Living Cationic Polymerization.

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Doctor of Philosophy

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SUMMARY

The kinetics of the polymerization of styrene initiated by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride have been studied. Dilatometry studies at 25 °C were conducted and the orders of reaction were established. Molecular weight studies were conducted for these experiments using size exclusion chromatography. These studies indicated that transfer/termination reactions were present. The observed kinetics may be explained by a polymerization mechanism involving a single propagating species which is present in low concentrations.

Reactions at 0 °C and -15 °C have shown that a "living" polymerization could be obtained at low temperatures. A method was derived to study the kinetics of a "living" polymerization by following the increase in degree of polymerization with time.

Polymerizations of styrene were conducted using 1,4-bis(bromomethyl)benzene as a difunctional co-catalyst. These reactions produced polymers with broad or bimodal molecular weight distributions. These observations may be explained by the rate of initiation being slower than the rate of propagation or the presence of transfer/termination reactions.

Reactions were conducted using a co-catalyst produced by the addition of 1,1-diphenylethane to 1,4-bis(bromomethyl)benzene. Size exclusion chromatography studies showed that the polymers produced had a narrower molecular weight distribution than those produced by polymerizations initiated by 1,4-bis(bromomethyl)benzene alone. However the polydispersity was still observed to increase with reaction time. This may also be explained by slow initiation compared to the rate of propagation.

Polymerizations initiated by both difunctional initiators were examined using the method of studying reaction kinetics by following the change in number average degree of polymerization. The results indicated that a straight line relationship could also be obtained with a non-living polymerization.

Homo-polymerizations of oxetane were studied using 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride. These reactions were found to be non-living. Block co-polymerizations of styrene and oxetane were conducted, but no co-polymer was produced. These results may be explained by the styryl cation or the oxonium ion formed by the addition of a styryl cation to oxetane being to stable to initiate polymerization. Alternatively the polymerization of oxetane may be initiated by proton transfer from the propagating centre.

Keywords: Styrene; Tin (IV) chloride; Difunctional co-catalyst; Oxetane.

To Mum and Dad, for everything.

Cheers.

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Chapter 1: Introduction.

1.1: General introduction.

Polymerizations can be divided into two main categories; step growth, or condensation, and chain growth, or addition, depending on the mechanisms and reactions involved. This distinction was first made by Carothers (1). Step growth polymerization (2) reactions involve the combination of monomers, dimers and oligomers to form larger molecules, usually occurring with the elimination of a small molecule such as H_2O, CO_2 or NH_3. Chain growth polymerization, which includes ring-opening polymerization, proceeds by the successive addition of monomer to a growing polymer chain end and, unlike step growth, involves at least three distinct reactions; initiation, propagation and termination or transfer. Chain growth polymerization reactions can be further sub-divided according to the nature of the growing chain end. These reactions have been documented and include free-radical polymerization(3) ionic polymerization, both anionic(4) and cationic(5), chain ends and coordinative systems, such as Ziegler-Natta(6), metathesis(7), or group transfer(8) polymerizations where propagation involves both the monomer and growing polymer chain being bonded to a catalytic centre. Termination in coordinative polymerization is more complicated but debonding of either the monomer, polymer or other ligand from the active centre may destroy the propagating centre.

1.2: Cationic polymerization.

Cationic polymerization comprises two major areas, carbocationic and onium ion reactions, depending on the nature of the propagating chain end. In carbocationic polymerization the positive charge of the growing chain end is based on a carbon atom. Reactions where the positive charge is based on a hetero atom such as oxygen, sulfur, nitrogen or phosphorus are called onium ion polymerizations. A third category, which resembles carbocationic polymerization, is the pseudo-cationic mechanism, which involves a strongly delocalised carbocation and promotes the polymerization of monomers such as aldehydes or acetals.

Some of the oldest reported examples of polymerization reactions are carbocationic. In the 19th century metal halides, for example BF_3, were used in the resinification of oil of turpentine(9). In 1866 polystyrene was synthesised by Berthelot(10) and in 1873 polyisobutene by Butlerov(11), both reactions involved initiation by sulphuric acid.

1.2.1: Monomers for carbocationic polymerization.

For a monomer to undergo cationic polymerization it must have a site that is susceptible to electrophilic attack, and generate a species with a sustained life-time as a propagating cation. The most common of these molecules are alkenyl compounds. The substituents on the carbon-carbon double bond of an alkene influence the ability of a monomer to polymerize cationically; electron donating substituents enhance the reactivity of the double bond and these monomers are suitable for cationic polymerization. Examples of such monomers that are suitable for carbocationic polymerization are styrene and vinyl ethers. Electron withdrawing substituents reduce the reactivity of the double bond that, in some cases, can prevent the addition of the initiating cation to the monomer. Other substituents may react with the initiating species in preference to the double bond. Vinyl monomers that do not undergo cationic polymerization include acrylates, vinyl halides, vinyl esters and acrylonitrile.

Aliphatic alkenes, such as ethene, propene and isobutene, can be polymerized cationically and the tendency to polymerize generally depends on the stability of the cation formed. Thus isobutene is more reactive than propene which in turn is more reactive than ethene, whereas the enthalpies of propagation would have predicted the opposite trend(12), because the primary cations formed with ethene or propene are very reactive and undergoes termination reactions. The tertiary cation formed in the polymerization of isobutene is stabilised by the two methyl groups making propagation the preferred reaction. Initiation 1,2-disubtituted and trisubstituted alkenes is rapid and produces a stable cation, however steric crowding around the propagating centre makes propagation slow compared to the rate of transfer and so leads to low molecular weight polymers. Cyclic alkenes in particular cyclopentene, cyclohexene and their derivatives have been polymerized cationically(13). Other related monomers are methylenecyclo compounds similar to those shown in figure 1.1.

Methylenecyclobutane β-pinene

Figure 1.1: Methylenecyclo compounds.

Aromatic alkenes such as styrene and its derivatives are suitable for cationic polymerization because the propagating positive charge can be resonance stabilised. The presence of a methyl group on the carbon attached to the aromatic ring (α-methylstyrene) increases the nucleophilic character of the double bond and therefore the monomer polymerizes more readily than styrene, however α-methylstyrene has a lower ceiling temperature (see below). If the substituent is a second benzene ring (1,1-diphenylethene) then initiation is rapid forming a highly stable cation, however steric hindrance prevents propagation and only a dimer is formed before the active centre is destroyed by transfer or termination. Substitution of a methyl group at the β-carbon (β-methylstyrene) reduces the reactivity of the monomer through steric hindrance between the propagating cation and the incoming monomer leading to low rates of polymerization and molecular weights. Substitution on the aromatic ring also affects the polymerization of these monomers. Electron withdrawing groups, e.g. halogens or nitro groups, at the para position decrease the reactivity of the double bond whereas electron donating groups, such as $-CH_3$ or -OR, increase the reactivity of the monomer. Electron donating substituents, such as $-OCH_3$, may increase the reactivity of the double bond, but others may react with the propagating carbocation. *p*-Cyanostyrene, polymerizes very slowly, and *p*-aminostyrenes do not propagate but form an ammonium salt upon initiation. Other aromatic alkenes that readily polymerize are indene, acenaphthylene and 2-alkenylfurans.

Amongst the most reactive monomers towards carbocationic polymerization are alkenes with electron donating groups bonded to the unsaturated carbon, which generally results in an increased tendency towards polymerization. The exception to this occurs when substituents that activate the monomer also lead to stabilisation of the propagating centre which in the extreme prevents polymerization. Monomers in this category include vinyl ethers, $CH_2=CH-OR$, where R is a linear or branched alkyl, an alkyl group with an aromatic ring attached or a halo-substitute alkyl group. Vinyl sulfides, $CH_2{=}CH{-}SR$, behave in a similar manner. N-vinylamines, $CH_2{=}CH{-}NR_2$, will readily react with cationic initiators but the resulting cation can undergo rearrangement reactions to form very stable ammonium ions and so rates of propagation are slow, see scheme 1.1.

$$CH_3{-}C^{+}H{-}NR_2 \longleftrightarrow CH_3{-}CH{=}N^{+}R_2 \rightleftharpoons CH_2{=}CH{-}N^{+}HR_2$$

Scheme 1.1: Formation of a stable ammonium ion in the polymerization of N-vinylamines.

In monomers where the nitrogen participates in a conjugated ring system, such as N-vinylcarbazole, N-vinylbenzopyrrole and N-vinylpyrrole (figure 1.2) the nitrogen cannot readily convert to the corresponding ammonium ion because the lone pair of electrons is required to generate the aromatic sextet. These monomers are amongst the most reactive towards cationic polymerization.

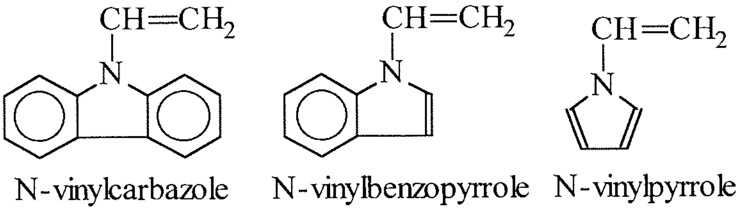


Figure 1.2: Easily polymerized nitrogen containing monomers.

Another class of monomers for carbocationic polymerization is highly strained cyclicalkanes, particularly substituted cyclopropanes. These monomers polymerize by a ring opening mechanism similar to that for heterocyclic molecules, section 1.2.7.

The possibility of a monomer forming a polymer is defined, in thermodynamic terms, by the free energy of polymerization of the pure monomer (ΔG_p) given by equation 1.1.

$$\Delta G_p = \Delta H_p - T\,\Delta S_p \qquad (1.1)$$

The free energy of polymerization will be independent of the polymerization mechanism, provided that the polymer formed has the same structure. For example styrene$^{(14)}$ has a standard enthalpy of polymerization for pure monomer (ΔH_p) of -73.1 kJ mol^{-1} and a standard entropy (ΔS_p) of -104 J K^{-1} mol^{-1}. In 1958 Dainton and Ivin(15) showed that for any monomer that polymerizes exothermically there exists a ceiling temperature above which the monomer is thermodynamically stable. The ceiling temperature (T_c) is the temperature at which the free energy of polymerization changes from a negative to positive value as the temperature increases. This can be calculated from equation 1.1, when ΔG_p equals zero;

$$T_c = \frac{\Delta H_p}{\Delta S_p}. \qquad (1.2)$$

Thus for styrene the ceiling temperature will be 430 °C for pure monomer, whereas α-methylstyrene has a ceiling temperature of 61 °C. The more reactive monomer has a lower ceiling temperature because it has a lower enthalpy of polymerization (-34.1 kJ mol^{-1}). For reactions in solution each monomer concentration has a ceiling temperature associated with it. At such temperatures there will an equilibrium between propagation and depropagation. From thermodynamics the free energy for an equilibrium can be written as;

$$\Delta G_p = -RT \ln K \qquad (1.3)$$

for polymerization reactions this becomes;

$$\Delta G_p = RT \ln [M]_e \qquad (1.4)$$

where $[M]_e$ is the concentration at equilibrium. By combining equations 1.1 and 1.4 the equilibrium constant can be calculated from;

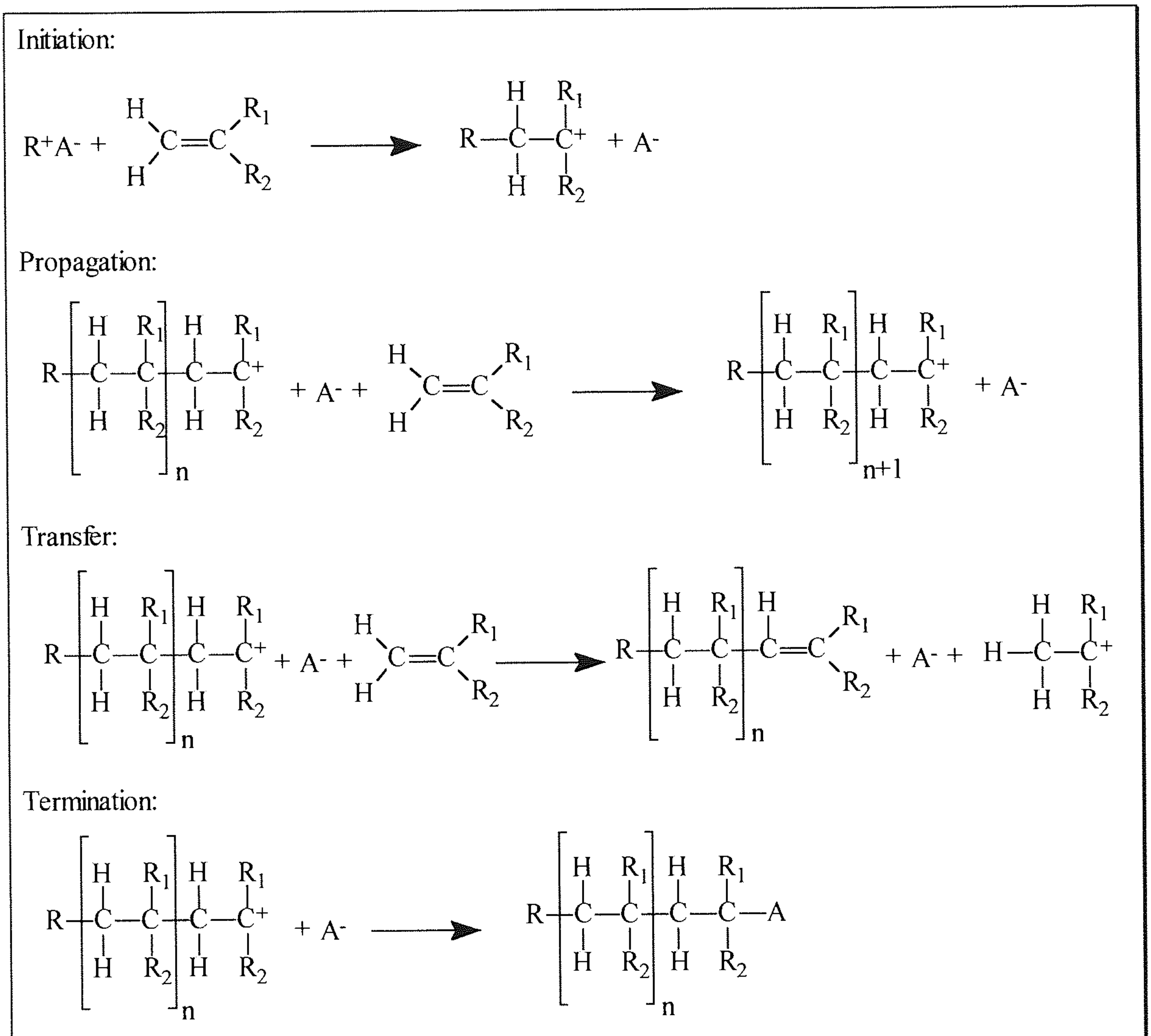
$$\ln[M]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R} \qquad (1.5)$$

thus the equilibrium concentration for styrene(16) is of the order of 10^{-7} mol dm^{-3} at 0 °C and in the range 10^{-4} to 10^{-3} mol dm^{-3} at temperatures of 100 - 150 °C. Therefore there will be an insignificant contribution from depropagation over a wide range of temperatures and concentrations.

1.2.2 General mechanism for carbocationic polymerization.

Scheme 1.2 shows a general mechanism for the carbocationic polymerization of an alkene monomer $CH_2=CR^1R^2$, as described in section 1.2.1. The mechanism is divided into four main reaction stages. Initiation occurs by generation of a cation that adds to the carbon-carbon double bond of a monomer molecule to give the propagating chain end. Propagation occurs by addition of a monomer molecule to the propagating chain end.

Growth of the polymer chain is stopped by either transfer of a proton from the propagating chain end to another molecule or termination by a reaction of the chain end with a molecule other than the monomer.



Scheme 1.2: General mechanism for the carbocationic polymerization of alkenes.

Carbocationic polymerization is initiated by the formation of a cation, such as a proton or carbocation, followed by the addition the cation to a monomer molecule to give the propagating chain end. The formation of the initiating cation also generates a counter or gegen-ion (A^-) the nature of which may affect the polymerization. Section 1.2.3 describes initiator systems used in carbocationic polymerization.

Propagation occurs through the repeated addition of monomer to the carbocationic chain end, by insertion between the propagating centre and the counter ion.

Monomer addition usually occurs in a head-to-tail manner to retain the more stable cation. The reactivity of the propagating chain end will depend on the charge density on the carbon centre. For example a benzyl cation ($\sim C^{+}H(Ph)$) will be more reactive than a diphenyl carbocation ($\sim C^{+}(Ph)_2$). The rate of propagation, however, increases with increasing monomer nucleophilicity, e.g. N-vinylcarbazole > vinyl ethers > para-methoxystyrene > para-methylstyrene > a-methylstyrene > styrene > indene(5).

The propagating species in cationic polymerization may be free ions or ion pairs depending on the nature of the monomer, solvent and counter ion (see section 1.2.4). In cationic polymerization, however, it has been shown that free ion and ion pairs have similar reactivities. Sigwalt(17) studied the polymerization of *p*-methoxystyrene initiated by $Ph_3C^{+}SbCl_6^{-}$ in dichloromethane. The dissociation constant for $Ph_3C^{+}SbCl_6^{-}$ was determined by conductance studies and the mole fraction of free ions present (γ) calculated. The rate of initiation k_i can then be given by:

$$k_i = \gamma k_{i+} + (1-\gamma)k_{i\pm} \qquad (1.6)$$

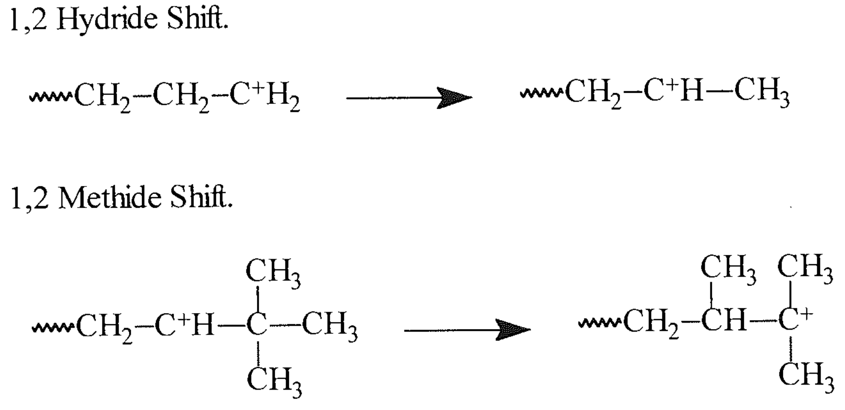
where k_{i+} = rate constant for initiation by free ions,

$k_{i\pm}$ = rate constant for initiation by ion pairs.

The mole fraction of free ions was varied by changing the concentration of the polymerization solution or by the addition of quaternary ammonium salts of SbCl6-. The results of these experiments showed that rate constants of initiation showed little variation with γ, demonstrating that $k_{i+} \approx k_{i\pm}$. Similar results have been observed for the polymerization of cyclopentadiene under similar conditions(18). Matyjaszewski *et al.*(19) studied the polymerization of oxepane initiated by 1,3-dioxolan-2-ylium hexafluoroantimonate salt, which is a vary rapid initiator, in dichloromethane, nitrobenzene and a mixture of the two solvents. The degree of dissociation into free ions was calculated from conductance experiments and the degree of dissociation modified by the addition of salts sharing a common counter with the propagating centre. The results showed that the rate of polymerization did not vary with the degree of dissociation of ions proving that ion pairs and free ions have equal reactivities in cationic polymerization.

The reason for the similarity in reactivity of free ions and ion pairs in cationic polymerization is that most of the counter ions involved are relatively large and hence their centre is relatively far away from the propagating cation. Therefore the influence of the counter ion on the reactivity of the propagating species is small, making the reactivities of ion pairs and free ions similar.

Propagation can be complicated by intramolecular rearrangement by 1,2 hydride and 1,2 methide shifts, see scheme 1.3. Reactions where propagation involves rearrangements are known as isomerization polymerization.

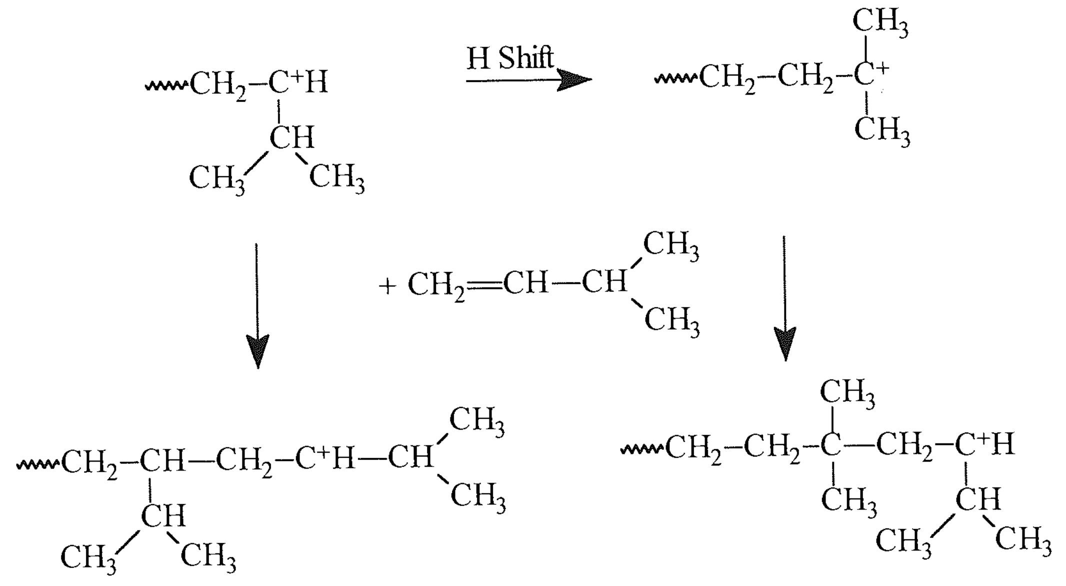


$$\sim CH_2{-}CH_2{-}C^+H_2 \longrightarrow \sim CH_2{-}C^+H{-}CH_3$$

$$\sim CH_2{-}C^+H{-}C(CH_3)_2{-}CH_3 \longrightarrow \sim CH_2{-}CH(CH_3){-}C^+(CH_3)_2$$

Scheme 1.3: Rearrangement reactions in carbocationic polymerization.

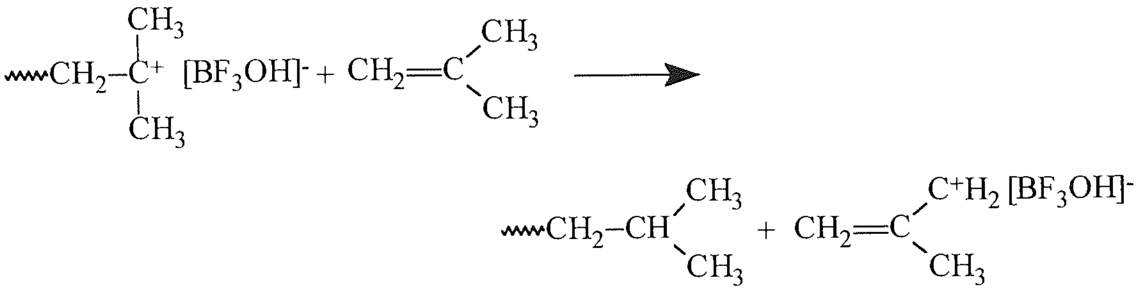
The extent of rearrangement in a polymerization depends on the relative stability of the cation formed by propagation compared to the ion formed by rearrangement and the relative rates of propagation, transfer, termination and rearrangement. Therefore monomers such as styrenes, vinyl ethers or isobutene polymerize without rearrangement. The propagating benzyl-, oxy- or tertiary-cations formed are relatively stable and there is no rearrangement route to a more stable carbocation. Monomers such as propene, 1-butene and higher 1-alkenes undergo extensive rearrangement during polymerization(20) and give a highly irregular structure. For example propene will undergo a combination of rearrangement reactions to give $-CH_2-CH_2-CH_2-$, $-CH_2-CH(CH_3)-$ and $-C(CH_3)_2-$ repeat units. The polymers produced are usually of low molecular weight because the rates of propagation or rearrangement are unfavourable compared to those of transfer and termination. Rearrangement reactions will lead to high molecular weight polymers if the rearrangement is simple and relatively stable cations are involved. For example the polymerization of 3-methyl-1-butene(21) gives a high molecular weight polymer containing two different repeat units from the first-formed cation and from a 1,2 hydride shift (see scheme 1.4). The relative quantities of the two repeat units depend on the reaction temperature.



Scheme 1.4: Propagation in the polymerization of 3-methyl-1-butene.

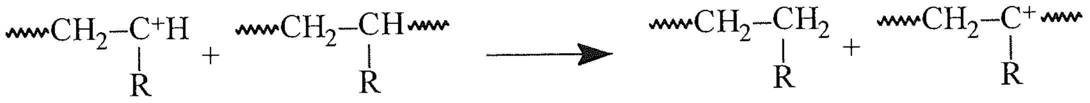
In carbocationic polymerization the growing polymer chain can be terminated by either transfer or termination. Transfer reactions can occur to a variety of species such as monomer molecules, polymer chain or the counter ion. Transfer reactions do not destroy the propagating centre since a new propagating centre is formed. Termination usually involves reactions that destroy the propagating centre.

The main chain-breaking process in carbocationic polymerization is generally transfer to monomer, as shown in scheme 1.2. The reaction occurs by transfer of a β-proton from the polymer chain end to a monomer molecule, yielding a terminal unsaturated group and a new propagating centre. The activation energy for transfer to monomer is usually higher than for propagation and so can be suppressed at low temperatures. Transfer to monomer can also occur by the transfer of a hydride ion from a monomer molecule to the propagating centre giving a saturated chain end, see scheme 1.5. This reaction is usually observed in the polymerization of 1-alkenes(22) where propagation in not favourable. This process is often referred to as degradative chain transfer because the ion-pair formed can be too stable to propagate



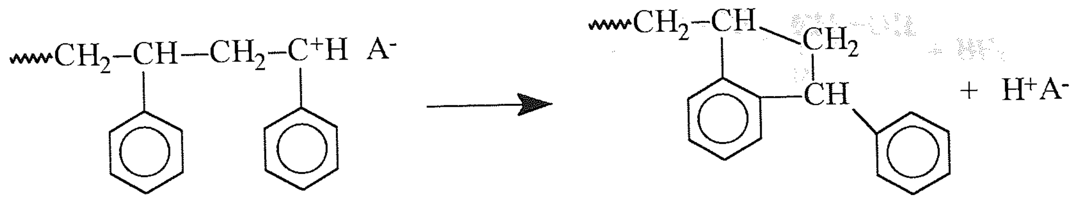
Scheme 1.5: Termination of a polymer chain by transfer of a hydride ion from a monomer molecule to the propagating centre.

Transfer can occur to a polymer chain, either by transfer of a hydride ion or by an electrophilic aromatic substitution. Transfer by hydride ion, scheme 1.6, results in a saturated polymer chain end. Since the propagating centre is transferred to a polymer chain this reaction leads to the formation of branched chains. Transfer to polymer chain can also be an intramolecular reaction.



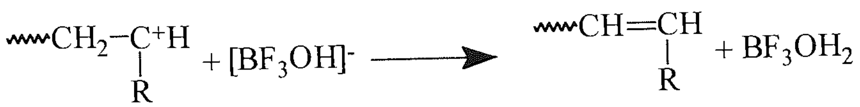
Scheme 1.6: Transfer to polymer by hydride ion.

Transfer by aromatic substitution usually occurs by an intramolecular backbiting reaction with transfer of a proton from the aromatic ring to the counter ion, see scheme 1.7. The product of this reaction is polymer with an indenyl end group. Further polymerization may be initiated by the proton transferred to the counter ion. Transfer by aromatic substitution can also occur by an intermolecular process leading to branched chains.



Scheme 1.7: Transfer to polymer by electrophilic aromatic substitution.

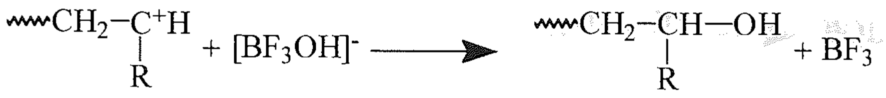
Transfer can occur by a rearrangement of the propagating centre and counter ion. An example of this is in polymerization initiated by boron trifluoride and water. The transfer of a proton to the counter ion reforms the catalyst/co-catalyst complex and gives a terminal unsaturated group on the polymer chain, see scheme 1.8.



$$\sim\!\sim CH_2-\underset{R}{\underset{|}{C^+H}} + [BF_3OH]^- \longrightarrow \sim\!\sim CH{=}\underset{R}{\underset{|}{CH}} + BF_3OH_2$$

Scheme 1.8: Transfer to counter ion.

Termination in cationic polymerization can occur by the formation of a covalent bond between the propagating cation and the counter ion as shown in scheme 1.2. This occurs in polymerization initiated by protonic acids. In polymerizations initiated by Lewis acids/co-catalyst complexes, see section 1.2.3, termination occurs by combination of the propagating centre and a fragment of the anionic counter ion. For example, in polymerizations initiated by boron trifluoride and water termination occurs through formation of a covalent bond between the propagating cation and the hydroxyl group from the counter ion, see scheme 1.9. The fragment of the counter ion that bonds with the propagating centre depends on the strength of the bond formed. Thus in polymerization initiated by BF_3/H_2O leads to a hydroxyl terminated polymer chain, whereas polymerization by BCl_3/H_2O termination yields a chlorine end group. This is because a boron-fluorine bond is stronger than a boron-oxygen bond which is stronger than a boron-chlorine bond.



$$\sim\!CH_2\!-\!\underset{R}{\overset{|}{C^{+}H}} + [BF_3OH]^- \longrightarrow \sim\!CH_2\!-\!\underset{R}{\overset{|}{CH}}\!-\!OH + BF_3$$

Scheme 1.9: Termination by combination with an anionic fragment of the counter ion.

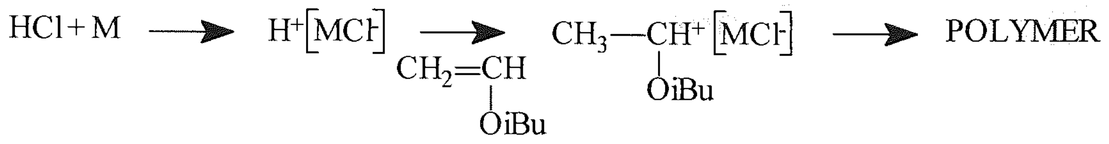
1.2.3: Initiators for carbocationic polymerization.

Initiators for carbocationic polymerization can be classed in four groups: protonic (Brønsted) acids, Lewis acids, carbenium ion salts and physical techniques.

1.2.3.1: Initiation by protonic acids.

Brønsted acids (HA) initiate polymerization by the addition of a proton to the carbon-carbon double bond of the monomer to give the propagating cation. The effectiveness of protonic acids as initiators depends on two factors; the acid must be strong enough to yield a reasonable concentration of cations to permit propagation and the anion formed (A^-) cannot be highly nucleophilic as a covalent bond would then be formed between the anion and the propagating centre leading to termination. For example, under most conditions hydrogen halides are generally ineffective as an initiator since a 1:1 addition product of the monomer is formed. The exception to this is with the most reactive monomers that form the most stable propagating cation, such as N-vinylcarbazole, can be polymerized by HCl(23). Other protonic acids such as perchloric, sulfuric, phosphoric, fluoro- and chlorosulfonic, methanesulfonic or trifluoromethanesulfonic which have less nucleophilic anions can initiate polymerisation in polar solvents.

The lifetime of a propagating carbocation, initiated by a Brønsted acid, before termination occurs can be extended by complexation of the counter ion with a metal(24), e.g. Ni, Co, Fe or Ca, or metal oxide, such as V_2O_5, PbO_2, SiO_2 or active Al_2O_3 (see scheme 1.10). Complexation of the counter-ion with a Lewis acid can also be used to give high molecular weight polymers (see section 1.2.3.2).



$$HCl + M \longrightarrow H^{+}[MCl^{-}] \xrightarrow{\underset{\displaystyle OiBu}{CH_2=\overset{}{CH}}} \underset{\displaystyle \quad\;\; OiBu}{CH_3-CH^{+}}[MCl^{-}] \longrightarrow \text{POLYMER}$$

Scheme 1.10: Complexation of counter-ion with metal in the polymerization of isobutyl vinyl ether initiated by hydrogen chloride.

1.2.3.2: Initiation by Lewis acids.

The most important class of initiators for carbocationic polymerization is the Lewis acids such as metal halides ($AlCl_3$, BF_3, $SnCl_4$, $SbCl_5$, $ZnCl_2$, $TiCl_4$ and PCl_5), organometallic derivatives ($RAlCl_2$, R_2AlCl or R_3Al) and oxyhalides ($POCl_3$ or CrO_2Cl). These may initiate polymerization on their own by a bimolecular self ionisation process (25), as shown in scheme 1.11.

$$2AlBr_3 \rightleftharpoons AlBr_2^{+}(AlBr_4^{-})$$

$$AlBr_2^{+}(AlBr_4^{-}) + M \longrightarrow AlBr_2{-}M^{+}(AlBr_4^{-})$$

Scheme 1.11: Initiation by bimolecular self ionisation of Lewis acid.

A similar process to this is the ionisation of mixtures of Lewis acids such as $FeCl_3$ and BCl_3 or $TiCl_4$ and $AlBr_3$(26), as shown in scheme 1.12.

$$FeCl_3 + BCl_3 \rightleftharpoons FeCl_2^{+}(BCl_4^{-})$$

$$FeCl_2^{+}(BCl_4^{-}) + M \longrightarrow FeCl_2{-}M^{+}(BCl_4^{-})$$

Scheme 1.12: Initiation by mixed Lewis acids.

Polymerization may be initiated by the direct addition of a Lewis acid to the monomer, see scheme 1.13.

$$TiCl_4 + M \longrightarrow TiCl_3\text{—}M^+Cl^-$$

Scheme 1.13: Initiation by direct addition of Lewis acid.

However, Lewis acids are not normally active on their own and usually require a cation source, R^+A^- in scheme 1.2, know as the co-catalyst (or initiator). The need for this co-catalyst was demonstrated by Evans *et al.*(27) who found that BF_3 alone will not initiate polymerisation of isobutene under anhydrous conditions. However, when trace quantities of water are present the reaction proceeds rapidly. The co-catalyst, RA, can be a proton donor, e.g. H_2O, HX, ROH or RCOOH, or a cation donor, e.g. 2-chloro-2-methyl-propane (*t*-butyl chloride, $(CH_3)_3CCl$) or (Ph_3CCl). For polymerization to take place an ionisation process is required to form the initiating cation (R^+), see scheme 1.14.

$$MX_n + RS \rightleftharpoons R^+[SMX_n]^-$$

Scheme 1.14: Ionisation of co-catalyst.

In general, the complex counter ion formed is less nucleophilic than the anion in protonic acid initiated systems and so termination reactions are slower and higher molecular weight polymers can be formed. The activity of the complex, $R^+[SMXn]^-$ towards initiation, depends on its ability to donate the carbocation to a monomer. The ability to initiate polymerization generally increases with increasing acidity(28) such that $AlCl_3 > AlRCl_2 > AlR_2Cl > AlR_3$ and $AlR_2I > AlR_2Br > AlR_2Cl$. As the acidity of the co-catalyst increases its ability to initiate polymerization increases(29), e.g. HCl > acetic acid > nitroethane > phenol > H_2O > methanol > acetone for the polymerization of isobutene with tin (IV) chloride(30). As the stability of the cation (R^+) increases the concentration of initiating species will increase but their reactivity decreases.

The difference in stability of the initiating cation and propagating centre is important; if the growing chain end ($R\text{-}M^+$) is significantly less stable than the co-catalyst (R^+) then initiation will be slow or a low concentration of propagating species will be formed. For example Ph_3C^+ and $C_7H_7^+$ are too stable to initiate the polymerization of styrene or isobutene but will polymerize more reactive monomers such as *p*-

methoxystyrene, vinyl ethers and N-vinylcarbazole. In the presence of the more active Lewis acids, such as AlR_3 or R_2AlCl, halogens can be used as initiators by formation of a halonium ion, X^+, as shown in scheme 1.15.

$$AlR_3 + I_2 \rightleftharpoons I^+[AlR_3I^-]$$

Scheme 1.15: Ionisation of halogen by Lewis acid.

1.2.3.3: Initiation by carbocationic salts.

The more stable cations are available as salts, e.g. $Ph_3C^+[SbCl_6^-]$, $C_7H_7^+[SbCl_6^-]$, and these salts can be used to initiate polymerization(31). Since these salts will exist as ions in polar solvents the ion generation process (scheme 1.14) can be eliminated. However due to the high stability of the ion formed these initiators are usually restricted to the more active monomers.

1.2.3.4: Initiation by physical methods.

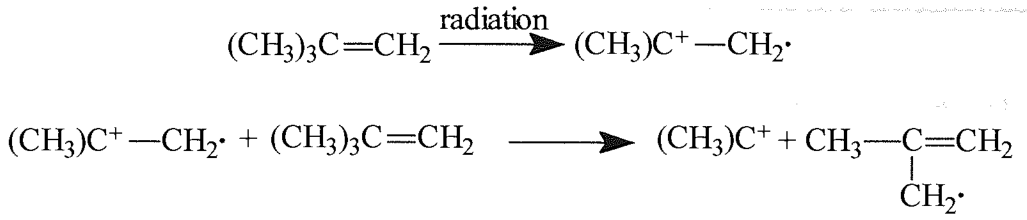
Physical methods of initiation include photoinitiation and ionising radiation. Effective photoinitiators for cationic polymerization are diaryliodonium ($Ar_2I^+Z^-$) and triarylsulfonium ($Ar_3S^+Z^-$) salts(32), where Z^- is a photostable, non-nucleophilic anion such as BF_4^-, SbF_6^- or PF_6^-. Photolytic cleavage of an Ar-I or Ar-S bond yields a radical cation (scheme 1.16). This reacts with a co-catalyst, HY, to give a catalyst-co-catalyst complex which acts as a proton donor to initiate polymerization. HY can be a solvent molecule or an added substance, such as an alcohol, with a labile hydrogen.

$$Ar_2I^+(PF_6^-) \xrightarrow{h\upsilon} ArI^{+\cdot}(PF_6^-) + Ar\cdot$$

$$ArI^+(PF_6^-) + HY + Ar\cdot \longrightarrow H^+(PF_6^-) + Y\cdot + ArI$$

Scheme 1.16: Photoinitiation

Ionising radiation such as electrons, neutrons, γ- and β-rays, can initiate polymerization(33). The first stage of the reaction is the formation of a radical cation from a monomer by ejection of a π electron (scheme 1.17). This radical cation can undergo further reactions to form cationic, anionic or radical species. The actual mechanism of polymerisation depends on the reaction conditions and the monomer. For example, styrene undergoes polymerization by all three mechanisms, under super dry conditions at 25 °C the major mechanism is cationic with approximately 2.5% anionic and negligible radical reactions. As the temperature increases radical polymerization becomes the dominant process. The presence of protogenic impurities, e.g. water, decreases the extent of the ionic reactions compared to radical polymerisation.



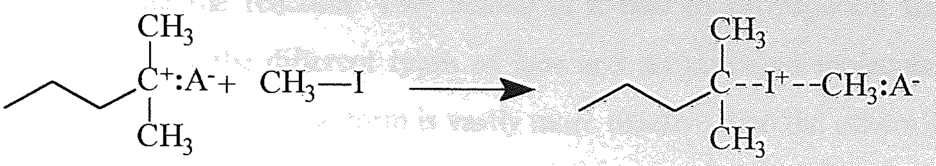
$$(CH_3)_3C{=}CH_2 \xrightarrow{\text{radiation}} (CH_3)C^+{-}CH_2\cdot$$

$$(CH_3)C^+{-}CH_2\cdot + (CH_3)_3C{=}CH_2 \longrightarrow (CH_3)C^+ + CH_3{-}\underset{\displaystyle CH_2\cdot}{\underset{|}{C}}{=}CH_2$$

Scheme 1.17: Initiation by ionising radiation.

1.2.4: Solvent and counter-ion effects.

Carbocationic polymerization propagation reactions involve ions or ion pairs and so the nature of the solvent and gegen ion will be important. A good solvent must be able to dissolve the monomer, catalyst and co-catalyst as well as the polymer formed over a wide range of molecular weights. It is important also that the solvent does not react or complex with the propagating centre to affect the rate of polymerization and the molecular weight of the product. For example isobutene readily polymerizes when initiated by diethyl aluminium chloride (Et_2AlCl) with 2-chloro-2-methylpropane (*t*-BuCl) as the co-catalyst in CH_3Cl, but in CH_3Br the rate is greatly reduced and no reaction takes place in CH_3I(34). This is because the growing carbocation forms a stable complex with iodomethane preventing propagation, see scheme 1.18. The stability of the halonium ion formed depends on the polarizability of the C-I bond (C-I > C-Br > C-Cl). As the stability of the halonium ion increases propagation reactions become more unfavouarble compaired to termination and transfer reactions. A similar effect is observed with the polymerization of isobutene in solvents such as diethyl ether, where an oxonium ion can be formed.



Scheme 1.18: Complexation of propagating centre with iodomethane in the polymerization of isobutene by Et_2AlCl/t-BuCl.

The active species in carbocationic polymerization can exist in a range of forms from a covalently bonded molecule through to free ions depending on the distance between the ions, see scheme 1.19 below. This distance is determined by the solvent and gegen ion. A polar solvent such as dichloromethane, dielectric constant (ε) = 9.1, will stabilise ions and therefore the equilibrium shown in scheme 1.19 will lie further to the right. In a non-polar solvent, e.g. hexane (dielectric constant = 1.9), the equilibrium will lie towards the close contact ion pairs and even covalently bonded molecules. In these cases initiation may be slow. In solvents with low dielectric constant but containing electron donating groups, such as 1,4-dioxane (ε = 2.2), the equilibrium lies towards the solvent separated ion pairs because the solvent complexes with the cation.

$$\underset{\text{covalent}}{RX} \rightleftharpoons \underset{\substack{\text{polarised}\\ \text{molecule}}}{\overset{\delta+\ \ \delta-}{R{-}{-}X}} \rightleftharpoons \underset{\text{ion pair}}{R^+X^-} \rightleftharpoons \underset{\substack{\text{solvent separated}\\ \text{ion pair}}}{R^+//X^-} \rightleftharpoons \underset{\text{free ions}}{R^+ + X^-}$$

Scheme 1.19: Equilibrium between different propagating species in carbocationic polymerization.

In general the rate constant for propagation for free ions will be higher than that involving the related ion pair. In addition an increase in distance between ions will reduce the steric restrictions on the incoming monomer. Thus polymerizations in solvents with a greater polarity tend to show higher rates of propagation, for example isobutyl vinyl ether polymerizes at a faster rate in dichloromethane than in hexane when the HI/I_2 system(35) is used as the initiator. If interconversion between ion pairs, solvent separated ions and free ions is rapid each propagating centre will exist in all the forms at various different times during the reaction. This results in a rate of propagation that is the average of the rates for the different types of ions and an averaged molecular weight distribution will be obtained. If one form is vastly more reactive than the others and there is rapid exchange between the different propagating species then the molecular weight distribution will be that associated with the faster reacting ion only. However, if the propagating centres do not readily interconvert then a broad or even multi-modal molecular weight distribution will be formed because different polymer chains grow at different rates and individual distributions are superimposed on each other.

1.2.5: Kinetics of carbocationic polymerization.

In order to formulate a general kinetic scheme for cationic polymerization it is necessary to make some assumptions. Since free ions exist only under the purest conditions(36), it will be assumed that propagation occurs via ion pairs and that there is only one type of propagating species. It is also assumed that chain transfer reactions are absent or, since the propagating centre is retained, such reactions do not affect the rate of polymerization. The rate of polymerization (R_p) can be equated to the rate of consumption of monomer and therefore the rate of propagation;

$$R_p = \frac{-d[M]}{dt} = k_p[P_n^+\{SMX_n\}^-][M] \qquad (1.7)$$

where [M] = concentration of monomer,

$[P_n{}^+\{SMX_n\}^-]$ = concentration of ion pair propagating centres,

and k_p = rate constant of propagation.

