LIVING CATIONIC POLYMERIZATION OF STYRENE MONOMERS

By

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A thesis submitted for the Degree of Doctor of Philosophy of
Aston University

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TO MY SON, MY HUSBAND AND MY PARENTS.

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ABSTRACT

This thesis describes an experimental investigation of synthesis of polystyrene under various polymerization conditions such as solvent polarity, temperature, initial concentrations of initiator, catalyst, monomer and added salts or co-catalyst, which was achieved using the living cationic polymerization technology in conjunction with gel permeation chromatography (GPC) and NMR spectroscopy.

Polymerizations of styrene were conducted using 1-phenyl ethylchloride (1-PEC) as an initiator and tin tetrachloride ($SnCl_4$) as a catalyst in the presence of tetra-*n*-Butylammonium chloride (nBu$_4$NCl). Effects of solvent polarity varied by mixing dichloromethane (DCM) and less polar cyclohexane (C.hex), temperature, initial concentrations of $SnCl_4$, 1-PEC and nBu$_4$NCl on the polymerizations were examined, and the conditions under which a living polymerization can be obtained were optimised as: $[\text{styrene}]_0 \sim 0.75 - 2$ M; $[\text{1-PEC}]_0 \sim 0.005 - 0.05$ M; $[SnCl_4]_0 \sim 0.05 - 0.4$ M; $[n\text{Bu}_4\text{NCl}]_0 \sim 0.001 - 0.1$ M; DCM/C.hex ~ 50/0 – 20/30 v/v; T ~ 0 to -45°C. Kinetic studies of styrene polymerization using the Omnifit sampling method showed that the number average molecular weight (M_n) of the polymers obtained increased in direct proportion to monomer conversion and agreed well with the theoretical M_n expected from the concentration ratios of monomer to initiator. The linearities of both the $\ln([M]_0/[M])$ vs. time plot and the M_n vs. monomer conversion plot, and the narrow molecular weight distribution (MWD) measured using GPC demonstrated the

livingness of the polymerizations, indicating the absence of irreversible termination and transfer within the lifetimes of the polymerizations. The proposed 'two species' propagation mechanism was found to apply for the styrene polymerization with 1-PEC/$SnCl_4$ in the presence of nBu$_4$NCl.

The further kinetic experiments showed that living styrene polymerizations were achieved using the 1-PEC/$SnCl_4$ initiating system in mixtures of DCM/C.hex 30/20 v/v at -15°C in the presence of various bromide salts, tetra-*n*-butylammonium bromide, tetra-*n*-pentylammonium bromide, tetra-*n*-heptylammonium bromide, and tetra-*n*-octylammonium bromide, respectively. The types of the bromide salts were found to have no significant effect on monomer conversion, M_n, polydispersity and initiation efficiency.

Living polymerizations of styrene were also achieved using titanium tetrachloride ($TiCl_4$) as a catalyst and 1-PEC as an initiator in the presence of a small amount of 2,6-di-*tert*-butylpyridine or pyridine instead of nBu$_4$NCl. GPC analysis showed that the polymers obtained had narrow polydispersities (P.D. < 1.3), and the linearities of both the $\ln([M]_0/[M])$ vs. time plot and the M_n vs. monomer conversion plot demonstrated that the polymerizations are living, when the ratio of DCM and C.hex was less than 40 : 10 and the reaction temperature was not lower than -15°C. The reaction orders relative to $TiCl_4$ and 1-PEC were estimated from the investigations into the rate of polymerization to be 2.56 and 1.0 respectively.

^{1}H and ^{13}C NMR analysis of the resultant polystyrene would suggest the end-functionality of the product polymers is chlorine for all living polymerizations.

Keywords: styrene; halide salts; tin tetrachloride; titanium tetrachloride; pyridine; GPC; NMR.

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CHAPTER 1

INTRODUCTION

Styrene is a readily and commercially available vinyl monomer, which has been utilised in cationic polymerizations. Because of its lack of a strongly electron donating group (substituent), styrene is among the more poorly reactive monomers in cationic polymerizations. When polymerized with conventional cationic initiators, styrene produces an unstable growing carbocation, resulting in chain transfer, termination, and other undesirable side reactions. The cationic polymerization of styrene has been considered to be difficult to control in contrast to its anionic polymerization.

In recent years, living cationic polymerization of monomers has rapidly become more attractive to polymer scientists **[1]**, since they can produce controllable polymers with narrow molecular weight distributions (MWD) and consistent molecular weights, which are to be used in fuel or oil additive applications. In living cationic polymerizations, the polymer chains could be modified to form specific polymers such as end-functionalised polymers, telechelic polymers and star polymers.

Truly living cationic polymerization of isobutyl vinyl ether, using hydrogen iodide (HI) and iodine (I) as an initiating system, was first reported in 1984 by Higashimura, Sawamoto and Miyamoto **[2]**, and shortly thereafter by Faust and Kennedy for isobutylene **[3]**. However, living cationic polymerization of styrene, a monomer with no electron-donating substitutent, is still practically difficult, because the stability of the propagating carbocation is quite poor and controlling the polymerization is difficult. Despite such difficulties, it has been proved that a near-perfect living cationic polymerization is indeed feasible for styrene by carefully selecting an

initiating system, for example, tin tetrachloride as a catalyst and 1-phenyl ethylchloride (1-PEC) an initiator **[4]**.

The objectives of this project were to study the effects of added salt, initiator, catalyst, solvent polarity and temperature on the cationic polymerization of styrene monomers in terms of polydispersity, molecular weight and initiator efficiency etc., optimising the conditions under which a living cationic polymerization of styrene could be achieved. Tin tetrachloride ($SnCl_4$) and titanium tetrachloride ($TiCl_4$) were used as catalysts. Halide salts such as tetra-*n*-butylammonium chloride (nBu$_4$NCl), tetra-*n*-butylammonium bromide (nBu$_4$NBr), $C_{20}H_{44}NBr$, $C_{28}H_{60}NBr$, $C_{32}H_{68}NBr$, and pyridines were added to render polymerization living.

The literature on cationic polymerization is surveyed in Chapter 2, before the main experimental techniques are described in Chapter 3 including high vacuum techniques and some transfer techniques used to prevent the polymerization from contamination by impurities. Chapter 4 details the systematic investigations into the effects of solvent polarity, temperature, the initial concentrations of salt, catalyst, and initiator on the styrene polymerization (Styrene/1-PEC/$SnCl_4$/ nBu$_4$NCl system). Further kinetic studies on the rate of polymerization and the orders of reaction for the Styrene/1-PEC/$SnCl_4$/ nBu$_4$NCl polymerization system are reported in Chapter 5. Chapter 6 presents the results for the styrene polymerization in the presence of bromide salts (nR$_{4n}$NBr) instead of nBu$_4$NCl, in which the terminal structure was analysed by NMR spectroscopy. Polymerizations of styrene with 1-PEC/$TiCl_4$ as the initial system in the presence of 2,6-di-*tert*-butylpyridine (DTBP) and pyridine are described in Chapter 7, followed by main conclusions and further work in Chapter 8. Finally, an example for MS Excel Calculation Sheet is enclosed at the end.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Polymerization can categorised into two main areas: step growth (or condensation), and chain growth (or addition), depending upon the mechanisms and reactions involved **[5]**. In the step growth polymerization, monomers, dimers and oligomers combine to form larger molecules, involving the elimination of a small molecule such as water, CO_2 or NH_3 **[6]**. Chain growth polymerization can be addition or ring-opening polymerization; comprising at least three reactions: initiation, propagation and termination or transfer **[7-9]**.

2.2 Conventional cationic polymerization

Cationic polymerization falls into two major areas, carbocationic and onium ion reactions, according to the nature of the propagating chain end **[8]**. For carbocationic polymerization, there is a positive charge of the growing chain end on a carbon atom;

while the positive charge is based on a hetero atom such as oxygen, sulfur, nitrogen or phosphorus in the onium ion polymerization.

2.2.1 Definition

Polymerizations are generally considered as being 'cationic' when they involve a positively charged active species acting as an electrophile towards the monomer. Generally, the active species is located at the end of a growing polymer molecule and reacts with the monomer as nucleophile. In some cases the situation may be reversed if the monomer is activated by an acid **[10]**. Conventional cationic polymerization can be defined as an addition polymerization reaction mediated by a propagating carbocation that is derived from a monomer and an initiator **[11]**.

As the growing carbocations are, in general, highly reactive, but unstable, and subject to a number of side reactions, polymers produced by the conventional cationic polymerization have broad molecular weight distributions (MWDs) with little control of molecular weight (MW) because termination reactions involved.

2.2.2 Monomers suitable for carbocationic polymerization

The monomers suitable for carbocationic polymerization must have a site that is susceptible to electrophilic attack and generate a species that is sufficiently stable to act as a propagating cation. Alkenes are the most common monomeric compounds. The ability of alkenes to polymerise cationically is affected by the substituents on the carbon-carbon double bond of the alkenes **[12]**. Styrene and vinyl ethers are such monomers that are suitable for cationic polymerization, as they have electron-donating substituents that can enhance the reactivity of the carbon-carbon double bond.

The ability of a monomer to form a polymer can be predicted in term of the free energy of polymerization of the pure monomer (ΔG_p), which is given by

$$\Delta G_p = \Delta H_p - T\Delta S_p \qquad (1)$$

where ΔH_p and ΔS_p are respectively the enthalpy and entropy of polymerization of the pure monomer, and T is the absolute temperature. The free energy of polymerization is dependent upon the structures of the monomer and polymer, not the mechanism of formation. For any monomer there exists a ceiling temperature above which the free energy of polymerization changes from a negative value to a positive one as the temperature increases, and the monomer is thermodynamically stable **[13]**. The ceiling temperature (T_c) can be calculated from equation (1), when ΔG_p equals to zero:

$$T_c = \frac{\Delta H_p}{\Delta S_p} \qquad (2)$$

Styrene has a standard enthalpy of polymerization for pure monomer of -73.1 kJ mol^{-1} and a standard entropy of -104 J mol^{-1} K^{-1} **[14]**, so the ceiling temperature will be 430 °C for pure monomer. The more active monomer, for example, α-methylstyrene, has a low ceiling temperature of 61 °C, as it has a lower enthalpy of polymerization of -34.1 kJ mol^{-1}.

2.2.3 General mechanism of carbocationic polymerization

The cationic polymerization includes four main steps: initiation, propagation, chain transfer and termination **[15]**. The general description given is for vinyl monomers of the type CH_2 = CH-R, where the R- group represents various functionalities, e.g. -H, -CH_3, -Ph, -$OCH_2CH(CH_3)_2$.

2.2.3.1 Initiation

The initiation step involves the generation of a cationic species by ionisation. This can be obtained by the ionisation of an initiator (AB, an acidic material) or by use of a Lewis acid catalyst in conjunction with a suitable base (see section 2.4). The cationic species generated (A^+) tends to attack the carbon-carbon double bond of a vinyl

monomer (CH_2 = CH-R) to give the propagating chain end (A-CH_2-C^+H-R), initiating the polymerization (**Fig. 2.1**). Meanwhile, a counter anion or gegen-ion (B^-) is also generated, the nature of which may affect the polymerization.

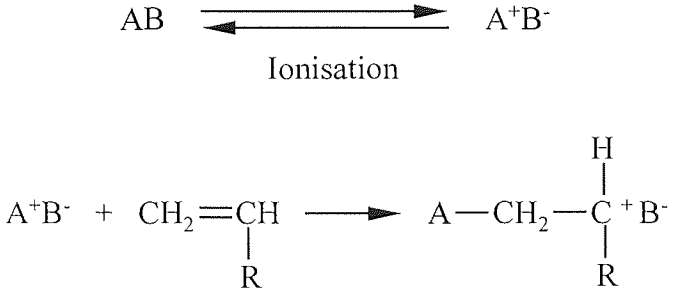


Fig. 2. 1. Initiation.

2.2.3.2 Propagation

Propagation, shown in Fig. **2.2**, occurs by the repeated insertion of a vinyl monomer molecule between the carbocationic chain end and the counter anion. The chain growth and formation of a propagating end (the right part in **Fig. 2.2**) is dependent on the reaction conditions. The propagation reaction competes with transfer and termination reactions, described in the next two sections.

