected was discarded.

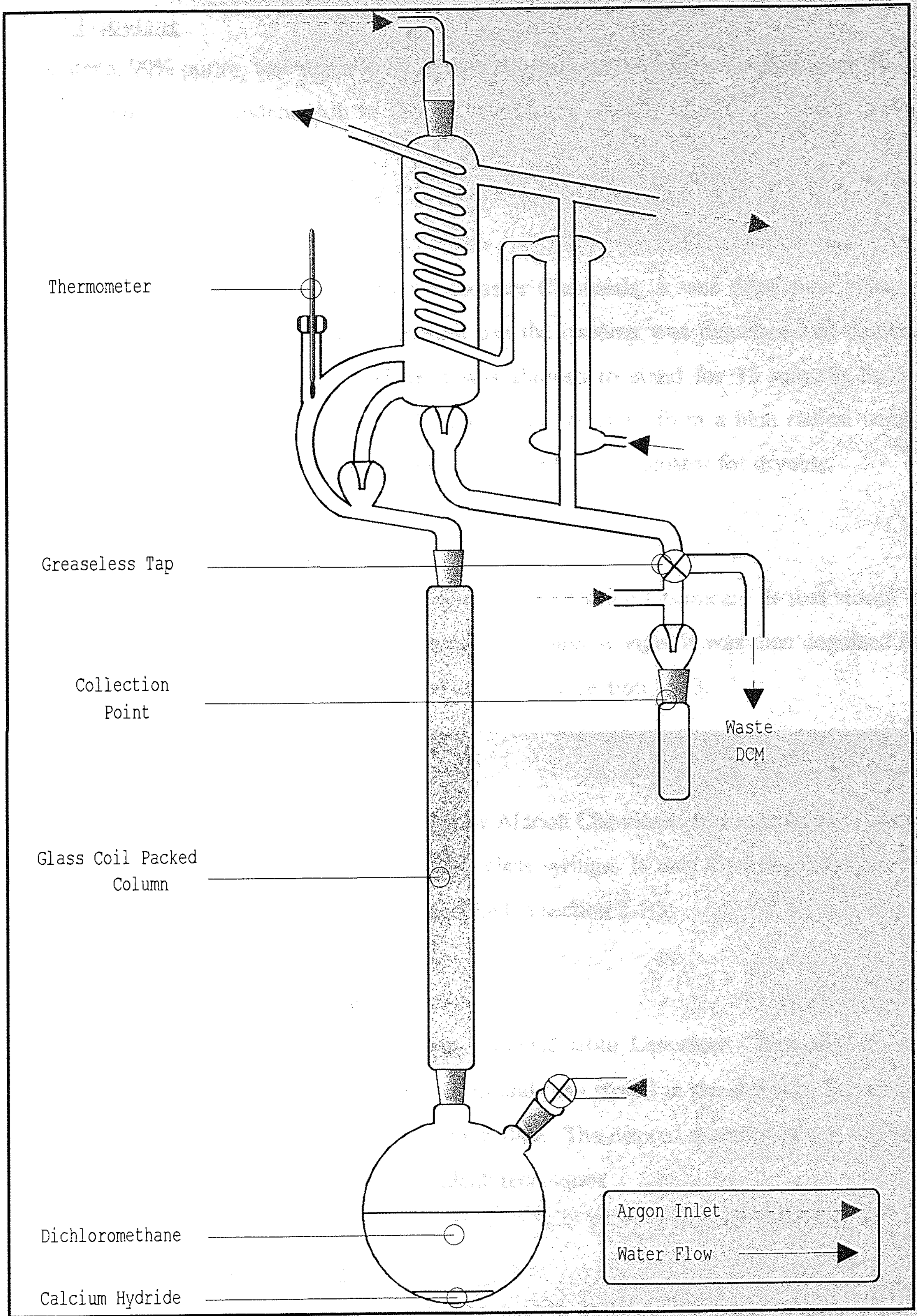


Figure 2.4. Dichloromethane still.

2.3.3 Isobutene

Isobutene, 99% purity, was supplied by Aldrich Chemicals. The gas was passed over silica-gel columns prior condensation in the polymerization vessel, which was fixed to the vacuum line.

2.3.4 Oxetane

99% purity oxetane was obtained from Lancaster Chemicals, it was dried over calcium hydride and stored in a refrigerator. Before use the oxetane was degassed and distilled onto sodium and benzophenone, where it was allowed to stand for 15 minutes before degassing a second time. Sodium and benzophenone react to form a blue radical anion, which is sensitive to moisture, and as such can be used as an indicator for dryness.

2.3.5 Titanium (IV) chloride

Titanium (IV) chloride, 99% purity, was supplied by Aldrich Chemicals. It was stored in the dry box and transferred as required using a dry glass syringe. It was then degassed on the vacuum line by the freeze thaw method described in section 2.1.3.

2.3.6 Tin (IV) chloride

Tin (IV) chloride, 99% purity, was supplied by Aldrich Chemicals. It was stored in the dry box and transferred as required using a dry glass syringe. It was then degassed on the vacuum line by the freeze thaw method described in section 2.1.3.

2.3.7 Tetrabutylammonium chloride

Tetrabutylammonium chloride (99 %) was obtained from Lancaster Chemicals. It was dried for 24 hours at 80 °C in a vacuum oven and then stored in the dry box. For use, a solution with DCM was prepared in a vacuum flask. The desired quantity of the solution was injected into the reaction vessel by Schlenk techniques.

2.3.8 1-Chloro-1-phenylethane

1-chloro-1-phenylethane, 99 % purity, was obtained from Acros Organics. It was stored in the glove box and used without further purification. It was transferred to a vacuum vessel (figure 2.3) using a dry syringe and degassed. A solution was prepared in either dichloromethane or cyclohexane. The desired quantity was injected into the reaction flask using Schlenk techniques.

2.3.9 1-Bromo-1-phenylethane

1-Bromo-1-phenylethane, 99 % purity, was obtained from Acros Organics. It was stored in the glove box and used without further purification. It was transferred to a vacuum vessel (figure 2.3) using a dry syringe and degassed. A solution was prepared in either dichloromethane or cyclohexane. The desired quantity was injected into the reaction flask using Schlenk techniques.

2.3.10 t-Butyl chloride

t-Butyl chloride, 99 % purity, was supplied by Aldrich Chemicals. It was stored in the glove box and used without further purification. It was transferred to a vacuum vessel (figure 2.3) using a dry syringe and degassed. A solution was prepared in either dichloromethane or cyclohexane. The desired quantity was injected into the reaction flask using Schlenk techniques.

2.3.11 Pyridine

Anhydrous pyridine (99 %) was obtained from Aldrich Chemicals. It was stored in the glove box and used without further purification. It was transferred to a vacuum vessel (figure 2.3) using a dry syringe and degassed. A solution was prepared in either dichloromethane or cyclohexane. The desired quantity was injected into the reaction flask using Schlenk techniques.

2.3.12 2,6-Di-t-butyl-pyridine

Di-tert-butylpyridine (D^{t}BP), 97 % purity, was supplied by Aldrich Chemicals. Prior to use it was vacuum distilled, using a conventional distillation apparatus, to remove any mono-substituted pyridine. The distillate was stored in the glove box and treated as the unsubstituted pyridine.

2.3.13 1,1-Diphenylethene

1,1-Diphenylethene, 97%, was supplied by Aldrich Chemicals. Prior to use it was dried for 24 hours over calcium hydride and then distilled as required into another vessel.

2.3.14 Methanol

S.L.R grade methanol was obtained from Fissons and used as supplied.

2.3.15 Calcium hydride

Calcium hydride, 90-95 % purity, 40 mesh, was used without further purification from Avocado.

2.3.16 Silica-gel

Silica-gel desiccant, ACS Reagent, was dried at 240 °C for 48 hours prior to use.

2.3.17 Sodium metal

Sodium metal was obtained in paraffin oil from BDH. The oil was removed by washing with cyclohexane prior to use.

2.3.18 Benzophenone

Benzophenone, 99% purity, was used without further purification from Janssen Chimica.

2.3.19 Phenol

Redistilled phenol, 99 % purity, was obtained from Aldrich and used without further purification.

2.4 Polymerization procedure

2.4.1 Batch polymerization

Solutions of the initiator and electron donor in cyclohexane were prepared prior to the reaction. Polymerizations were carried out in a two-armed glass flask fitted with Teflon Rotaflow taps (figure 2.5). The vessel was attached to the vacuum line, evacuated and filled with argon.

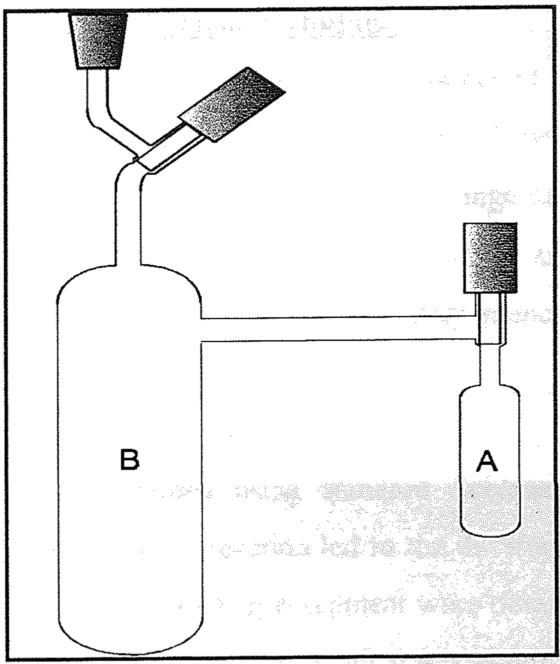


Figure 2.5 Polymerization vessel.

A typical polymerization was carried out as described below. The catalyst solution was injected into arm A in the glove box, under an inert atmosphere using a dry syringe, and then degassed using the freeze-thaw technique on the vacuum line. To ensure chamber B was free from HCl gas and any residual catalyst it was evacuated and flamed. 20 ml of dichloromethane were distilled into the vessel, and the required quantities of initiator and electron-donor solutions injected into bulb B using the Schlenk technique described in section 2.1.5. The flask was then immersed in liquid nitrogen, and 30 ml of cyclohexane were distilled using the trap to trap method. Finally the isobutene was condensed into vessel. The flask was then allowed to warm to the desired temperature by immersion in a bath containing acetone/dry ice mixtures. Polymerization was commenced when the contents of the two arms were mixed with vigorous shaking. Degassed methanol was injected into the flask using Schlenk technique to quench the reaction.

The polymerization solvent was evaporated and the crude product redissolved in cyclohexane. Catalyst residues could then be removed by filtration. In turn the cyclohexane was also evaporated leaving the polymer residue in the form of a viscous oil. The polymer was dried to constant weight in a vacuum oven at 50 °C.

2.4.2 Sampling reactions using Schlenk technique

The removal of samples was attempted during the course of a polymerization using a Schlenk technique. The main tap of the reaction vessel was removed and samples withdrawn under argon using a dry syringe. Separate syringe needles were used for each sample taken. Prior to use all of the needles had been dried at 240 °C for 4 hours and allowed to cool under argon. The sample was immediately quenched in methanol.

2.4.3 Sampling reactions using Omnifit fittings

The unreproducible results obtained using standard Schlenk technique for sampling polymerizations during the course of reaction led to the development of the vessel shown in figure 2.6. The fittings for the sampling equipment were obtained from Omnifit. Half of a 10 mm glass chromatography column was attached to the side of the vessel, onto which was a 3-way column bleed valve equipped with a Luer lock syringe adapter.

The procedure for carrying out the polymerization remained the same as for a bulk polymerization (section 2.4.1). Once the polymerization was initiated the vessel was re-attached to the vacuum-line and maintained under a blanket of argon. A sample could then be taken by opening the three way valve to the vessel and drawing out a quantity of the polymerization solution into a dry syringe. The valve was then closed to the vessel and the sample injected into methanol. The syringe and Teflon tubing leaving the vessel were then washed with dry dichloromethane and cyclohexane in preparation for the next sample. In this way samples of the polymer could be taken without contamination of the remaining polymerization

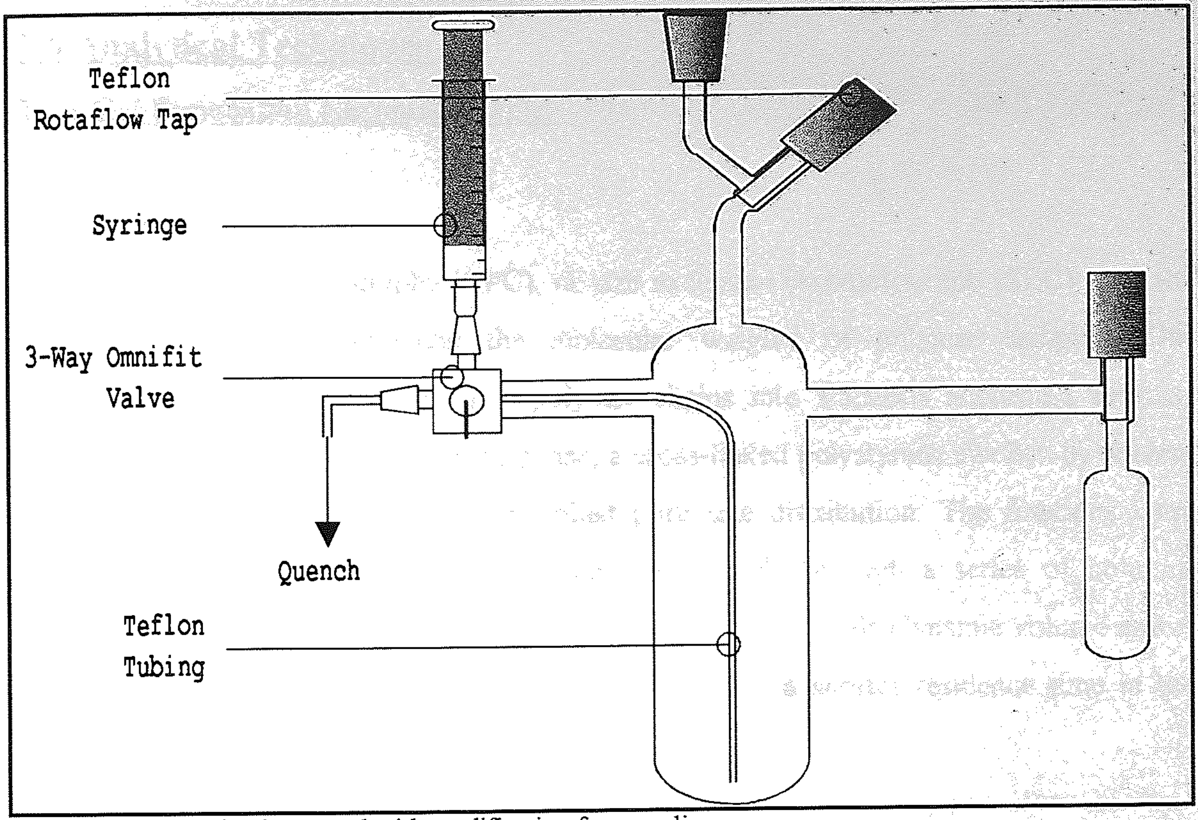


Figure 2.6 Polymerization vessel with modification for sampling.

2.4.4 Phenol capping reaction

The polymerization of isobutene was conducted as described in section 2.4.1, using the vessel shown in figure 2.6. A magnetic stirring bar was included in the vessel. The polymerization was taken to completion, before a solution of phenol in dichloromethane was added through the 3-way valve. The flask was then fitted with a water condenser at the B24 ground glass joint, and an argon bleed was fitted to the 3-way valve. The reaction mixture was refluxed under argon, with stirring, for 6 hours. The reaction was quenched by the careful addition of 2 ml of water. The resultant solution was washed 3 times with 10% NaOH solution and dried over $MgSO_4$. The polymer was recovered by removal of the solvent, and dried under vacuum to constant weight.

2.6 Analytical Techniques

2.6.1 Gel-Permeation Chromatography

2.6.1a Introduction

Gel-permeation chromatography (GPC), or size exclusion chromotograph (SEC), was the technique used for determining the molecular weights of polymer samples. This chromatographic technique separates polymer chains into fractions according to their hydrodynamic volume. The stationary phase, a cross-linked polystyrene swollen by solvent (the gel), possessed pores with a controlled pore size distribution. The fractions were separated by passing a solution of the polymer sample through a series of columns containing the stationary phase. Since a polymer with a large hydrodynamic volume enters fewer pores than molecules with smaller volumes it has a shorter residence time in the columns, and is therefore eluted more rapidly.

2.6.2b Apparatus

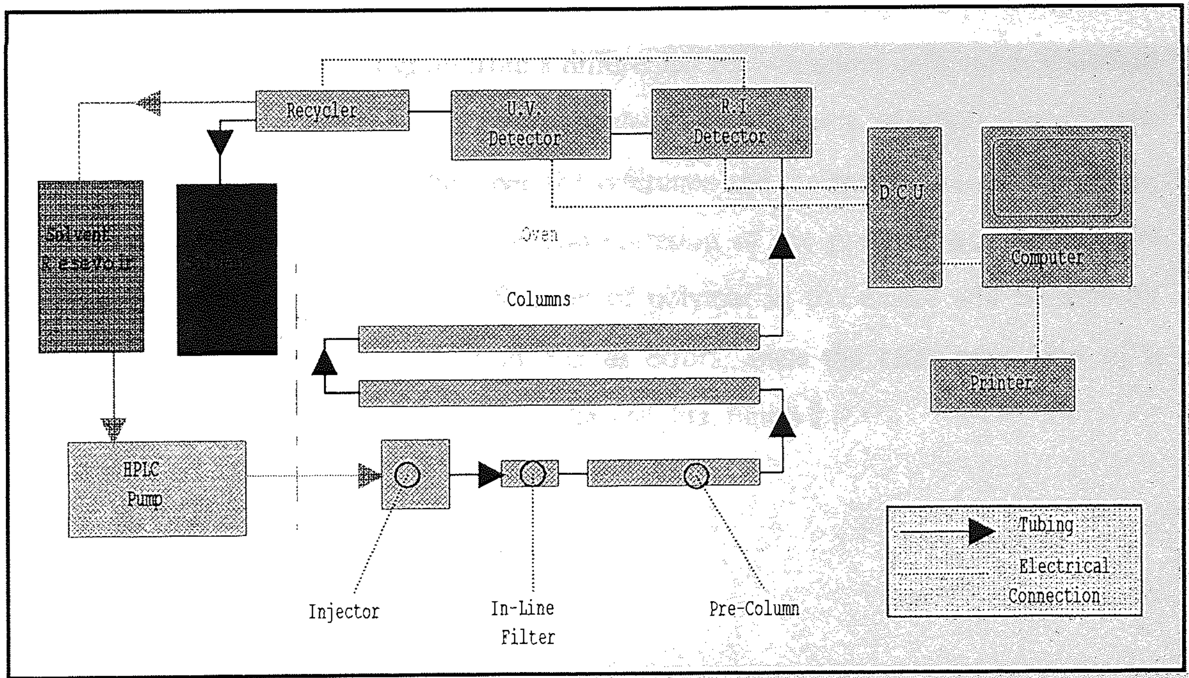


Figure 2.7 Schematic of gel-permeation chromatography equipment.

The GPC apparatus used is illustrated in the schematic diagram, figure 2.7. The mobile phase, HPLC grade THF, was pumped at a rate of 1 ml/min by a Knauer HPLC pump. A 0.5% w/v solution of polymer in THF was introduced into the system by a Rheodyne injector equipped with a 100 μL loop. The sample was passed through a 0.5 μm in-line filter and then a 5 μm Polymer Labs guard column, to remove any particulates. Two gel columns were used, a single bead 10^3 A μ-PL and a mixed B. The eluted solution was then passed through a Knauer differential refractometer and UV detector, the outputs from which were monitored by a Polymer Labs DCU and analysed using PL Caliber® software.

2.6.2c Theory

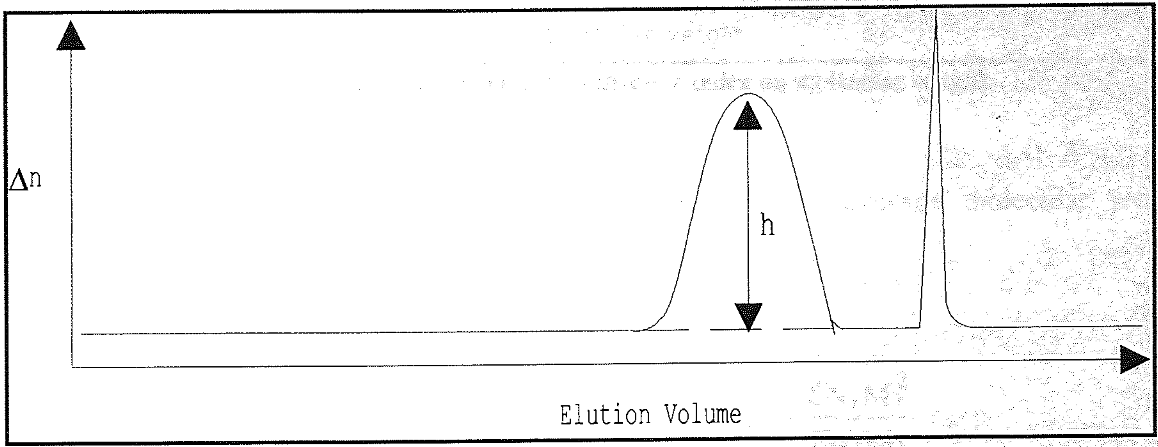


Figure 2.8. Example GPC trace.

An example of a GPC chromatogram from a differential refractometer detector is shown in figure 2.8. The height of the trace, at any particular elution volume, is proportional to the difference in refractive index (Δn) between the reference and the eluent. It is assumed that the refractive index is dependent on the concentration of the polymer and not on the molecular weight. Hence, the weight fraction of polymer in the eluent will be directly related to Δn. However, the assumption creates errors, since the refractive index of a polymer will considerably vary at low molecular weights, figure 2.9.

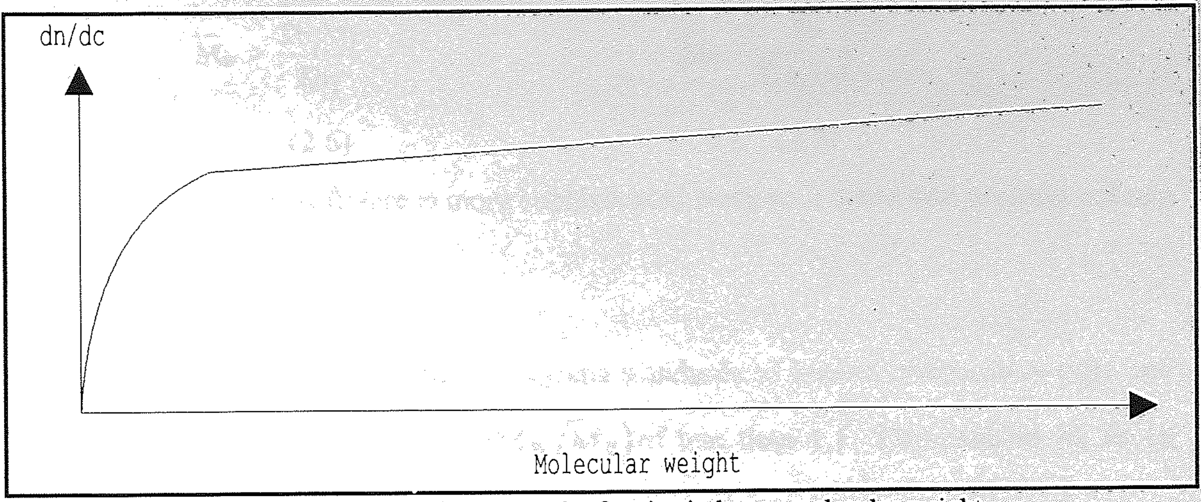


Figure 2.9. Dependency of a polymers incremental refractive index on molecular weight.

The number average molecular weight $\left(\overline{M}_n\right)$ and weight average molecular weight $\left(\overline{M}_w\right)$ are defined by:

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \qquad (2.1) \qquad\qquad \overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \qquad (2.2)$$

where;

N_i = number of molecules of molecular weight M_i.

The mass of polymer, W_i, with molecular weight, M_i, can be described by the following:

$$W_i = N_i M_i / N_A \qquad (2.3)$$

N_A = Avogadro's constant.

Therefore;

$$\overline{M}_n = \frac{\Sigma W_i}{\Sigma\, W_i / M_i} \qquad (2.4) \qquad\qquad \overline{M}_w = \frac{\Sigma W_i M_i}{\Sigma W_i} \qquad (2.5)$$

Since the height of the GPC trace is dependent on the weight fraction of polymer the molecular weights can be calculated from:

$$\overline{M}_w = \frac{\Sigma h_i M_i}{\Sigma h_i} \qquad (2.6) \qquad\qquad \overline{M}_n = \frac{\Sigma h_i}{\Sigma h_i/M_i} \qquad (2.7)$$

although the computer software is more sophisticated because it takes into account column broadening.

The columns were calibrated using polystyrene standards of known molecular weight and with molecular weight distributions $\left(\overline{M}_w/\overline{M}_n\right)$ of less than 1.1. This enabled M_i to be determined for any particular elution volume or time. A typical calibration curve is shown in figure 2.10.

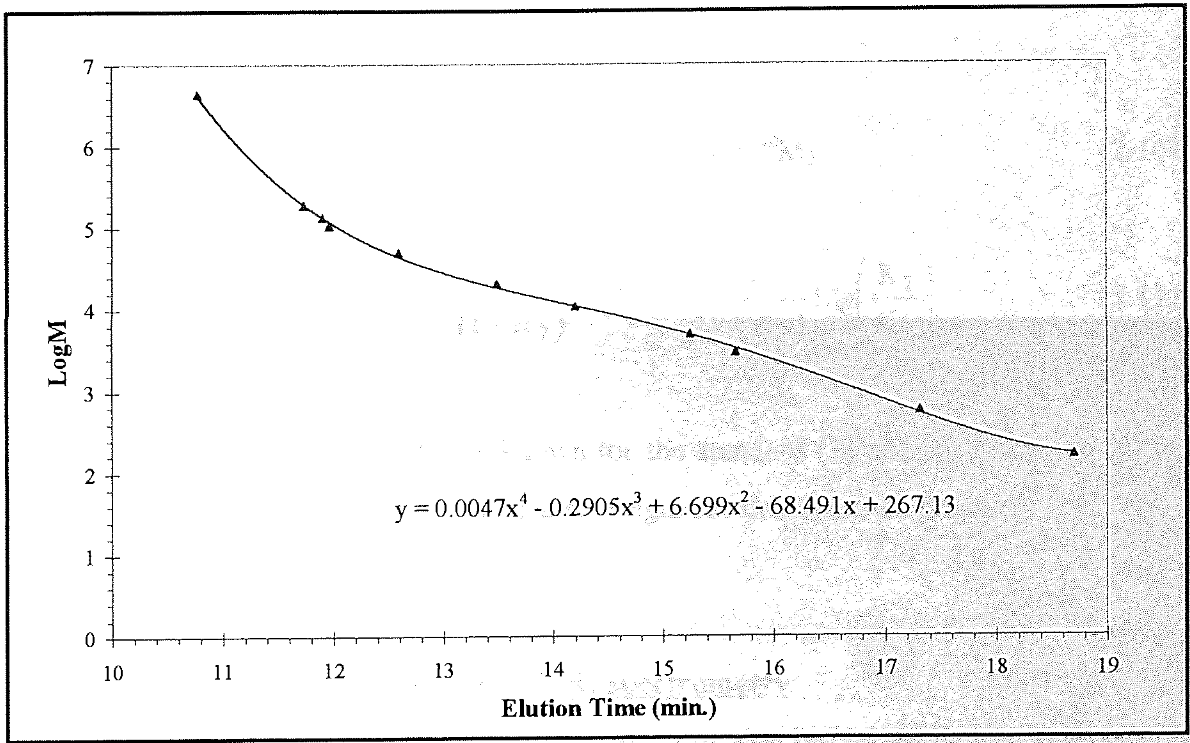


Figure 2.10. Calibration curve for GPC.

For a particular molecular weight different types of polymer may have different hydrodynamic volumes, in a given solvent. The calibration curve obtained gives absolute molecular weight values for polystyrene only, the molecular weights of other polymer types must be quoted in terms of polystyrene equivalents, or can only be obtained if the Mark-Houwink parameters are known for the calibrant and sample in the solvent used.

It is possible then to obtain absolute molecular weights of other polymers by the use of a universal calibration curve. It is known that the hydrodynamic volume of a polymer molecule in solution is the product of its intrinsic viscosity (η) and molecular weight (M), two polymers (1 and 2) eluting at the same volume must have the same hydrodynamic volume :

$$\eta_1 M_1 = \eta_2 M_2 \tag{2.8}$$

The Mark-Houwink equation relates the intrinsic viscosity to molecular weight:

$$\eta = KM^{\alpha} \tag{2.9}$$

K and α are constants for a given polymer in a specific solvent.

Polymers eluting at the same volume:

$$K_1 M_1^{\alpha 1} M_1 = K_2 M_2^{\alpha 2} M_2 \tag{2.10}$$

Re-arranging:

$$\log M_2 = \frac{(1+\alpha_1)}{(1+\alpha_2)} \log M_1 + \frac{1}{(1+\alpha_2)} \log\left(\frac{K_1}{K_2}\right) \tag{2.11}$$

If the Mark Houwink constants are known for the standard (1) and the unknown (2) it is possible to determine an absolute molecular weight for the unknown polymer.

2.6.2 Nuclear magnetic resonance (NMR) spectrometry

A Bruker AC300 spectrometer was used to carry out high resolution Fourier transform ^{1}H and ^{13}C NMR. Samples were dissolved in deuterated chloroform ($CDCl_3$) with a small quantity of tetramethyl silane (TMS) as reference material. The spectra were analysed and edited using WinNMR, software marketed by Bruker.

A pulse technique P.E.N.D.A.N.T. was used for ^{13}C analysis. Signals from the corresponding carbon are edited, methyl and methine carbons appear as positive peaks, methylene and quaternary carbons appear as negative peaks.

A second technique was also used for ^{13}C analysis, S.P.E.E.D. Signals from carbonyl and quaternary carbons are enhanced, while methine, methylene and methyl carbons are decoupled.

Chapter 3: Development of a living isobutene polymerization system

3.1 Introduction

A review of the literature (section 1.3.4, table 1.1) shows that the majority of living polymerizations for isobutene use tertiary alkyl halides, such as 2-chloro-2-phenylpropane (CumCl) or 2,4,4-trimethyl-2-chloropentane (TMPCl), as initiators (section 1.2.4d, figure 1.20). The catalysts used are almost exclusively boron trichloride or titanium tetrachloride and these are employed in the presence of an electron donor, such as triethylamine. A mixed solvent system, typically chloromethane and hexane in a ratio of 40/60 (v/v), controls the nature of the propagating end. The role of each of these compounds in the mechanism of a living cationic polymerization has been discussed in chapter 1.

Before we go on to study the production of narrow molecular weight polymers it is necessary to establish suitable polymerization conditions.

3.2 Isobutene polymerization systems

Cationic systems that polymerize styrene in a living manner tend to use a single solvent, such as dichloromethane (DCM), with tin tetrachloride as catalyst in conjunction with a salt, tetrabutyl ammonium chloride [82, 132,133]. The purpose of the salt is to reduce the lifetime of the active propagating species, such that the probability of propagation predominates over transfer and irreversible termination. It was thought that a similar system might also be used to polymerize isobutene in a living manner. Living polymerizations of isobutene are characterised by the fact that the structure of the propagating end is controlled by the polarity of the solvent. Therefore, it was speculated that like some polymerizations of styrene addition of salt could be used to control the propagating species in polymerizations of isobutene, instead of the solvent. The chloride ions generated from the salt and catalyst should force the isobutene chain carriers to take a more covalent form, thus lowering the instantaneous concentration of active species and its lifetime. If the use of a salt were successful, the polymerization system could be potentially useful in the one pot synthesis of isobutene-styrene co-polymers.

A series of experiments was designed to evaluate the feasibility of applying the catalyst/initiator/salt system to the polymerization of isobutene (the results are shown in table 3.1). $SnCl_4$ was used as the catalyst and 1-chloro-1-phenylethane (1-PEC) as the initiator. The effect of the concentration of salt, Bu_4NCl, on the polymerization was investigated using the experimental method described in section 2.4.1. Such a system was typical of those used for the polymerization of styrene.

$[Bu_4NCl]$ /mol L^{-1}	[1-PEC] /mol L^{-1}	[IB]/ [1-PEC]	% Conv.	$\overline{M_n}$ /g $mole^{-1}$	$\overline{DP_n}$	MWD	% I_{eff}
0	0.014	100	90	9380	170	2.46	53
0.014	0.014	60	70	1810	32	1.53	125
0.029	0.014	125	45	1840	33	1.46	164
0.045	0.015	80	37	1360	24	1.68	125

Table 3.1. The dependence of conversion and molecular weight distributions on the concentration of Bu_4NCl. Temperature = -30 °C, $[SnCl_4]$ = 0.08 mol L^{-1}, 40 ml DCM, reaction time = 2 hrs.

The results in table 3.1 show that in the absence of nBu_4NCl the polymer was produced in high yield but had a broad molecular weight distribution, as would be expected from a conventional polymerization. In an attempt to reduce the number of termination and transfer steps relative to those of propagation, the effect of the concentration of salt in the system was examined. Addition of the salt in a 1:1 molar ratio to the initiator led to a significant narrowing of the molecular weight distribution and was accompanied by a reduction in the yield. Conversion was suppressed even more when the concentration of the salt was raised further. These results suggest that the rate of propagation was slowed, consistent with the equilibrium shifting in favour of the more covalent species. In this way the instantaneous concentration of the active propagating chains was decreased and the contribution of highly reactive species to propagation was reduced. However, the efficiencies of the initiator were high and none of the polymerizations went to completion, even after two hours. A question arises as to why the efficiency of initiation increased with the addition of salt, a phenomenon that has also been observed by other fellow worker in our laboratories [11]. An increased efficiency of initiation would be consistent with chain transfer, therefore it might be possible that the salt behaved as a chain transfer agent, illustrated in figure 3.1.

$$P_n^+ B^- + R_4N^+Cl^- \rightleftharpoons R^+B^- + P_nR_3N^+Cl^-$$

Figure 3.1. Chain transfer to salt.

An alternative explanation may also account for the observed rise in the efficiency of initiation with the addition of Bu_4NCl. In the absence of salt it is probable that reactions occur which involve chain transfer to monomer, and backbiting to initiator. Chain backbiting to initiator results in the formation of cyclic oligomers, termination of propagating species, and hence low efficiencies of initiation. Addition of salt may have suppressed these cyclisation reactions but the transient lifetime of the active propagating species may still not have been sufficiently shortened so as to prevent chain transfer reactions. Under these conditions the loss of initiator caused by the formation of oligomers would have been prevented, but the previously masked transfer reactions would now be prevalent, resulting in an observed increase in the efficiency of initiation.

In the presence of salt, the narrowing of the molecular weight distributions would suggest that the number of termination and transfer steps are being reduced. However, the molecular weight distributions obtained, under the conditions given in table 3.1, remain relatively broad in comparison to those produced by classical living polymerization systems. It remains unclear if the broadening was caused by the suggested transfer to salt mechanism, or by other transfer and termination processes inherent to the system.

$TiCl_4$ is preferred as a catalyst for living isobutene polymerizations. The above experiments were repeated with $TiCl_4$ as the catalyst instead of $SnCl_4$. The experimental conditions and results are shown in table 3.2, the corresponding GPC traces can be found in figure 3.2.

Exp. No.	Bu_4NCl /mol L^{-1}	[IB]/ [1-PEC]	% Conversion	$\overline{M_n}$ /g $mole^{-1}$	$\overline{DP_n}$	MWD	% I_{eff}
1	0	87	85	9150	163	1.40	45
2	0.014	68	100	4370	78	1.29	87
3	0.029	88	100	6090	109	1.28	81

Table 3.2. The dependence of conversion and molecular weight distributions on the concentration of Bu_4NCl. Temperature = -30 °C, $[TiCl_4]$ = 0.11 mol L^{-1}, 50 ml DCM, reaction time = 2 hrs [1-PEC] = 1.5 ±0.1 × 10^{-2} mol L^{-1}.