If initiation is by a Lewis acid co-catalyst combination, then the rate of initiation (Ri) will be;

$$R_i = k_i[R^+\{SMX_n\}^-][M] \qquad (1.8)$$

where k_i = rate constant for initiation,

and $[R^+\{SMX_n\}^-]$ = concentration of catalyst - co-catalyst complex,

The equilibrium constant for the ionisation (K) of the co-catalyst by the catalyst is given by,

$$K = \frac{[R^+\{SMX_n\}^-]}{[RS][MX_n]}. \qquad (1.9)$$

Assuming that termination is a first order process involving the recombination of the active centre and co-catalyst fragment, as shown in scheme 1.2, then the rate of termination (R_t) will be;

$$R_t = k_t[Pn^+\{SMX_n\}^-] \tag{1.10}$$

If a steady state in the concentration of active centres is established such that;

$$\frac{d[Pn^+\{SMX_n\}^-]}{dt} = R_i - R_t = 0 \tag{1.11}$$

then combination of equations 1.8, 1.10 and 1.11 will lead to,

$$k_i[R^+\{SMX_n\}^-][M] = k_t[Pn^+\{SMX_n\}^-] \tag{1.12}$$

from which;

$$[P_n^+\{SMX_n^-\}] = \frac{k_i}{k_t}[R^+\{SMX_n\}^-][M] \tag{1.13}$$

and equation 1.9 can be rearranged to give;

$$[R^+\{SMX_n\}^-] = K[RS][MX_n] \tag{1.14}$$

So the overall rate of polymerization can be rewritten as;

$$R_p = \frac{k_p k_i}{k_t} K[RS][MX_n]\ [M]^2. \tag{1.15}$$

Whilst this is not rigorously applicable to all cationic systems it does give a reasonable description of cationic polymerization based on the general mechanism described in scheme 1.2. Since the rate constant for polymerization is $k_p k_i/k_t$, the overall activation energy E will be given by;

$$E = E_p + E_i - E_t \tag{1.16}$$

where E_p, E_i and E_t are the activation energies for propagation, initiation and termination respectively.

Table 1.1 shows selected rate constants for cationic polymerizations.

System	k_i/l mol^{-1} s^{-1}	k_p/l mol^{-1} s^{-1}	k_t/s^{-1}
α–Methylstyrene			
$H_2O/BuTiCl_3$/DCM/-70 °C	17 ± 6	2.2 * 10^4 ± 1.1 * 10^4	0.54 ± 0.05
$H_2O/BuTiCl_3$/DCM/-30 °C	120 ± 20	1300 ± 500	1 ± 0.1
p-Methoxystyrene			
$Ph_3C^+SbCl_6^-$/DCM/-15 °C	0.03	7.4 * 10^4	0.25
$Ph_3C^+SbCl_6^-$/DCM/-10 °C	0.28	2.8 * 10^4 ± 5.0 * 10^4	0.08 ± 0.05
Isobutyl vinyl ether			
$Ph_3C^+SbCl_6^-$/DCM/-40 °C	0.3	930	0.01
$Ph_3C^+SbCl_6^-$/DCM/0 °C	5.4	7000	0.19
$Ph_3C^+SbCl_6^-$/DCM/20 °C	16	1.6 * 10^4	0.8

Table 1.1: Selected rate constants for cationic polymerization.

1.2.6: Molecular weight distributions in cationic polymerization.

For a polymerisation which follows the kinetic scheme described above and in which transfer reactions are absent, the number average degree of polymerization (Dp_n) will be given by;

$$\overline{Dp_n} = \frac{R_p}{R_t} = \frac{k_p[P_n^+\{SMX_n^-\}][M\ ]}{k_t[P_n^+\{SMX_n^-\}]} = \frac{k_p}{k_t}[M]. \tag{1.17}$$

By using the Arrhenius equation to obtain expressions for the rate constants,

$$\overline{Dp_n} = \frac{A_p}{A_t}.e^{-\left(E_p-E_t/R_t\right)}.[M] \tag{1.18}$$

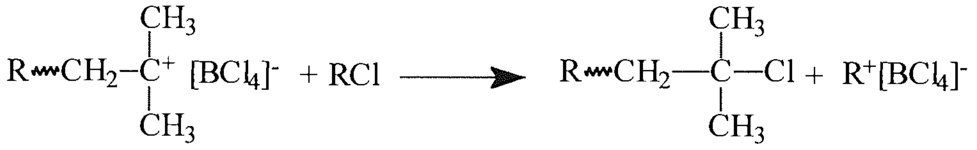
So the molecular weight will be dependent on the temperature of reaction, by way of the difference in activation energies, and the monomer concentration. However the molecular weight is independent of the concentration of propagating centres. If termination of the growing polymer chain is by transfer to monomer (scheme 1.2) then the Dp_n will be given by,

$$\overline{Dp_n} = \frac{R_p}{R_{tm}} = \frac{k_p[P_n^+\{SMX_n^-\}][M]}{k_{tm}[P_n^+\{SMX_n^-\}][M]} = \frac{k_p}{k_{tm}} = \frac{A_p}{A_{tm}}.e^{-\left(\frac{E_p-E_t}{R_t}\right)} \tag{1.19}$$

and so the only control over the degree of polymerisation is through the temperature.

1.2.7: Telechelic polymers by cationic polymerization.

A telechelic polymer is a relatively low molecular weight polymer with functional end groups. These end groups can be used in further reactions to synthesise copolymers or for forming networks. Cationic polymerization can be used to prepare telechelic polymers by using the initiator-transfer, or inifer systems as reported by Kennedy(37). The initiating catalyst/co-catalyst system is prepared from a Lewis acid and an alkyl or aryl halide, i.e. BCl_3 and RCl, as shown in scheme 1.14 above. When a monomer, such as isobutene, is added, propagation can proceed as shown in scheme 1.2 and the growing polymer chain can undergo a transfer reaction with the co-catalyst to produce a halogenated chain end and regenerate the initiating catalyst/co-catalyst complex, see scheme 1.20. Bifunctional telomers can also be synthesised by using a dihalogenated co-catalysts, for example 1,4-bis(α,α-dimethylchloromethyl)benzene, $Cl(CH_3)_2CC_6H_4C(CH_3)_2Cl$.



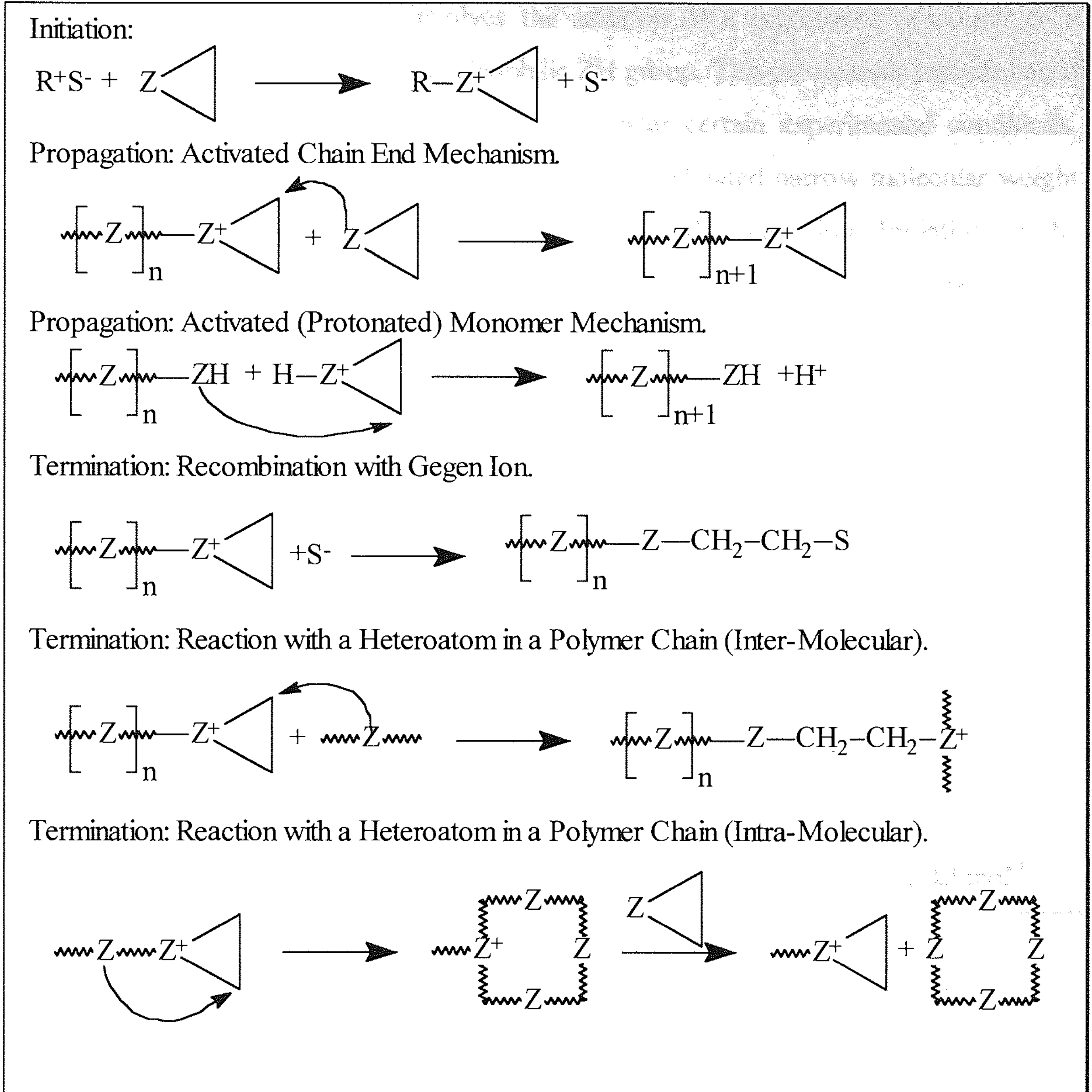
$$R\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}\;[BCl_4]^- + RCl \longrightarrow R\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl + R^+[BCl_4]^-$$

Scheme 1.20: Transfer to co-catalyst in the polymerization of isobutene by BCl_3/RCl.

In these polymerization reactions, as termination mainly occurs by transfer, the molecular weight of the telechelic polymers can be controlled by varying the reaction temperature, see section 1.2.6. For this method of preparing telechelic polymers the rate constants of initiation and transfer must be higher than the rate constant of transfer to monomer. Functional groups other than halogens can be obtained by performing further reactions once polymerization is complete, for example dehyrohalogenation by sterically hindered bases to give a terminal carbon-carbon double bond(38). These end groups can undergo further reaction, such as; conversion to hydroxyl groups by hydroboration followed by alkaline oxidation(39), epoxide groups by oxidation with a per acid and silane end groups by reaction with $HSi(CH_3)_2Cl$ followed by reduction with $LiAlH_4$(40).

1.2.8: Onium ion polymerization.

As stated previously onium ion polymerization involves a polymerization where the positive charge is located on an atom other than carbon. Monomers in this category are usually heterocyclic compounds such as cyclic ethers(41), cyclic amines(42), lactones(43) or lactams(44) and the polymerization involves a ring opening process. The principles discussed previously for carbocationic polymerization generally can be applied to cationic ring opening polymerization, but there are differences and these are discussed below. Scheme 1.21 describes the general mechanism of onium ion polymerization for a simple three membered ring containing a hetero-atom Z, usually oxygen, nitrogen or sulfur.



Scheme 1.21: General mechanism for ring opening onium ion polymerization.

1.2.8.1: Initiation in onium ion polymerization.

Initiation involves the addition of a cation (R^+) to a monomer molecule to form the onium ion; R^+ can be a proton or a carbocation. Usually catalyst and co-catalysts used for alkene polymerization can also be used in cationic ring opening polymerization.

1.2.8.2: Propagation in onium ion polymerization.

Propagation can take place by two different mechanisms, which may occur concurrently, the activated chain end mechanism (ACE) and the activated monomer mechanism (AMM). In the activated chain end mechanism the propagating chain end is a cyclic onium ion. Propagation occurs through the opening of the cyclic onium ion by nucleophilic attack of the heteroatom of a monomer molecule on the onium ion. The activated monomer mechanism involves the addition of a protonated monomer to a growing chain end with a terminal nucleophilic ZH group. This mechanism was proposed by Penczek(45) to explain the observation that under certain experimental conditions, particularly slow addition of monomer, polyoxiranes exhibited narrow molecular weight distributions and an increase of molecular weight with conversion. Initiation of the polymerization was by an alcohol in the presence of a protonic acid. The monomer was admitted slowly so that, at any instant, its concentration is of the same order as the initiator concentration. The acid protonates the monomer as is the case for the activated chain end mechanism (scheme 1.21). However, because of the low concentration of monomer the only nucleophile present that is capable of attacking the onium ion is the alcohol.

The tendency for a cyclic monomer to undergo ring opening polymerization depends on the ring size. The main driving force for polymerization is the relief of ring strain caused by bond angle distortion, conformational strain and non-bonded interactions in the ring. For example, table 1.2 lists some common cyclic ethers with their ring size, ring stain and heat of polymerization.

Monomer	Ring Size	Ring Strain/kJ mol^{-1}	ΔHp/kJ mol^{-1}
Ethylene oxide	3	114	-94.5
Trimrthylene oxide	4	107	-81
Tetrahydrofuran	5	23	-15
Tetrahydropyran	6	5	~0
Hexamethylene oxide	7	33	33.5

Table 1.2: Ring size, ring strain and heat of polymerization for some common cyclic ethers.

1.2.8.3: Termination in Onium Ion Polymerization.

In the activated chain end polymerization termination can occur through a variety of methods including recombination with the gegen ion or transfer of a proton as in alkene polymerization. Termination can also occur by nucleophilic attack of an in chain hetero-atom on the propagating onium ion to form a stable onium ion which will not undergo further propagation(see scheme 1.21). If this attack is inter-molecular then a branched polymer is formed. In the case of an intra-molecular reaction a macrocyclic species is formed. These cyclic oligomers are in equilibrium with straight chain molecules and their formation is normally described by the Jacobson-Stockmayer equation(46),

$$[R_n] = K_n n^{-5/2} \tag{1.20}$$

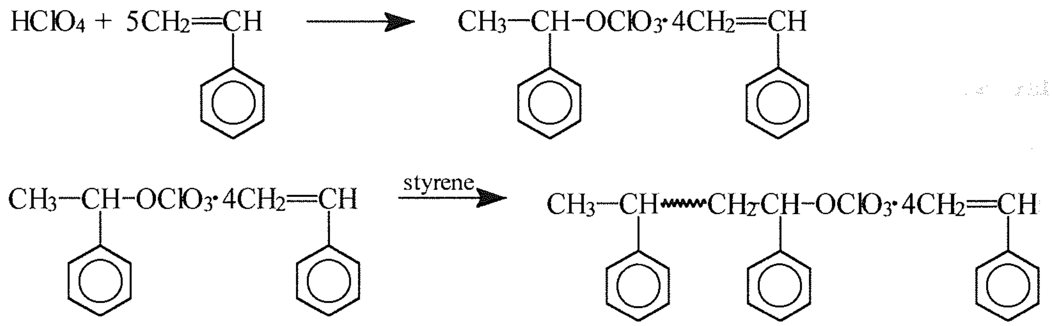
where $[R_n]$ = concentration of macrocyclic species of n repeat units,

and K_n = equilibrium constant for the formation of oligomers of n repeat units.

The activated monomer mechanism has no formal termination step, however reaction between the propagating species and impurities can take place to interrupt the polymerization.

1.2.9: Pseudo-cationic polymerization.

In 1966 Gandini and Plesch used spectophotometry and conductivity measurements to investigate the polymerization of styrene initiated by perchloric acid(47), and showed that ions were not present during the reaction. To explain these observations Plesch proposed the pseudo-cationic mechanism(48) where the propagating species are esters (scheme 1.22).



Scheme 1.22: Pseudo-cationic mechanism for the polymerization of styrene.

It is possible for certain systems to polymerize either by a conventional carbocationic or a pseudo-cationic mechanism, the exact nature depending on the reaction conditions. For example, at high acid concentrations, the pseudo-cationic system may change to a carbocationic mechanism, or at low temperatures the rate of pseudo-cationic polymerization may become very slow whilst the rate for the conventional mechanism remains high(49).

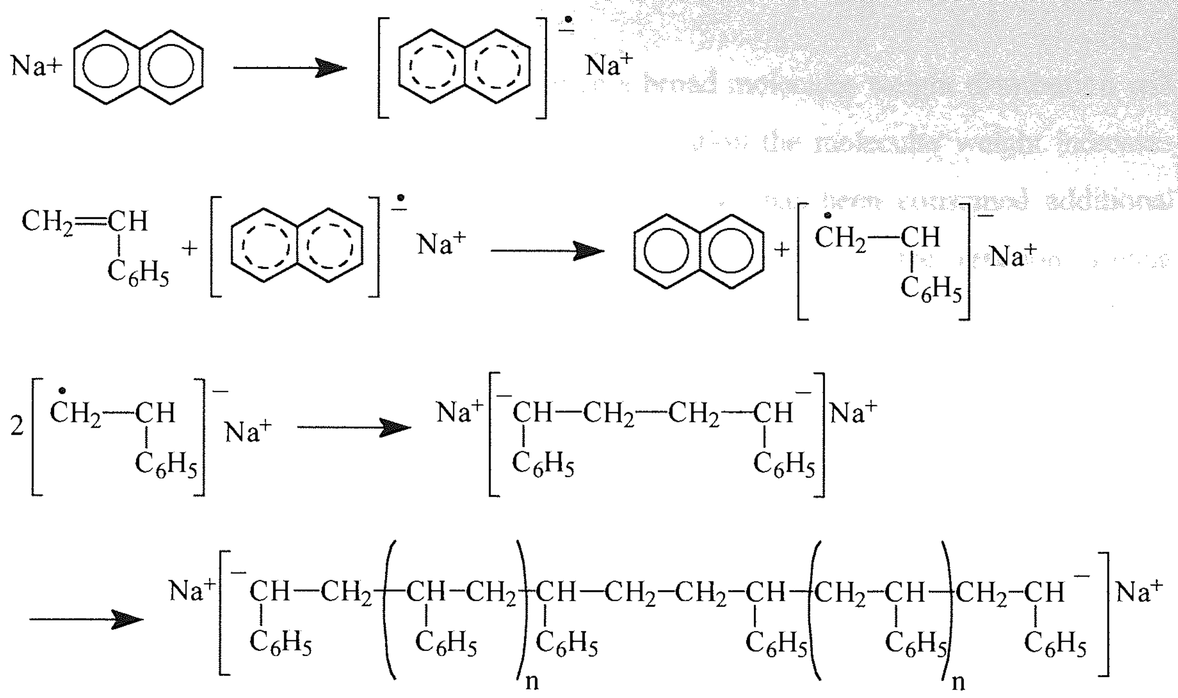
The term pseudo-cationic polymerization is also applied to polymerizations where the positive charge is delocalized, as in the polymerization of aldehydes and acetals, see scheme 1.23.

$$\sim\!\sim\!\sim O\overset{+}{=}CH_2 + O{=}CH_2 \longrightarrow \sim\!\sim\!\sim O-CH_2-O\overset{+}{=}CH_2$$

Scheme 1.23: Polymerization of an aldehyde by a pseudo-cationic mechanism.

1.3: Living polymerization.

A living polymerization is defined as a polymerization in which propagation proceeds in the absence of termination or transfer reactions and the growing chain ends remain active once all monomer has been consumed. However, since all the chain ends will eventually isomerise, react with their surroundings or otherwise decompose, this definition has been relaxed and a polymer is considered living if the growing centre remains active long enough for any further synthesis to be completed. One of the first living polymerizations, reported by Szwarc(50), was the anionic polymerization of styrene initiated by sodium naphthalide (scheme 1.24). Sodium was added to a solution of naphthalene in THF to produce the green naphthyl radical-anion. Addition of styrene leads to transfer of an electron from the naphthyl radical-anion to the monomer producing a red styryl radical-anion. Two of these radical-anions will combine to give a dianion that propagates from both ends. The living nature of this polymerization was demonstrated by the persistence of the red colour from the styryl radical-anion when all the monomer had been consumed. Further evidence of the living nature was obtained by adding a second batch of monomer to the completed polymerization where upon an increase in molecular weight was observed.



Scheme 1.24: Living polymerization of styrene initiated by sodium naphthalide.

Living polymerization is well established in the area of anionic polymerization(51), and more recently cationic polymerization (see section 1.3.2). As well as ionic reactions living polymerizations have been achieve in the areas of group transfer polymerization(52) and more recently free radical polymerization(53).

1.3.1: Characteristics of living polymerization.

One of the major characteristics of living polymerization is the ability to control the molecular mass of the polymer. If the rate of initiation is fast compared to the rate of propagation, so that all the polymer chains are initiated at approximately the same time and the reaction mixture is homogeneous, so that all the polymer chains grow a the same rate then polymers with narrow molecular weight distributions will be obtained. The molecular weight distribution will then have a Poisson distribution (54-56) give by;

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + \frac{\overline{M}_n}{\left(\overline{M}_n + 1\right)^2} \qquad (1.21)$$

Under these conditions and if each initiating molecule gives rise to one discreet polymer chain then the number average degree of polymerization will be given by;

$$\overline{Dp_n} = \frac{[M]_0 - [M]}{[I]_0}. \qquad (1.22)$$

However, if the rate of initiation is slow then a broad molecular weight distribution will be obtained. For reactions with a high rate of initiation the molecular weight increases linearly with monomer conversion. Once all monomer has been consumed additional polymerization will take place if more monomer is added to the reaction. Living polymerization can be deliberately terminated by adding a reagent that will react with the propagating chain end, for example water, alcohols or protic acids depending on the nature of the active centre.

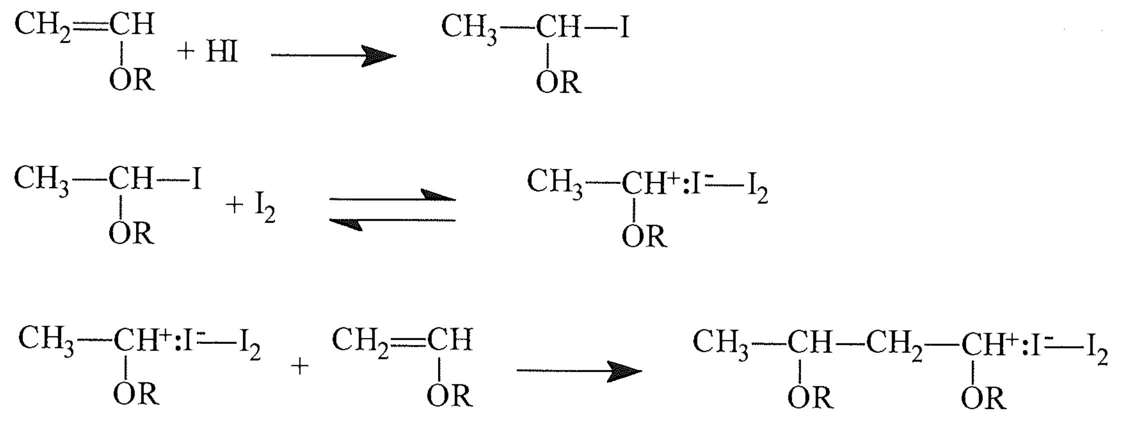
1.3.2: Living carbocationic polymerization.

The first developments in the area of living cationic polymerization were the quasiliving carbocationic polymerization(57-59). This approximation to living polymerization was achieved under certain restrictive reaction conditions. Spontaneous termination and combination with counter ion have to be reversible or suppressed. There must be no other chain breaking reactions present. The life time of the propagating species can be extended by the continuous very slow addition of monomer. The incoming monomer is almost entirely consumed by propagation preventing transfer to monomer from taking place. An example of a quasiliving polymerization is the polymerization of α-methylstyrene initiated by $C_6H_5(CH_3)_2Cl/BCl_3$ in a mixture of dichloromethane and methylcyclohexane solvent at -50 °C. These reactions have some of the characteristics of a living polymer and have been used in the synthesis of telechelic polymers and block copolymers.

The first living cationic polymerization, reported by Higashimura et al(60), was the polymerization of vinyl ethers initiated by hydrogen iodide and iodine at temperatures below 0 °C in non-polar solvents, such as toluene, or below -15 °C in more polar solvents, e.g. dichloromethane. This polymerization exhibited all the characteristics of a living polymer. The number average degree of polymerisation increased linearly with conversion and was found to be given by;

$$\overline{Dp_n} = \frac{[M]_0 - [M]}{[I]_0}. \qquad (1.23)$$

A narrow molecular weight distribution was obtained and after complete conversion of the monomer propagation continued on addition of more monomer. ^1H and ^{13}C NMR(61) studies showed that the living polymer had a terminal carbon-iodine bond. Scheme 1.25 shows the proposed mechanism for this reaction. Initiation is by the rapid addition of hydrogen iodide to a monomer molecule forming an inert iodide, alternatively the iodide can be prepared prior to the polymerization. This iodide then complexes with an iodine molecule to form a close contact ion pair. Propagation is by insertion of a monomer into the ion pair.

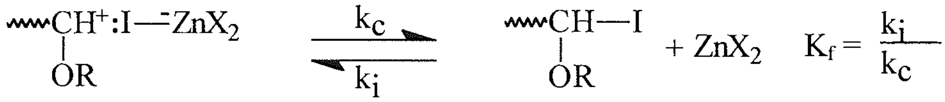


Scheme 1.25: Polymerization of vinyl ethers by hydrogen iodide/iodine.

It was found that this polymerization exhibited a narrow molecular weight distribution even at ratios of $[I_2]$ to $[HI] < 1$, indicating that not all the polymer chains are active at once and that there is an exchange reaction taking place between the inert iodide and the active species. The rate of this exchange is faster than propagation. Lewis acids such as ZnX_2 and SnX_2, where X = Cl, Br or I, proved to be more efficient catalysts than iodine(62). The rates of polymerization using these Lewis acids were higher than that of reactions catalysed by iodine. Concentrations 50 times lower than those of iodine produced similar rates of polymerization. The temperature range over which the polymerization was shown to be living increases from that catalysed by iodine when using zinc halides to -40 °C to +40 °C in toluene and -40 °C to 0 °C in dichloromethane. This is because ZnX_2 will not initiate polymerization on its own where as iodine will at these higher temperatures and such polymerization will be conventional cationic reactions. Stronger Lewis acids, e.g. BCl_3 or $SnCl_4$, will induce polymerization with hydrogen iodide but these reactions are not living.

In a conventional polymerization the life time of the active centres is only a few seconds before it combines with a counter ion fragment (termination) or undergoes loss of a β-proton to monomer or counter ion (transfer). For a polymerization to be living it is necessary to prevent these reactions from occurring.

Theoretically termination by the collapse of an ion pair into a covalent molecule, is a reversible reaction, see scheme 1.26. For a polymerization to be living there must be a rapid exchange between the ion pairs and covalent molecules. If $1/k_i$, the time for a covalent molecule to form an ion pair, is less than the time for polymerisation then the process is considered reversible and the covalent molecule is a dormant polymer chain. If, however, $1/k_i$ is greater than the time for polymerisation the covalent species is regarded as the product of an irreversible termination reaction.



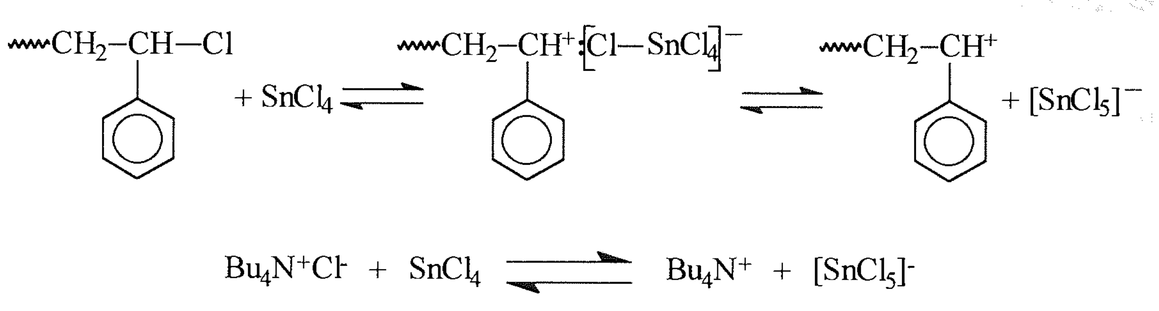
$$\underset{\text{OR}}{\sim\!\text{CH}^+}\text{:I}\text{—}^-\text{ZnX}_2 \underset{k_i}{\overset{k_c}{\rightleftharpoons}} \underset{\text{OR}}{\sim\!\text{CH}}\text{—I} + \text{ZnX}_2 \qquad K_f = \frac{k_i}{k_c}$$

Scheme 1.26: Equilibrium between ion pairs and covalent species in the polymerization of vinyl ether by HI/ZnX_2.

The equilibrium constant for the formation of ion pairs, K_f, decreases as the nucleophilicity of the counter ion increases. This increases the shelf life of the polymer as more of the potentially active sites are converted to the dormant species. This conversion to the dormant species decreases the rate of propagation. If the decrease in the rate of propagation is too great, polymerization may be prevented completely. For example N-vinylcarbazole will polymerize with hydrogen iodide because the value of K_f is large enough to give a reasonable rate of propagation. Vinyl ethers however cannot be polymerized by hydrogen iodide alone because K_f is too low and propagation is extremely slow, a Lewis acid is thus needed to reduce the nucleophilicity of the iodide and increase K_f.

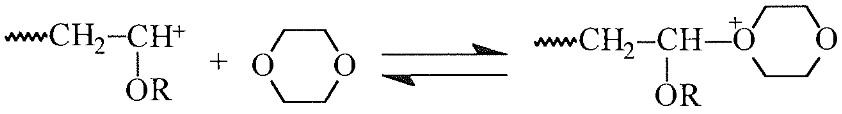
The second problem in a living polymerization is chain transfer. Matyjaszewski(63) showed that the life time of a close contact ion pair, before it collapses back to a covalent molecule, is shorter than that of free ions. This means that transfer to monomer reactions can be suppressed in polymerizations where the propagating species is an ion pair because the life time of the close contact ion pair is less than the time required for a transfer reaction to take place. This is illustrated by the differences in the polymerisation of vinyl ethers by ZnX_2 and $SnCl_4$. $SnCl_4$ is the stronger Lewis acid and forms free ions allowing transfer reactions to occur.

The nature of the propagating species can be controlled using the common ion salt method. In a polymerization the active centre can be present in several forms as discussed in section 1.2.3 (see scheme 1.19). While close contact ion pairs may undergo a living polymerization the looser ion pairs and free ions will tend to participate in transfer as well as propagation reactions. This leads to a broad, and possibly multi-modal molecular weight distribution. The formation of the free ionic form in the equilibrium can be suppressed by the addition of a salt containing an anion capable of complexing with the catalyst. For example the polymerization of styrene by tin (IV) chloride and 1-chloro-1-phenylethane is non-living producing a broad, multi-modal molecular weight distribution. Scheme 1.27 shows the equilibrium between active and dormant species in this reaction. However, if the reaction is conducted in the presence of tetrabutyl ammonium chloride a narrow molecular weight distribution is obtained and the polymer is living$^{(64)}$. The ammonium salt will react with the tin (IV) chloride to give a stable ammonium ion and a pentachloro-tin anion. The excess $[SnCl_5]^-$ produced by this reaction drives the equilibrium between chain ends towards the covalent species suppressing the formation of free ions almost completely and leaving only the short lived ion pairs to undergo living polymerization.



Scheme 1.27: Equilibrium between chain ends in the polymerization of styrene by tin (IV) chloride/1-chloro-1-phenylethane in the presence of tetrabutylammonium chloride.

The other method to produce a living system is to reduce the rate of transfer. This can be achieved by a number of methods. One method is to control the rate of transfer by increasing the stability of the carbocation, this can be achieved by complexation with another molecule. For example the polymerization of vinyl ethers initiated by $(C_2H_5)AlCl_2$ and a cationogen, e.g. water, is a non-living reaction. The polymerization becomes living on the addition of an excess of an ester, such as ethyl acetate or ethyl benzoate(65), or an ether, for example dioxane or diethyl ether(66). The ester or ether combines with the active centre to produce an unreactive onium ion which is in rapid equilibrium with the propagating carbocation, as shown in scheme 1.28. The rapid interconversion between the different ions gives the propagating species a very short lifetime preventing transfer from occurring.



Scheme 1.28: Formation of an oxonium ion in the polymerization of vinyl ethers initiated by $Al(C_2H_5)$ in the presence of 1,4-dioxane.

Another method of controling transfer reactions is to make the formation of the products of transfer unfavourable. For example, the polymerization of N-vinylcarbazole initiated by hydrogen chloride is a non-living polymerization because the elimination of HCl is too fast. However the same reaction initiated by hydrogen iodide produces a living polymerization because the hydrogen-iodine bond is ~100 kJ mol^{-1} weaker and so elimination of HI is a slower reaction.

Many living cationic polymerizations have been developed for a range of monomers by selecting the correct solvent, counter ion, temperature and additives to control the stability of the growing carbocation. Table 1.3 lists some monomers and initiating systems for living cationic polymerization.

Monomer	Initiator System	Notes	Ref N°
vinyl ethers	HI/I_2	Toluene -5 °C to -35 °C, hexane -15 °C.	60
	HI/ZnI_2	Toluene -40 °C to 40 °C, dichloromethane -40 °C to 0 °C.	62
	$CH_3CH(OR)X/ZnI_2$	X = Cl, I. A wide range of HX adducts of vinyl ethers have been used to initiate polymerization.	
	Triflic acid/$Bu_4N^+I^-$	Dichloromethane -40 °C.	67
	$R^1R^2PO_2H/ZnCl_2$	R1/R2 = Ph/H; Ph/Ph; OPh/OPh. Toluene, < 0 °C.	68
	$HCl/TiCl_{4-n}(OR)_n$	$R = -CH_2(CH_3)_2$, n = 2-3. Dichloromethane -15 °C.	69
	HI/MX_n	$MX_n = ZnI_2$. $ZnBr_2$, $ZnCL_2$,SnI_2 and $SnCl_2$	70
	1-isobutylethyl acetate/$EtAlCl_2$/X-C_6H_4-$COOCH_2CH_3$ or R-$COOCH_3$	X = CH_3O, CH_3, H, Cl. R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$. Hexane, + 40 °C.	71
	α-chloro-iodo and α-iodo esters/$Bu_4N^+ClO_4^-$	Dichloromethane -30 °C	72

Monomer	Initiator System	Notes	Ref N°
Isobutyl vinyl ether	$CH_3CH(OiBu)OCOCH_3$/ $EtAlCl_2$/cyclic ether	Hexane, 0 °C. Cyclic ethers used were THF, THP, oxepane, 1,4-dioxane, 1,3-dioxane.	73
	$R_4N^+ClO_4^-$ $(KClO_4;LiClO_4)/CH_3CH(OR)I$		74
	Carbon Black/$ZnCl_2$	Polymerization initiated by carboxyl groups on carbon black. Toluene	75
	Diphenylphosphate/ZnI_2		76
	$EtAlCl_2$/2,6-dimethylpyridine		77
	$HI/R_4N^+A^-$	Dichloromethane -40 °C to -15 °C. R = C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17} or $C_{12}H_{25}$ and A = ClO_4, or R = C_4H_9 and A = I, NO_3, PF_6, BF_4 or $B(C_6H_5)_4$.	78
	Me_3SiI/Lewis Acid/Acetone	ZnI_2; toluene < 0 °C. I_2; toluene -40 °C.	79

Monomer	Initiator System	Notes	Ref N°
Isobutyl vinyl ether	HI/M(acetyacetonate)$_n$	Toluene or dichloromethane, 0 °C. M = Zn (n = 2); toluene or dichloromethane -40 °C, Fe (n = 3); dichloromethane -40 °C, Al (n = 3); dichloromethane -40 °C.	80
	Me_3SiY/ZnX_2/ p-methoxybenzaldehyde	Toluene, -15 °C. X = I, Br or Cl and Y = I, Br.	81
	HCl/MX_n	Dichloromethane, -15 °C. MX_n = $ZnCl_2$; $SnBr_4$; $SnCl_4$ in the presence of $Bu_4N^+Y^-$ or $Bu_4P^+Y^-$. Y = Br, Cl, I, CH_3CO_2	82
2-Chloroethyl vinyl ether	$R_4N^+ClO_4^-$ ($KClO_4$;$LiClO_4$)/ $CH_3CH(OR)I$		74
	$CH_3CHI(OCH_2CH(CH_3)_2)$/ $Bu_4N^+ClO_4^-$		83
Cyclohexyl vinyl ether	HI or HCl/$Bu_4N^+X^-$	X = Cl, Br, I. Toluene -15 °C, Dichloromethane -30 °C.	84

Monomer	Initiator System	Notes	Ref N°
N-vinylcarbazole	HI	Toluene -40 °C. Dichloromethane -78 °C with $Bu_4N^+Cl^-$.	85
	$I_2/Bu_4N^+I^-$		86
Styrene	Methanesulfonic acid/ $SnCl_4/Bu_4N^+Cl^-$	Dichloromethane -15 °C to 0 °C.	87
	1-Chloro-1-phenylethane $/SnCl_4/Bu_4N^+Y^-$	Dichloromethane -15 °C. Y = I, Br or Cl.	64
	1,4 Bis(1-chloroethyl)benzene/ $SnCl_4$/2,4-ditertbutyl pyridine	Chloroform -15 °C.	88
	1-Chloro-1-phenylethane/$SnCl_4$	Chloroform, -15 °C.	89
	$HCl/TiCl_{4-n}(OR)_n/Bu_4N^+Cl^-$	$R = CH_2(CH3)_2$; n = 1. Dichloromethane -15 °C.	69
α-methylstyrene	$CH_3CHCl(OCH_2CH_2Cl)/SnBr_4$	Dichloromethane, -78 °C.	90

Monomer	Initiator System	Notes	Ref N°
p-methoxystyrene	$HI/I_2/Bu_4N^+X^-$	Dichloromethane -15 °C. Y = I, Br or Cl.	91
	HI/ZnI_2	Toluene or dichloromethane < 0 °C. $HI/ZnI_2 = 1/5$	92
Isobutene	Blocked difunctional initiators/$TiCl_4$/2,6-ditertbutyl pyridine	Initiators used: 5-*t*-butyl-1,3-dicumyl chloride, 5-*t*-butyl-1,3-dimethyl ether and 5-*t*-butyl-1,3-dicumyl-acetate. Dichloromethane/hexane (40 : 60 v : v) -80 °C.	93
	BCl_3/proton trap	Chloromethane, dichloromethane or 1,2-dicholoroethane. -60 °C to -25 °C.	94
	Tertiary Chloride/$TiCl_4$ or BCl_3/Electron Donor	60/40 % v/v chloroform/hexane -40 °C. Tertiary chloride = 2-chloro-2-phenylpropane or 2-chloro-2,4,4-trimethypentane. Electron donor = dimethylsulfoxide or dimethylacetamide.	95

Monomer	Initiator System	Notes	Ref N°
Isobutene	Dicumyl Chloride/BCl_3/ Electron Donor	Chloroform -80 °C. Electron donors = N,N-dimethylacetamide, acetophenone, benzophenone, ethylisobutyrate, methylbenzoate, dimethyl 5-t-butyl-benzene-1,3-carboxylate, dimethyl phthalate & dioctyl phthalate	96
	1,4-Bis(1-azido-1-methylethyl) benzene/Et_2AlCl	Dichlorormethane -50 °C to -20 °C.	97
	Dicumyl chloride/$TiCl_4$/Pyridine	60/40% v/v hexane/dichloromethane -80 °C.	98
	5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)-benzene/$TICl_4$/2,6-di-*tert*-butylpyridine	60/40% v/v hexane/dichloromethane -80 °C.	99
	2-chloro-2,4,4-trimethypentane/ $TiCl_4/Bu_4N^+Cl^-$	60/40% v/v hexane/dichloromethane -80 °C to -40 °C.	100

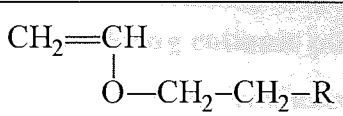
Table 1.3: Living cationic polymerization systems.

1.3.3: Synthetic applications of living carbocationic polymerization.

Living polymerization can be used to prepare a variety of polymers with controlled molecular weight and structure. The molecular weight of the polymer can be controlled by varying the monomer to initiator ratio. If the rate of initiation is faster than the rate of propagation then near monodispers polymers can be produced. This is often achieved by using co-catalysts that are analogues of the monomer. For example the HX adducts of the monomer, e.g. 1-chloro-1-phenylethane for styrene, 2-chloro-2-methylpropane for isobutene or 1-iodo-1-(2-methylpropoxy)ethane for isobutyl vinyl ether.

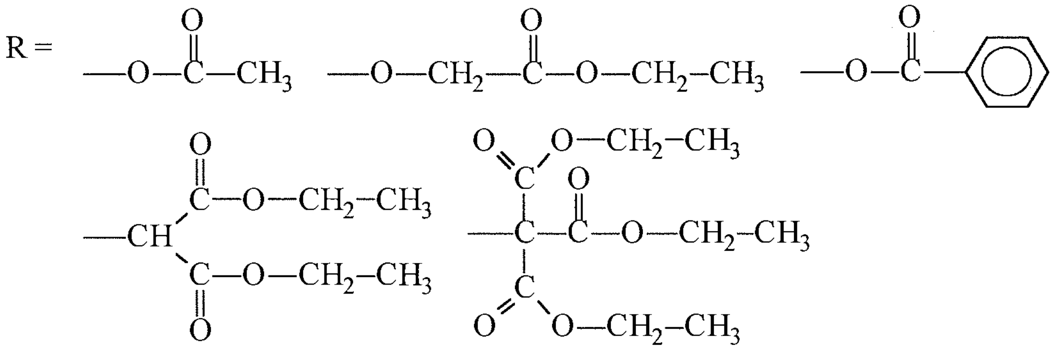
1.3.3.1: Polymers containing pendant functional groups.

Polymers containing pendent functional groups can be synthesised using living polymerization. These groups often result in side reactions in classical cationic polymerizations, but the increased stability of the active centre in living polymerization allows the use of functional monomers. For example, the hydrogen iodide/iodine or zinc iodide initiating system has been used with a range of functional monomers such as; saturated ester(101), unsaturated esters(102), ethers(103), polyoxyethylenes(104), trialkylsilyoxyl(105), phthalimide(106) and perfluoroalkyl sulfonamide(107), see figure 1.3.

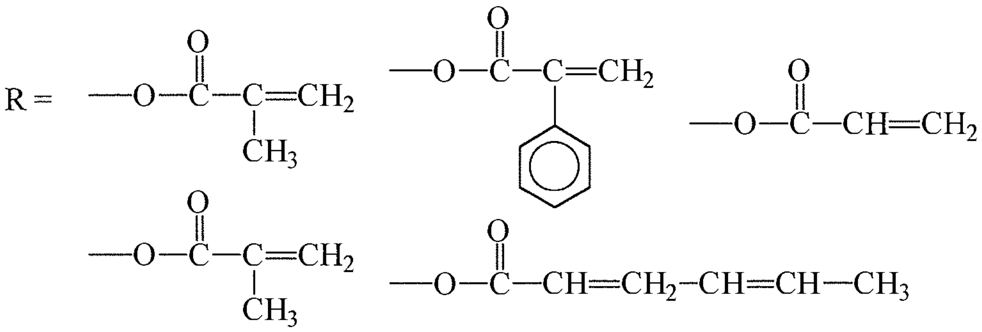


$CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}R$

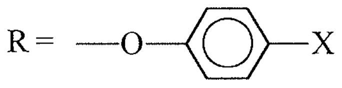
Saturated Esters.



Unsaturated Esters.

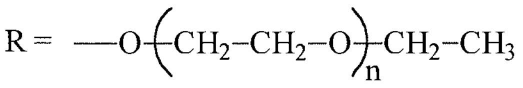


Ethers.



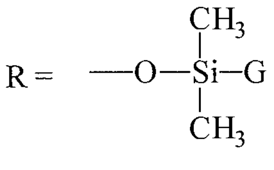
X = H, OCH$_3$, Cl

Polyoxyethylenes.



$R = {-}O{-}(CH_2{-}CH_2{-}O)_n{-}CH_2{-}CH_3$

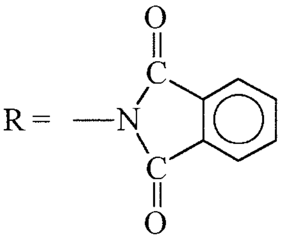
Trialkylsilyloxyl.



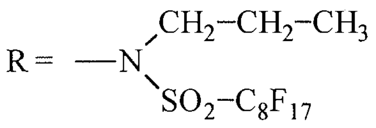
$R = {-}O{-}Si(CH_3)_2{-}G$

G = CH$_3$, *t*-C$_4$H$_9$

Phthalimide.



Perfluoroalkyl sulfonamide



$R = {-}N(CH_2{-}CH_2{-}CH_3)(SO_2{-}C_8F_{17})$

Figure 1.3: Functional vinyl ethers for living cationic polymerization.

1.3.3.2: Telechelic polymers by living cationic polymerization.