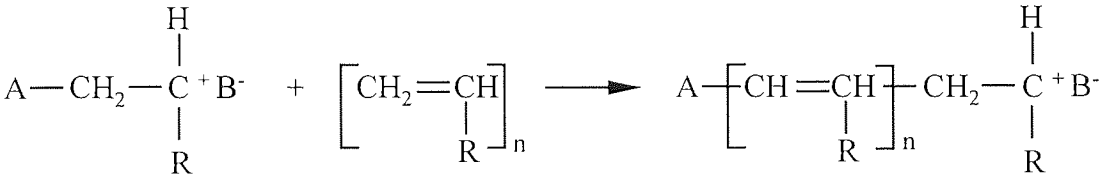


Fig. 2. 2. Propagation.

The propagating chain end may exist in the form of free ions or ion pairs. The structure is dependent on the monomer, solvent polarity, temperature and counter ions, described in Section 2.3.2.2 in more detail. Low temperatures, less polar

solvents and unstable counter ions favour the formation of the propagating chain end as ion pairs.

It has been shown that the free ions and ion pairs may have similar reactivities in some cases. This has been demonstrated by the equal rate constants for initiation by free ions or ion pairs in the polymerization of p-methoxystyrene initiated by $Ph_3C^+SbCl_6^-$ in dichloromethane **[16]**, and in the cationic polymerization of cyclopentadiene under similar conditions **[17]**. The difference in size between the chain end and the counter anions involved in the polymerization is the reason for the similarity in reactivity of free ions and ion pairs. In most instances, the counter ions involved are relatively large resulting in their centre being relatively far away from the propagating chain end, hence has a small influence on the reactivity of the propagating species.

The reactivity of the propagating chain end depends largely on the charge density associated with it, which is affected by the nature of monomer, i.e. the substituents. For example, the propagating end $\sim C^+HCH_3$ with a high charge density at the carbon atom will be more reactive than $\sim C^+(CH_3)_2$ when the charge is stabilised.

2.2.3.3 Chain transfer

Chain transfer can terminate a growing polymer chain and at the same time initiate a new chain. Different transfer reactions can take place, including transfer to monomer molecules, transfer to polymer chain or the counter ion **[18, 19]**.

Fig. 2.3 shows the main chain-breaking process in the transfer to monomer reaction. The β-hydrogen atom (proton) at the propagating end is inherently acidic and thus is abstracted by the vinyl monomer which is a nucleophilic or basic species. During the chain transfer process, transfer terminates the growth of one chain but initiates the growth of another, which gives rise to chains of different lengths, resulting in a polymer with a broad molecular weight distribution because of the statistics of such processes.

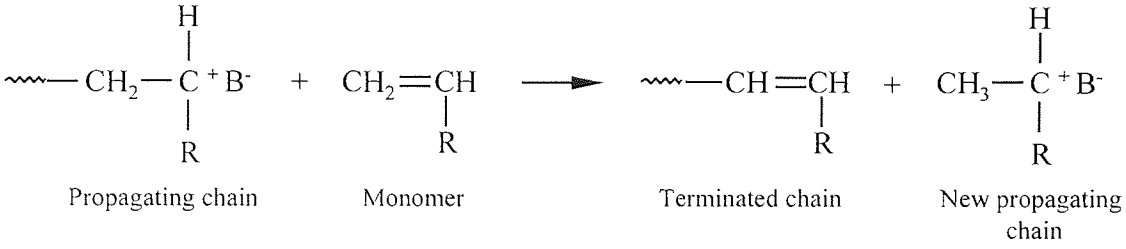


Fig. 2. 3. Chain transfer to monomer.

Transfer to polymer chain occurs either by transfer of a hydride ion or by an electrophilic aromatic substitution. The transfer of a hydride ion will result in a saturated polymer chain end (**Fig. 2.4**, top scheme), leading to the formation of branched chains. Transfer by electrophilic aromatic substitution usually involves an intramolecular backbiting reaction with transfer of a proton from the aromatic ring to the counter ion, as shown in the top scheme in **Fig. 2.4**, resulted in the product being a polymer chain with an indanyl end group.

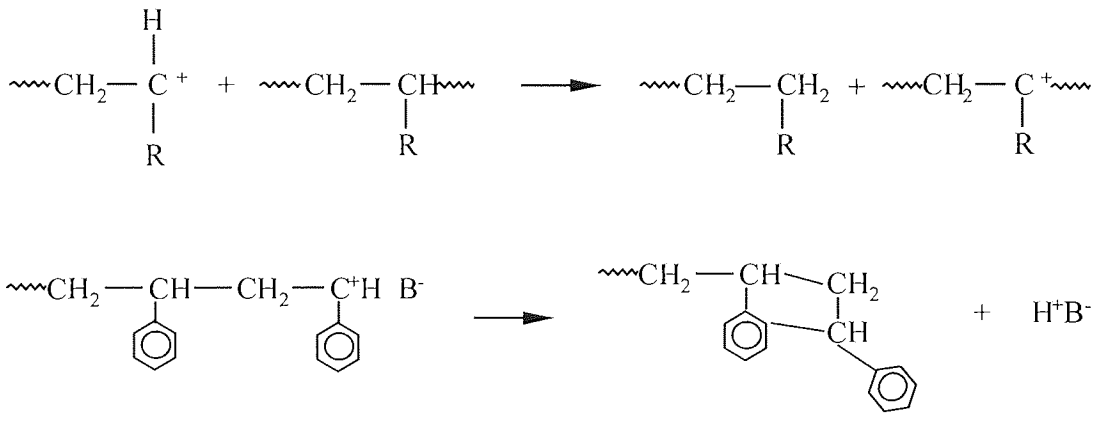


Fig. 2. 4 Chain transfer to polymer.

Transfer to counter ions can be achieved by a rearrangement of the propagating centre and counter ion (**Fig. 2.5**), leading to reformation of the original catalyst / initiator complex **[20]**, which can continue to propagate another chain.

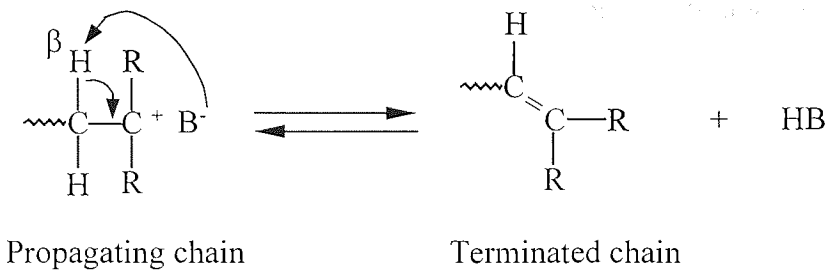


Fig. 2. 5 Chain transfer to counter ion.

2.2.3.4 Termination

The propagating chain end can be terminated by reversible self-rearrangement (**Fig. 2.4**), which is caused by the combination of an acidic β-hydrogen atom with the counter anion (B^-) to form a covalent bond between the propagating cation and the counter ion. In addition, the growing chain can be terminated by the quenching of the propagating chain by the addition of a nucleophile such as methanol **[15]**.

Quenching by some undesirable impurities, such as water, can also result in termination as well. In practice, the quenching agent is deliberately added to stop the polymerization in order to obtain polymer with controllable molecular weights.

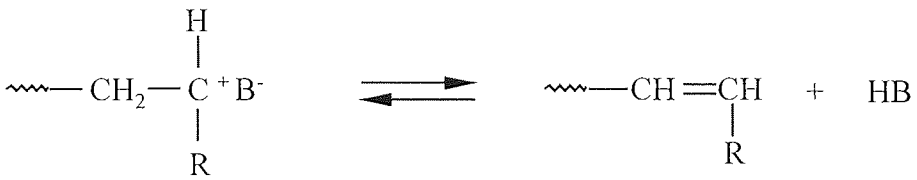


Fig. 2. 6 Termination.

2.2.4 Characteristics

Because of the high reactivity of the carbenium ions (propagating carbocation chain), the classical cationic polymerization is difficult to control. The accompanying side reactions, such as transfer reactions, slow initiation, and slow exchange between

various active sites with different reactivities or different lifetimes result in low molecular weights and high polydispersities when polymerization is carried out at ambient and higher temperatures **[21]**. At ambient temperature, the lifetimes of active ions and ion pairs in cationic polymerization are usually different **[22]**, resulting in high polydispersities, although they seem to have similar reactivities **[23-25]**. Therefore, the formation of a broad molecular weight distribution is inevitable in the conventional cationic polymerization.

2.2.5 Kinetics of cationic polymerization

The number of complex factors involved make it impossible to derive a general kinetic scheme for cationic polymerization. A single active species is assumed to be responsible for propagation, and the propagation occurs via ion pairs since free ions exist only under the purest conditions **[26]**. It has been assumed that chain transfer reactions are absent, or do not influence the rate of polymerization since the propagating centre is retained. For the sake of simplicity, the propagation reaction is assumed to be second order. Although too many assumptions have been questioned and for the most part found false or unsubstantiated the formulation of a general kinetic scheme may highlight some characteristics of interest.

Assuming chain propagation in terms of a single active species, the rate of polymerization (R_p) can be equated to the rate of consumption of monomer, which is given by

$$R_p = -\frac{d[M]}{dt} = k_p[P^+][M] \tag{3}$$

where t is the time,

k_p is the rate constant of propagation,

$[P^+]$ is the concentration of active propagating species, and

$[M]$ is the concentration of monomer.

For a Lewis acid co-catalyst combination as initiation system, the rate of initiation (R_i) is expressed as

$$R_i = k_i[I][M] \tag{4}$$

where k_i is the rate constant of initiation, and

$[I]$ is the concentration of the active initiator species.

The rate of termination is given by:

$$R_t = k_t[P^+] \tag{5}$$

where k_t is the rate constant of termination.

If it is assumed that a steady state in the concentration of propagating species is established, one obtains

$$\frac{d[P^+]}{dt} = R_i - R_t = 0 \tag{6}$$

Substituting equations (4) and (5) into equation (6) yields

$$[P^+] = \frac{k_i}{k_t}[I][M] \tag{7}$$

Then the rate of polymerization can be derived by substituting equation (7) into equation (3), given as

$$R_p = \frac{k_p k_i}{k_t}[I][M]^2 \tag{8}$$

For a polymerization, in which transfer reactions are absent and termination is unimolecular, the degree of polymerization can then be given by

$$\overline{DP_n} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p}{k_t}[M] \tag{9}$$

If the Arrhenius equation is used to replace the rate constants, equation (9) becomes

$$\overline{DP_n} = \frac{A_p}{A_t} e^{-\left(E_p - E_t / RT\right)}[M] \tag{10}$$

where A_p and A_t are the activation energies of propagation and termination respectively, E and E_t are the respective Arrhenius parameters, T is the polymerization temperature and R is the gas constant, 8.31441 J mol^{-1} K^{-1}.

In the presence of chain transfer to some agent, C, (e.g. monomer, then [C] = [M]), the degree of polymerization can be given by the following expression **[27]**:

$$\overline{DP_n} = \frac{R_p}{R_{tm}} = \frac{k_p}{k_{tm}} = \frac{A_p}{A_{tm}} e^{-\left(E_p - E_t / RT\right)} \tag{11}$$

As can be seen from the Equations (10) and (11), the degree of polymerization is dependent upon the initial concentration of the monomer and the polymerization temperature, not on the concentration of the active chains or the concentration of the initiator. Therefore, manipulation of the polymerization temperature and monomer concentration is the way for controlling cationic polymerization.

2.3 Living cationic polymerization

2.3.1 Principles

Truly living cationic polymerizations are polymerizations in the absence of side reactions such as termination and chain transfer to monomers, polymers and counter ions **[28]**, and the growing chain ends remain active towards further monomer addition for a desired period once all monomer has been consumed **[29]**. Owing to these features, the resulting polymers can be controlled in terms of molecular weight distribution and molecular weight. However, isomerisation of the propagating chain ends is eventually inevitable. The propagating end will react with the surroundings or otherwise decomposes.

In recent years, investigations into the mechanisms of propagation have revealed that living cationic polymerization can still be achieved even involving the reversible formation of inactive species, such as reversible termination **[30]**. Matyjaszewski and Muller **[31]** have defined a living polymerization as a chain polymerization in the absence of irreversible chain breaking reactions or side reactions, probably involving slow initiation and reversible termination. However, the rate of initiation must be greater than that of propagation, in order to obtain polymers with a narrow unimodal MWD with the MW determined by the ratio of monomer to initiator. The definition of a living polymerization excludes the presence of any irreversible termination and transfer reactions during chain propagation.