Under the conditions shown above the molecular weight distributions of the polymers are narrower than those obtained from the polymerizations using $SnCl_4$ as catalyst, even without the addition of salt. Therefore, under these conditions propagation was more favourable than termination or transfer. $TiCl_4$ is known to dimerise and these dimers (discussed in detail in section 4.4) are likely to have a lower Lewis acidity than $SnCl_4$. Therefore, the propagating centres activated by $TiCl_4$ would be expected to have a greater covalent character than those activated by $SnCl_4$, with accordingly shorter transient lifetimes in the active state. This shortened lifetime was caused by the rate constant of collapse being increased over that of formation (or ionisation). In this situation transfer would be suppressed, because the lifetime of the active species is less than the time required for a transfer reaction to occur. Thus, each time a polymer chain became active, the probability of it propagating was greater than that of it transferring.

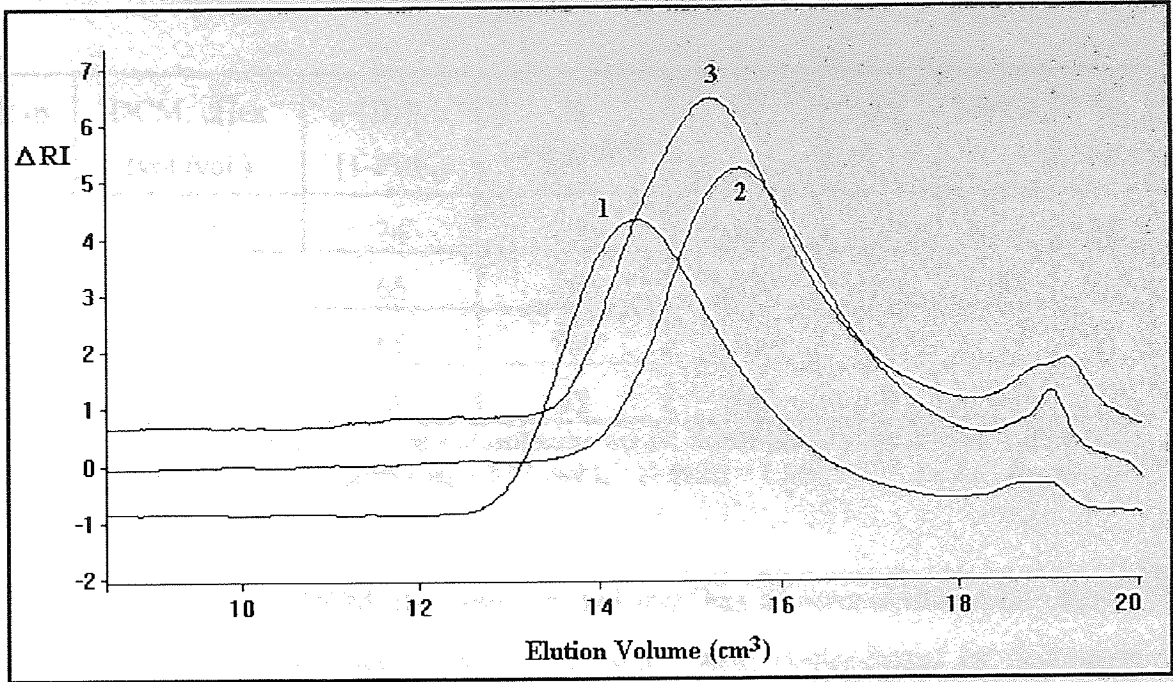


Figure 3.2. GPC traces for increasing salt concentrations.

The addition of a salt to the polymerization causes the molecular weight distribution to narrow and the monomer was completely converted to polymer, as would be consistent with living behaviour. However, the molecular weights of the polymer samples in table 3.2 were higher than predicted. The observation might be explained by either the irreversible termination of some of the polymer chains and/or the rate of initiation being slow. In both of these cases the concentration of the propagating polymer chains, in at least some stages of the polymerization, would be lower than predicted and would thus lead to increased molecular weights and an apparent reduction in the efficiencies of initiation. Raising the salt concentration above that of the initiator does not seem to serve any useful purpose, although it is likely that the polymerization rate is slower.

The final system studied utilised pyridine as an electron donor in a mixed solvent of dichloromethane (DCM) and cyclohexane (cHex). Storey et al. adopted a similar system using a combination of dicumyl chloride, $TiCl_4$ and pyridine in a 40/60 (v/v) chloromethane to hexanes solvent mixture [79] and concluded that the polymerization behaved as a living system. The polymerization described below was initiated by 1-PEC/$TiCl_4$ in the presence of pyridine. A series of experiments was conducted using a range of solvent mixtures, the results of these experiments can be found in table 3.3, and figure 3.3.

Exp. No.	DCM: cHex (vol./vol.)	[IB]/ [1-PEC]	% Conversion	$\overline{M}_n$ /g mole^{-1}	$\overline{DP}_n$	MWD	% I_{eff}
1	100:0	74	100	6590	118	1.24	63
2	60:40	65	100	3610	65	1.19	100
3	40:60	65	100	4600	82	1.17	80
4	20:80	102	42	1860	33	1.22	77

Table 3.3. The dependence of conversion and molecular weight distributions on the solvent. Temperature = -30°C, [$TiCl_4$] = 0.33 mol L^{-1}, [Pyridine] = 0.03 mol L^{-1}, [1-PEC] = $1.5 \pm 0.1 \times 10^{-2}$ mol L^{-1}. 40 ml scale, reaction time = 3 hrs.

In a single solvent of DCM the resultant polymer has a narrow molecular weight distribution, but the GPC trace shows it to be significantly contaminated by oligomeric material. Reducing the polarity of the solvent both reduces the quantity of oligomeric material and narrows the polydispersity. However, the formation of oligomer may also account for the low initiator efficiencies in experiments 3 and 4.

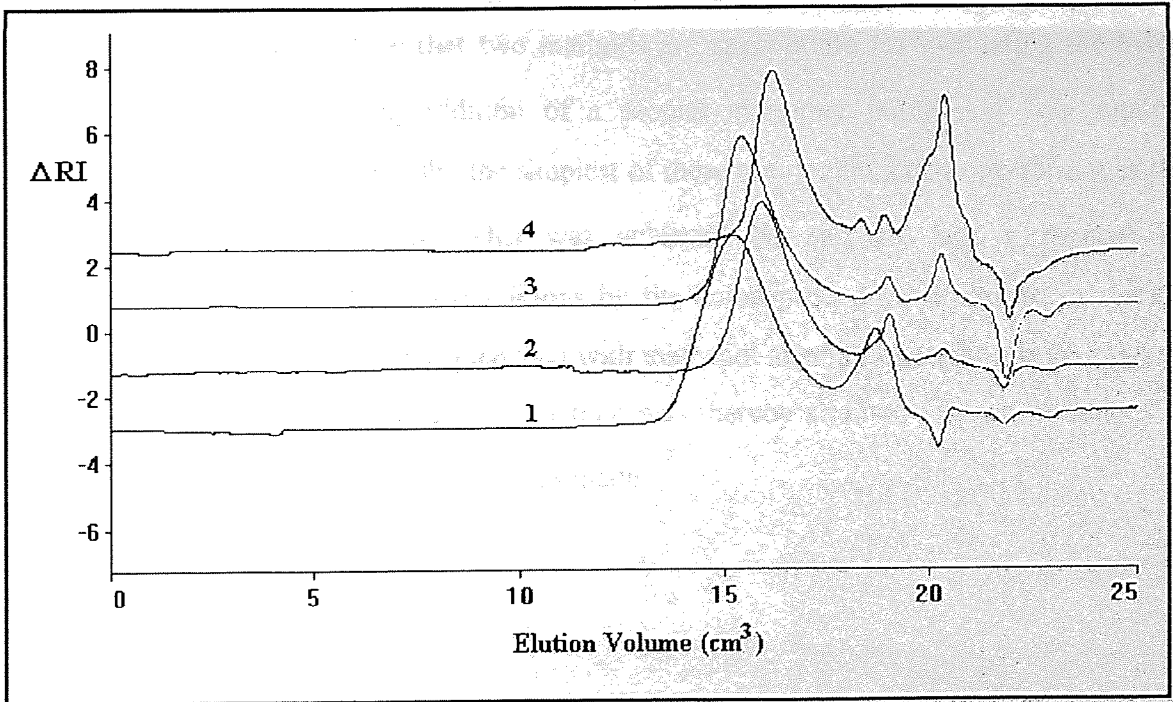


Figure 3.3. GPC traces of polymerizations conducted in DCM/cHex. solvent compositions.

In experiment 4 the polymerization did not go to completion even after 3 hours. This may be explained by the fact that the chain carriers in relatively low polarity solvents will be in a more covalent state and the overall rate of polymerization retarded. If adequate time were given it is likely the polymerization would have gone to 100 % conversion.

Reviewing the experimental data obtained, it is apparent that the polymerization systems that use pyridine as an electron donor show the best potential to be living. In a 40/60 (v/v) DCM to cHex solvent ratio the polydispersities were low with close to quantitative initiation. Further, the reaction conditions were comparable to many known living systems reported in the literature.

3.3 The living nature of polymerizations initiated by 1-PEC/$TiCl_4$ in the presence of pyridine.

The previous section demonstrated that the polymerization system initiated by 1-PEC/$TiCl_4$/pyridine in a mixed solvent showed potential for living behaviour. It was therefore decided to test the living nature of this polymerization. In the introduction (section 1.3.5) it was shown that two methods are appropriate for evaluating the living nature of a polymerization, addition of a second monomer batch and $\overline{M}_n$ against conversion plots. Experimentally, the simplest of these two techniques to perform was the $\overline{M}_n$ against conversion plot. This was achieved by carrying out a number of polymerizations under identical conditions by the batch procedure described in section 2.4.1. Each polymerization was quenched with methanol after an increasing time interval. A series of conversions as a function of time was thereby attained (shown in table 3.4) and a plot of $\overline{M}_n$ against conversion was made.

Time /seconds	$\overline{M_n}$ /g mole^{-1}	% Conversion	MWD	ln(M$_0$/M)	% I$_{eff}$
335	1230	5	1.23	0.078	45
620	2710	20	1.25	0.229	73
1240	4630	40	1.19	0.470	86
2200	6020	50	1.20	0.683	93
6180	10940	85	1.16	1.999	85

Table 3.4. Dependence of conversion on time. Temperature = -30°C, [$TiCl_4$] = 0.22 mol L^{-1}, [Pyridine] = 0.02 mol L^{-1}, [1-PEC] = 5×10^{-3} mol L^{-1}, [IB] = 1 mol L^{-1}, 20 ml DCM, 30 ml cHex.

Some consideration of the error in the above data should be considered. Molecular weight calculations by GPC's are generally estimated to be accurate to within 10 %. However, it should be noted that the degree of error will be considerably greater for polymers of low molecular weight, such as those at low conversions in table 3.4. The source of the difficulty is the non-linearity of dn/dc with molecular weight, as previously discussed in section 2.6.2c of the experimental. Another area of concern is the determination of conversion. Quantities of polymer were unavoidably lost during transfer between vessels and by the evaporation of oligomeric material in gravimetric analysis. It was conservatively estimated that up to 0.1 g of polymer could be lost when dealing with samples weighing 2.0 g. This calculated to a reserved value of ±5 % error in conversion determination. The impact is displayed as error bars on the plot in figure 3.4.

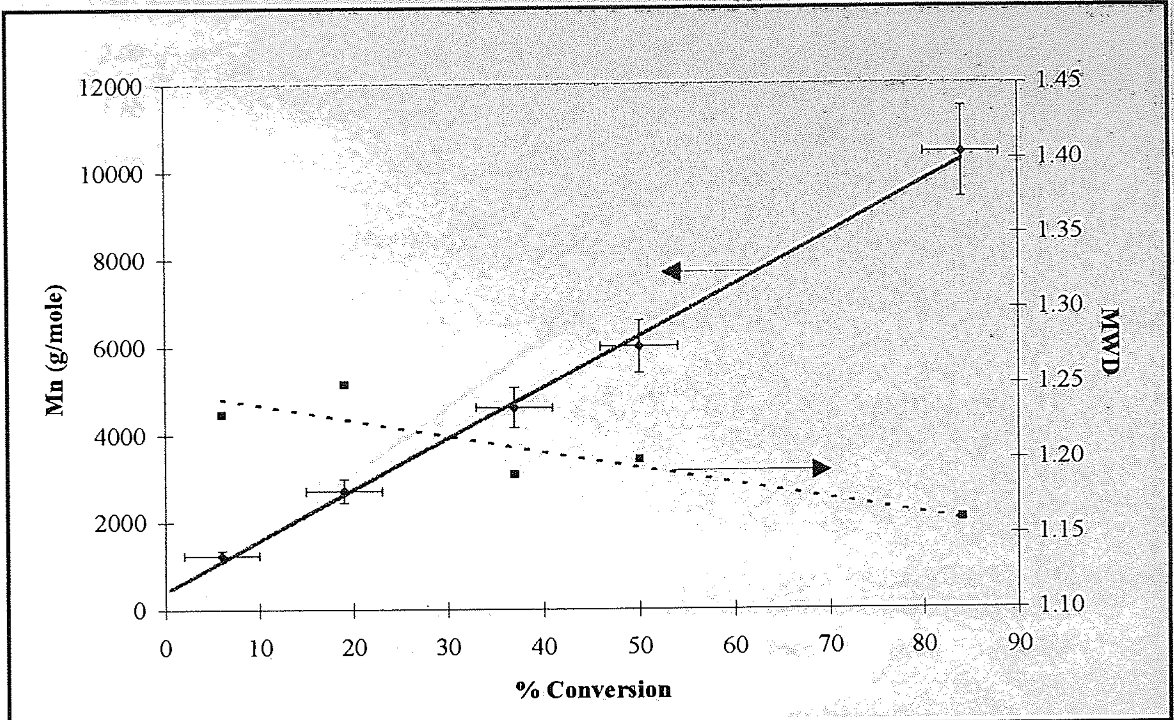


Figure 3.4. Plot of $\overline{M_n}$ vs. conversion for the polymerization of isobutene by $TiCl_4$/1-PEC/pyridine in a 40/60 (v/v) DCM to cHex. solvent mixture at -30°C.

Given that experiments of this type are prone to some degree of error, the linearity of the plot in figure 3.4 demonstrates the absence of chain transfer during the polymerization under the conditions described. The line passes near but does not intercept the origin. The deviation may be caused by an induction period during initiation, in which the equilibrium involving the chain carriers is establishing itself. However, such comments can only be tentative because the data is within experimental error.

The initially broad molecular weight distribution narrows as the polymerization proceeds, which is indicative of a living system. The initial breadth was believed to be caused by slow initiation, which is probably not complete until approximately 10 minutes into the reaction. However, the impact of slow initiation on the polymers molecular weight distribution and molecular weight at high conversions is small in this instance.

Values of $[M_o]/[M]$ were calculated from the fractional conversions, which enabled $\ln([M_0]/[M])$ to be plotted against time, as described in section 1.3.5. The graph in figure 3.5 demonstrates the polymerization is first order with respect to monomer concentration.

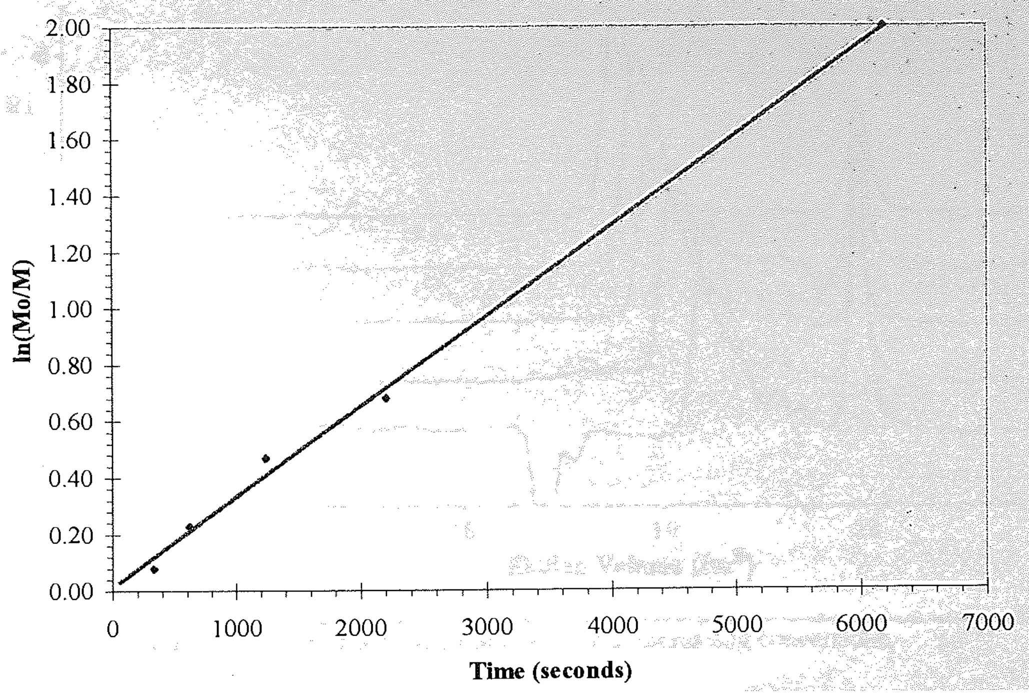


Figure 3.5. Pseudo first-order plot for monomer concentration.

The linearity of the plot demonstrates a constant number of propagating sites, indicating the absence of irreversible termination and that over the time-scale of the polymerization initiation is fast relative to propagation. Although the above plot shows initiation to be fast the initiator efficiency is not 100 % for these polymerizations. Examination of the GPC traces (figure 3.6) shows that the polymers consistently contain oligomeric material. The oligomers appear to be produced in the early stages of polymerization, and could account for the reduced initiator efficiency. A more detailed study of the nature of the oligomer and its mechanism of formation is given in section 3.5.

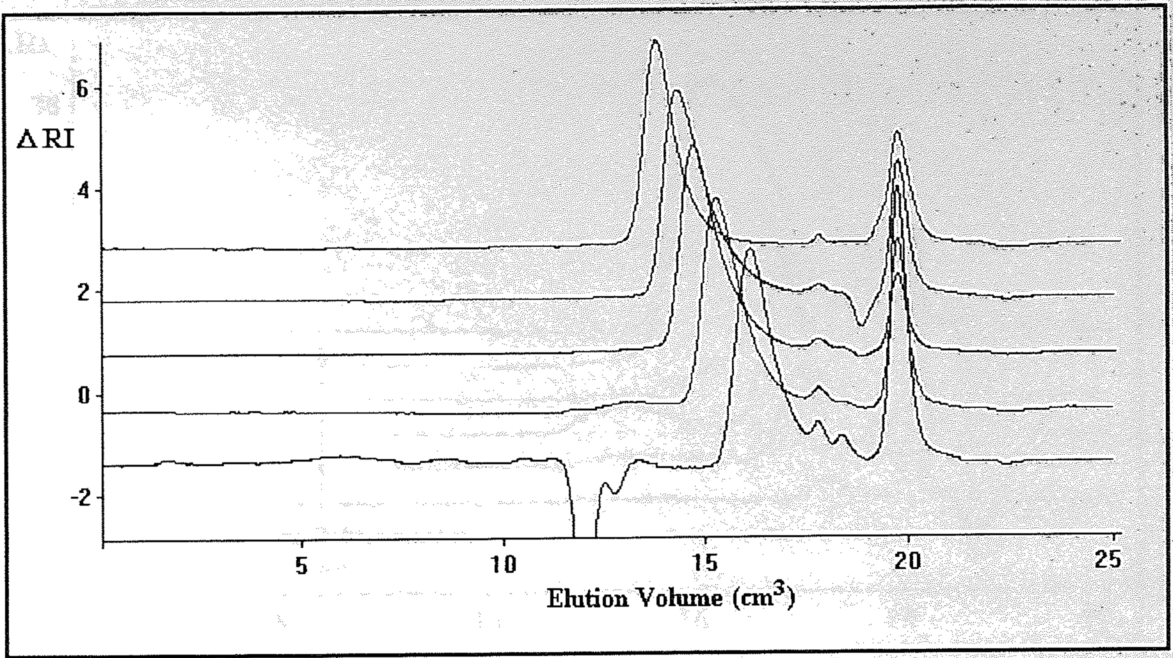


Figure 3.6. GPC traces for the polymerization of isobutene at increasing conversions.

3.4 Sampling reactions

To allow the polymerization process of a single reaction to be followed as a function of time, a method of removing samples was developed. This eradicated the need to carry out multiple polymerizations to obtain a single pseudo first order kinetic plot. Obtaining the required data from a single reaction liquor is beneficial, since any anomalies in the conditions between reactions will be minimised. Two methods of drawing samples are discussed.

3.4.1 Schlenk sampling technique

First attempts at removing samples were made by using a dry syringe under a blanket of argon, as described in section 2.4.2. The GPC traces obtained from such an experiment are shown in figure 3.7 with the experimental conditions given underneath.

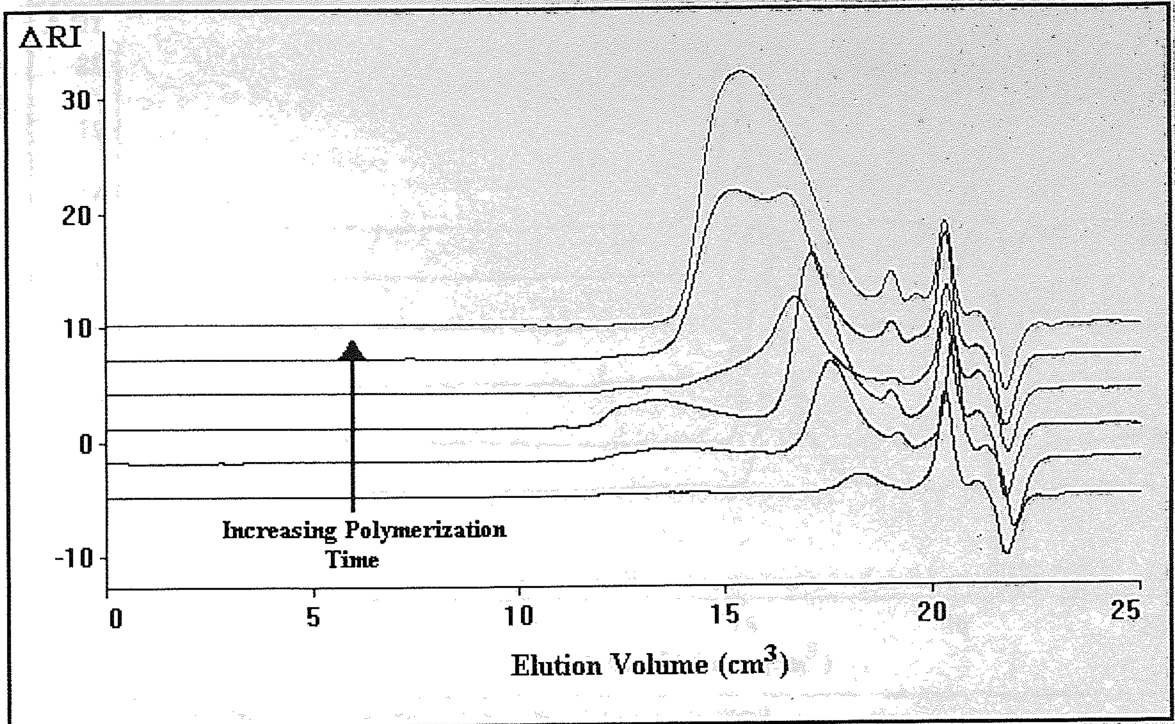


Figure 3.7. GPC traces for a sampling reaction of the polymerization of isobutene; [IB] = 1 mol L^{-1}, [1-PEC] = 0.01 mol L^{-1}; [Pyridine] = 0.03 mol L^{-1}, [$TiCl_4$] = 0.33 mol L^{-1}, 40/60 (v/v) DCM/cHex., temperature = -30°C, total time of polymerization = 20 min.

A single peak that increases in molecular weight as the polymerization proceeds is observed in the initial sample only. This polymer fraction may be attributed to that formed by the living chain carrier. However, in subsequent samples a second peak at high molecular weight is clearly visible. The intensity of the second peak increases and eventually merges with that of the lower molecular weight material. The rapid formation of high molecular weight material can be attributed to the formation of uncontrolled non-living propagating species, initiated from impurities introduced by the sampling procedure. Despite attempts to modify the sampling procedure accurate measurements could not be obtained. This technique is therefore unsuitable for examining the polymerization mechanism.

3.4.2 Omnifit sampling technique

To combat the problems of introducing impurities when taking samples the experimental technique described in section 2.4.3 was developed. The experimental conditions were kept the same as for the previous experiment and the new equipment was used to extract samples. The GPC traces obtained are illustrated in figure 3.8 and the experimental data in table 3.5.

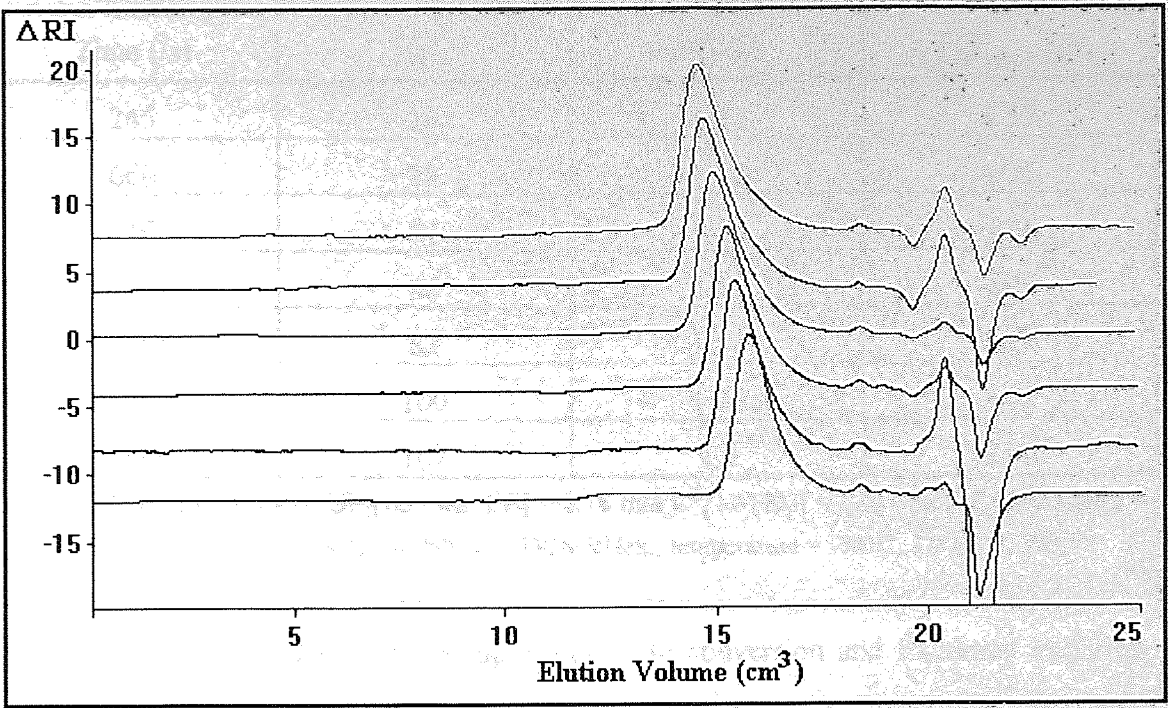


Figure 3.8. GPC traces of a reaction sampled by Omnifit equipment.

Samples withdrawn using the new method show a single distinct polymer peak that moves to higher molecular weight with time. The undesirable high molecular weight polymer that is a feature of the Schlenk sampling method was not present. It was now possible to study the dependence of molecular weight of a single polymerization as a function of time.

The small quantity of sample taken each time made it difficult to calculate the fractional conversion of polymer in that sample. Each sample contained polymer that was contaminated with an uncertain quantity of catalyst residue. Furthermore, at low conversions the mass of catalyst residue was greater than that of the polymer, and owing to the small quantities involved purification of the product was not feasible. Therefore, the necessary information required to plot pseudo first order plots of the form $\ln(M_0/M)$ vs. time was unattainable. An alternative method was required.

The kinetic derivation as described by Endsor [89] and given in section 1.3.3 was utilised as an alternative. The value of $\overline{DP}_n$ for any aliquot was readily obtained from GPC data, enabling plots of $\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$ against time to be made.

Time (/s)	$\overline{DP}_n$	MWD	$\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$
265	28	1.15	4.57
660	48	1.16	4.35
910	61	1.13	4.16
1210	66	1.18	4.08
1740	82	1.18	3.76
2110	100	1.16	3.21
2735	107	1.2	2.88

Table 3.5. The dependence of $\overline{DP}_n$ on time. [IB] = 1.18 mol L^{-1}, [1-PEC] = 0.011 mol L^{-1}; [Pyridine] = 0.03 mol L^{-1}, [$TiCl_4$] = 0.33 mol L^{-1}, 40/60 (v/v) DCM/cHex., temperature = -30°C. $\overline{DP}_{n\infty}$ = 125.

A theoretical value of $\overline{DP}_{n\infty}$ based upon complete conversion and fractional initiation was calculated, which enabled $\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$ against time to be plotted. The value of the intercept was noted and used to calculate a new value of $\overline{DP}_{n\infty}$, this was subsequently re-entered into the equation to create a new plot. The iterative process was continued by computer calculations until the value of $\overline{DP}_{n\infty}$ initially entered into the equation agreed with that given by the y-intercept. In the case given in table 3.5 the value was found to be 125, and the plot in figure 3.9 was produced. The theoretical value originally calculated was 107, suggesting an initiator efficiency of 85 %, which is in agreement with the efficiencies found in previous batch polymerizations.

When producing plots such as those given in figure 3.9 the significance of error in the data will increase as $\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$ approaches 0 and must be considered, as has already been discussed in section 1.3.5 of the introduction.

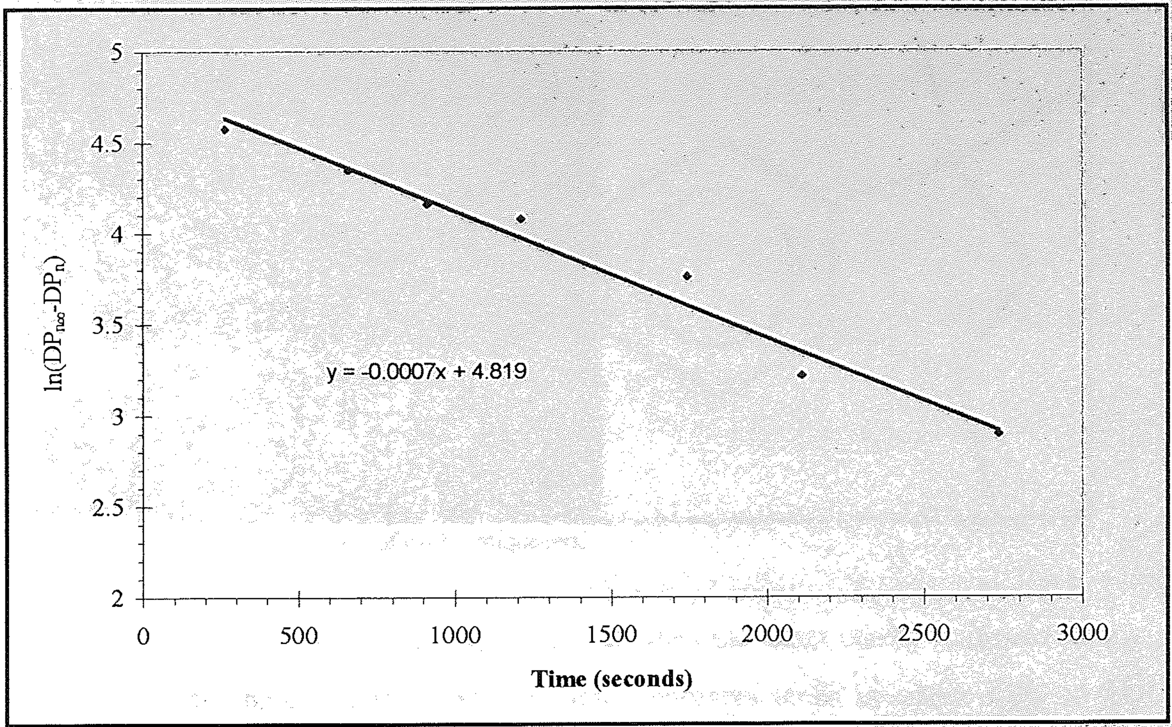


Figure 3.9. Graph of $\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$ against time.

From the gradient of the line the apparent rate constant of polymerization (k_{app}) is estimated at 7×10^{-4} s^{-1}.

3.5 Oligomer formation

A characteristic of polymerizations conducted in the presence of pyridine at -30 °C is the manifestation of an oligomeric peak in the gel-permeation chromatographs. The presence of such oligomers in living isobutene polymerizations has been previously noted in the literature and is associated only with aromatic initiators [127]. The flexibility of the polyisobutene chain allows a backbiting reaction to occur onto the aromatic ring of the initiator. The mechanism of reaction is believed to be a classical Friedel-Crafts alkylation, with the side-product formed thought to be a cyclic indanyl type structure (figure 3.10). The example displayed shows the insertion of a single isobutene unit, but it is both feasible and likely that chains of a greater length could backbite.

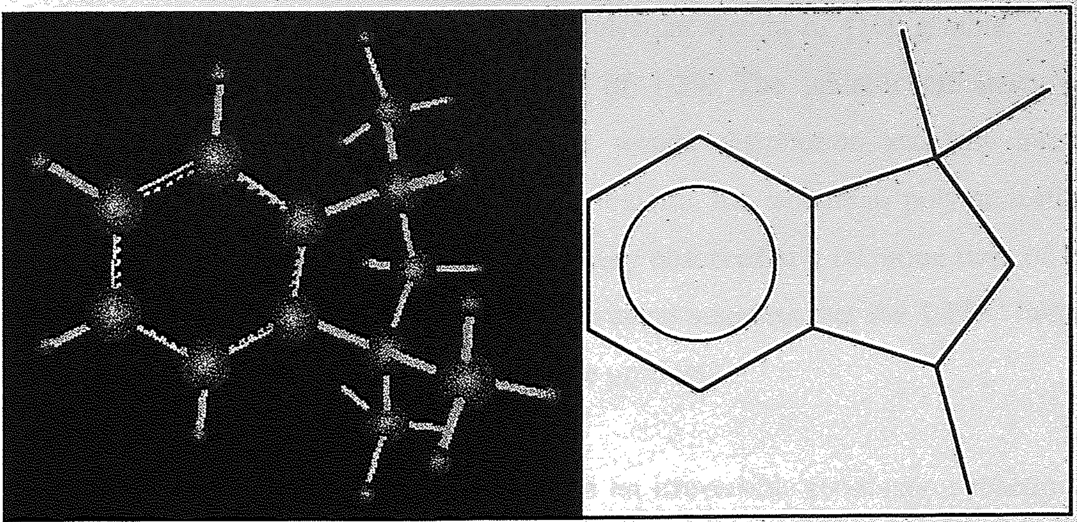


Figure 3.10 Suggested structure of cyclic oligomers.

The probability of alkylation occurring is greatest when the chain carrier is closest to the initiator function. Therefore, formation of these oligomers tends to occur early in the course of polymerization. If the oligomeric peak is a cyclic structure, as suggested above, then removal of the aromatic component should prevent their formation. tert-Butyl chloride (^{t}BuCl) was considered to be a satisfactory initiator, although it is known to act only slowly because of its inability to ionise rapidly. A polymerization was carried out according to the method described in section 2.4.1, using a ^{t}BuCl/$TiCl_4$/pyridine initiating system under the conditions given in figure 3.11.