Living polymerization can be used to synthesise telechelic polymers by two methods; functionalised co-catalysts or end functionalisation. If there are no transfer reactions taking place and in the absence of impurities, such as water which will initiate polymerization, all the polymer chains will contain the initiating cation, R^+ in scheme 1.2. Therefore a functional group can be included in the polymer chain end by using a functionalised co-catalyst. Examples of this method include; HCl or HI adducts of the functional monomers shown in figure 1.20 with the RI/I_2 initiator system for vinyl ethers(108) or the $RCl/SnCl_4/Bu_4N^+Cl^-$ initiating system for styrene(109). Ester functional groups have been included in polyisobutene using the co-catalysts shown on figure 1.4 in combination with titanium tetrachloride.

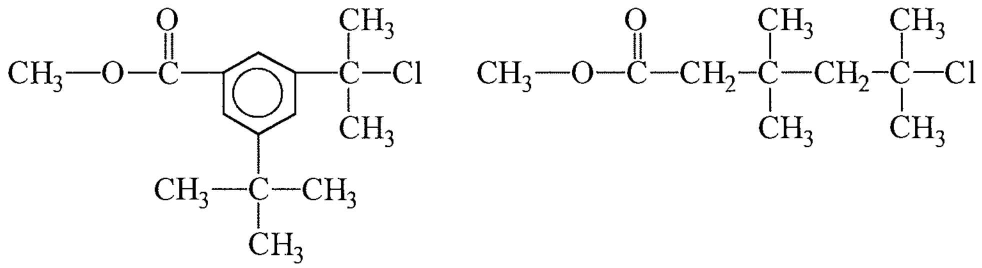
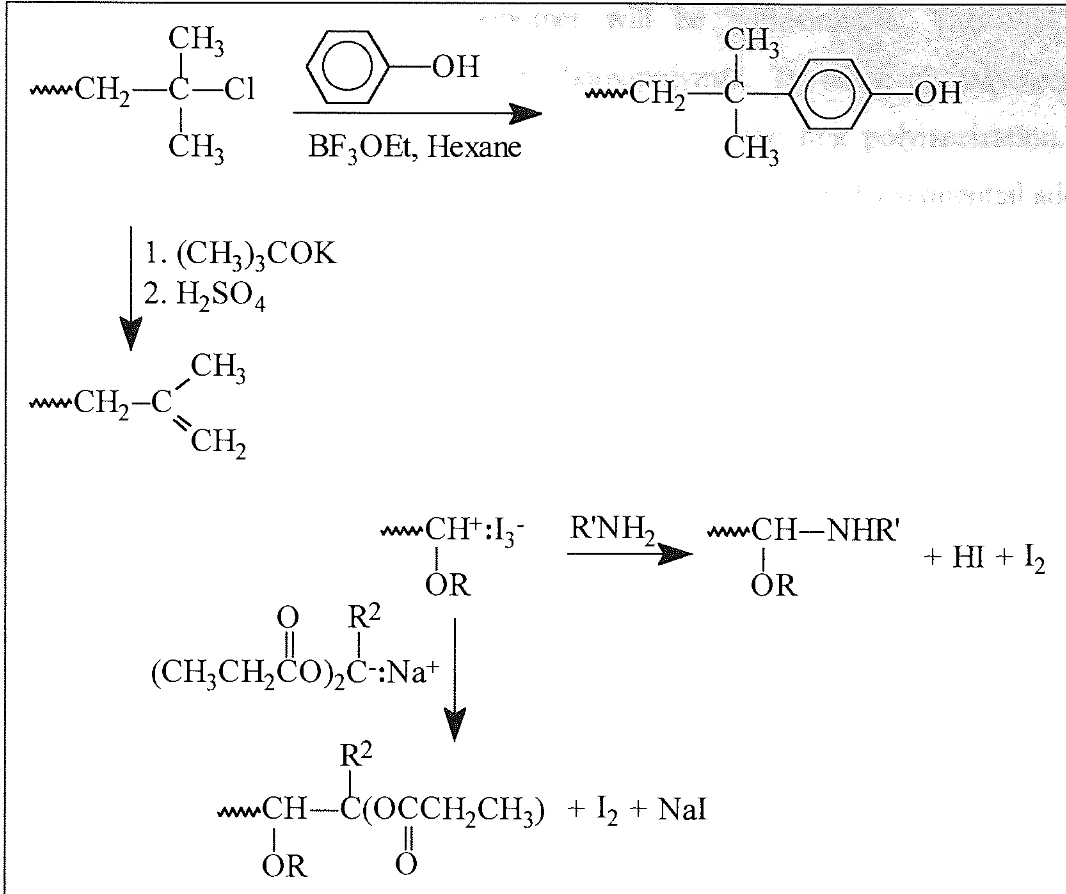


Figure 1.4: Functional co-catalysts for the polymerization of isobutene.

Telechelic polymers can also be synthesised by capping the growing polymer chain end by reacting it with a functional nucleophile. Terminally halogenated polymers are often formed when a polymerization initiated by Lewis acid/organic halide is quenched by the addition of methanol. Examples of reagents used for the synthesis of telechelic polymers by the end capping method are; dehydrochlorination of chlorine terminated polyisobutene initiated by $TiCl_4/RCl$ to give a vinyl end group(110) or reaction with phenol to give a hydroxyl end group. Poly(vinyl ethers) with terminal amino groups can be obtained from the HI/I_2 system by reaction with excess RNH_2(111) where R = $CH_3CH_2CH_2CH_2$-, $NH_2CH_2CH_2CH_2CH_2$-, C_6H_5-, $NH_2C_6H_4$-, $HOOCC_6H_4$-, $CH_3CH_2OOCC_6H_4$-. Sodiomalonic esters $(C_2H_5COO)_2C^-R{:}Na^+$ can be used to produce functional end groups(112), see scheme 1.29.

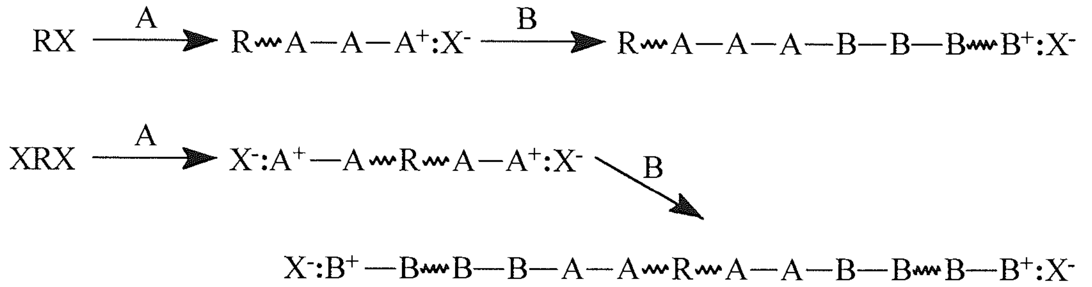


Scheme 1.29: Telechelic polymers by the end capping method.

Difunctional telechelic polymers can be synthesised by combining the functional co-catalyst and end capping methods or by using a difunctional co-catalyst to give a polymer chain that is growing from both ends and then performing a capping reaction on the propagating centre.

1.3.3.3: Block co-polymers by living cationic polymerization.

Block copolymers can be prepared, free of homopolymer, using living polymerization by a process known as sequential monomer addition. This method involves polymerizing the first monomer to completion and then adding the second monomer. For the sequential monomer addition method to be effective it is necessary for both monomers to undergo a living polymerization under the same conditions, solvent and counter ion. The second monomer must be at least as reactive towards polymerization as the first. If the cation formed by the addition of a molecule of the second monomer to the polymer chain end produces a less stable cation then initiation of polymerization of the second monomer will be unfavourable. This will lead to contamination of the co-polymer with homopolymer. Tri-block co-polymers can be formed by using a difunctional co-catalyst to initiate the first polymerization. Scheme 1.30 shows the formation of di-block and tri-block co-polymers by sequential addition.

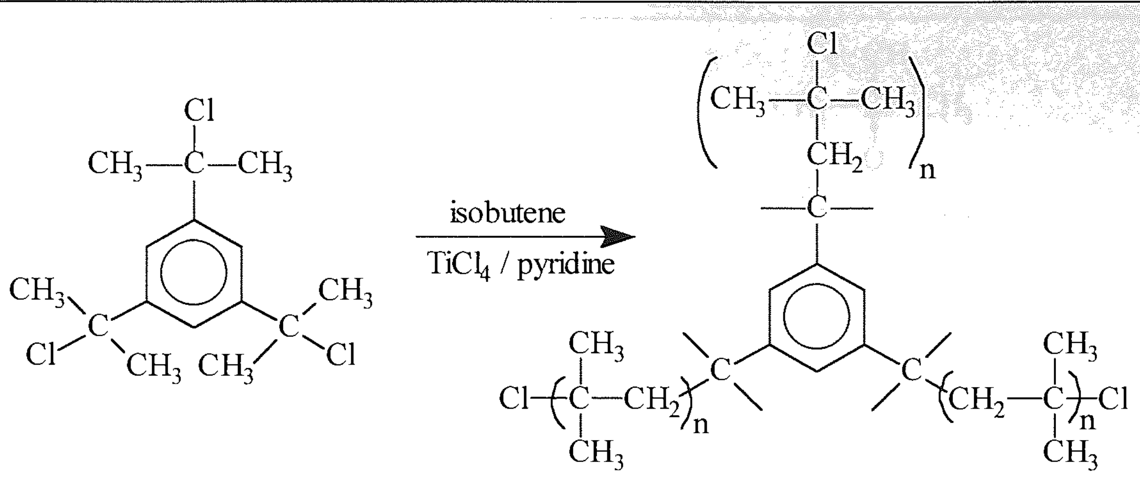


Scheme 1.30: Synthesis of block co-polymers by sequential monomer addition.

Examples of block co-polymers synthesised by living cationic polymerization are; poly(styrene-*b*-isobutene-*b*-styrene) using $TiCl_4$/dicumylchloride/pyridine initiator system(113), poly(indene-*b*-isobutene-*b*-indene) with $TiCl_4$/1,4-bis(2-methoxy-2-propyl) benzene/N,N-dimethylacetamide/2,6-di-*tert*-butylpyridine initiator(114) and poly(para-methoxystyrene-*b*-isobutylvinylether) by the HI/I_2 initiating system(115).

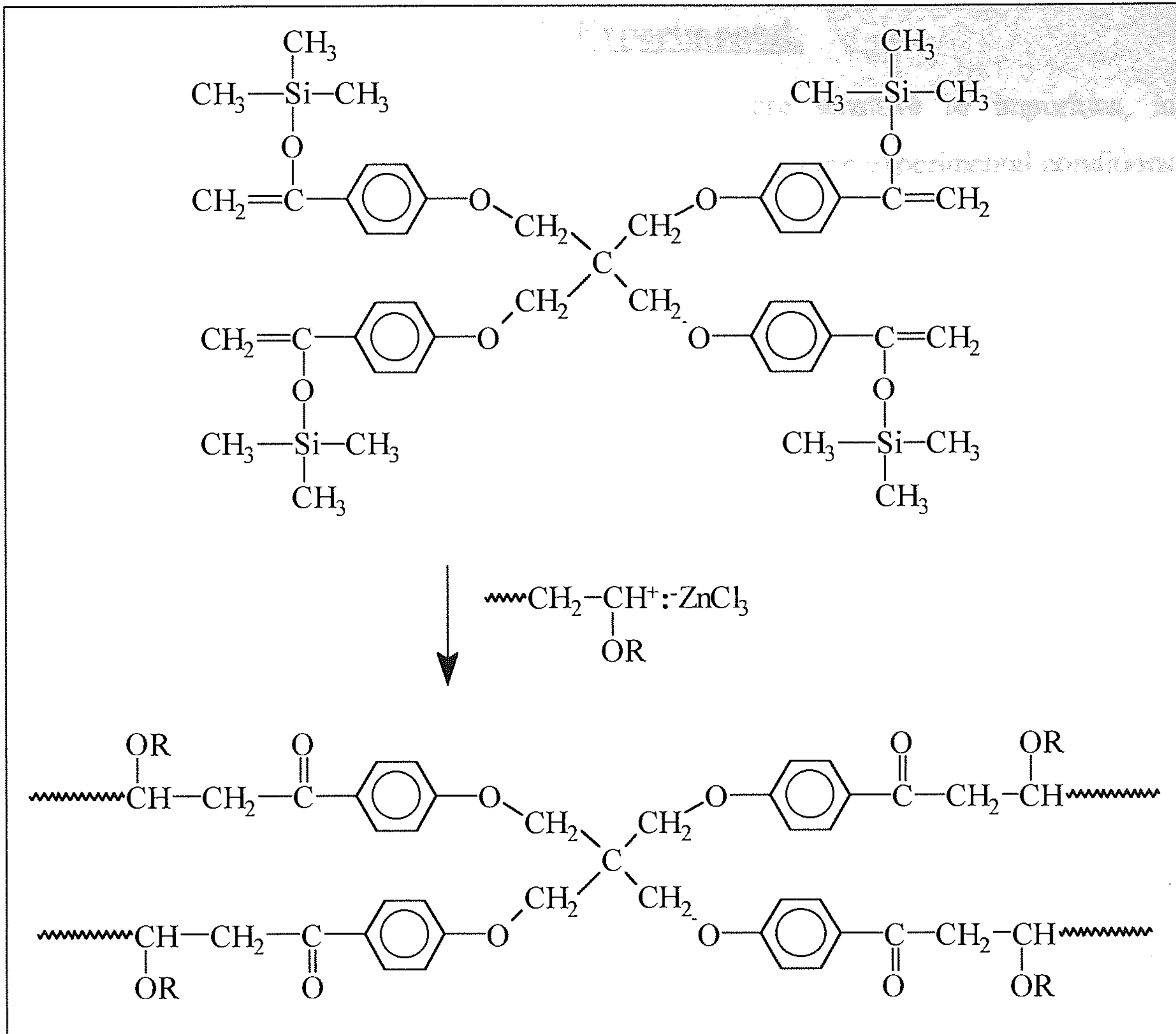
1.3.3.4: Star shaped polymers by living polymerization.

Star shaped polymers can be prepared by living cationic polymerization by two methods; using the 'core first' method of growing a number of polymer chains from a single co-catalyst molecule, or by using a coupling reaction to join together several polymer chains. The core first method involves initiating a polymerization using a multi-functional co-catalyst. A problem with this method is that initiation at all the active sites on a co-catalyst molecule must be rapid to give a polymer with uniform length arms and avoid production of linear polymer. An example of this is the polymerization of isobutene initiated by tricumylchloride/$TiCl_4$/pyridine(116), as shown in scheme 1.31.



Scheme 1.31: Star shaped polymers by the multi-functional initiator method.

Star shaped polymers can also be synthesised by using a coupling agent to link several living polymer chains. Scheme 1.32 shows an example of this method using a tetra functional silyl enol ether to couple together living poly vinyl ether initiated by $ZnCl_2$/RCl (117). Using this method it is necessary to have an accurate stoichiometric ratio of living ends to linking agent of 4:1 other wise the star shaped polymer may contain linear polymer chains either from; unreacted polymer chains if the ratio is too high, or from linking agents reacting with only 1 or 2 polymer chains if the ratio is too low.



Scheme 1.32: Synthesis of star shaped polymers by a coupling reaction.

Many of these applications of living polymerization have been used in combination with each other to produce the desired polymers. For example star shaped block co-polymers, block co-polymers containing pendant functional groups or star shaped polymer with functional end groups.

1.4: Scope of the project.

Living polymerization offers a wide range of opportunities for the synthesis of speciality polymers. The scope of this project is to study the polymerization of styrene using the common ion salt method, to obtain information about the mechanism of polymerization and to study the potential use in the synthesis of functional polymers and block co-polymers.

Chapter 2: Experimental.

Ionic, and especially living polymerizations, are sensitive to impurities, in particular moisture or oxygen and require the use of highly pure experimental conditions to minimise side reactions.

All glassware was first washed with toluene or acetone to remove any polymer and organic residues and then soaked in a solution Decon 90 to remove any high vacuum silicon grease before being thoroughly rinsed with water. Prior to use all glassware was oven-dried at 200 °C and transferred to either the vacuum line or the dry box.

2.1 Vacuum techniques.

The vacuum line, shown in figure 2.1 below, was constructed of glass and consisted of a manifold (A) and two sub-manifolds (B) connected via PTFE greaseless taps. A series of B19 ground glass joints were connected to the manifold by means of PTFE taps. The manifolds were connected to a Leybold Tri-Vac Rotary vacuum pump, which reduced pressures to 10^{-3} to 10^{-4} mm Hg, through a main tap. Two liquid nitrogen cold traps were present to protect the vacuum pump from any vapour coming from the manifold. The pressure inside the system was measured by use of a Pirani gauge. An argon supply was connected to the manifold to allow manipulation of materials under an inert atmosphere rather than a vacuum.

2.1.1: Freeze-thaw degassing.

In order to remove dissolved gases and facilitate distillation of materials under high vacuum, liquids were degassed using a freeze-thaw procedure. The flask containing the material to be degassed was attached to the vacuum line with the tap closed and the manifold evacuated. The contents of the flask were then frozen by immersing the flask in liquid nitrogen. Once the material was frozen the relevant taps were opened and the flask evacuated. When the pressure in the flask was minimised the main tap, or sub-manifold tap, was closed and the frozen liquid was melted releasing any gases trapped by the freezing process to enter the manifold. The tap on the flask was closed, and the main tap opened to evacuate the manifold. The contents of the flask were frozen and the degassing procedure repeated until no further gas was released during the thawing process.

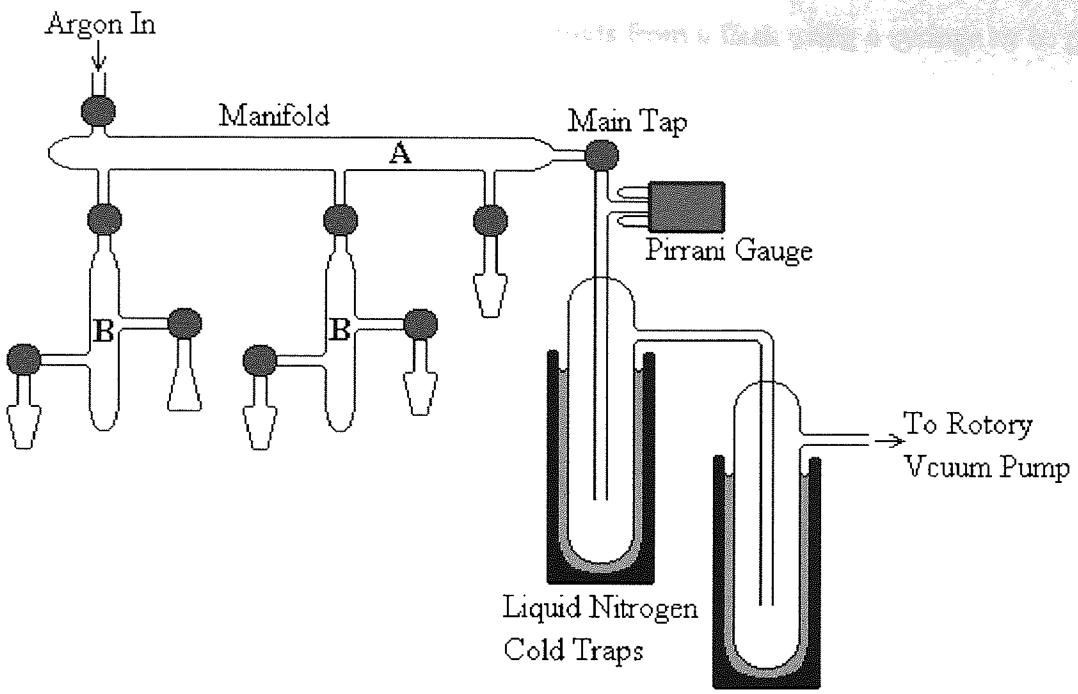


Figure 2.1: Vacuum line.

2.1.2: Trap-to-trap distillation.

Once degassed liquids could be transferred to a second vessel using the vacuum line by a trap-to-trap distillation procedure. The flask containing the degassed material was attached to one of the sub-manifolds and the vacuum line was evacuated. The receiver flask was then attached to the same sub-manifold and, if empty, evacuated and then immersed in liquid nitrogen. The sub-manifold was isolated from the vacuum pump by closing the relevant tap then the taps on the appropriate ground glass joints and flasks were opened to allow the material to distil.

2.1.3: Schlenk techniques.

To enable the handling of sensitive materials under an inert atmosphere an argon supply was connected to the vacuum line. So that the Schlenk technique could be used the apparatus to be used was attached to the manifold, evacuated and then the main tap was closed. Argon was introduced into the manifold and flask and a slight positive pressure was maintained. This pressure was monitored by an oil bubbler connected in parallel to the argon supply. The tap on the apparatus was then removed and materials could be introduced into the apparatus using dry syringes with an argon stream flowing. Similar methods were also used to remove liquids from a flask using a syringe or to place a solid material into a flask.

2.2: Argon dry-box.

To enable materials to be stored and manipulated under an inert atmosphere, a dry-box supplied by Halco Engineering Ltd was used. This maintained an argon atmosphere which was constantly re-circulated through absorbent columns to remove oxygen and water from the atmosphere. Typically, a BASF R311 catalyst was used to remove oxygen and 3Å molecular sieve to absorb moisture to below 1 ppm and 5 ppm respectively. To prevent air entering the system access to the dry box was via a double door posting port. The inner door of the port was sealed, the outer door opened and the apparatus placed into the port. The outer door was closed and the port was then evacuated and filled with argon; this operation was repeated three times before opening the inner door to bring the apparatus into the main part of the dry-box.

2.3: Materials and purification.

2.3.1: Styrene.

Styrene, 99% purity, inhibited with 0.005% 4-tertbutylcatechol, was supplied by Fluka Chemicals. The inhibitor was removed by standing the monomer over sodium hydroxide pellets for 24 hours before distilling the material, using the trap-to-trap method, into a flask containing calcium hydride. The styrene was finally degassed by opening the flask to the vacuum pump and stored over the calcium hydride in a refrigerator.

2.3.2: Dichloromethane.

SPS grade dichloromethane (DCM) 99.9% purity, unstabilised, was obtained from Romil Chemicals and stored in the dry box. Prior to use it was dried over calcium hydride (CaH_2) for at least 24 hours and then refluxed for several hours under an inert atmosphere using the distillation apparatus shown in figure 2.2. DCM was then distilled into a solvent flask discarding the first 10%, degassed on the vacuum line and distilled using the trap-to-trap method as required.

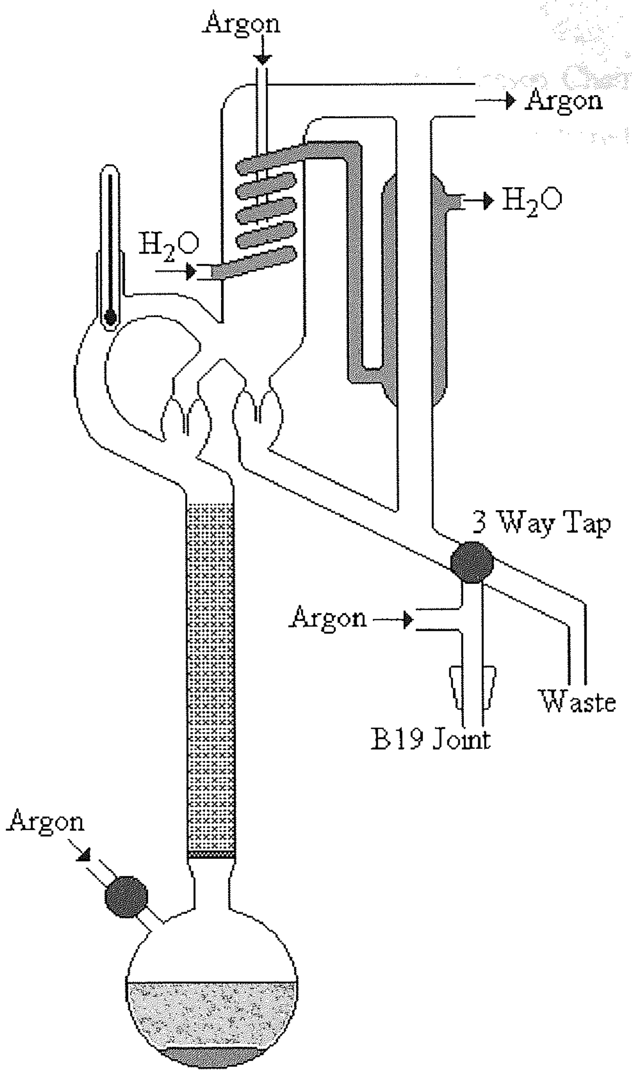


Figure 2.2: Dichloromethane still.

2.3.3: Tin (IV) chloride.

Tin tetrachloride, 99% purity, obtained from Aldrich Chemicals, was stored in the dry box and was transferred as required to a flask using a dry syringe. It was then degassed using the freeze-thaw method, distilled into a catalyst flask by trap-to-trap distillation and a solution in DCM prepared.

2.3.4: Tetrabutyl ammonium chloride.

Tetrabutyl ammonium chloride, 99% purity, supplied by Lancaster Chemicals was dried in a vacuum oven at 80 °C for 24 hours and stored in the dry box. A solution was then prepared in dichloromethane in a catalyst flask in the dry box and degassed.

2.3.5: 1-Chloro-1-phenylethane.

1-Chloro-1-phenylethane (99%) obtained from Janssen Chemica, was stored in the dry box and used without further purification. It was transferred to a catalyst flask using a dry syringe, degassed using the trap-to-trap procedure and a solution in DCM prepared.

2.3.6: 1,4-Bis(bromomethyl)benzene.

1,4-Bis(bromomethyl)benzene, 97%, supplied by Aldrich was dried in a vacuum oven at 80 °C for 24 hours and stored in the drybox. A solution in DCM was prepared in the dry box and degassed on the vacuum line.

2.3.7: 1,1-Diphenylethene.

1,1-Diphenylethene, 97% purity, was obtained from Aldrich Chemicals, dried over calcium hydride for 24 hours, distilled into a catalyst flask using the trap-to-trap method and a solution in dichloromethane prepared.

2.3.8: Oxetane.

Oxetane, 99% purity, obtained from Lancaster Chemicals, was dried and stored over calcium hydride in a refrigerator. Prior to use the oxetane was distilled into a flask containing benzophenone and sodium, was degassed and left to stand for 10-15 minutes. This acted as a check for dryness as the sodium/benzophenone radical anion formed has a characteristic blue colour, but is extremely sensitive to moisture and oxygen.

2.3.9: Methanol.

S.L.R. grade methanol, obtained from Fisons Chemicals, was used as supplied and degassed by bubbling argon through it.

2.3.10: Calcium hydride.

Powdered anhydrous calcium hydride, 90-95% purity, 40 mesh, was obtained from Aldrich Chemical Company and used as supplied.

2.3.11: Sodium hydroxide.

A.C.S. grade sodium hydroxide (97+% purity) in pellet form was supplied by Aldrich Chemical Company and used as supplied.

2.3.12: Sodium metal.

Sodium metal was supplied in paraffin oil by B.D.H. Chemicals. The paraffin oil was removed by washing with hexane and any tarnished pieces of metal removed prior to use.

2.3.13: Benzophenone.

Benzophenone, 99% purity, was obtained from Janssen Chimica and used as supplied.

2.3.14: Phosphorous pentoxide.

Phosphorous pentoxide, 98% purity, was obtained from Fisons Chemicals and used as supplied.

2.3.15: Magnesium sulfate.

A.C.S. grade (97%) magnesium sufate was obtained from Aldrich Chemicals. Prior to use the magnesium sufate was dried in an oven at 200 °C for at least 48 hours.

2.3.16: Proton sponge (1,8-bis(dimethylamino)naphthalene).

Proton sponge, supplied by Aldrich Chemicals, was stored in the dry box, solutions in dichloromethane were prepared and degassed on the vacuum line before use.

2.3.17: 3Å Molecular sieves.

3Å molecular sieves were obtained from Lancaster Synthesis. Prior to use the molecular sieves were dried in oven at 200 °C for at least 48 hours.

2.4: Polymerization techniques.

2.4.1: Homopolymerization procedure.

Homopolymerization reactions were carried out in a side-arm vessel, such as that shown in figure 2.3. Prior to the reaction, solutions of the catalyst, co-catalyst and ammonium salt were prepared. The reaction vessel was attached to the vacuum line and evacuated. In a typical experiment the required amount of catalyst and ammonium salt solutions were injected into bulb B by dry syringe using the Schlenk technique described earlier. The tap to the flask was then replaced, the contents of the bulb frozen with liquid nitrogen and the flask re-evacuated. The co-catalyst solution was then added to the main body of the flask (A), the contents frozen and the vessel evacuated. Styrene was distilled into the main bulb of the vessel using the trap-to-trap method, as was the required volume of solvent also.

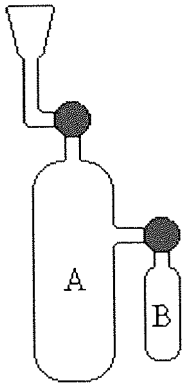


Figure 2.3: Homopolymerization vessel.

The apparatus was then immersed in a constant temperature bath for 30 minutes, either a thermostated water bath for reactions at room temperature, an ice bath for reactions at 0 °C or a Dewar flask containing acetone and solid carbon dioxide for reaction temperatures below 0 °C. The polymerization was then initiated by opening the appropriate tap and pouring the catalyst and ammonium salt solution into the main body of the flask then closing the tap. The vessel was shaken vigorously to ensure efficient mixing and returned to the constant temperature bath. The reaction was terminated by attaching the flask to the vacuum line and injecting degassed methanol into the vessel using the Schlenk technique described above. The polymer was then recovered by pouring the terminated reaction solution into approximately 200 cm^3 of methanol; the solid polymer was then removed by filtration and dried in a vacuum oven at 50 °C for 24 hours.

2.4.2: Co-polymerization procedure

Reactions that required the addition of a second batch of monomer were conducted using a three armed vessel as shown in figure 2.4. The vessel was attached to the vacuum line and evacuated. The required amount of co-catalyst solution was transferred into bulb B using the Schlenk technique. Solutions of the catalyst and ammonium salt were injected into bulb C. The contents of the flask were then frozen by immersing the bulbs into liquid nitrogen and the flask was evacuated. The second monomer or co-monomer was distilled into bulb D and the first monomer distilled into the main body of the flask (A) using the trap-to-trap method. The reaming volume of solvent was then distilled into the main body of the flask.

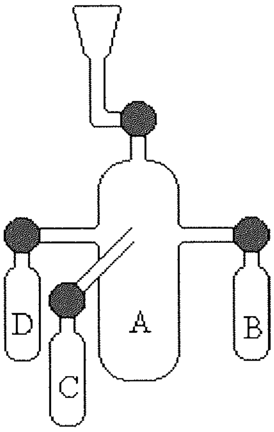


Figure 2.4: Co-polymerization vessel.

The apparatus was first immersed in a constant temperature bath, as described above, for 30 minutes. The polymerization was then initiated by first mixing the monomer and co-catalyst solutions, shaking vigorously before adding the catalyst and ammonium salt solutions, again shaking vigorously. The flask was replaced in the constant temperature bath. After four hours the flask was attached to the vacuum line, still in the constant temperature bath, a sample removed with a dry syringe using the Schlenk method and the polymerization terminated by injecting the solution into a beaker containing degassed methanol. The flask was resealed, the second monomer was then added to the reaction mixture and shaken then replaced in the constant temperature bath. The reaction was terminated by attaching the flask to the vacuum line and injecting degassed methanol into the vessel using the Schlenk technique.

2.5: Dilatometry.

During the polymerization reactions studied in this project there is a change in density as monomer is converted to polymer. This change in density can be measured by dilatometry (118) and used to monitor the extent of conversion during the reaction.

2.5.1 Principle.

The polymerizing reaction mixture is contained in a bulb of known volume attached to a capillary tube of uniform cross sectional area. The accuracy of this technique is dependent on a number of factors. The reaction must be conducted at a constant temperature since rate constants are temperature dependent and to avoid thermal fluctuations in the volume of solution. If the reaction is exothermic the heat evolved must be readily conducted away from the reaction solution. The capillary tube of the dilatometer should be of uniform cross sectional area and narrow enough to detect small changes in volume. Reaction should be carried out at rates that allow the reaction to be followed readily. The concentration of the polymer formed in polymerization reactions must be low enough to avoid the formation of a viscous solution which would impair the movement of the meniscus.

Given these constraints on the use of dilatometry if the meniscus in the capillary moves a distance Δh cm then the volume change ΔV (cm^3) would be:

$$\Delta V = \pi r^2 \Delta h \tag{2.1}$$

where r = radius of capillary /cm.

If m grams of monomer are completely converted to m grams of polymer to produce this volume change then:

$$\Delta V = V_p - V_m = \frac{m}{\rho_p} - \frac{m}{\rho_m} = m\left(\frac{\rho_m - \rho_p}{\rho_m \rho_p}\right) \tag{2.2}$$

where V_p = volume of m grams polymer /cm^3,

V_m = volume of m grams monomer /cm^3,

ρ_p = density of polymer /g cm^{-3},

and ρ_m = density of monomer /g cm^{-3}.

Therefore:

$$m = \frac{\Delta V \rho_m \rho_p}{\left(\rho_m - \rho_p\right)} \tag{2.3}$$

If the number of moles of monomer polymerized is ΔM then

$$\Delta M = \frac{m}{M_m} \tag{2.4}$$

where M_m = relative molecular mass of monomer.

Assuming the volume of the polymerization is much greater than the total volume change, the change in monomer concentration Δ[M] can be approximated to:

$$\Delta[\mathrm{M}] = \frac{\Delta \mathrm{M}}{\mathrm{V}} \qquad (2.5)$$

where V = volume of dilatometer /dm^3.

Substituting equations 2.1, 2.3 and 2.4 into equation 2.5 then gives;

$$\Delta[\mathrm{M}] = \frac{\pi r^2 \Delta h \rho_m \rho_p}{\mathrm{V} \mathrm{M}_m (\rho_m - \rho_p)} \qquad (2.6)$$

so the change in monomer concentration can be related to the change in the height of liquid in the capillary by equation 2.6.

2.5.2 Experimental.

Prior to the polymerization a solution of styrene in dichloromethane was prepared by distilling the required volumes of monomer and solvent into a monomer flask (as shown in figure 2.5).

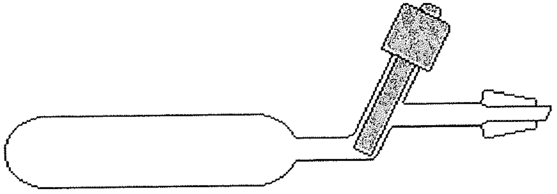


Figure 2.5: Monomer solution flask.

Figure 2.6 shows the dilatometer used in these investigations. The dilatometer was attached to the vacuum line by a ground glass joint (A) and taps H, J and K were opened. The dilatometer was then evacuated and the taps closed. The monomer flask was attached to the dilatometer at B and taps H and I were opened. Tap H was then closed and tap J opened and the tap on the monomer flask opened carefully allowing the monomer solution to run into the lower bulb (D). The amount of monomer solution used was determined by the difference in weight of the dilatometer when evacuated and when containing the solution. The required volume of co-catalyst solution was injected into the dilatometer in the dry box through the suba seal (E) and run into the lower bulb (D) and the solutions of the catalyst and ammonium salt were injected into and retained in the upper bulb (C). The dilatometer was put in a thermostated water bath and allowed to stand for 30 minutes. Tap J was opened and the reactants mixed. Tap K was opened allowing the reaction mixture to run into the dilatometer bulb (F) and capillary (G), tap K was closed and the decrease in meniscus height observed using a cathetometer. The reaction was terminated by opening taps J and K and injecting a small quantity of methanol.

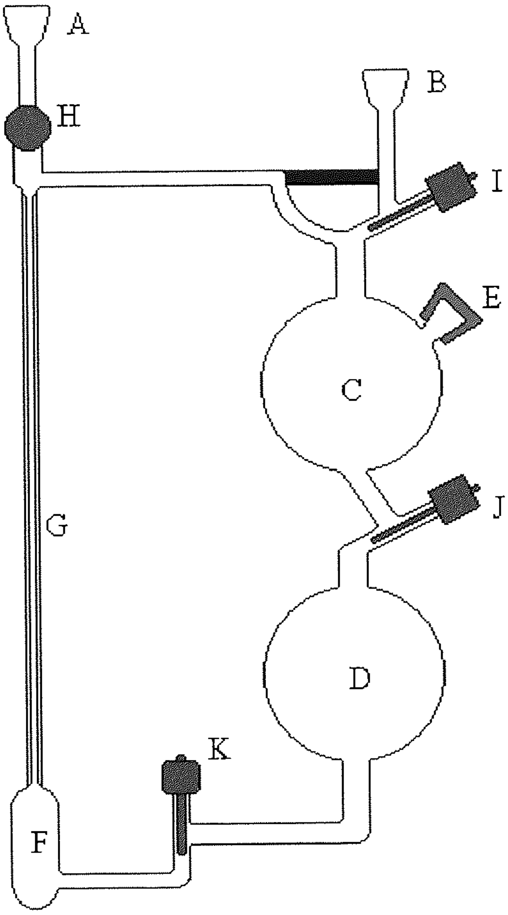


Figure 2.6: Dilatometer.

2.6: Sampling techniques.

Experiments were conducted to monitor the change in molecular weight as the reaction progressed by removing samples from the polymerization. Two methods were used for this; the Schlenk technique or running off samples using the apparatus shown in figure 2.7.

2.6.1: Schlenk technique sampling.

Reactions were prepared using the method for homopolymerizations described above (section 2.4.1). The reaction was initiated, the flask attached to the vacuum line and a constant temperature bath placed around it. The flask was then filled with argon and samples removed with dry syringes using the Schlenk technique.

2.6.2: Run-off sampling

To eliminate the possibility of introducing impurities into a reaction by using a syringe the apparatus shown in figure 2.7 was used to sample the reaction in progress. Before the reaction a solution of monomer in dichloromethane was prepared in a monomer flask (figure 2.5). The reaction vessel was attached to the vacuum line by joint A, the monomer flask was attached at B and a receiver flask at C. Taps E, F and G were opened, the vessel evacuated and then the taps closed. The apparatus was isolated from the vacuum line, tap E opened and the monomer solution run into the reaction vessel. Thermostated water was pumped through the jacket and the apparatus allowed to stand for 30 minutes. Tap F was opened and the vessel filled with dry argon. Solutions of the co-catalyst and ammonium salt were introduced to the apparatus through tap D using the Schlenk techniques. The polymerization was initiated by using the Schlenk method to inject a solution of the catalyst into the vessel. With all the taps closed, samples were taken at specified times. The tap on the receiver flask was opened then tap G was opened and a small sample of the reaction mixture allowed to run into the receiver flask. Tap G was closed and 2 cm^3 of degassed methanol injected into the receiver flask to quench the polymerization.

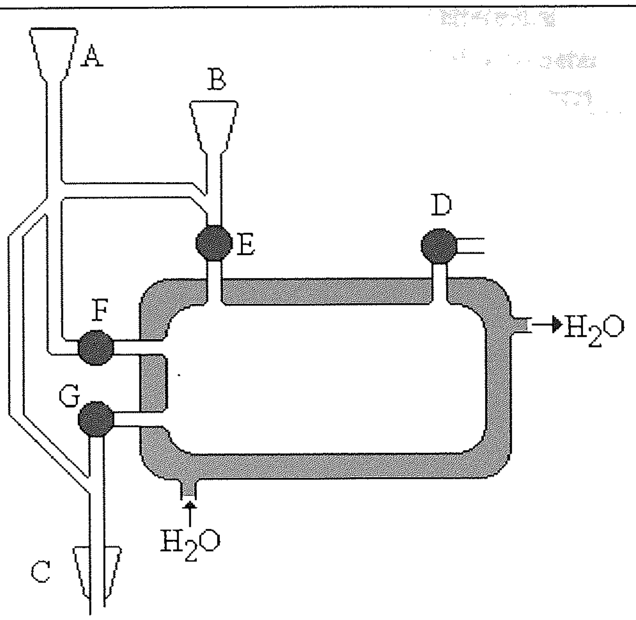


Figure 2.7: Sampling vessel.

2.7: Size exclusion chromatography.

Size exclusion chromatography (S.E.C.), otherwise known as gel permeation chromatography (G.P.C.) is a technique for determining the molecular weight distribution of a polymer sample. The polymer sample is separated into fractions by a sieving action according to the hydrodynamic volume of the molecules. This is achieved by passing a solution of the sample through a series of columns containing a stationary phase of cross linked polystyrene swollen by solvent. The swollen stationary phase contains pores whose size distribution is controlled. Polymer molecules with large hydrodynamic volume can enter a smaller fraction of the pores and hence are eluted more rapidly than smaller molecules to which a larger volume of solvent is accessible.

2.7.1: Apparatus.

Figure 2.8 shows a schematic diagram for the size exclusion chromatograph used in these studies.

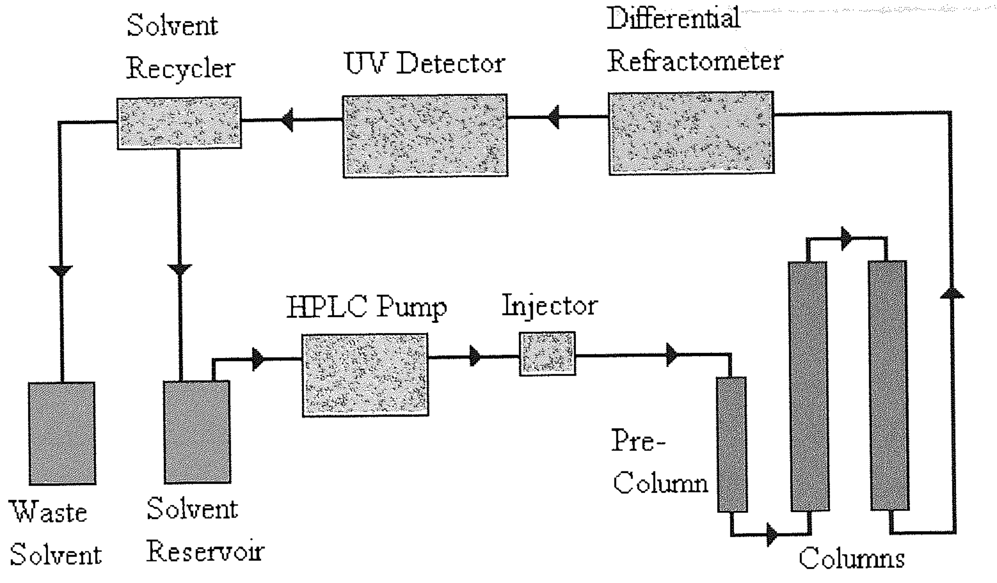


Figure 2.8: Size exclusion chromatograph

The mobile phase, HPLC grade THF, was pumped at 1 cm^3 by a Knauer HPLC pump. Solutions of the polymer sample, ~ 0.25% w/v, were prepared in THF and introduced to the system by means of a 100 μL valve and loop injector. The sample was pumped through a Polymer Laboratories 5 μm guard column, to remove any undissolved material, then a series of columns supplied by Polymer Laboratories. The columns used were a mixed B and a μ-PL gel column with an exclusion limit of 10^3 Å. The eluted solution was then passed through a Knauer differential refractometer and variable wavelength UV detector connected in series, the outputs from these were passed to a Polymer Laboratories DCU and analysed using PL Caliber® software.

2.7.2: Theory.

Figure 2.9 shows a typical S.E.C. trace. If a differential refractometer is used as a detector then the difference in refractive index (Δn) at any elution volume is proportional to the height, h, at that point. The difference in refractive index will depend on the concentration of polymer in the elutent and hence the weight fraction of polymer at that elution volume.

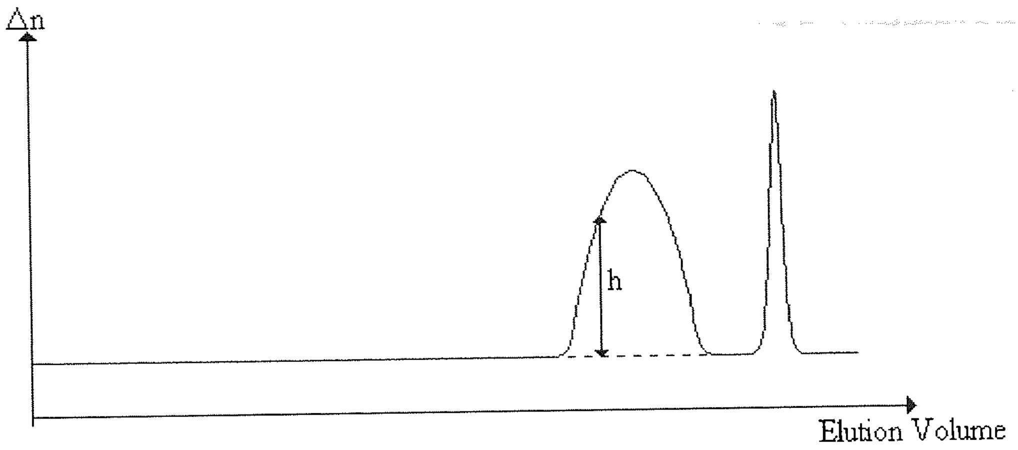


Figure 2.9: Typical S.E.C. trace.