2.3.2 Methods to produce a living polymerization

As conventional cationic polymerization is associated with an unstable growing carbocation, the fulfilment of living cationic polymerization demands stabilising this unstable propagating chain end (**Fig. 2.2**). There are two ways that have been used to achieve this aim, addition of a highly nucleophilic counter-anion or an externally added Lewis base **[1]**. Both methods are based on the reduction of the cationic charge

of the propagating end, hence the acidity of the β-proton and eventual suppression of chain transfer.

2.3.2.1 Suppression of side reactions

In practice, suppression of termination and chain transfer to monomers can be achieved by maximising the rate of propagation (**Fig. 2.2**) over the rates of chain transfer to monomer (**Fig. 2.3**) or to polymers (**Fig. 2.4**) or to counter ions (**Fig. 2.5**) and termination (**Fig. 2.6**).

Since the activation energies of chain transfer and termination are normally higher than that of propagation, the side reactions can be suppressed at low polymerization temperatures **[32, 33]**. However, a living polymerization is not achieved simply by lowering the polymerization temperature.

One method of achieving a living polymerization is to reduce the rate of transfer by increasing the stability of the propagating chain end or carbocation by complexation with another molecule. A conventional non-living cationic polymerization of vinyl ethers initiated by $(C_2H_5)AlCl_2$ and a cationogen, e.g. water has shown to be non-living. However, a living polymerization can be achieved if an excess of an ester, such as ethyl acetate or ethyl benzoate **[34]**, or an ether, for example dioxane or diethyl ether **[35]** is added. As shown in **Fig. 2.7**, ester or ether may combine with the active propagating chain end, producing a nonreactive onium ion which is in rapid equilibrium with the active chain end, and so the propagating species has a very short life time, not long enough for transfer reactions to occur.

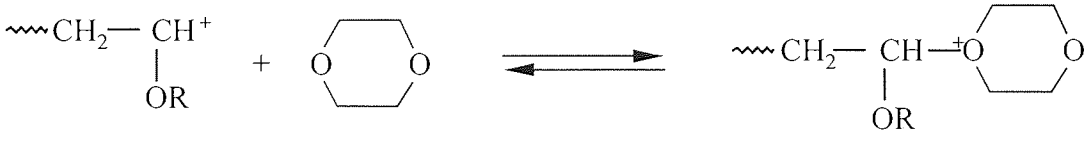


Fig. 2. 7 Formation of an oxonium ion in vinyl ether polymerization initiated by $Al(C_2H_5)$ in the presence of 1,4-dioxane.

2.3.2.2 Common-ion effect

Addition of a compound into a conventional cationic polymerization may result in a living polymerization; the compound does not react with respect to the polymerization, but can complex with the counter ion and so mediate it through the common-ion effect **[21]**. The effect is explained in terms of the stages of the active propagating species. As a consequence, the dissociation states of the propagating chain species are of importance in determining whether the cationic polymerization is living.

According to the description by Kennedy and Higashimura **[36, 37]**, the active species i.e. propagating chain species (growing chain) in cationic polymerization can exist in a variety of states, from a covalently bonded molecule to free ions depending on the distance between the ions, as demonstrated spectrum as follows by the Winstein ionicity:

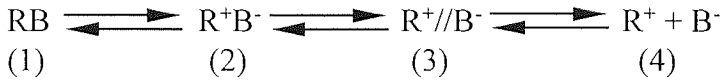


Fig. 2. 8 Winstein ionicity spectrum.

where (1) is the covalent species, (2) the associated ion pairs, (3) the solvent separated or dissociated ion pairs, and (4) fully solvated or free ions. Which state a propagating chain end takes depends upon the environment, such as the nature of the cation, counter ion and solvent. Factors that favour the covalent species (1), stabilise the charges on the ions and further stabilise the polymerization. But stable counter ions and polar solvent will favour the ionic species (4).

The covalent species (1) is much less active than the other species, propagation taking the order of months **[2]**, and these species can be considered as dormant in the polymerization. In contrast to the covalent species, the free ions (4) are highly reactive, resulting in a very fast polymerization (minutes) and a more likely tendency

to simultaneous chain transfer to monomer (side reactions). In addition an increase in distance between ions reduces steric hindrance to the incoming monomer. A rapid equilibrium between active and covalent species is now regarded as the essential condition for living cationic polymerization in which the counter ions stabilise the cation, suppressing termination and transfer reactions.

The active species in cationic polymerization can also coexist in different states, as illustrated in **Fig. 2.8**. Such multiplicity of propagating species has been proposed in the literature **[38]**. If the interconversion between the propagating species of different forms is slow, the polymers obtained will have a broad or even multi-modal molecular weight distribution, since the different propagating chains grow at different rates and individual distributions are superimposed on each other. A unimodal distribution will be obtained if the rate of exchange between these different species is high, because the total rate of propagation will be the average of the rates for different types of species and an averaged molecular weight distribution will be obtained.

2.3.2.3 Electron pair donors

Evidence has shown that electron pair donors can induce a living cationic polymerization in certain systems **[28, 39]**. For example, conventional cationic polymerization of isobutane with 2,4,4-trimethyl-2-pentyl acetate (TMPOAc)/BCl_3 became living after the addition of 1,1,1-triphenyl acetate $(C_6H_5)_3COAc$ to the system.

The effects of electron pair donors has been mainly attributed to three mechanisms: stabilising the propagating chain end, reducing the nucleophilicity of the catalyst by co-ordinating with it, and trapping impurities such as moisture. However, no clear explanation has been given.

2.3.3 Characteristics of living polymerization

2.3.3.1 Slow polymerization

In a living polymerization, the rate of initiation can be greater than that of propagation, provided that the initiating system is chosen properly. Such systems result in a low transient concentration of carbenium ions (propagating carbocation or growing chain end) and a slower polymerization that can be easily controlled.

2.3.3.2 Narrow molecular weight distribution (MWD)

Living polymerization proceeds with transfer and termination reactions being excluded. If the initiation reaction is fast in comparison with chain propagation, all the polymer chains are initiated at approximately the same time and grow at the same rate, so that the polymers produced will have narrow molecular distributions and the degree of polymerization can be controlled. In living cationic polymerizations, there is a rapid equilibrium between low concentrations of active growing chains and large amounts of either dormant covalent species or dormant onium ions **[40]**. The total concentration of active centres (growing chain and dormant species) is usually equal to the initial concentration of initiator, if the initiator efficiency is 100 %. The similar reactivity of the various active species in cationic polymerization as described in Winstein ionicity spectrum, or the rapid exchange between them in comparison to propagation should lead to polymers with narrow molecular weights MWDs **[40, 41]**.

For living cationic polymerization, a Poisson distribution can be used to describe the molecular weight distribution **[42-44]**

$$\frac{\overline{M_W}}{\overline{M_n}} = 1 + \frac{\overline{M_n}}{\left(\overline{M_n} + 1\right)^2} \qquad (12)$$

The number average ($\overline{M_n}$) and weight average ($\overline{M_W}$) molecular weights of polymers will be described in the next chapter in more detail.

Assuming one initiator molecular produces one discreet polymer chain, the number average degree of polymerization ($\overline{DP_n}$) equals the ratio of the concentration of the reacted monomer to the initial initiator concentration **[45]**, as shown as:

$$\overline{DP_n} = \frac{[M]_0 - [M]}{[I]_0} \tag{13}$$

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

$[M]$ is the instantaneous monomer concentration, and

$[I]_0$ is the initiator concentration.

If the chain propagation is regarded as a first order, the concentration of monomer can be expressed as follows **[45]**:

$$[M] = [M]_0 e^{-k_{app}t} \tag{14}$$

where t is the time, and

k_{app} is the apparent rate constant.

Rearranging Equation (14) yields

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_{app}t \tag{15}$$

Plotting ln ($[M]_0/[M]$) versus time should produce a linear relationship with the gradient equal to the apparent rate constant of propagation. Obviously equations (14) and (15) do not take into account the concentrations of the initiator or the propagating chain end.

The major characteristics of living cationic polymerization can be summarised as the following **[2, 46]**:

a) The number-average molecular weight ($\overline{M_n}$) increases in directly proportional to monomer conversion; the polymer chain number equals to the molecular number of initiator initially supplied ([I]), thus,

$$\overline{M_n} = \text{(weight of polymerized monomer)} / [I]_0$$

b) The molecular weight distribution is near monodisperse ($\overline{M_w} / \overline{M_n} \leq 1.1$) throughout the polymerization.

c) Increasing the initial concentration of the initiator does not affect polymer molecular weight but accelerates polymerization.

2.4 Monomers

As styrene was chosen as monomer in this project, the review in this section is mainly focused on the polymerizations of styrene and its derivatives as monomers. Although styrene and its derivatives are less reactive and the propagating carbocations formed less stable than those from vinyl ethers **[2]**, several workers have proved that the living cationic polymerization of styrene and its derivatives is possible by carefully selecting an initiating system **[1]**.

2.4.1 Styrene (St)

Living cationic polymerization of styrene has been achieved using different initiators and solvents. Faust and Kennedy firstly studied an arylacetate (p-$CH_3C_6H_4CH(CH_3)$-$OCOCH_3$ / BCl_3 initiating system in CH_3Cl solvent **[47]**, but the resulting polymers had broad molecular weight distributions (MWDs). Lin and Matyjaszewski used 1-phenylethyl trichloroacetate as an activator instead of arylacetate and CH_2Cl_2 as a

solvent **[48]**. Ishihama et al. **[49]** reported an initiating system of CH_3SO_3H / tin tetrachloride ($SnCl_4$) / tetra-*n*-butylammonium chloride (nBu_4NCl).

Higashimura et al. **[50]** and Matyjaszewski et al. **[21]** found that 1-phenyl ethylchloride (1-PEC), coupled with tin tetrachloride ($SnCl_4$) in the presence of tetra-*n*-butylammonium chloride (nBu_4NCl) in methylene chloride (CH_2Cl_2) solvent, gives living polystyrenes with very narrow molecular weight distributions in which the number of polymer molecules equals the molecular number of 1-PEC initiator molecules used. Later, Higashimura et al. **[4]** achieved living polystyrene with the use of initiating systems comprising 1-phenylethyl halide (PhE-X; X = Br, Cl) and tin tetrachloride ($SnCl_4$) in conjunction with added tetra-*n*-butylammonium halide (nBu_4NY; Y = Cl, Br, I) in methylene chloride (CH_2Cl_2) solvent; X and Y may be either the same or different. The resulting living polymers had very narrow molecular weight distributions MWDs ($\overline{M_w} / \overline{M_n}$ = 1.1 - 1.2).

At the same time, Choi et al. **[51]** synthesised living polystyrene using 1-phenyl ethylchloride (1-PEC) as a initiator and tin tetrachloride ($SnCl_4$) as a catalyst in CH_3Cl solvent in the absence of salts. More recently, Stover et al **[52]** presented their work on the living polymerization of styrene initiated by 1-phenylethyl bromide (1-PEB) and tin tetrachloride in chloroform (CH_2Cl_2) or CH_3Cl; they found that the polymerization is about two times slower than the corresponding 1-phenylethyl chloride-based initiating system because of the lower activity of the bromine substitute **[51]**. The 'colourless nondissociated ion pair' was assumed as the reason allowing the polymerization to be controlled, although this mechanism was doubted later **[53]**.

More recently, Endsor **[27]** studied the polymerization of styrene monomers initiated by 1-phenyl ethylchloride/ tin (IV) chloride in chloroform in the presence of tetrabutylammonium chloride. A living polymerization was obtained at 0 °C and -15 °C. Dilatometry studies were used to prove the liveness of polymerization reactions although data of polydispersity ($\overline{M_w} / \overline{M_n}$) have not presented in the literature **[27]**.

2.4.2 Styrene derivatives

2.4.2.1 Strongly electron-donating groups

A styrene monomer with an electro-donating group as a substitute can undergo living polymerization using initiating systems that were originally developed for alkyl vinyl ethers **[2]**. The strongly electro-donating group both enhances the reactivity of monomers and stabilises the propagating carbocation (growing chain). Based on this principle, the living polymerizations of *p*-alkoxystyrene **[54, 55]** and *p*-alkylstyrene **[56]** were carried out using HI / ZnX_2 and tertiary acetate / BCl_3 as the initiating systems. Living polymerizations of alkylstyrenes (*p*-methyl- and 2,4,6-trimethylstyrenes) were also achieved using acetyl perchlorate **[57]**, HI /$ZnCl_2$ **[56]** or aryl ester / BCl_3 **[47]** as initiating systems. Because of the low activity of *p*-methylstyrene monomer, the living polymerization occurred with the use of $ZnCl_2$, a stronger Lewis acid than ZnI_2 and the concentration of $ZnCl_2$ was high and in excess over hydrogen iodide **[56]**.