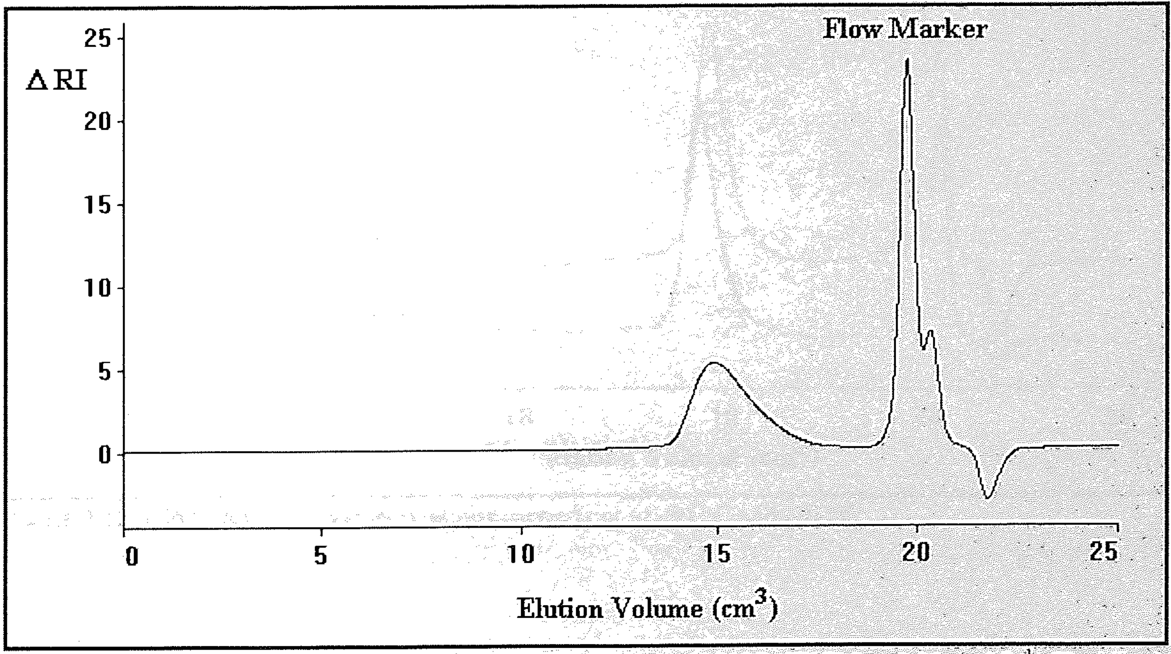


Figure 3.11. Polymerization initiated by ^{t}BuCl. Temperature = -30°C, [$TiCl_4$] = 0.33 mol L^{-1}, [Pyridine] = 0.03 mol L^{-1}, [^{t}BuCl] = 0.020 mol L^{-1}, [IB] = 0.93 mol L^{-1}, 20 ml DCM, 30 ml cHex.

The polymer produced had a number average molecular weight of 4100 g mole^{-1} with a relatively broad molecular weight distribution of 1.39. The initiator efficiency was calculated to be 64 %. The broad molecular weight distribution and low initiator efficiency are expected, since ^{t}BuCl is a slow initiator for isobutene polymerizations. However, it is important that the oligomer, normally observed at a retention time of 18.2 minutes, was absent from the polymer. The experiment suggests that the 1-PEC initiator is involved in the formation of the oligomeric side products.

The oligomerisation process is considered to be an irreversible termination reaction. A general kinetic scheme that was derived for cationic polymerizations shows that the rate constant of propagation can be maximised over that of termination by reducing the temperature of polymerization (section 1.2.2). If this is the case then lowering the polymerization temperature should reduce the quantity of oligomeric material. Two reactions were carried out at -70 °C and -50 °C using the 1-PEC/$TiCl_4$/pyridine initiation system , the results of which are given in figure 3.12 and table 3.6.

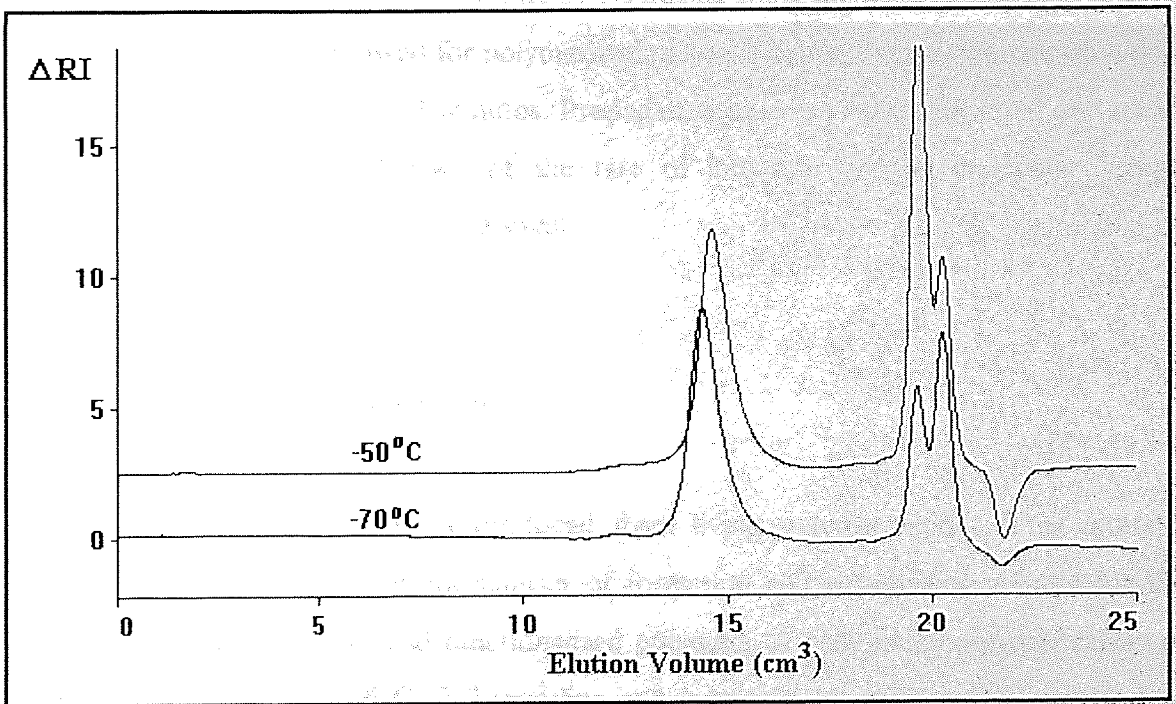


Figure 3.12. GPC traces of a polymerizations carried out at -50 °C and -70 °C.

Temperature (°C)	[IB]/[1-PEC]	% Conversion	$\overline{M}_n$ (/g mole^{-1})	MWD	% I_{eff}
-50	50	100	6970	1.11	42
-70	63	100	8100	1.11	43

Table 3.6. Experimental data of polymerizations carried out at -50 °C and -70 °C. [1-PEC] = 0.017 mol L^{-1}, [$TiCl_4$] = 0.33 mol L^{-1}, [Pyridine] = 0.03 mol L^{-1}, 20 ml DCM, 30 ml cHex., time of polymerization = 2 hrs.

At both of these lower temperatures oligomer formation is absent. The molecular weight distributions of the polymers have also narrowed. The narrowing is expected since the activation energies of termination and transfer are greater than that of propagation, therefore low temperatures favour propagation.

Unfortunately the initiator efficiency has been halved from that of polymerizations carried out at -30 °C. The presence of slow initiation would normally cause a broadening of the molecular weight distribution. However, polymerizations carried out under the conditions given in table 3.6 clearly show narrow distributions and as such the data appears to be conflicting. An explanation can be found by examining subsequent results given in chapter 4.2. Although the time allowed for polymerization was 2 hours, the polymerization would have been complete within 2-3 minutes. Propagation must be extremely rapid and under such conditions the significance of the rate of initiation on the molecular weight distribution might be expected to be small.

3.6 Polymer characterisation

The structures of the polymers produced from living polymerizations is of interest, providing evidence as to the mechanism of formation and establishing a basis for the structural determination of end-functionalised polymers. A truly living polymerization of isobutene initiated by 1-PEC/$TiCl_4$/pyridine and quenched by methanol is expected to show aromatic and chlorine capped chains. Whereas a polymerization that contains transfer reactions will exhibit chains that possess vinyl end-caps.

The polymer characterised in this study was prepared by the technique given in section 2.4.1 The polymerization was conducted with a [$TiCl_4$] of 0.22 mol L^{-1}, [Pyridine] of 0.02 mol L^{-1}, [1-PEC] of 5×10^{-3} mol L^{-1}, [IB] of 1 mol L^{-1} at -30°C in 20 ml dichloromethane, 30 ml cyclohexane and quenched with methanol after 10 minutes. The polymer synthesised had a number average molecular weight of 2710 g $mole^{-1}$ and a molecular weight distribution of 1.25, by GPC analysis.

3.6.1 NMR model by computer prediction software

It is well documented in the literature that, regardless of the quenching agent, living polymerizations of isobutene are almost exclusively chlorine end-capped. When the initiator used is 1-PEC the following structure is predicted (figure 3.13) for the polymer obtained.

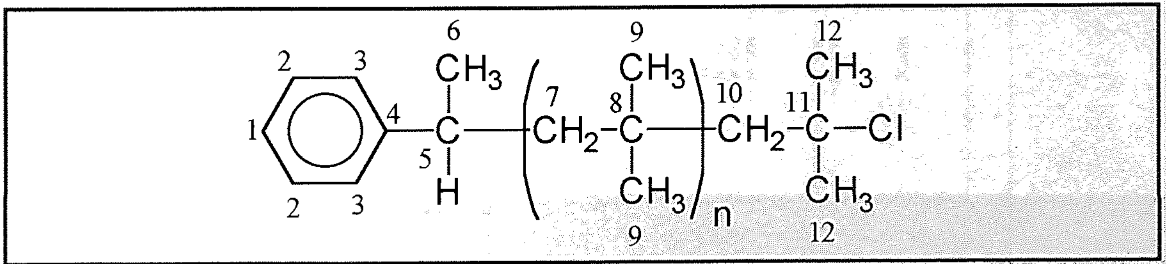


Figure 3.13. Projected polymer product, α-(1-phenylethyl)-ω-(*tert*-chloro)polyisobutene.

The ^{13}C NMR chemical shifts for the structure shown in figure 3.13 were predicted by utilising Specinfo, a UNIX based NMR modelling program [128]. The results obtained are give in figure 3.14.

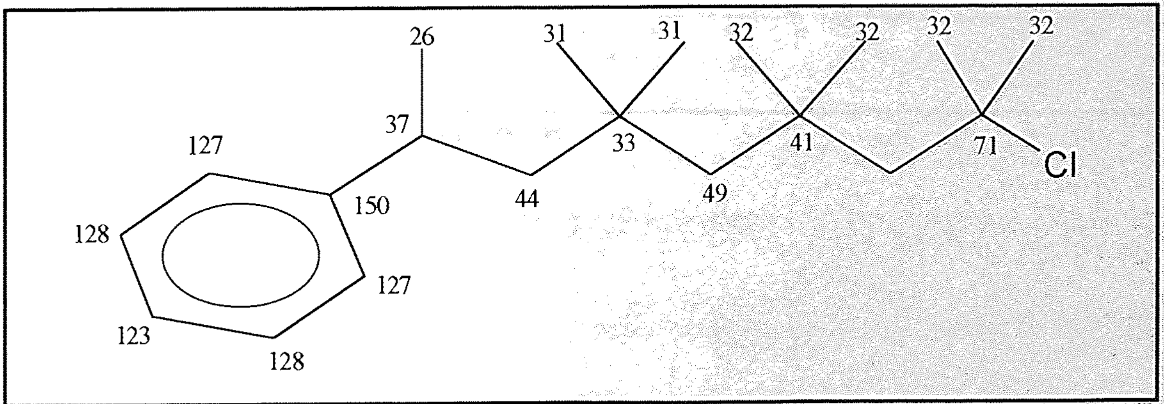


Figure 3.14. Predicted chemical shifts in ppm of ^{13}C-NMR spectrum of polyisobutene.

The above data were used to help correlate assignments in the NMR spectrum obtained for the polymer.

3.6.2 ^{13}C-PENDANT NMR of polyisobutene

NMR analysis was carried out as described in the experimental section 2.6.2. ^{13}C-PENDANT NMR is a technique in which resonances from methyl and methine carbons exhibit themselves in the spectrum as positive peaks, whereas signals from methylene and quaternary carbons are apparent as negative peaks. Figure 3.15 shows the spectrum of the prepared polyisobutene sample, the assignments of which are given in table 3.7.

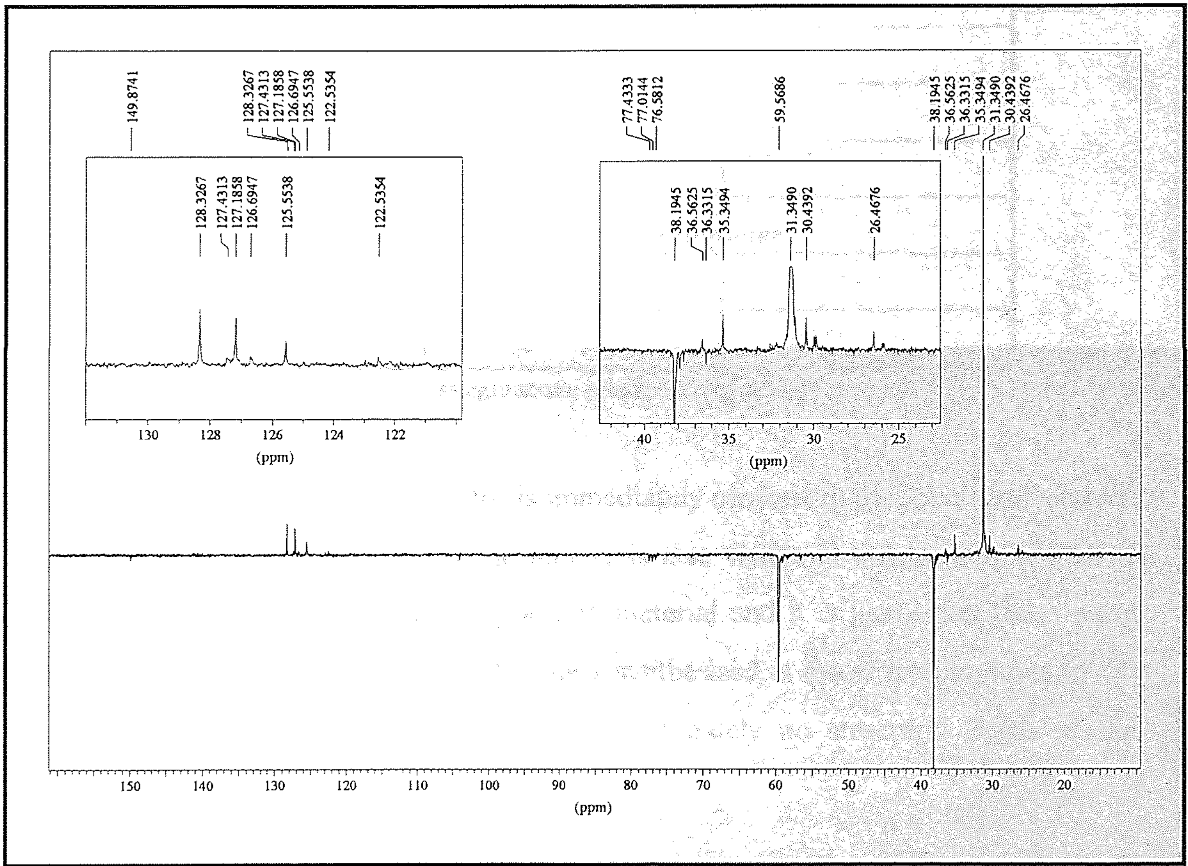


Figure 3.15. ^{13}C NMR spectrum of polyisobutene.

δ (ppm)	Assignment (Carbon Number in Fig. 3.15)
26.5	6
30.4	12 (?)
31.3	9
36.6	5
38.2	7
59.6	8
76.6	$CDCl_3$ (solvent)
77.0	$CDCl_3$ (solvent)
77.4	$CDCl_3$ (solvent)
122.5	*Oligomer*
125.6	1
126.7	*Oligomer*
127.2	3
127.4	*Oligomer*
128.3	2
149.9	4

Table 3.7. ^{13}C NMR assignments, relative to figure 3.15.

The aromatic functionality of the initiator is immediately obvious in the spectrum between 125 and 128 ppm but a second aromatic moiety is also visible in this region. The GPC shows the polymer to contain some oligomeric material and it is likely that these extra peaks are from the aromatic oligomer. Polymers synthesised at lower temperatures (<-50 °C) do not display these extra resonances. Unfortunately no structural detail of the oligomer can be deduced.

Computer modelling of the NMR from the proposed structure predicts a peak at approximately 71 ppm for the quaternary carbon bearing the terminal chlorine atom. No evidence of its presence can be seen in the NMR spectrum. This problem is recognised in the literature, which relies on the ^1H NMR spectrum to locate the chlorine end group. This methine is notoriously difficult to observe, producing weak signals because of its long relaxation time [134].

3.6.3 ^{1}H-NMR of polyisobutene

Figure 3.16 shows the ^{1}H NMR spectrum of a polyisobutene sample; the assignments of the resonance's are given in table 3.8.

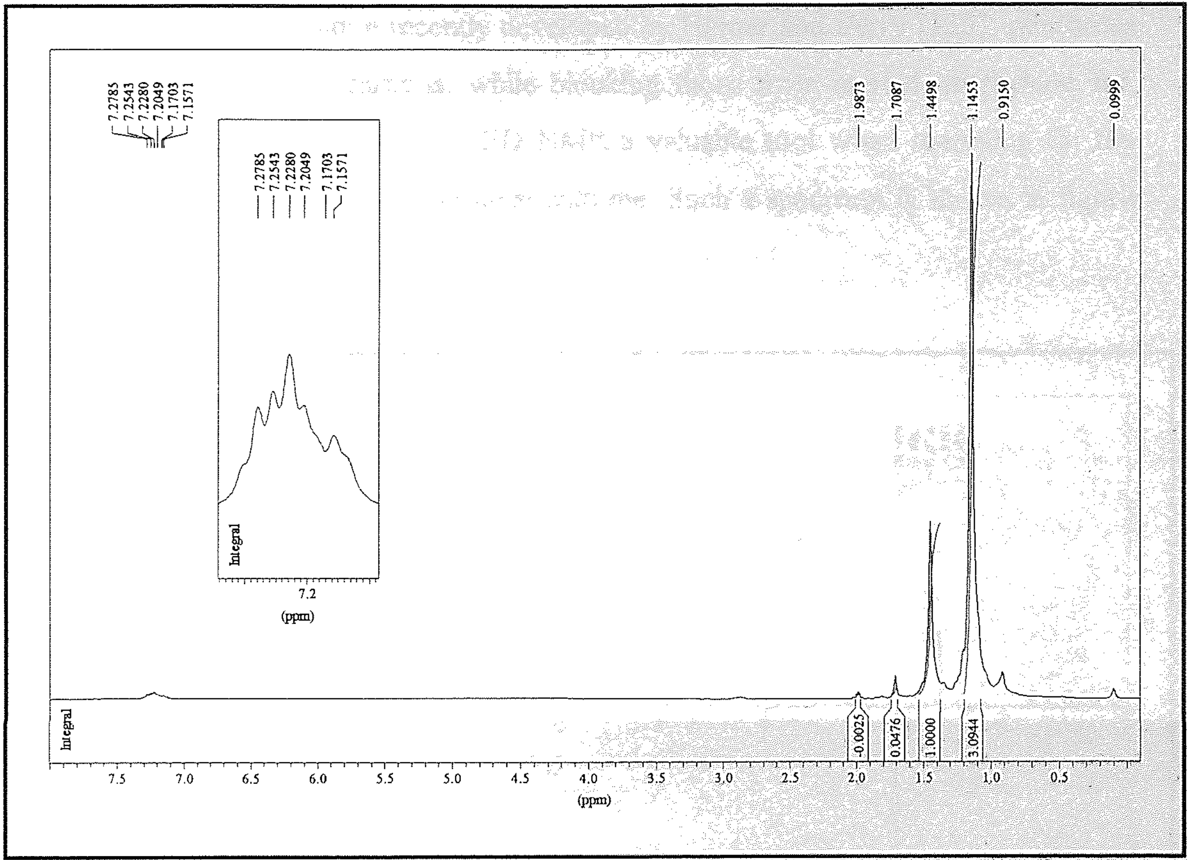


Figure 3.16. ^{1}H-NMR spectrum of polyisobutene.

δ (ppm)	Multiplicity	Assignment
1.15	singlet	-$\mathbf{CH_3}$ on polymer backbone
1.45	singlet	-$\mathbf{CH_2}$- on polymer backbone
1.70	singlet	-$\mathbf{CH_3}$ adjacent to -Cl end group
1.98	singlet	-$\mathbf{CH_2}$- adjacent to -Cl end group
7.1-7.4	multiplet	Aromatic Initiator Function

Table 3.8. ^{1}H-NMR assignments of polyisobutene.

The ratio of the areas of the peaks of the backbone -CH_2- to -CH_3 is 1:3. The singlets at 1.70 and 1.98 ppm are respectively assigned to the -CH_3 and -CH_2 groups adjacent to the terminal -Cl [129,130,131]. An absence of resonance in the region 3.5-6.0 ppm shows that there are no vinylic end groups, indicating that no detectable transfer to monomer occurs during the polymerization.

3.6.4 ^{13}C SPEED NMR of polyisobutene

^{13}C-SPEED NMR, a technique recently developed by Homer and Perry [135], reinforces the signal from quaternary carbons, while blocking those from methyl, methylene and methine carbons. This may make SPEED NMR a valuable tool when searching for the quaternary carbon adjacent to the terminal chlorine. Such a spectrum is shown in figure 3.17 for polyisobutene.

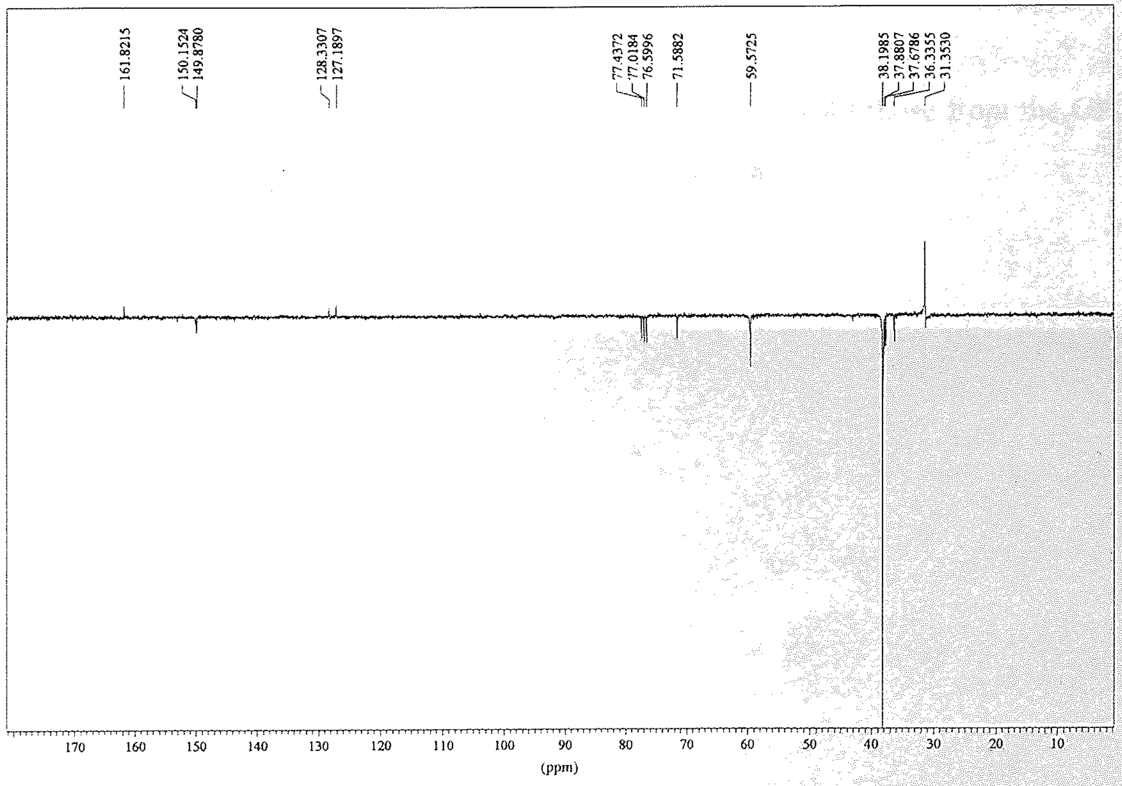


Figure 3.17. ^{13}C-SPEED NMR of polyisobutene.

The peaks at 31.2 and 59.6 ppm are the remains of the -CH_3 and -CH_2- resonance's respectively. The feature at 38.2 ppm is the much enhanced quaternary carbon from the polymer backbone. An extra resonance is now seen at 71.6 ppm, the predicted shift for the end carbon. SPEED is not a quantitative technique and therefore no information can be gained from the ratio of the peak areas.

3.6.5 Elemental chlorine analysis

Two polymer samples, prepared under the conditions described at the beginning of the section, were submitted for elemental chlorine analysis. The results are given in table 3.9. The $\overline{M}_n$ and molecular weight distributions were obtained by GPC analysis. The $\overline{DP}_n$, calculated from the elemental analysis results, were made by assuming one chlorine atom caps one polymer chain.

GPC Analysis			Elemental Analysis	
$\overline{M}_n$ (/g mole^{-1})	$\overline{DP}_n$	MWD	% Cl (mass/mass)	Calculated $\overline{DP}_n$
2690	48	1.25	1.35	46
3640	65	1.22	0.99	63

Table 3.9. Elemental chlorine analysis results.

The $\overline{DP}_n$ calculated from the chlorine analysis correlate well with those from the GPC, indicating that the polymer chains possessed chloro end caps.

Chapter 4: The nature of the dynamic equilibrium in living cationic polymerizations

4.1 Introduction

It has already been suggested in chapter 3 that the dielectric constant of the solvent and temperature influence the rate of polymerization. Such occurrences have been noted in the literature. It has been shown by various workers [79, 84] that increasing the polarity of the solvent and decreasing temperature will increase the polymerization rate. The cause of this effect might be attributed to the presence of a dynamic equilibrium between covalent and active species (section 1.3.2b). Lower temperatures and increased dielectric constant favour the ionised species. Although the influences of such factors have been noted, little has been proposed to qualify the observations for living cationic systems. However, some work has been carried out to explain such effects in anionic systems.

The anionic polymerization of styrene initiated by polystyrl-lithium in mixtures of THF and benzene has been examined by Worsfold [137] and Van-Beylan [138]. Equations developed by Fuoss [139] and Kirkwood [140] applicable to ion-pairs in solution were used to establish the dependence of the observed rate constant of propagation (k_{pobs}) on dielectric constant (ε). A plot of $\ln k_{pobs}$ against $1/\varepsilon$ was shown to be linear. Complications were found with THF and dioxane solvent mixtures and attributed to the preferential aggregation of dioxane around the ion-pair.

4.2 The effect of temperature on a living cationic polymerization

To develop a model relating the apparent rate constant of polymerization to temperature the living polymerization system described in section 3.3 (1-PEC/$TiCl_4$/pyridine) was investigated. As discussed in section 1.3.2b the active species is assumed to be an ion-pair, $[P^{+-}Ti_2Cl_2]$, in equilibrium with a dormant, covalently bonded species [P-Cl], shown in figure 4.1. The concentration of the active species is believed to be small, such that the rate constant of ionisation, k_1, is much less than the rate constant of collapse, k_2. The ion-pairs react with the monomer, M, to propagate with a rate constant, k_p. It may be assumed that at equilibrium the degree of dissociation into ion-pairs, α, is constant, since propagation regenerates an identical species. Studies by other workers [79] and work discussed in section 4.4 show that the order of reaction with respect to the $TiCl_4$ is 2. The concentration of $TiCl_4$ is normally in excess of that of the initiator and hence also that of the polymer chains.

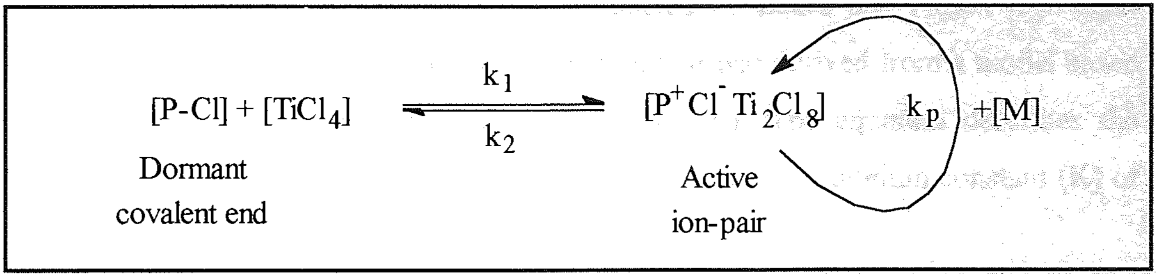


Figure 4.1. Mechanism of propagation.

The observed rate of polymerization (R_p) will be dependent on the concentration of the ion-pairs, monomer, and k_p:

$$R_p = -\frac{d[M]}{dt} = k_p\left[P^+Cl^-Ti_2Cl_8\right][M] \tag{4.1}$$

The concentration of the active species in the above equation can be expressed in terms of an equilibrium constant, K_p, and the concentration of the catalyst and initiator, to give the following:

$$R_p = -\frac{d[M]}{dt} = k_p K_p [PCl][TiCl_4][M] \tag{4.2}$$

Expressing k_p in the Arrenhius form gives:

$$R_p = -\frac{d[M]}{dt} = A_p e^{-E_p/RT} K_p [PCl][TiCl_4][M] \tag{4.3}$$

where;

E_p = activation energy of propagation.

The Gibb's free energy of the equilibrium is given by:

$$\Delta G = -RT \ln K_p \tag{4.4}$$

Substituting 4.4 into 4.3 and simplifying leads to:

$$R_p = -\frac{d[M]}{dt} = A_p[PCl][TiCl_4][M]e^{-(Ep+\Delta G)/RT} \qquad (4.5)$$

If the contribution from ΔG in equation 4.5 is greater than E_p then the equilibrium constant will control the energetics of polymerization. Provided the forwards reaction, k_1, is exothermic, K_p and hence R_p will increase with decreasing temperature. A suitable model for the polymerization would then need to incorporate the concentration and nature of the ion-pair.

Studies of ion-pairs in solution have been conducted by Beard and Plesch [5]. Their treatment relied upon the use of the Fuoss equation that was derived from a model based upon an equilibrium similar to that shown in figure 4.1. The equation describes the ionisation of a covalent species into an ion-pair in terms of an equilibrium constant (K) of ionisation, where K is given by:

$$\ln K = \ln\left(\frac{4\pi N_A a^3}{3000}\right) + \frac{e^2}{a\varepsilon kT} \qquad (4.6)$$

e - charge on the electron

N_A - Avogadros number

It was shown, by examination of the salt methyltriethylammonium iodide, that the interionic distance a increases with decreasing temperature, a situation that could be potentially comparable to that of the active species in cationic polymerizations. Equation 4.6 takes account of both the nature of the ion-pair (described by a) and its concentration (described by K). It is now possible to derive a treatment based upon the Fuoss equation.

For a given solvent and ion-pair it can be assumed a, e and ε are constant. It is now possible to reduce equation 4.6 to show the dependence of K_p on temperature as:

$$\ln K_p \propto \frac{1}{T} \qquad (4.7)$$

From figure 4.1 it is possible to express K_p in terms of the mole fraction of the active species, α:

$$K_p = \frac{\left[P^+Cl^-Ti_2Cl_8\right]}{[PCl][TiCl_4]} = \frac{\alpha}{(1-\alpha)[TiCl_4]} \qquad (4.8)$$

Since $k_2 >> k_1$ then α is small, such that:

$$K_p = \alpha/[TiCl_4] \tag{4.9}$$

The apparent rate constant is given by

$$k_{app} = \alpha k_p \tag{4.10}$$

So substituting 4.9 into 4.10 gives:

$$k_{app} = K_p k_p [TiCl_4] \tag{4.11}$$

Therefore, for a given $[TiCl_4]$:

$$\ln k_{app} \propto \ln K_p \tag{4.12}$$

Substitute 4.12 into 4.7:

$$\ln k_{app} \propto \frac{1}{T} \tag{4.13}$$

Plotting $\ln k_{app}$ against 1/T should produce a linear relationship if the nature (interionic distance) of the ion-pair remains unchanged. Any structural change in the propagating species would be expected to manifest itself as a deviation from linearity. The relation does not take account of dielectric constant changes of the solvent with temperature, which are considered small and negligible.

A series of experiments, based on the polymerization of isobutene by 1-PEC/$TiCl_4$/Pyridine, was designed to test the derived relationship (4.13). Values of k_{app} were calculated at intervals between -10 and -55 °C. Because of experimental constraints it was not possible to expand the temperature range outside these limits. The boiling point of isobutene is -5.6 °C and so the upper limit was set at -10 °C. Polymerizations performed at temperatures below -55 °C proved to be extremely rapid and difficult to follow with the equipment used. The experimental conditions and the results for each reaction are given in table 8.1 of Appendix 1. Figure 4.2 shows the $\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$ against time plots from which k_{app} could be determined as a function of temperature. To avoid systematic errors the polymerizations were conducted in a random order.

Experiments repeated at -30 °C (table 3.5, figure 3.9), along with error analysis conducted in section 4.3, showed k_{app} to be reproducible to within 3 %, an accuracy that is tolerable in the values given in table 4.1.

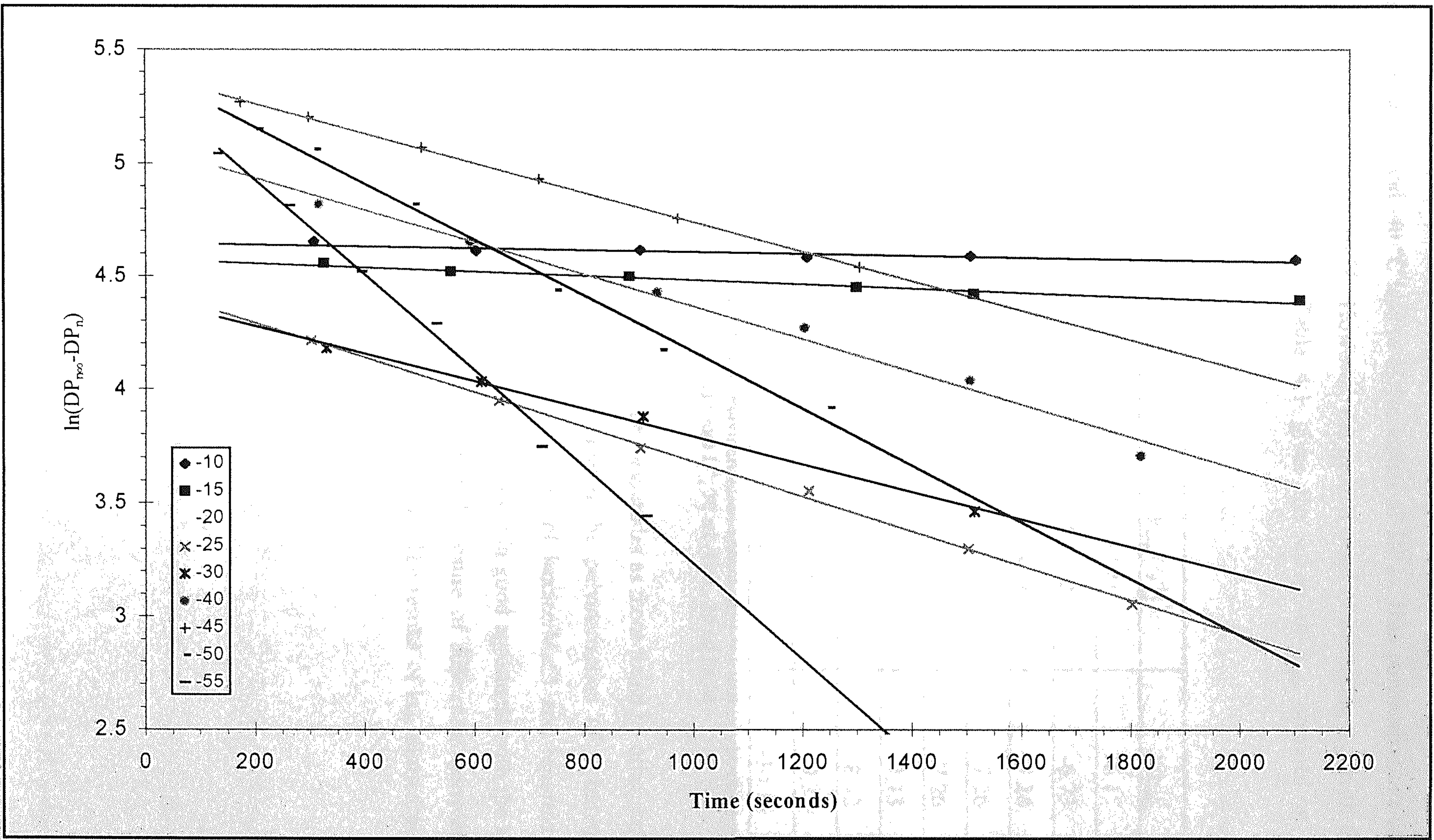


Figure 4.2 Plot of ln($\overline{\text{DP}}_{n\infty}$ - $\overline{\text{DP}}_n$) against time over a temperature range of -10 to -55 °C.