The number average ($\overline{M_n}$) and weight average ($\overline{M_w}$) molecular weights of a polymer can be calculated from;

$$\overline{M_n} = \frac{\Sigma N_i M_i}{\Sigma N_i} \quad \text{and} \quad \overline{M_w} = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \tag{2.7}$$

where N_i = number of molecules of molecular weight M_i.

If W_i is the weight fraction of polymer at molecular weight M_i then;

$$W_i \propto N_i M_i \quad \text{and} \quad N_i \propto \frac{W_i}{M_i} \tag{2.8}$$

and;

$$\overline{M_n} = \frac{\Sigma W_i}{\Sigma W_i / M_i} \quad \text{and} \quad \overline{M_w} = \frac{\Sigma W_i M_i}{\Sigma W_i}. \tag{2.9}$$

Given the above relationships the molecular weights can be calculated from the SEC trace by;

$$\overline{M_n} = \frac{\Sigma h_i}{\Sigma h_i / M_i} \quad \text{and} \quad \overline{M_w} = \frac{\Sigma h_i M_i}{\Sigma h_i}. \tag{2.10}$$

In order to obtain values for M_i it was necessary to determine how the molecular weight of eluted polymer varied with elution volume. This was achieved by calibrating the columns using polystyrene standards of known molecular weight and molecular weight distribution ($\overline{M_w}/\overline{M_n}$) less than 1.1. The logarithm of the molecular weight was plotted against elution volume and a 3rd order polynomial equation obtained. Figure 2.10

shows the calibration curve obtained.

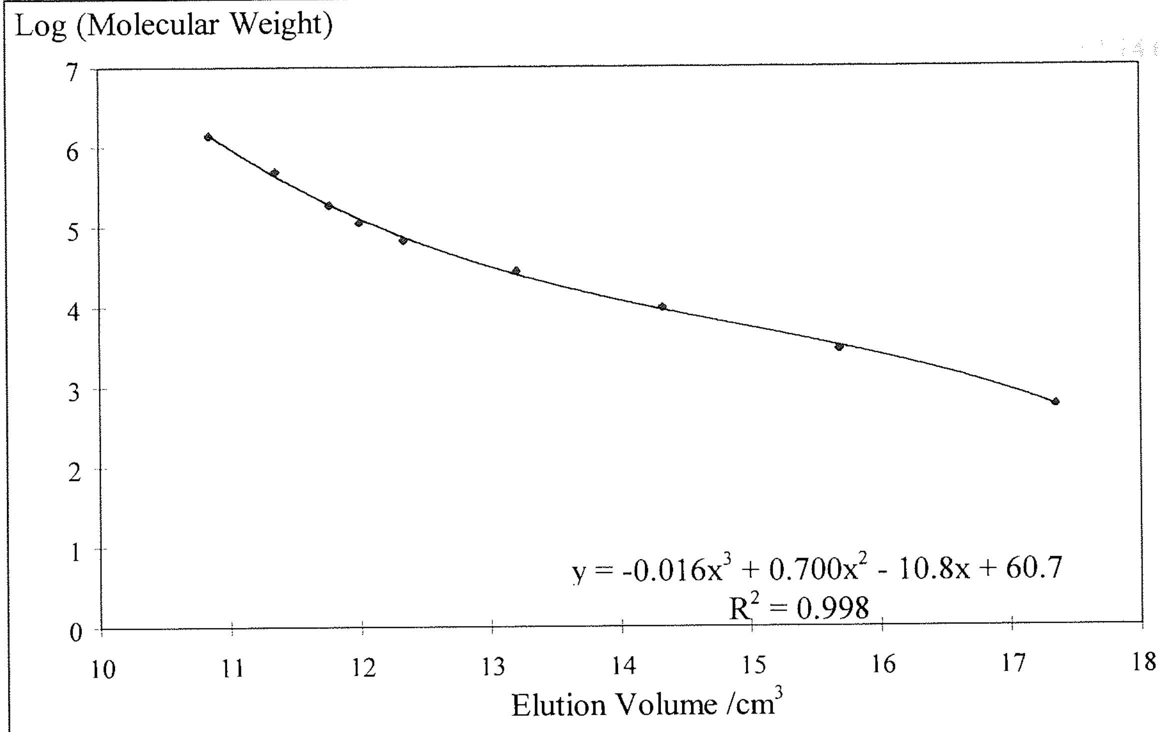


Figure 2.10: Calibration curve for S.E.C. using polystyrene standards.

Since the hydrodynamic volume of a given molecular weight varies with polymer type, this calibration only provides absolute molecular weights for samples of polystyrene. However, it is possible to obtain absolute molecular weights for polymers other than the calibrant by using the universal calibration method. The hydrodynamic volume of a polymer molecule in solution can be shown to be proportional to its intrinsic viscosity and molecular weight. Two polymers eluting at the same elution volume must have the same hydrodynamic volume therefore;

$$\eta_1 M_1 = \eta_2 M_2 \tag{2.11}$$

where η_1 and η_2 are the intrinsic viscosities of the two polymers

and M_1 and M_2 their molecular weights.

The intrinsic viscosity of a polymer is related to its molecular weight by the equation

$$\eta = Km^{\alpha} \tag{2.12}$$

where K and α are the Mark Houwink constants for polymers in different solvents.

Therefore for co-eluting polymers:

$$K_1 M_1^{\alpha 1} M_1 = K_2 M_2^{\alpha 2} M_2 . \tag{2.13}$$

Rearranging equation 2.13 gives:

$$\log M_2 = \frac{(1+\alpha_1)}{(1+\alpha_2)}\log M_1 + \frac{1}{(1+\alpha_2)}\log\left(\frac{K_1}{K_2}\right). \qquad (2.14)$$

Therefore if the Mark Houwink constants are known for both the calibrant standard and the polymer then absolute molecular weights may be determined.

2.8: Nuclear magnetic resonance spectroscopy.

Fourier transform high resolution ^{1}H and ^{13}C N.M.R. were carried out using a Bruker AC 300 spectrometer. Solutions of the samples were prepared in deuterated chloroform with a small quantity of tetramethyl silane as reference. For ^{13}C analysis the P.E.N.D.A.N.T pulse technique was used, with methyl and methine carbons appearing as positive peaks and methylene and quaternary carbons as negative peaks. The spectra were analysed using WinNMR software supplied by Bruker.

Chapter 3: Polymerization of styrene by the monofunctional initiator 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride.

3.1: Introduction.

The living polymerization of styrene by the 1-halo-1-phenylethane/tin (IV) chloride initiating system in the presence of tetrabutylammonium salts is an example of the common ion salt method of living cationic polymerization, see section 1.3.2. This polymerization was first reported by Higashimura *et al.*(64) who studied the effects of various catalysts, co-catalysts and ammonium salts on reactions at -15° in dichloromethane(119). It was found that polymerizations were living in the presence of tetrabutylammonium chloride, bromide and iodide with the rates of polymerization decreasing with increasing size of the halide. 1-Chloro-1-phenylethane and 1-bromo-1-phenylethane both proved to be effective initiators and again chloride gave a higher rate of polymerization than the bromide. This trend is consistent with the behaviour shown by the tetrabutylammonium salts . These trends in the rate of polymerization were attributed to $SnCl_4$ being a stronger Lewis acid than $SnCl_3Br$ or $SnCl_3I$. Further work by Higashimura *et al.* used functional co-catalysts based on the HCl adduct of vinyl ethers carrying pendant substituents to synthesise telechelic polymers. Work by Choi *et al.*(89) demonstrated that a living polymerization can be obtained in the absence of tetrabutylammonium salts by using a less polar solvent such as chloroform.

3.2: Dilatometry studies at 25 °C.

The aim of this work was to investigate the dependence of the rate of polymerization on the concentration of the various reactants to determine the mechanism of the polymerization and establish the conditions for living polymerization.

3.2.1: Effect of initial concentration of 1-chloro-1-phenylethane on the rate of polymerization.

Studies using dilatometry to determine the rate of polymerization were conducted as described in section 2.5, using dichloromethane as solvent at 25 °C. The initial concentrations of monomer, catalyst and ammonium salt were kept constant; $[\text{styrene}]_0 = 0.5$ mol dm^{-3}, $[SnCl_4]_0 = 0.05$ mol dm^{-3}, $[Bu_4N^+Cl^-]_0 = 0.02$ mol dm^{-3}, and in this series of experiments the concentration of 1-chloro-1-phenylethane was varied. The change in monomer concentration was then calculated using the equation derived in section 2.5.1.

$$\Delta[M] = \frac{\pi r^2 \Delta h \rho_m \rho_p}{V M_m (\rho_m - \rho_p)} \qquad (3.1)$$

The radius of the capillary was measured as being 0.05 cm and the volume of the dilatometer was measured as 20.5 cm^3. The density of monomer used was that quoted by the supplier, 0.906 g cm^{-3} and the density of polystyrene used was 1.04 g cm^{-3}. This value was chosen because it was the lowest quoted for polystyrene(120) (1.04 - 1.065 g cm^{-3}). Data was not available for the rate of change of density with molecular weight over the range studied. For a classical polymerization the molecular weight rapidly reaches a maximum so the change in density with molecular weight is not significant. However. for a living polymerization the molecular weight will increase initially with monomer conversion, which may introduce errors into the subsequent calculations of the conversion from the height change observed. Other sources of error may be variations in the radius of the capillary, temperature fluctuations and inaccuracies in the concentrations of reactants.

Studies on living cationic polymerization have shown that it is not unreasonable to consider the polymerization to be first order in the concentration of styrene. As such therefore in a living polymerization system in which the concentration of active centres remains constant during the polymerization, the rate of polymerization may be expressed as;

$$-\frac{d[M]}{dt} = k_{app}[M]. \qquad (3.2)$$

which is solved to give;

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_{app}\,t \tag{3.3}$$

where [M] is the concentration of monomer at any time t,

$[M]_0$ is the initial concentration of monomer,

and k_{app} is the measured rate constant.

Figure 3.1 below shows a plot of $\ln([M]_0/[M])$ against time for reactions over a range of concentrations of co-catalyst.

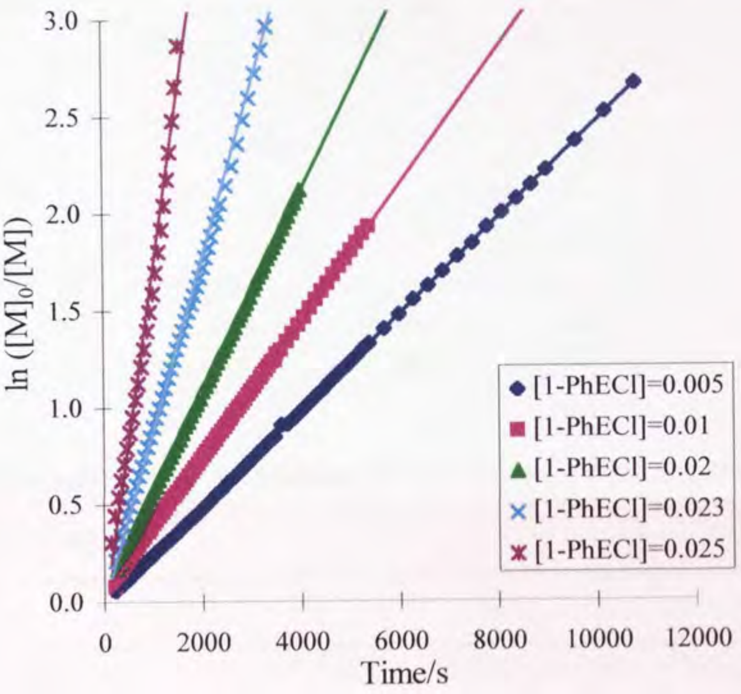


Figure 3.1: Graph of $\ln([M]_0/[M])$ against time for reactions at 25°C.

The plots of $\ln([M]_0/[M])$ against time provide good straight line fits despite the possible problems associated with the change in density of the polymer. This may be because over the range of molecular weights of polymer present during these reactions, up to approximately 4000, the change in density is not significant

The measured rate constant (k_{app}), which is expected to depend on the concentration of active propagating centres, may be obtained from the slope of the plot of $\ln([M]_0/[M])$ against time. Experiments were carried out to establish the effect of concentration of 1-chloro-1-phenylethane on the value of the apparent rate constant. The first 10 to 15 points of each $\ln([M]_0/[M])$ against time graph were taken and the gradient calculated to obtain a value for k_{app}, figure 3.2 shows an example of such a plot for

[1-chloro-1-phenylethane]$_0$ = 0.020 mol dm^{-3} Table 3.1 shows the dependence of rate constant on concentration of 1-chloro-1-phenylethane.

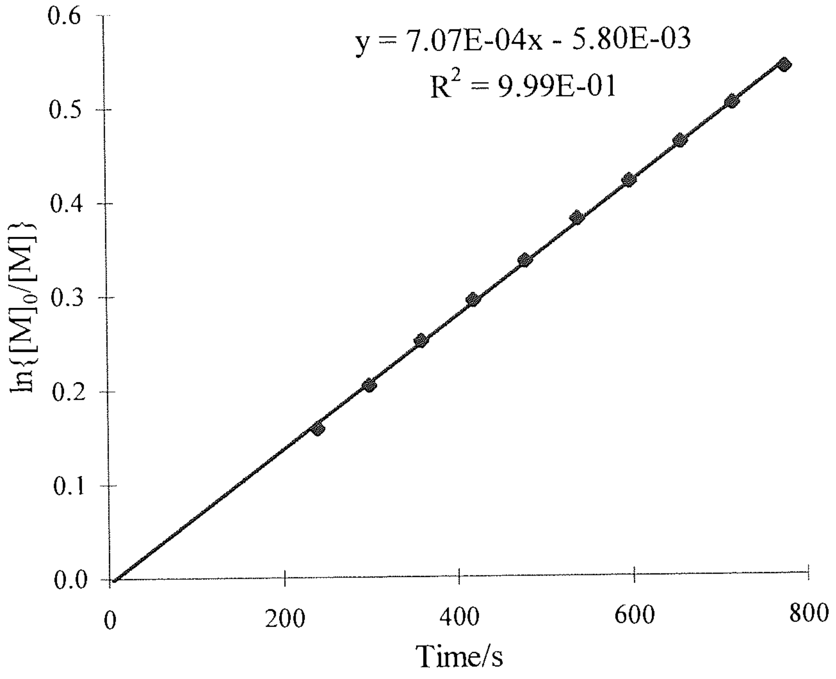


Figure 3.2: Example of the determination of apparent rate constant from a plot of ln ([M]$_0$/[M]) versus time.

[1-PhECl]$_0$/mol dm^{-3}	10^4*k$_{app}$/s^{-1}	log ([1-PhECl]$_0$/mol dm^{-3})	log (k$_{app}$/s^{-1})
0.005	2.41	-2.30	-3.62
0.010	4.35	-2.00	-3.36
0.010	4.10	-2.00	-3.39
0.018	4.83	-1.76	-3.32
0.018	6.00	-1.76	-3.22
0.020	5.59	-1.70	-3.25
0.020	7.07	-1.70	-3.15
0.023	8.92	-1.65	-3.05
0.025	14.4	-1.60	-2.84

Table 3.1: Dependence of apparent rate constant of polymerization on initial co-catalyst concentration.

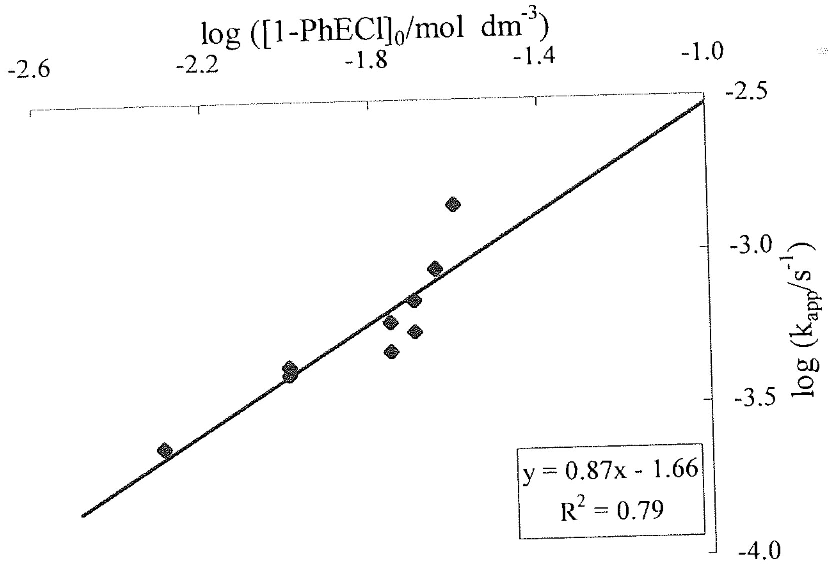


Figure 3.3: Graph of log k_{app} against log $[1\text{-PhECl}]_0$ for reactions at 25 °C.

The order of reaction with respect to the co-catalyst was estimated from a plot of log [1-chloro-1-phenylethane]$_0$ against log k_{app}, figure 3.3. The straight line through the points has a gradient of 0.9, which indicates that the apparent rate constant has a first order dependence on the initial concentration of co-catalyst. There is a significant difference between the sets of data at concentrations of co-catalyst of 0.018 and 0.020 mol dm^{-3}. This may be due to experimental error in determining the concentration of reactants or variations in the reaction temperatures resulting in the observed variation in rate of polymerization.

Figure 3.4, below, shows a plot of the apparent rate constant against initial concentration of 1-chloro-1-phenylethane. The data suggest a first order plot with the exception of the point when the initial concentration of 1-chloro-1-phenylethane was 0.025 mol dm^{-3}. The deviation from predicted behaviour at this concentration of co-catalyst may be a result experimental error in determining the concentration of co-catalyst solution or due to a higher than expected concentration of free ions present in this system. In turn this would lead to an increase in the rate of polymerization by conventional cationic routes. The first order kinetics with respect to the co-catalyst agrees with results reported by Matyjaszewski an co-workers(121).

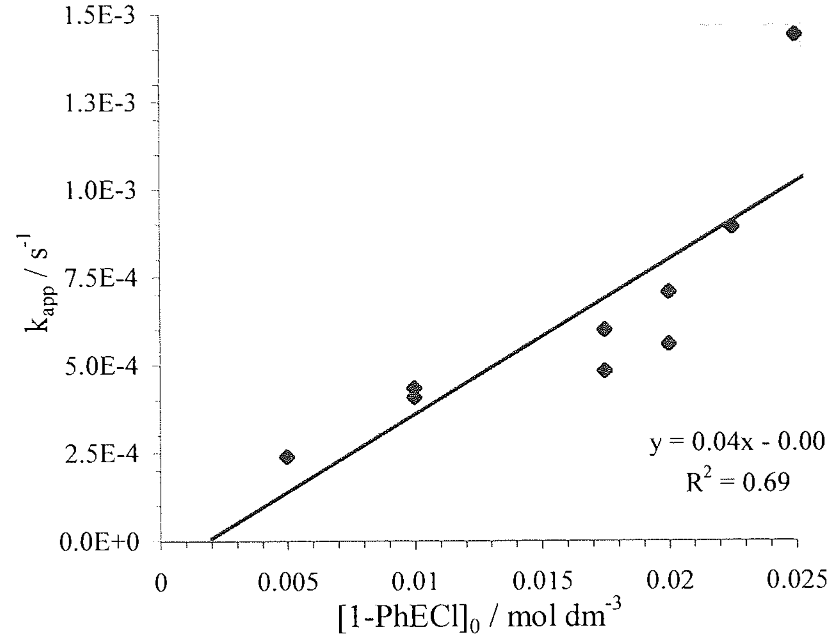


Figure 3.4: Graph of apparent rate constant against initial concentration of co-catalyst.

3.2.2: Effect of initial concentration of tin (IV) chloride on rate of polymerization.

Reactions were conducted to study the effect on the polymerization of varying the concentration of catalyst. Rates of polymerization were measured by dilatometry conducted in dichloromethane at 25° C. The initial concentrations of monomer, co-catalyst and tetrabutylammonium chloride were kept constant; $[\text{styrene}]_0$= 0.5 mol dm^{-3}, $[1\text{-PhECl}]_0$= 0.02 mol dm^{-3}, $[Bu_4N^+Cl^-]_0$= 0.02 mol dm^{-3} and the concentration of tin (IV) chloride varied. Plots of ln $([M]_0/[M])$ against time were made for each experiment and the apparent rate constant for each experiment was obtained from the gradients of the resulting plot. The dependence of apparent rate constant on the concentration of tin (IV) chloride is shown in table 3.2.

$[SnCl_4]_0$/mol dm^{-3}	$10^4 k_{app}$/s^{-1}	log ($[SnCl_4]_0$/mol dm^{-3})	log (k_{app}/s^{-1})
0.03	1.21	-1.52	-3.92
0.03	1.25	-1.52	-3.90
0.05	7.07	-1.30	-3.15
0.05	5.59	-1.30	-3.25
0.06	10.0	-1.22	-3.00
0.06	9.16	-1.22	-3.04
0.06	10.7	-1.22	-2.97
0.08	14.4	-1.10	-2.84
0.08	12.5	-1.10	-2.90
0.15	65.9	-0.82	-2.18

Table 3.2: Dependence of apparent rate constant of polymerization on initial concentration of tin (IV) chloride.

The polymerization conducted at an initial concentration of tin (IV) chloride of 0.15 mol dm^{-3} proved to be too fast to be studied accurately using dilatometry. The high rate of polymerization in this experiment suggests that the polymerization was due not only to living but also a conventional carbocationic mechanism. Therefore this data was not used in any further calculations.

The order of reaction with respect to catalyst was estimated from the plot of log k_{app} against log $[SnCl_4]_0$ for these experiments, shown in figure 3.5. The gradient of a straight line through the points has a gradient of 2.5 which may indicate that the apparent rate constant has a second order dependence on the initial concentration of catalyst. Figure 3.6 shows a plot of apparent rate constant against $[SnCl_4]_0^2$. A straight line through the points provides a relatively good fit.

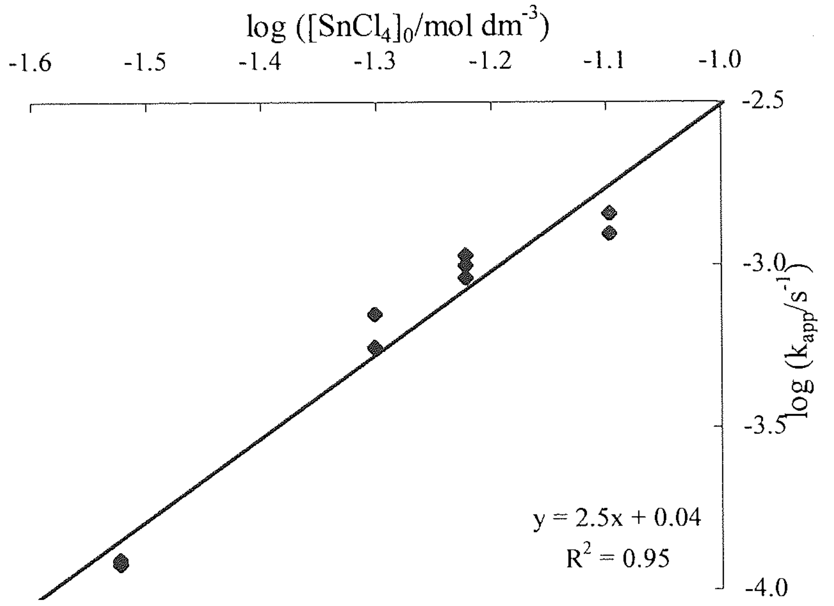


Figure 3.5: Graph of log k_{app} against log $[SnCl_4]_0$ for reactions at 25 °C.

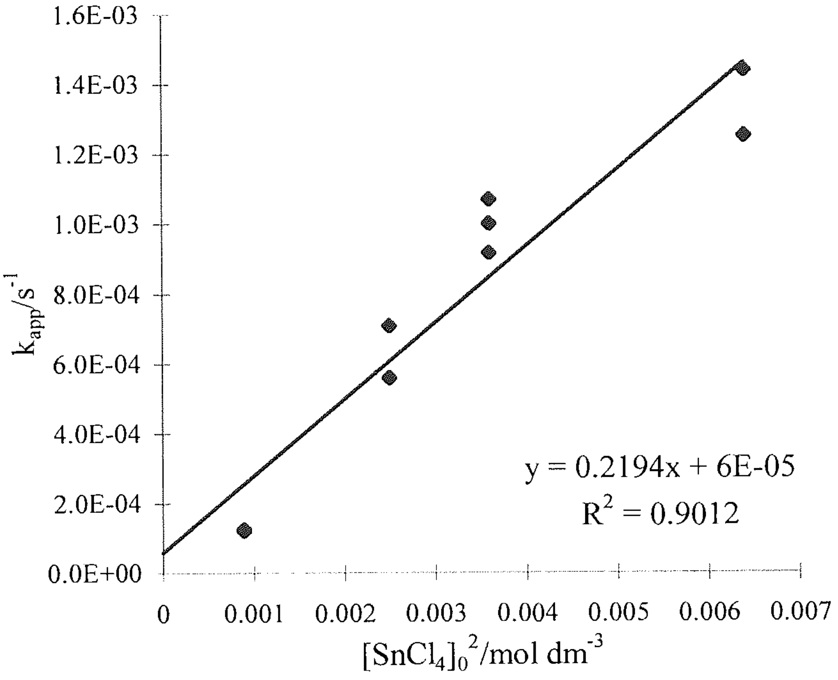


Figure 3.6: Graph of k_{app} against $[SnCl_4]_0^2$ for reactions at 25 °C.

However Matyjaszewski and co-worker reported a first order rate dependence on the concentration of tin (IV) chloride(121). In light of the reported results the measured rate constant was plotted against the concentration of tin tetrachloride, figure 3.7, which suggests a first order dependence on the concentration of catalyst. From the graph of apparent rate constant versus initial concentration of tin (IV) chloride there appears to be a threshold concentration of catalyst of 0.024 mol dm^{-3} necessary for polymerization to take place. This value is close to the initial concentration of tetrabutylammonium chloride (0.020 mol dm^{-3}). Since the catalyst and tetrabutylammonium chloride are mixed together before being added to the reaction solution it is possible that the effective concentration of tin (IV) chloride will be the initial concentration minus the concentration of tetrabutylammonium chloride. Table 3.3 shows the dependence of apparent rate constant on the difference between the concentration of tin (IV) chloride and tetrabutylammonium chloride.

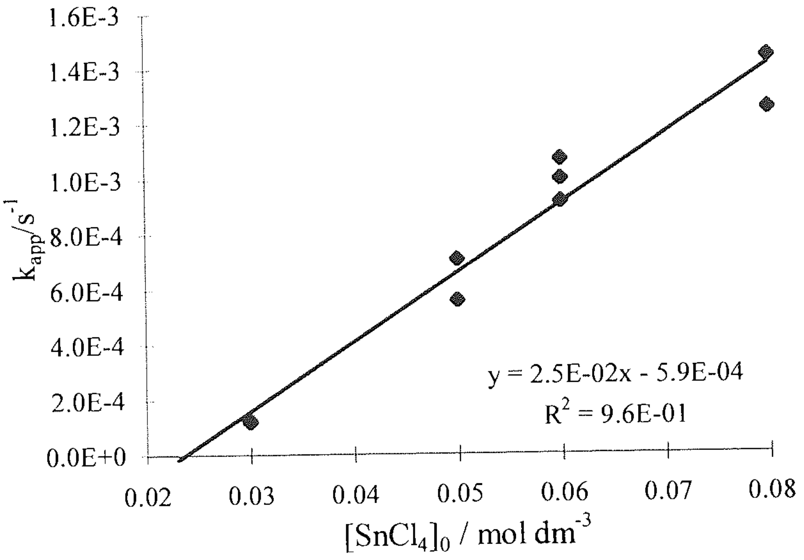


Figure 3.7: Graph of apparent rate constant against initial concentration of catalyst.

$[SnCl_4]_0$-$[TBAC]_0$/mol dm^{-3}	10^4*k_{app}/s^{-1}	log($[SnCl_4]_0$-$[TBAC]_0$)	log (k_{app}/s^{-1})
0.01	1.21	-2.00	-3.92
0.01	1.25	-2.00	-3.90
0.03	7.07	-1.52	-3.15
0.03	5.59	-1.52	-3.25
0.04	10.0	-1.40	-3.00
0.04	9.16	-1.40	-3.04
0.04	10.7	-1.40	-2.97
0.06	14.4	-1.22	-2.84
0.06	12.5	-1.22	-2.90

Table 3.3: Dependence of rate constant on the concentration of tin (IV) chloride minus concentration of tetrabutylammonium chloride.

Figure 3.8 shows a graph of log (k_{app}) against log ($[SnCl_4]_0$-$[TBAC]_0$). The straight line plot of this data has a gradient of 1.4, which might indicate a first order dependence of the apparent rate constant on $[SnCl_4]_0$-$[TBAC]_0$. The graph of apparent rate constant against the concentration of tin (IV) chloride minus the tetrabutylammonium chloride, figure 3.9, suggests a first order plot.

These results suggest that the apparent rate constant does not have a simple order of dependence on the initial concentration of catalyst. This may be due to propagation taking place by more than one species and tin (IV) chloride being involved in two competing equilibria.

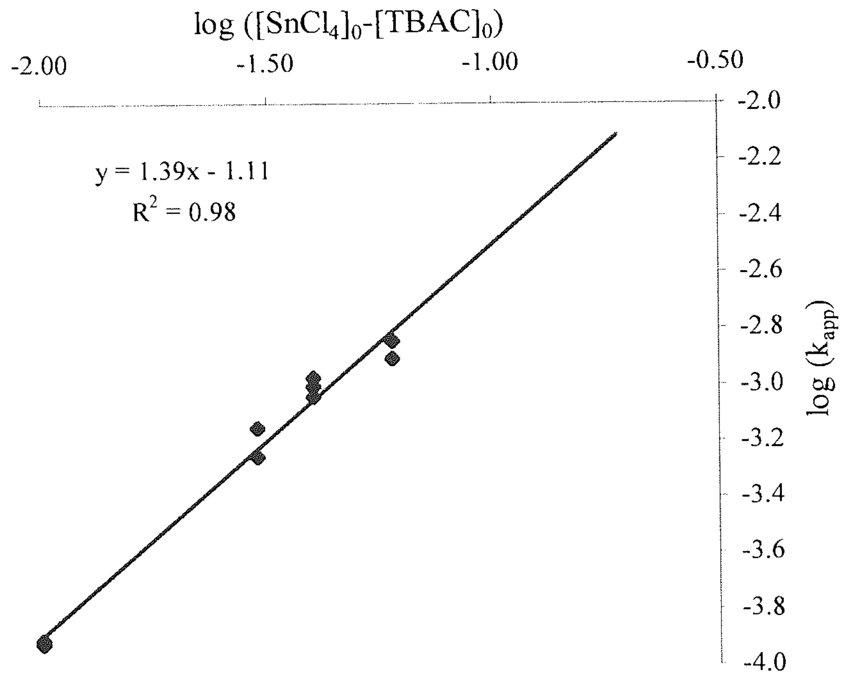


Figure 3.8: Graph of log (k$_{app}$) against log ([SnCl$_4$]$_0$-[TBAC]$_0$).

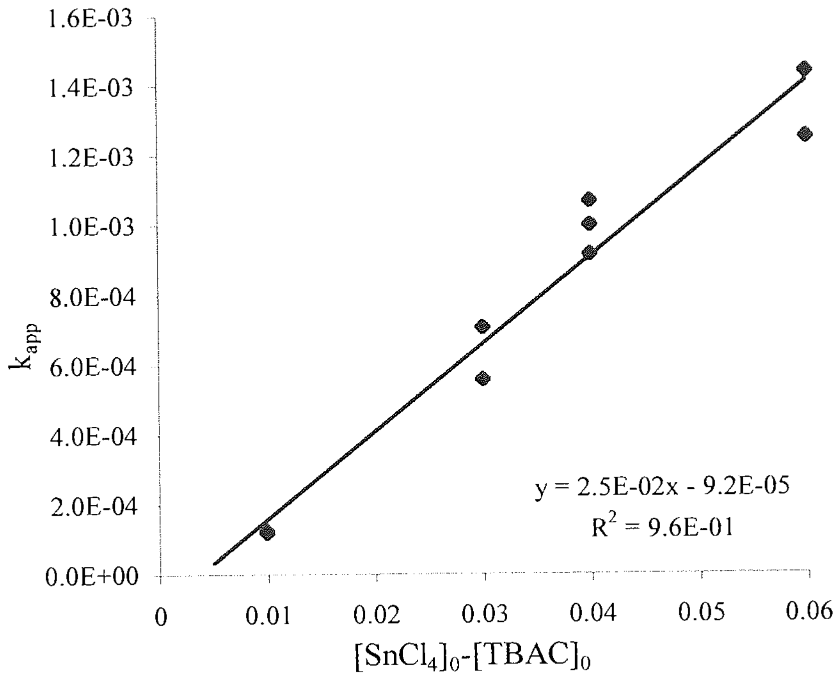


Figure 3.9: Graph of apparent rate constant against concentration of tin (IV) chloride minus concentration of tetrabutylammonium chloride.

3.2.3: Effect of the initial concentration of tetrabutylammonium chloride on rate of polymerization.

Experiments were conducted to study what effect varying the concentration of tetrabutylammonium chloride had on the rate of polymerization. The rate of polymerization was measured by dilatometric studies using dichloromethane as solvent at 25 °C. The initial concentrations of monomer, co-catalyst and catalyst were kept constant with; $[\text{styrene}]_0 = 0.5$ mol dm^{-3}, $[\text{1-PhECl}]_0 = 0.02$ mol dm^{-3}, $[\text{SnCl}_4]_0 = 0.05$ mol dm^{-3} and the concentration of tetrabutylammonium chloride varied over the range 0.005-0.4 mol dm^{-3}. Plots of ln $([M]_0/[M])$ against time were constructed for each experiment and the apparent rate constants under the polymerization conditions obtained from the gradients of the lines. The dependence of apparent rate constant on the concentration of tetrabutylammonium chloride is shown in table 3.4.

$[\text{Bu}_4\text{N}^+\text{Cl}^-]_0$/mol dm^{-3}	$10^4 * k_{app}/s^{-1}$	log ($[\text{Bu}_4\text{N}^+\text{Cl}^-]$/mol dm^{-3})	log (k_{app}/s^{-1})
0.005	9.12	-2.30	-3.04
0.005	7.56	-2.30	-3.12
0.02	7.14	-1.70	-3.15
0.03	6.00	-1.52	-3.22
0.04	1.82	-1.40	-3.74
0.04	1.82	-1.40	-3.74

Table 3.4: Dependence of apparent rate constant of polymerization on initial concentration of tetrabutylammonium chloride.

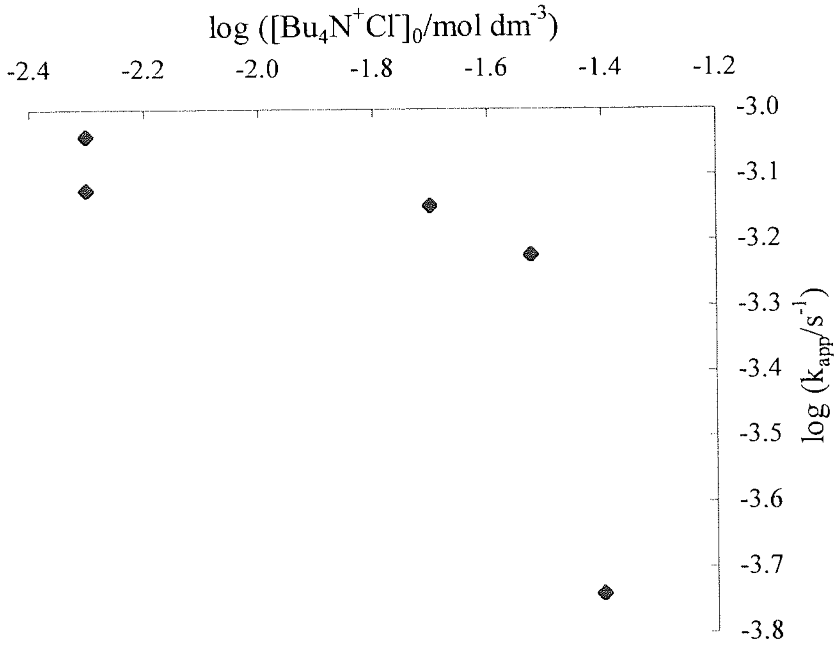


Figure 3.10: Graph of log k_{app} against log $[Bu_4N^+Cl^-]_0$ for reactions at 25 °C.

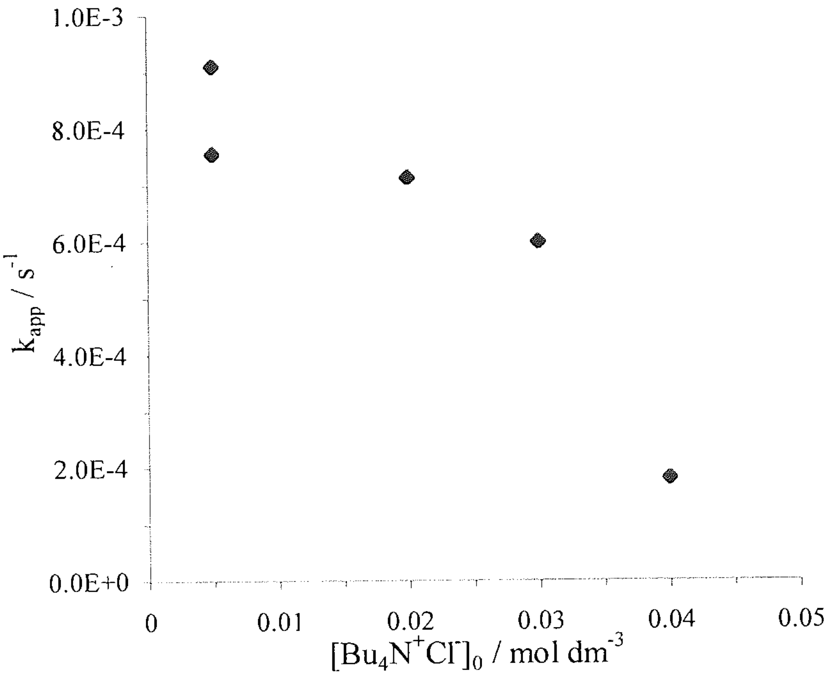


Figure 3.11: Graph of apparent rate constant against initial concentration of tetrabutylammonium chloride.

The graph of log k_{app} against log $[Bu_4N^+Cl^-]_0$, figure 3.10 suggests that the rate of polymerization does not have a simple order dependence on the initial concentration of tetrabutylammonium chloride. A plot of apparent rate constant against initial concentration of tetrabutylammonium chloride, figure 3.11, shows a decrease in the rate of polymerization as the concentration of ammonium salt increases. The decrease of the rate of polymerization caused by the addition of tetrabutylammonium chloride has been observed by other workers(119-120) and is believed to be associated with the suppression of the polymerization by the very active conventional polymerization and the enhancement of the controlled or living polymerization process.

Further to the relationship observed in section 3.2.2 between the apparent rate constant and the difference between the initial concentrations of tin (IV) chloride and tetrabutylammonium chloride, table 3.5 shows this dependence for experiments with varying concentration of tetrabutylammonium chloride.

$[SnCl_4]_0$-$[TBAC]_0$/mol dm^{-3}	$10^{-4}*k_{app}/s^{-1}$
0.045	9.12
0.045	7.56
0.03	7.14
0.02	6.00
0.01	1.82
0.01	1.82

Table 3.5 Dependence of k_{app} on $[SnCl_4]_0$-$[TBAC]_0$ for experiments with varying $[TBAC]_0$.

Figure 3.12 shows the plot of apparent rate constant against $[SnCl_4]_0$-$[TBAC]_0$. The graph does not indicate a straight line relationship between k_{app} and $[SnCl_4]_0$-$[TBAC]_0$ which suggest that the dependence of the rate constant on the concentration of tetrabutylammonium chloride is more complex than this simple relationship. A more complex dependence would be expected if the product of the reaction between tin (IV) chloride and tetrabutylammonium chloride affects the equilibrium between the various propagating species.

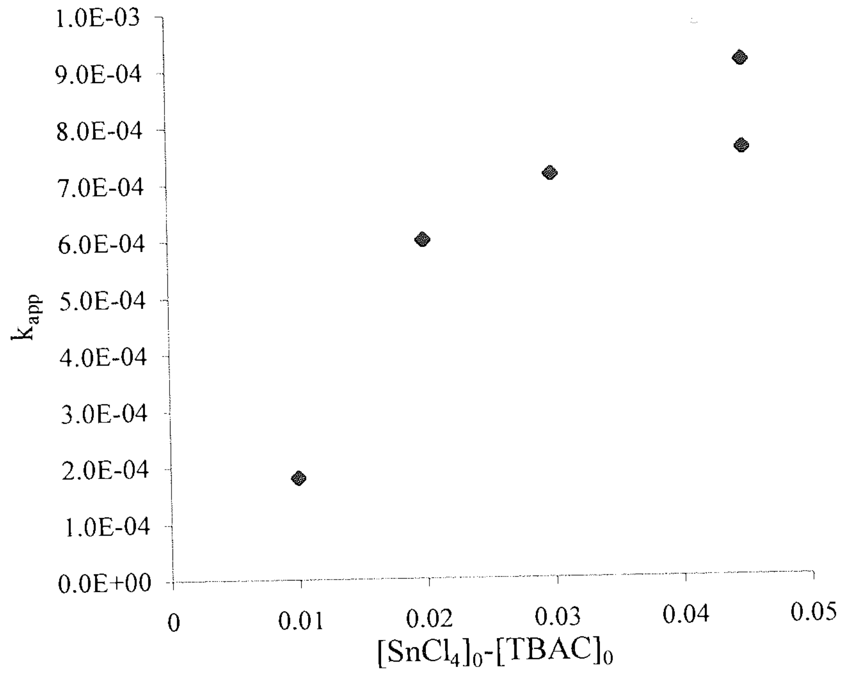


Figure 3.12: Graph of k_{app} against [tin (IV) chloride] - [tetrabutylammonium chloride] for experiments with varying $[TBAC]_0$.

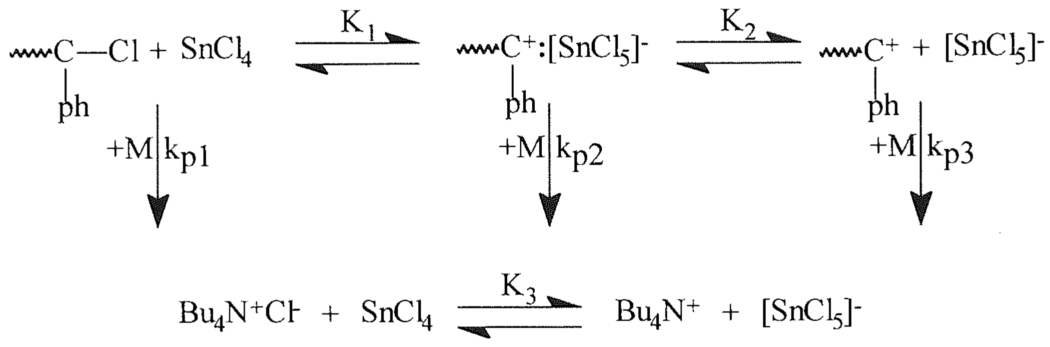
3.2.4: Effect of monomer concentration.

The straight line relationship for the graph of $\ln\{[M]_0/[M]\}$ against time, figure 3.1, infers that the rate of polymerization is first order with respect to monomer concentration, which differs from the kinetic scheme described in section 1.25, where the relationship was shown to be second order. This suggests that initiation is rapid and the concentration of active species is independent of the monomer concentration.

3.2.5: Discussion.

3.2.5.1: Propagation by two species.

Scheme 3.1 shows the proposed mechanism for the polymerization of styrene by 1-chloro-1-phenylethane and tin (IV) chloride in the presence of tetrabutylammonium chloride(121). The propagating centre is present in three possible forms; a covalent species, a close contact ion-pair and a dissociated ion.



Scheme: 3.1: Proposed mechanism for the polymerization of styrene by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride.

Under these conditions the apparent rate constant can be written as;

$$k_{app} = k_{p1}[P_1] + k_{p2}[P_2] + k_{p3}[P_3] \tag{3.4}$$

where $[P_1]$= concentration of chain ends present as covalent species,

$[P_2]$= concentration of chain ends present as close contact ion pairs,

$[P_3]$= concentration of chain ends present as free ions,

k_{p1}, k_{p2}, k_{p3} are the rate constants of propagation for the relevant chain ends shown in scheme 3.1.