2.4.2.2 Electron-withdrawing groups

For styrene and most styrenic derivatives, which possess an electro-withdrawing group, are less reactive and require special initiating systems to achieve living cationic polymerization. Recent development of initiating systems encouraged many workers to investigate living polymerizations of such less reactive monomers.

Living cationic polymerization of α-methylstyrene (αMeSt) was achieved by Higashimura et al. using the HCl - adduct of 2-chloroethyl vinyl ether as an initiating system in CH_2Cl_2 solvent **[58]**. Matyjaszewski et al. carried out living polymerization of αMeSt using cumyl chloride / tetra-butylammonium chloride (Bu_4NCl) / $SnCl_4$ or BCl_3 initiator in CH_2Cl_2 / toluene solvent mixture **[59]**. Stover et al. studied living polymerization of αMeSt using an initiating system of 1-halogenethylbenzene / $SnCl_4$ in $CHCl_3$ solvent **[52]**.

The cationic polymerization of 4-methylstyrene (4MeSt) has also reported recently. Using initiating systems of hydrogen iodide (HI) / zinc dichloride ($ZnCl_2$) and HI / I_2 in toluene and CH_2Cl_2 solvents, Kojima K. et al. **[56]** obtained living polymers of fairly narrow molecular weight distributions ($\overline{M_w} / \overline{M_n}$ = 1.1 - 1.2). More recently, Stover at al. reported that living polymerizations of 4MeSt were initiated by 1-phenylethyl bromide (1-PEB) and tin tetrachloride ($SnCl_4$) in chloroform **[52]**, although they obtained polymers with number-average weights ($\overline{M_n}$) in agreement with the calculated values, but with broad MWDs ($\overline{M_w} / \overline{M_n} \approx 1.5$).

Living polymerization of *p*-chlorostyrene (pClSt) was firstly carried out by Kennedy et al. **[60]**, although the polymers obtained did not have narrow molecular weight distributions even at very low temperatures. More recently, well designed initiating systems consisting of HCl - adduct ($CH_3CH(R)Cl$; R = Ph, or OCH_2CH_2Cl) / SnX_4 (X = Br, Cl) / nBu$_4$NCl were extended to polymerize less reactive styrenic derivatives such as *p*-chlorostyrene (pClSt), *p*-chloromethylstyrene (pCMSt) and *p*-acetoxymethylstyrene (pAcOMSt) **[61]**, monomers with an electro-withdrawing functional group is attached to a phenyl ring. The pClSt polymerized with 1-phenylethyl chloride / $SnCl_4$/nBu$_4$NCl initiating system in CH_2Cl_2, resulting in living polymers with unimodal and very narrow molecular weight distributions ($\overline{M_w} / \overline{M_n} \approx$ 1.1). In contrast, both pCMSt and pAcOMSt were unable to produce living polymer.

2.4.3 Protected *p*-hydroxystyrenes

Poly(*p*-hydroxystyrene) and poly(*p*-methyl-*p*-hydroxystyrene), two typical polymers of protected *p*-hydroxystyrenes which have been found wide use as photoresist, were polymerized with BF_3OEt_2 in CH_2Cl_2 or liquid sulphur dioxide to give polymers with fairly high molecular weights (number-average weight $\overline{M_n}$ up to 157,600) in high yield **[62]**.

2.4.4 Bifunctional styrene monomer

Bifunctional styrenic monomer with p-alkoxystyrene-type vinyl groups were polymerized with $(C_6H_5)_2I^{\oplus}PF_6$ / $Cu(II)(OOC\text{-}C_6H_5)_2$ initiating system **[63]**; the polymerization rates were greater than those of the corresponding divinyl ethers. Formation of linear polymers is specific for bifunctional styrenes. The polymerizations of *p*- and *m*-diisopropenylbenzene involve a repetitive intermolecular Friedel-Crafts alkylation of the growing styryl cation onto the phenyl ring to give polymers comprising (bis) indane-type repeat units **[64]**.

2.4.5 Other monomers

The living cationic polymerization was firstly achieved for non-styrene monomers. Higashimura et al. **[65]** reported a truly living cationic 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. Since then a number of researchers have been devoted considerable efforts to develop living cationic polymerization for a range of monomers by selecting suitable solvent, temperature, counter ion and additives to control the stability of the propagating chain end. **Table 2.1** lists some monomers, excluding styrene and its derivatives, whose details have been documented in the previous sections, initiating systems that have been used successfully in living polymerization.

Table 2. 1 Living cationic polymerization systems.

Monomer	Initiator	Catalyst	Solvent	Additive	Ref.
Vinyl	HI	I_2	Toluene Hexane		**[65]**
	HI	ZnI_2	Toluene		**[66]**

			DCM		
	Triflic acid		DCM	$Bu_4N^+I^-$	**[67]**
	$R^1R^2PO_2H$ R1/R2 = Ph/H; Ph/Ph; OPh/OPh	$ZnCl_2$	Toluene		**[68]**
	HCl	$TiCl_{4-n}$ (OR)n	DCM	R=-$CH_2(CH_3)_2$, n=2-3	**[69]**
	HI	MXn = ZnI_2-Cl_2, SnI_2, $SnCl_2$			**[70]**
Isobutane	$CuOA_C$	BCl_3	CM	X	**[28,71]**
	CuCl	BCl_3, $TiCl_4$	CM / C.hex	DMSO; DMA	**[72]**
	DiCuCl	$TiCl_4$	CM / Hex.	pyridine	**[73,74]**
	TMPOH	BCl_3	M	1-methyl-2-pyrrolidinone	**[75]**
	DiCuAzide	Eth_2AlCl	DCM	X	**[72]**
	t-BuOBenzene	$TiCl_4$	DCM	D^{t}BP	**[76]**
	5-tert-butyl-1,3-bis(2-chloro-2-propyl)-	$TiCl_4$	DCM / Hexane	D^{t}BP	**[77]**

	benzene				
IBVE	HCl	$SnCl_4$	Toluene	nBu_4NCl	**[78,79]**
	CH3COOH	$EtAlCl_2$	Hex.	Esters/ethers	**[34]**
N-vinylcarbazole	HI	NBu_4NI	Toluene	-	**[80]**

2.5 Initiating systems: (initiator + activator)

The initiating system refers to a combination of two and more reagents that generate propagating species from a styrene monomer. It is obvious that the initiating system is very important in achieving controlled living polymerizations. The initiating systems established for vinyl ethers **[2]** cannot be directly extended to styrene and *p*-alkylstyrenes, which are far less reactive and their growing carbocations are much less stable than those for vinyl ethers and *p*-alkoxystyrene which have an electro-donating group rendering the growing chain stable. In general, the initiating systems used for vinyl ethers are simply ineffective for polymerizing styrene and their derivatives, or where the initiator and activator (catalyst) do affect polymerization, the polymerizations are less or uncontrolled.

2.5.1 Friedel-Craft initiation

Friedel-Craft initiating systems are widely used for the cationic living polymerizations of vinyl monomers (CH_2 = CH-R). They consist of a Lewis acid activator (catalyst) and a Lewis base (initiator). The hydrogen iodide (HI) / iodine (I_2) initiating system used for vinyl ether (CH_2 = CH-OR) living polymerization is an original Friedel-Craft initiating system **[2]**. As can be see in **Fig. 2.9**, hydrogen iodide (HI) acts as an 'initiator' which generates the living growing end (1) with the nucleophilic iodide anion (I^-); iodine (I_2) serves as an activator (behaving as a Lewis acid) and activates

the dormant carbon-iodine linkage in (2) and (3) through an electrophilic interaction **[1, 2]**; further addition of monomer leads to a living polymer (3).

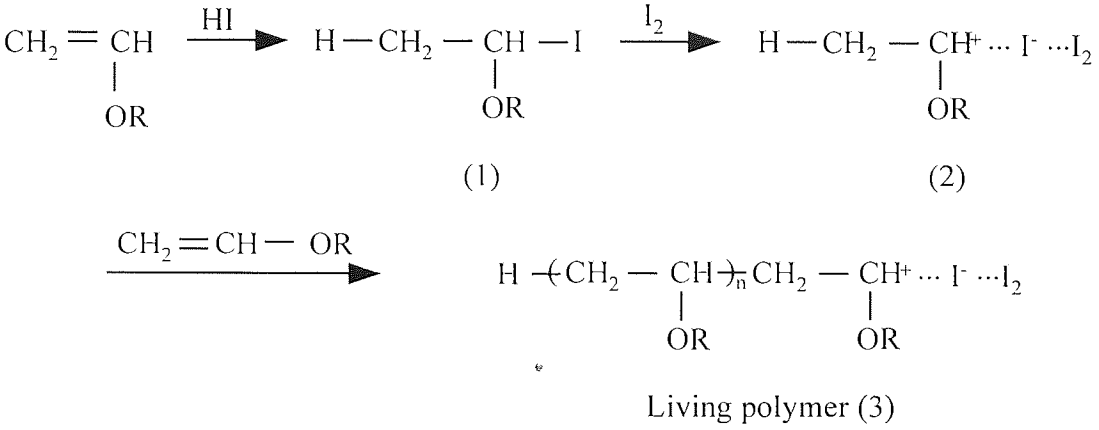
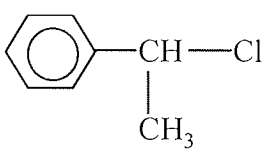
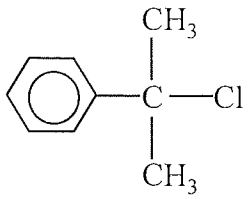
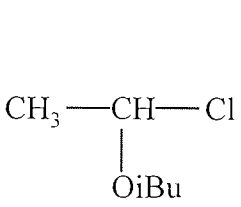


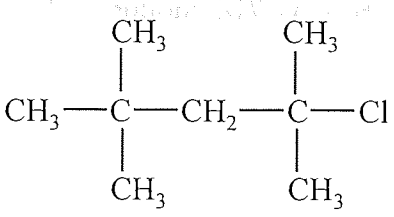
Fig. 2. 9 HI / I_2 initiating system for vinyl ether living polymerization.

1-Phenylethyl halides ($PhCH(CH_3)X$; X = Br, Cl) are commonly used as initiators, coupled with Lewis acids (SnX_4; X = Br, Cl), in living cationic polymerizations of styrene and their derivatives **[4, 21]**. They behave as Lewis bases in living polymerizations. **Fig. 2.10** summarises initiators commonly used in living cationic polymerizations.

CH_3COOH Acetic acid **[47]**	HI Hydrogen iodide **[54, 55]**
 1-Phenylethyl chloride **[50]**	 2-Chloro-2-phenylpropane **[81]**



IBVE / HCl adduct **[82]**



2,4,4-Trimethyl-2-chloropentane **[83]**

Fig. 2. 10 Common Friedel-Craft initiators.

2.5.2 Friedel-Craft activators (catalysts)

Selecting the Lewis acid (as activators) to suit for the monomer reactivity is recognised as one of the keys to living or controlled cationic polymerization. An initiating system consisting of acetic acid (CH_3COOH) as an initiator and BCl_3 as an activator was used in living polymerization of *p*-methylstyrene **[47]**. The resulting polymers had controlled molecular weights but rather broad molecular weight distributions ($\overline{M_w} / \overline{M_n} \approx 5$ - 6).

The tin tetrachloride ($SnCl_4$) based initiating system has been found to be one of the most efficient initiating systems, inducing living and better-controlled cationic polymerizations of styrenes in terms of molecular weight and molecular weight distribution **[49, 50, 4]**. In conjunction with 1-phenylethyl chloride (1-PEC) and in the presence of tetra-*n*-butylammonium chloride (nBu$_4$NCl), these initiating systems lead to polystyrenes with narrow MWDs ($\overline{M_w} / \overline{M_n} \sim 1.1$) and molecular weight controlled by the monomer / initiator mole ratio. The efficiency of $SnCl_4$ could be attributed to the use of a suitable Lewis acid for the monomer reactivity.