A preliminary inspection of the plot shows that there appears to be two sets of data. The set between -55 and -40 °C lead to higher values of $\overline{DP}_{n\infty}$ than polymerizations carried out between -30 and -10 °C. However, the general trend of increasing k_{app} with falling temperature was observed. Table 4.1 gives the values of k_{app} obtained at each temperature.

Temperature (/K)	1/Temperature (/K)	k_{app} (/s^{-1})	$\ln k_{app}$
218	0.00459	0.0021	-6.17
223	0.00448	0.0012	-6.73
228	0.00439	0.0007	-7.26
233	0.00429	0.0007	-7.26
243	0.00412	0.0007	-7.26
248	0.00403	0.0008	-7.13
253	0.00395	0.0002	-8.52
258	0.00388	0.00009	-9.32
263	0.00380	0.00004	-10.13

Table 4.1. Dependence of k_{app} on temperature. Polymerization system, [IB] = 1 mol L^{-1}, [1-PEC] = 0.01 mol L^{-1}, [Pyridine] = 0.02 mol L^{-1}, [$TiCl_4$] = 0.15 mol L^{-1}, 30 ml cHex., 20 ml DCM.

The values obtained for k_{app} are of the same magnitudes as those found by other workers for similar systems. Storey et al [79], initiated the polymerization of isobutene by DCC/$TiCl_4$ in a 60/40 (vol/vol) solvent mixture of hexane/MeCl and reported rate constants of the magnitude 10^{-4} s^{-1} at -30 °C. This is in good agreement with the above data. Exact comparability would not be expected because of differences between the polymerization systems and experimental conditions. The results of k_{app} plotted against temperature are given in figure 4.3.

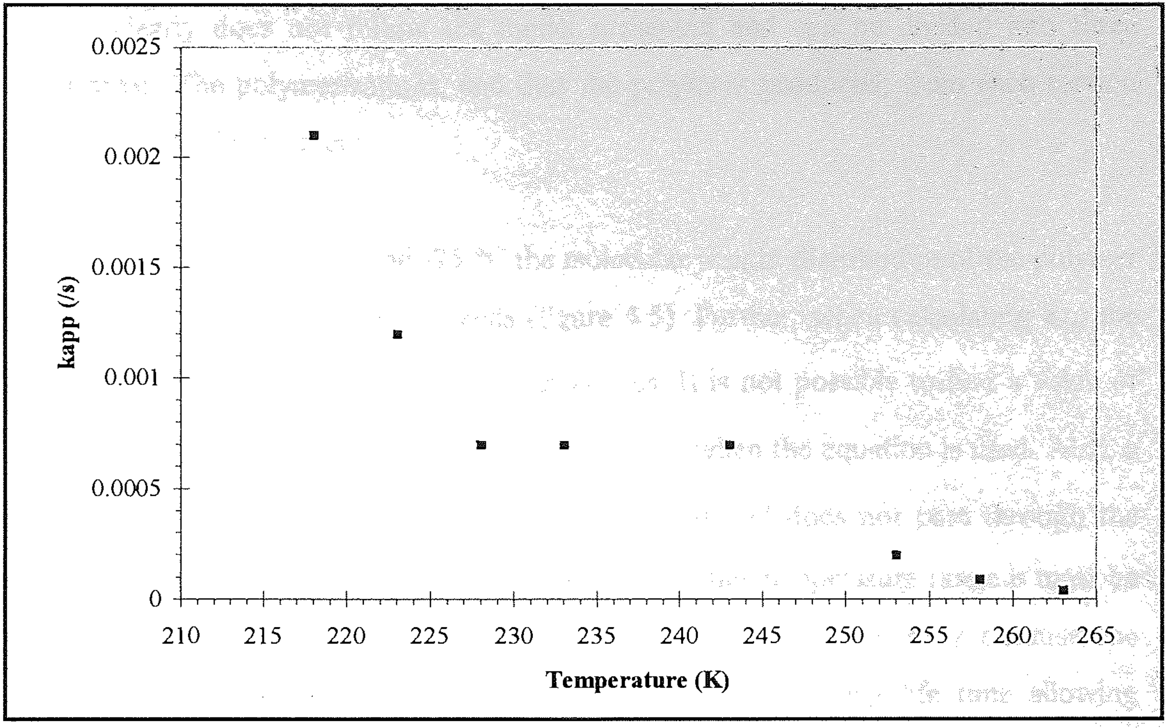


Figure 4.3. Dependence of k_{app} on temperature.

The observation of two data sets in figure 4.2 becomes immediately apparent in figure 4.3 with a cross-over region occurring in the middle of the data series.

Plotting $\ln k_{app}$ against 1/temperature as described by equation 4.13 produces the plot in figure 4.4.

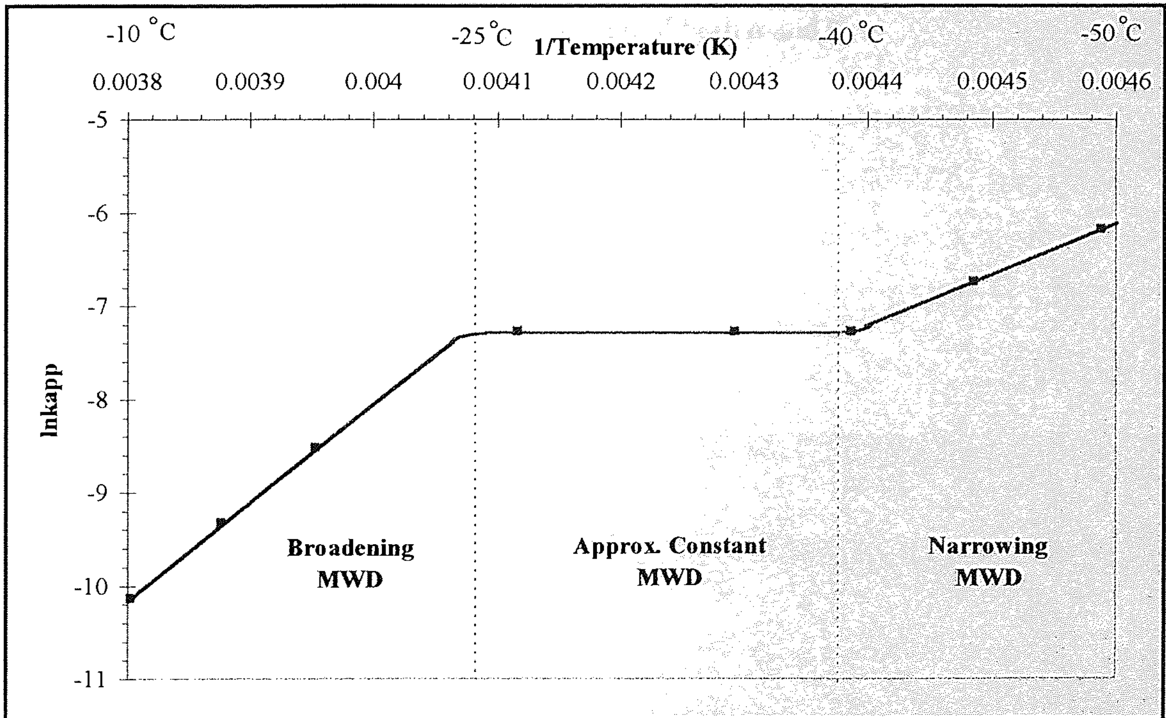


Figure 4.4. Plot of lnkapp against 1/temperature.

The plot clearly does not follow the model presented and can be divided into three distinct areas. The polymerizations, and thus the polymers produced, from each section are characteristically different.

At temperatures between -10 and -25 °C the molecular weight distribution of the polymer increases as the polymerization proceeds (figure 4.5). Further, when calculating k_{app} the equation $\ln(\overline{DP}_{n\infty} - \overline{DP}_n) = -k_{app}t$ no longer applies. It is not possible to find a value of $\overline{DP}_{n\infty}$ that corresponds to the value of the y-intercept when the equation is used. Also, a plot of $\overline{M}_n$ against conversion at -20 °C is non-linear and does not pass through the origin (figure 4.6; Appendix 1, table 8.2). Therefore, in this temperature range it must be concluded that the polymerization is not a truly living system, possibly because the equilibrium is slow and the active ion-pairs have a relatively long life time allowing transfer and termination reactions to occur. However, in this region of the plot in figure 4.4, $\ln k_{app}$ shows an inverse linear relationship to temperature. So although a truly living polymerization is not witnessed, equation 4.13 derived from the Fuoss expression applies between temperatures of -10 and -25 °C. Therefore, across the given temperature range the same ion-pairs must be responsible for propagation, because if the ion-pairs were changing in nature, i.e. the interionic distance a was increasing, then the relation would not hold. In such circumstances the Fuoss equation (4.6) predicts that the equilibrium constant, K_p , and hence k_{app}, is a complex function of both a and T.

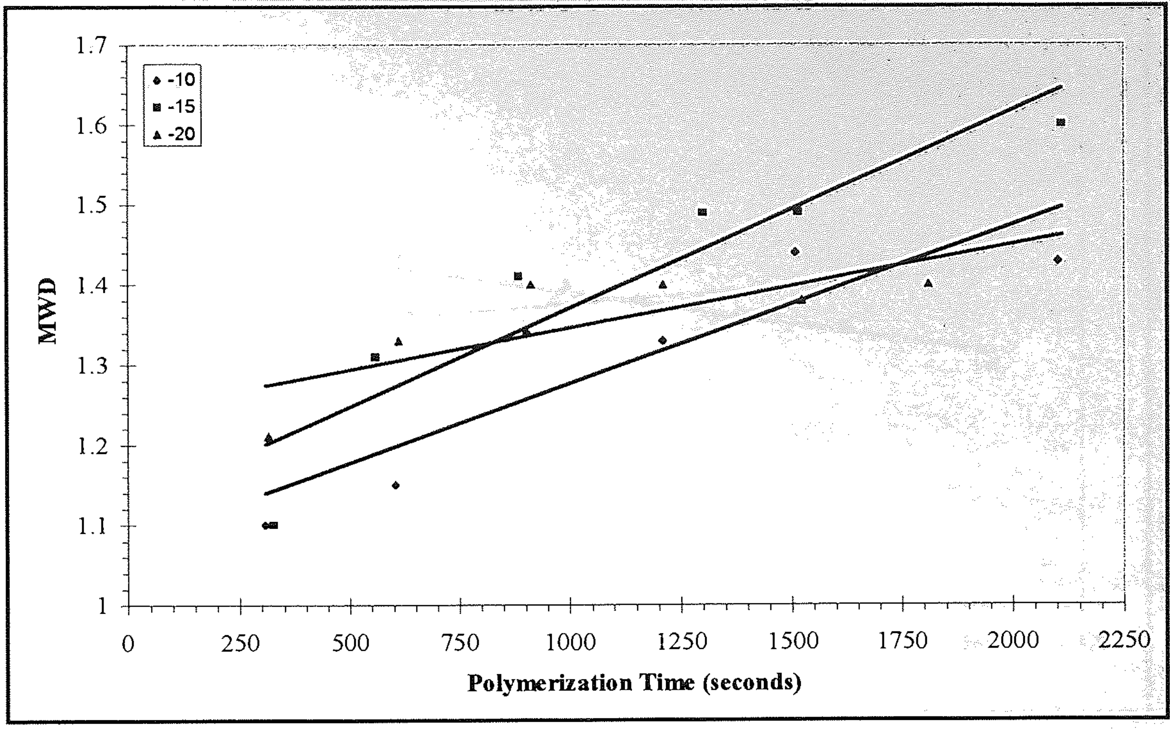


Figure 4.5. Molecular weight distribution trends at -10 to -20 °C.

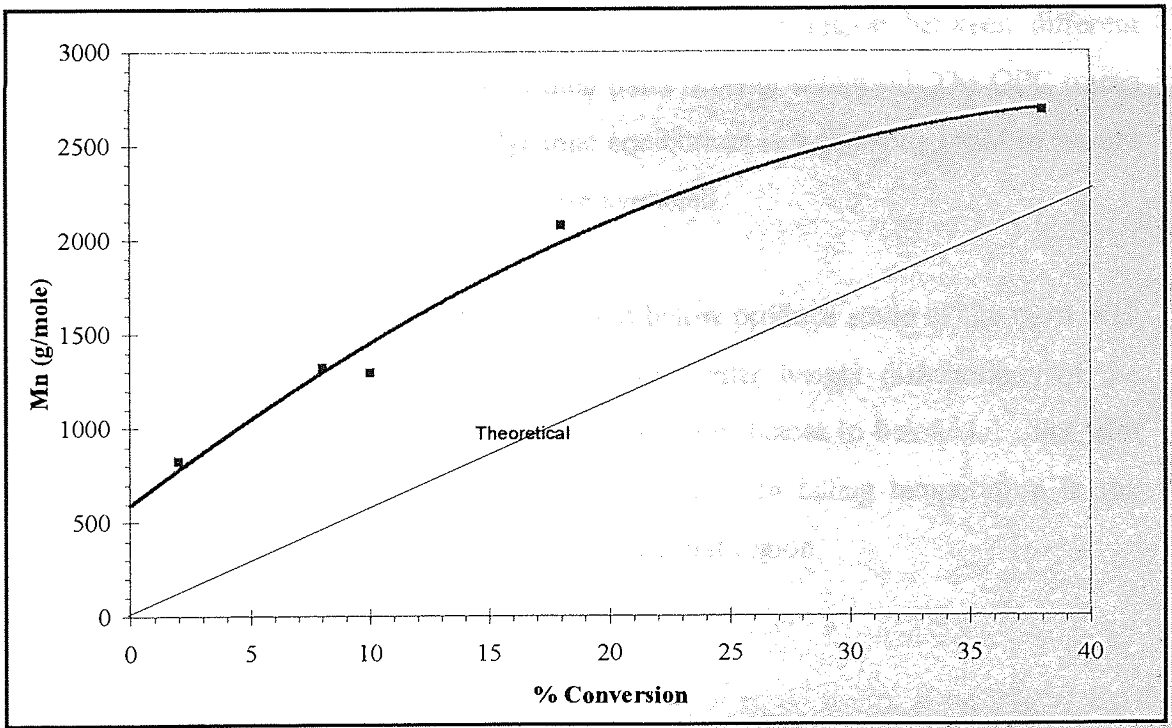


Figure 4.6. Plot of $\overline{M_n}$ vs. conversion at -20 °C.

The central region of figure 4.4 seems to be an intermediate between the two extremes. In the temperature range of -25 to -40 °C only a small change is observed in the molecular weight distributions of the polymers, typically from 1.17 to 1.24.

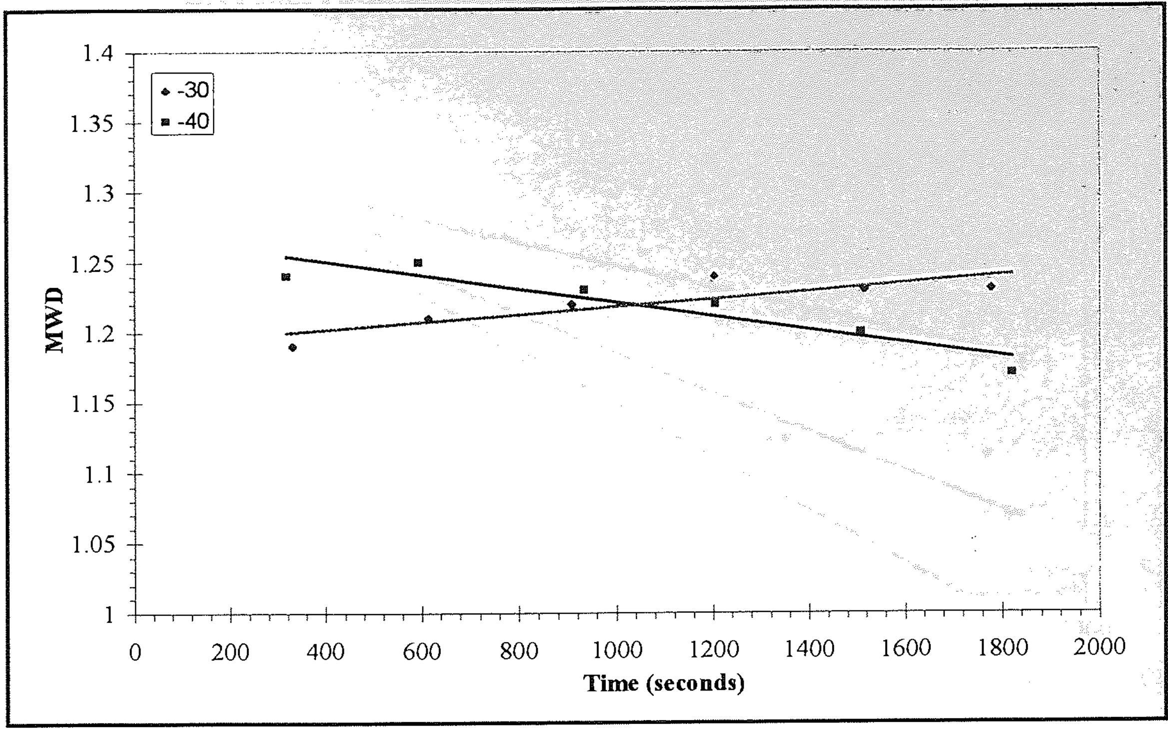


Figure 4.7. Molecular weight distribution trends at -30 to -40 °C.

The living nature of this polymerization at -30 °C has already been demonstrated in section 3.3. If this segment of figure 4.4 is a cross over region between different propagating species then the summation of their parts is being witnessed. The GPC traces are not bimodal, probably because the dynamic equilibrium is sufficiently rapid to ensure that the contributions from different species are averaged.

Finally polymerizations carried out at -40 °C and below produce some of the most well defined polymers. As shown in figure 4.8, the molecular weight distributions of the polymers noticeably decrease with conversion, in some instances to below 1.1 . As with the first section of the plot, k_{app} once again increases with falling temperature in the manner predicted, but at a different rate to that in the first region.

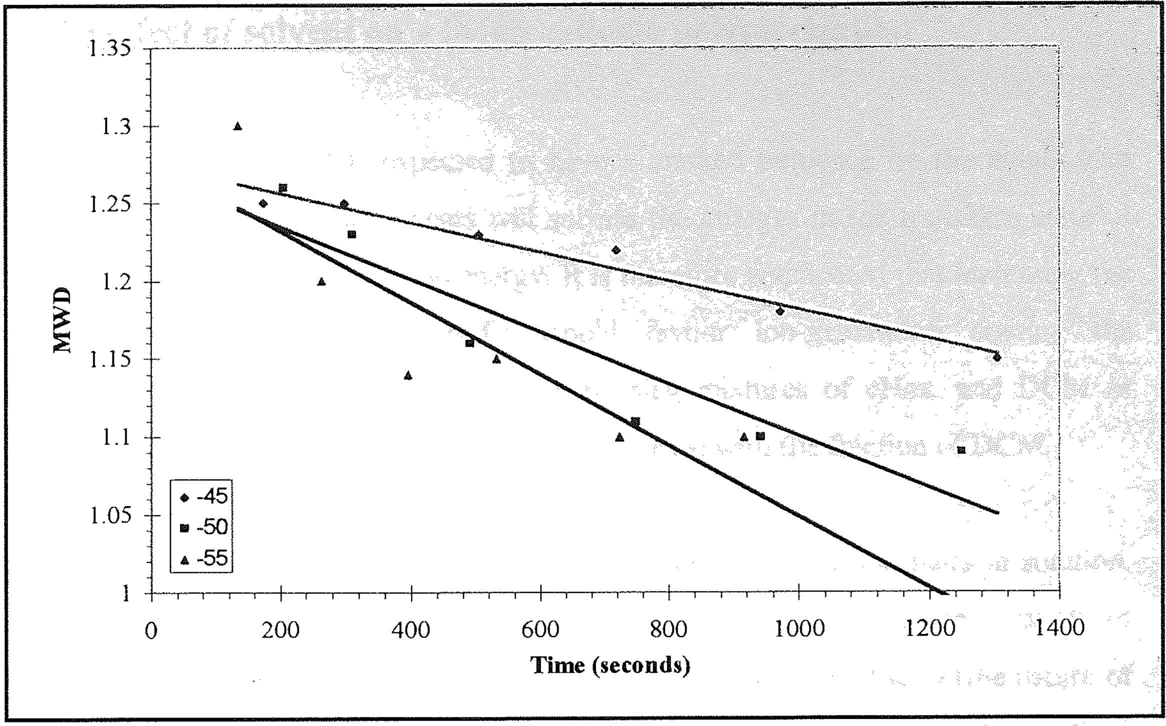


Figure 4.8. Molecular weight distribution trends at -45 to -50 °C.

The predicted values of $\overline{DP}_{n\infty}$ are much larger than expected at temperatures below -40 °C and are in agreement with batch polymerizations carried out in section 3.5. Slow initiation is the most likely cause of high $\overline{DP}_n$. In the temperature range -10 °C to -40 °C initiator efficiencies are between 80 to 90 %. However, at -40 °C the efficiencies start to fall, down to 40 to 50 % at below -45 °C. Since fewer polymer chains have been initiated, the concentration of active ion-pairs must be lower. Thus, it is expected that k_{app} will be reduced at these lower temperatures. It is then reasonable to propose that the results shown in figure 4.4 represent the overlapping trends of two distinct polymerization mechanisms, one exhibiting high initiator efficiency the other low.

An indication of the cause of this reduced initiator efficiency can be found by comparing the gradients of the plot in the first and later regions of figure 4.4. If only the fraction of ion-pairs had changed then the gradients of the line in the two areas would be the same. However, the change in gradient between the two extremes shows that a reduction in number of propagating species alone cannot account for the witnessed behaviour. Examining Fuoss's model shows that a change in gradient can only be accounted for by a difference in the nature of the ion-pair. The value of a, and thus k_p, must have altered, accounting for the different rate at which $\ln k_{app}$ increases with 1/temperature.

4.3 The effect of solvent on a living cationic polymerization

The polarity of the solvent is expected to have a marked influence on the equilibrium described in figure 4.1. Polar solvents will solvate the charges in the transition state of ionisation and so lower its activation energy. It is therefore anticipated that increasing the polarity of the polymerization media would favour ion-generation causing the concentration of ion-pairs to rise. Thus, when using mixtures of cHex. and DCM as solvent the rate of polymerization is expected to increase with the fraction of DCM.

Ramsey et al. [142] have carried out extensive investigations into ion pairs in solution. They examined salts of tetra-n-butylammonium picrate, and perchlorate, in a variety of mixed solvents, including dichloromethane and hexane. It was found that a (the nature of the ion-pair) is independent of dielectric constant. The conclusion was drawn from application of the Fuoss equation, for a given salt at constant temperature, plots of log K against 1/ε were linear. If this relation also holds true for living cationic polymerizations then changes in rate can only be attributed to a change in the concentration of active species, cause by a shift in the equilibrium. This would be in contravention of some workers who speculate that increasing rate is because of a rise in the ionicity of propagating species.

It is possible to derive a relationship between the k_{app} of polymerization and the dielectric constant of the solvent, by using the same arguments that were applied to temperature in section 4.2. Thus the following expression can be deduced:

$$\ln k_{app} \propto \frac{1}{\varepsilon} \tag{4.15}$$

A series of experiments was conducted to test the above relation. The dielectric constant of the polymerization medium was altered by using various compositions of DCM and cHex. In the absence of experimental data, the dependence of dielectric constant on the solvent composition was estimated by comparison with literature values. Imanishi et al [143] measured ε for various mixtures of DCM and hexane (Appendix 1; table 8.3 and figure 8.1). The relationship between ε and the mole fraction of DCM/hexane is not linear but a second order polynomial fit can be found. The polynomial relationship was assumed to be also applicable for DCM/cHex. mixtures and literature values for the pure solvents [145] were inserted into the equation. This provided a curve estimating the dependence of dielectric constant on the mole fraction solvent composition of DCM and cHex (figure 4.9). Unfortunately the values are estimated for a temperature of 20 °C, it was not possible to derive values at the polymerization temperature of -30 °C because of a lack of data. It is assumed that the effect of temperature on dielectric constant is relatively small, and can be neglected for the purposes of this investigation.

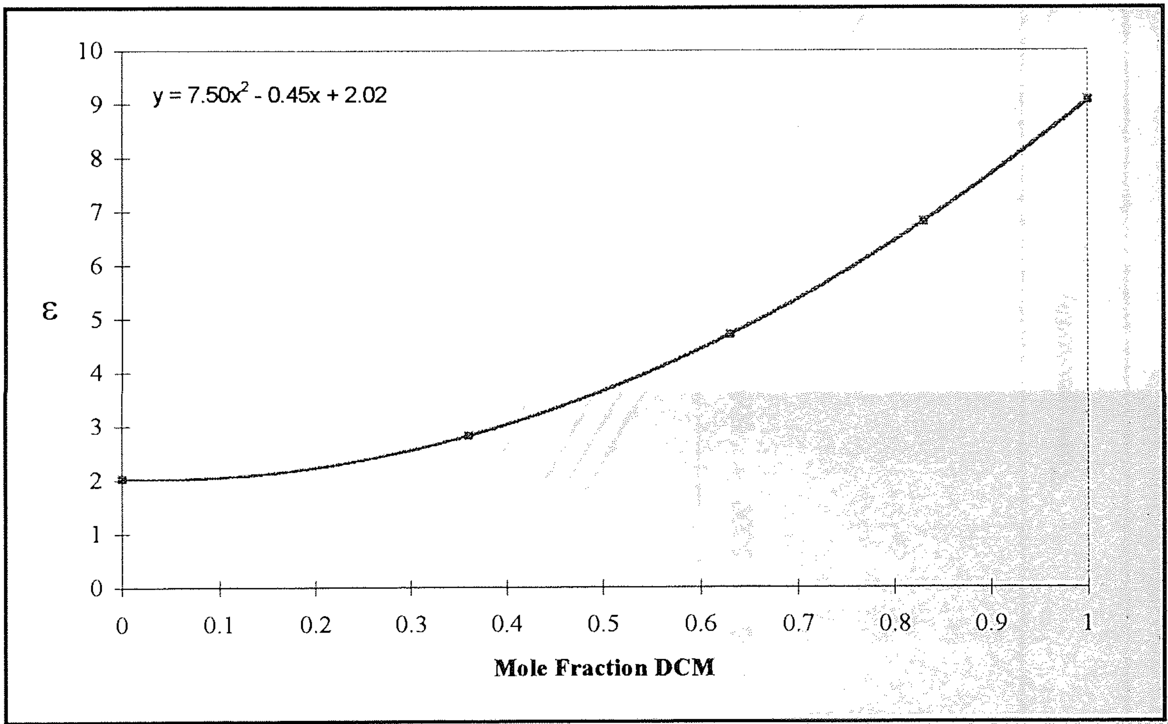


Figure 4.9. Dependence of dielectric constant on mole fraction of DCM in cHex.

The experimental data for each polymerization carried out in a given solvent are presented in Appendix 1, table 8.4 and the $\ln(\overline{DP}_{n\infty} - \overline{DP}_{n})$ against time plots from which k_{app} was found are presented in figure 4.10.

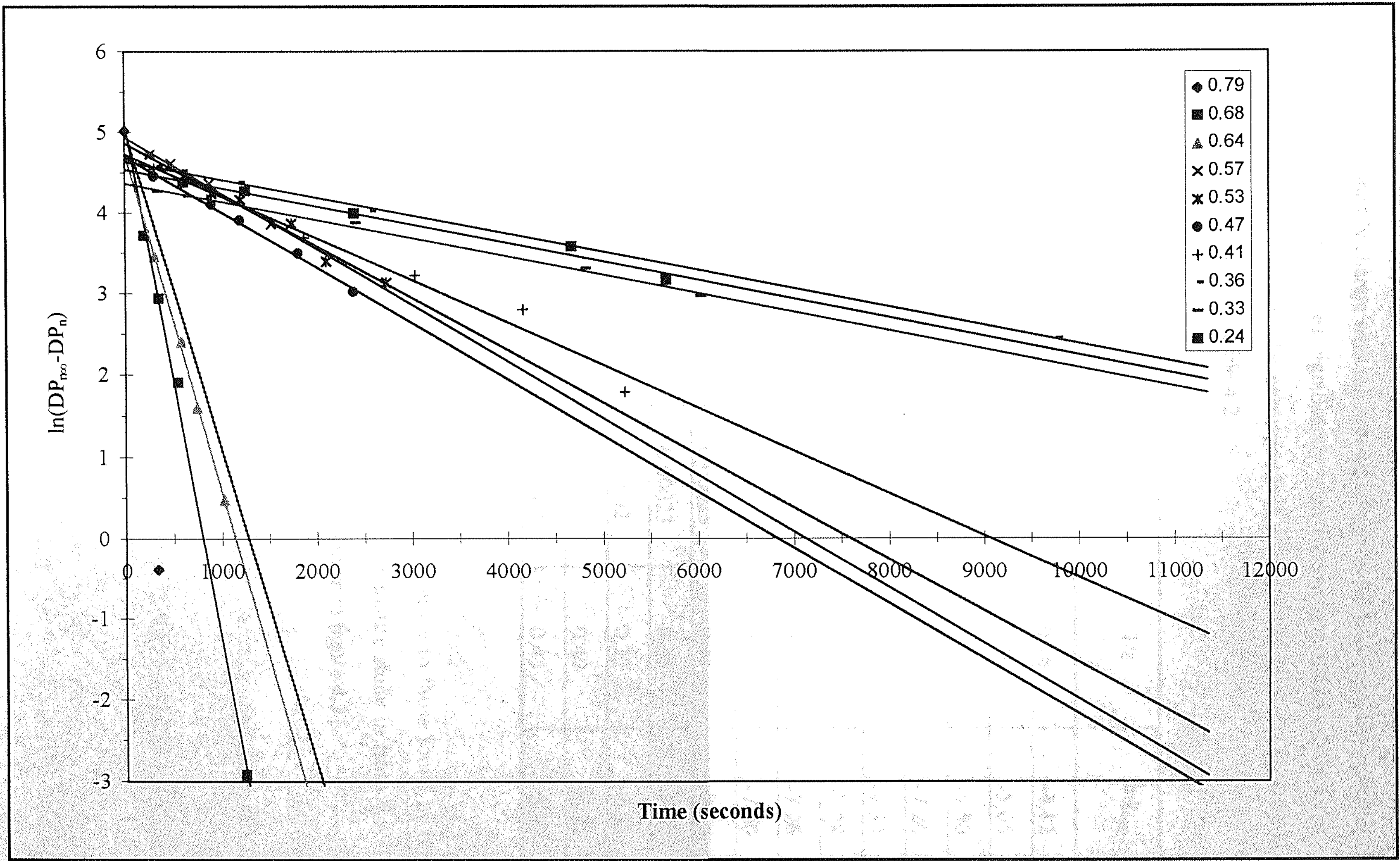


Figure 4.10. Plot of ln($\overline{DP}_{n\infty}$ - $\overline{DP}_n$) against time for a given mole fraction of DCM.

It appeared that the polymerizations clustered themselves into one of three groups and that k_{app} did not linearly change with the solvent composition. However, the apparent rate constant of polymerization rises significantly with increasing fraction of DCM in the solvent. The values of k_{app} and the corresponding ε (calculated from figure 4.9) for a given mole fraction are shown in table 4.2.

Solvent composition, mole fraction DCM	ε	k_{app} (/s^{-1})	1/ε	$\ln k_{app}$
0.79	6.4	0.0162	0.16	-4.12
0.68	5.2	0.0064	0.19	-5.05
0.64	4.8	0.0041	0.21	-5.50
0.57	4.2	0.0007	0.24	-7.26
0.53	3.9	0.00065	0.26	-7.34
0.53	3.9	0.00069	0.26	-7.28
0.47	3.5	0.0007	0.29	-7.26
0.41	3.1	0.0005	0.32	-7.60
0.36	2.8	0.00025	0.35	-8.29
0.36	2.8	0.00023	0.35	-8.52
0.33	2.7	0.0002	0.37	-8.52
0.28	2.5	0.0002	0.40	-8..52
0.24	2.3	0.0002	0.43	-8.52

Table 4.2. Dependence of k_{app} on solvent composition.

The values obtained for k_{app} are once again similar in magnitude to those found by other workers [79] and comparable to those found in the temperature study in table 4.1. The change in k_{app} with the apparent dielectric constant is shown in figure 4.11.

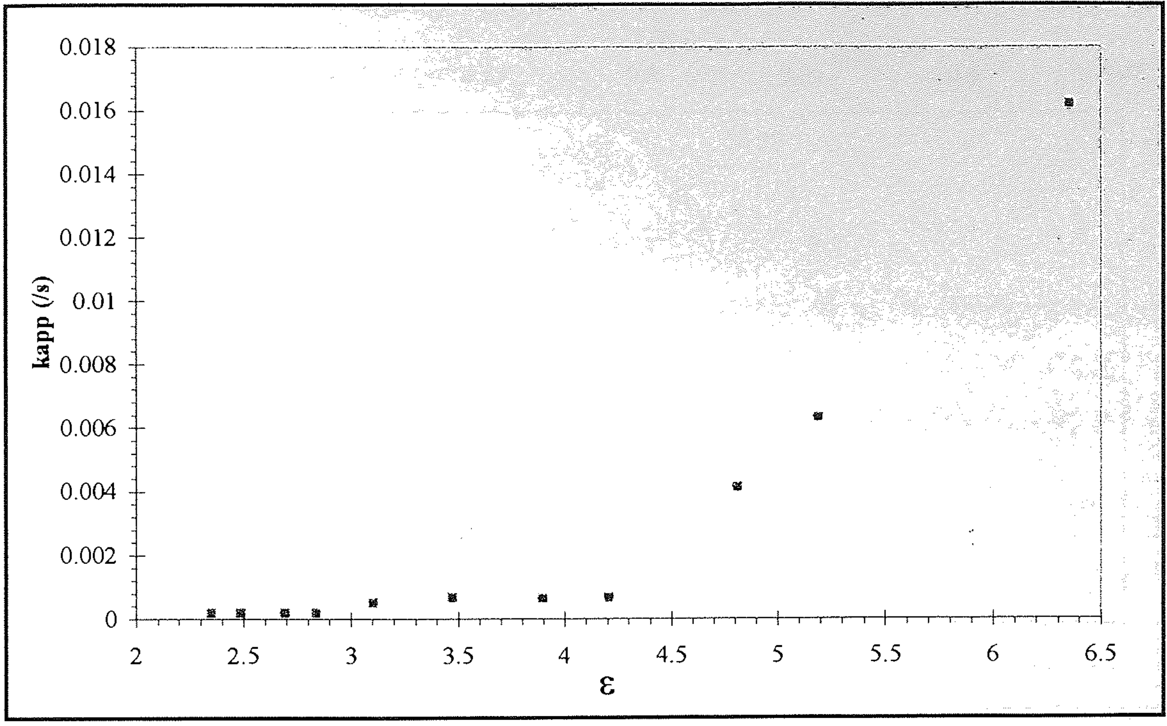


Figure 4.11. Dependence of k_{app} on dielectric constant.

To begin with, k_{app} falls rapidly from 0.016 to 0.0007 s^{-1}, as dielectric constant decreases from 6.4 to 4.2. As dielectric constant decreases further, from 3.9 to 2.3, the reduction in k_{app} is far less profound, from 0.0007 to 0.0002 s^{-1}. Therefore, the polymerization is most sensitive to changes of solvent composition in relatively polar mixtures of above 45/55 (v/v) DCM/cHex ratio.

Experiments repeated at DCM fractions of 0.53 and 0.36 showed k_{app} to be reproducible to within 3 %, an accuracy that is tolerable in the above values.