If there exists the series of equilibria shown in scheme 3.1 then the equilibrium constants for the formation of the propagating species will be;

$$K_1 = \frac{[P_2]}{[P_1][SnCl_4]} \tag{3.5}$$

and

$$K_2 = \frac{[P_3][SnCl_5^-]}{[P_2]}. \tag{3.6}$$

Rearranging these gives $[P_2]$ and $[P_3]$ in terms of $[P_1]$ as;

$$[P_2] = K_1[SnCl_4][P_1] \tag{3.7}$$

and

$$[P_3] = \frac{K_2[P_2]}{[SnCl_5^-]} = \frac{K_1K_2[SnCl_4]}{[SnCl_5^-]}[P_1].. \tag{3.8}$$

Substituting equations 3.7 and 3.8 into 3.4 gives,

$$k_{app} = k_{p1}[P_1] + k_{p2}K_1[P_1][SnCl_4] + \frac{k_{p3}K_1K_2[P_1][SnCl_4]}{[SnCl_5^-]} \tag{3.9}$$

which can then be rewritten as;

$$k_{app} = \left\{ k_{p1} + [SnCl_4]\left(k_{p2}K_1 + \frac{k_{p3}K_1K_2}{[SnCl_5^-]} \right) \right\}[P_1]. \tag{3.10}$$

The concentration of $SnCl_5^-$ can be calculated from the concentration of chain ends present as free ions plus the concentration of tetrabutylammonium chloride that has reacted with tin (IV) chloride, so that:

$$[SnCl_5^-] = [TBAC]_0 - [Cl^-] + [P_3] \tag{3.11}$$

where $[TBAC]_0$= initial concentration of tetrabutylammonium chloride

and $[Cl^-]$= concentration of free chloride anion.

If the chloride anions readily react with tin (IV) chloride and the formation of $SnCl_5^-$ drives the equilibrium shown in scheme 3.1 towards the covalent species then it can be assumed that the $[Cl^-]$ and $[P_3]$ are small compared to $[TBAC]_0$ in which case, since almost all the $SnCl_5^-$ is formed by reaction of tin (IV) chloride and tetrabutylammonium chloride, equation 3.11 approximates to;

$$[SnCl_5^-] \approx [TBAC]_0, \tag{3.12}$$

Substituting this into equation 3.10 gives;

$$k_{app} = \left\{ k_{p1} + [SnCl_4]\left(k_{p2}K_1 + \frac{k_{p3}K_1K_2}{[TBAC]_0} \right) \right\}[P_1]. \tag{3.13}$$

It is reasonable to assume that the covalent species (P1) does not contribute significantly to the rate of polymerization, so that equation 3.13 becomes;

$$k_{app} = \left(k_{p2}K_1 + \frac{k_{p3}K_1K_2}{[TBAC]_0} \right)[SnCl_4][P_1]. \tag{3.14}$$

If the concentration of propagating species present as close contact ion pairs is likely to be small compared to the concentration present as covalent species then the following approximations can be made;

$$[P_1] = [I]_0 - [P_2] - [P_3] \approx [I]_0 \tag{3.15}$$

and

$$[SnCl_4] = [SnCl_4]_0 - [P_2] - [SnCl_5^-] \approx [SnCl_4]_0 - [TBAC]_0. \tag{3.16}$$

Substituting equations 3.15 and 3.16 into equation 3.14 gives;

$$k_{app} = \left(k_{p2}K_1 + \frac{k_{p3}K_1K_2}{[TBAC]_0} \right)\left([SnCl_4]_0 - [TBAC]_0\right)[I]_0. \tag{3.17}$$

The assumptions made during the derivation of this equation are similar to those made by Kennedy *et al.*(122) in their kinetic treatment of the living cationic polymerization of isobutylene by 2-chloro-2,4,4-trimethylpentane/$TiCl_4$ in the presence of tetrabutylammonium chloride. This equation accounts for the observed first order relationship between the apparent rate constant and the initial concentration of co-catalyst and the relationship between the initial concentration of tin (IV) chloride minus the concentration of tetrabutylammonium chloride, if the concentration of ammonium salt is kept constant. The complex order dependence on the concentration of tetrabutylammonium chloride is also explained. If the relationship in equation 3.16 is true then a graph of $k_{app}/([SnCl_4]_0-[TBAC]_0)$ against $1/[TBAC]_0$ will be a straight line. Table 3.6 shows the dependence of $k_{app}/([SnCl_4]_0-[TBAC]_0)$ on $1/[TBAC]_0$.

$1/[TBAC]_0$ / mol^{-1} l	$k_{app}/([SnCl_4]_0-[TBAC]_0)$
200	0.020
200	0.017
50	0.024
33	0.030
25	0.018
25	0.018

Table 3.6: Dependence of $k_{app}/([SnCl_4]_0-[TBAC]_0)$ on $1/[TBAC]_0$.

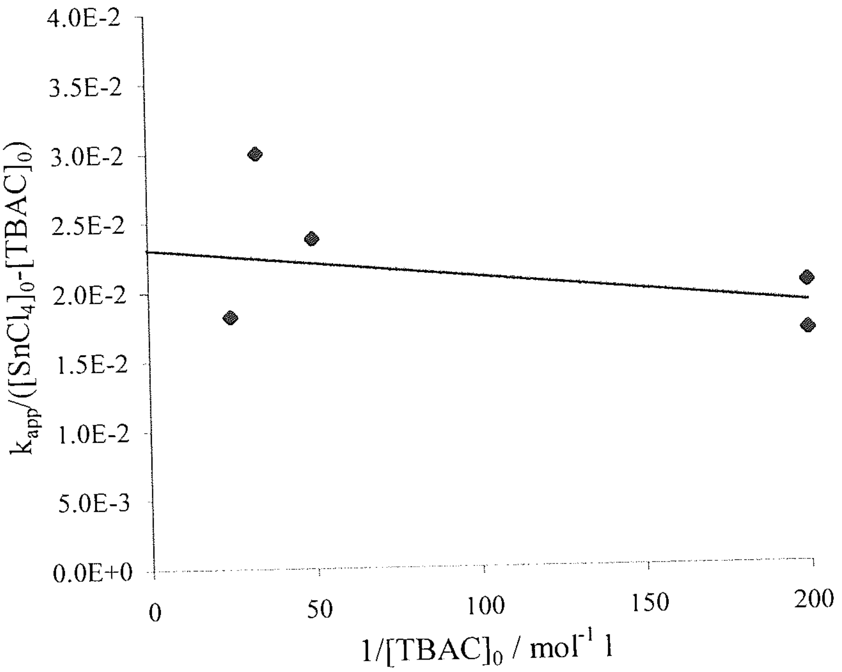


Figure 3.13: Graph of $k_{app}/([SnCl_4]_0-[TBAC]_0)$ against $1/[TBAC]_0$.

Figure 3.13 shows a graph of $k_{app}/([SnCl_4]_0-[TBAC]_0)$ against $1/[TBAC]_0$. However, the error on this plot is to great to draw any conclusions from the graph. This discrepancy may be due to experimental error or the proposed reaction mechanism may be incorrect.

3.2.5.2: Propagation by a single species.

An alternative possible mechanism for the polymerization of styrene by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride is one where the dormant polymer chains are in equilibrium with a single propagating species. In this model the decrease in rate of polymerization might be explained if the reaction between tetrabutylammonium chloride and tin (IV) chloride reduces the effective concentration of catalyst, so reducing the rates of initiation and propagation and as such there is no distinction in mechanism between conventional and living systems. The reduction in concentration of active polymer chain ends would also make transfer reactions unfavourable. Such behaviour is akin to the competitive type of inhibition in Michaelis-Menten kinetics for enzyme catalysis. Scheme 3.2 shows the reaction scheme for this type of kinetics, where E is the enzyme, S the substrate, ES the enzyme/substrate complex, P the product, I the inhibitor and EI the enzyme/inhibitor complex.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_p} E + P$$

$$E + I \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EI$$

Scheme 3.2: Reaction scheme for competitive Michaelis-Menten kinetics.

The rate of reaction (v) for competitively inhibited Michaelis-Menten kinetics is given by equation 3.18;

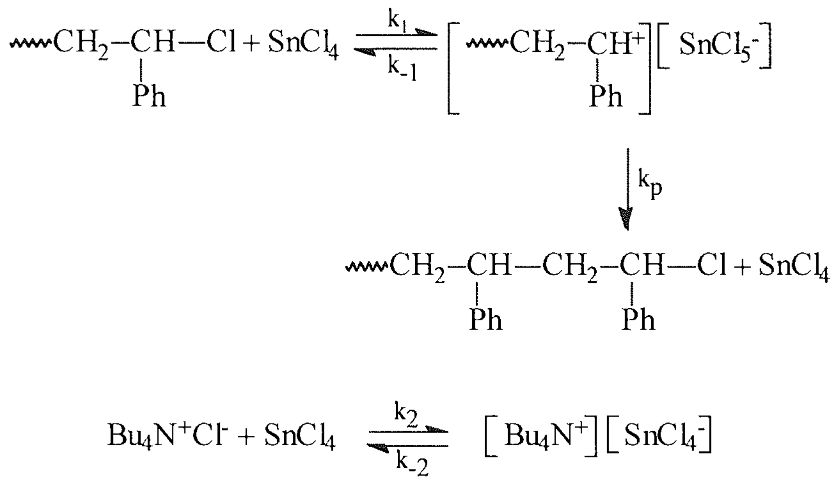
$$v = \frac{d[P]}{dt} = k_p[ES] = k_p[E]_0 \left\{ \frac{1}{1 + \frac{K}{[S]}\left(1 + \frac{[I]}{K_2}\right)} \right\} \tag{3.18}$$

$$K = \frac{k_{-1} + k_p}{k_1} \tag{3.19}$$

where K= Michaelis-Menten constant

and K_2= equilibrium constant for the reaction between enzyme and inhibitor.

In the case of this polymerization the substrate can be considered as a polymer chain of n repeat units, the product a polymer chain of n+1 repeat units, the enzyme tin (IV) chloride, ES the active propagating polymer chain and the inhibitor a chloride anion from the tetrabutylammonium chloride, as shown in scheme 3.3.



Scheme 3.3: Proposed mechanism of polymerization for propagation by a single species.

If initiation is rapid and the concentration of the active polymer chain ends is small then, since the product of the reaction (P) may also act as a substrate molecule (S), the concentration of substrate will be equal to the initial concentration of co-catalyst. The rate of polymerization will then be given by;

$$\frac{-d[M]}{dt} = k_p[SnCl4]_0[M]\left\{\frac{1}{1+\frac{K}{[1-PhECl]_0}\left(1+\frac{[Cl^-]}{K_2}\right)}\right\} \tag{3.20}$$

and therefore;

$$k_{app} = k_p[SnCl4]_0\left\{\frac{1}{1+\frac{K}{[1-PhECl]_0}\left(1+\frac{[Cl^-]}{K_2}\right)}\right\}. \tag{3.21}$$

Inversion of equation 3.21 gives;

$$\frac{1}{k_{app}} = \frac{1}{k_p[SnCl4]_0}\left\{1+\frac{K}{[1-PhECl]_0}+\frac{K[Cl^-]}{K_2[1-PhECl]_0}\right\} \tag{3.22}$$

and therefore the reciprocal of the apparent rate constant will have a straight line dependence on the concentration of chloride anions if the concentrations of catalyst and co-catalyst are kept constant. The concentration of the free chloride can be related to the initial concentration of tetrabutylammonium chloride. Table 3.7 shows the dependence of $1/k_{app}$ on the initial concentration of tetrabutylammonium chloride.

$[Bu_4N^+Cl^-]_0$	$1/k_{app}$
0.005	1096
0.005	1323
0.02	1401
0.03	1667
0.04	5495
0.04	5495

Table 3.7: The dependence of the reciprocal of the apparent rate constant on the concentration of tetrabutylammonium chloride.

Figure 3.14 shows the plot of the reciprocal of the apparent rate constant against the initial concentration of tetrabutylammonium chloride. The graph does not show a complete straight line relationship, with the points at higher concentration of tetrabutylammonium chloride having a value of $1/k_{app}$ higher than would be expected. The initial region of the plot is of interest because the Michaelis-Menten kinetic scheme appears to apply. The deviation from Michaelis-Menten kinetics at high concentrations might be explained by the formation of $SnCl_5^-$ in the reaction between tin (IV) chloride and tetrabutylammonium chloride. In Michaelis-Menten kinetics the product of the reaction between the enzyme and inhibitor is inert. However, if propagation proceeds via free ions then the formation of $SnCl_5^-$ will further effect the equilibrium between active and dormant chain ends.

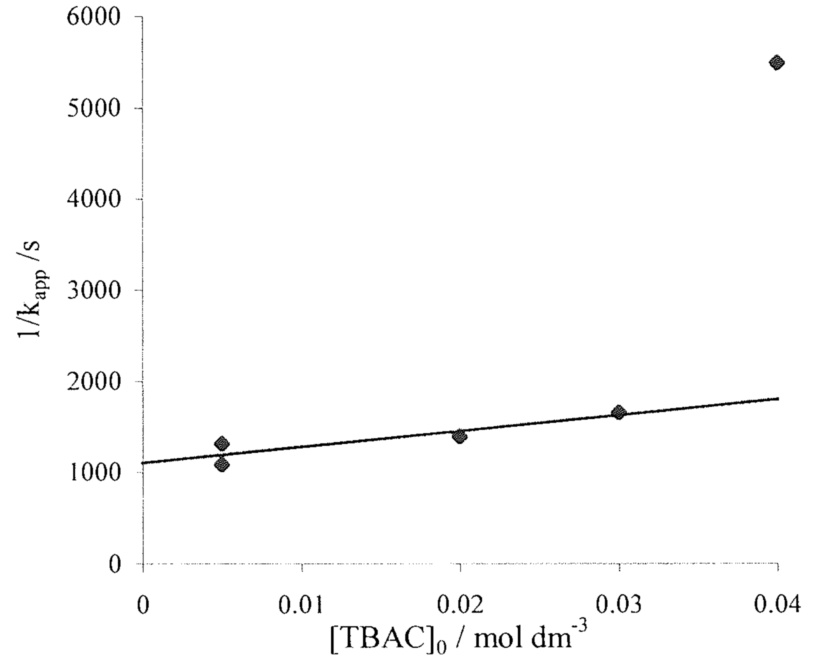


Figure 3.14: Graph of $1/k_{app}$ against concentration of tetrabutylammonium chloride.

On the basis of this analysis it is not possible to rule out the likelihood that there is only one active species, (i) which is present in low concentration and (ii) whose lifetime in the active state is extremely short. It is then possible to explain "living" polymerization in terms of a short-lived/dormant conventional polymerization. In this case the active species has time to propagate but not terminate or transfer.

3.3: Molecular weight studies of polymerizations at 25 °C.

The polymers produced by the reactions studied in section 3.1.2 were analysed by size exclusion chromatography, as described in section 2.7.

Studies have shown that, for a living polymerization in which initiation is rapid and each co-catalyst molecule leads to one discrete polymer chain, the number average molecular weight can be calculated from;

$$M_n = \frac{[M]_0 - [M]}{[I]_0} Mm \qquad (3.23)$$

where M_n= number average molecular weight,

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

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

$[I]_0$= initial concentration of catalyst

and Mm= relative molecular mass of monomer.

Table 3.8 shows the dependence of molecular weight on the initial concentration of 1-chloro-1-phenylethane along with the theoretical M_n based on the monomer conversion calculated from the dilatometry results.

$[1\text{-PhECl}]_0$/mol dm^{-3}	M_n	M_w	M_w/M_n	Calculated M_n	E_I	$1/[1\text{-PhECl}]_0$ /mol^{-1} dm
0.005	3800	4300	1.14	9690	2.6	200
0.01	3000	3300	1.11	4226	1.4	100
0.01	3000	3300	1.12	4454	1.5	100
0.018	2200	2400	1.12	2648	1.2	57
0.018	2300	2600	1.13	2510	1.1	57
0.02	2100	2400	1.12	2291	1.1	50
0.02	2100	2300	1.13	2574	1.2	50
0.023	1900	2200	1.12	2274	1.2	44
0.025	1700	1900	1.13	1990	1.2	40

Table 3.8: Dependence of molecular weight on the initial concentration of co-catalyst; $[\text{styrene}]_0$= 0.5 mol dm^{-3}, $[SnCl_4]_0$= 0.05 mol dm^{-3}, $[Bu_4N^+Cl^-]_0$= 0.02 mol dm^{-3}.

Figure 3.15, below, shows a plot of the number average molecular weight calculated using equation 3.23 and that determined by size exclusion chromatography against $1/[1\text{-PhECl}]_0$. As the initial concentration of catalyst decreases (1/[1-PhECl] increases) there is an increasing discrepancy between the observed number average molecular weight and that calculated using equation 3.23 and the monomer conversion determined from the dilatometry data. This difference may be attributed to transfer reactions increasing the number of polymer chains or termination of a propagating chain before the polymerization is complete. Another possible cause of the discrepancy between the observed and calculated molecular weight might be the presence of impurities such as water which could initiate polymerization to give a greater number of growing chains. At low concentrations of 1-chloro-1-phenylethane impurities are likely to be significant which would lead to the large discrepancy between observed and theoretical M_n at low [1-phECl] while a higher concentrations the difference is not as marked.

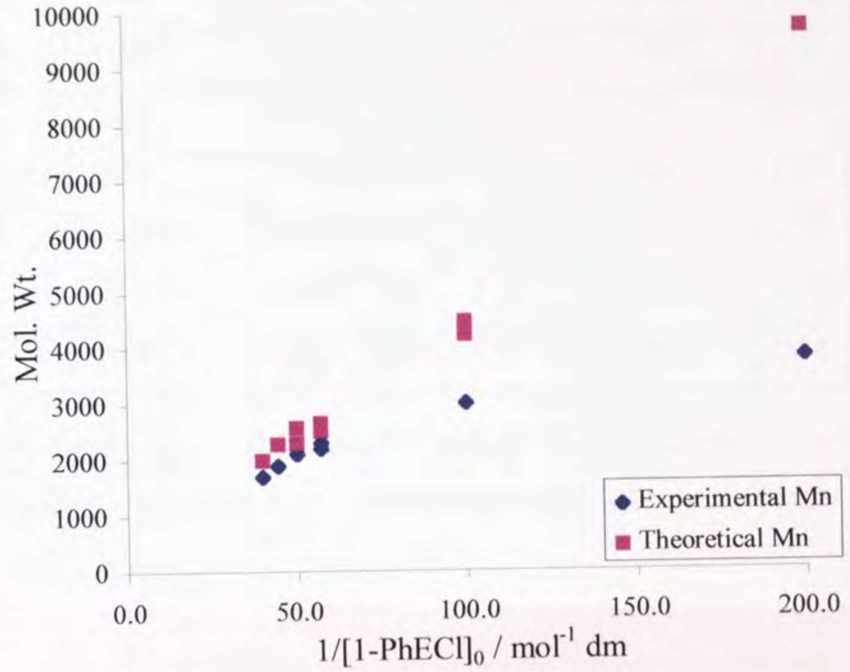


Figure 3.15: Graph of experimental and calculated number average molecular weight against 1/[1-chloro-1-phenylethane]$_0$.

The efficiency of the initiator, E_I, is defined as the ratio of calculated M_n to experimental M_n and is an indication of the number of polymer chains formed per molecule of co-catalyst. Tables 3.9 and 3.10 show the dependence of molecular weight on the initial concentration of catalyst and tetrabutylammonium salt respectively.

[SnCl$_4$]$_0$/mol dm^{-3}	M_n	M_w	M_n/M_w	Calculated M_n	E_I
0.02	2100	2400	1.14	2291	1.09
0.03	1800	2100	1.14	2574	1.43
0.03	1800	2100	1.14	2597	1.44
0.05	2100	2400	1.12	2566	1.22
0.05	2100	2300	1.13	2528	1.20
0.06	2000	2300	1.14	2217	1.11
0.06	2100	2300	1.10	2492	1.19
0.08	2100	2300	1.13	2601	1.24
0.08	1900	2200	1.15	2284	1.20
0.08	2100	2400	1.12	2403	1.14

Table 3.9: Dependence of molecular weight on the initial concentration of catalyst; [styrene]$_0$= 0.5 mol dm^{-3}, [1-PhECl]$_0$= 0.02 mol dm^{-3}, [Bu$_4$N$^+$Cl$^-$]$_0$= 0.02 mol dm^{-3}.

[Bu$_4$N$^+$Cl$^-$]$_0$/mol dm^{-3}	Mn	Mw	Mn/Mw	Calculated Mn	EI
0.005	2000	2300	1.15	2386	1.19
0.005	2100	2400	1.14	2542	1.21
0.02	2100	2400	1.12	2291	1.09
0.02	2100	2300	1.13	2574	1.23
0.03	1900	2100	1.14	2571	1.35
0.04	1300	1500	1.15	1641	1.26
0.04	1700	1900	1.12	2067	1.22

Table 3.10: Dependence of molecular weight distribution on the initial concentration of tetrabutylammonium chloride; [styrene]$_0$ = 0.5 mol dm^{-3}, [1-PhECl]$_0$ = 0.02 mol dm^{-3}, [SnCl$_4$]$_0$= 0.05 mol dm^{-3}.

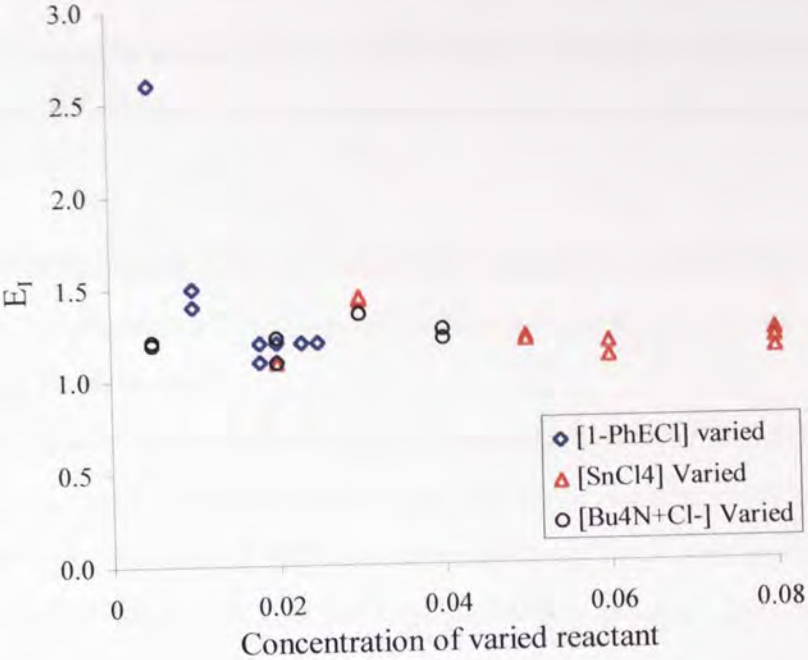


Figure 3.16: Graph of initiator efficiency against concentration for series of experiments with varying concentration of either co-catalyst, catalyst or added salt.

Figure 3.16 shows a plot of initiator efficiency against concentration for the three series of experiments varying the concentration of 1-chloro-1-phenylethane, tin (IV) chloride and tetrabutyl ammonium chloride. The efficiency is always greater than one which indicates that more polymer chains are being formed than expected. The initiator efficiency appears to be independent of the initial concentration of tin (IV) chloride and tetrabutylammonium chloride and increases with decreasing concentration of co-catalyst.

The high initiator efficiencies may be due to a slow equilibrium between the active and dormant polymer chain ends. However this would appear unlikely because the initiator efficiency is independent of the initial concentrations of tin (IV) chloride and tetrabutylammonium chloride, which would effect position of equilibrium between active and dormant polymer chain ends.

Another possible reason for the high initiator efficiencies might be the presence of impurities, such as water or alcohol, which may act as a co-catalyst. The extent of this effect would be independent of the concentration of tin (IV) chloride and tetrabutylammonium chloride and would be more pronounced at lower concentrations of 1-chloro-1-phenylethane. Initiation could also occur through a thermally induced method.

A third possible reason for the high initiator efficiencies might be that, under these experimental conditions, the propagating polymer chain ends may undergo transfer reactions.

3.4: Investigations into the effect of various drying agents on reactions at 25 °C.

A series of experiments was conducted to determine if initiation by advantageous impurities could be eliminated.

Reactions were conducted at higher concentration of monomer to determine the effect of any adventitious impurities on the molecular weight distributions of the polymers. The concentrations of reactants were $[\text{styrene}]_0$ = 2.5 mol dm^{-3}, $[\text{1-PhECl}]_0$= 0.020 mol dm^{-3}, $[SnCl_4]_0$= 0.050 mol dm^{-3} and $[\text{TBAC}]_o$= mol dm^{-3}. The polymerization reaction was carried out in a side-arm flask as described in section 2.4.1. The resultant polymer had an Mn of 7700, Mw of 11900 and a polydispersity of 1.54.

Figure 3.17 shows the size exclusion chromatography trace obtained using a single mixed B column for the polymer produced in this experiment. It shows a bimodal molecular weight distribution, which could be caused by the presence of two different propagating species having different rates of polymerization or life times.

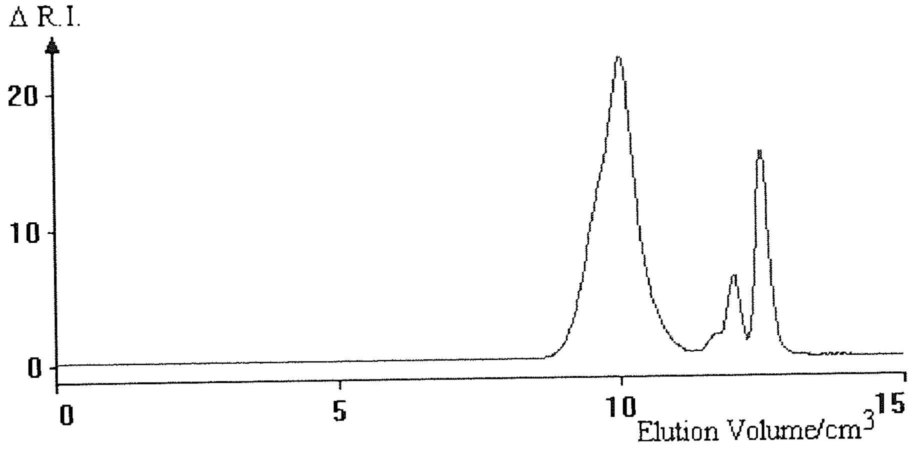


Figure 3.17: Size exclusion chromatogram for polymerization conducted at high monomer concentration.

It was considered possible that complications might have arisen from thermal polymerization of styrene. A solution of styrene in dichloromethane was prepared on the vacuum line and then placed in a constant temperature bath at 25 °C for four hours. After this period of time the solution was poured into an excess of degassed methanol. No polymer was precipitated and after evaporating the liquid off in a vacuum oven no low molecular weight polymer residue was observed. Thermal initiation was not considered to be responsible for the bimodal molecular weight distribution.

To attempt to dry further the styrene monomer before use, it was first distilled from calcium hydride via the vacuum line into a flask containing phosphorus pentoxide and allowed to stand for two hours. However this produced a viscous liquid, suggesting that the phosphorus pentoxide had polymerized the styrene.

The bimodal molecular weight distribution could also be explained in terms of moisture leaking into the reaction system through one of the taps or suba-seal of the dilatometer. A second dilatometer was designed to overcome this problem, which is shown in figure 3.18 shows this second dilatometer. Solutions of the catalyst and tetrabutylammonium chloride were placed into the side-arm bulb of the apparatus and the monomer, co-catalyst and solvent in the central bulb. After mixing, the reaction solution was run into the capillary. Table 3.11 shows the concentration of reactants used and the molecular weights of the polymers produced and figure 3.19 shows the size exclusion chormatograms for these polymerizations, obtained using a single mixed B column.

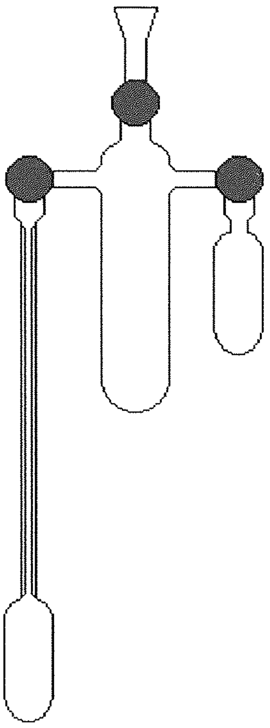


Figure 3.18: Dilatometer.

$[M]_0$	$[I]_0$	$[SnCl]_0$	$[TBAC]_0$	Mn	Mw	Pdi	E_I
0.5	0.020	0.050	0.020	1800	2200	1.25	1.5
1.0	0.040	0.10	0.040	2100	2700	1.31	1.3

Table 3.11: Concentration of reactants and molecular weights for reactions in an alternative dilatometer.

The polymers produced have a unimodal molecular weight distribution, but higher polydispersities than those analysed in sections 3.2 and 3.3. The initiator efficiencies observed were in the same range as those reported in section 3.3. This indicates that moisture entering the system through leaking taps or suba-seals was unlikely to have been the cause of the high initiator efficiencies observed in section 3.3.

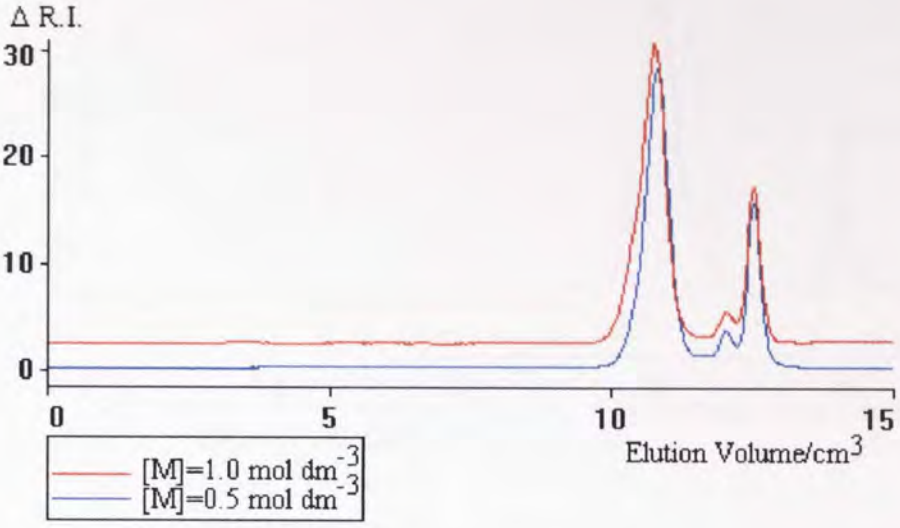


Figure 3.19: S.E.C traces for reactions conducted using a side-arm dilatometer.

To try to remove any moisture remaining in the dichloromethane after distillation, it was distilled before use into a flask containing 3Å molecular sieves. The dichloromethane was then distilled into the reaction vessel using the trap-to-trap method. Table 3.12 shows the concentration of reactants for experiments conducted using solvent dried in this manner, along with the molecular weights of the polymers produced.

$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[TBAC]_0$/ mol dm^{-3}	Mn	Mw	Pdi	% conversion	E_I
0.7	0.04	0.1	0.04	2200	2600	1.21	76.7	0.7
1.7	0.04	0.1	0.04	4200	5500	1.31	97.5	1.1
1.8	0.04	0.1	0.04	4133	5709	1.38	88.0	1.0

Table 3.12: Concentration of reactants and molecular weight data for experiments conducted with dichloromethane dried with 3Å molecular sieves.

Figure 3.20 show the S.E.C. traces for the polymers produced in these reactions, obtained using four single pore columns. The reactions at higher concentration of monomer show a bimodal molecular weight distribution, Indicating that either the adventitious impurities are still present or the bimodality is caused by transfer or termination reactions.

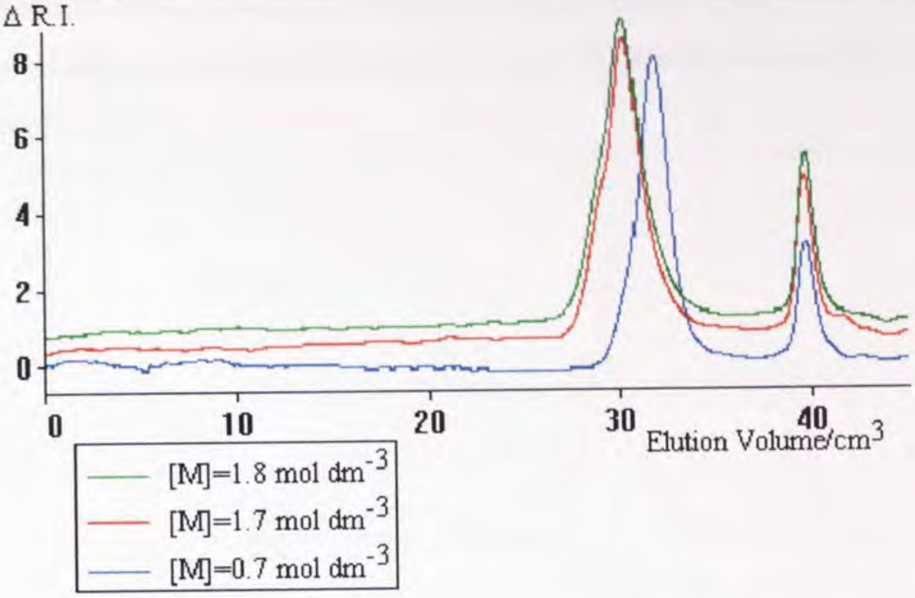


Figure 3.20: S.E.C. traces for reactions conducted using DCM dried using 3Å molecular sieves.

An alternative method to remove any moisture remaining in the dichloromethane was to dry it using magnesium sulfate. Prior to use the dichloromethane was distilled into a flask containing magnesium sulfate and allowed to stand for 24 hours. The dichloromethane was then distilled into the reaction vessel on the vacuum line using the trap-to-trap method. Table 3.13 shows the concentration of reactants for experiments conducted using solvent dried in this manner, along with the molecular weights of the polymers produced.

$[M]_0$	$[I]_0$	$[SnCl_4]_0$	$[TBAC]_0$	M_n	M_w	Pdi	Yield	E_I
2.0	0.04	0.1	0.04	4500	6400	1.42	95	1.1
2.4	0.04	0.1	0.04	4800	6600	1.39	93	1.2
3.3	0.04	0.1	0.04	6900	9900	1.43	86	1.1

Table 3.13: Concentration of reactants and molecular weight data for experiments conducted with dichloromethane dried with $MgSO_4$.

Figure 3.21 shows the S.E.C. traces for the polymers produced in reactions using dichloromethane dried with $MgSO_4$. All polymers show a bimodal molecular weight distribution, with a shoulder on the high molecular weight side of the peak. This would indicate that should any adventitious impurities still be present they are not removed by magnesium sulfate or the bimodal molecular weight distribution is caused by transfer or termination reactions.

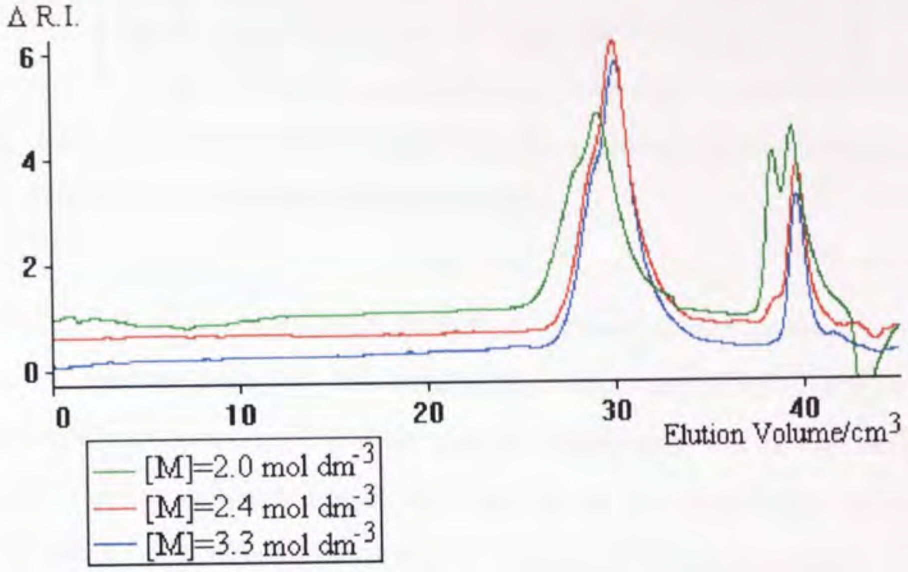


Figure 3.21: S.E.C. traces for reactions conducted using DCM dried using $MgSO_4$.

3.5: Reactions in the presence of a proton sponge (1,8-bis(dimethylamino) naphthalene).

To attempt to prevent initiation by protons from adventitious impurities such as water and to prevent chain transfer involving a proton, reactions were conducted in the presence of a proton trap (1,8-bis(dimethylamino)naphthalene). The proton sponge is highly basic and will easily react with a proton. However owing to the steric hindrance in the molecule 1,8-bis(dimethylamino)naphthalene is not a strong nucleophile and does not readily react with electrophiles other than protons.

A solution of the proton sponge was prepared in dichloromethane prior to a reaction. Polymerizations were conducted in a side arm flask with the proton sponge being added to the reaction before the mixture of tin (IV) chloride and tetrabutylammonium chloride was added and the reaction started. Table 3.14 shows the concentration of reactants in these experiments.

$[M]_0$	$[1\text{-PhECl}]_0$	$[SnCl_4]_0$	$[TBAC]_0$	[Proton Sponge]$_0$
2.2	0.04	0.1	0.04	0.08
2.3	0.04	0.1	0.04	0.06
2.8	0.04	0.1	0.04	0.04
1.8	0.04	0.1	0.04	0.02

Table 3.14: Concentration of reactants for polymerizations conducted in the presence of 1,8-bis(dimethylamino)naphthalene.

Table 3.15 below shows the molecular weights of the polymers produced by reactions in the presence of 1,8-bis(dimethylamino)naphthalene. The experiments conducted at a concentration of proton sponge greater than that of co-catalyst did not produce any polymer which indicates that there is an interaction between the polymer chain end and 1,8-bis(dimethylamino)naphthalene preventing propagation from taking place.

[Proton Sponge]:[I]	M_n	M_w	Pdi	M_n calc	% conversion	E_I
2 : 1	--	--	--	0	0	--
1.5 : 1	--	--	--	0	0	--
1 : 1	7300	9600	1.3	6194	83	0.84
0.5 : 1	4400	6300	1.4	4701	97	1.1

Table 3.15: Molecular weight distributions for polymerizations in the presence of a proton sponge.

Figure 3.22 shows the size exclusion chromatograms for reactions conducted with a concentration of proton sponge equal to or lower than the concentration of co-catalyst. The polymers have a bimodal molecular weight distribution which indicated that the transfer process taking place is not prevented by the proton sponge.

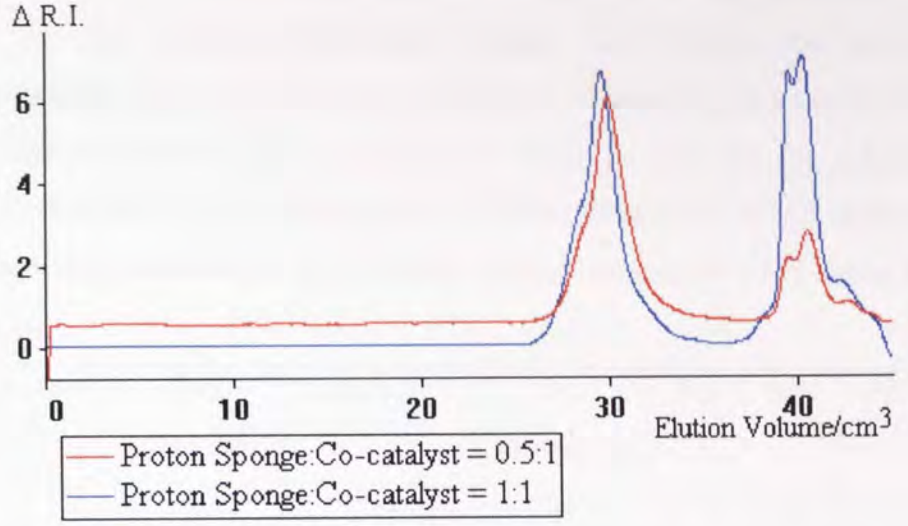


Figure 3.22: Size exclusion chromatography traces for reactions in the presence of 1,8-bis(dimethylamino)naphthalene.

3.6: Effect of temperature on molecular weight distribution.

To determine whether the bimodal molecular weight distribution observed in sections 3.4 and 3.5 was caused by transfer reactions or not, a series of experiments were conducted at various temperatures. In cationic polymerization the activation energy for transfer reactions is greater than the activation energy for propagation. So that as the reaction temperature is decreased the rate of transfer will decrease more rapidly than the rate of propagation. Table 3.16 shows the reaction temperature and the concentration of reactants for this series of experiments.

Temperature / °C	$[M]_0$ / mol dm^{-3}	[1-PhECl]$_0$ / mol dm^{-3}	[SnCl$_4$]$_0$ / mol dm^{-3}	[TBAC]$_0$ / mol dm^{-3}
0	2.8	0.035	0.087	0.035
-15	0.72	0.042	0.11	0.042
-15	1.0	0.040	0.10	0.040

Table 3.16: Temperature and concentration of reactants for polymerizations at temperatures below ambient.

Table 3.17 shows the percentage conversion and the dependence of the molecular weights on the reaction temperature. Figure 3.21 shows the size exclusion chromatography results for this series of reactions. Comparing these results with those for reactions conducted at 25 °C (section 3.4) it can be seen that the polymers have a lower polydispersity, 1.1-1.2 compared to 1.5. The reaction at 0 °C still shows a bimodal molecular weight distribution, however the polymerizations at -15 °C have a unimodal distribution.

Temperature / °C	$[M]_0$ / mol dm^{-3}	Conversion	M_n theoretical	Mn	Mw	Pdi	E_I
0	2.8	0.94	7843	8400	9800	1.17	0.94
-15	0.72	0.85	1658	2000	2300	1.14	0.83
-15	1.0	0.95	2615	2600	3000	1.14	0.99

Table 3.17: Dependence of molecular weights on reaction temperature.

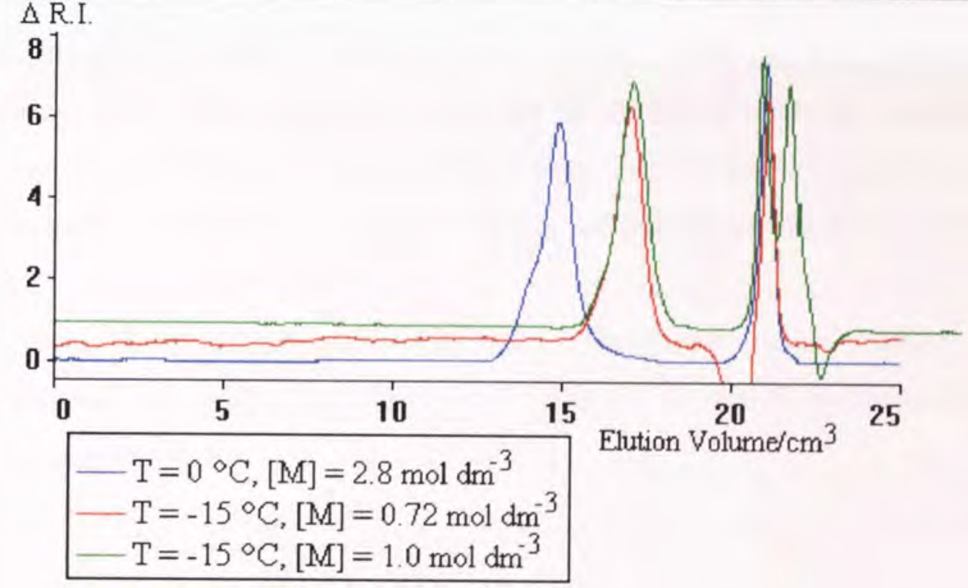


Figure 3.23: S.E.C. results for polymerizations at below ambient temperatures.

From these results would seem be seen that, as the polymerization temperature is decreased, the molecular weight distribution changes from bimodal to unimodal and the polydispersity of the polymers decreases. This evidence indicates that at 25 °C transfer reactions are present in the polymerization of styrene by 1-chloro-1-phenylethane and tin

(IV) chloride in the presence of tetrabutylammonium chloride. As the polymerization temperature is decreased the rate of transfer reactions is decreased compared to the rate of propagation and at -15 °C these transfer reactions become unfavourable leading to a "living" polymerization.

At temperatures below ambient the polymerization shows the characteristics of a living polymerization. These results are in agreement with those presented by higashimura and co-workers(119). It was then decided to attempt to investigate the kinetics of the polymerization at these temperatures and to study the changes in the molecular weight distribution as the reaction progresses.