Recent research on $TiCl_4$ proved that $TiCl_4$ based initiating systems, in the presence of a nitrogen base including *N*,*N*-dimethylacetamide and sterically hindered pyridines **[84, 85]**, activated polymerizations of styrenes resulting in polymers with controlled

molecular weights, but broader molecular weight distributions MWDs ($\overline{M_w}/\overline{M_n}$ ~ 1.8) in comparison to those with the $SnCl_4$ based initiating systems.

Addition of nucleophilic compounds **[4, 49, 50]** to modulate the Lewis acidity of metal halides with substituents is also a method of effectively weakening strong Lewis acids to control cationic polymerization. In-situ mixing of $TiCl_4$ and $Ti(OR)_4$ was used as activators in the living polymerization of *p*-methylstyrene **[86]** and α-methylstyrene **[87]**. The living cationic polymerization was achieved with the use of substituted titanium (IV) chlorides, such as $TiCl_2(OiPr)_2$ **[88]** and $TiCl_3(OnBu)$ **[89]**, where their Lewis activities are modulated by electro-donating alkoxy groups introduced onto the metal, so as to be suitable for the cationic reactivity of the monomers.

More recently, Hasebe et al. **[33]** studied living polymerization of styrene with the use of titanium (IV)-based Lewis acids ($TiCl_{4-n}X_n$) modified by the number and nature of the substituents (X = O*i*Pr, OPh, Cp), in conjunction with 1-phenylethyl chloride (1-PEC) as an initiator. Living cationic polymerizations of styrenes were achieved with $TiCl_3(OiPr)$ and $TiCl_3(OPh)$, resulting in polymers of narrow molecular weight distributions MWDs ($\overline{M_w}/\overline{M_n}$ ~ 1.1 and 1.3, respectively). However, $TiCl_2(OiPr)_2$, having a weaker Lewis acidity was unable to activate the living polymerization of styrene, although it induced the living polymerization of vinyl ethers **[88]**.

2.5.3 Bifunctional initiating systems

A new bifunctional initiating system, 1,4-bis(1-chloroethyl)-benzene (**Fig. 2.11**) / $SnCl_4$, in the presence of 2,6-di-*tert*-butylpyridine (2,6-DtBP), was used to carried out living cationic polymerization of styrene **[90]**. The polymers obtained had narrow molecular weight distributions MWDs ($\overline{M_w}/\overline{M_n}$ < 1, 2) and number-average molecular weights increasing with monomer conversion.

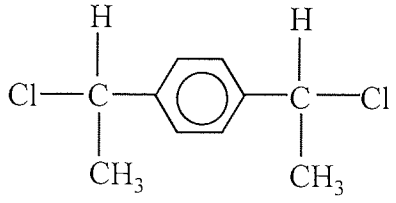


Fig. 2. 11 1,4-bis(1-chloroethyl)-benzene.

2.5.4 Other initiating systems

Nuyken et al reviewed some newly developed initiating systems, for examples, the NR_4ClO_4 ($KClO_4$; $LiClO_4$) / CH_3CHI-OR system was used to initiate vinyl ether monomer to obtain a living cationic polymerization **[91]**.

2.6 Living polymers

Living polymerization has been used to synthesis polymers with controlled molecular weight and structures, which may contain quantitative functionalisation at the chain end. Since the molecular weight plays a very important role in determining the physical characteristics and the chemical reactivity of polymers when reacted with other compounds, control of molecular weight distribution needs to be fulfilled. This can be achieved by varying the monomer to initiator ratio.

Living cationic polymerizations of styrene and its derivatives can produce end-functionalised, telechelic or star polystyrenes, depending on the initiating systems used.

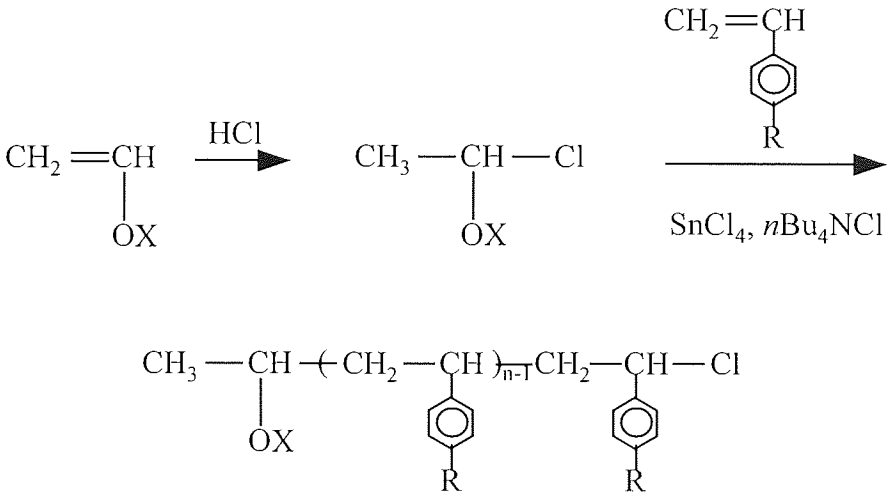
2.6.1 End-functionalised polymers

End-functionalised polymers are those with terminal functional groups. They can be synthesised by living cationic polymerization, at which chain transfer to monomer,

which results in olefinic or other useless terminal groups, is directly eliminated by stabilising the propagating carbocations. Two methods were used in the living cationic polymerization, as follows **[1]**:

2.6.1.1 Functionalized initiator method

End-functionalized initiator method involves an initiation of living polymerization with an initiator carrying a functional group to be incorporated into a polymer as a head or α-end group.



End-functionalized polymer

R = H (styrene), CH_3 (*p*-methylstyrene)

Fig. 2. 12 Polymerization of end-functionalized polymer.

A series of α-end-functionalized polymers of styrene and *p*-methylstyrene were achieved by living cationic polymerization in CH_2Cl_2 at -15 °C, initiated with the HCl adducts of vinyl ethers carrying pendant substituents X that serve as the terminal functionalities in the products (**Fig. 2.12**); $CH_3CH(OCH_2CH_2X)Cl$; X = chloride (Cl), benzoate [OC(O)B], acetate [$OC(O)CH_3$], phthalimide [$N(CO)_2B$], methacrylate [$OC(O)C(CH_2)CH_3$] **[92]**. By coupling with $SnCl_4$ (activator), which activated the carbon-chlorine bond of the HCl adducts, in the presence of tetra-*n*-butylammonium

chloride (nBu$_4$NCl), the obtained polymers had narrow molecular weight distributions MWDs ($\overline{M_w} / \overline{M_n} < 1.2$) with controlled molecular weights.

Table 2. 2 End-functionalized reactions of living cationic polystyrene

End-capping reagent		Polymer	
A-Z	Formulation	ω-end (Z)	MWD
Methanol	MeOH	Cl-	1.11
Trimethylsilyl methacrylate	CH_2=C(CH_3)CO-OSi(CH_3)$_3$	CH_2=C(CH_3)CO-O-	1.13
Trimethylsilyl acetate	CH_3COOSi(CH_3)$_3$	CH_3COO-	1.13
Allyltrimethylsilane	CH_2=CHCH_2Si(CH_3)$_3$	CH_2=CH_2-	1.10

2.6.1.2 End-capping method

In the end-capping method, a living cationic polymer is quenched with a nucleophilic reagent having the functional group to be attached to a 'tail' group (ω-end) of the polymer. Quantitative addition of the nucleophilic reagent is essential for eliminating side reactions, particularly β-proton elimination. In addition, the efficiency of the end-capping reagents is dependent upon the nature of the polymer ends as well as the nature of the quenching reagents **[93]**.

Synthesis of end-functionalized polystyrene with organosilicon end-capping reagents (**Table 2.2**) was carried out in the living cationic polymerization of styrene initiated with the 1-phenylethyl chloride (1-PEC) / tin tetrachloride ($SnCl_4$) / tetra-n-butylammonium chloride (nBu$_4$NCl) system in CH_2Cl_2 at -15°C. In the living polystyrene, the appropriate nucleophilic reagents (A-Z), which may have functional groups such as chloride, methacryloxy, acetoxy and allyl, react with the growing

polystyryl terminal to give ω-end-functionalized polystyrenes with narrow molecular weight distributions MWDs. The formation of end-functionalized polymers was attributed to the high affinity of silicon toward chlorine. Four silyl compounds were found effective in the end-capping of the living polystyrene, enabling quantitative end-functionalizations, but their concentrations must be high enough (usually 200-fold molar excess over the initiator or the living end), so that the end-capping polymerizations can occur.

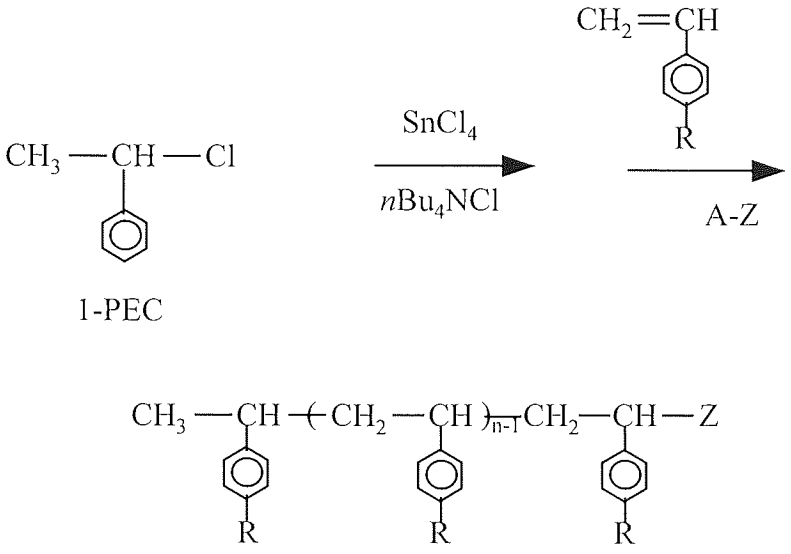


Fig. 2. 13 Formation of end-functionalized polystyrene.

2.6.2 Telechelic polymers

Telechelic polymers can be obtained when the living polymer in the functional initiator method (right part in **Fig. 2.12**) is terminated with an end-capping reagent (**Fig. 2.13**). As can be seen in **Fig. 2.14**, combination of the two methods for the synthesis of functionalized polymers leads to the formation of telechelic polymers.

It is well known that a bulky 2,6-disubstituted pyridine such as 2,6-di-*tert*-butylpyridine (2,6-DtBP) does not react with electrophiles other than a proton, owing to steric hindrance around the nitrogen **[90]**. 2,6-DtBP was used as an end-capping

reagent in the living polymerization as it inhibits proton-initiated polymerization by capturing the protons from the system. Kwon et al **[90]** reported that living cationic polymerization of styrene was achieved with the use of 1,4-bis(1-chloroethyl)benzene (initiator) / $SnCl_4$ (activator) initiating system in chloroform at -15 °C in the presence of the proton trap, 2,6-di-*tert*-butylpyridine (2,6-DtBP). The polymers obtained had narrow molecular weight distributions ($\overline{M_w} / \overline{M_n}$ < 1.2) with better regulation of molecular weights. The similar rates of polymerization in the presence and absence of 2,6-DtBP implies that 2,6-DtBP does not stabilise propagating carbocations in contrast to the effect of adding Lewis bases **[2]**, but only traps protons and then suppresses side reactions arising from protogenic impurities produced by adventitious water.

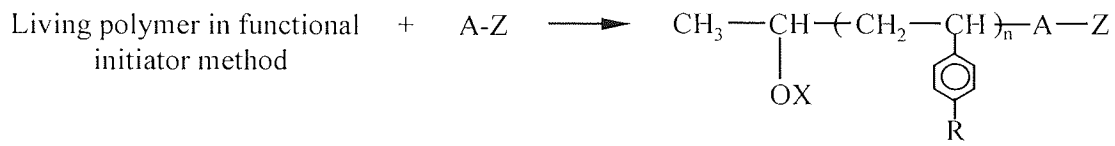


Fig. 2. 14 Telechelic polymer.