Plotting $\ln k_{app}$ as a function of $1/\varepsilon$ as described by equation (4.14) produces the graph shown in figure 4.12.

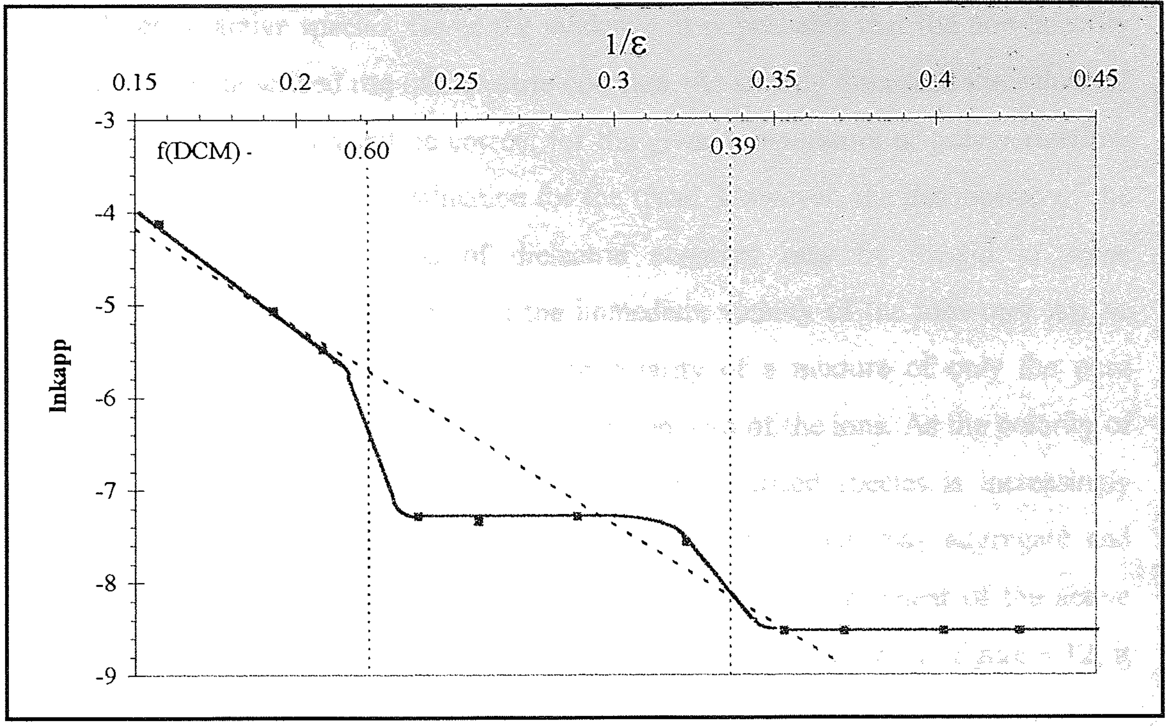


Figure 4.12. Plot of $\ln k_{app}$ against 1/ε.

At high mole fraction DCM content of above 0.60 the plot follows the predicted relationship, represented by the dashed line. However, at a mole fraction of DCM of approximately 0.60 the trend flattens out to form a plateau, which steps down again at a mole fraction of approximately 0.39. There is little to distinguish between the polymers produced from different solvent compositions. The initiator efficiencies and molecular weight distributions are all comparable. The only notable differences are the rates of polymerization and that polymers produced in DCM mixtures of above 0.60 tend to have broader molecular weight distributions; typically 1.29 compared to ≈1.18. This is accountable by an increased value of k_1 over k_2, causing the concentration of ion-pairs to be raised with longer transient life times. The longer lifetimes of the active species, i.e. a slowing in the equilibrium, would have resulted in an increased probability of transfer, thus broadening the molecular weight distributions.

There is no evidence to suggest a change in the type of propagating species, particularly considering the similarity of the polymers produced from the different regions. Such behaviour would also contradict Ramsey et al's work [142] on ion-pairs, who found the interionic distance to be independent of dielectric constant. Therefore, it is not possible to confidently attribute the existence of the plateau in figure 4.12 to an exchange region between different active species. Given the evidence, it is probable that the non-linearity was caused by the described use of dielectric constant. As already discussed the values of dielectric constant used may not be correct for the given temperature of polymerization, but should provide a reasonable estimation for the trend. However, the description of the polarity of the solvent in terms of dielectric constant may be invalid in some circumstances. The dielectric constant in the immediate vicinity of the ions may not be that in bulk. Dielectric constant describes the polarity of a mixture of only the pure solvents and does not necessarily describe the environment of the ions. As the polarity of the solvent mixture is reduced, aggregation between polarised species is increasingly likely. Thus the DCM and ion-pairs in the polymerization system may aggregate and although the polarity of the solution in bulk is lowering, the environment of the active species may not. Thus, in certain solvent mixtures, such as those shown in figure 4.12, it would appear that k_{app} does not depend on dielectric constant.

4.4 The effect of the catalyst and electron donor on the equilibrium

The precise role of the electron pair donor (ED) has been the subject of some debate in the literature. Three theories have been presented to explain its function, proton trapping, carbocation stabilisation, and co-ordination with the catalyst. The details of each are discussed in section 1.3.3b.

A series of experiments was designed to investigate the influence of pyridine (ED) in a living isobutene polymerization system. The nature of the polymerization was first examined in the absence of ED and then the influence of its concentration on k_{app} was studied.

Table 4.3 gives the results obtained from two experiments, one with pyridine, the second without. The corresponding GPC traces can be found in figure 4.13. The polymerization in the presence of pyridine precipitates a yellow solid that is lost in quenching. The solid is only witnessed when both the catalyst and pyridine are present. Therefore, it is likely to be a complex of $TiCl_4$ and pyridine.

[Pyridine] (/mol L^{-1})	[IB]/ [1-PEC]	% Conversion	$\overline{M}_n$ /g mole^{-1}	MWD	% I_{eff}
0.03	65	100	4600	1.17	80
0	58	100	4660	1.22	70

Table 4.3. Polymerization of IB in the absence of pyridine. Temperature = -30 °C, 20 ml DCM, 30 ml cHex., time = 3 hrs.

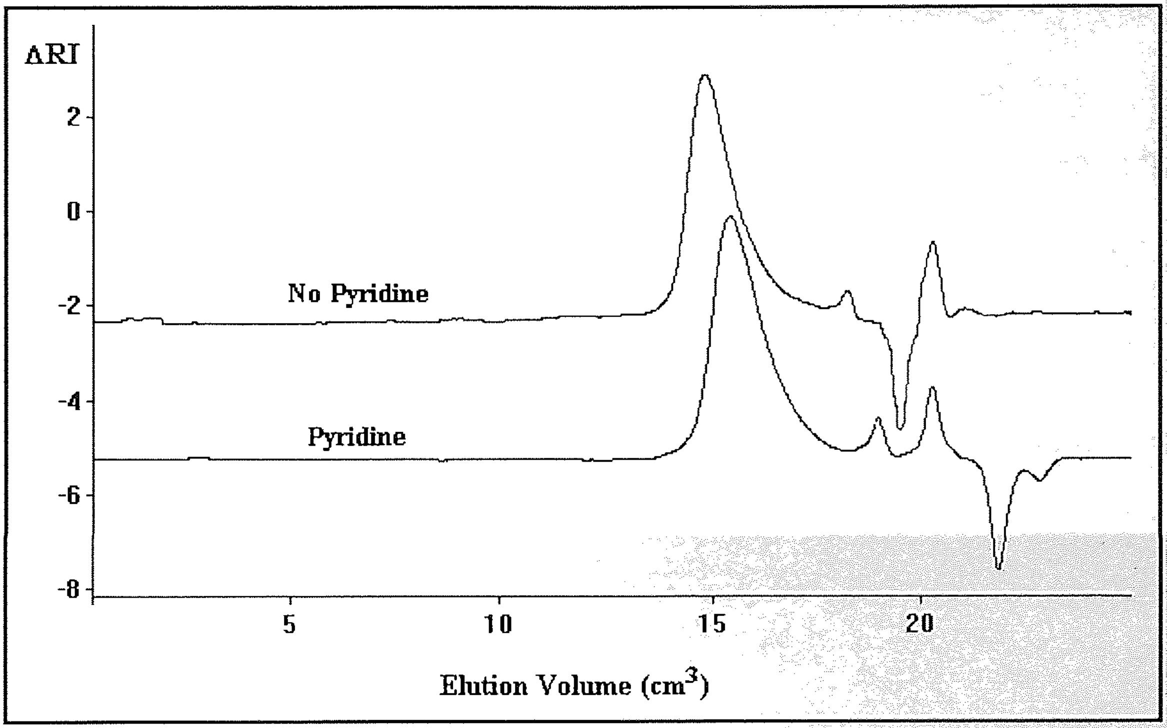


Figure 4.13. Comparison between polymerizations conducted with and without pyridine.

Superficially it first appears that there is little difference between the two polymerizations. The reaction carried out without pyridine has only a slightly lower initiator efficiency of 70% as oppose to 80%, and a broader molecular weight distribution of 1.22 as oppose to 1.17. However, a successful polymerization without pyridine is more difficult to achieve. Even with high vacuum techniques great care must be exercised to avoid contamination of the reaction with such impurities as water. The difficulty is such that a sampling polymerization proved impossible to achieve. The collected samples were invariably contaminated with high molecular weight material so it must be concluded that at least part of the function of pyridine is to negate the effect of impurities, i.e. by proton trapping.

It has been reported by numerous workers that the addition of an ED retards the rate of polymerization. To examine this effect a series of experiments were conducted to find k_{app} as a function of the concentration of pyridine. The complete experimental data are given in appendix 1, table 8.4, figure 4.14 displays the $\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$ versus time plots from which k_{app} is found.

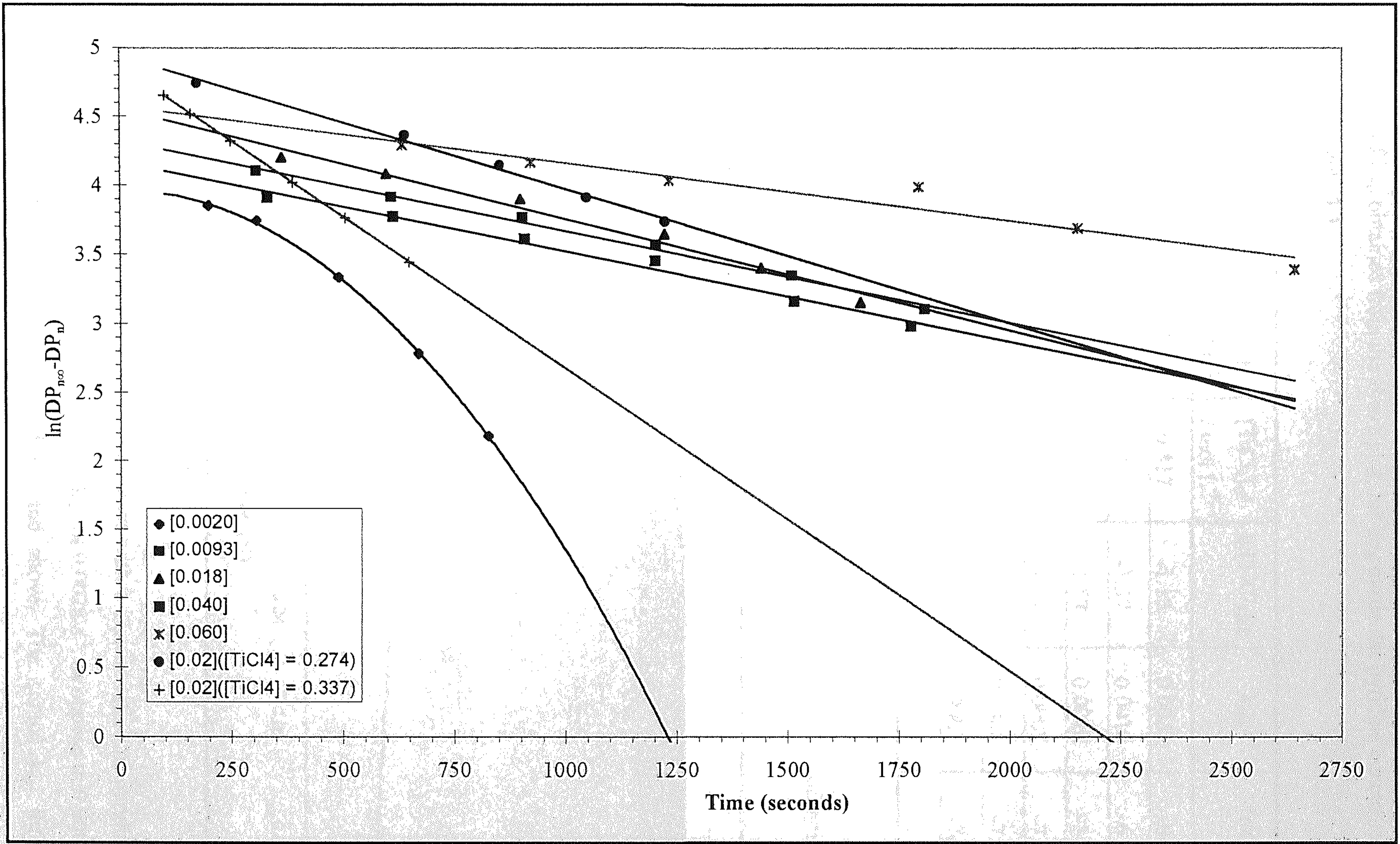


Figure 4.14. Effect of pyridine concentration on pseudo first order kinetics.

The values of k_{app} obtained from the above plot, for any particular pyridine concentration, are given in table 4.4.

[Pyridine] /mol L^{-1}	ln[Pyr]	$[TiCl_4]_0$ / mol L^{-1}	$[TiCl_4]_{eff}$ / mol L^{-1}	$\ln[TiCl_4]_{eff}$	k_{app}	$\ln k_{app}$
0.02	-3.91	0.337	0.317	-1.15	0.0022	-6.1
0.02	-3.91	0.274	0.254	-1.37	0.0010	-6.9
0.002	-6.21	0.210	0.280	-1.57	0.0028	-5.9
0.009	-4.68	0.210	0.201	-1.61	0.0007	-7.3
0.018	-4.02	0.210	0.192	-1.65	0.0008	-7.1
0.04	-3.22	0.210	0.17	-1.77	0.0007	-7.3
0.06	-2.81	0.210	0.15	-1.90	0.0004	-7.8

Table 4.4. Effect of pyridine concentration on k_{app}.

Figure 4.15 shows the values of k_{app} plotted as a function of the concentration of pyridine.

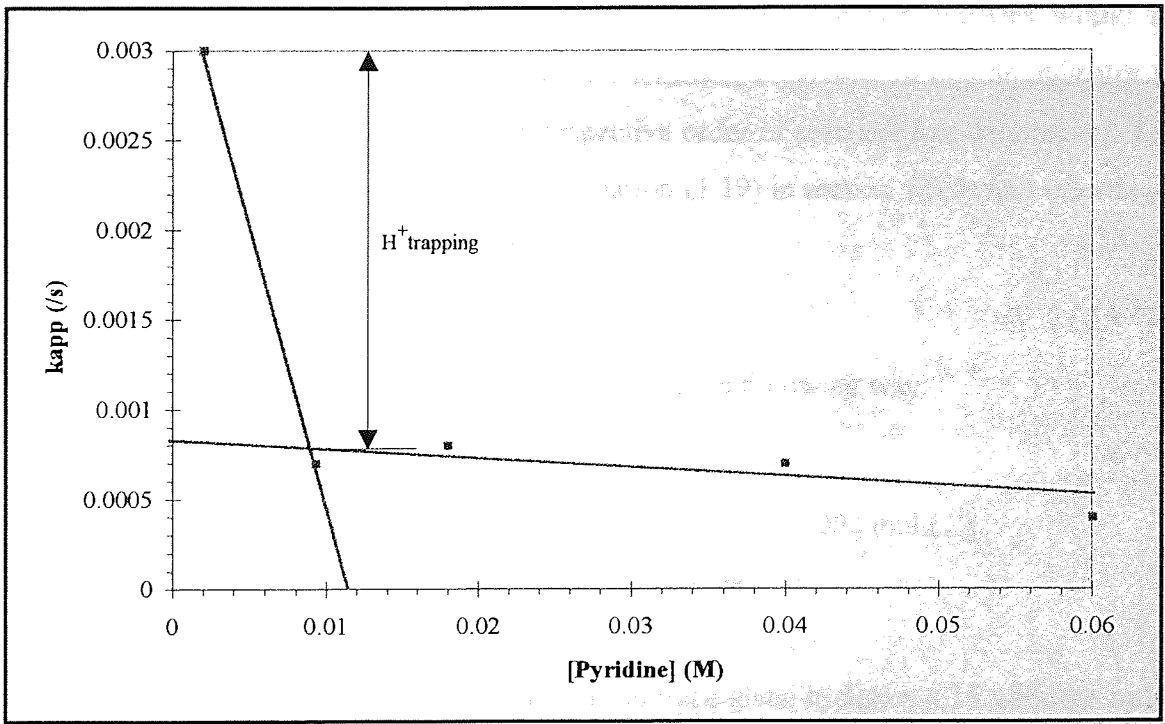


Figure 4.15. Dependence of k_{app} on pyridine concentration.

Table 4.4 shows that the polymerization conducted with a concentration of pyridine of 0.002 mol L^{-1} had a significantly higher average k_{app} of 0.0028 s^{-1}, as oppose to 0.0007 s^{-1} at pyridine concentrations of 0.009 mol L^{-1} and above. The quoted k_{app} for this polymerization was an average, estimated by assuming a linear relationship through the points of the pseudo first order plot shown in figure 4.14 (◆). The pseudo first order plot for the polymerization demonstrates that k_{app} increased during the course of reaction. An increase in k_{app} is normally associated with a rise in the number of active propagating species and might be explained by uncontrolled initiation by protic contamination. For such initiation to occur the concentration of impurities would need to be greater than or at least equal to that of the pyridine. The concentration of protic impurities within the system would have almost certainly increased as the sampling experiment proceeded. The contribution of uncontrolled chain growth to the overall rate of propagation would explain the observation of an unusually high average $k_{app.}$ The concentration of protic impurities can now be estimated to be between 0.002 and 0.009 mol L^{-1}.

Figure 4.15 also shows that even after the level of pyridine has reached that of the impurities further reductions in k_{app} still occur. Apart from proton trapping the electron donor may be having some other influence on the polymerization. The possibilities are co-ordination with the catalyst or carbocation stabilisation. The two theories would be expected to present distinctly different kinetic schemes. Therefore, to find an indicator to the mechanistic role of the pyridine the respective order of reaction was determined. The order was found by adopting the general equation (1.19) in section 1.3.5. and inserting a term for the free pyridine in the system:

$$k_{app} = k_p[P^+B^-][Pyr] \tag{4.15}$$

The concentration of free pyridine was estimated in the following way:

$$[Pyr.] = [Pyr]_0 - [H^+] \tag{4.16}$$

where; $[H^+]$ = concentration of protic impurities (0.002 mol L^{-1})

$[Pyr]_0$ = initial concentration of pyridine

Plotting $\ln k_{app}$ against ln[Pyridine] produced the trace given in figure 4.16 with the order of reaction being calculated from the gradient.

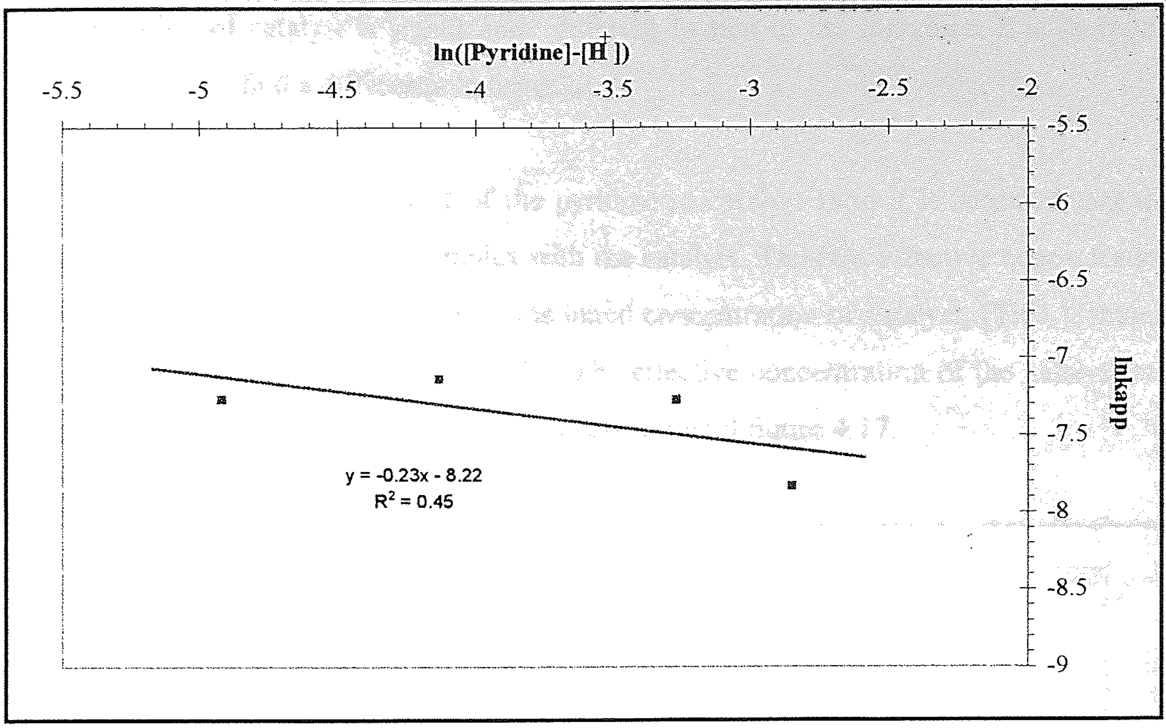


Figure 4.16. Order of reaction with respect to pyridine concentration.

The order of reaction for pyridine from figure 4.16 was approximated to be -0.23, although errors were large it is comparable to -0.28 cited in the literature for similar systems [79]. The negative value is expected since the rate of polymerization falls with increasing concentration of pyridine. However, no mechanistic interpretations are immediately obvious, suggesting the problem to be complex. The scatter in the plot was caused by the insensitivity of the polymerizations rate to the concentration of pyridine. In the above experiments the effect of over a six-fold increase in the concentration of pyridine was evaluated, which resulted in an overall doubling of k_{app} (table 4.4). Such small differences of rate approach the detectable limits of the technique and errors start to become significant. The trend might be better observed under different polymerization conditions that give a greater variation of rate, such as higher catalyst levels.

Concurrent work by Storey et al. published in 1997 first fully realised the function of the ED [144]. It was shown that the ED scavenges protic impurities (as above) and then co-ordinates with the catalyst lowering its effective concentration. Then, by action of the concentration of catalyst on the equilibrium in figure 4.1, the instantaneous concentration of propagating ends is reduced. Therefore, the order of reaction found from figure 4.16 will be dependent on the ratio of $TiCl_4$ to pyridine. In the above experiments the concentration of catalyst is significantly different to that in the literature, it is therefore unremarkable to find a difference in order.

In order to investigate the effect of the pyridine to catalyst ratio it is assumed that the available pyridine forms a 1:1 complex with the catalyst. Thus the effective concentration of free catalyst, $[TiCl_4]_{eff}$, is equal to the initial concentration of catalyst, $[TiCl_4]_0$, minus that of the available pyridine, $[Pyr]_0-[H^+]$. The effective concentration of the catalyst can now be calculated, and its relationship to k_{app} is shown if figure 4.17.

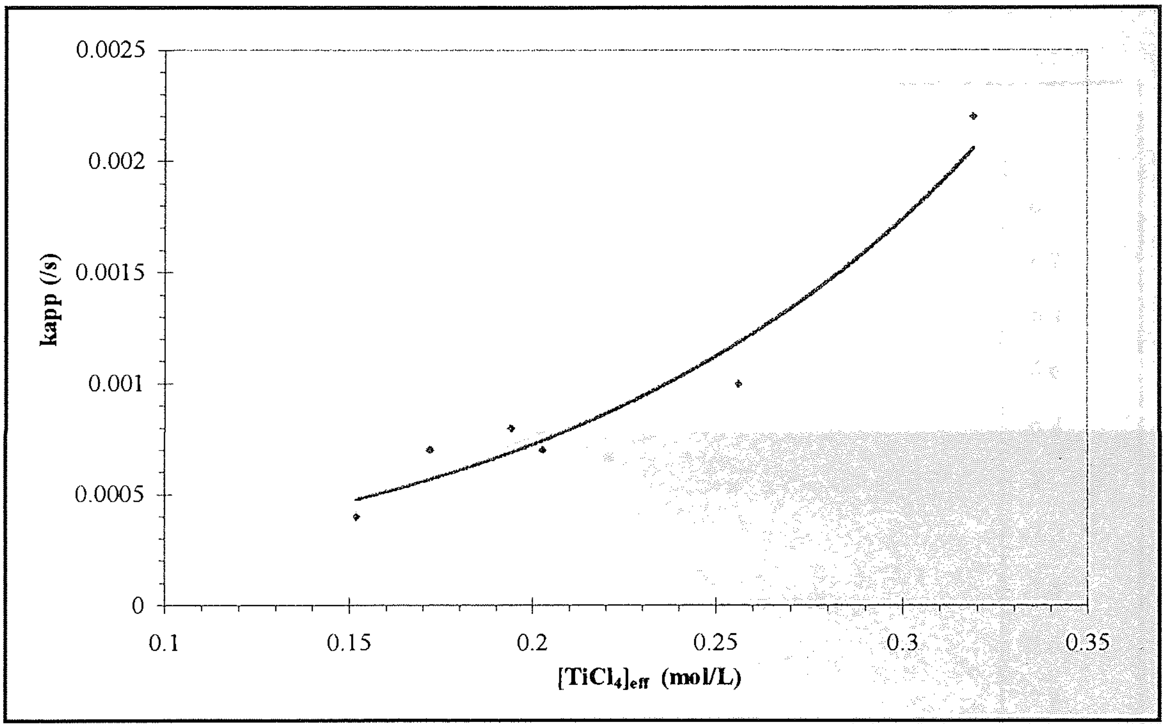


Figure 4.17. Plot of k_{app} against $[TiCl_4]_{eff}$.

Given the function of the pyridine, the kinetic scheme for the polymerization can now be derived:

$$R_p = -\frac{d[M]}{dt} = k_p[P^+Cl^-TiCl_4][M] = k_{app}[M] \tag{4.17}$$

where;

$$k_{app} = k_p[P^+Cl^-TiCl_4] \tag{4.18}$$

the equilibrium constant K_p is defined as follows;

$$K_p = \frac{[P^+Cl^-TiCl_4]}{[TiCl_4]_{eff}[PCl]} \tag{4.19}$$

substituting (4.19) into (4.18) gives;

$$k_{app} = K_p k_p [P - Cl][TiCl_4]^y \tag{4.20}$$

for a given initiator concentration and conditions, [P-Cl] will be constant;

$$\ln k_{app} \propto y \ln[TiCl_4]_{eff} \tag{4.21}$$

where;

$$[TiCl_4]_{eff} = [TiCl_4]_0 - [Pyr] \tag{4.22}$$

Plotting $\ln[k_{app}]$ against $\ln[TiCl_4]_{eff}$ should give a linear plot with the gradient equal to the order of reaction with respect to the catalyst (figure 4.18).

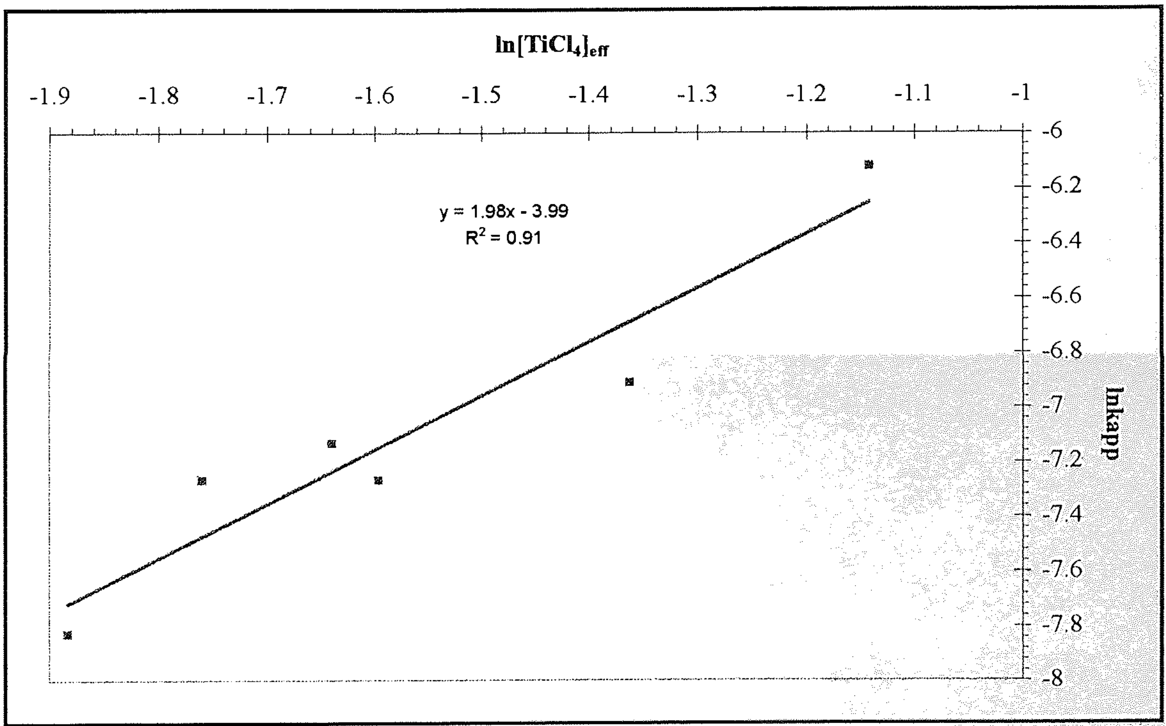


Figure 4.18. Order of reaction with respect to the catalyst.

The order of reaction with respect to the catalyst (y) was found to be 1.98. Within experimental error this can considered to be a second order dependency. This is in agreement with other workers who have attributed the order to the formation of dimeric $Ti_2Cl_9^-$ anions:

$$TiCl_4 + TiCl_5^- \rightleftharpoons Ti_2Cl_9^-$$

Figure 4.19. Dimerisation of $TiCl_4$.

The significance of the work is that the order of reaction with respect to the catalyst has been demonstrated by predominately altering the concentration of the pyridine. Thus, it can be concluded that the role of the pyridine is to prevent undesirable protic initiation by impurities and that the excess will then retard the rate of polymerization by co-ordinating with the catalyst, rendering it inactive.

Chapter 5: Synthesis of low molecular weight polyisobutene

5.1 Introduction

Low molecular weight polyisobutenes have a variety of uses and therefore their syntheses are of interest. For example, end-functionalised polyisobutenes with a degree of polymerization of 20 and a polydispersity less than 1.6 are useful fuel or oil additives [146]. Furthermore, the low molecular weight of the chains aids the structural determination of the polymer by normal analytical techniques such as NMR, because the concentration of end groups relative to the number of backbone monomer units is increased. Thus end-functions will be more prominent in analysis.

The aim of this section of work was to modify the 1-PEC/$TiCl_4$/pyridine polymerization system to produce polyisobutene within the specifications given above.

5.2 Slow initiation at high 1-PEC concentrations

Because the polymerization system under study was a living system the first logical step in synthesising low molecular weight polymer was to increase the concentration of the initiator system (1-PEC/$TiCl_4$/pyridine) relative to the concentration of isobutene. Accordingly, it was desirable to study the effect of the initiator concentration on the polymerization. To this end a series of experiments was carried out using the experimental method described in section 2.4.1. The concentration of isobutene was maintained constant for all polymerizations but the concentration of the initiator system was increased, such that the theoretical degree of polymerization ranged from 10 to 150. The reaction conditions and the results obtained therefrom are given in table 5.1.

[IB]/[1-PEC]	[TiCl$_4$] (mol L^{-1})	% Conversion	$\overline{DP}_n$	MWD	% I$_{eff}$
150	0.1	20	40	1.23	85
100	0.15	46	40	1.21	83
50	0.30	86	67	1.22	63
20	0.75	100	56	1.21	38
10	1.5	100	39	1.34	28

Table 5.1. Effect of increasing initiator concentration; [IB] = 1 mol L^{-1}, [Pyridine] = 0.013 mol L^{-}, 20 ml DCM, 30 ml cHex., Temperature = -30 °C, reaction time = 1 hr.

The results in table 5.1 show that the molecular weight distributions for all the polymerizations are comfortably within the given criteria of 1.6. Unfortunately at high initiator concentrations the desired degree of polymerization of 20 units was not attained. Even a ratio of initiator to monomer of 10 did not lead to low molecular weight polymer at high conversion. As the initiator concentration increased from 6.67×10^{-3} mol L^{-1} to 0.1 mol L^{-1} the efficiency of initiation reduced from 85 % to 28 %. The reduction is demonstrated in figure 5.1 by plotting the initiator efficiency as a function of initiator concentration.

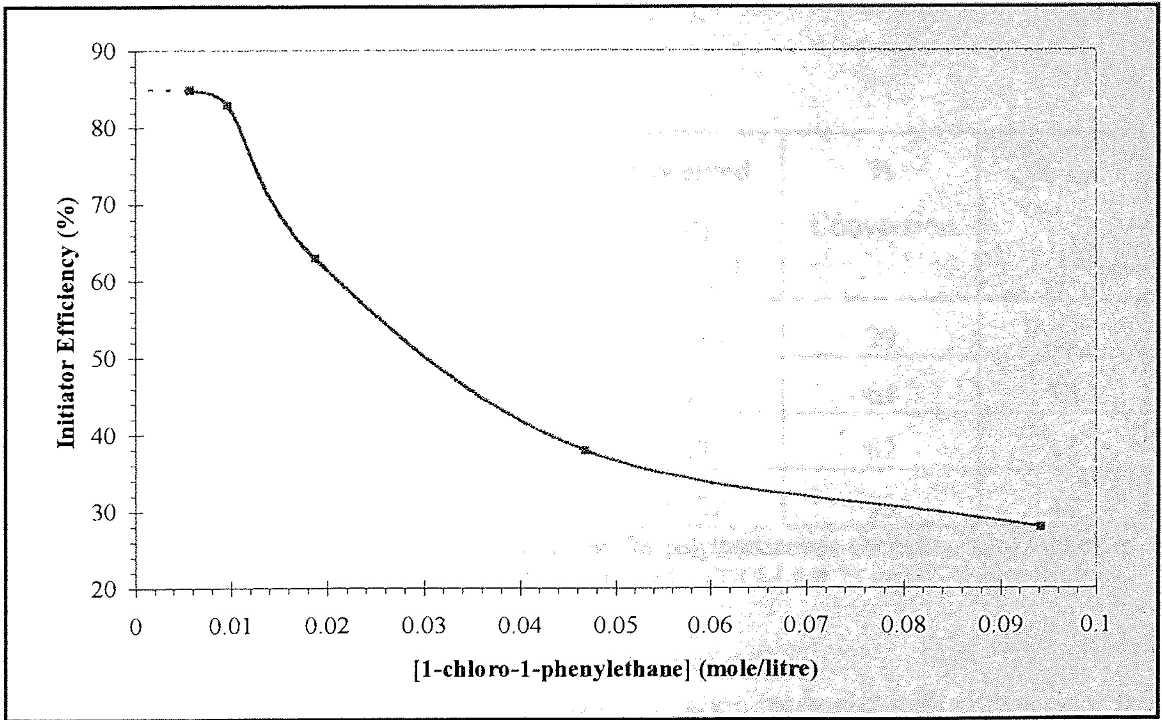


Figure 5.1. Effect of initiator concentration on initiator efficiency.

The plot shows that at molar ratios of isobutene to initiator above 100 the initiator efficiency remains above 80 %, as has been previously found in other experiments. Synthesis of polyisobutene with a degree of polymerization in excess of 100 offers little difficulty, at least until transfer reactions become important. At ratios below 100 the initiator efficiency begins to rapidly decrease to approximately 25-30 %. Thus, the propagating polymer chains attain molecular weights that are higher than predicted.