3.7: Kinetic studies of reactions at 0 °C by sampling.

To study the kinetics of polymerizations at 0 °C, experiments were conducted and samples of the reaction solution obtained as described in section 2.6.2. The initial experimental plan was to quench the samples with methanol, allow the precipitated polymer to settle and use gas chromatography to determine the concentration of remaing monomer. However, it was found that as the polymer settled monomer and solvent would become trapped in the polymer network rendering the subsequent gas chromatography results meaningless. Since, for the method of removing sample used, the exact sample size was not known a methodology was devised to study the kinetics of polymerization by the number average degree of polymerization after different time periods.

For a living polymerization with rapid initiation the number average degree of polymerization can be given by equation 3.24 if all the co-catalyst molecules lead to one growing polymer chain.

$$Dp_n = \frac{[M]_0 - [M]}{[I]_0} \tag{3.24}$$

where Dp_n= number average degree of polymerization,

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

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

and $[I]_0$= initial concentration of catalyst.

The concentration of monomer at a given time, t, can be given by;

$$[M] = [M]_0 e^{-kt}. \tag{3.25}$$

where k= apparent rate constant.

Substituting equation 3.25 into 3.24 gives;

$$Dp_n = \frac{[M]_0\left(1 - e^{-kt}\right)}{[I]_0}. \tag{3.26}$$

If, after a long time period, all the monomer is consumed then the final degree of polymerization at this time will be given by;

$$Dp_{n\infty} = \frac{[M]_0}{[I]_0}. \tag{3.27}$$

Substituting equation 3.27 into equation 3.26 gives;

$$Dp_n = Dp_{n\infty}\left(1 - e^{-kt}\right). \tag{3.28}$$

Rearranging and taking the natural logarithm of equation 3.28 gives;

$$\ln\left(1 - \frac{Dp_n}{Dp_{n\infty}}\right) = -kt. \tag{3.29}$$

equation 3.29 can then be rewritten as;

$$\ln\left(Dp_{n\infty} - Dp_n\right) = \ln\left(Dp_{n\infty}\right) - kt \tag{3.30}$$

Therefore for a living polymerization a plot of $\ln(Dp_{n\infty}-Dp_n)$ against time will be a straight line with a gradient given by (minus) the apparent rate constant of the reaction and an intercept equal to the final number average degree of polymerization. This approach is most infromative in the early stages of polymerization because, as the reaction approaches completion, i.e. as Dp_n tends to $Dp_{n\infty}$, slight inaccuracies in ($Dp_{n\infty}$-Dpn), a small number, lead to large errors in $\ln(Dp_{n\infty}-Dp_n)$. Therefore the most accurate points are those early in the polymerization. For this reason the final data for the final sample was recorded but not necessarily used in the plot of $\ln(Dp_{n\infty}$-Dpn) against time.

An experiment was conducted as described in section 2.6.2, with $[\text{styrene}]_0$= 2.8 mol dm^{-3}, $[\text{1-PhECl}]_0$= 0.038 mol dm^{-3}, $[\text{SnCl}_4]_0$= 0.097 mol dm^{-3} and $[\text{TBAC}]_0$= 0.039 mol dm^{-3}. Samples of the polymerization were taken at specified times and the resultant polymers analysed by S.E.C. as described in section 2.7. Table 3.18 shows the dependence of molecular weight distribution and degree of polymerization on time.

Time/s	Mn	Mw	Pdi	Dpn	ln (76-Dpn)
250	2200	2500	1.11	21.4	4.0
1125	5300	5600	1.06	50.7	3.2
1950	6600	7000	1.07	63.2	2.6
3585	7500	8200	1.09	72.4	1.3
5400	7900	8800	1.12	75.6	-0.93

Table 3.18: Dependence of molecular weight and degree of polymerization on time for reaction at 0 °C.

The final number average degree of polymerization ($Dp_{n\infty}$) was assumed to be at least that of the final sample and this value was used to plot a graph of ln($Dp_{n\infty}$-Dpn) against t, as shown in figure 3.24. which gave a linear plot. From the intercept of this plot the value of $Dp_{n\infty}$ was calculated as being 67 which compares reasonably with the expected number average degree of polymerization (Dp_n= 73) calculated using equation 3.24. The apparent rate constant was estimated from the gradient of the graph as being $8.1 * 10^{-4}$ s^{-1}.

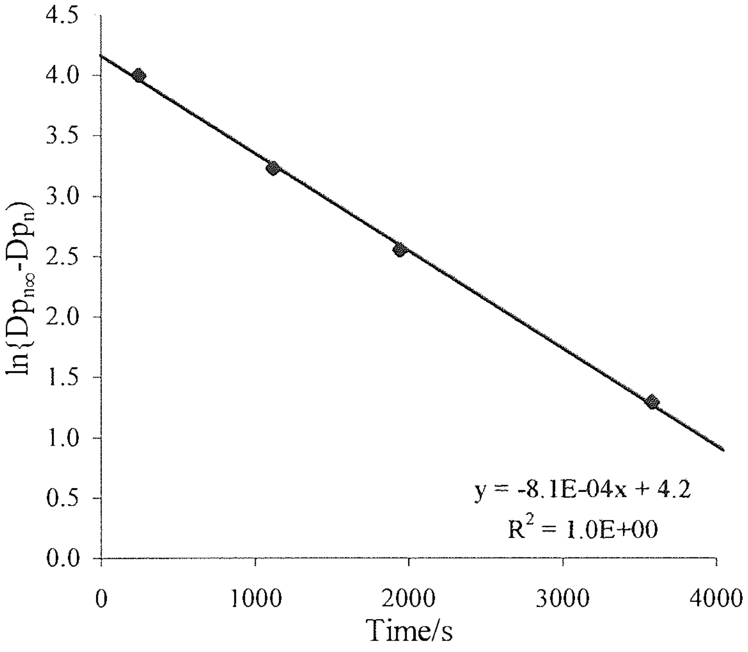


Figure 3.24: Graph of ln($Dp_{n\infty}$-Dpn) against time for polymerization at 0 °C.

A further experiment was conducted as described above changing the concentration of styrene leaving all other concentrations unchanged i.e. with $[\text{styrene}]_0$= 1.6 mol dm^{-3}, $[1\text{-PhECl}]_0$= 0.038 mol dm^{-3}, $[SnCl_4]_0$= 0.093 mol dm^{-3} and $[TBAC]_0$= 0.037 mol dm^{-3}. Table 3.19 shows the dependence of molecular weight distribution and degree of polymerization on time.

Time/s	Mn	Mw	Pdi	Dpn
355	3087	3375	1.09	29.6
1025	3721	4085	1.10	35.7
1870	3997	4464	1.12	38.4
3330	4343	4865	1.12	41.7
4973	3969	4656	1.17	38.1
6125	3196	4245	1.33	30.7

Table 3.19: Dependence of molecular weight and degree of polymerization on time for reaction at 0 °C.

The samples at 4973 and 6125 seconds show a decrease in the degree of polymerization compared to that at 3330 s and an increase in polydispersity. It is likely that the reaction became contaminated whilst a sample was being removed and this data was not used in any further calculations. Table 3.20 shows the dependence of ln($Dp_{n\infty}$-Dpn) on time for the value of $Dp_{n\infty}$ calculated using equation 3.24.

Time/s	ln (42-Dpn)
355	2.5
1025	1.8
1870	1.3
3330	-1.2

Table 3.20: Dependence of ln($Dp_{n\infty}$-Dpn) on time.

The data shown in table 3.20 was plotted, as shown in figure 3.25, and the value of $Dp_{n\infty}$ calculated from the intercept of a straight line through the points.

From this graph the apparent rate constant was estimated as 1.2 * 10^{-3} s^{-1}. However this plot shows a curved relationship between $\ln(Dp_{n\infty}\text{-}Dp_n)$ and time with an increase in rate constant with increasing time, also the value of $Dp_{n\infty}$ obtained from the intercept of the plot, which has a value of 22, does not agree with that used in the calculation of $\ln(Dp_{n\infty}\text{-}Dp_n)$.This could indicate that additional polymer chains were being initiated either by impurities such as moisture entering the system or because the rate of initiation was slow.

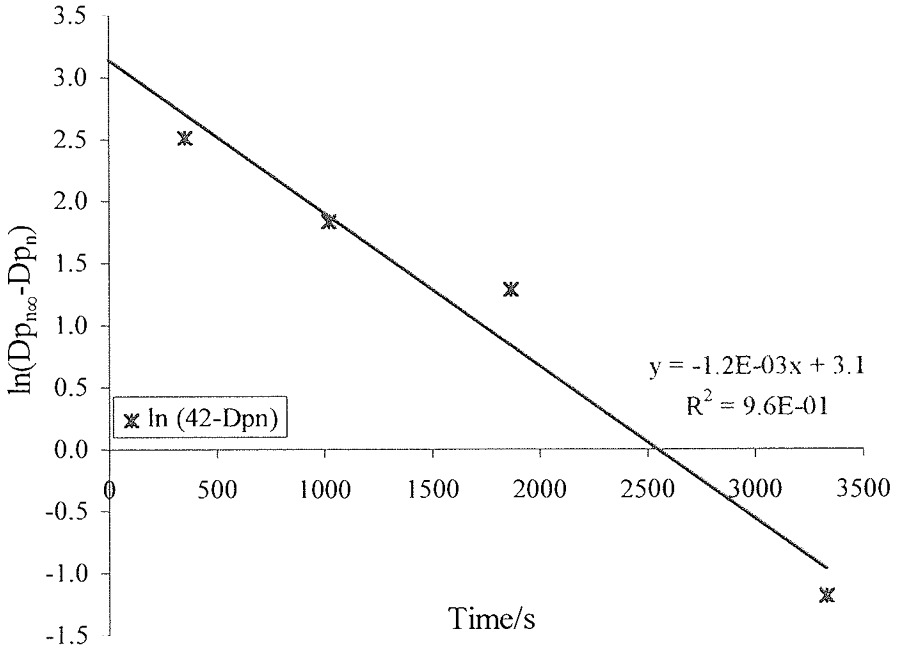


Figure 3.25: Graph of $\ln(Dp_{n\infty}\text{-}Dpn)$ against time for polymerization at 0 °C.

3.7.1: Measurement of the initial rate of polymerization by sampling reactions at 0 °C.

To measure the initial rate of polymerization, reactions were conducted as described above, with samples being taken in the early stages of polymerization. The reaction was the allowed to continue for 2 hours to determine the final degree of polymerization and $\ln(Dp_{n\infty}\text{-}Dp_n)$ was then plotted against time for the samples.

Table 3.21 shows the dependence of molecular weight and degree of polymerization on time for a reaction carried out as detailed above with $[\text{styrene}]_0 = 2.4$ mol dm^{-3}, $[\text{1-PhECl}]_0 = 0.039$ mol dm^{-3}, $[\text{SnCl}_4]_0 = 0.094$ mol dm^{-3} and $[\text{TBAC}]_0 = 0.039$ mol dm^{-3}.

Time/s	Mn	Mw	Pdi	Dpn
50	580	810	1.39	5.6
165	1900	2100	1.12	17.9
328	2500	2700	1.10	23.6
482	2900	3200	1.09	28.0
630	3300	3600	1.08	32.0
9000	6500	7400	1.14	62.4

Table 3.21: Dependence of molecular weight on sample time for reactions to study the initial rate of polymerization.

The ln $(Dp_{n\infty}-Dp_n)$ was calculated for a value of $Dp_{n\infty}$ of 63, as shown in table 3.22. The data was plotted against time and the intercept of the straight lines used to calculate a value for $Dp_{n\infty}$. Figure 3.26 shows the graph of ln $(Dp_{n\infty}-Dp_n)$ against time. The plot of ln $(Dp_{n\infty}-Dp_n)$ against time appears to show a decrease in slope as the reaction proceeds. This may be due to either some of the propagating chains being terminated as the first sample was removed or experimental error due to the low reaction time and conversion at this point. Since the propagating centre is in equilibrium with a dormant species at low reaction time the amount of time the polymer chains have spent in the active state may not have averaged out. This may also be responsible for the relatively high polydispersity observed for this sample. This change in gradient could lead to inaccuracies in any calculations based on these plots.

Time/s	ln(63-Dpn)
50	4.1
165	3.8
328	3.7
482	3.6
630	3.4
9000	-0.57

Table 3.22: Dependence of ln ($Dp_{n\infty}$-Dp_n) on time for a reaction to study the initial rate of polymerization.

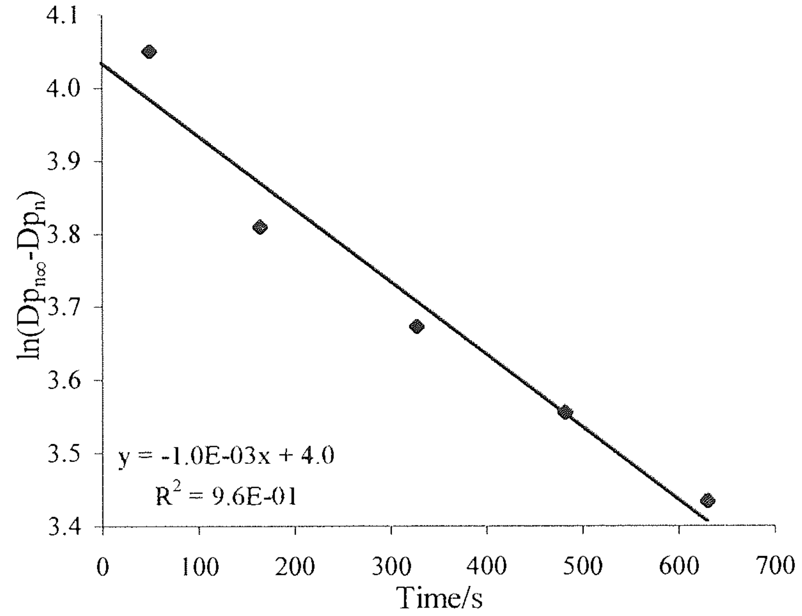


Figure 3.26: Graph of ln ($Dp_{n\infty}$-Dp_n) versus time for experiment to measure the initial rate of polymerization at 0 °C.

The value of $Dp_{n\infty}$ calculated form the intercept of figure 3.26 was 57 which is within experimental error of both the value used in the calculation of ln ($Dp_{n\infty}$-Dp_n) and the theoretical value of 62 calculated using equation 3.24. From the plot of ln ($Dp_{n\infty}$-Dp_n) against time the apparent rate constant was estimated to be $1.0 * 10^{-3}$ s^{-1}.

A second experiment was carried out to study the initial rate of polymerization at 0 °C with $[\text{styrene}]_0 = 3.2$ mol dm^{-3}, $[\text{1-PhECl}]_0 = 0.041$ mol dm^{-3}, $[\text{SnCl}_4]_0 = 0.099$ mol dm^{-3} and $[\text{TBAC}]_0 = 0.041$ mol dm^{-3}. Table 3.23 shows the dependence of molecular weight on the reaction time and $\ln(Dp_{n\infty}-Dp_n)$ for a $Dp_{n\infty}$ of 95 which was the value for the final polymer sample. The $\ln(Dp_{n\infty}-Dp_n)$ was plotted against time (figure 3.27) and the intercept value of $Dp_{n\infty}$ calculated.

Time/s	Mn	Mw	Pdi	Dp_n	$\ln(95-Dp_n)$
45	2000	2200	1.11	18.8	4.3
180	3400	4000	1.17	32.9	4.1
320	4500	5100	1.14	42.9	4.0
475	5000	5700	1.15	47.9	3.9
735	6100	7000	1.15	58.1	3.6
8100	9900	14000	1.420	94.6	-0.88

Table 3.23: Dependence of molecular weight and $\ln(Dp_{n\infty}-Dp_n)$ on reaction time for a reaction to study the initial rate of polymerization.

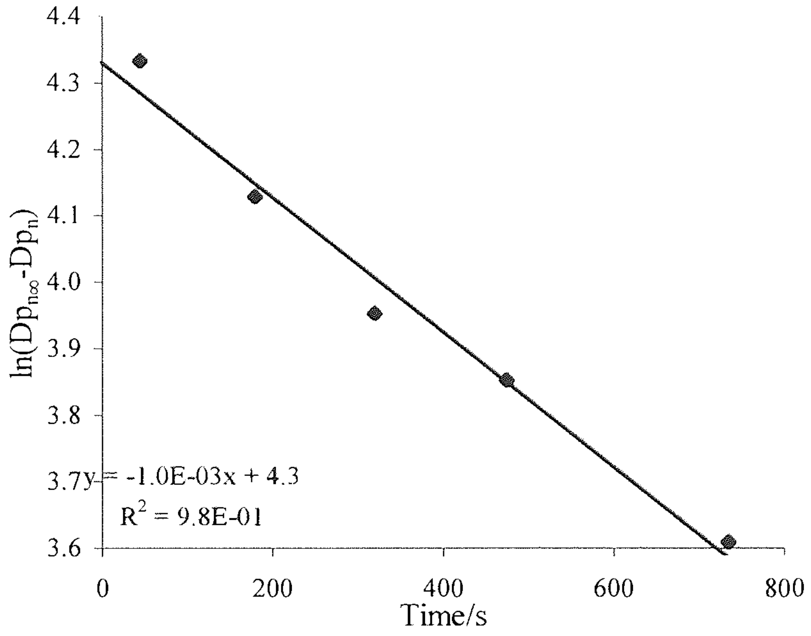


Figure 3.27: Plot of $\ln(Dp_{n\infty}-Dp_n)$ against time for a reaction to study the initial rate of polymerization.

The value of $Dp_{n\infty}$ determined from the plot of ln ($Dp_{n\infty}$-Dp_n) against time was 76, which compares with the theoretical value of 78. However, this value is significantly lower than the degree of polymerization of the final sample. The discrepancy between the values of $Dp_{n\infty}$ may be due to impurities entering the system as samples were removed; the relatively high polydispersity of the final sample compared to the other samples suggests that this is so. From the gradient of the plot of ln($Dp_{n\infty}$-Dp_n) the apparent rate constant was estimated to be $1.0 * 10^{-3}$ s^{-1}.

Comparing the values of k_{app} obtained from sampling experiments at 0 °C the average value is $1.0 * 10^{-3}$ s^{-1} with a standard deviation of $1.6 * 10^{-4}$.

These results show that the polymerization of styrene by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride is 'living' at temperatures below ambient. From this it can be infered that a plot of ln($Dp_{n\infty}$-Dp_n) against time can be used as a "test" for a living polymerization. The accuracy of the kinetic data derived from this relationship is limited by that of size exclusion chromatography, which is approximatly ±10%. The main drawback of this method is that the final value of the degree of polymerization is not that predicted from the ratio of monomer to co-catalyst, due to either errors in the calculation of the concentrations of reactant or because of incomplete initiation. In these cases it is necessary to ensure the reaction has gone to completion to obtain a value of $Dp_{n\infty}$.

3.8: Reactions involving the addition of a second batch of monomer.

One of the major features of "living" polymerization is that once all the monomer has been consumed in a reaction addition of a further batch of monomer to the reaction will cause polymerization to continue. To test the living nature of the cationic polymerization of styrene initiated by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride reactions were conducted as described in section 2.4.2 at -15 °C. The initial batch of styrene was allowed to polymerize for 4 hours, after which time a small sample (2 cm^3) of the reaction solution was removed and terminated by addition to excess methanol. The second batch of monomer was then added and the polymerization continued for a further 4 hours at which time the reaction was terminated by the addition of degassed methanol. The polymers produced were then analysed by size exclusion chromatography.

Table 3.24 shows the concentration of reactants for an experiment carried out as described above along with the extent of monomer conversion and the theoretical molecular weight.

Monomer Batch	$[M]_0$/ Mol dm^{-3}	[1-PhECl]$_0$/ Mol dm^{-3}	[SnCl$_4$]$_0$/ Mol dm^{-3}	[TBAC]$_0$/ Mol dm^{-3}	Conversion	Calculated M_n
1st	1.1	0.040	0.10	0.022	99%	3005
2nd	0.92	0.036	0.089	0.02	97%	5579

Table 3.24: Concentration of reactants, percentage conversion and theoretical molecular weight for an experiment with the addition of a second monomer batch.

Table 3.25 shows the molecular weights of the polymers produced by this experiment. The results for the polymerization of the first monomer batch show a narrow, unimodal molecular weight distribution which is common to many living polymerizations. After polymerization of the second batch of monomer an increase in molecular weight was observed. However, the polymer possessed a bimodal molecular weight distribution; figure 3.28 shows these size exclusion chromatography results. The position of the lower molecular weight peak of this bimodal distribution corresponds to the position of the peak for the first polymer sample. This indicates that the removal of the sample after the first monomer batch had been polymerized may have introduced impurities into the reaction which terminated some of the growing polymer chains.

Monomer Batch	Mn	Mw	Mp	Pdi
1st	2750	3241	2705	1.18
2nd	4306	5365	5175	1.25

Table 3.25: Molecular weight distributions for experiment with the addition of a second batch of monomer.

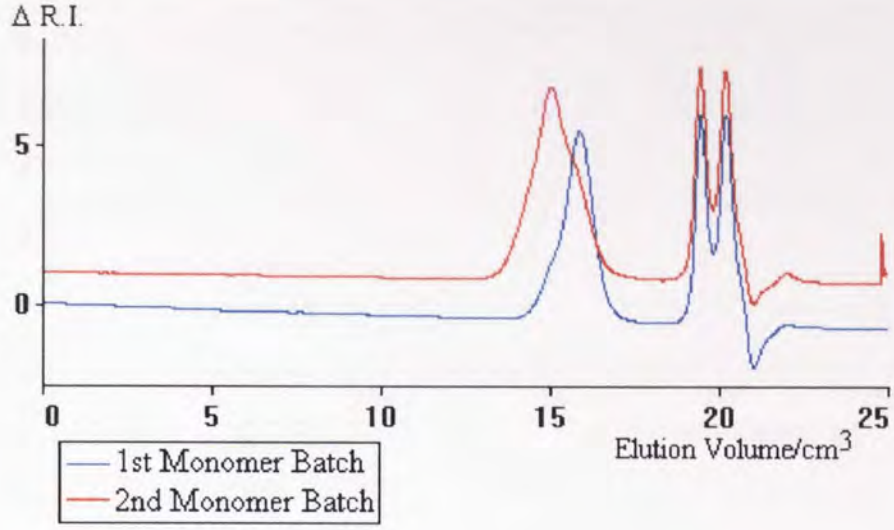


Figure 3.28: Size exclusion chromatograms for a reaction with the addition of a second batch of monomer.

A second experiment was conducted as described above, table 3.26 lists the concentration of reactants. Figure 3.29 shows the size exclusion chromatography results for this experiment. Again a unimodal molecular weight distribution was observed for the first polymer sample and a bimodal distribution of the second sample. This suggests that the termination of some of the polymer chains when the first sample is removed is a problem with the experimental technique and an alternative method needs to be devised.

Monomer Batch	$[M]_0$/ mol dm^{-3}	[1-PhECl]$_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	[TBAC]$_0$/ mol dm^{-3}	Conversion	Calculated M_n
1st	1.0	0.044	0.11	0.045	95%	2383
2nd	0.94	0.04	0.099	0.04	97%	4757

Table 3.26: Concentration of reactants, percentage conversion and theoretical molecular weight for an experiment with the addition of a second monomer batch.

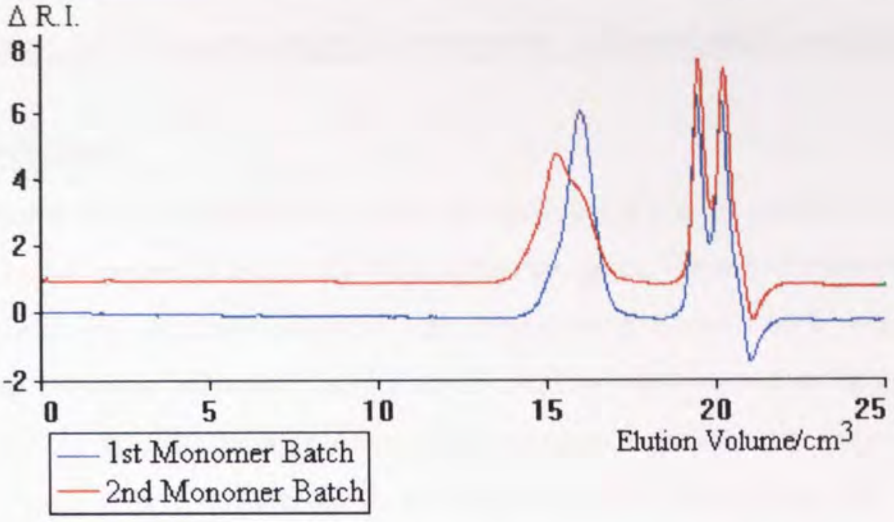


Figure 3.29: Size exclusion chromatograms for a reaction with the addition of a second batch of monomer.

Monomer Batch	Mn	Mw	Mp	Pdi
1st	2425	2788	2375	1.15
2nd	3399	4217	4335	1.24

Table 3.27: Molecular weight distributions for experiment with the addition of a second batch of monomer.

These results suggest that the cationic polymerization of styrene by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride is not a truly "living" polymerization and that a small amount of transfer or termination reactions are taking place. However the propagating centre is sufficiently long lived to allow the control of the molecular weight of the polymer produced and for further reactions to be conducted on the polymer chain ends.

Chapter 4: Polymerization of styrene by difunctional co-catalysts.

4.1: Introduction.

Difunctional co-catalysts are of interest since they allow the synthesis of polymers that have active centres at both ends of the polymer chain. These polymers can then be used to synthesise telechelic polymers with functional groups on both polymer chain ends. These telechelic polymers can be used in coupling reactions and in the synthesis of macrocyclic compounds. In copolymerization reactions a difunctional initiator can be used to prepare P(ABA) type tri-block copolymers by first polymerizing the central, B, block and then forming the outer, A, blocks.

The first living anionic polymerizations initiated by radical anions, for example sodium naphthalene(50), form a difunctional initiator by the combination of two radicals (section 1.3). Other difunctional initiators for anionic polymerization are dilithium compounds formed by the addition of a lithium alkyl compound to an aromatic divinyl precursor, such as *m*-diisopropenylbenzene(123), *m*-divinylbenzene(124) or 1,3-bis(1-phenylethenyl)benzene(125).

In cationic polymerization difunctional initiators have been used in inifer polymerizations, an example of this is dicumyl chloride(37). Examples of difunctional co-catalysts that have been used in living cationic polymerization are; 1,4-bis(1-chloroethyl)benzene(88), 1,4-bis(1-bromomethylethyl)benzene(93), 1,4-bis(1-azido-1-methylethyl)benzene(97) and 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene(99).

4.2: Polymerization of styrene using 1,4-bis(bromomethyl)benzene as a difunctional co-catalyst.

In this section the polymerization of styrene by the initiator system 1,4-bis(bromomethyl)benzene/tin (IV) chloride in the presence of tetrabutylammonium chloride will be discussed. This co-catalyst was chosen because the potential active sites are structurally similar to those on the monofunctional initiator, reported in chapter 3. The bromine atom should be relatively labile and the material is readily available. The object of these studies was to investigate the use of this difunctional co-catalyst on the molecular weight distribution, reaction kinetics and the "living" nature of the polymerization.

4.2.1: Polymerization reactions in a side-arm flask.

A polymerization initiated by 1,4-bis(bromomethyl)benzene/tin (IV) chloride in the presence of tetrabutylammonium chloride was conducted in dichloromethane as solvent at 0 °C as described in section 2.4.1. The concentrations of reactants were $[\text{styrene}]_0 = 1.7$ mol dm^{-3}, $[\text{1,4-bis(bromomethyl)benzene}]_0 = 0.019$ mol dm^{-3}, $[SnCl_4]_0 = 0.095$ mol dm^{-3} and $[Bu_4N^+Cl^-]_0 = 0.039$ mol dm^{-3}. The polymerization was allowed to proceed for 4 hours at which point the reaction was terminated by the addition of methanol, the polymer recovered and examined using size exclusion chromatography. Table 4.1 shows the results of the size exclusion chromatography and figure 4.1 shows the S.E.C. trace for this polymer.

Theoretical M_n	M_n	M_w	M_p	Pdi	E_I
9584	13400	19700	19600	1.47	0.72

Table 4.1: Molecular weight distribution for polymerisation using 1,4-bis(bromomethyl)benzene as the co-catalyst.

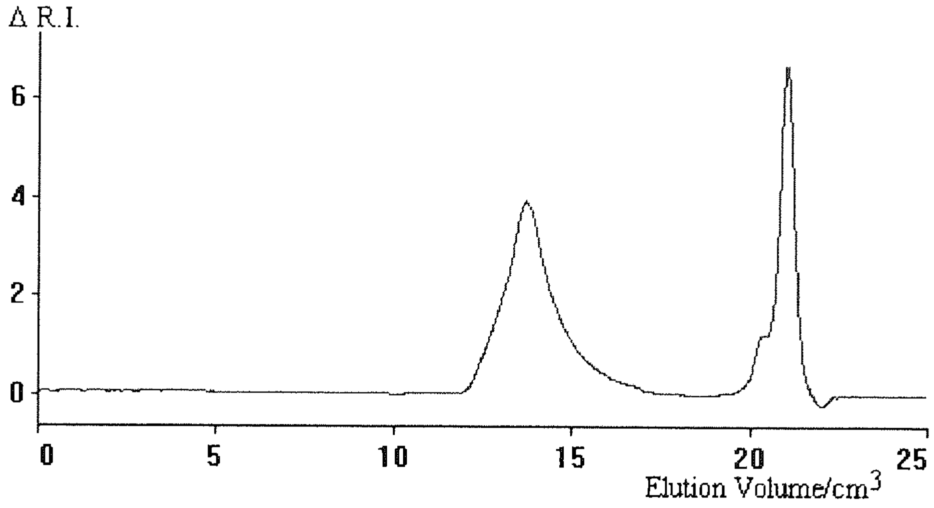


Figure 4.1: S.E.C. trace for polymer produced by a reaction initiated by 1,4-bis(bromomethyl)benzene.

The polymer sample shows a broader molecular weight distribution than observed for similar reactions using a monofunctional initiator. The polymer has a polydispersity of 1.5 compared to polydispersities in the range of 1.1-1.2 for unimodal co-catalysts and the observed molecular weight of the polymer is greater than that expected for a living polymerization, with an initiator efficiency significantly less than one. These observations may be due to transfer or termination reactions taking place. Another possible explanation for the broad molecular weight distribution may be that the rate of initiation for the polymerization initiated by 1,4-bis(bromomethyl)benzene being slower than the rate of propagation. If this is the case then not all the co-catalyst molecules initiate polymer chains at the same time leading to a broadening of the molecular weight distribution.

4.2.2: Sampling reactions at 0 °C.

Experiments were conducted to study the kinetics of the polymerization of styrene initiated by 1,4-bis(bromomethyl)benzene/tin (IV) chloride in the presence of tetrabutylammonium chloride and to observe the variation of molecular weight with time. Reactions were carried out as described in section 2.6.2 at 0 °C in dichloromethane.

A reaction was conducted with $[\text{styrene}]_0 = 2.1$ mol dm^{-3}, $[\text{1,4-bis(bromomethyl)benzene}]_0 = 0.019$ mol dm^{-3}, $[SnCl_4]_0 = 0.096$ mol dm^{-3} and $[Bu_4N^+Cl^-]_0 = 0.038$ mol dm^{-3}. Table 4.2 shows the dependence of molecular weight on time of samples extracted from this reaction.

Time/s	M_n	M_w	M_p	Pdi	Dpn
270	1900	2200	2100	1.15	18.5
672	3500	3900	3700	1.10	33.8
1114	4600	5100	5200	1.11	44.2
2625	7700	8900	9500	1.16	73.8
5122	11400	14400	15300	1.26	110
6457	13800	18000	17700	1.31	132

Table 4.2: Dependence of molecular weight on sample time.

The polymer samples show an increase in polydispersity which may indicate that more polymer chains are initiated as the reaction progresses. The living character of the polymerization was tested using the equation derived in section 3.7, by plotting ln ($Dp_{n\infty}$-Dp_n) against time. Table 4.3 shows the dependence of ln ($Dp_{n\infty}$-Dp_n) on time for this experiment. This series of data was plotted against time, but the final value was excluded because the final datum point was likely to contain the largest error (section 3.7).

Time/s	ln (133-Dp_n)
270	4.7
672	4.6
1114	4.5
2625	4.1
5122	3.1
6457	-0.18

Table 4.3: Dependence of ln ($Dp_{n\infty}$-Dp_n) on time.

Figure 4.2 shows a graph of ln ($Dp_{n\infty}$-Dp_n) against time for a value of $Dp_{n\infty}$ = 133. This value was chosen because it was the value for the final polymer sample, however, since the monomer conversion for this sample was not known the use of this value may lead to errors. The value of $Dp_{n\infty}$ was then estimated from the intercept of the straight line plot through the points. Figure 4.2 shows a good straight line relationship between ln ($Dp_{n\infty}$-Dp_n) and time. The values of $Dp_{n\infty}$ used to calculate ln ($Dp_{n\infty}$-Dp_n) and that obtained from the intercept of figure 4.2 of 133 and 127 respectivly show a close agreement. However, both these valuse are significantly larger than that predicted by equation 3.24 of 110. From the graph of ln ($Dp_{n\infty}$-Dp_n) against time the apparent rate constant was accordingly estimated to be $3.2 * 10^{-4}$ s^{-1}.

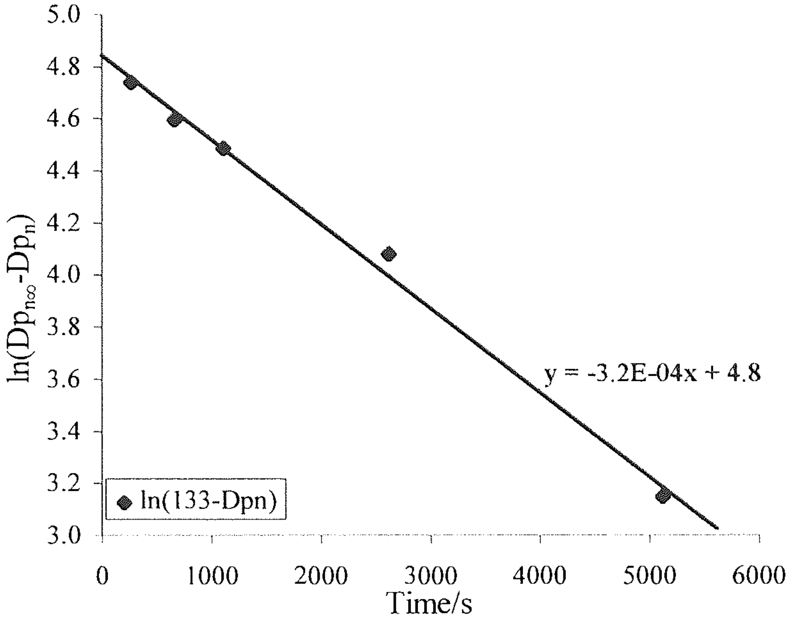


Figure 4.2: Graph of ln ($Dp_{n\infty}$-Dp_n) against time.

A further reaction was conducted as described above with $[\text{styrene}]_0$= 2.3 mol dm^{-3}, $[\text{1,4-bis(bromomethyl)benzene}]_0$= 0.020 mol dm^{-3}, $[SnCl_4]_0$= 0.10 mol dm^{-3}, $[\text{tetrabutylammonium chloride}]_0$= 0.041 mol dm^{-3}. Table 4.4 shows the dependence of molecular weight on polymerization time for this reaction. Again the samples show an increasing polydispersity with time which may indicate that transfer or termination reactions are taking place or polymer chains are continuously produced as the reaction progressed, due to either slow initiation or impurities entering the system.

Time/s	M_n	M_w	M_p	Pdi	Dp_n
360	2800	3000	2900	1.07	26.7
720	4000	4300	4000	1.07	38.5
1200	5000	5500	5600	1.12	47.7
2640	7700	9000	9400	1.17	74.1
5280	11300	14400	15600	1.27	108
9000	16100	22600	21300	1.40	154

Table 4.4: Dependence of molecular weight distribution on sample time for a polymerization initiated by 1,4-bis(bromomethyl)benzene.

ln ($Dp_{n\infty}$-Dp_n) was calculated for a value of $Dp_{n\infty}$ of 155, again this value was selected because it was slightly higher than the degree of polymerization of the final sample. Table 4.5 shows the dependence of ln ($Dp_{n\infty}$-Dp_n) on time. A graph of ln ($Dp_{n\infty}$-Dp_n) against time was plotted, again excluding the final datum point. From the intercept of this graph the value of $Dp_{n\infty}$ was estimated and compared to that used in the calculation of ln ($Dp_{n\infty}$-Dp_n).

Time/s	ln(155-Dpn)
360	4.9
720	4.8
1200	4.7
2640	4.4
5280	3.8
9000	-1.8

Table 4.5: Dependence of ln ($Dp_{n\infty}$-Dp_n) on time.

Figure 4.3 shows the plot of ln ($Dp_{n\infty}$-Dp_n) against time for the polymer samples from this reaction. The graph shows a straight line relationship between ln ($Dp_{n\infty}$-Dp_n) and the sampling time. Comparing the values of $Dp_{n\infty}$ used in the calculation of ln ($Dp_{n\infty}$-Dp_n) of 155 and that estimated from the intercept of figure 4.3 of 137, it can be seen that there is a noticeable difference between the two values. There is also a significant difference between these values of $Dp_{n\infty}$ and the theoretical value of 115. This discrepancy may be due to the increase in the molecular weight distribution as the reaction progresses. From this plot the apparent rate constant was estimated to be 2.0 * 10^{-4} s^{-1}.

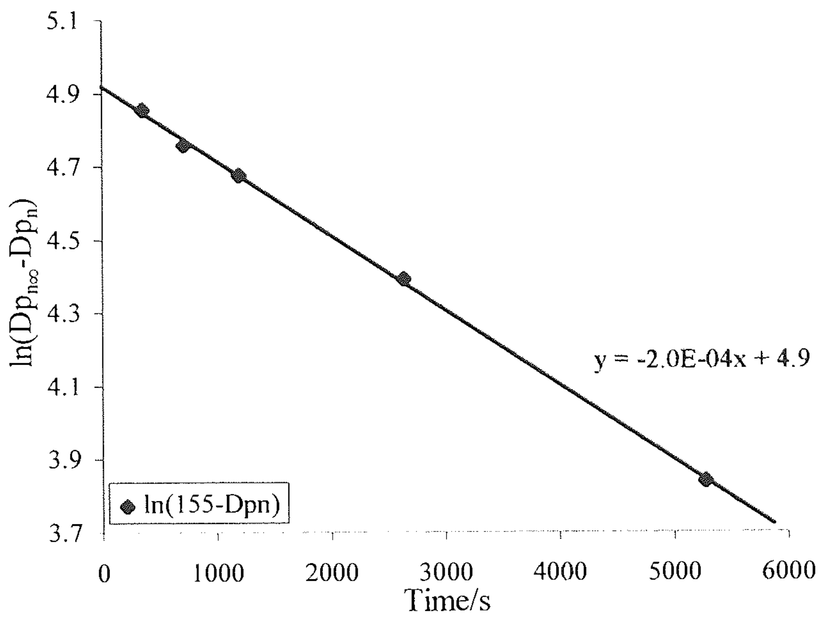


Figure 4.3: Plot of ln ($Dp_{n\infty}$-Dp_n) versus time.

Since the monomer conversion was not known experiments were conducted to determine whether the polymerization was complete or not after the reaction time used in the previous experiments, 4 hours. Reactions were carried out as described in section 2.6.2 with sample taken over a period of 8-9 hours.

A reaction was conducted at 0 °C in dichloromethane solvent with $[\text{styrene}]_0$ = 1.5 mol dm^{-3}, $[\text{1,4-bis(bromomethyl)benzene}]_0$ = 0.021 mol dm^{-3}, $[\text{tin (IV) chloride}]_0$ = 0.10 mol dm^{-3} and $[Bu_4N^+Cl^-]_0$ = 0.042 mol dm^{-3}. Table 4.6 shows the dependence of molecular weight on sample time for this reaction.

Time/s	M_n	M_w	M_p	Pdi	Dp_n
5625	8300	10400	11700	1.26	79.6
9064	13200	17000	16023	1.29	126
14270	16000	23400	19400	1.46	154
21350	17000	27417	20900	1.62	163
26750	18700	30523	21300	1.63	179
32080	18300	32231	20900	1.76	176
over night	19600	34589	21800	1.77	188

Table 4.6: Dependence of molecular weight distribution on time for reaction over a long time period.

Figure 4.4 shows the size exclusion chromatography traces for this reaction. As the reaction progresses the polymer develops a shoulder on the S.E.C. peak which separates into a bimodal molecular weight distribution. The bimodal molecular weight distribution produced by this experiment may be explained by termination or transfer reactions occurring at only one of the active sites on a growing polymer. This would lead to a mixture of polymer chains that are growing from either one or both potential active sites, which would lead to a bimodal molecular weight distribution. The observed molecular weight distribution may also be explained in terms of the rate of initiation being lower than the rate of propagation for this co-catalyst. If this is the case then it is conceivable that some co-catalyst molecules will initiate polymerization at both the available sites while others will initiate polymerization at only one. This would lead to some polymer chains growing at twice the rate of others, giving rise to the bimodal molecular weight distribution observed. These observations suggest that the polymerization of styrene initiated by 1,4-bis(bromomethyl)benzene/tin (IV) chloride in the presence of tetrabutylammonium chloride is not a living system either due to transfer reactions taking place or a slow rate of initiation.

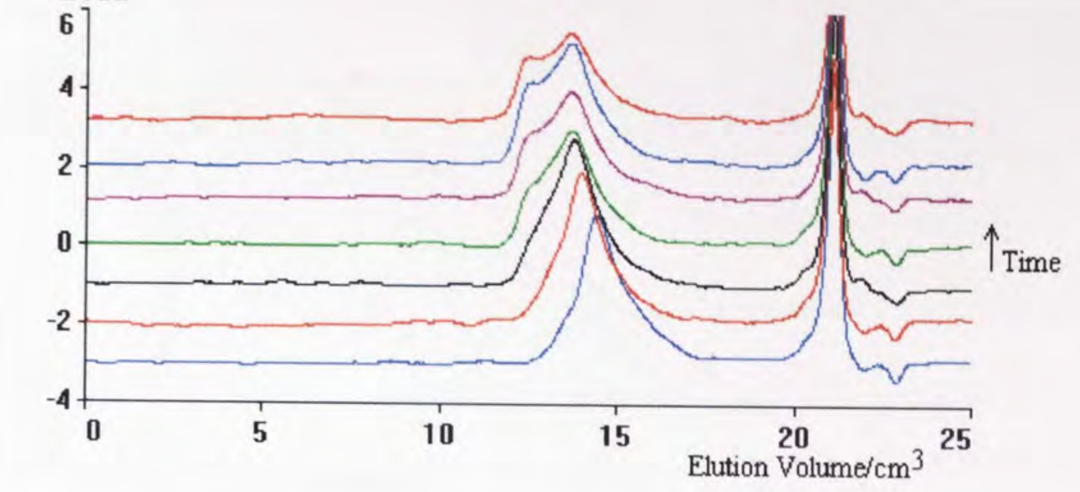


Figure 4.4: Size exclusion chromatograms for polymerization of initiated by 1,4-bis(bromomethyl)benzene at 0 °C.

Adopting the test of living polymerization used previously, if initiation is slow or transfer/termination reactions are present, then a plot of ln ($Dp_{n\infty}$-Dp_n) against time will not give a straight line. However if the rate of propagation is significantly larger than the rate of initiation, then it is possible that, after a short induction period, no further initiation will take place and the monomer is consumed by propagation alone. If this is the case then a plot of ln ($Dp_{n\infty}$-Dp_n) versus time will have a straight line relationship. Table 4.7 shows the dependence of ln ($Dp_{n\infty}$-Dp_n) on sample time for a $Dp_{n\infty}$ of 188 this value was chose since it was that of the final polymer sample.

Time/s	ln(188-Dpn)
5625	4.7
9064	4.1
14270	3.5
21350	3.2
26750	2.2
32080	2.5

Table 4.7: Dependence of ln ($Dp_{n\infty}$-Dp_n) on sample time.