2.6.3 Star polymers

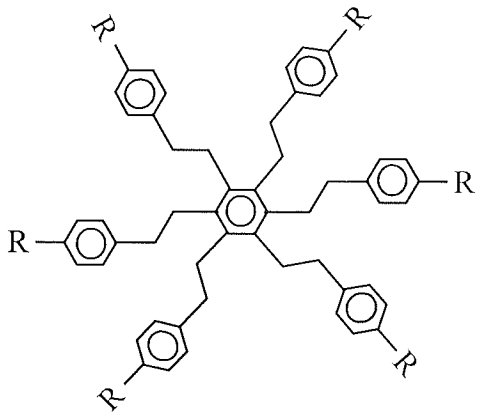
Star-shaped polymers have three dimensional shapes and highly branched structures with more compact occupation of space, so that they present different properties compared to normal linear polymer. There are a number of different methods employed to produce multiple branched, star polymers.

2.6.3.1 Arm-first method

The arm-first method involves a synthesis of a linear 'living' polymer and its treatment with a polyfunctional deactivating reagents **[94]**. The copolymerization of a 'living' linear polymer with a bifunctional monomer can lead to a star central core forming the basis of a star polymer; however, there was a problem with the stability of the star functionality **[95]**.

2.6.3.2 Core-first method

The core-first method employs a polyfunctional initiator from which branches can be grown. The functionality of the resulting star depends upon the initiator if all of the active sites of the initiator leads to branches. The synthesis of such polyfunctional initiator was encouraged by the perfunctionalization of polymethylaromatics induced by $Fe(\eta\text{-}C_5H_5)^+$ **[96]**.



R = CH(Cl)Me

Fig. 2. 15 Hexafunctional initiator $C_6[(CH_2)_2p\text{-}C_6H_4CH(Cl)Me]_6$

A hexafunctional initiator $C_6[(CH_2)_2p\text{-}C_6H_4CH(Cl)Me]_6$ (**Fig. 2.15**) was firstly synthesised by $Fe(\eta\text{-}C_5H_5)^+$ induced hexabenzylation of C_6Me_6 followed by regiospecific acetylation, $NaBH_4$ reduction **[97]**. Hexaarm star-shaped polystyrenes were achieved using this hexafunctional initiator in the presence of tin tetrachloride ($SnCl_4$) and tetra-*n*-butylammonium chloride (nBu_4NCl) in CH_2Cl_2 at -15 °C **[97]**. The star-shaped polymers were 'living' and approached monodispersity ($\overline{M_w} / \overline{M_n} \sim 1.1$).

2.6.3.3 Polymer linking (microgel) method

The microgel-based, start-shaped polymers can be synthesised through the linking reaction of linear living polymers with a small amount of a divinyl compound **[95]**. A

living polymer, which was obtained through the polymerization of *p*-methoxystyrene (pMOS) initiated with HI/I_2 initiating system in methylene chloride at -15 °C (**Fig. 2.16**), reacted with a small amount of a divinyl compound (linking agent) $[CH_2=CHC_6H_4O(CH_2)_3OC_6H_4CH=CH_2]$, resulting in star-shaped polymers that consist of poly(*p*-alkoxystyrene) arms and a microgel core of the divinyl compound **[98]**.

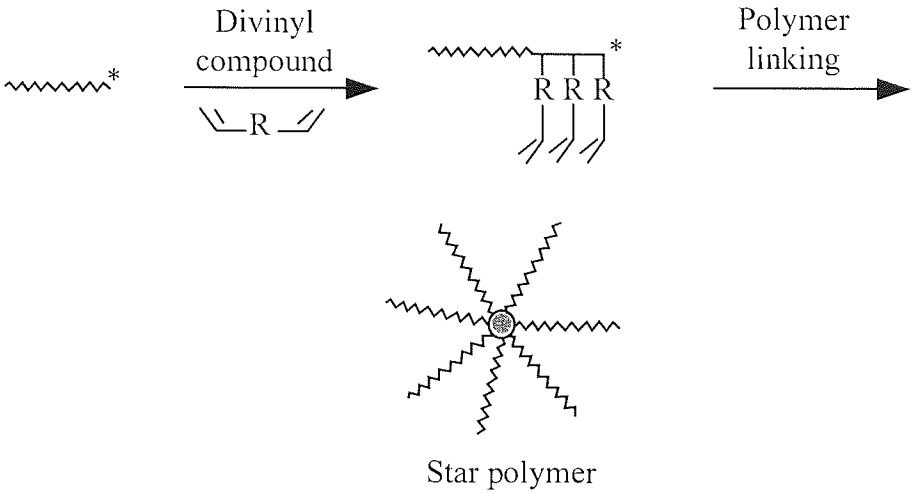


Fig. 2. 16 Polymerization of star-shaped polystyrene.

Similar star-shaped polymers were also obtained with *p-tert*-butoxystyrene which has a bulkier subsituent than pMOS **[98]**.

It has been shown that use of another linking agent, a bifunctional vinyl ether $[CH_2=CHOCH_2CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH_2OCH=CH_2]$, resulted in a significant decrease in the yield of the start-shaped polymers **[98]**.

2.6.4 Ring-shaped polymer

A new method based on cyclization was developed to synthesis ring-shaped polymers with predictable molecular weights and narrow molecular weight distributions. The cyclization is based on a unimolecular 'end-to-end' coupling reaction. The encounter probability of the two functional ends (X, Y) of a single chain depends mainly on the distance between these two functional ends. High dilution conditions favour

intermolecular coupling, and thus facilitate the cyclization reaction. This method involves firstly a living polymerization of a linear polymer possessing two reactive function ends, which are then cyclized under high dilution by the selection reaction of one function with the other one, yielding a cyclized poly block (see **Fig. 2.17**).

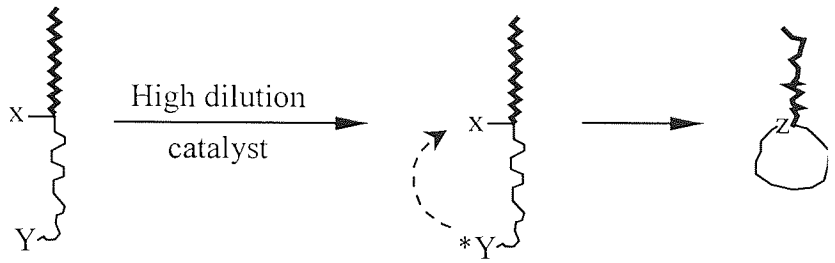


Fig. 2. 17 A ring-shaped polymer.

Using the method, Beinat et al. **[99]** obtained cyclic diblock copolymers of poly(hydroxyethyl vinyl ether) and linear polystyrene, comprising by a cycle hydrophilic block on which a linear hydrophobic polymeric tail is attached.

2.7 Factors affecting living cationic polymerization

2.7.1 Salt

The addition of salts has been used successfully for improving the 'livingness' of polymerizations of vinyl ethers **[1]**. The proportion of free ions and their lifetimes were reduced by adding the salts with anions capable of forming covalent species reversibly.

In cationic polymerization of styrene and its derivatives, the added salts can provide a sufficient concentration of anions, which seemingly exerts an additional carbocation stabilisation. This can be explained in terms of the dissociation of carbocationic ion

pairs (propagating chains) according to the Winstein ionicity spectrum described in Section 2.2.2.2; i.e., the added salts dissociate completely into anions and cations, and the free-anions will render the spectrum in **Fig. 2.8** move to the left to suppresses the dissociation of the growing carbocation, resulting in living polymerizations.

Kojima et al **[55]** studied the effect of added salts (nBu$_4$NX; X = I, Br, Cl, ClO$_4$) on the cationic polymerization of *p*-methoxystyrene (pMOS) with the use of hydrogen iodide / zinc iodide (HI / ZnI$_2$) initiating system. The molecular weight distributions (MWDs) of the obtained polymers were bimodal in the absence of the salts (nBu$_4$NX). However, addition of a small amount of nBu$_4$NI (1.0 mol % to HI) lead to polymers with very narrow MWDs ($\overline{M_w} / \overline{M_n} \leq 1.1$), indicating that polymerizations became living. Similar living polymers were obtained in the presence of nBu$_4$NBr and nBu$_4$NCl; but nBu$_4$NClO$_4$ was found to have no effect on the polymerizations.

Addition of halide salts (nBu$_4$NX; X = I, Br, Cl) was also reported to have significant effect on the cationic polymerizations of styrenes using 1-phenylethyl halide (PhE-X; X = Br, Cl) and tin tetrachloride (SnCl$_4$) initiating systems in methylene chloride at -15 ° C **[4]**. In the absence of halide salts, the initiating systems formed polymers with bimodal molecular weight distributions (MWDs); but in the presence of the salts, living polystyrene with narrow MWDs ($\overline{M_w} / \overline{M_n}$ = 1.1 - 1.2) were obtained. Obviously the addition of the salts facilitated cabocation stabilisation during polymerization.

Lin et al **[21]** also investigated the effect of tetra-*n*-butylammonium chloride (nBu$_4$NCl) on the kinetics and molecular weight distribution in the cationic polymerization of styrene initiated by 1-phenylethyl chloride (1-PEC) / SnCl$_4$ initiating system. The addition of the salt suppressed the dissociation of the growing carbocation ion pairs and thus slowed down the polymerization; the polymerization rates decreased about five times in the presence of a small amount of salt ([salt] / [SnCl$_4$] < 0.1). Eventually the addition of salts leaded to the decrease in polydispersities of the polymers.

2.7.2 Solvent

Cationic polymerization involves the ionisation of initiators and ions or ion pairs, the nature of the solvent is of importance. Firstly, the solvent must has the capability of dissolving the monomer, initiator, catalyst and / or additives that may be added as well as the polymers over a wide range of molecular weight. Secondary, the solvent must not react or complex with the propagating chain end to influence the rate of propagation and the molecular weight of the resultant polymers.

As the dissociation of the growing chain end (carbocation ion pairs) depends upon the dielectric permmittivity of solvent, solvent polarity will remarkably affect the rates of cationic polymerization and the molecular weight distribution (MWD) of the polymers. In general, living cationic polymerization would be more difficult to occur in polar solvents compared to the cases in non-polar solvents **[55]**. According to the Winstein ionicity spectrum (**Fig. 2.8**), polar solvents tend to favour the more ionised species of the growing chain (propagating carbocation) during polymerization, since their polarities allow them to stabilise the charges on the dissociating ions, resulting in less stable propagating carbocations.

In polar solvents, multiple growing species may exist with different ionic dissociation states of the propagating cabocations, which was demonstrated by the bimodal molecular weight distributions of the product polymers **[100]**. Typical examples of double-peaks molecular weight distribution were shown in the polymerizations of styrene carried out in relatively polar solvents such as methylene chloride (CH_2Cl_2) **[101, 102]**.

Studies on the effects of solvent polarity on the cationic polymerization showed that polymerizations in polar and less-polar solvents result in polymers with completely different molecular weight distributions MWDs **[55]**. In the presence of toluene, a non-polar solvent, polymers of p-methoxystyrene with nearly monodisperse MWDs were achieved using the hydrogen iodine (HI) / zinc iodine (ZnI_2) initiating system. In contrast, polymers with bimodal molecular weight distributions were obtained in a

polar CH_2Cl_2 solvent, especially at low monomer conversions. The formation of the two-peaks MWD is due to the overlap of the peak at the lower polymer fraction, which increasing with the polymerization, and the other peak at the higher polymer fraction, which remain constant during the whole polymerization.

2.7.3 Temperature

As described in the former Section 2.2.2.1, low temperature facilitates suppressing of side reactions (chain transfer to monomer and termination) and renders living cationic polymerization possible. Most of living cationic polymerizations of styrenes and its derivatives have been carried out at low temperatures, usually -15 °C **[1, 2]**.

However, living cationic polymerizations may occur even at room temperature by selecting appropriate initiating systems. For examples, living polymers with narrow molecular weight distributions MWDs ($\overline{M_w} / \overline{M_n} \leq 1.1$) were synthesised even at + 25 °C in polar methylene chloride CH_2Cl_2 solvents using a HI / ZnI_2 initiating system **[55]**.

The polymerization of *p*-chlorostyrene (pClSt) at +25 °C with the use of 1-phenyl ethylchloride (1-PEC) / tin tetrachloride ($SnCl_4$) / tetra-*n*-butylammonium chloride ($n$$Bu_4NCl$) (20 / 100 / 40 mM) was also given living polymers with narrow molecular weight distributions MWDs ($\overline{M_w} / \overline{M_n} = 1.13$) **[61]**. However, the corresponding polymerization of styrene was not living at +25 °C. The polymerization of styrene at 0 °C with the same system 1-PEC / $SnCl_4$ / $n$$Bu_4NCl$ (20 / 100 / 40 mM) leaded to polymers with relative narrow MWDs ($\overline{M_w} / \overline{M_n} = 1.28$) but double-peak MWDs.