It is possible that the effective concentration of the initiator is being reduced by impurities but this is unlikely and would be expected to be more pronounced at low initiator concentrations. The most probable cause of a low efficiency of initiation is incomplete consumption of initiator i.e. slow initiation. As the concentration of initiator rises, the rate of propagation relative to that of initiation becomes significant, the monomer is consumed before all of the 1-PEC has had time to react. To establish whether slow initiation was the cause of molecular weight broadening, a series of experiments was designed to follow molecular weight as a function of conversion. Using the method described in section 2.4.1 polymerizations using a monomer to initiator ratio of 20 were allowed to go to successively increasing conversions, before being quenched with methanol. The results of these experiments and the conditions under which they were carried out under are given in table 5.2.

Reaction time (/seconds)	W_p (/g)	$\overline{M}_n$ (g mole^{-1})	MWD	Observed [P] (/mol L^{-1})	% Conversion	% I_{eff}
130	0.8	1260	1.18	0.013	29	24
300	1.6	2100	1.27	0.017	64	30
480	1.9	2210	1.22	0.021	82	35
720	2.6	2420	1.41	0.022	93	43

Table 5.2. Molecular weight as a function of conversion for polymerizations exhibiting slow initiation; [IB] = 1 mol L^{-}, [1-PEC] = 0.05 mol L^{-}, [Pyridine] = 0.03 mol L^{-}, [$TiCl_4$] = 0.75 mol L^{-}, temperature = -30 °C, 20 ml DCM, 30 ml cHex.

From table 5.2 it is apparent that the efficiency of initiation increased with conversion. It can be seen that the concentration of polymer chain ends [P] increased with time and the molecular weight distribution broadened. It must be concluded therefore that slow initiation is the factor impeding the successful synthesis of low molecular weight polymer particularly with a narrow polydispersity. The effect of slow initiation in a polymerization can also be shown by using the above data to make standard kinetic plots of molecular weight against conversion and $\ln[M_0]/[M]$ against time, as described in section 1.3.5.

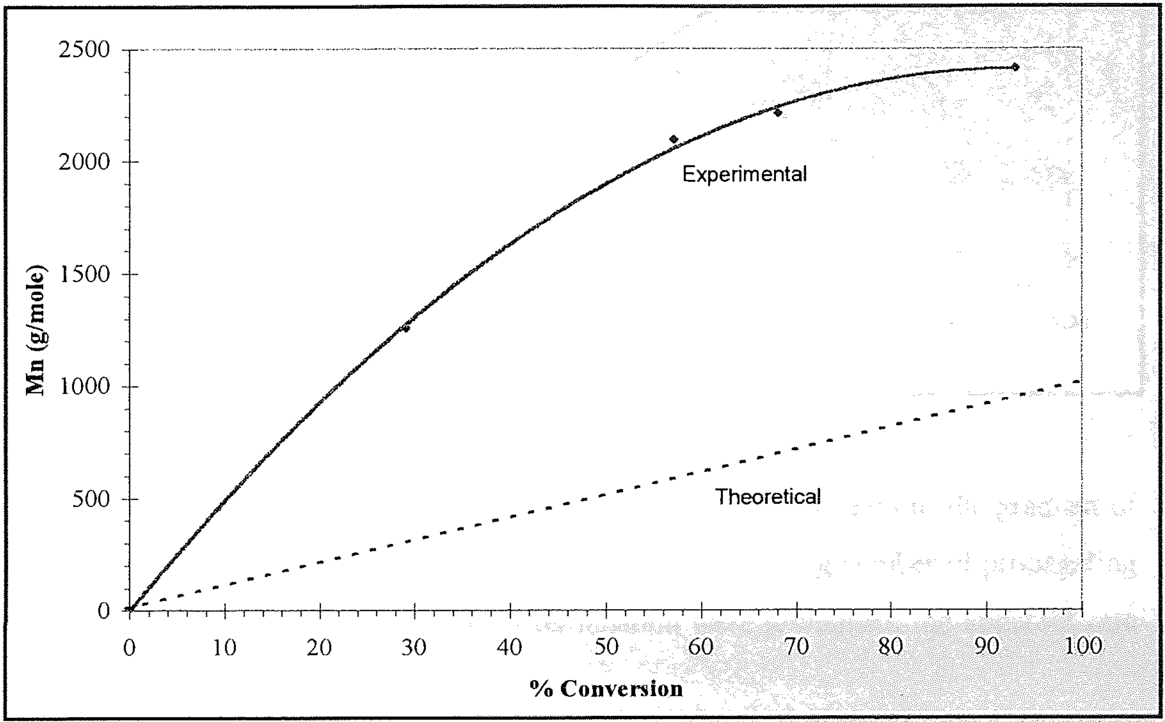


Figure 5.2. A plot of $\overline{M}_n$ against conversion.

Figure 5.2 shows a plot of molecular weight as a function of conversion and demonstrates a non-linear relationship. The non-linearity of the plot was caused by a slow increase in the concentration of propagating chains. As the concentration of chains increased the demand for monomer also rose and therefore the rate of increase of molecular weight as a function of conversion was slowed. The lower than predicted concentration of propagating species also leads to the molecular weights being higher than theoretically calculated (represented by the dash line). However, the presence of some termination would also cause higher than predicted values of molecular weight but the curvature of the relationship shows otherwise. The significance of termination can be discounted when examining a plot of $\ln[M_0]/[M]$ against time, shown in figure 5.3.

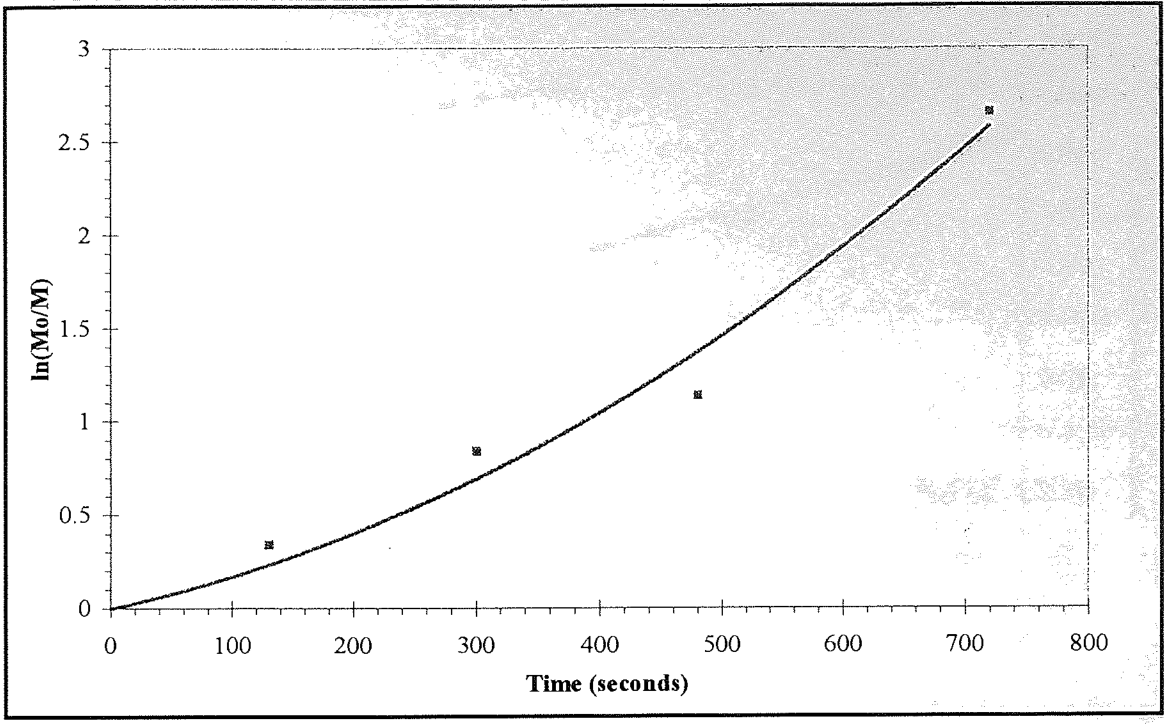


Figure 5.3. Pseudo first order kinetic plot.

Figure 5.3 demonstrates that the apparent rate constant of polymerization (the gradient of the plot) increased with time. This is consistent with an increasing number of propagating species with no significant termination. If termination were prominent, the apparent rate constant would decrease with time.

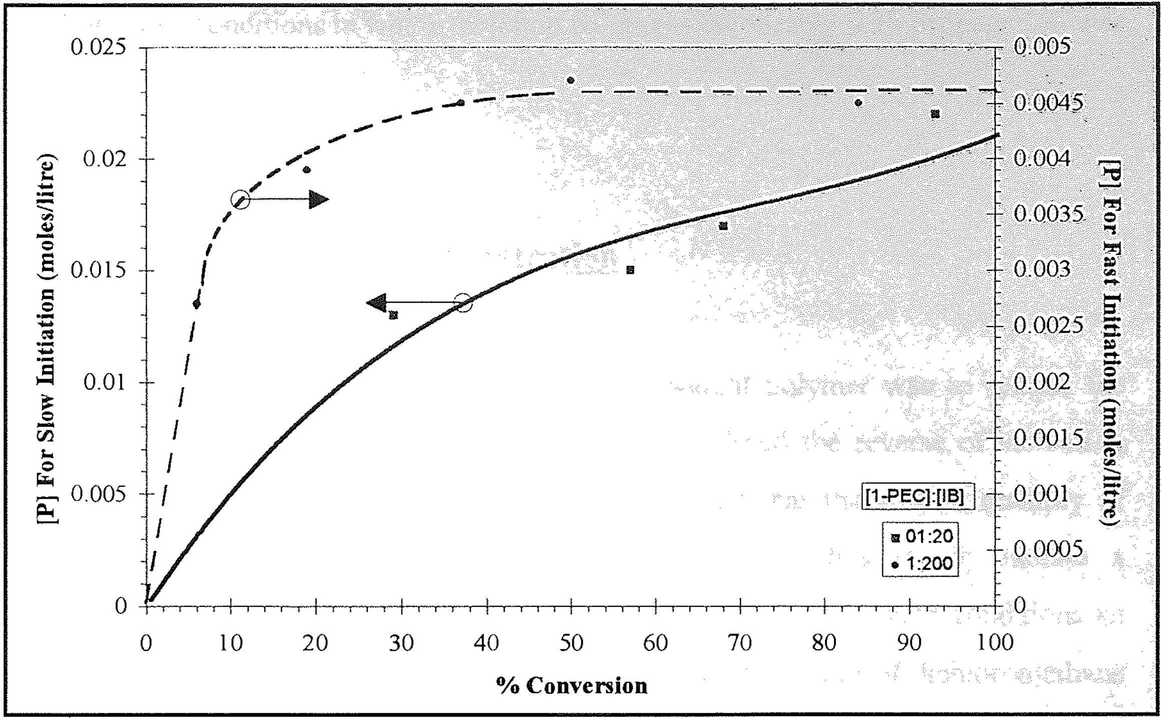


Figure 5.4. Concentration of polymer chains as a function of conversion.

The problem of slow initiation in these experiments can be compared to polymerizations in which the rate of initiation is fast relative to propagation. Figure 5.4 shows the concentration of polymer chains as a function of conversion for fast and slow initiating scenarios. The dashed line represents a polymerization with fast initiation, the results from a series of polymerizations previously described in table 3.4, in which the monomer to initiator ratio was 200. In this instance initiation was nearly complete at conversions of 20-30 %. The solid line represents the results obtained from a series of polymerizations with slow initiation that was described in table 5.2, with a monomer to initiator ratio of 20. The concentration of propagating chains in this latter case did not rise sharply, as with a fast initiating system, but steadily increased as the polymerization proceeded. At 100 % conversion initiation was still not complete.

The synthesis of low molecular weight polyisobutene ($\overline{DP}_n$ < 20) by 1-PEC/$TiCl_4$/pyridine under the described conditions was not achieved by polymerizations that were taken to complete conversion. The limiting factor in polymerizations that contain a high proportion of initiator over monomer is the slow rate of initiation, that inevitably leads to higher than predicted molecular weights. Therefore, an alternative method or set of conditions in which initiation competes favourably with propagation was required.

5.3 Reduction of monomer concentration

A different approach to synthesising low molecular weight polymer was to reduce the concentration of monomer. Such an approach was considered the reverse of increasing the concentration of initiator. However, it was anticipated that the smaller quantity of initiator would take less time to completely activate and thus rapidly initiate a polymerization. To examine the feasibility of a polymerization under such conditions an experiment was carried out at -30°C in a 40:60 v/v solvent mixture of dichloromethane and cyclohexane, using the method described in section 2.4.1. The concentration of initiator was 0.01 mol L^{-1}, pyridine 0.02 mol L^{-1} and $TiCl_4$ 0.15 mol L^{-1}, the same as that used in the more successful polymerizations described in section 3.3 . The concentration of the monomer however was reduced to 0.38 mol L^{-1} instead of 1 mol L^{-1}. The polymerization was quenched in methanol after 15 minutes to yield a polymer with an average degree of polymerization of 21 and a polydispersity of 1.21. At the time of quenching 18 % conversion had been attained and an initiator efficiency of 33 % was calculated.

The results indicate that reducing the concentration of monomer does not lead to the desired low molecular weight polymer at high conversions. The rate of initiation relative to propagation was still slow. Although the approach used was the reverse to that of increasing the concentration of initiator, the limiting kinetics of slow initiation are essentially identical to those described previously in section 5.3. The main difference in this latter experiment was a reduction in the rate of polymerization, caused by a lower concentration of reagents. Even if the method were successful it would be of limited practical use. The quantity of polymer produced from such a polymerization is small (approx. 0.5-1g) on the current experimental scale and the reaction time relatively long. Such small quantities of material would make successful sampling reactions, with which to follow the kinetics, difficult to achieve. The production of larger quantities of material would require a significant increase in the volume of the reaction vessel, being both costly and wasteful.

Variation of the monomer to initiator ratio alone has proven unsuccessful in producing low molecular weight polymer, at least under the conditions described. To attempt to optimise the relative rates of initiation and propagation it would be of value to examine the effect of the reaction conditions such as, temperature and the concentrations of pyridine and catalyst, on the polymerization. Further work will now centre on these aspects.

5.4 Modification of the initiator system

5.4.1 Mechanism of initiation

Following the previous unsuccessful attempts at synthesising low molecular weight polyisobutene, by variation of the monomer to initiator feed ratios, it was decided to focus attention on the initiator system. Using this approach attempts were made to increase the rate of initiation over that of propagation. The mechanism of initiation for the 1-PEC/$TiCl_4$/pyridine type system is shown in figure 5.5.

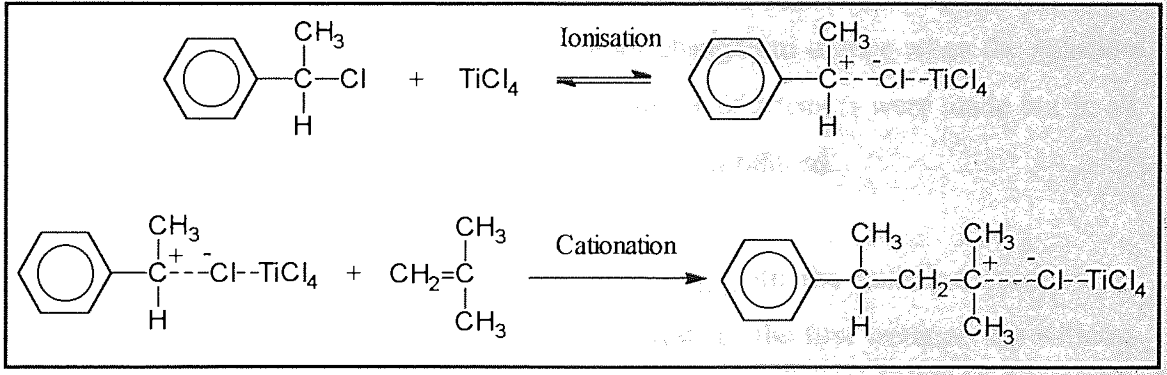


Figure 5.5. Initiation.

As has previously been discussed in the introduction (section 1.2.2a) initiation is considered to be a two step process. The first step involves the generation of a cation, ionisation, and the addition of the first monomer unit to that cation, cationation. In this instance it is so far unclear which of the two steps is rate determining. However, various techniques such as, ageing, seeding and use of more labile initiator were employed, to make one or other of these steps more favourable.. The following sections will discuss each of these techniques in detail.

5.4.2 Ageing the initiation system

If the slow rate of initiation were due to the slow establishment of the equilibrium of ionisation it may be possible to give adequate time for the process to establish itself by ageing the initiator solution before the addition of monomer. In this way a higher concentration of cations might be established before the polymerization is initiated. If the generation of cations is normally slow and rate determining, then the efficiency of initiation should be improved.

To attempt such a polymerization a modification to the batch polymerization procedure described in section 2.4.1 was required. A solution containing 2.5×10^{-3} moles of initiator and 2×10^{-3} moles of pyridine in 20 ml of dichloromethane was added to the side arm, *A*, of the polymerization vessel (figure 2.5) along with 0.038 moles of $TiCl_4$. The mixture was allowed to age at -30 °C for 5 hours before being added to 0.06 moles of monomer and 30 ml of cyclohexane in the second part of the vessel, initiating the polymerization. The reaction mixture was quenched by the addition of methanol after 35 minutes.

When the initiator, pyridine and catalyst were pre-mixed a deep red solution formed and then a yellow precipitate was observed. The colour changed to orange when the solution was added to the monomer and cyclohexane. A number of attempts were made but in all cases insignificant quantities of ill-defined polymer were produced.

It was believed that the pyridine might be interfering with the initiation reaction by combining with either the generated cation or catalyst. In the first instance the initiator might be rendered inactive and in the latter the Lewis acidity of the catalyst could be significantly reduced. Therefore, an experiment was attempted under conditions identical to those described for the previous reaction, except the pyridine was not present during the ageing process but added with the monomer.

Using this second method the polymerization went to completion and yielded a polymer with an average degree of polymerization of 43 and a polydispersity of 1.51. Evidently the presence of pyridine in the ageing process must inhibit initiation, although the exact mechanism by which it does this is unknown. The molecular weight distribution is relatively broad but is still within the criteria given earlier. The cause of the broadening is unclear, although it is likely to arise from the action of impurities in the system. The initiator efficiency was greater than a polymerization without ageing, 50 % compared to 38 %. However, if the broad molecular weight distribution is indicative of protic impurities initiating chain growth and (or) transfer is present then the functional purity of the polymer must be questioned.

5.4.3 Alternative initiator

If the ionisation equilibrium lies to the left in favour of the reagents, and is the rate determining step, then it was considered that a more labile initiator might aid the overall rate of initiation. For example, carbon-bromine bonds are weaker and therefore more readily ionisable than carbon-chlorine bonds. Thus, the equivalent bromo derivative, 1-bromo-1-phenylethane (1-PEB), would be expected to be more labile and generate cationic species rapidly. If ionisation is the rate determining step in initiation the use of 1-PEB should show an increased rate of initiation over 1-PEC. Experiments were carried out to investigate the advantages of using 1-bromo-1-phenylethane (1-PEB), shown in figure 5.6, over its more often used chloro counterpart.

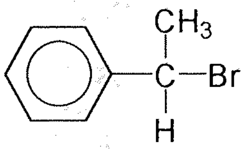


Figure 5.6. 1-Bromo-1-phenylethane.

A batch polymerization was carried out at -30°C as described in section 2.4.1, using 1-PEB instead of 1-PEC. The conditions under which the polymerization was carried out were analogous to those of previous experiments, using a 40:60 v/v ratio of dichloromethane to cyclohexane solution containing 1.1 mol L^{-1} isobutene, 0.05 mol L^{-1} 1-PEB, 0.04 mol L^{-1} pyridine, and 0.75 mol L^{-1} $TiCl_4$.

Under these conditions no polymer was produced because it is believed that there was a reaction between the 1-PEB and the pyridine. Mixing the two reagents together was found to produce a crystalline solid, whereas the chloro derivative and pyridine showed no such reaction. It is known that many bromo compounds form quaternary ammonium salts with pyridine, figure 5.7.

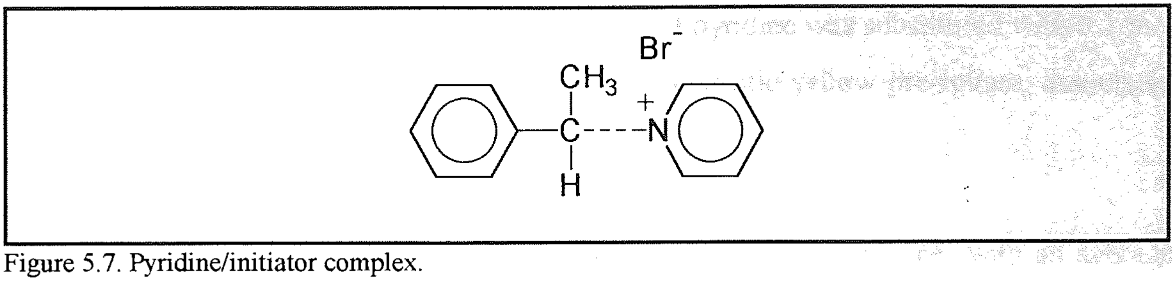


Figure 5.7. Pyridine/initiator complex.

Consequently, pyridine was not considered to be a satisfactory electron donor/proton scavenger. The problem was solved by using a sterically hindered electron donor that cannot react with the bromo initiator but can still scavenge protic impurities. An electron donor fulfilling these criteria is 2,6-di-*tert*-butyl pyridine (DtBP) shown in figure 5.8. Examining the spatial model makes it possible to envisage how the two substituent side-groups prevent large molecules from approaching the lone-pair of electrons on the nitrogen (labelled as blue in figure 5.8). However, smaller species such as H^+ may still approach.

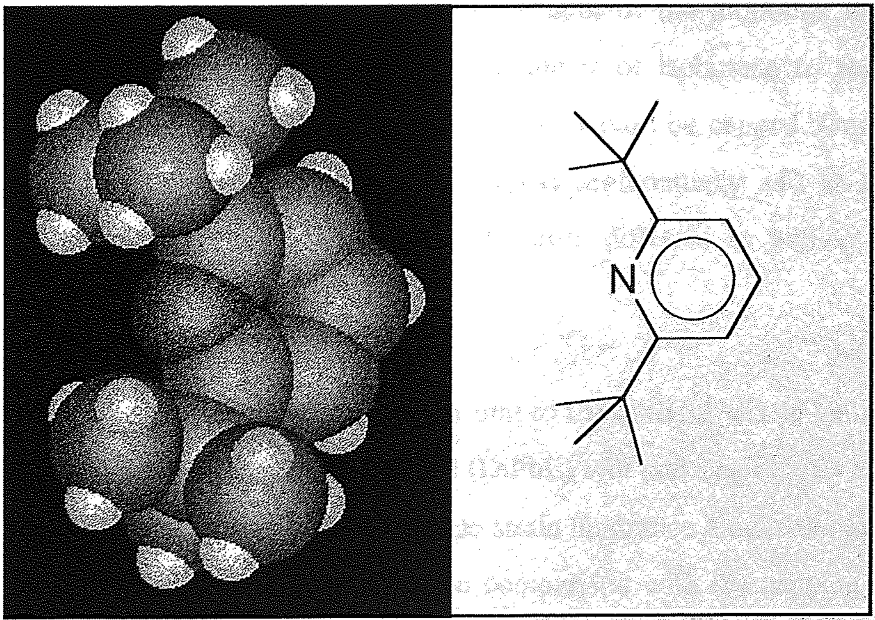


Figure 5.8. 2,6-Di-*tert*-butylpyridine.

The above electron donor has been used previously by other workers in living cationic polymerizations [74] and has been found not to co-ordinate with the catalyst but will still trap protic impurities.

A batch polymerization using 0.045 mol L^{-1} of bromo initiator was carried out at -30 °C in a 40:60 v/v ratio of dichloromethane to cyclohexane. The concentrations of reactants were 1.0 mol L^{-1} isobutene, 0.75 mol L^{-1} $TiCl_4$, and pyridine was substituted with 0.1 mol L^{-1} of DtBP. During the polymerization the characteristic yellow precipitate, associated with the pyridine, was not observed.

The polymerization was complete in 35 minutes and yielded a polymer with an average degree of polymerization of 60 and a polydispersity of 1.28. The efficiency of initiation was 37 %, which is comparable to 38 % found for 1-PEC. The desired low molecular weight polymer was not synthesised and the use of 1-PEB in this situation is not of advantage. The ease of ionisation of the bromo derivative has been clearly demonstrated by its tendency to form complexes with pyridine. Therefore, if ionisation were slow then some improvement in the initiator efficiency would be expected. It is more likely therefore that the slow step in the initiation mechanism is cationation and not ionisation.

5.4.4 Seeding technique

Seeding a polymerization involves capping the initiator species with a single monomer molecule, such that cationisation occurs before the bulk of the monomer is added. It would be of little benefit to add an equimolar quantity of isobutene to the initiator, because it is unlikely that all of the initiator molecules would be capped. Once the first few chains had started growing the monomer would preferentially add to these over newly activated initiator. The situation would be little different to adding the entire monomer batch at the start.

A potential method of adding a single monomer unit to the initiator would be by using an unpolymerizable monomer. 1,1-Diphenylethene (DiPhE) will add one unit to a generated carbocation but will not continue further because steric hindrance blocks the approach of a second molecule (section 1.4.3). Isobutene in comparison with the capping reagent is much smaller and should be able to approach the cation. The cationation step in initiation would now be as shown in figure 5.9.

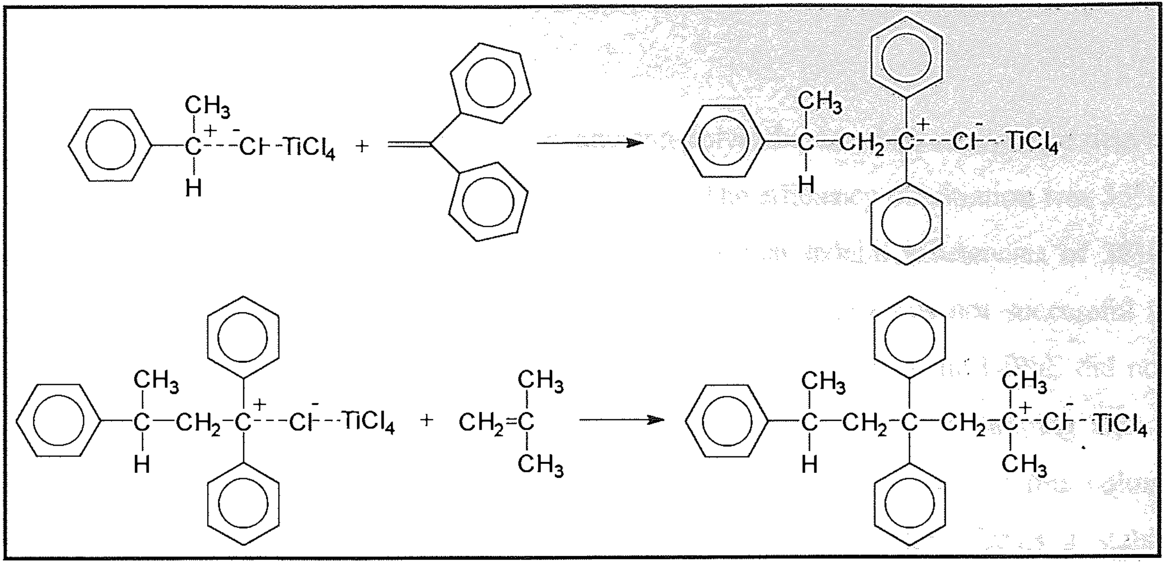


Figure 5.9. Seeding with 1,1-diphenylethane.

Such a method is expected to have a two fold effect on the polymerization. Firstly, by capping the initiator the ionisation step in initiation will be forced to completion. As the ionised products are consumed the ionisation equilibrium will be shifted to the formation of active species. Secondly the cationation step, of adding the first DiPhE unit, will also be able to go to completion, provided adequate reaction time is given. The final question will then be whether or not the isobutene adds rapidly to the cation to begin chain growth.

A polymerization was attempted using the seeding technique by making some small modifications to the procedure described in section 2.4.1. A solution of the initiator (1-PEC), catalyst and DiPhE in 20 ml of dichloromethane were prepared in the side arm of the polymerization vessel. The solution was aged for 4.5 hours, to allow all of the initiator to react, before its addition to the main chamber of the vessel containing 30 ml of cylcohexane, isobutene and pyridine. The concentrations of reactants were 0.95 mol L^{-1} isobutene, 0.05 mol L^{-1} 1-PEC, 0.05 mol L^{-1} DiPhE, 0.1 mol L^{-1} pyridine, and 0.75 mol L^{-1} $TiCl_4$.

The catalyst, initiator and capping agent turned deep red upon mixing and slowly changed to dark green as the solution was aged. The dark green colour remained when the aged solution was added to the monomer and was lost when the polymerization was quenched after 20 minutes.

The polymerization went to completion, producing polyisobutene with an average degree of polymerization of 57 and a polydispersity of 1.35. The efficiency of initiation was 33%, which is no advantage over standard polymerizations that exhibit efficiencies of 38%. There are a number of possible reasons why the seeding method was not successful in narrowing the molecular weight distribution. Firstly it is possible that the DiPhE did not cap the initiator. The dark green colour must be associated with the capping agent, because it is not observed under any other conditions. The persistence of this colour throughout the polymerization would suggest that the DiPhE either forms a stable cationic species, which fails to initiate polymerization, or a stable complex with the $TiCl_4$. In the former case, addition of an isobutene unit to a cation that is resonance stabilised by two aromatic rings would be unfavourable, since a less stable charged species will be produced. In this situation it might be expected that the rate of initiation would be slow. The two phenyl rings could also hinder the attack of isobutene sterically (figure 5.10) or provide a site for backbiting.

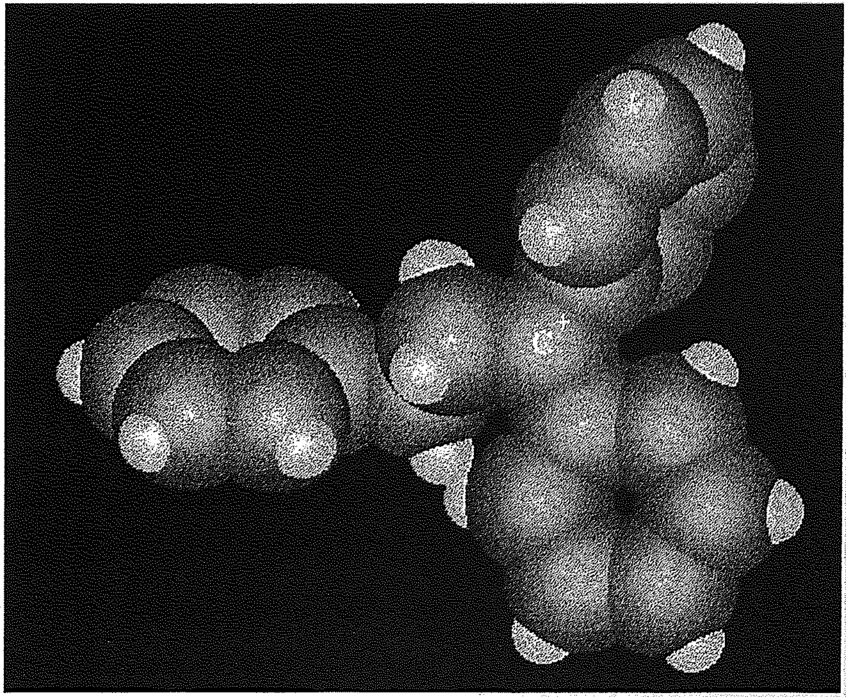


Figure 5.10. Spatial model of DiPhE capped initiator

1-PEC on its own has been shown to be susceptible to oligomer formation by the growing chain folding back upon itself and alkylating the aromatic ring (section 3.5). Given the steric constraints it would be unsurprising if the capped initiator is even more susceptible to oligomer formation.

5.5 Optimising reaction conditions

5.5.1 Optimal catalyst/pyridine concentration

In an attempt to improve the initiator efficiency experiments were designed to reduce the rate of consumption of monomer and so provide a longer period over which initiation could take place. Considering the initiation mechanism described in figure 5.1 the following rate equation may be derived:

$$R_i = k_i[M][1-PEC][TiCl_4] \qquad (5.1)$$

where k_i is a constant:

$$k_i = K_i k_{cat} = \frac{k_{ion}}{k_{col}} k_{cat} \qquad (5.2)$$

As already discussed in section 4.2, the rate of propagation may be expressed as:

$$R_p = K_p k_p [M][PCl][TiCl_4] \qquad (5.3)$$

where:

$$K_p = \frac{k_1}{k_2} \qquad (5.4)$$

It was thought that decreasing the catalyst concentration would reduce the rate of propagation, but the effect on the rate of initiation might not be as pronounced. Therefore, a series of experiments was designed to investigate the possibility that the relative rates of initiation and propagation could be controlled by adjusting the concentration of catalyst.

From experiments in section 4.4 it was found that the effective concentration of catalyst is dependent on the concentration of the pyridine. The polymerizations were thus designed such that a single catalyst concentration was chosen and its effective concentration was varied by increasing the concentration of pyridine. The method by which these experiments were performed is described in section 2.4.1 and the results are given in table 5.3.

[Pyridine] (/mol L^{-1})	$[TiCl_4]_{eff}$ (/mol L^{-1})	[IB]:[1-PEC]	% Conversion	$\overline{DP}_n$	MWD	% I_{eff}
0	0.35	25	82	-	Bi	-
0.010	0.34	17	64	46	1.45	24
0.025	0.33	26	68	43	1.41	42
0.050	0.30	20	70	38	1.27	37
0.10	0.25	18	84	29	1.25	62
0.15	0.20	15	68	35	1.27	30
0.20	0.15	20	7	19	1.19	10

Table 5.3. Effect of $[TiCl_4]_{eff}$ on I_{eff}. [1-PEC] = 0.05 mol L^{-1}, 20 ml DCM, 30 ml cHex., temperature = -30 °C, reaction time = 11 mins.

The results in the above table show that, in the absence of pyridine, an expected bimodal polymer is produced, because of uncontrolled protic initiation. The optimal effective catalyst concentration was found to give rise to a polymerization exhibiting an efficiency of initiation 62 %. This value corresponds to an initiator system with a molar ratio of 1-PEC/pyridine/$TiCl_4$ of 1/2/7. When the effective concentration of catalyst was reduced further, below the above value, the efficiency of initiation dramatically lowered. This was presumably caused by a greater decline in the rate of initiation over that of propagation.

5.5.2 Optimal temperature

The rate constants given in section 5.5.1 are all dependent on temperature. It was thought that there might be a temperature at which the relative rate of initiation would be optimised over that of propagation.

Previous experiments described in section 3.5 showed that the efficiency of initiation decreases at temperatures below -40 °C. Thus, it was believed that studying polymerizations below -40 °C would not provide increased efficiencies of initiation in these experiments. However, it is also known that the rate of polymerization slows as temperature increases. Therefore, at temperatures above -40 °C it may be possible to slow the rate of propagation more than that of initiation. The efficiencies of initiation in polymerizations using the optimal initiator system ratio (previous section) were evaluated at temperatures between -10 °C and -40 °C. The conditions of polymerization are given in table 5.4 and the procedure has been described in section 2.4.1.

Temperature (/ °C)	[IB]:[1-PEC]	% Conversion	$\overline{DP}_n$	MWD	% I_{eff}
-10	17	30	17	1.33	30
-20	24	36	25	1.34	36
-30	20	86	32	1.26	54
-40	17	78	49	1.19	27

Table 5.4. Effect of temperature on I_{eff}. [1-PEC] = 0.05 mol l^{-1}, [Pyridine] = 0.010 mol l^{-1}, [$TiCl_4$] = 0.35 mol l^{-1}, 20 ml DCM, 30 ml cHex., reaction time = 11 mins.

The results in table 5.4 show that, as predicted, the efficiency of initiation decreases at -40 °C to below 30 %. At temperatures above -30 °C the efficiency also lowers, from 54 % to 30 %. Therefore, the optimal temperature indicated by these experiments is -30 °C. The polymerization at this temperature is effectively a repeat of the optimal polymerization found in the previous section. The efficiency of initiation was lower than previously found. The cause is unknown but can likely be attributed to the cleanliness of the polymerization.