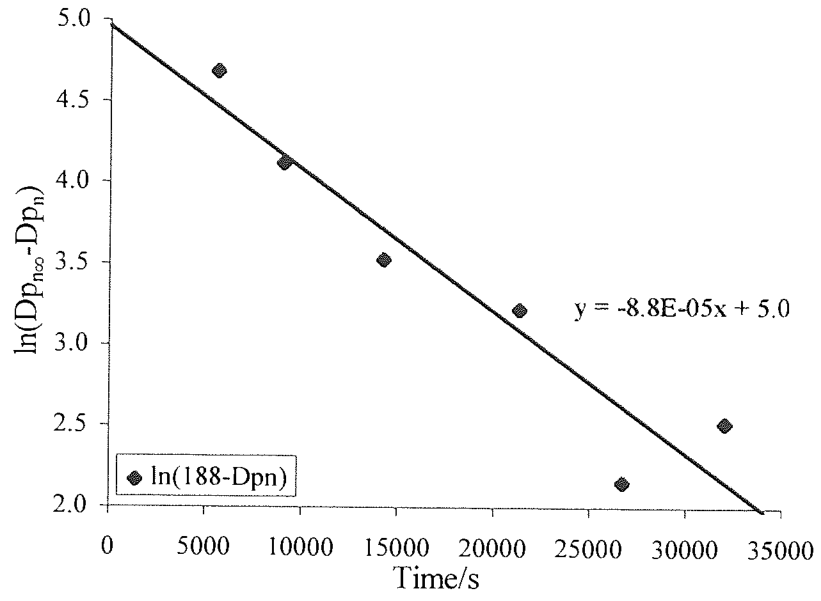


Figure 4.5: Graph of ln ($Dp_{n\infty}$-Dp_n) against time.

Figure 4.5 shows the plots of ln ($Dp_{n\infty}$-Dp_n) versus time. The graph appears to show a straight line relationship between ln ($Dp_{n\infty}$-Dp_n) and time, however there is a large scatter of the data points. Due to the bimodal nature of the molecular weight distribution this plot does not have any real significance, however, it does demonstrate that is possible to get a straight line plot for a non-living polymerization so limiting the usefulness of this method.

4.2.3: Second addition of monomer.

To determine if the polymerization of styrene initiated by 1,4-bis(bromomethyl)benzene has any "living" character, experiments were conducted as described in section 2.4.2 in which a study was made of the effect of adding a second monomer batch to a polymerization once the first had been consumed.

Table 4.8 shows the concentration of reactants for such an experiment. For the second batch of monomer the concentration of co-catalyst is the number of polymer chains assuming each 1,4-bis(bromomethyl)benzene molecule produces only one polymer chain, whether it has an active centre on both chain-ends or only one. To ensure complete conversion of the first batch of monomer, polymerization was carried out overnight, for approximately 18 hours, at 0 °C, before 1 cm^3 of the reaction solution was removed. The second monomer batch was then added and allowed to react for a further 8 hours.

Monomer Batch	$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[Bu_4N^+Cl^-]_0$/ mol dm^{-3}
1st	2.0	0.031	0.099	0.039
2nd	1.2	0.029	0.091	0.036

Table 4.8: Concentration of reactants for experiment with the addition of a second batch of monomer.

Figure 4.6 shows the size exclusion chromatography traces and table 4.9 gives the molecular weight distribution for this experiment. The first monomer batch shows the bimodal molecular weight distribution observed in the previous experiments. The polymer produced after addition of the second batch of monomer shows an increase in the molecular weight and a broadening of the molecular weight distribution with a shoulder on the low molecular weight side of the peak. The general shift of the peak to higher molecular weight may indicate that the polymerization has some living character. However the bimodal distribution observed for the first monomer batch becomes a broad unimodal distribution after polymerization of the second batch of monomer. This may be caused by termination of some of the polymer chains. The shoulder on the low molecular weight end of the S.E.C. peak might be caused by impurities, such as moisture, entering the reaction system as the sample was removed and acting as a co-catalyst initiating further polymerization.

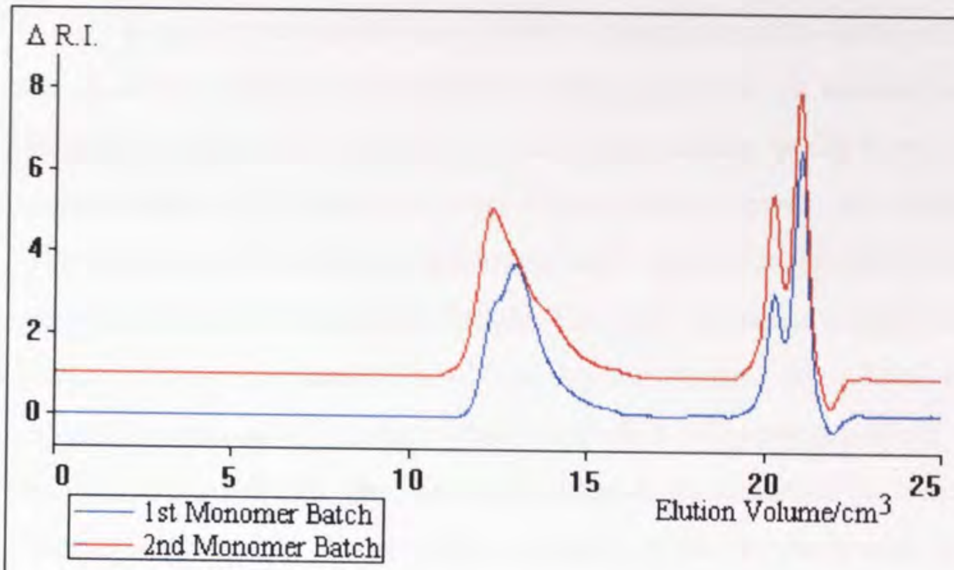


Figure 4.6: S.E.C. trace for experiment with the addition of a second batch of monomer.

Monomer Batch	M_n	M_w	M_p	Pdi
1st	25000	44400	41100	1.77
2nd	25500	58500	97900	2.29

Table 4.9: Molecular weight distribution for a polymerization with the addition of a second monomer batch.

A further experiment was conducted as described above. Table 4.10 shows the concentration of reactants for this polymerization. The first batch of monomer was polymerized for approximately 19 hours at 0 °C, after this time 1.5 cm^3 removed. The second monomer batch was allowed to react for 8 hours.

Monomer Batch	$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[Bu_4N^+Cl^-]_0$/ mol dm^{-3}
1st	2.3	0.045	0.14	0.059
2nd	1.7	0.039	0.13	0.051

Table 4.10: Concentration of reactants for experiment with the addition of a second batch of monomer.

Figure 4.7 shows the size exclusion chromatography traces and table 4.11 gives the molecular weight distribution for this experiment. A bimodal molecular weight distribution was also observed for the polymerization under these conditions. After polymerization of the additional batch of monomer a trimodal distribution was observed. The distribution from the first monomer batch appears unchanged and a third peak has developed at a lower molecular weight. This may be caused termination of the growing chains. Another explanation could be impurities being introduced into the reaction system on removal of a sample which terminated the growing polymer chains. Initiation of new polymer chains may then have occurred by impurities such as moisture or any unreacted co-catalyst. These results indicate that the polymerization of styrene by 1,4-bis(bromomethyl)benzene/tin (IV) chloride in the presence of tetrabutylammonium chloride is unlikely to be living.

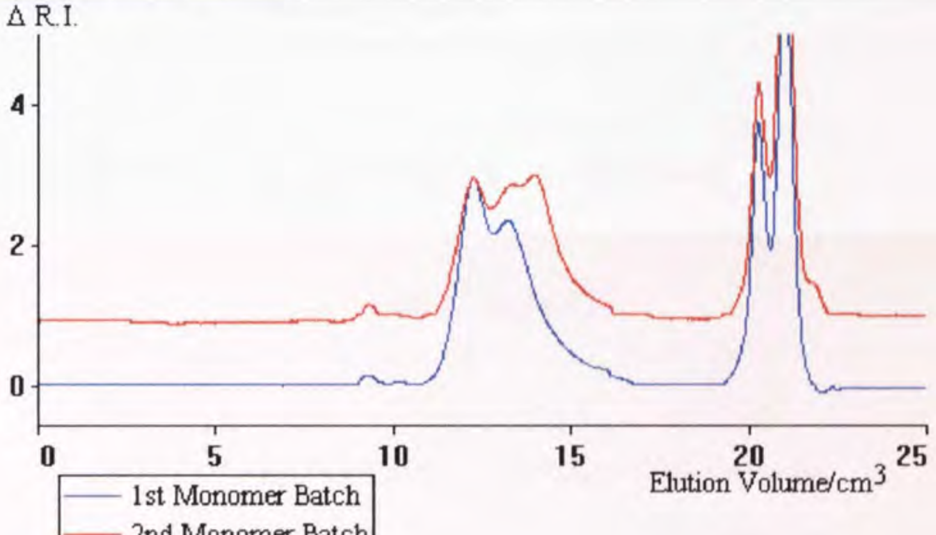


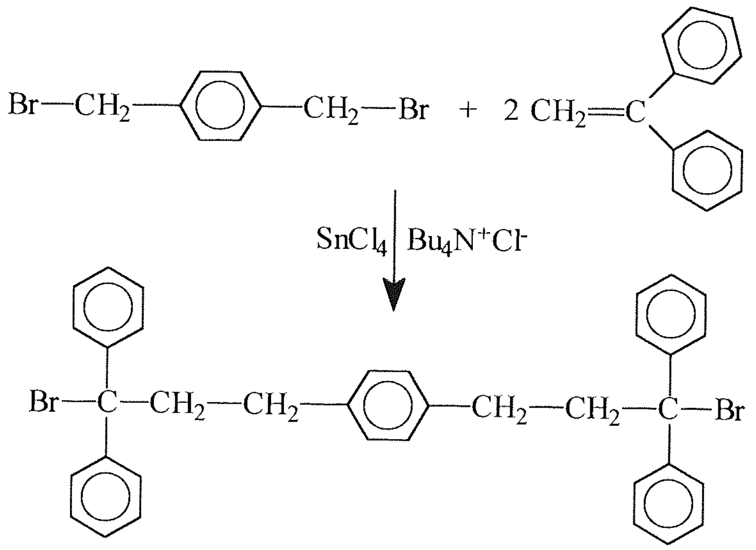
Figure 4.7: Size exclusion chromatograph for an experiment with the addition of a second monomer batch.

Monomer Batch	M_n	M_w	M_p	Pdi
1st	23700	60300	109000	2.54
2nd	17700	44800	16000	2.54

Table 4.11: Molecular weight distribution for polymerization with the addition of a second monomer batch.

4.3: Polymerization of styrene using 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene as a co-catalyst.

To determine if there were any problems of slow initiation associated with using 1,4-bis(bromomethyl)benzene as the co-catalyst and, if so, attempt to overcome them, reactions were conducted using 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene. The 1,1-diphenylethene added to the co-catalyst in a manner similar to the addition of a styrene molecule during initiation in a polymerization reaction. However, because of the steric hindrance of the two phenyl rings attached to the same carbon atom of 1,1-diphenylethene, the addition of a second molecule of 1,1-diphenylethene to a diphenyl chain-end is highly unlikely. Since styrene possesses only one phenyl ring the steric hindrance will be less for its addition and so styrene should be able to add to the diphenyl chain-end. Scheme 4.1 shows the addition of 1,1-diphenylethene to 1,4-bis(bromomethyl)benzene.



Scheme 4.1: Capping of 1,4-bis(bromomethyl)benzene with 1,1-diphenylethene.

4.3.1: Reactions in a side-arm flask.

Reactions were conducted in a side arm flask, similar to those described in section 2.4.1. Solutions of 1,4-bis(bromomethyl)benzene, 1,1-diphenylethene, tetrabutylammonium chloride and tin (IV) chloride were injected into the side arm of the flask by dry syringes using the Schlenk technique described in section 2.1.3. The solutions were then degassed using the freeze-thaw method. Styrene and dichloromethane were distilled into the main bulb of the flask. The apparatus was then placed in a thermostated water bath at 0 °C for 4 hours, to allow the 1,4-bis(bromomethyl)benzene and 1,1-diphenylethene to react, at which point polymerization was initiated by mixing the reactants. Table 4.12 shows the concentration of reactants used for these experiments.

$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	[1,1-DPE]$_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[Bu_4N^+Cl^-]_0$/ mol dm^{-3}
2.1	0.022	0.044	0.10	0.043
2.0	0.019	0.039	0.096	0.038

Table 4.12: Concentration of reactants for polymerizations initiated by 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene.

The polymerizations were terminated by injecting 2ml of degassed methanol into the reaction and the resulting polymers were precipitated by pouring the solutions into an excess of methanol. The products were then examined by size exclusion chromatography. Table 4.13 and figure 4.8 show the S.E.C. results for these experiments.

A comparison of the capped co-catalyst with those for the uncapped 1,4-bis(bromomethyl)benzene, section 4.2.1, the polymers produced using the capped co-catalyst show a narrower molecular weight distribution and higher initiator efficiency. This suggests that the rate of initiation is greater for the 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene than for the uncapped co-catalyst or that the rate of any transfer reactions is slower. Both reactions have number average molecular weights greater than those calculated by equation 3.17. This suggests that not all the co-catalyst molecules are initiating a polymer chain. The first reaction, $[M]_0 = 2.1$ mol dm^{-3}, has a higher monomer conversion and polydispersity than the polymerization with $[M]_0 = 2.0$ mol dm^{-3}. This may indicate that the rate of propagation is still greater than the rate of initiation because of the greater steric hindrance associated with adding a styrene molecule to a chain end containing two phenyl rings as opposed to the hindrance involved with a chain end possessing only one phenyl ring.

$[M]_0$	% conversion	Theoretical M_n	M_n	M_w	M_p	Pdi	E_I
2.1	85	8982	11200	14000	15300	1.25	0.80
2.0	50	5794	7200	8000	8600	1.12	0.80

Table 4.13: Molecular weight distribution for polymerizations with a capped co-catalyst at 0 °C.

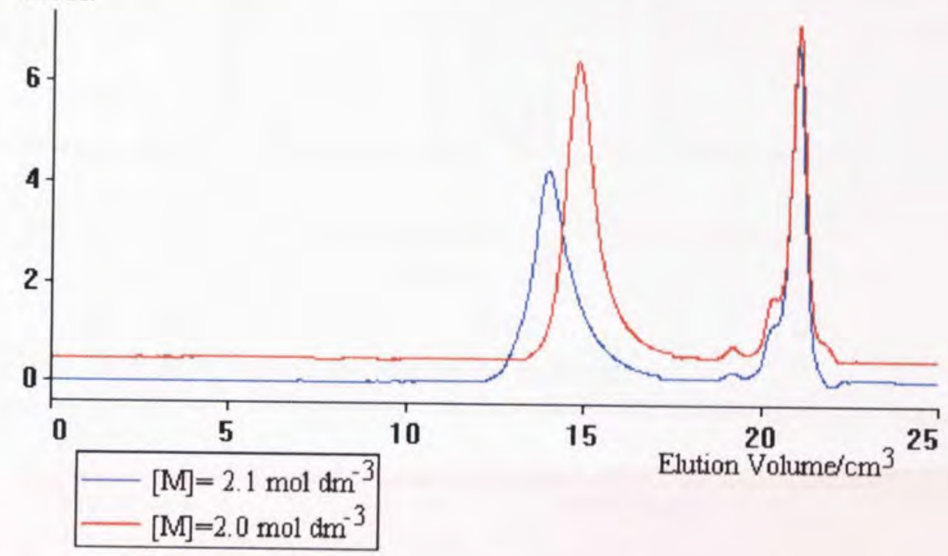


Figure 4.8: Size exclusion chromatograph for polymerizations with a capped co-catalyst at 0 °C.

4.3.2: Analysis of co-catalyst by N.M.R.

A sample of the capped co-catalyst was prepared by injecting solutions of 1,4-bis(bromomethyl)benzene, 1,1-diphenylethene, tetrabutylammonium chloride and tin (IV) chloride into a flask using the Schlenk technique described in section 2.1.3. The solution was then placed in a thermostatted bath at 0°C for 4 hour after which time an excess of methanol was introduced to the vessel. The solvent and methanol were evaporated and the ^{1}H and ^{13}C N.M.R. of the product obtained. Figure 4.9 shows the ^{1}H N.M.R. results for this experiment and table 4.14 details the peaks for the ^{1}H N.M.R. spectrum and their assignment.

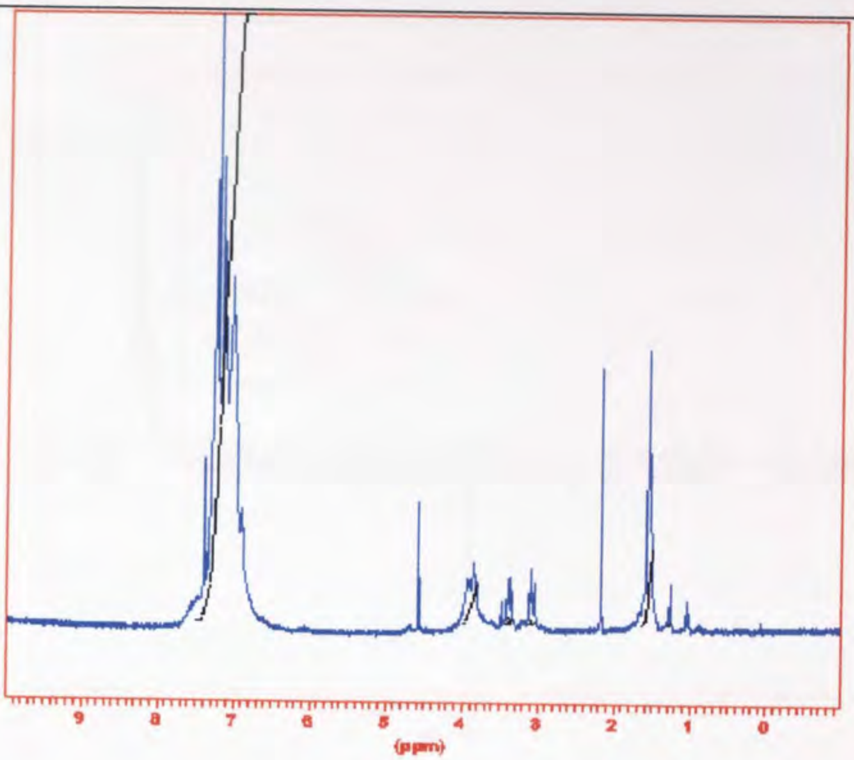


Figure 4.9: ^{1}H N.M.R. spectrum of capped co-catalyst.

δ/ppm	Multiplicity	Assignment
1.3	singlet	$\mathbf{CH_3}$-C(Ph)$_2$Cl from addition of HCl to 1,1-diphenylethene
1.6	singlet	residual proton peak from water in $CDCl_3$
2.2	singlet	
3.1	triplet	Br-(Ph)$_2$C-C$\mathbf{H}_2$-CH$_2$-Ph-CH$_2$-C$\mathbf{H}_2$-C(Ph)$_2$-Br
3.4	triplet	Br-(Ph)$_2$C-CH$_2$-C$\mathbf{H}_2$-Ph-C$\mathbf{H}_2$-CH$_2$-C(Ph)$_2$-Br
3.9	triplet	
4.6	singlet	-C$\mathbf{H}_2$- from 1,4-bis(bromomethyl)benzene
6.8-7.4	multiplet	aromatic

Table 4.11: 1H N.M.R. results for capped co-catalyst.

Figure 4.10 shows the ^{13}C N.M.R. spectrum for the sample of capped co-catalyst. The 3 negative peaks at 77 ppm are from the deuterated chloroform solvent. The series of peaks at 125 - 130 ppm were assigned to the aromatic -**C**H- peaks whilst the aliphatic carbons were not detected using this method.

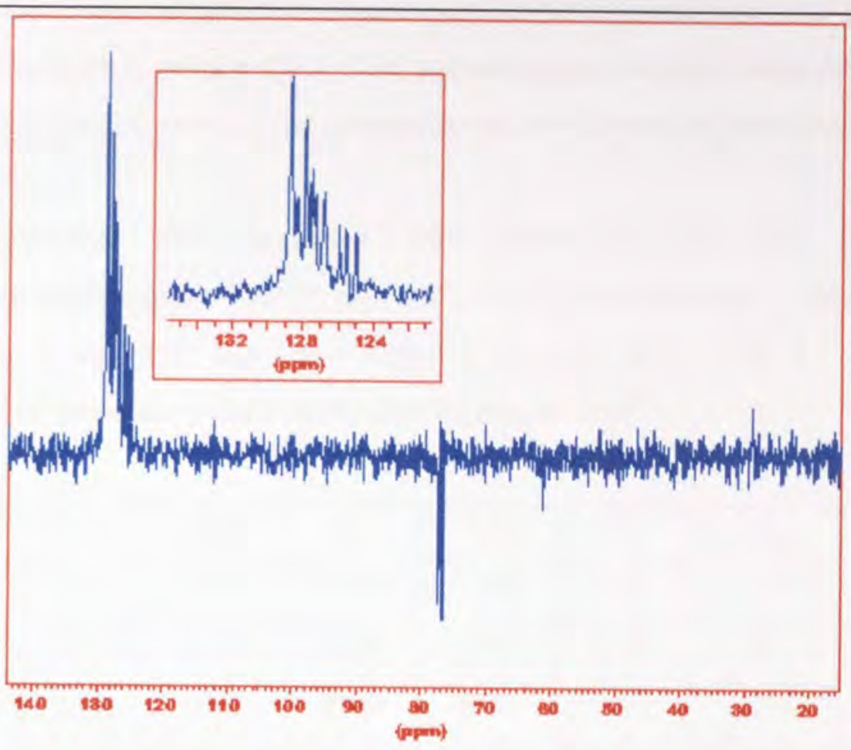


Figure 4.10: ^{13}C **N.M.R. spectrum of capped co-catalyst.**

The results of the N.M.R. studies of the capping of 1,4-bis(bromomethyl)benzene with 1,1-diphenylethene proved inconclusive. The spectra show aromatic rings in various different environments. There is some evidence of the capped product in the ^1H N.M.R.. However the results suggest that the reaction has not gone to complete conversion, with peaks corresponding to the uncapped co-catalyst and the product of addition of HCl, produced by the reaction of $SnCl_4$ with methanol, to 1,1-diphenylethene. These results suggest that the polymerization may be initiated by a mixture of mono- and di-capped co-catalyst and also the uncapped 1,4-bis(bromomethyl)benzene.

4.3.3: Sampling reactions at 0°C.

To study the kinetics of polymerizations initiated by 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene, reactions were conducted as described in section 2.6.2 at 0 °C with the following changes. Solutions of 1,4-bis(bromomethyl)benzene, 1,1-diphenylethene, tetrabutylammonium chloride and tin (IV) chloride were injected in to a small monomer flask (figure 2.5) by dry syringe using the Schlenk technique. This solution was degassed by the freeze thaw method and the reaction mixture placed in a thermostatted bath for 4 hours. A solution of styrene in dichloromethane was prepared in a monomer flask and introduced into the reaction vessel as described in section 2.6.2. The polymerization was then start by adding the solution of catalyst, co-catalyst and ammonium salt to the reaction vessel using the same technique.

A reaction was conducted with [styrene]$_0$= 2.2 mol dm^{-3}, [1,4-bis(bromomethyl)benzene]$_0$= 0.020 mol dm^{-3}, [1,1-diphenylethene]$_0$= 0.042 mol dm^{-3}, [SnCl$_4$]$_0$= 0.10 mol dm^{-3} and [Bu$_4$N$^+$Cl$^-$]$_0$= 0.040 mol dm^{-3}. Table 4.15 shows the dependence of molecular weight distribution on sample time.

Time/s	M_n	M_w	M_p	Pdi	Dp_n
325	1100	1300	1000	1.22	10
870	2100	2400	2300	1.11	20
2705	4300	4700	4600	1.09	41
5400	6400	7100	7300	1.10	62
8940	8300	9700	10400	1.17	80
12620	11400	12700	12800	1.12	109

Table 4.15: Dependence of molecular weight on time for a reaction initiated using a co-catalyst capped with 1,1-diphenylethene.

The polymer samples all show a narrow molecular weight distribution common to many "living" polymerizations. Table 4.16 shows the dependence of ln ($Dp_{n\infty}$-Dp_n) on time for a value of $Dp_{n\infty}$ which was slightly higher than that of the final sample. These data series were plotted against time again omitting the final datum point, as shown in figure 4.11.

Time/s	ln(110-Dpn)
325	4.6
870	4.5
2705	4.2
5400	3.9
8940	3.4

Table 4.16: Dependence of ln ($Dp_{n\infty}$-Dp_n) on time.

The data suggests a straight line relationship. The intercept of the straight line plot of ln ($Dp_{n\infty}$-Dp_n) versus time was used to estimate the value of $Dp_{n\infty}$ as 99. There is reasonable comparison between the value used in the calculation and that estimated from the graph and good agreement between the degree of polymerization of the final sample and that predicted by equation 3.24, 109 and 110 respectively. From this plot the apparent rate constant was estimated as being $1.4 * 10^{-4} s^{-1}$.

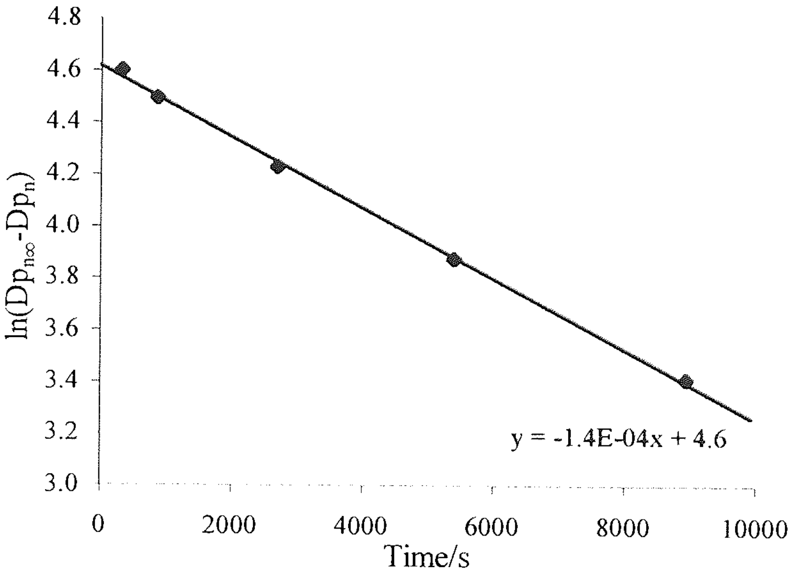


Figure 4.11: Plots of ln ($Dp_{n\infty}$-Dp_n) versus time for a polymerization using 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene as co-catalyst.

To determine if the reaction was complete after 4 hours, a reaction was conducted as described above and samples were taken over a period of 8 hours with the final sample being allowed to react overnight. The concentration of reactants for this experiment were [styrene]$_0$= 2.2 mol dm^{-3}, [1,4-bis(bromomethyl)benzene]$_0$= 0.015 mol dm^{-3}, [1,1-diphenylethene]$_0$= 0.030 mol dm^{-3}, [$SnCl_4$]$_0$= 0.076 mol dm^{-3} and [$Bu_4N^+Cl^-$]$_0$= 0.030 mol dm^{-3}. Table 4.17 shows the relationship between molecular weight and sample time.

Time/s	M_n	M_w	M_p	Pdi	Dp_n
5065	6800	7200	7200	1.06	65
8414	8800	9700	10200	1.10	85
14188	10300	12400	14300	1.21	99
20930	13600	16500	17800	1.22	131
26910	14300	18500	19300	1.29	137
31742	15800	20000	20000	1.26	152
--	18500	24900	21300	1.34	178

Table 4.17: Dependence of molecular weight on time for a reaction initiated using a capped co-catalyst.

The polymer shows an increase in molecular weight throughout the reaction which suggests that the reaction was not complete in the time scale used for the previous experiments. The polymer samples show an increase in polydispersity as the reaction progresses which may be due to slow initiation as discussed in section 4.3.1. or the presence of transfer/termination reactions. The ln ($Dp_{n\infty}$-Dp_n) was calculated for $Dp_{n\infty}$=178, the degree of polymerization for the final sample. Table 4.18 shows the dependence of ln ($Dp_{n\infty}$-Dp_n) on sample time. A graph of ln ($Dp_{n\infty}$-Dp_n) against time was plotted, figure 4.12, and the intercept of the line used to estimate $Dp_{n\infty}$. It has to be appreciated that for the reasons described previously the most reliable data obtained from this technique is that produced early in the conversion

Time/s	ln (178-Dpn)
5065	4.7
8414	4.5
14188	4.4
20930	3.9
26910	3.7
31742	3.3

Table 4.18: Dependence of ln ($Dp_{n\infty}$-Dp_n) on time for a reaction initiated by a capped co-catalyst.

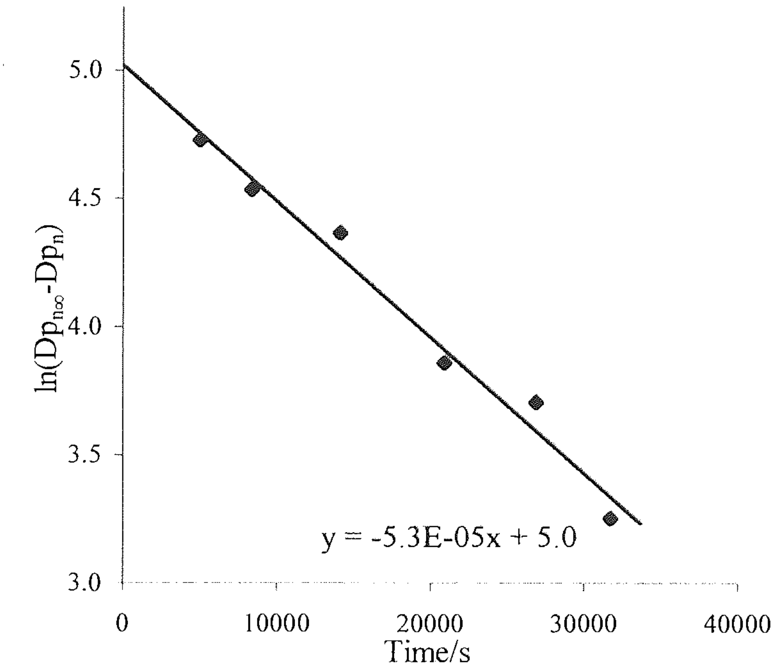


Figure 4.12: Graph of ln ($Dp_{n\infty}$-Dp_n) versus time for a polymerization using a capped co-catalyst for a range of values of $Dp_{n\infty}$.

The plot of ln (Dp_n-$Dp_{n\infty}$) against time shows a straight line relationship. Comparison of the value of $Dp_{n\infty}$ obtained from the final polymer sample, 178, and the value estimated from the intercept of figure 4.12 which was 148 shows a significant difference. This difference may be attributable to either transfer/termination reactions or a slow initiation process causing a change in the concentration of active centres during the reaction. The number average degree of polymerization of the final sample is also higher than the value predicted by the ratio of monomer to co-catalyst which was 147.

4.3.4: Effect of temperature on molecular weight distribution for reactions initiated by 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene.

To determine if the increase in the polydispersity as the polymerizations proceeds was due to transfer reactions, experiments were conducted at decreasing temperatures. Reactions were conducted as described in section 4.3.1 at -15 °C, table 4.19 gives details of the concentration of reactants used in this polymerization. The polymerizations were allowed to proceed for 5 hours after which time the polymers produced by these reactions were examined by size exclusion chromatography. Figure 4.13 shows the S.E.C. traces.

$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	[1,1-DPE]$_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[Bu_4N^+Cl^-]_0$/ mol dm^{-3}
1.8	0.022	0.043	0.11	0.045
0.92	0.023	0.045	0.12	0.047

Table 4.19: Concentration of reactants for polymerizations at -15 °C initiated with 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene.

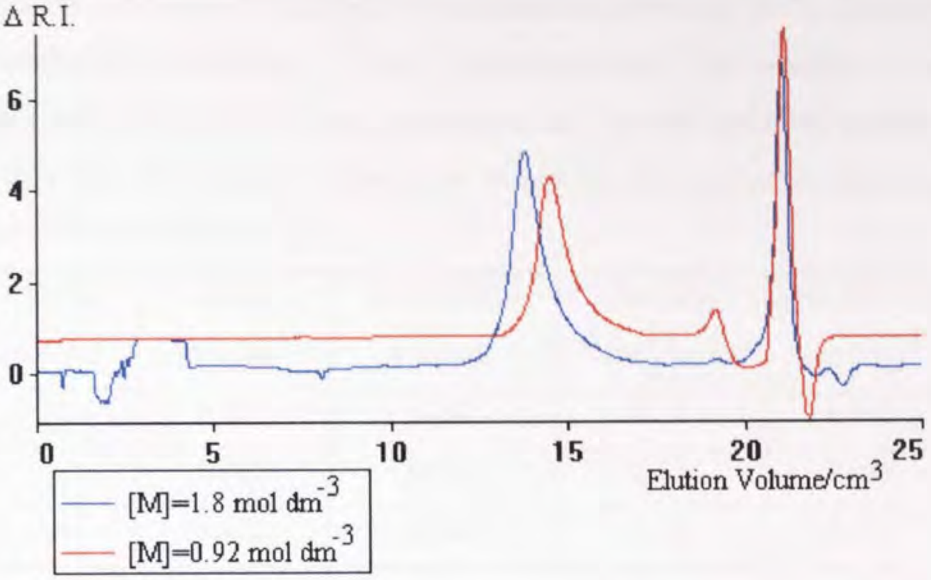


Figure 4.13: S.E.C. traces for polymerizations at -15 °C initiated with 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene.

Table 4.20 shows the monomer conversion, theoretical number average molecular weight based on the ratio of monomer to co-catalyst and the monomer conversion and experimental molecular weight distribution for the reactions at -15 °C. These reactions show similar polydispersities to the polymers produced by reactions at 0 °C, section 4.3.1, however there is a larger discrepancy between the theoretical number average molecular weight and that measured by size exclusion chromatography, shown by the low initiator efficiencies.

This suggests that the decrease in temperature has reduced the rate of initiation compared to the rate of propagation such that not all of the co-catalyst molecules initiate polymerization.

$[M]_0$/mol dm^{-3}	% Conversion	Theoretical M_n	M_n	M_w	M_p	Pdi	E_I
1.8	71	6494	13700	16800	18700	1.23	0.47
0.92	60	2875	8700	10100	11100	1.17	0.33

Table 4.20: Molecular weight distribution for polymerizations initiated with a capped co-catalyst at -15 °C.

Further reactions were carried out as described above at -30 °C. Table 4.27 lists the concentration of reactants for these polymerizations. The reaction at an initial monomer concentration of 1.2 was polymerized for 5 hours, while the other reactions were polymerized for 8 hours. Figure 4.14 shows the size exclusion chromatography results for these experiments

$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	[1,1-DPE]$_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[Bu_4N^+Cl^-]_0$/ mol dm^{-3}
1.2	0.020	0.042	0.11	0.042
1.3	0.022	0.044	0.11	0.043
0.48	0.022	0.044	0.10	0.044

Table 4.21: Concentration of reactants for polymerizations at -30 °C initiated with 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene.

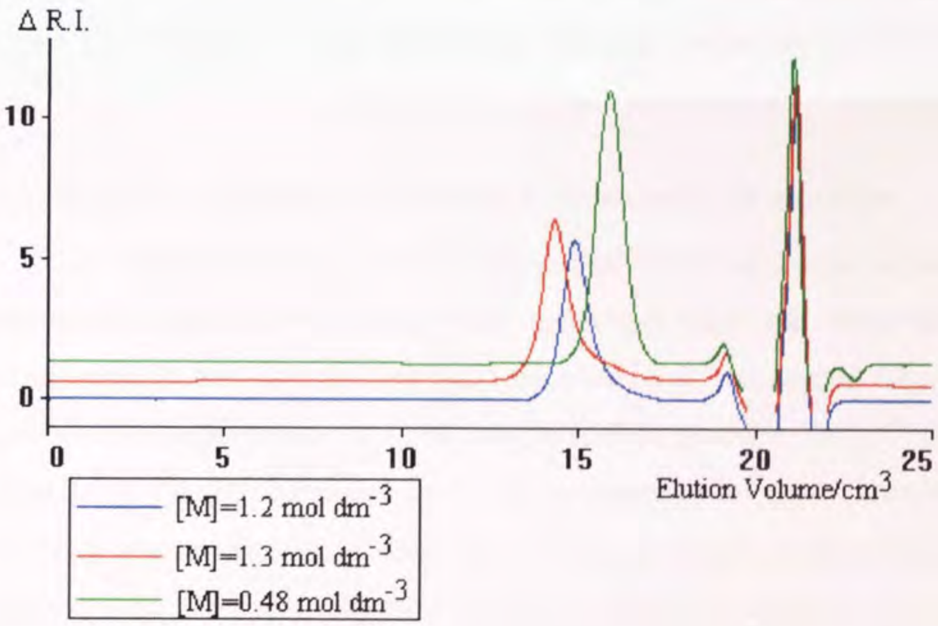


Figure 4.14: S.E.C. traces polymerizations at -30 °C initiated with 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene.

Table 4.22 shoes how the monomer conversion, the observed molecular weights and molecular weight distributions and theoretical number average molecular weight compare for polymerizations initiated by a capped co-catalyst at -30 °C. All experiments show a relatively low monomer conversion, which indicates that the rate of reaction is slower than for reactions at higher temperature and the polymers have number average molecular weights significantly higher than expected with initiator efficiencies similar to those for reactions at -15 °C. These two facts suggest the apparent rate constants are low and that a fraction of the co-catalyst molecules initiate polymerization because only high molecular weight polymers with narrow molecular weight distributions are obtained.

$[M]_0$/ mol dm^{-3}	% Conversion	Theoretical M_n	M_n	M_w	M_p	Pdi	E_I
1.2	34	2337	7400	8200	8600	1.11	0.38
1.3	59	4256	10200	11800	12700	1.15	0.42
0.48	57	1920	4300	4600	4400	1.06	0.45

Table 4.22: Molecular weight distribution for polymerization at -30 °C.

4.3.5: Reactions involving the addition of second batch of monomer.

To determine the "living" nature of the polymerization of styrene initiated by 1,4-bis(bromomethyl)benzene experiments were conducted study the effect of adding a second monomer batch once the first had been consumed. The capped co-catalyst was prepared as describe in section 4.3.1 and polymerizations conducted at 0 °C as described in section 2.4.2. The first monomer batch was polymerized for approximately 18 hours (overnight) to ensure complete conversion after a small sample of the reaction solution had been removed the second monomer batch was added and allowed to polymerize for 6 hours. Table 4.23 shows the concentration of reactants for this experiment.

Monomer Batch	$[M]_0$ / mol dm^{-3}	$[I]_0$ / mol dm^{-3}	$[1,1\text{-DPE}]_0$ / mol dm^{-3}	$[SnCl_4]_0$ / mol dm^{-3}	$[Bu_4N^+Cl^-]_0$ / mol dm^{-3}
1st	1.9	0.017	0.034	0.086	0.034
2nd	1.1	0.016	N/A	0.075	0.030

Table 4.23: Concentration of reactants for experiment with the addition of a second batch of monomer initiated by 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethene.

The polymers were examined using size exclusion chromatography, Table 4.24 shows the molecular weight distributions for these reactions. The first polymer sample has a bimodal molecular weight distribution, see figure 4.15. This may be due to some of the co-catalyst molecules initiating polymerization at both active sites while others only initiate polymer chains that have only growing chain end. After addition of the second batch of monomer the bimodal molecular weight distribution from the first part of this experiment has increased in molecular weight, which indicates the polymerization possesses some "living" character. A third peak is present in the S.E.C. of the second polymer sample. This might be caused by impurities such as moisture entering the reaction as the first sample was removed and initiating polymerization. Alternatively unreacted co-catalyst may initiated polymerization when the second batch of monomer was added.

Monomer Batch	Theoretical M_n	M_n	M_w	M_p	Pdi
1st	12266	14300	19200	15500	1.35
2nd	19427	12500	21800	24600	1.74

Table 4.24: Molecular weight distribution for polymerization initiated by a capped co-catalyst with the addition of a second monomer batch.

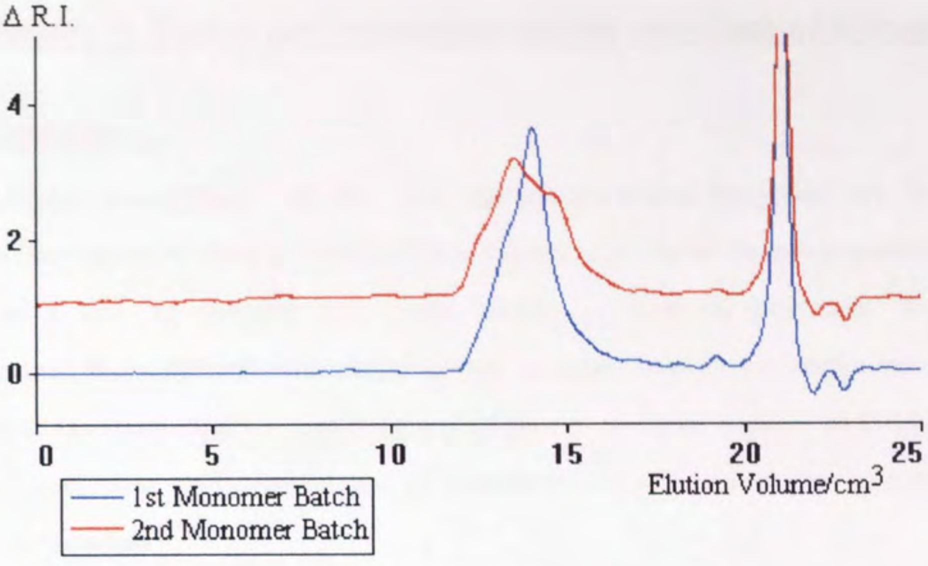


Figure 4.15: Size exclusion chromatography trace for polymerization initiated by a capped co-catalyst with the addition of a second monomer batch.

Chapter 5: Homo- and co-polymerization reactions with oxetane.

5.1: Introduction.

Block co-polymers of the type styrene-*b*-oxetane-*b*-styrene are of interest because they could be used as thermoplastic elastomers. These materials contain an inner block of a low T_g polymer and outer blocks of high T_g polymers. At ambient temperatures thermoplastic elastomers behave as cross-linked elastomeric materials, but at elevated temperatures they can flow and behave in a similar manner to thermoplastics. Oxetane, and other cyclic ethers, are of interest because they can also be converted to energetic materials.(126)

Previous work has shown super acids, such as concentrated sulfuric, fluorosulfonic or trifluoromethane sulfonic acid(127), to be effective initiators for the polymerization of cyclic ethers. Other initiators that have been used include Lewis acids(128), for example BF_3, BF_3OEt_2, $SnCl_4$ or PF_5, in conjunction with a co-catalyst such as H_2O, ROH, $MeCO_2H$ or HBr, and oxonium ions for example $R_3O^+[SbF_6]^-$.(129)

5.2: Homopolymerization of oxetane by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride.

Experiments were conducted to determine whether oxetane could be polymerized using the initiating system 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride. Reactions were carried out as described in section 2.4.1 with dichloromethane as the solvent at -15 °C. The polymerizations were continued for 4 hours. Table 5.1 shows the concentration of reactants for these experiments.

$[M]_0$/ mol dm^{-3}	[1-PhECl]$_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	[TBAC]$_0$/ mol dm^{-3}	$[M]_0$/ [1-PhECl]$_0$
1.0	0.046	0.11	0.047	21.7
1.0	0.020	0.10	0.042	50.0
0.92	0.011	0.10	0.041	83.6
0.74	0.0051	0.094	0.038	145

Table 5.1: Concentration of reactants for the polymerization of oxetane by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride.

When the catalyst was added to the reaction solution fumes were evolved. The reactions were terminated by the addition of 5 ml of degassed methanol. The polymers produced in these experiments were soluble in methanol and so the polymer was recovered by allowing the solvent and unused monomer to evaporate overnight before the viscous liquid remaining was dried in a vacuum oven at 80 °C for 24 hours.

Since the polymers were viscous liquids removing all the solvent and methanol was difficult. This meant determination of the monomer conversion was difficult. The polymers produced were analysed using size exclusion chromatography, figure 5.1 shows the S.E.C. results.

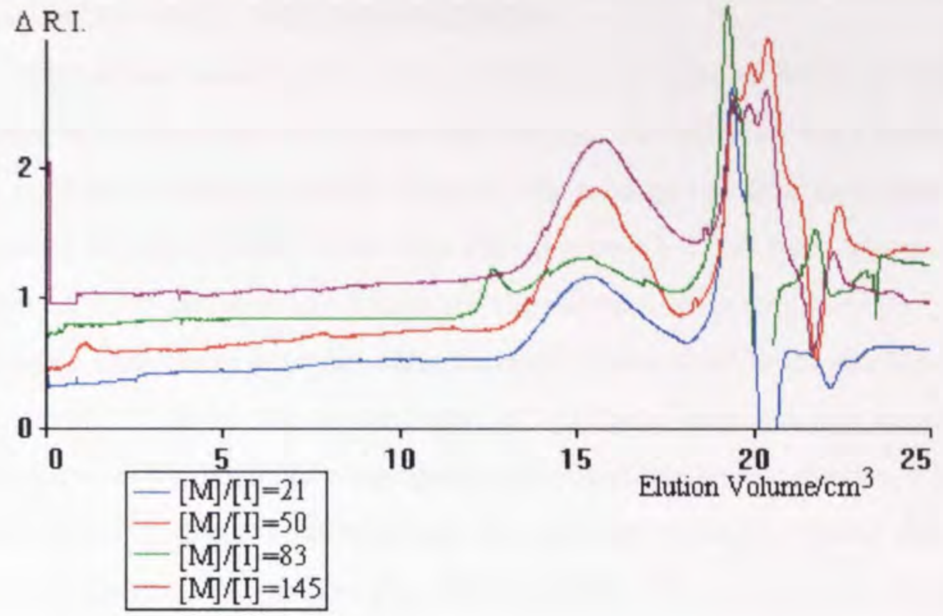


Figure 5.1: S.E.C. results for the polymerization of oxetane.