More recently, polymerization of styrene with 1-phenylethyl chloride (1-PEC) / $TiCl_3$(OiPr) / $n$$Bu_4NCl$ in CH_2Cl_2 polar solvent were carried out at different temperatures: -15, -40 and -78 °C **[33]**. Lowering temperature increased the reaction rate, which was attributed to the increase in solvent polarity with lowering temperatures and/or the negative activation energy for propagation. The number-

average molecular weights of the polymers obtained at -15 °C were slightly smaller than the calculated values, probably resulting from chain transfer side reactions. The polymers obtained at -15 and -40 °C had narrow MWDs ($\overline{M_w}/\overline{M_n}$ < 1.1); where those at -80 °C possessed a slightly broad MWD ($\overline{M_w}/\overline{M_n}$ = 1.3), which was attributed to the slow interconversion between the dormant and the activated species **[33]**.

CHAPTER 3

EXPERIMENTAL DESIGN

Controlling the experimental environment is clearly vital to living cationic polymerization, since trace contamination by materials such as air or moisture can lead to the formation of non-living systems with a multimodal molecular weight distribution and high dispersity or low catalyst destruction.

3.1 High vacuum techniques

The high vacuum technique is one of several types of experimental technique that can be employed to control the experimental environment, preventing the cationic polymerization from being affected by the presence of oxygen, water and, less commonly, carbon dioxide. As the intermediates involved in living cationic polymerizations, such as the propagating active species, are sensitive to impurities, the distillations and purification of solvents or monomers were carried out using either high vacuum techniques or an inert atmosphere of argon surely trying to avoid atmospheric contamination.

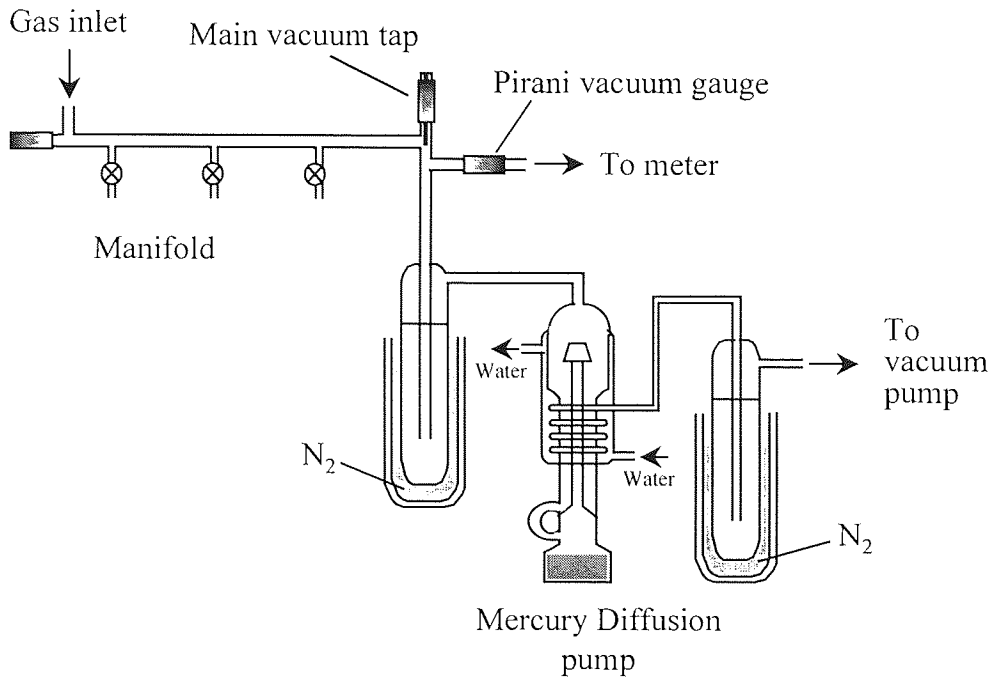


Fig. 3. 1. The vacuum line.

3.1.1 The vacuum line

Fig. 3.1 illustrates the vacuum line used in this work. A vacuum line is almost always efficient for laboratory scale operations. The vacuum line is constructed from glass and consists of a manifold with greaseless Teflon® taps connected to a Metrovac® rotary vacuum pump in conjunction with a mercury diffusion pump, in which mercury is heated so that it boils vigorously to produce a stream of mercury vapour, and then condensed on the walls of the water condenser. The rotary pump used to generate a pressure of approximately 10^{-2} mm Hg, and the whole system is capable of achieving pressures of 10^{-5} mm Hg. The pressure was measured by a Pirani vacuum gauge. Prior to use the glassware was flamed with a Bunsen, while under vacuum, to remove any moisture that may be adsorbed onto the inside surface.

Two cold traps were used to trap volatile materials from the line on their way to pumps, the vapour and any pumping fluid is condensed before it can enter the line by back diffusion. The coolant used for the traps was liquid nitrogen (b.p. -195.8 °C).

3.1.2 Treatment of glassware

Flasks were specially designed for the high vacuum techniques used in the work to dry and store monomers and solvents. These flasks were fitted with PTFE taps and joints which allowed direct connection to the manifold vacuum line.

Organics are commonly found on glass (silica) surface. Some aqueous solvents, which have the capability of either dissolving the impurities or dissolving the substrate glass to undercut the impurities, have been used to clean glass surfaces. In this work, all the glass parts of the system likely to come into contact with the test solutions were cleaned thoroughly with a Decon solution and acetone. The glassware was also immersed in a concentrated hydrochloride acid solution for 24 hours in order to remove particularly resistant materials such as high vacuum silicon based greases and traces of surfactants and polymers. Once cleaned all of the flasks and reaction vessels were kept in an oven at 240 °C for a few hours prior to use.

3.1.3 Degassing

The gases such as oxygen, carbon dioxide or hydrogen, dissolved in the liquids to be distilled, need to be removed before vacuum distillation can be carried out. The conventional 'freeze - thaw degassing' method was employed for removing the dissolved gases in the work.

The solvent to be degassed stored in the flask as shown in **Fig. 3.2** was frozen using liquid nitrogen in a Dewar vessel placed around the flask. The flask was then evacuated until a vacuum was established. The frozen solvent was then allowed to warm by opening the main tap, resulting in bubble off of the dissolved gasses as the solvent melted or thawed. The same cycle was repeated until the dissolved gas had been removed.

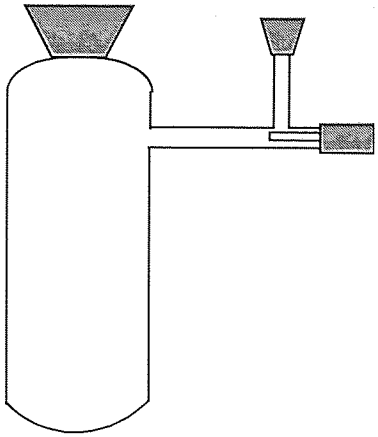


Fig. 3. 2 A solvent flask.

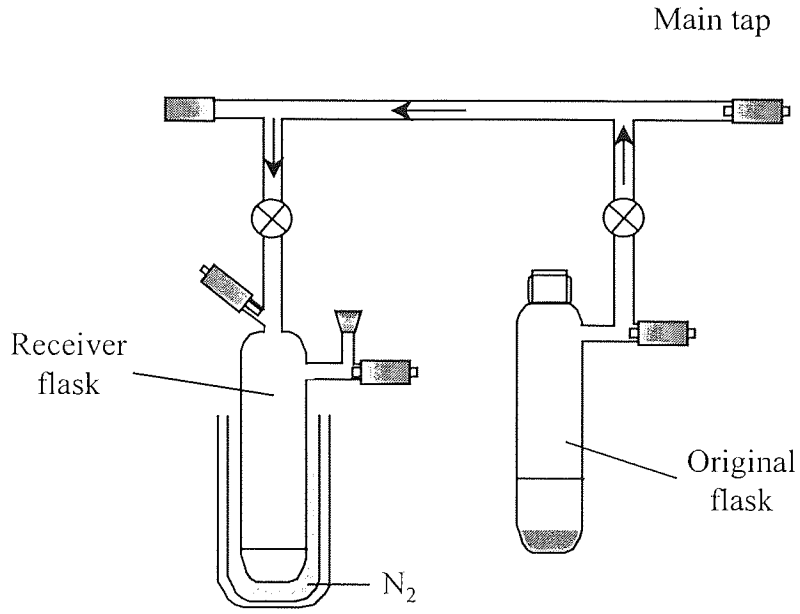


Fig. 3. 3 Vacuum line distillation.

3.1.4 Vacuum distillation

The trap to trap vacuum distillation technique was used to transfer degassed solvent or monomer from a solvent flask to another storage flask (receiver flask) using the vacuum line. As shown in **Fig. 3.3**, the receiver flask was attached to the vacuum line,

evacuated and cooled by immersing into a Dewar vessel filled with liquid nitrogen. The manifold was then isolated from the vacuum pump by closing the appropriate Teflon tapes. The pure dry contents of the original flask were then distilled into the receiver flask by opening the taps between the two flasks in the vacuum system.

3.1.5 Inert gas techniques

Since many of the reactants involved in the cationic polymerization are sensitive to oxygen and moisture, a number of inert gas techniques were employed to prevent their decomposition or reaction with the atmosphere. Argon is the commonly used inert gas for this purpose. It is based on the higher density of argon than air, so that it provides a protective layer of argon gas above the liquid solution and diffuses only slowly through seals. As shown in **Fig. 3.4**, dry argon, supplied by BOC with purity guaranteed less than 3 ppm moisture and oxygen, was introduced into the flasks with the use of a needle through a rubber septum. Known quantities of materials could than be removed by syringe from the storage vessel without contaminating the contents.

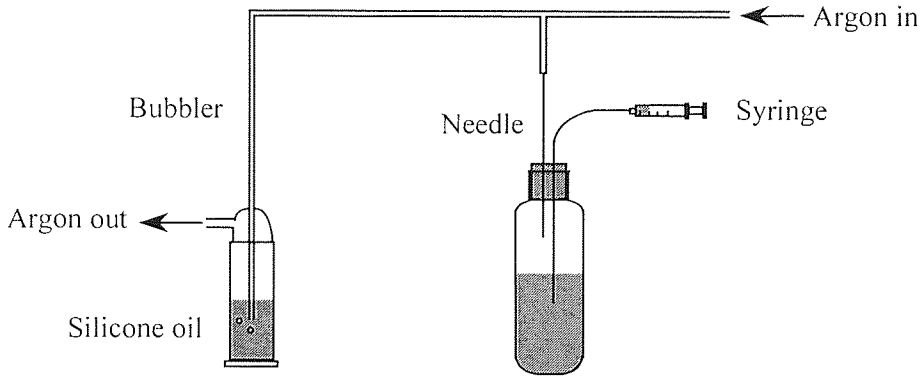


Fig. 3. 4 Inert gas technique.

3.1.6 Schlenk techniques

The Schlenk technique was used in the experiments described in chapter, in which the polymerization time was fixed to three hours. The use of the inert gas technique allowed the handling of monomer and solvents under an inert argon atmosphere

instead of vacuum. The vessels, between which the transfer would take place, were attached to the manifold via Teflon taps. The manifold, and as appropriate the flasks, were evacuated, and followed by isolation from the pumps by means of closing the appropriate taps. Argon was introduced into the line by use of the inert gas techniques. An oil bubbler was employed in order to maintain a positive pressure throughout the process. Having removed the taps to the vessels, a transfer was carried out by the use of a dry syringe.

3.1.7 Glove box techniques

Glove box techniques were used to store and transfer in an inert atmosphere air and moisture sensitive reagents, such as initiators and polymerization solvents. The Halco Engineering Ltd glove box used for this purpose had a recirculation system with argon being as the inert gas. The box maintained a dry argon environment at a positive pressure relative to the surroundings with a constant argon flow of 45 litre per minute through three absorbent columns containing 3 °A molecular sieve, BASF R311 catalyst and BDH activated charcoal. As confirmed by the manufacturer, a moisture level below 5ppm oxygen was achieved by means of the periodically reforming the columns. Flasks, syringes and other equipment were introduced into the glove box by the use of a side port, which was evacuated and purged with argon three times before opening the main door. Furthermore, an Edwards rotary vacuum pump vented to a fume cuppoard was used to evacuate the port, so as to minimise contamination with the outside atmosphere.