Chapter 6: End-functionalisation of polyisobutene

6.1 Phenol end-capping

6.1.1 Introduction

Polyisobutene chains that have phenol end-groups are useful precursors in the additives industry. It was of interest therefore to attempt the synthesis of phenolated polymers by making use of the Friedel-Crafts conditions that are present in the polymerization reaction. If successful this approach could then lead to a one-pot synthesis route to functionalised polymers. Phenolation has only been achieved hitherto by a two pot process. Kennedy pioneered the technique with a polymerization of isobutene initiated by a blocked cumyl chloride in the presence of BCl_3 and N,N-dimethylacetamide (DMA) [91]. The chloride end-capped polyisobutene ($\overline{M}_n$ = 4100, MWD = 1.29) was then purified and a Friedel-Crafts alkylation carried out in a second step as shown in figure 6.1. The reaction was catalysed by boron trifluoroetherate ($BF_3.OEt_2$) in hexane.

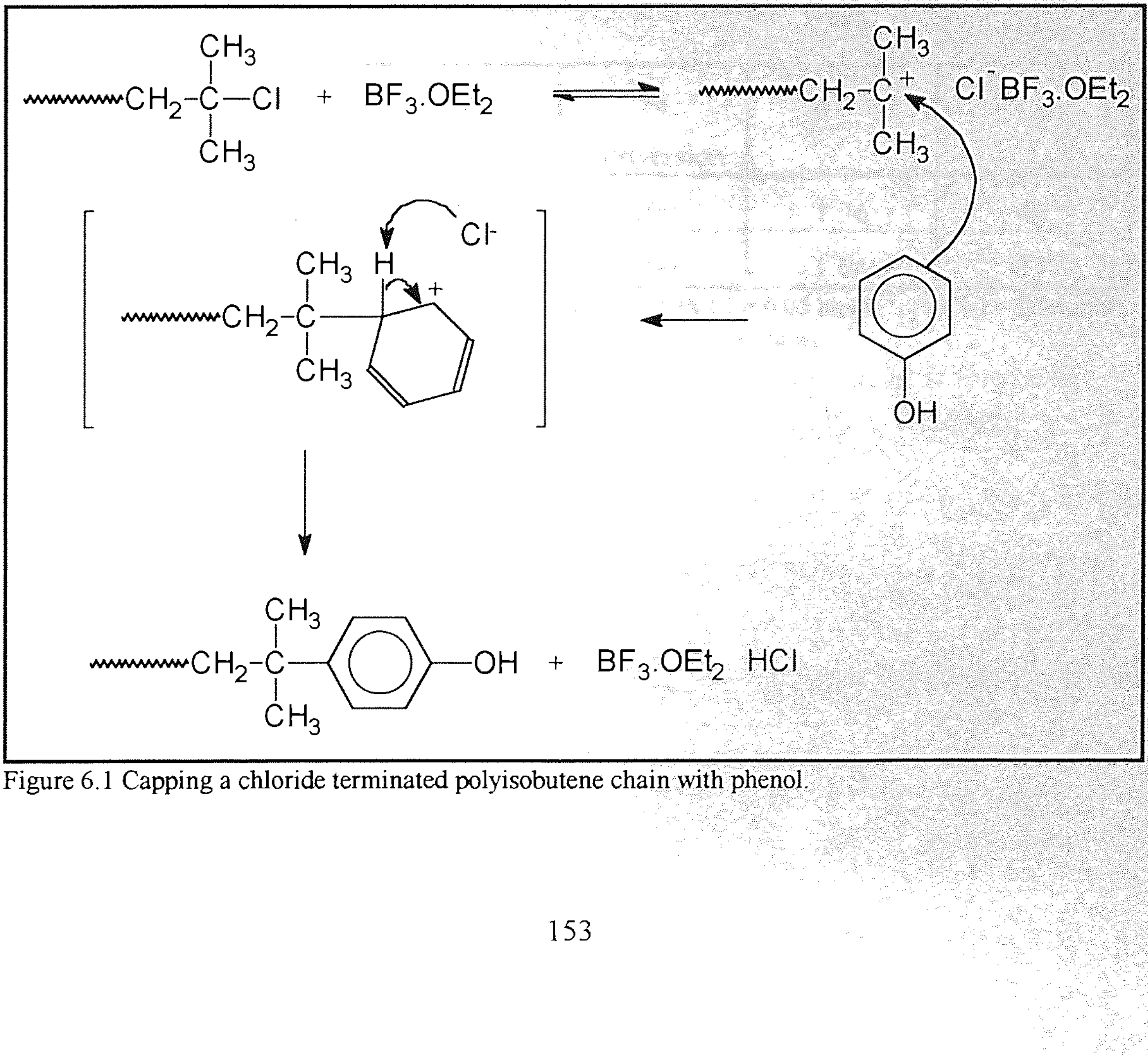


Figure 6.1 Capping a chloride terminated polyisobutene chain with phenol.

The structure of the telechelic polymer was derived from analysis of the ^{1}H-NMR spectrum, which showed aromatic doublets at 7.2 and 6.7 ppm. No evidence was found for the presence of $-CH_3$ groups adjacent to a terminal chloride and so it was concluded that complete functionalisation had occurred.

6.1.2 Polymerization and phenolation

The potential application of the functionalised polymer required the synthesis of a polymer with a $\overline{DP}_n = 20$. Such polymers are of sufficiently short chain length for NMR to be used as a technique to analyse end groups. Therefore, the polymerization was performed under the optimal conditions described in the previous chapter for the synthesis of low molecular weight polyisobutene. The experimental procedure was similar to that used for a batch polymerization, but before quenching the reaction phenol was added, and the system was then refluxed as described in section 2.4.4. To help ensure that each aromatic ring was alkylated by only one chain the phenol was added in molar excess to the initiator. Two experiments were attempted using identical procedures, the results from which are given in table 6.1 and figure 6.2.

[IB]/[1-PEC]	[Pyridine] (/ mol L^{-1})	$\overline{DP}_n$	% Conversion	MWD	% I_{eff}
18	0.03	45	100	1.36	40
20	0.15	26	100	1.64	77

Table 6.1. Polymerization followed by the addition of phenol. [1-PEC] = 0.05 mol L^{-1}, [$TiCl_4$] = 0.36 mol L^{-1}, 20 ml DCM, 30 ml cHex., temperature = -30 °C, reaction time = 15 mins.

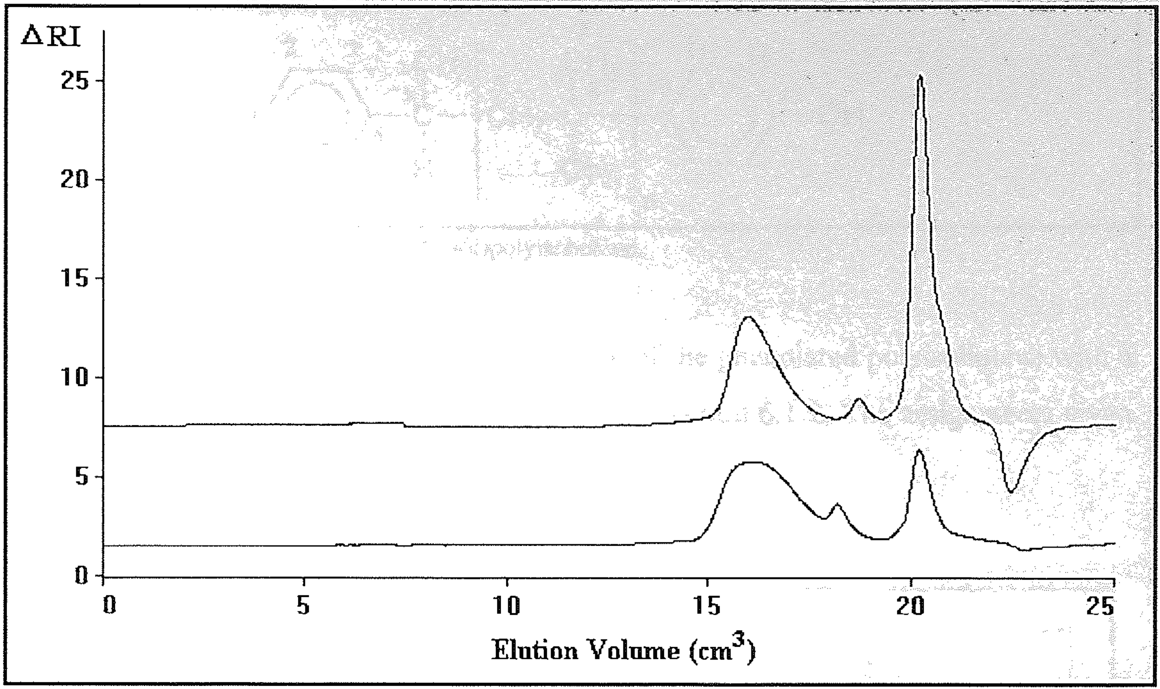


Figure 6.2. GPC traces of phenolated polymer.

From table 6.1 it can be seen that both polymerizations went to completion, but the second had a considerably lower molecular weight. The molecular weight distribution of the second polymer was also much broader and it is unclear whether the increase in polydispersity occurred during the polymerization or the subsequent phenolation. In both experiments the GPC traces show the presence of oligomeric material. The structures of the polymers were determined by NMR, which is discussed in section 6.1.3.

6.1.3 NMR characterisation of modified polyisobutene

The success of the functionalisation procedure was evaluated by using NMR techniques that have been previously described in section 2.6.2. The target telechelic polymer is shown in figure 6.3 and is referred to when analysing the subsequent spectra. In accordance with Kennedy's work the structure given displays functionalisation at the para position of the phenol. However, the phenolic hydroxy group is known to be equally para and ortho activating. Therefore, it is possible for some ortho isomer to be also produced.

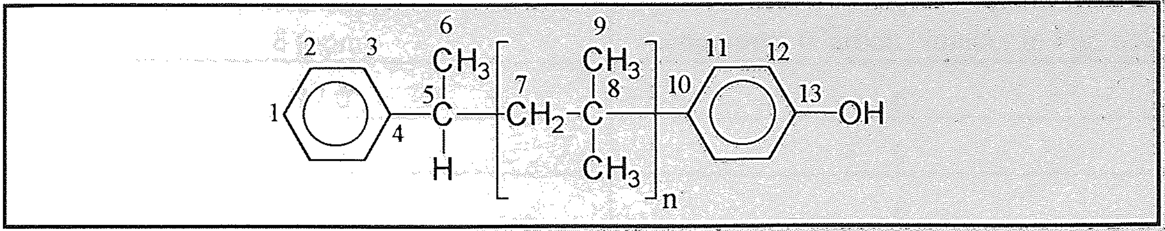


Figure 6.3. α-(1-phenylethyl)-ω-(*para*-phenol)polyisobutene.

Figure 6.4 shows the ^{13}C-Pendant NMR spectrum of the phenolated polyisobutene with a degree of polymerization of 26 that was prepared in section 6.1.2. The assignments given to the resonances are shown in table 6.2.

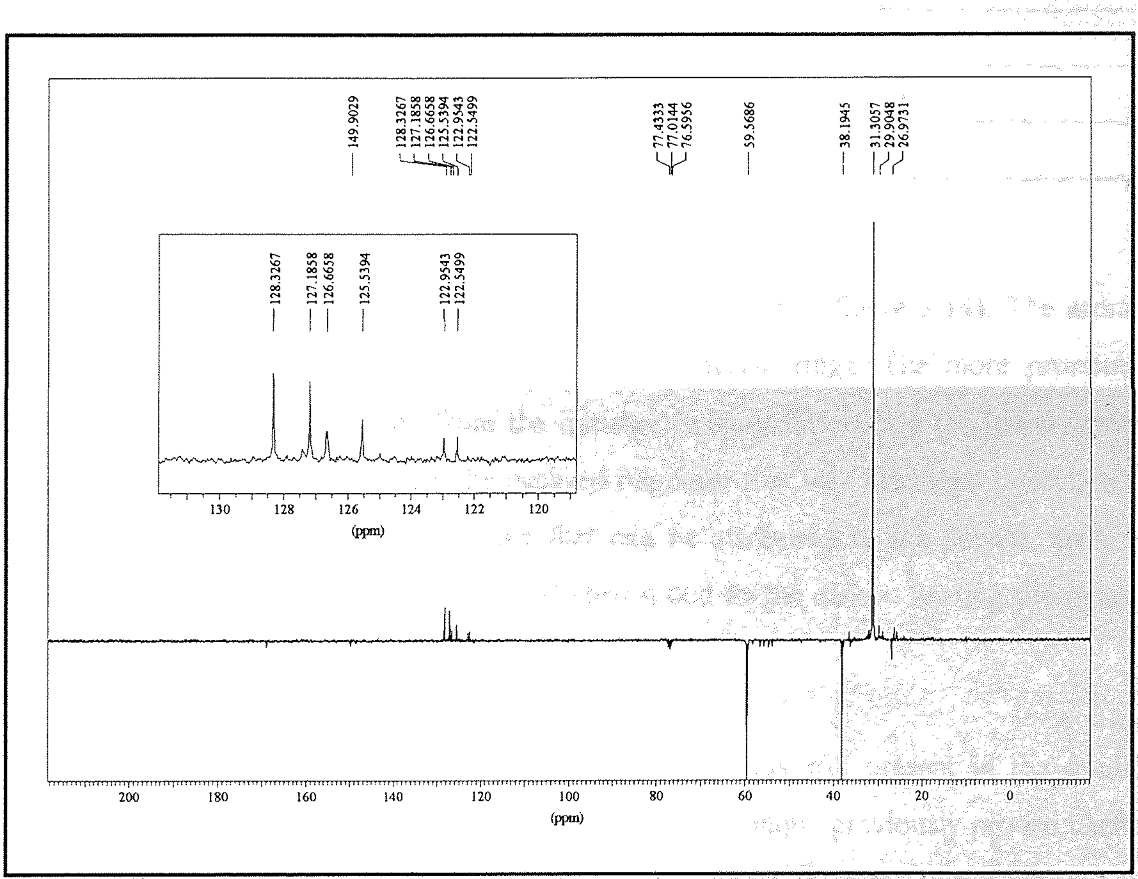


Figure 6.4. ^{13}C-Pendant NMR of phenolated isobutene

δ (ppm)	Assignment (Carbon Number in Fig. 6.4)
27.0	6
31.3	9
38.2	8
59.6	7
76.6 - 77.4	$CDCl_3$
122.5	Oligomer
123.0	Oligomer
125.5	1
126.6	Oligomer
127.2	3
128.3	2
149.9	4

Table 6.2. ^{13}C-NMR assignments of the NMR given in figure 6.4.

The spectrum is very similar to that of the original polymer (figure 3.14). The aromatic region once again shows the presence of two different rings. The more pronounced resonances are believed to be from the initiator functionality, while the lower intensity peaks correspond to those from the cyclised oligomer that was discussed in section 3.6. There are no signs of any resonances that can be attributed to the phenol, such as a negative signal at 155 ppm which would correspond to the carbon bearing the hydroxyl group [91].

In an attempt to find whether the chloride end-cap was still present in the modified polymers the ^{13}C-SPEED NMR was examined. The technique previously proved useful in identifying the quaternary carbon adjacent to the terminal chloride atom (section 3.6.4). Figure 6.5 shows the ^{13}C-SPEED NMR spectrum of a polymer obtained in this series of experiments.

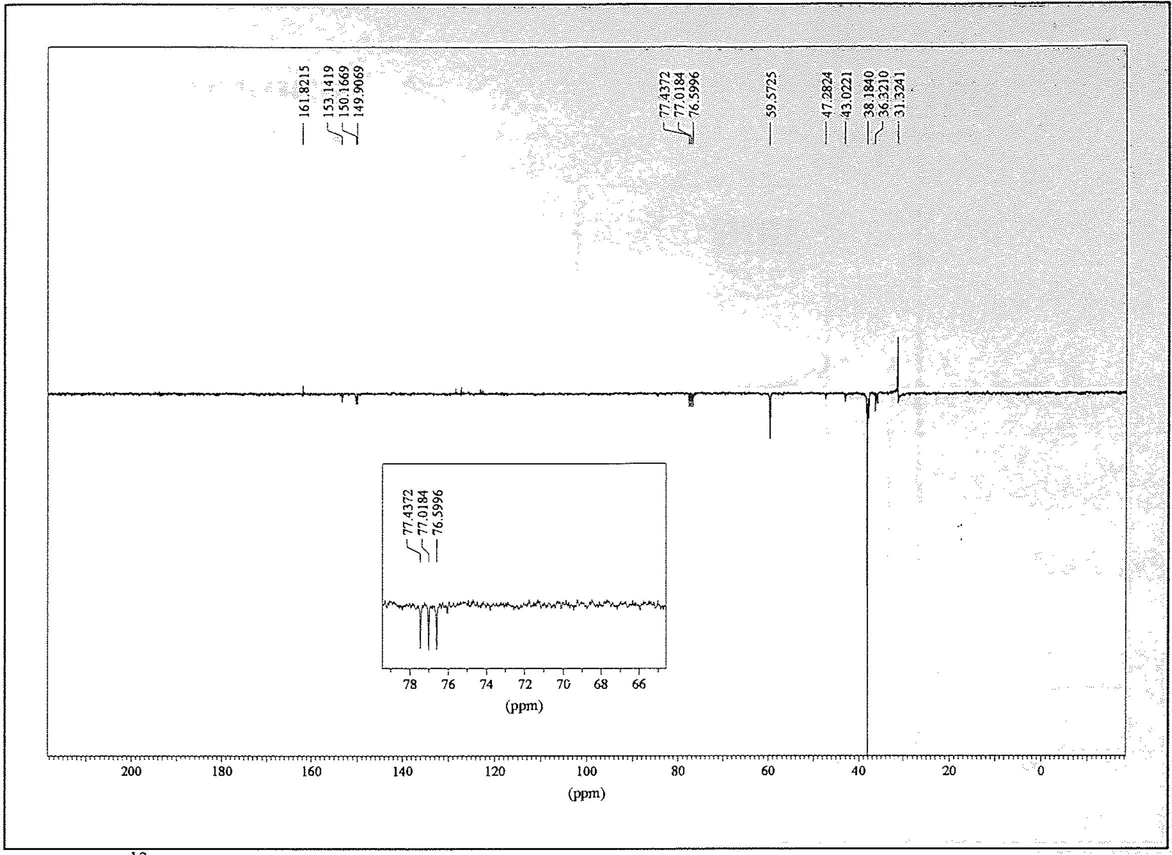


Figure 6.5. ^{13}C-SPEED NMR of polyisobutene.

The most significant feature of the above spectrum is the absence of a resonance at 71.6 ppm which would have been assigned to a quaternary carbon adjacent to a chloride. Therefore, the spectrum would suggest that the terminal functionality is no longer chloride. However, no indication as to the true terminal group can be found either.

^{1}H-NMR is the technique most commonly used to detect the functionality of polyisobutene. Figure 6.6 shows the spectrum from the phenolated polymer. The assignments of which are given in table 6.3.

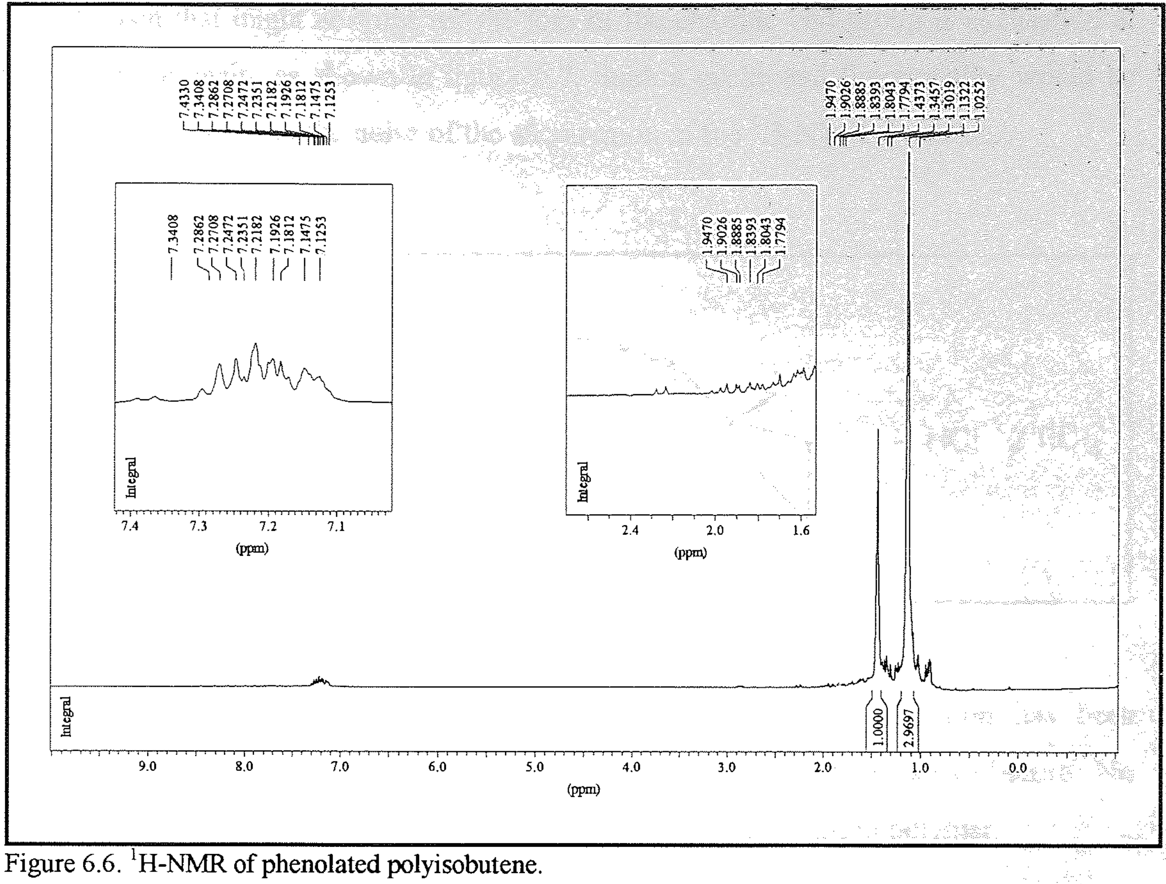


Figure 6.6. ^{1}H-NMR of phenolated polyisobutene.

δ (ppm)	Multiplicity	Assignment
1.15	singlet	$-CH_3$ on polymer backbone
1.45	singlet	$-CH_2$ on polymer backbone
7.1-7.4	multiplet	Aromatic Initiator Function

Table 6.3. ^{1}H-NMR assignments given to the spectrum of phenolated polyisobutene.

Resonances at 1.7 and 1.98 that respectively originate from terminal $-CH_3$ and $-CH_2-$ groups adjacent to a -Cl are not present in figure 6.6. The absence of such resonances suggests that the natural terminating functionality of the polymer has been altered. However, the poor resolution in the aromatic region makes quantitative analysis of the actual end functionalities extremely difficult. Nevertheless, the spectrum in the aromatic region is almost identical to that of unfunctionalised polymer, suggesting that capping did not occur. Further, there is no signal observed at around 5.7 ppm, which would be expected from an aromatic -OH group. Thus the ^{1}H-NMR spectrum shows that the terminal functionalities of the polymer are neither chloro or phenol and can offer no alternative.

A mechanism that might account for the loss of the chloride end-group is cyclisation at the end of the chain, as shown in figure 6.7. Such a cyclic end functionality would be difficult to distinguish in the noise of the alkyl region of the ^{1}H-NMR spectrum.

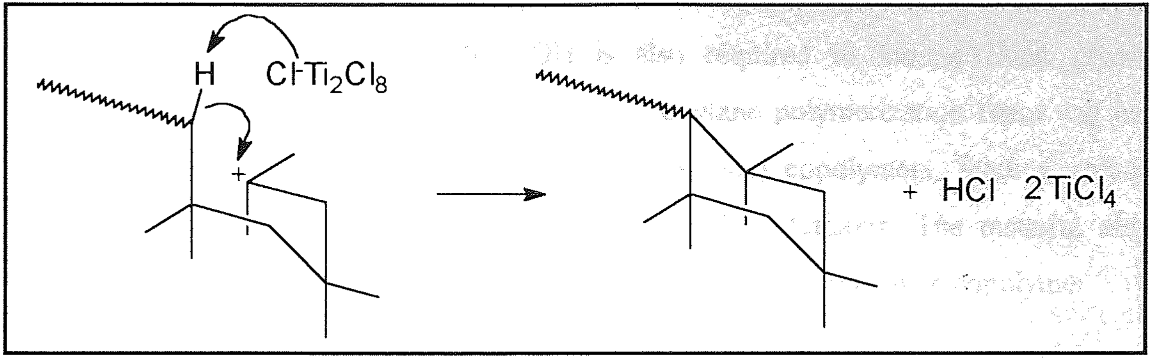


Figure 6.7. Mechanism of cyclisation at the end of the chain.

The available spectroscopic evidence suggests that the terminal function has been transformed from a chloride but the identity of the true end-cap remains obscure. No indication was found to support the existence of phenol functionalised polymer.

6.2 Oxetane end-capping

6.2.1 Introduction

A primary alcohol is a desirable end-function for a polyisobutene chain. Such a group would facilitate subsequent reactions that are not normally possible with chloride termini. The synthesis of polymers with novel terminal groups might then be possible. One conceivable method of introducing an alcohol functionality would be to cap the chain with oxetane and then quench with water as shown in figure 6.8.

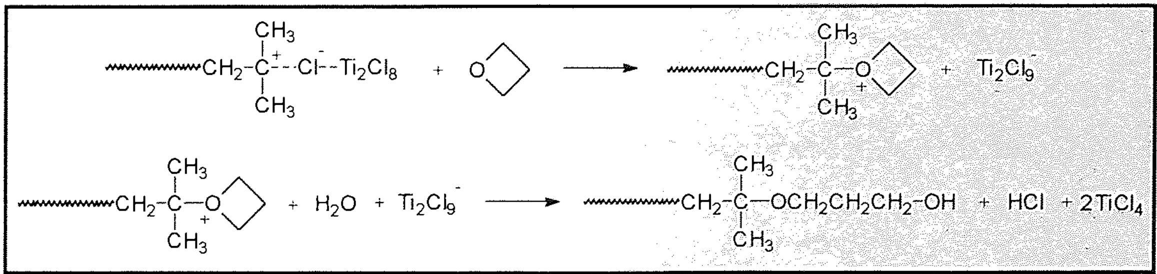


Figure 6.8. Capping living PIB chain with oxetane and quenching with water.

Oxetane is recognised to polymerize under cationic conditions similar to those employed in the polymerization of isobutene [147]. The monomer has been found to undergo onium ring opening polymerization in the presence of various Lewis acid catalysts, BF_3, BF_3OEth_2, $SnCl_4$, $SbCl_5$, $AlCl_3$, $FeCl_3$, and PF_5. Normally the presence of a co-catalyst such as H_2O, ROH, HX or MeCOOH is also required to initiate chain growth. Therefore, if the living isobutene chain initiates oxetane polymerization there will be a distinct possibility of forming poly(isobutene-b-oxetane) copolymers. Such a polymer would be expected to exhibit interesting physical characteristics. The material might possess both hydrophobic and hydrophilic regions and be an amphiphilic copolymer.

If oxetane polymerization is initiated the reaction conditions will have to be carefully manipulated to produce the desired alcohol termini. It would be difficult to add a single oxetane unit onto the polyisobutene chain, but addition of short blocks may be possible. Under the conditions used for the polymerization of isobutene it is unlikely that the oxetane will polymerize in a living manner. Control of chain length would then be troublesome and the production of oxetane homopolymer a matter for concern. However, if some control can be gained, there is potential for the synthesis of novel materials.

6.2.2 Homopolymerization of oxetane

First attempts focused on the homopolymerization of oxetane under conditions identical to those used for isobutene. The ability of the initiator 1-PEC/$TiCl_4$/pyridine system to polymerize oxetane was evaluated. Two reactions with different concentrations of initiator were attempted, using the method described in section 2.4.1. Each polymerization was carried out at ambient temperature and allowed to continue for 1 hour before quenching with excess methanol. The conditions used are given in table 6.4.

DCM ($/cm^3$)	cHex. ($/cm^3$)	[Oxetane] ($/mol\ L^{-1}$)	[1-PEC] ($/mol\ L^{-1}$)	[Pyridine] ($/mol\ L^{-1}$)	[$TiCl_4$] ($/mol\ L^{-1}$)
20	30	0.34	0.0032	0.0068	0.05
20	30	0.34	0.0062	0.0140	0.10

Table 6.4. Homopolymerization of oxetane; temperature = 16 °C, reaction time = 1 hour.

No polymer was isolated from either of these reactions. It may be that the initiator was ineffective and that any carbocations generated do not complex with the oxetane to form onium ions. This ability will be influenced by the Lewis acidity of the $TiCl_4$ and the strength of Cl^- as a base. If the catalyst does not adequately ionise the initiator the polarised chloride-carbon bond may be too strong for the oxetane to break. Furthermore, assuming the onium ion is generated, a weak catalyst may not facilitate the ring opening of the monomer to cause polymerization. The presence of pyridine might also be detrimental. The electron donor could prevent propagation by stabilising the onium-ion and delocalising the cationic charge.

To establish some understanding of the inactivity of the system, a polymerization was carried out under the same conditions as the second experiment in table 6.4, but without pyridine and using ethanol as initiator. Alcohols have been extensively used to initiate ring opening polymerizations of cyclic ethers. If polymerization occurs under these conditions then the inactivity of the systems in table 6.4 can be attributed either to the pyridine or 1-PEC.

No polymer was isolated from the polymerization and therefore the inactivity of the system in previous experiments cannot necessarily be attributed to the initiator, 1-PEC, or pyridine. The constituents remaining unchanged are the solvent and catalyst. The catalyst almost certainly generated H^+ when combined with ethanol, which was expected to initiate the polymerization. However, propagation is not being promoted, which could be ascribed to the catalyst combination not reacting to open the oxetane ring. A stronger acid, such as BF_3OEt_2, would be expected to promote the formation of species with higher charge densities thus making ring opening more likely, polar solvent systems also promote the formation of charged species. The generated cations in polar solvents will be better stabilised by solvation and their rate of formation increased. The use of pure dichloromethane would then increase the rate of polymerization.

The difficulties of polymerizing oxetane by the isobutene system show that a one pot block copolymerization is unlikely to be possible. However, the opportunity to block copolymerize the monomers in two distinctive steps still remains, but for the moment is out of the scope of this project.

6.2.3 End-capping polyisobutene with oxetane

From the results gained in the previous section, copolymerization using the 1-PEC/$TiCl_4$/pyridine system appears to be improbable. If the propagating cation is being capped with an oxetane, but does not lead to ring opening, then it might be still possible to cap the isobutene chain with a single unit. Such a reaction was attempted by first polymerizing the isobutene at -30 °C for 40 minutes according to the method described in section 2.4.3. A sample was removed by the Omnifit technique and quenched for GPC analysis. The vessel was then allowed to warm to ambient temperature, before the oxetane was injected by the Schlenk technique. The reaction was allowed to continue for a further 20 minutes before quenching with 'wet' DCM. The experimental data for the reaction is given in table 6.5 and the GPC traces are shown in figure 6.9.

IB polymerization (-30 °C)				Oxetane polymerisation (16 °C)		
[1-PEC] (/mol L^{-1})	[IB] (/mol L^{-1})	$\overline{DP}_n$	MWD	[Oxetane] (/mol L^{-1})	$\overline{DP}_n$	MWD
0.017	0.75	81	1.48	0.34	88	1.39

Table 6.5. Copolymerization of isobutene and oxetane (1). [$TiCl_4$] = 0.26 mol L^{-1}, [Pyridine] = 0.034 mol L^{-1}, 20 ml DCM, 30 ml cHex.

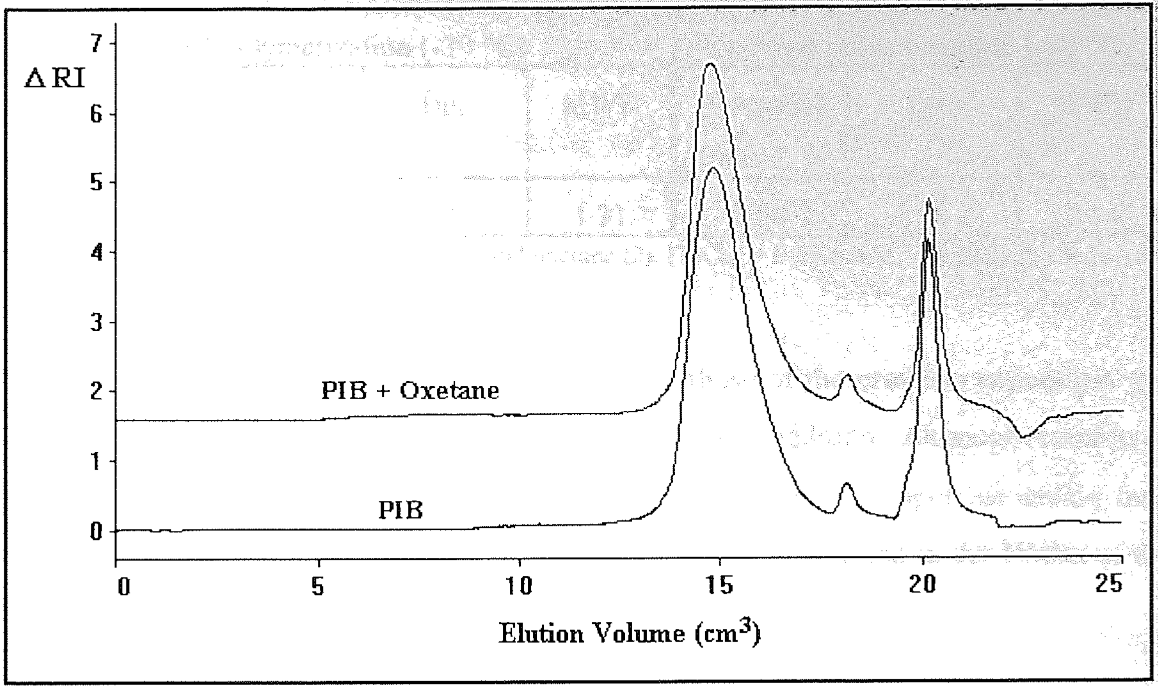


Figure 6.9. GPC traces before and after oxetane addition.

The GPC traces in figure 6.9 of the polymer taken before and after the addition of oxetane are very similar. However, as shown in table 6.5, there was a small increase in $\overline{DP}_n$ of 7 after the oxetane has been added and allowed to react. Unfortunately neither polyisobutene or polyoxetane are absorbent in the UV, so the extent of any copolymerization can not be assessed by comparison of UV and ΔRI GPC traces.

The increase in $\overline{DP}_n$ is not very significant and may be largely explained by GPC errors or continued isobutene polymerization. Any copolymerization or end-capping that has occurred should be detectable by NMR analysis of the polymer, and is dealt with in subsequent sections.

One concern with the above methodology was that the reaction was warmed before addition of oxetane. It has already been shown that the polymerization is not living at higher temperatures. The isobutene chain carriers may transfer and terminate under such conditions, hindering the capping reaction. In the following experiment the oxetane was added and polymerized at -30°C. The experimental data is given in table 6.6.

IB polymerization (-30 °C)				Oxetane polymerization (-30 °C)		
[1-PEC] (/mol L^{-1})	[IB] (/mol L^{-1})	$\overline{DP}_n$	MWD	[Oxetane] (/mol L^{-1})	$\overline{DP}_n$	MWD
0.017	0.46	51	1.31	0.34	58	1.34

Table 6.6. Copolymerization of isobutene and oxetane (2). [$TiCl_4$] = 0.26 mol L^{-1}, [Pyridine] = 0.034 mol L^{-1}, 20 ml DCM, 30 ml cHex.

The GPC traces (not shown) were very similar to those of the previous experiment and there was a small increase in $\overline{DP}_n$ after the oxetane addition. Although considered unlikely, and certainly not significant, it is unclear whether any copolymerization took place. The possibility of end-capping still remains and was assessed in the NMRs of the polymer.

6.2.4 NMR spectrum of oxetane capped polyisobutene

The polymers synthesised in the two reactions in the previous section have identical NMR spectra, despite the different experimental methods. Therefore, only one set of data is given treatment in this section, but the analysis is applicable to both experiments. The techniques used for NMR characterisation are described in the experimental section 2.6.2.