Table 5.2 shows the dependence of molecular weight distribution on the ratio of monomer to co-catalyst. There does not appear to be any correlation between the ratio of monomer to co-catalyst. This indicates that the polymerization is a non-living reaction with transfer/termination reactions taking place or the macrocyclic compounds being formed. The fumes evolved may indicate that moisture was present in the monomer solution which could initiate polymerization, or there was reaction between the tin (IV) chloride and oxetane. The molecular weight distribution of the polymers is relatively narrow, with polydispersities of 1.2-1.3.

$[M]_0/[1\text{-PhECl}]_0$	% conversion	M_n	M_w	M_p	Pdi
21.7	71	3800	5000	4300	1.33
50.0	60	3700	4700	4100	1.26
83.6	66	4100	5200	4500	1.25
145	19	3300	4200	3600	1.28

Table 5.2: Dependence of molecular weight distribution on the ratio of oxetane to 1-chloro-1-phenylethane.

5.3: Co-polymerization of styrene and oxetane.

Experiments were carried out as described in section 2.4.2 to designed to synthesise block copolymers of styrene and oxetane. The reactions were conducted at -15 °C in dichloromethane solvent. Styrene was used as the first monomer and was polymerized for 4 hours after which time a small sample (~2 ml) was removed. Oxetane was then added to the reaction solution and the polymerization continued for a further 4 hours. Again fumes were observed when the oxetane was added to the reaction mixture.

Table 5.3 shows the concentration of reactants for a reaction carried out as described above. The $[I]_0$ is the concentration of co-catalyst for the reaction, which is the concentration of 1-chloro-1-phenylethane, the polystyryl cation produced then initiated the polymerization of the oxetane $[I]_0$ polymer chains. The reaction was terminated by the addition of 2 cm^3 of degassed methanol and the polymers recovered by precipitating the in an excess of methanol.

Monomer Batch	$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[TBAC]_0$/ mol dm^{-3}
Styrene	1.0	0.04	0.04	0.10
Oxetane	0.90	0.038	0.038	0.094

Table 5.3: Concentration of reactants for the co-polymerization of styrene and oxetane.

The polymers produced in this reaction were examined by size exclusion chromatography using two detector systems, the differential refractometer used to analyse the previous polymers and a variable wavelength ultraviolet detector set at 254 nm. The two detectors were used to estimate the relative quantities of the two monomers incorporated into the polymers since only styrene has a chromophore at the wavelength used. Table 5.4 shows the molecular weights for the polymers produced after each part of the reaction. The data for the monomer batch labelled "oxetane" refers to the polymer recovered after the addition of oxetane to the styrene polymerization.

Monomer Batch	M_n	M_w	M_p	Pdi	Area R.I./ Area U.V.
Styrene	2600	3000	2600	1.14	0.135
Oxetane	2600	3000	2600	1.14	0.133

Table 5.4: Molecular weight distribution for co-polymerization of styrene and oxetane.

There is no increase in molecular weight after the addition of the oxetane and the ratio of the areas of the peaks from the refractive index and ultraviolet detectors is the same, figure 5.2 shows the S.E.C. results from the differential refractometer for this experiment. This indicates that no polymerization of oxetane has taken place. This may be due to impurities entering the polymerization when the sample was removed. Another possible reason for no co-polymer being produced is that the oxonium ion produced by the addition of an oxetane molecule to the polystyrene chain is too stable, see scheme 5.1, to propagate or the styryl cation is to stable to attack oxetane.

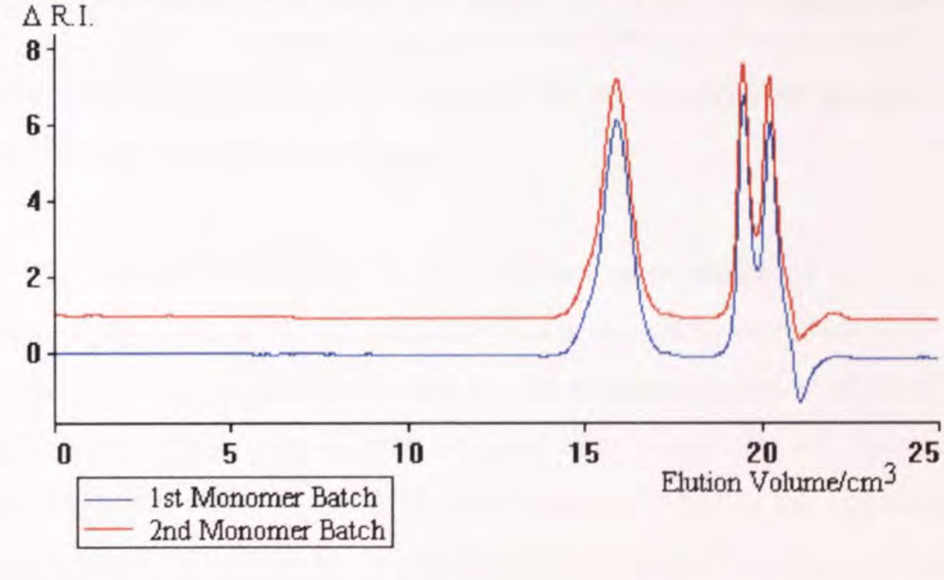
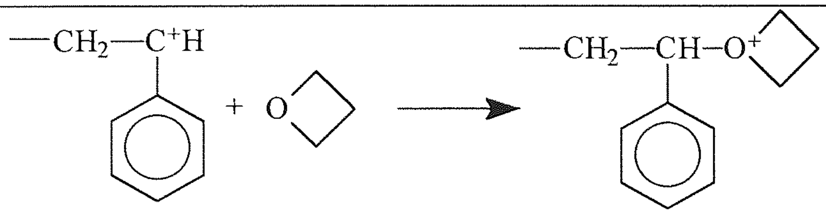


Figure 5.2: Size exclusion chromatography results for the co-polymerization of styrene and oxetane.



Scheme 5.1: Formation of oxonium ion in the polymerization of oxetane initiated by styryl cation.

A second experiment was conducted as described above, table 5.5 shows the concentration of reactants for this experiment. As for the previous experiments fumes were evolved as the oxetane was added to the reaction mixture. The polymer was recovered by precipitation in methanol. After the solid polymer had been removed by filtration the solvent and methanol was allowed to evaporate overnight, yielding a viscous liquid which was then dried in a vacuum oven.

Monomer batch	$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[TBAC]_0$/ mol dm^{-3}
Styrene	0.83	0.038	0.097	0.039
Oxetane	1.0	0.035	0.091	0.036

Table 5.5: Concentration of reactants for an experiment involving the co-polymerization of styrene and oxetane.

The polymers produced by this reaction were examined by size exclusion chromatography using both the refractive index and ultraviolet detectors. Table 5.6 shows the molecular weight distribution for the polymers produced by each section of the reaction and of the viscous liquid obtained from evaporating off the methanol and solvent. Again the monomer batch labelled "oxetane" refers to the polymer recovered after the addition of oxetane to the styrene polymerization. The "viscous liquid" results are for the product recovered after evaporation of the solvent and methanol.

Polymer sample	M_n	M_w	M_p	Pdi	Area R.I./ Area U.V.
Styrene	2300	2700	2300	1.16	0.126
Oxetane	2300	2600	2300	1.15	0.130
Viscous Liquid	3800	6400	6200	1.67	1.17

Table 5.6: Molecular weight distribution for polymers produced by an attempted co-polymerization of styrene and oxetane.

Figure 5.3 shows the size exclusion chromatograms for the polymers precipitated in methanol. As with the previous experiment there in no change in the polymer upon the addition of the oxetane monomer, with the peaks having the same ratio of peak areas from the refractive index and ultraviolet detectors. However the S.E.C. traces for the liquid polymer, figure 5.4, have a much higher ratio of areas along with a broader molecular weight distribution. This data along with the liquid nature of the polymer suggests that it was oxetane homopolymer. This homo-polymerization was most probably initiated by water which entered the reaction when a sample of the solution was removed.

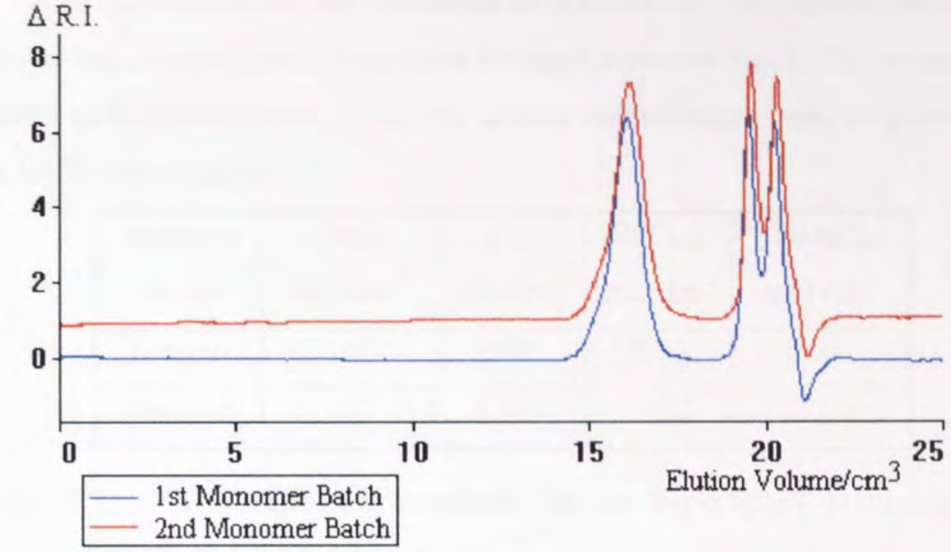


Figure 5.3: S.E.C. for polymers produced by an attempted block co-polymerization of styrene and oxetane.

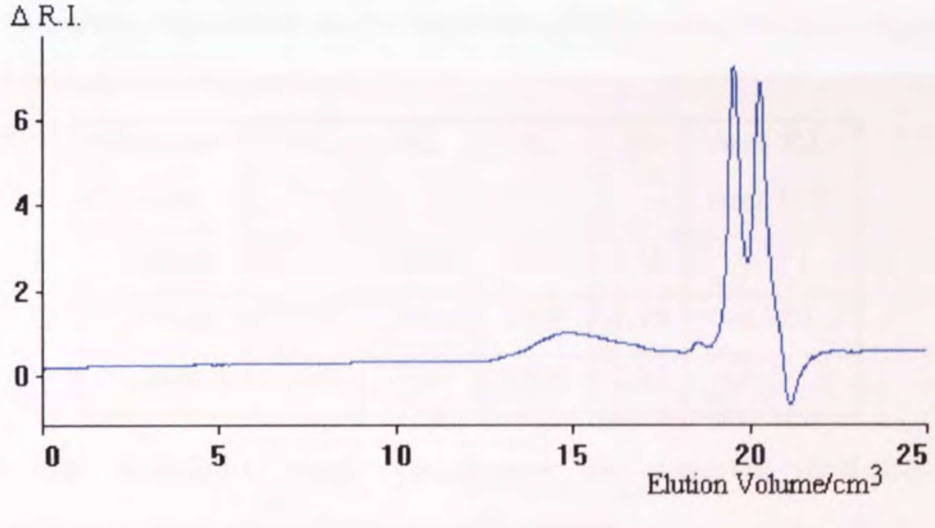


Figure 5.4: S.E.C. of oxetane homopolymer produced during a co-polymerization of styrene and oxetane.

A further experiment was conducted as described for the previous reaction, table 5.7 shows the concentration of reactants for each monomer batch. The polymers were recovered as described above. Again the solvent and methanol were evaporated off to give a highly viscous liquid.

Monomer batch	$[M]_0$/ mol dm^{-3}	$[I]_0$/ mol dm^{-3}	$[SnCl_4]_0$/ mol dm^{-3}	$[TBAC]_0$/ mol dm^{-3}
Styrene	0.65	0.40	0.10	0.041
Oxetane	1.2	0.037	0.092	0.038

Table 5.7: Concentration of reactants for an experiment involving the co-polymerization of styrene and oxetane.

Table 5.8 shows the molecular weight distributions of the polymers produced in this experiment. As with the previous attempts at co-polymerization the was no increase in molecular weight observed for the styrene containing polymer. Oxetane homopolymer was also observed. Figures 5.5 and 5.6 show the size exclusion chromatographs for the polymers produced in this reaction.

Monomer batch	M_n	M_w	M_p	Pdi	Area R.I./ Area U.V.
Styrene	1700	1900	1600	1.15	0.121
Oxetane	1700	1900	1600	1.15	0.120
Liquid	3300	7400	9500	2.22	

Table 5.8: Molecular weight distribution for polymers produced by an attempted co-polymerization of styrene and oxetane.

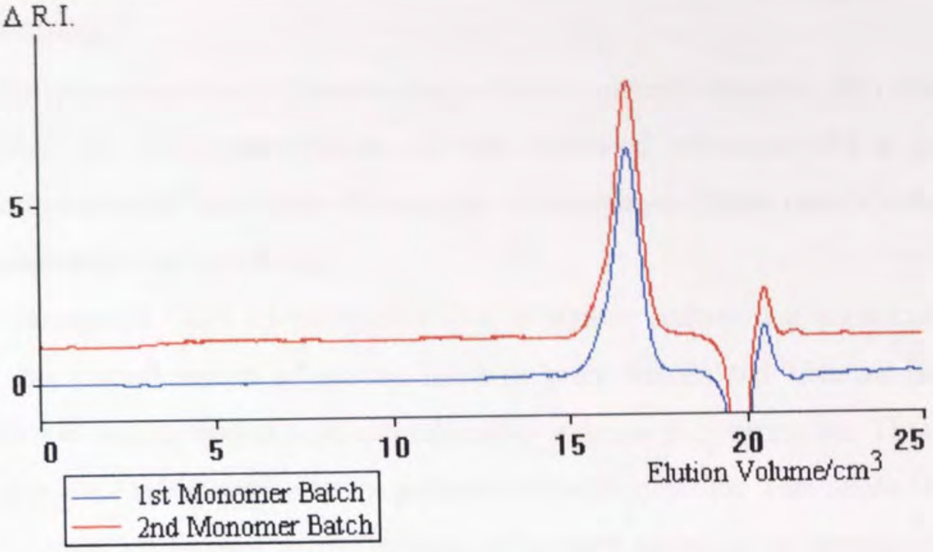


Figure 5.5: S.E.C. for polymers produced by an attempted block co-polymerization of styrene and oxetane.

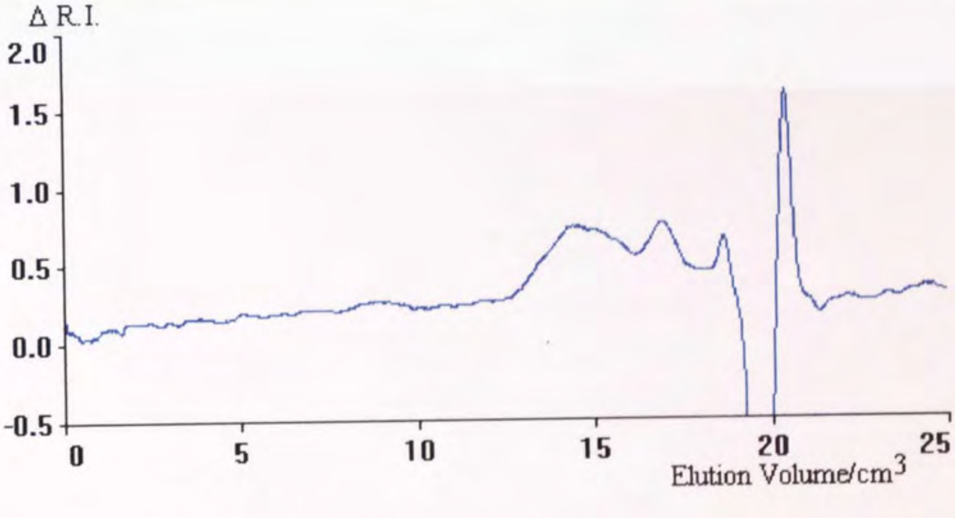


Figure 5.6: S.E.C. of oxetane homopolymer produced during a co-polymerization of styrene and oxetane.

5.4: Discussion.

The polymerization of oxetane by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride produced polymers with a molecular weight independent of the ration of monomer to co-catalyst. These results indicate that the polymerization was not living.

Attempts at block co-polymerizations of styrene and oxetane produced no co-polymer, but a small amount of oxetane homo polymer was formed. Oxetane has a high ring strain and basicity and as such should readily undergo polymerization. These results suggest that the hindrance to oxetane polymerization is initiation. This might be caused by the oxonium ion formed by the addition of a styryl cation to an oxetane molecule being to stable to initiate polymerization. Alternatively the problem may be that the styryl cation is to stable to attack the oxetane, this is conceivable if propagation in this system is by close contact ion pairs as suggested by Higashimura and co-workers(119). A third possibility is that there is a reaction between the oxetane and the catalyst which initiates polymerization.

Chapter 6: Conclusions and further work.

6.1: Conclusions.

The work presented in this thesis has investigated the kinetics and the molecular weight distributions of 'living' polymerizations of styrene. The kinetics of polymerizations were studied at 25 °C using dilatometry. It is appreciated that the density of polystyrene is not constant over the initial range of conversion. However, the error introduced by this is likely to be within the accuracy of dilatometry because (i) the linearity of the $\ln([M]_0/[M])$ plot extends over a long time period when such effects are negligible and (ii) for the available data (1.04 -1.065 g cm^{-1}) there is an error of less than 3% for such density measurements. The polymerization of styrene initiated by 1-chloro-1-phenylethane in the presence of tetrabutylammonium chloride was found to have a first order rate dependence on the concentration of monomer and the initial concentration co-catalyst. Results indicated that the apparent rate constant had either a second order dependence on the initial concentration or a first order dependence on the difference between the initial concentrations of catalyst and ammonium salt. The reaction was found to have a complex order with respect to the concentration of tetrabutylammonium chloride. The first order kinetics with respect to the monomer and co-catalyst are in agreement with the results reported by Matyjaszewski and co-workers(121) who also obtained similar results for the dependence of the rate of polymerization on. the concentration of tetrabutylammonium chloride. However, they report a simple first order dependence of the rate on the concentration of tin (IV) chloride.

In section 3.2.5.1 an equation was derived for the rate of polymerization based on a living polymerization with propagation taking place by ion pairs and free ions in equilibrium with a dormant covalent species. This was similar to the theoretical approach used by Kennedy and co-workers(122) in their studies of the polymerization of isobutylene initiated by 2-chloro-2,4,4-trimethylpentane/$TiCl_4$ in the presence of $Bu_4N^+Cl^-$. This equation explained the observed orders of reaction. However, the plot of $\{k_{app}/([SnCl_4]_0-[Bu_4N^+Cl^-]_0)\}$ against $\{1/[Bu_4N^+Cl^-]_0\}$ which was expected to be linear did not show this relationship. This relationship results from the fraction of propagation attributable to free ions which, if this mechanism is correct, should be small. This may be the reason for the large error observed in the plot of $\{k_{app}/([SnCl_4]_0-[Bu_4N^+Cl^-]_0)\}$ against $\{1/[Bu_4N^+Cl^-]_0\}$.

The kinetics of polymerization, involving propagation by a single species in equilibrium with a dormant covalent species, were compared to the Michaelis-Menten model for a competitively inhibited enzyme catalysed reaction$^{(130)}$. Over a range of concentration of tetrabutylammonium chloride of 0.005 mol dm^{-3} to 0.03 mol dm^{-3}, the polymerization followed this behaviour, but above this range the model does not apply. This novel approach fits the model within limits and accuracy of the data.

Molecular weight studies of the products of polymerizations at 25 °C showed a number average molecular weight below that which would be expected for a 'living' polymerization. This discrepancy was shown to be due to transfer reactions taking place at 25 °C and a 'living' polymerization was obtained by conducting the polymerizations at -15 °C.

The presence of transfer or termination reactions at 25 °C my be the reason that the kinetic studies proved inconclusive under these conditions. The presence of transfer reactions may be consistent with the Michaelis-Menten treatment for propagation by a single cationic species. The propagating species will be in an active state for a given time. During this time the active centre may undergo a propagation reaction, a transfer reaction or collapse back to a dormant covalent species. The probability of a transfer reaction occurring will increase with the time a propagating chain spends in the active state and the ratio of $k_t/(k_p+k_t)$.

The living nature of the polymerization at -15 °C initiated by 1-chloro-1-phenylethane was tested by experiments involving the addition of a second batch of monomer once the first had been polymerized. The results showed an increase in the molecular weight indicating the polymerization has some living character. However, a bimodal molecular weight distribution. This may be a result of impurities being introduced into the reaction as a sample was removed and terminating some of the polymer chains. An alternative explanation for these observations may be that transfer or termination reactions are still present but at a low rate such that only some of the growing chains have been terminated by the time the polymerization of the first monomer batch was complete. These results suggest that it is possible to conduct further reaction on the growing polymer chains but the resultant product may be contaminated with styrene homopolymer with uncontrolled end groups.

An equation (5.1) was developed to study the kinetics of a ''living' polymerization, without knowing the monomer conversion, by the increase in the number average degree of polymerization with time.

$$\ln\left\{\overline{Dp}_{n\infty} - \overline{Dp}_{n}\right\} = \ln\left\{\overline{Dp}_{n}\right\} - kt. \qquad 6.1$$

Dilatometry studies were most accurate over long time periods, conversely this method is most accurate during the initial time period. Studies of the polymerization of styrene, initiated by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride, at 0 °C give a straight-line dependence of $\ln\{Dp_{n\infty}\text{-}Dpn\}$ on time suggesting that the polymerization is living.

The polymerization of styrene using 1,4-bis(bromomethyl)benzene as a difunctional co-catalyst has been studied. The polydispersity of the polymers produced increased and molecular weight distribution became bimodal as the polymerization proceeded. These observations may be explained by slow initiation reactions leading to the number of propagating chain ends increasing throughout the polymerization. This slow initiation process could be explained by two reasons; First, if initiation by 1-chloro-1-phenylethane is slow attempts to produce a propagating centre with two positive charges, $^{+}CH_2\text{-}C_6H_4\text{-}CH_2^{+}$, are going to be even more difficult. To get initiation at both the active sites on a co-catalyst molecule, monomer must be added to one site to move the positive charge away from the original phenyl ring before the other can be activated. Second a propagating cation on a polymer chain end will be more stable than a cation on a co-catalyst molecule because of the electron donating effects of the methylene group of the polymer chain. This will make an active centre on a polymer chain more reactive towards polymerization than the co-catalyst. These problems have also been observed in attempts to produce low molecular weight poly(isobutene) by living cationic polymerization using similar initiating systems where only high molecular weight polymers have been obtained(131). Alternatively the bimodal molecular weight distribution may be caused by transfer or termination reaction occurring at only one growing end of some of the polymer chains.

The living character of the polymerization of styrene was tested by adding a further batch of monomer once all the initial monomer had been consumed. However this resulted in very broad, multi-modal, molecular weight distributions. This feature may be due to the slow initiation process described above or transfer reactions terminating the polymer chains. These results indicate that the polymerization of styrene initiated by 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride is not a living polymerization.

Reactions involving capping the 1,4-bis(bromomethyl)benzene with 1,1-diphenylethene prior to the initiation of polymerization were studied. This approach is similar to that used in the polymerization of styrene by butyllithium in hexane solvent where problems of side reactions were solved by seeding the reaction with diphenylethene(56). These polymerizations yielded polymers with narrower molecular weight distributions than those initiated by 1,4-bis(bromomethyl)benzene. This can be explained by a cation on the diphenyl carbon will be more stable than a phenyl carbocation and with the increased separation between the active sites there will not be the problems of initiation occurring at both potential active sites simultaneously. These results are in agreement with the above argument that the broad molecular weight distribution was a result of slow initiation

An increase in the polydispersity with time was still observed. This can be explained by the steric hindrance of the active centre, an incoming monomer will encounter a greater steric hindrance from the two benzene rings present on the co-catalyst than from the single phenyl ring on a growing polymer chain end. This difference in steric hindrance will result in a rate of initiation lower than the rate of propagation. The increased stability of the diphenyl carbocation may also contribute to the lower rate of initiation.

The living nature of the polymerization initiated by 1,4-bis(bromomethyl)benzene capped with 1,1-diphenylethane was investigated by the addition of a second batch of monomer to the polymerization. These experiments showed the polymerization possessed only a small amount of living character however a multi modal molecular weight distribution was obtained.

The method of studying the kinetics described above, equation 6.1, was further tested using polymerizations initiated by both the capped and uncapped 1,4-bis(bromomethyl)benzene. Both series of experiments gave an apparently straight line relationship between $\ln\{Dp_{n\infty}\text{-}Dpn\}$ and time. These results indicate that this method cannot be used to determine the living character of a polymerization. It may still be possible to use the equation to study systems that are known to be living, however, unless the initiator is 100% efficient it is necessary to determine the monomer conversion so that $Dp_{n\infty}$ can be determined.

The polymerization of oxetane was studied using 1-chloro-1-phenylethane/tin (IV) chloride in the presence of tetrabutylammonium chloride as the initiator. These reactions showed the molecular weight to be independent of the ratio of monomer concentration to co-catalyst concentration. These observations may be explained by the polymerization of oxetane being a non-living reaction, as expected, with transfer/termination reactions and the formation of macrocyclic species taking place.

Copolymerization reactions were attempted by first polymerizing styrene and then, upon complete consumption of the styrene, adding oxetane to the reaction. Size exclusion chromatography studies of the polymers showed that no oxetane had been added to the polystyrene chain ends. However a small amount of oxetane homopolymer was produced. The failure to produce any copolymer may be explained by the stability of the oxonium ion formed. The oxetane homopolymer produced may be due to initiation by impurities, such as water, by transfer of a proton from the polystyrene chain end to the oxetane monomer or by reaction of the catalyst with oxetane.

6.2: Further work.

The main area of interest for future work is to use the polymerizations studied to develop a true living polymerization of styrene. Possible methods for achieving this may be to change the Lewis acid to a less active species, such as $TiCl_4$ or $SnBr_4$, or to change the solvent to a less polar material. Both these methods would reduce the concentration of chain ends present in the active state. The reduction of solvent polarity would also alter the position of the active species on the ionisation spectrum to an ion pair centre. Another method for obtaining a living polymerization may be to further reduce the temperature. It would be advantageous to develop an experimental technique for removing samples from a polymerization without impurities such as moisture entering the system, so that initiation or termination caused by these impurities will not affect the polymers produced. Some work has already been conducted in this area using a polymerization vessel with a three way tap to which a syringe may be attached to remove a sample of the polymerization solution without opening the flask.

The synthesis of block copolymers of styrene and oxetane may be achieved using methods other than the sequential addition of monomers. One method would be to use established initiating systems for cyclic ether such as ethanediol/boron trifluoride dietherate to produce poly(oxetane) with terminal hydroxyl groups. The hydroxy-telechelic poly(oxetane) could then be used as a difunctional 'macro-initiator' for the polymerization of styrene. Alternatively the hydroxyl group could be converted to another functional group such as a chloride or ∝-chloroether. An alternative approach to producing block copolymers of styrene and oxetane may be to use a living polymerization to produce telechelic polystyrene which could then be used in a coupling reaction with poly(oxetane). If these reactions proved successful then the formation of copolymers with substituted oxetanes would be of interest.

To produce telechelic polymers of styrene with functional groups on both chain ends and having a controlled molecular weight, investigations should be conducted using difunctional co-catalysts which will have a rate of initiation greater than that of propagation, such as 1,4-bis(2-chloro-2-propyl)benzene (dicumyl chloride).

The kinetics of polymerizations at -15 °C, reactions initiated by difunctional co-catalysts and any reactions involving macroinitiators need to be studied. Another possible area of study of the kinetics of polymerization is to measure the rate constants for the formation of an active species from a dormant polymer chain, propagation, transfer and the collapse of an active centre to a inactive species. This would allow the probability of a propagating species either adding a monomer to the chain, undergoing a transfer reaction or forming a dormant species to be calculated. This information could then be used to control the molecular weight of polymerizations where transfer is present.

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Appendix 1: Dilatometry results.

Results for varying concentration of 1-chloro-1-phenylethane, $[\text{styrene}]_0=0.5$ mol dm^{-3}, $[\text{tin (IV) chloride}]_0=0.05$ mol dm^{-3}, $[\text{tetrabutylammonium chloride}]_0=0.02$ mol dm^{-3}.

[1-PhECl]=0.005		[1-PhECl]=0.010				[1-PhECl]=0.018	
Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$
240	0.06	465	0.18	240	0.08	240	0.12
360	0.08	540	0.24	300	0.13	360	0.19
480	0.11	600	0.27	360	0.16	490	0.26
600	0.14	660	0.29	420	0.19	600	0.32
720	0.17	720	0.32	485	0.21	720	0.37
840	0.20	780	0.34	540	0.23	840	0.43
960	0.23	840	0.36	600	0.25	960	0.49
1080	0.26	900	0.39	660	0.27	1080	0.54
1210	0.29	960	0.41	720	0.29	1200	0.59
1325	0.32	1020	0.43	780	0.32	1320	0.65
1440	0.34	1080	0.46	840	0.34	1440	0.70
1560	0.37	1140	0.48	910	0.36	1560	0.76
1680	0.40	1200	0.50	960	0.38	1680	0.80
1800	0.43	1260	0.52	1020	0.40	1810	0.85
1920	0.46	1325	0.55	1080	0.42	1920	0.91
2040	0.49	1390	0.57	1140	0.44	2040	0.96
2160	0.52	1440	0.59	1200	0.46	2160	1.01
2280	0.55	1500	0.61	1260	0.48	2280	1.06
2400	0.58	1565	0.64	1320	0.50	2400	1.11
2525	0.61	1625	0.66	1380	0.53	2525	1.16
2640	0.64	1680	0.68	1440	0.55	2640	1.20
2760	0.67	1745	0.70	1500	0.57	2760	1.25
2880	0.70	1800	0.72	1560	0.59	2880	1.30
3000	0.73	1860	0.74	1620	0.61	3000	1.35

Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}
3120	0.76	1920	0.77	1680	0.63	3120	1.39
3240	0.79	1980	0.79	1740	0.65	3250	1.44
3360	0.82	2040	0.81	1800	0.67	3360	1.48
3480	0.85	2100	0.83	1860	0.69	3485	1.53
3600	0.91	2160	0.85	1920	0.71	3600	1.57
3720	0.91	2225	0.88	1980	0.73	3720	1.61
3840	0.94	2285	0.90	2040	0.75	3840	1.65
3960	0.97	2340	0.92	2100	0.77	3960	1.69
4080	1.00	2400	0.94	2160	0.79	4080	1.73
4200	1.03	2460	0.97	2220	0.82	4200	1.77
4340	1.06	2520	0.99	2280	0.84	4320	1.81
4440	1.09	2590	1.01	2340	0.86	4440	1.84
4560	1.12	2650	1.04	2400	0.88	4560	1.88
4680	1.15	2710	1.06	2460	0.90	4680	1.92
4800	1.18	2760	1.07	2520	0.92	4800	1.95
4920	1.21	2820	1.09	2580	0.94	4920	1.98
5040	1.24	2880	1.12	2620	0.96		
5160	1.27	2945	1.14	2700	0.98		
5280	1.30	3000	1.16	2760	1.00		
5400	1.33	3060	1.18	2820	1.02		
5700	1.40	3120	1.20	2880	1.04		
6000	1.48	3180	1.22	2940	1.07		
6300	1.55	3240	1.24	3000	1.09		
6600	1.63	3300	1.26	3060	1.11		
6900	1.70	3360	1.28	3120	1.13		
7200	1.78	3420	1.30	3195	1.15		
7500	1.84	3480	1.32	3240	1.17		
7800	1.93	3540	1.33	3300	1.19		

Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}
		3600	1.35	3360	1.21		
		3660	1.37	3420	1.23		
		3720	1.38	3485	1.24		
		3780	1.40	3520	1.28		
		3840	1.42	3600	1.30		
		3900	1.44	3720	1.34		
		3960	1.45	3840	1.38		
		4020	1.47	3960	1.42		
		4080	1.48	4080	1.46		
		4140	1.50	4200	1.51		
		4200	1.51	4320	1.55		
		4260	1.53	4440	1.60		
		4320	1.54	4560	1.64		
		4380	1.56	4685	1.68		
		4440	1.57	4800	1.73		
		4500	1.59	4920	1.76		
		4560	1.60	5040	1.81		
		4620	1.62	5160	1.85		
		4680	1.62	5280	1.89		
		4740	1.64	5400	1.93		
		4810	1.66				
		4860	1.67				
		4920	1.68				
		4980	1.69				

[1-PhECl]=0.018		[1-PhECl]=0.020				[1-PhECl]=0.023	
Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$
195	0.11	280	0.17	240	0.16	250	0.21
240	0.15	340	0.20	300	0.20	300	0.28
300	0.19	400	0.24	360	0.25	360	0.34
360	0.23	460	0.27	420	0.29	420	0.39
420	0.26	520	0.31	480	0.34	480	0.45
480	0.30	580	0.34	540	0.38	540	0.50
540	0.33	640	0.37	600	0.42	600	0.55
600	0.36	700	0.41	660	0.46	660	0.60
660	0.40	760	0.44	720	0.50	720	0.65
720	0.43	820	0.47	780	0.54	780	0.70
780	0.46	880	0.50	840	0.58	840	0.75
840	0.49	940	0.53	900	0.62	900	0.80
900	0.53	1000	0.56	960	0.66	960	0.85
965	0.56	1060	0.59	1020	0.69	1020	0.90
1020	0.59	1120	0.63	1085	0.73	1080	0.95
1080	0.62	1185	0.66	1140	0.77	1140	1.00
1140	0.65	1242	0.69	1200	0.81	1200	1.05
1200	0.68	1300	0.72	1260	0.84	1260	1.10
1260	0.71	1360	0.75	1320	0.88	1320	1.15
1320	0.74	1420	0.78	1380	0.92	1380	1.20
1380	0.76	1485	0.81	1440	0.95	1440	1.25
1440	0.79	1550	0.84	1500	0.99	1500	1.30
1500	0.82	1600	0.87	1560	1.03	1560	1.35
1560	0.85	1660	0.90	1620	1.07	1620	1.40
1620	0.88	1720	0.93	1680	1.10	1680	1.45
1680	0.91	1780	0.96	1740	1.14	1740	1.49
1740	0.93	1840	0.99	1800	1.18	1800	1.53

Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}
1800	0.96	1900	1.02	1865	1.22	1860	1.58
1860	0.99	1960	1.05	1920	1.25	1920	1.62
1920	1.02	2020	1.08	1980	1.29	1980	1.67
1985	1.05	2085	1.11	2040	1.33	2040	1.72
2040	1.08	2145	1.14	2100	1.37	2100	1.77
2100	1.10	2200	1.17	2170	1.41	2160	1.83
2160	1.13	2260	1.20	2220	1.45	2220	1.89
2225	1.16	2320	1.23	2280	1.48	2290	1.95
2280	1.19	2380	1.27	2340	1.52	2340	2.00
2340	1.21	2440	1.29	2400	1.56		
2400	1.24	2500	1.32	2460	1.60		
2520	1.30	2560	1.35	2520	1.64		
2640	1.35	2620	1.38	2580	1.68		
2760	1.40	2680	1.41	2640	1.72		
2880	1.45	2745	1.45	2700	1.76		
3000	1.52	2800	1.48	2760	1.80		
3120	1.55	2860	1.51	2820	1.84		
3240	1.55	2920	1.54	2885	1.89		
3360	1.63	2980	1.57	2940	1.93		
3480	1.67	3045	1.61	3000	1.97		
3600	1.71	3100	1.64				
3900	1.79	3160	1.67				
4200	1.86	3220	1.70				
		3280	1.73				
		3340	1.77				
		3400	1.80				
		3460	1.82				
		3520	1.85				

[1-PhECl]=0.025	
Time/s	$\ln\{[M]_0/[M]\}$
165	0.31
240	0.45
300	0.54
360	0.63
420	0.71
480	0.79
540	0.87
600	0.95
660	1.04
720	1.13
780	1.21
840	1.30
900	1.40
960	1.49
1020	1.59
1080	1.70
1140	1.80
1200	1.92

Results for varying concentration of tin (IV) chloride, [styrene]$_0$=0.5 mol dm^{-3}, [1-chloro-1-phenylethane]$_0$=0.02 mol dm^{-3}, [tetrabutylammonium chloride]$_0$=0.02 mol dm^{-3}.

[$SnCl_4$]=0.03				[$SnCl_4$]=0.05			
Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$
145	0.01	155	0.03	240	0.16	280	0.17
240	0.02	220	0.05	300	0.20	340	0.20
300	0.03	300	0.06	360	0.25	400	0.24
360	0.04	420	0.08	420	0.29	460	0.27
420	0.04	480	0.08	480	0.34	520	0.31
480	0.05	540	0.09	540	0.38	580	0.34
540	0.06	600	0.10	600	0.42	640	0.37
600	0.07	660	0.10	660	0.46	700	0.41
660	0.07	720	0.11	720	0.50	760	0.44
720	0.08	780	0.11	780	0.54	820	0.47
780	0.09	740	0.12	840	0.58	880	0.50
840	0.09	900	0.12	900	0.62	940	0.53
900	0.10	1920	0.20	960	0.66	1000	0.56
1815	0.19	3600	0.30	1020	0.69	1060	0.59
3600	0.31	5580	0.39	1085	0.73	1120	0.63
5400	0.40	11220	0.54	1140	0.77	1185	0.66
11520	0.53	12600	0.56	1200	0.81	1242	0.69
13860	0.54	14400	0.57	1260	0.84	1300	0.72
15100	0.54	15300	0.58	1320	0.88	1360	0.75
		16200	0.58	1380	0.92	1420	0.78
		17100	0.59	1440	0.95	1485	0.81
				1500	0.99	1550	0.84
				1560	1.03	1600	0.87
				1620	1.07	1660	0.90
				1680	1.10	1720	0.93

Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$
				1865	1.22	1900	1.02
				1920	1.25	1960	1.05
				1980	1.29	2020	1.08
				2040	1.33	2085	1.11
				2100	1.37	2145	1.14
				2170	1.41	2200	1.17
				2220	1.45	2260	1.20
				2280	1.48	2320	1.23
				2340	1.52	2380	1.27
				2400	1.56	2440	1.29
				2460	1.60	2500	1.32
				2520	1.64	2560	1.35
				2580	1.68	2620	1.38
				2640	1.72	2680	1.41
				2700	1.76	2745	1.45
				2760	1.80	2800	1.48
				2820	1.84	2860	1.51
				2885	1.89	2920	1.54
				2940	1.93	2980	1.57
				3000	1.97	3045	1.61
						3100	1.64
						3160	1.67
						3220	1.70
						3280	1.73
						3340	1.77
						3400	1.80
						3460	1.82
						3520	1.85

[SnCl4]=0.06						[SnCl4]=0.08	
Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}
420	0.41	240	0.25	240	0.22	180	0.23
480	0.49	300	0.31	300	0.30	240	0.32
540	0.55	360	0.38	360	0.37	300	0.41
600	0.60	420	0.45	420	0.42	360	0.48
660	0.66	480	0.51	480	0.49	420	0.56
720	0.71	540	0.57	540	0.55	485	0.64
780	0.77	600	0.64	600	0.61	540	0.70
840	0.82	660	0.70	720	0.73	600	0.77
900	0.87	720	0.76	840	0.84	660	0.84
960	0.92	780	0.83	960	0.95	720	0.91
1020	0.97	840	0.90	1080	1.07	780	0.98
1080	1.02	900	0.96	1200	1.19	840	1.05
1140	1.08	960	1.03	1320	1.31	900	1.12
1200	1.13	1020	1.10	1440	1.42	960	1.19
1320	1.23	1080	1.17	1560	1.55	1020	1.26
1440	1.34	1140	1.24	1680	1.67	1080	1.34
1560	1.44	1200	1.32	1800	1.80	1200	1.48
1680	1.54	1260	1.39	1935	1.94	1320	1.62
1800	1.65					2100	2.06
1920	1.76						
2040	1.86						
2160	1.97						

[SnCl4]=0.08		[SnCl4]=0.15	
Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$
240	0.31	144	0.57
300	0.45	186	0.81
360	0.55	230	1.04
420	0.64	274	1.27
480	0.72	330	1.60
540	0.80	383	1.98
600	0.88		
660	0.96		
720	1.04		
785	1.13		
840	1.20		
900	1.29		
960	1.37		
1020	1.46		
1080	1.54		
1140	1.63		
1200	1.73		
1260	1.82		
1320	1.91		

Results for varying concentration of tetrabutylammonium chloride, [styrene]$_0$=0.5 mol dm^{-3}, [1-chloro-1-phenylethane]$_0$=0.02 mol dm^{-3}, [tin (IV) chloride]$_0$=0.05 mol dm^{-3}.

$[Bu_4N^+Cl^-]=0.005$				$[Bu_4N^+Cl^-]=0.02$		$[Bu_4N^+Cl^-]=0.03$	
Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}	Time/s	ln{[M]$_0$/[M]}
420	0.36	630	0.38	240	0.16	240	0.14
540	0.48	720	0.45	300	0.20	365	0.22
600	0.53	840	0.54	360	0.25	480	0.29
660	0.59	960	0.63	420	0.29	600	0.36
720	0.64	1085	0.73	480	0.34	720	0.45
780	0.70	1200	0.82	540	0.38	840	0.52
840	0.75	1320	0.91	600	0.42	960	0.58
900	0.80	1440	1.00	660	0.46	1080	0.65
960	0.86	1560	1.09	720	0.50	1200	0.72
1020	0.91	1680	1.18	780	0.54	1320	0.78
1080	0.97	1800	1.27	840	0.58	1440	0.85
1140	1.03	1920	1.36	900	0.62	1560	0.91
1200	1.08	2040	1.45	960	0.66	1680	0.98
1500	1.37	2160	1.54	1020	0.69	1800	1.04
1800	1.67	2280	1.63	1085	0.73	1920	1.11
2100	1.99	2400	1.72	1140	0.77	2040	1.18
		2520	1.80	1200	0.81	2160	1.24
		2640	1.88	1260	0.84	2280	1.31
		2760	1.97	1320	0.88	2400	1.38
				1380	0.92	2520	1.45
				1440	0.95	2640	1.52
				1500	0.99	2760	1.59
				1560	1.03	2880	1.67
				1620	1.07	3010	1.74
				1680	1.10	3120	1.81
				1740	1.14	3240	1.88

Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$
				1865	1.22		
				1920	1.25		
				1980	1.29		
				2040	1.33		
				2100	1.37		
				2170	1.41		
				2220	1.45		
				2280	1.48		
				2340	1.52		
				2400	1.56		
				2460	1.60		
				2520	1.64		
				2580	1.68		
				2640	1.72		
				2700	1.76		
				2760	1.80		
				2820	1.84		
				2885	1.89		
				2940	1.93		
				3000	1.97		

$[Bu_4N^+Cl^-]=0.04$			
Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$
250	0.01	300	0.06
360	0.07	360	0.08
480	0.09	480	0.10
600	0.12	600	0.12
720	0.13	720	0.14
840	0.15	840	0.17
960	0.17	960	0.19
1080	0.19	1080	0.21
1200	0.21	1200	0.23
1320	0.23	1320	0.25
1440	0.24	1455	0.27
1560	0.26	1560	0.28
1680	0.28	1680	0.30
1800	0.29	1800	0.32
2100	0.34	2100	0.36
2400	0.38	2410	0.41
2700	0.42	2700	0.45
3000	0.45	3000	0.49
3300	0.49	3300	0.53
3600	0.53	3600	0.56
4200	0.60	4200	0.64
4800	0.66	4800	0.72
5400	0.73	5400	0.79
6000	0.80	6000	0.86
6600	0.86	6600	0.93
7200	0.93	7200	1.00
7800	0.98		

Time/s	$\ln\{[M]_0/[M]\}$	Time/s	$\ln\{[M]_0/[M]\}$
9000	1.08		
9600	1.14		
10200	1.19		
10800	1.23		
11400	1.28		
12000	1.32		
12600	1.36		
13200	1.40		
13800	1.43		
14400	1.47		
15000	1.49		
15600	1.52		
16200	1.54		
16800	1.56		
17400	1.58		