The ^{13}C-PENDANT NMR of the polymers (not shown) is identical to that of the chloro end-capped PIB described in section 3.6.2. There are no resonances corresponding to an oxetane unit which would be expected to show at 40 and 69 ppm for the -CH_2- and -OCH_2- groups respectively.

To detect the presence of any chloride end-caps the technique of ^{13}C-SPEED NMR was used and is shown in figure 6.10.

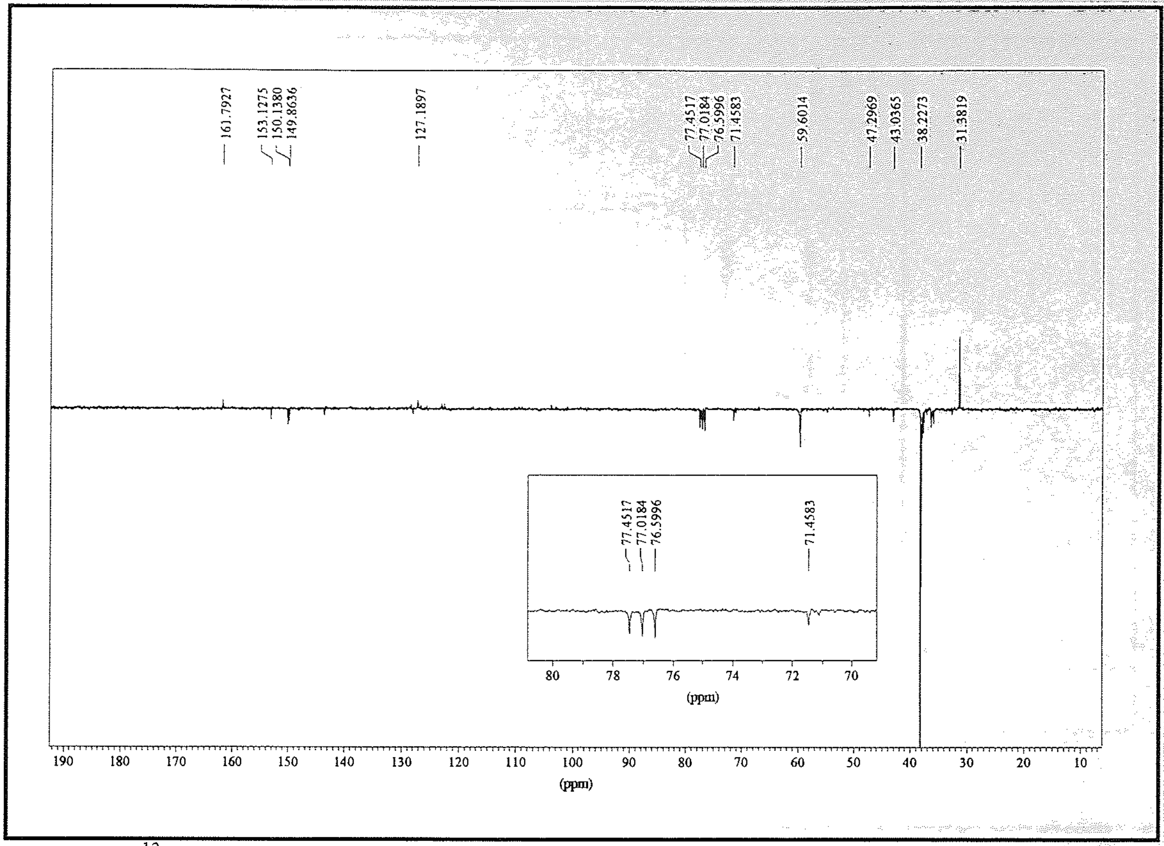


Figure 6.10. ^{13}C-SPEED NMR of oxetane capped polyisobutene.

The spectrum gives a little more information than the PENDANT, in that a resonance at 71.5 ppm is clearly visible. This suggests a chloride end-cap. However, the intensity of the peak is reduced when compared to that of the fully functionalised chloride end-capped polyisobutene in section 3.6.4. Therefore, it can be concluded that at least some of the polyisobutene chains still possess chloride functionalities. None of the ^{13}C spectra provide any evidence to support the presence of oxetane capped chains. It is a possibility that the number of carbon atoms from the oxetane were too few to see, because the NMR was not sensitive enough.

^{1}H-NMR analysis provided more information about the oxetane capped polymers. The spectrum of the polymer is shown in figure 6.11.

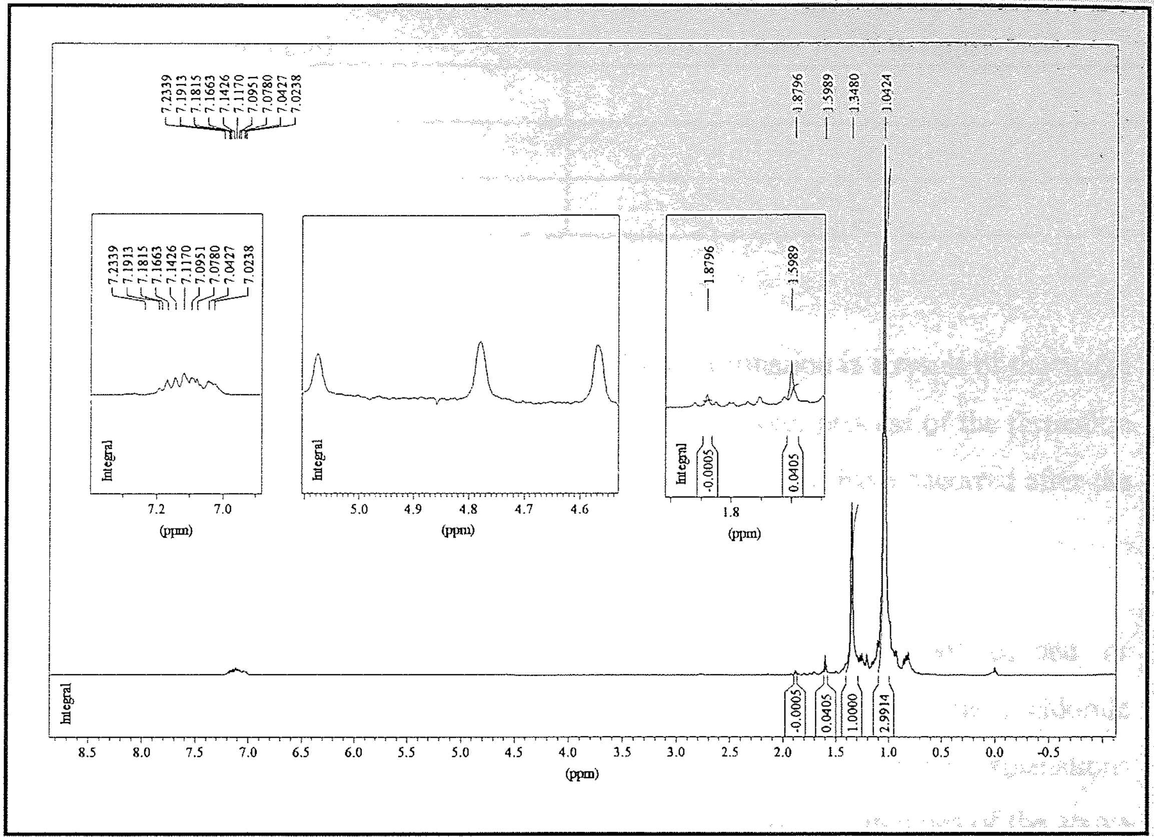


Figure 6.11. ^{1}H-NMR of oxetane capped polyisobutene.

The singlets at 1.6 and 1.9 ppm in figure 6.11 can be assigned to -CH$_3$ and -CH$_2$- groups adjacent to a terminal chloride. The ratios of the end-cap peak areas to those in the backbone are similar to that of a chloride end-capped polymer. Also faintly visible in the above spectrum are three singlets, in the region 4.5-5.1 ppm. These correspond to vinylic termini. The presence of two different types of vinylic end group (figure 6.12) would account for the three resonances.

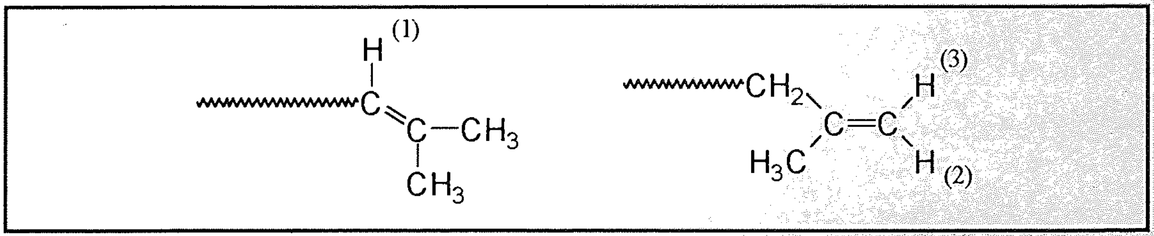


Figure 6.12. Structure of vinyl capped polyisobutene.

The assignments of the vinylic hydrogens to the resonances in figure 6.11 are given in table 6.7 [148].

δ (ppm)	Assignment to ^{1}H in figure 6.10
5.08	1
4.78	3
4.57	2

Table 6.8. Assignments of vinylic hydrogens.

Vinyl end-groups are characteristic of transfer and their formation is a result of the acidic nature of the β-hydrogen atoms (see section 1.2.1c). The exact process of the formation of vinyl groups in the above experiments is unclear but is likely to have occurred after the addition of oxetane by proton abstraction.

The available spectroscopic evidence indicates that oxetane has not capped or copolymerized with the isobutene. The synthesised polymer contains largely chloride termini with some vinylic contamination. There are a number of possible explanations why the capping reaction proved unsuccessful. It is known that the lifetimes of the active species in living polymerizations of isobutene are very short. Under such conditions the oxetane may not be given enough time to react with the active chain-end, similar to the case of transfer and termination reactions. Steric crowding around the chain end may also prevent reaction by blocking the approach of the comparatively bulky oxetane ring.

Chapter 7: Conclusions and further work

7.1 Conclusions

The work presented in this document investigated the polymerization of isobutene with emphasis placed upon living and controlled systems. The polymerization of isobutene conducted in dichloromethane at -30 °C, initiated by 1-chloro-1-phenylethane and $SnCl_4$ in the presence of tetrabutyl ammonium chloride was studied. Increasing the concentration of salt was found to reduce rates of conversion and molecular weight distributions, but increased the efficiency of initiation to over 100%. The increased efficiency of initiation was explained by the tetrabutyl ammonium chloride behaving as a chain transfer agent, which resulted in molecular weights being lower than theoretical. Molecular weight distributions of 1.46 were considered relatively broad, and it was decided that under the given conditions the system was not suitable for polymerizing isobutene in a controlled, living manner.

Polymerizations that used $TiCl_4$ instead of $SnCl_4$ were found to produce polymers with narrower molecular weight distributions, typically between 1.28 and 1.40, and the efficiencies of initiation were below 100%, normally between 80 and 90%. It was thought that the lower Lewis acidity of $TiCl_4$ dimers produced propagating centres with shorter transient lifetimes, suppressing transfer and irreversible termination reactions.

The system that showed the greatest potential for living character was initiated by 1-chloro-1-phenylethane and $TiCl_4$ in the presence of pyridine in a 40/60 (v/v) mixed solvent of dichloromethane and cylcohexane. Molecular weight distributions of 1.17 were considered narrow and efficiencies of initiation were between 80 and 100%. Control of molecular weight was demonstrated by a linear plot of $\overline{M}_n$ against conversion that passed through the origin and polydispersity reduced with conversion. A linear pseudo first order plot of $\ln([M_0]/[M])$ against time demonstrated a first order rate dependence on the concentration of monomer. It was concluded that over the time-scale of the polymerization initiation was fast and irreversible termination and transfer were below detectable limits. Such behaviour fits the criteria for a controlled living polymerization. Some of these reactions showed incomplete initiation. A small oligomer peak was observed in the GPC chromatograms and it was believed that these were cyclic species produced by a backbiting reaction to the aromatic ring which occurred early in the polymerization.

A technique of removing samples from a polymerization without introducing impurities was developed to enable the kinetics of a single polymerization to be followed. Successive samples that contained polymer of narrow molecular weight distribution were successfully withdrawn from the reaction vessel. The presence of catalyst residue made the determination of fractional conversion difficult. As a result the equation $\ln(\overline{DP}_{n\infty} - \overline{DP}_n) = -k_{app}t$ was introduced so that the apparent rate constant of polymerization could be determined from $\overline{DP}_n$ measurements made by GPC. A plot of $\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$ against time was linear.

The terminal functionality of the polymers was found to be chloride. Terminal $-CH_3$ and $-CH_2-$ groups were observed in the ^{1}H-NMR and the terminal carbon was observed by using a new technique, ^{13}C-SPEED NMR. Elemental chlorine analysis showed that, within experimental error, all chains were chloride capped.

The kinetics of polymerization involving propagation by active ion-pairs in equilibrium with dormant covalent species was studied. An equation (7.1) was derived from the Fuoss equation to relate the apparent rate constant of propagation to temperature. Such a treatment incorporated the effects of the equilibrium in the polymerization.

$$\ln k_{app} \alpha \frac{1}{T} \qquad (7.1)$$

The apparent rate constant of polymerization was found to increase over the temperature range of -10 to -55 °C. A plot of $\ln k_{app}$ against 1/temperature was linear between -10 and -25 °C, and -40 and -50 °, but between -25 °C and -40 °C a plateau formed. It was suggested that different ion-pairs were responsible for propagation and that the ion-pairs that predominated in the polymerization depended on the polymerization temperature.

The observed plateau could then be accounted for as an exchange period between the different types of propagating entities. A second equation (7.2) was derived for the effect of dielectric constant on the equilibrium, which related the apparent rate constant of polymerization to the dielectric permittivity of the solvent.

$$\ln k_{app} \alpha \frac{1}{\varepsilon} \tag{7.2}$$

The mole fraction of dichloromethane was varied between 0.24 and 0.79 in a mixture with cyclohexane. As the content of dichloromethane increased the dielectric constant and apparent rate of polymerization also increased. A plot of $\ln k_{app}$ against $1/\varepsilon$ was not linear. At high dichloromethane content the plot obeyed the given relationship but at 0.57 mole fraction DCM the trend flattened out to form a plateau, which stepped down again at a mole fraction of 0.41. It was thought that the concentration of active species increased with dielectric constant as predicted but aggregation of ions complicated matters. Under such conditions the dielectric constant in the immediate vicinity of the ions may be different to the bulk.

The pyridine or the electron donor used in the polymerization was believed to trap protic impurities. Undesirable protic initiation by impurities was thus prevented and the excess pyridine then retarded the rate of polymerization by co-ordinating with the catalyst rendering it inactive. The effective concentration of catalyst was calculated using equation 7.3.

$$[TiCl_4]_{eff} = [TiCl_4]_0 - ([Pyr]_0 - [H^+]) \tag{7.3}$$

By plotting k_{app} against [Pyr] the concentration of protic impurities in the system was estimated to be below 0.009 mol L^{-1}.

The reaction was shown to be second order with respect to the catalyst by plotting $\ln k_{app}$ against $\ln[TiCl_4]_{eff}$. Under the conditions of the experiment the concentration of the catalyst was held constant but that of the pyridine was increased, thereby reducing $[TiCl_4]_{eff}$. The second order dependency was attributed to the formation of dimeric $Ti_2Cl_9^-$ counter anions.

The syntheses of polyisobutenes with a $\overline{DP}_n$ of less than 20 was attempted. To achieve low molecular weights the concentration of 1-chloro-1-phenylethane was increased relative to the concentration of isobutene. As the concentration of initiator was raised the efficiency of initiation reduced and the desired $\overline{DP}_n$ could not be attained. Plots of $\overline{M}_n$ against conversion and $\ln([M_0]/[M])$ against time showed that the number of propagating centres was increasing with time. It was concluded that under conditions of high initiator concentration slow initiation was prevalent.

Attempts were made to improve the rate of initiation by ageing the initiation system, using a more labile initiator (1-bromo-1-phenylethane) and capping the initiator with 1,1-diphenylethene. In all cases no improvement was observed. Efforts were then made to optimise the conditions for maximum efficiency of initiation. A molar ratio of 1-PEC/pyridine/$TiCl_4$ of 1/2/7 at -30 °C were found to be optimal for a polymerization aiming at a $\overline{DP}_n$ of 20. The efficiency of initiation was found to be 54 % and the resultant polymer had a polydispersity of 1.26 and a $\overline{DP}_n$ of 32 at 86 % conversion.

Work to cap the short chain polyisobutene with phenol in a one pot synthesis route was undertaken. Phenol was added to the polymerization vessel when the monomer had been consumed. An NMR study of the resultant polymer could provide no evidence that end-capping had occurred.

Experiments were conducted to polymerize oxetane using the polyisobutene system initiated by 1-chloro-1-phenylethane and $TiCl_4$. In all attempts no polymer could be isolated. It was then concluded that under the above conditions it would not be possible to block copolymerize isobutene and oxetane in a single pot. It was thought that the oxetane might have capped the polyisobutene chain but did not then proceed to polymerize. The possibility arose that the oxetane end-capped polyisobutene might be synthesised, but quenching with water did not lead to a primary terminal alcohol group. Oxetane capping reactions were attempted at -30 °C and 16 °C but without success. The NMR of the resultant polymers showed the presence of chloride and vinyl termini only.

7.2 Further work

The polymerizations of isobutene that have been studied in this work have largely revolved around the use of 1-chloro-1-phenylethane as an initiator. This initiator is a good representation of the end group of a chloride terminated polystyrene that has been synthesised by living techniques. Given the success of these polymerizations of isobutene it should be possible to synthesis block copolymers of styrene and isobutene by using polystyrene as a macroinitiator.

In chapter 3 some success was achieved using 1-PEC/$TiCl_4$/Bu_4NCl/DCM to polymerize isobutene but was not further pursued, such a system has a close resemblance to those used for styrene polymerization. Living polymerizations of styrene normally use $SnCl_4$ as catalyst. Investigation of this system for both styrene and isobutene may be of interest, providing a potential route to the one-pot synthesis of copolymers.

Block copolymerizing oxetane and isobutene may be achieved by using a two step synthesis. Oxetane polymerization could be initiated by a chloride end-capped polyisobutene chain in the presence of boron triflouride dietherate. Such a polymerization would produce oxetane homopolymer that would require removal. Alternatively hydroxyl -telechelic polyoxetane could be produced by using ethanediol as an initiator in the presence of boron triflouride dietherate. The hydroxyl group could then be converted to a chloride for use as a macroinitiator in an isobutene polymerization.

End-capping living polyisobutene chains proved largely unsuccessful, with the exception of silyl enol ethers the literature is also bereft of such reactions. A reverse approach may be possible, in which the functional group is contained in the initiator. The choice of groups will be limited to those that are inactive in the polymerization. For example species containing phthalimide functionalities have been successfully used to initiate the polymerization of styrenes and isobutylvinylethers.

Chapter 4 was concerned with the kinetics of polymerization and in particular the equilibrium between active and dormant species that is believed to be involved. A useful addition to this work would be to measure the conductivity of the reactions as a function of temperature and dielectric constant. Such measurements would provide information about the concentrations and types of ions that are responsible for propagation and even allow calculation of equilibrium constants. Combining the findings from such a study with those in chapter 4 would provide valuable insight into the mechanism of polymerization.

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Appendix 1:

Results for sampling polymerizations conducted between -10 and -55 °C

Temperature (°C)	Time (seconds)	$\overline{M}_n$ (/g mole^{-1})	$\overline{DP}_n$	MWD	ln($\overline{DP}_{n\infty}$ - $\overline{DP}_n$)
-10	307	558	10	1.1	4.65
	603	808	14	1.15	4.61
	902	790	14	1.34	4.61
	1208	960	17	1.33	4.58
	1507	921	16	1.44	4.59
	2101	1000	18	1.43	4.58
$\overline{DP}_{n\infty}$ = 115	$e^{(\text{y-intercept})}$ = 104		I_{eff} = 88 %		k_{app} = 0.00004 s^{-1}
-15	325	733	13	1.1	4.55
	557	922	16	1.31	4.52
	882	1034	18	1.41	4.49
	1298	1261	23	1.49	4.45
	1513	1392	25	1.49	4.42
	2109	1512	27	1.60	4.39
$\overline{DP}_{n\infty}$ = 108	$e^{(\text{y-intercept})}$ = 97		I_{eff} = 87 %		k_{app} = 0.00009 s^{-1}
-20	314	742	13	1.21	4.38
	610	1042	19	1.33	4.31
	910	1354	24	1.40	4.23
	1208	1547	28	1.40	4.18
	1522	1965	35	1.38	4.06
	1810	2061	37	1.40	4.03
$\overline{DP}_{n\infty}$ = 93	$e^{(\text{y-intercept})}$ = 86		I_{eff} = 87 %		k_{app} = 0.0002 s^{-1}

Temperature (°C)	Time (seconds)	$\overline{M}_n$ (/g mole^{-1})	$\overline{DP}_n$	MWD	$\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$
-25	302	978	17	1.28	4.21
	644	1862	33	1.27	3.95
	903	2403	43	1.29	3.74
	1211	2798	50	1.35	3.56
	1504	3239	58	1.35	3.30
	1803	3571	64	1.35	3.06
$\overline{DP}_{n\infty} = 85$	$e^{(\text{y-intercept})} = 85$		$I_{eff} = 108$ %		$k_{app} = 0.0008$ s^{-1}
-30	330	1337	24	1.19	4.18
	613	1834	33	1.21	4.03
	908	2282	41	1.22	3.88
	1202	2406	43	1.24	3.83
	1515	3196	57	1.23	3.46
	1778	3765	67	1.23	3.08
$\overline{DP}_{n\infty} = 89$	$e^{(\text{y-intercept})} = 89$		$I_{eff} = 80$ %		$k_{app} = 0.0007$ s^{-1}
-40	316	2078	37	1.24	4.82
	592	3175	57	1.25	4.65
	933	4326	77	1.23	4.43
	1204	5013	90	1.22	4.27
	1507	5841	104	1.20	4.04
	1819	6731	120	1.17	3.71
$\overline{DP}_{n\infty} = 161$	$e^{(\text{y-intercept})} = 160$		$I_{eff} = 50$ %		$k_{app} = 0.0007$ s^{-1}
-45	174	1437	26	1.25	5.27
	298	2131	38	1.25	5.20
	504	3417	61	1.23	5.07
	718	4564	82	1.22	4.93
	971	5805	104	1.18	4.76
	1304	7071	126	1.15	4.54
$\overline{DP}_{n\infty} = 220$	$e^{(\text{y-intercept})} = 220$		$I_{eff} = 40$ %		$k_{app} = 0.0007$ s^{-1}

Temperature (°C)	Time (seconds)	$\overline{M}_n$ (/g mole^{-1})	$\overline{DP}_n$	MWD	ln($\overline{DP}_{n\infty}$ - $\overline{DP}_n$)
-50	205	2859	51	1.26	5.15
	310	3659	65	1.23	5.06
	490	5572	100	1.16	4.82
	748	7772	139	1.11	4.43
	941	8870	158	1.10	4.17
	1249	9676	173	1.09	3.92
$\overline{DP}_{n\infty}$ = 223	$e^{(\text{y-intercept})}$ = 223		I_{eff} = 40 %		k_{app} = 0.0012 s^{-1}
-55	135	3156	56	1.30	5.04
	263	4938	88	1.20	4.81
	395	6705	120	1.14	4.51
	531	7753	138	1.15	4.28
	723	9448	169	1.10	3.74
	915	10069	180	1.10	3.44
$\overline{DP}_{n\infty}$ = 211	$e^{(\text{y-intercept})}$ = 211		I_{eff} = 45 %		k_{app} = 0.0021 s^{-1}

Table 8.1. Polymerization of IB between -10 and -55 °C. [IB] = 1 M, [1-PEC] = 0.01 M, [Pyridine] = 0.02 M, [$TiCl_4$] = 0.15 M, 30 ml cHex., 20 ml DCM.

% Conversion	$\overline{M}_n$ (/g mole^{-1})	MWD
2	830	1.35
8	1325	1.43
10	1300	1.45
18	2080	1.65
38	2690	1.8

Table 8.2. $\overline{M}_n$ versus conversion at -20 °C. [$TiCl_4$] = 0.15 M, [IB] = 1 M, [1-PEC] = 0.01, [Pyridine] = 0.02 M, 20 ml DCM, 30 ml cHex.

Dependence of dielectric constant on DCM/hexane composition

Mole Fraction DCM	ε
1.00	14.9
0.83	10.7
0.63	6.8
0.36	4.0
0	2.0

Table 8.3. Literature values of ε for different DCM/hexanes solvent compositions at -80 °C.

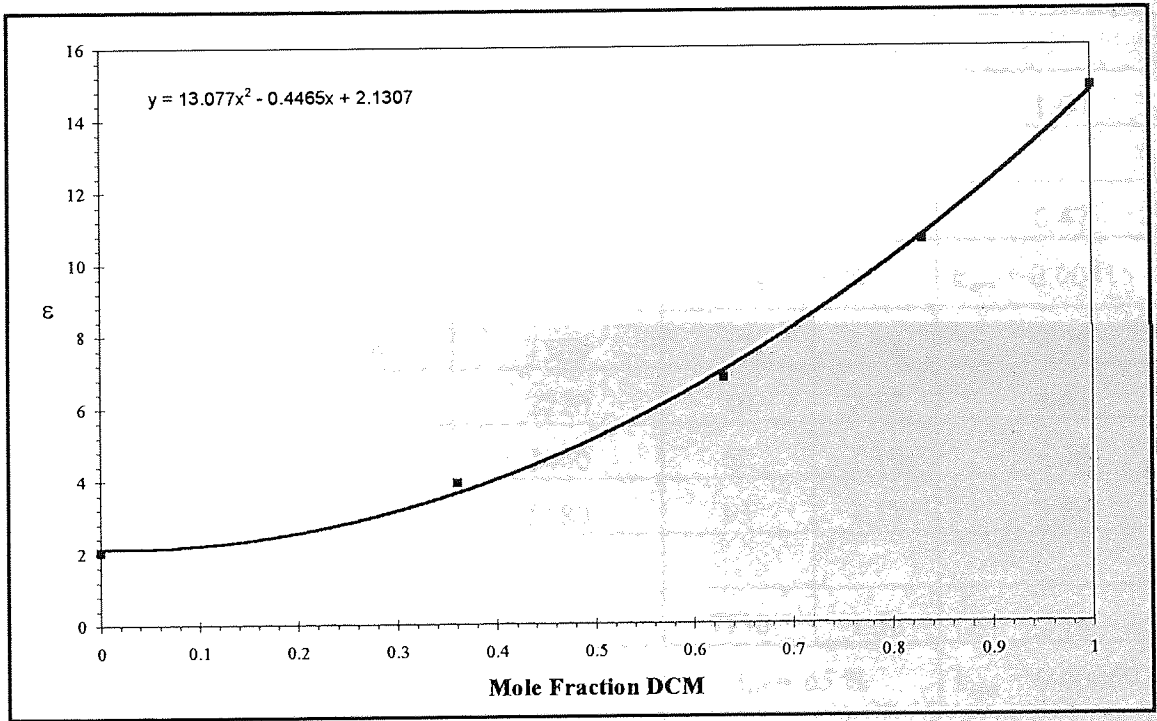

Figure 8.1. Literature values of ε for different DCM/hexanes solvent compositions at -80 °C.

Results from sampling polymerizations conducted in different solvents

Fraction DCM (mole/mole)	Time (seconds)	$\overline{M}_n$ (/g mole^{-1})	$\overline{DP}_n$	MWD	$\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$
0.79	0	0	0	-	5.02
	333	8418	150	1.18	-0.39
	532	7679	137	1.29	
	747	7164	128	1.34	
$\overline{DP}_{n\infty} = 151$	$e^{(\text{y-intercept})} = 151$		$I_{eff} = 100\ \%$		$k_{app} = 0.01623\ s^{-1}$
0.64	306	4950	88	1.19	3.45
	581	6100	109	1.25	2.40
	619	4620	83	1.26	
	746	6440	115	1.24	1.60
	947	6410	114	1.25	
	1031	6630	118	1.23	0.47
$\overline{DP}_{n\infty} = 120$	$e^{(\text{y-intercept})} = 115$		$I_{eff} = 61\ \%$		$k_{app} = 0.00415\ s^{-1}$
0.57	268	1500	27	1.12	4.73
	487	2220	40	1.12	4.61
	887	3460	62	1.10	4.36
	1529	5180	93	1.11	3.86
	2096	-	-	-	-
	3042	7750	7750	1.38	138
$\overline{DP}_{n\infty} = 140$	$e^{(\text{y-intercept})} = 140$		$I_{eff} = 65\ \%$		$k_{app} = 0.00069\ s^{-1}$
0.53	660	2660	48	1.16	4.412
	912	3400	61	1.13	
	1210	3660	66	1.18	4.16
	1743	4600	82	1.18	3.87
	2110	5620	100	1.16	3.39
	2740	6000	107	1.20	3.13
$\overline{DP}_{n\infty} = 130$	$e^{(\text{y-intercept})} = 130$		$I_{eff} = 80\ \%$		$k_{app} = 0.00065\ s^{-1}$

Fraction DCM (mole/mole)	Time (seconds)	$\overline{M}_n$ (/g mole^{-1})	$\overline{DP}_n$	MWD	$\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$
0.53	330	1340	24	1.19	4.18
	613	1830	33	1.21	4.03
	908	2280	41	1.22	3.88
	1202	2410	43	1.24	3.83
	1515	3200	57	1.23	3.28
	1778	3770	67	1.23	3.08
$\overline{DP}_{n\infty} = 89$	$e^{(\text{y-intercept})} = 89$		I_{eff} = *80* %		$k_{app} = 0.00069\ s^{-1}$
0.47	304	1340	24	1.14	4.46
	597				
	905	2781	50	1.13	4.10
	1200	3379	60	1.14	3.91
	1811	4325	77	1.15	3.49
	2389	5016	90	1.16	3.02
$\overline{DP}_{n\infty} = 110$	$e^{(\text{y-intercept})} = 110$		I_{eff} = *82* %		$k_{app} = 0.00069\ s^{-1}$
0.41	315	1024	18	1.23	4.55
	910	2509	45	1.12	4.22
	1873	4096	73	1.09	3.69
	3034	4931	88	1.16	3.22
	4164	5405	97	1.20	2.80
	5235	5992	107	1.18	1.79
$\overline{DP}_{n\infty} = 113$	$e^{(\text{y-intercept})} = 113$		I_{eff} = *73* %		$k_{app} = 0.00052\ s^{-1}$
0.36	348	750	13	1.17	4.57
	608	1041	19	1.18	4.51
	1208	1686	30	1.17	4.38
	2580	3054	55	1.14	4.02
	5202				
	9776	5515	98	1.22	2.44
$\overline{DP}_{n\infty} = 110$	$e^{(\text{y-intercept})} = 104$		I_{eff} = *96* %		$k_{app} = 0.00023\ s^{-1}$

Fraction DCM (mole/mole)	Time (seconds)	$\overline{M}_n$ (/g mole^{-1})	$\overline{DP}_n$	MWD	$\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$
0.36	365	540	10	1.15	4.70
	923	1300	23	1.12	4.57
	4020	3900	70	1.18	3.92
	6015	5030	90	1.17	3.40
	9153	6250	112	1.18	2.14
	12900	6370	114	1.19	1.82
$\overline{DP}_{n\infty} = 120$	$e^{(\text{y-intercept})} = 120$		$I_{eff} = 79$ %		$k_{app} = 0.00025$ s^{-1}
0.33	344	452	8	1.17	4.26
	665	700	13	1.20	4.20
	1198	-	-	-	-
	2417	1752	31	1.19	3.87
	4828	2916	52	1.15	3.29
	6035	3348	60	1.17	2.96
$\overline{DP}_{n\infty} = 79$	$e^{(\text{y-intercept})} = 79$		$I_{eff} = 77$ %		$k_{app} = 0.00023$ s^{-1}

Table 8.3. Polymerization of IB in different solvent compositions of DCM and cHex. Temperature = -30 °C, [$TiCl_4$] = 0.35 M, [Pyridine] = 0.03, [IB] = 1 M, [1-PEC] = 0.01 M.

Effect of pyridine concentration on isobutene polymerizations

[Pyridine] (/mol L^{-1})	Time (seconds)	$\overline{M}_n$ (/g $mole^{-1}$)	$\overline{DP}_n$	MWD	$\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$
0.002	198	2730	49	-	3.83
	307	2970	53	1.21	3.74
	491	3760	67	1.21	3.33
	670	4420	79	1.21	2.78
	827	4830	86	1.20	2.18
	1014	5020	90	1.20	1.67
$\overline{DP}_{n\infty} = 95$	$e^{(\text{y-intercept})} = 94$		$I_{eff} = 85$ %		$k_{app} = 0.0028$ s^{-1}
0.009	306	820	15	1.2	4.10
	610	1400	25	1.2	3.91
	904	1800	32	1.23	3.76
	1204	2240	40	1.24	3.56
	1510	2620	47	1.26	3.34
	1810	2950	53	1.27	3.10
$\overline{DP}_{n\infty} = 75$	$e^{(\text{y-intercept})} = 75$		$I_{eff} = 140$ %		$k_{app} = 0.0007$ s^{-1}
0.018	363	1570	28	1.19	4.20
	599	2020	36	1.21	4.08
	899	2550	46	1.22	3.90
	1224	3185	57	1.24	3.64
	1442	3640	65	1.23	3.40
	1666	4018	72	1.23	3.15
$\overline{DP}_{n\infty} = 95$	$e^{(\text{y-intercept})} = 95$		$I_{eff} = 105$ %		$k_{app} = 0.0008$ s^{-1}

[Pyridine] (/mol L^{-1})	Time (seconds)	$\overline{M}_n$ (/g $mole^{-1}$)	$\overline{DP}_n$	MWD	$\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$
0.04	330	830	15	1.12	3.91
	613	1200	22	1.20	3.77
	908	1560	28	1.23	3.61
	1202	1880	34	1.27	3.45
	1515	2320	41	1.24	3.16
	1778	2540	45	1.26	2.98
$\overline{DP}_{n\infty} = 65$	$e^{(\text{y-intercept})} = 65$		$I_{eff} = 105$ %		$k_{app} = 0.0007\ s^{-1}$
0.06	634	1340	24	1.20	4.29
	923	1830	33	1.21	4.16
	1234	2280	41	1.23	4.03
	1797	2410	43	1.31	3.99
	2155	3200	57	1.31	3.69
	2644	3770	67	1.29	3.39
$\overline{DP}_{n\infty} = 97$	$e^{(\text{y-intercept})} = 97$		$I_{eff} = 90$ %		$k_{app} = 0.0004\ s^{-1}$

Table 8.5a. Effect of pyridine concentration on IB polymerizations. Temperature = -30 °C, $[TiCl_4]$ = 0.210 mol L^{-1}, [1-PEC] = 0.01 mol L^{-1}, 20 ml DCM, 30 ml cHex.

$[TiCl_4]$ (/mol L^{-1})	Time (seconds)	$\overline{M}_n$ (/g $mole^{-1}$)	$\overline{DP}_n$	MWD	$\ln(\overline{DP}_{n\infty} - \overline{DP}_n)$
0.337	100	1520	25	1.22	4.65
	160	2130	38	1.23	4.52
	250	3050	54	1.25	4.33
	389	4180	75	1.22	4.02
	506	4880	87	1.20	3.76
	650	5530	99	1.22	3.44
$\overline{DP}_{n\infty} = 130$	$e^{(\text{y-intercept})} = 130$		$I_{eff} = 61$ %		$k_{app} = 0.0022\ s^{-1}$
0.274	174	1380	25	1.24	4.74
	324				
	640	3390	60	1.27	4.36
	853	4280	76	1.27	4.14
	1048	5000	89	1.25	3.91
	1225	5440	97	1.25	3.73
$\overline{DP}_{n\infty} = 139$	$e^{(\text{y-intercept})} = 139$		$I_{eff} = 65$ %		$k_{app} = 0.001\ s^{-1}$

Table 8.5b. Effect of pyridine concentration on IB polymerizations. Temperature = -30 °C, [Pyridine] = 0.02 mol L^{-1}, [1-PEC] = 0.01 mol L^{-1}, 20 ml DCM, 30 ml cHex.