3.1.8 Catalyst transfer techniques

A new transfer technique was used to transfer catalyst in the experiments reported in Chapter 5. This involved the use of the Aldrich Sure/Seal™ Value Cap system, as shown in **Fig. 3.5**. With the use of this system, catalysts were handled and stored without exposure to atmospheric moisture or oxygen. The catalyst comes in contact only with glass and Teflon®, yet it was readily transferred using standard syringe techniques.

The standard transfer was readily accomplished by first pressuring the Sure/Seal reagent bottle with dry, high-purity nitrogen following by filling the syringe as illustrated in **Fig. 3.5**. The nitrogen pressure is used to slowly fill the syringe with the desired volume plus a slight excess (to compensate for gas bubbles) of the reagent. The excess reagent along with and gas bubbles is forced back into the reagent bottle. The accurately measured volume of reagent in the syringe was quickly transferred to the reaction apparatus by puncturing a rubber septum on the reaction flask.

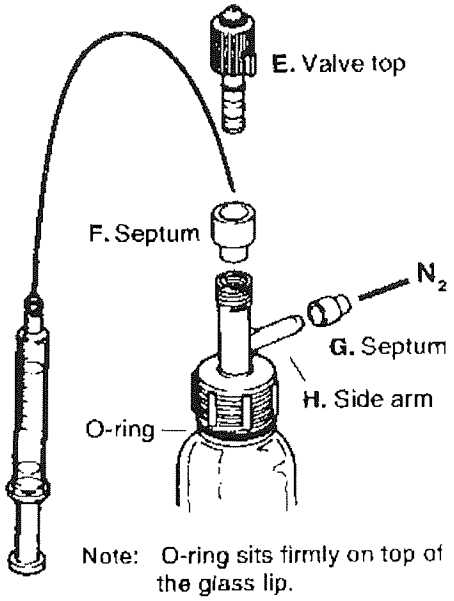


Fig. 3. 5 A solvent flask (Instructions for Aldrich Sure/Seal™ Value Cap system).

3.2 Preparation of materials

3.2.1 Monomer

Styrene monomer was purchased from Aldrich Co. As the commercial styrene monomer contains 4-tert-butylcatechol inhibitor to inhibit polymerization, sodium

hydroxide pellets were mixed with the styrene monomers in a vacuum solvent flask overnight so as to destroy the polymerization inhibitor.

The vacuum distillation technique was used to purify the styrene monomer. Both the original and receiver flasks were dried overnight in an oven at 220 °C prior to use. The styrene monomer stored in the original flask was then distilled under vacuum (as described in Section 3.1.4) into another receiver flask that contained calcium hydride, a drying agent. The styrene was allowed to stand for at least 48 hours to ensure any moisture present had been removed by reaction with CaH_2. The hydrogen evolved was then removed by using the degassing technique (Section 3.1.3). The flask was stored at a temperature below 0°C in a Dewar flask filled with liquid nitrogen in order to prevent polymerization. Finally, the pure monomer was distilled into a polymerization vessel as request.

3.2.2 Initiator

3.2.2.1 1-Phenylethyl chloride (1-PEC)

1-Phenylethyl chloride used as an initiator in the cationic polymerization of styrene monomers, was purchased from Acros. It was stored in the glove box and used without further purification. It was dissolved into in either DCM or a mixture of DCM and cyclohexane, and the resultant solution was transferred to a vacuum vessel using a dry syringe and degassed using the method described in section 3.1.3.

3.2.3 Catalyst (activator)

3.2.3.1 Tin tetrachloride ($SnCl_4$)

Tin tetrachloride having a purity of 99.999%, purchased from Aldrich Co., was used as a catalyst in the cationic polymerization of styrene monomer. To avoid contamination by moisture and oxygen, tin tetrachloride was stored in a dry box and transferred as required using a dry glass syringe. It was then degassed on the vacuum line by the repeated freeze thaw method described in section 3.1.3.

3.2.3.2 Titanium tetrachloride ($TiCl_4$)

Another catalyst used in the styrene cationic polymerization is titanium (IV) chloride ($TiCl_4$) with a purity of 99.999%, which is purchased from Aldrich Co. Again it was stored in a dry box and transferred as required using a dry glass syringe in order to minimise contamination by moisture and oxygen,. It was then degassed on the vacuum line by the freeze thaw method.

3.2.4 Solvents

3.2.4.1 Cyclohexane (C.hex)

Spectrophotometric grade cyclohexane was purchased from Aldrich Co. Before use it was dried and stored over calcium hydride for a period of at least 24 hours. As required it could then be freshly distilled using the method described in section 3.1.4.

3.2.4.2 Dichloromethane (CH_2Cl_2)

Dichloromethane CH_2Cl_2 (high purity grade, 99.9%), obtained from Romil Chemicals Co., was used to mix with cyclohexane to act as the polymerization solvent. Since dichloromethane (DCM) has a greater affinity for water than hydrocarbons, extra precautions were taken, including distillation technique and inert gas technique described in section 3.1.5. DCM was placed in a round bottom flask over calcium hydride and then distilled under an inert atmosphere of argon to prevent moisture contaminating the solvent. **Fig. 3.6** illustrates the scheme of the distillation apparatus. The pure solvent was collected from a still head at the top of a reflux column after a few hours distillation, and the first 25 ml collected was discarded.

3.2.4.3 Methanol

Methanol with S.L.R grade was purchased from Fisons and used as supplied.

3.2.4.4 Iso-propyl alcohol (propan-2-0l)

Iso-propyl alcohol with S.L.R grade was obtained from Fisons and used as supplied.

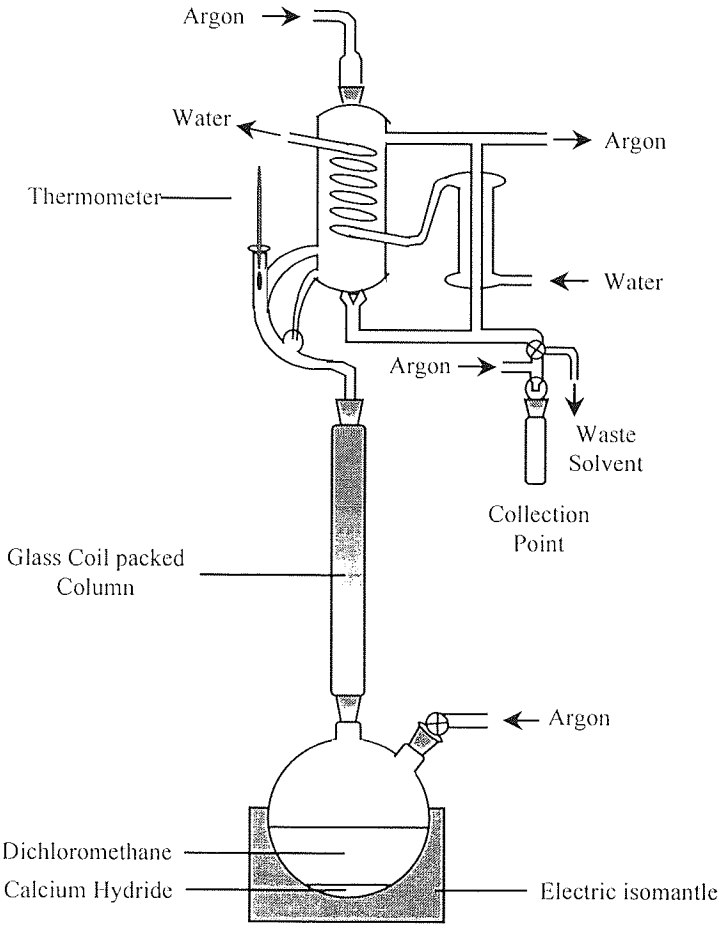


Fig. 3. 6 Distillation apparatus used for the purification of dichloromethane.

3.2.5 Additives

3.2.5.1 Tetra-*n*-butylammonium chloride (nBu$_4$NCl)

Tetra-*n*-butylammonium chloride, 99% purity, purchased from Aldrich Co., was dried under high vacuum at 90 °C prior to be used.

3.2.5.2 Tetra-*n*-butylammonium bromide (nBu$_4$NBr)

Tetra-*n*-butylammonium bromide, $C_{16}H_{36}NBr$, 99% purity, provided by Aldrich Co., was dried under high vacuum at 90 °C prior to be used.

3.2.5.3 $C_{20}H_{44}NBr$, $C_{32}H_{68}NBr$, $C_{28}H_{60}NBr$

Other bromide salts, tetra-*n*-pentylammonium bromide $C_{20}H_{44}NBr$ (nBu$_5$NBr), tetra-*n*-heptylammonium bromide $C_{28}H_{60}NBr$ (nBu$_7$NBr), and tetra-*n*-octylammonium bromide $C_{32}H_{68}NBr$ (nBu$_8$NBr), 99% purity, obtained from Aldrich Co., were dried under high vacuum at 90 °C prior to be used.

3.2.5.4 Pyridine

Pyridine, 99% purity, was purchased from Aldrich Chemicals. It was stored in the glove box and used without further purification. It was dissolved in either DCM or a mixture of DCM and cyclohexane, and the resultant solution was then transferred to a vacuum vessel using a dry syringe and degassed using the method described in section 3.1.3. The desired quantity was injected into the reaction flask using Schlenk techniques.

3.2.5.5 2,6-Di-t-Butyl-Pyridine (DTBP)

2,6-Di-t-Butyl-Pyridine, 99% purity, was purchased from Aldrich Co. Prior to use it was dried under high vacuum at 90 °C and vacuum distilled using conventional apparatus to remove any mono-substituted pyridine. The resulting distillate was stored in the glove box and treated as the un-subsituted pyridine.

3.2.5.6 Calcium hydride (CaH_2)

Calcium hydride, 90-95% purity, 40 mesh, was purchased from Aldrich Chemicals. A 40 mesh powder was found to be the most efficient to dry monomers and solvents such as dichloromethane.

3.2.5.7 Sodium Metal

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

3.2.5.8 Others

Sodium hydroxide pellets (Aldrich Co.) had a purity of 99.99%.

The Gel Permeation Chromatography solvent tetrahydrofuran (hplc grade) was purchased from Fisons Co. It was used to dissolve polymer samples for analysis.

3.3 Polymerization techniques

3.3.1 Procedure

Prior to use solutions of the initiator were prepared. A special vessel, as shown in **Fig. 3.7**, was designed for the polymerization of styrene monomers. It consists of a two armed glass flask fitted with Teflon Rotaflow taps, which used to place initiator, activator and additives such as salts. The flask was dried in an oven overnight at 220 °C prior to use, evacuated on the vacuum line and then filled with argon. The flask A was evacuated and flamed so as to ensure it was free from any residual catalyst.

A solution of the initiator was injected into the flask A using the Schlenk techniques described in section 3.1.6. By means of the inert gas technique, the catalyst (activator) was injected into the flask B under an insert atmosphere in the glove box. This solution was then degassed using the freeze-thaw technique. Pure styrene monomer and solvent were then distilled into the flask A containing the initiator. The flasks were then immersed into Dewar flasks, filled with solid CO_2, allowing them to be kept

at the required temperature. Eventually, the polymerization occurred when mixing the contents of the two flasks and shaking vigorously. The reaction was quenched after a specified period by injection of degassed methanol into the flask using the Schlenk technique.

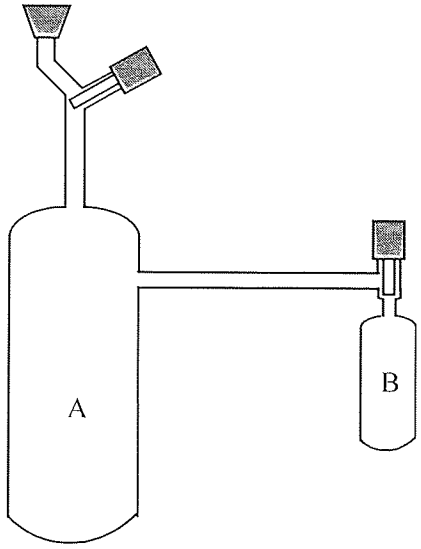


Fig. 3. 7 The polymerization vessel.

3.3.2 Purification of polymer products

Excess methanol was added under an argon atmosphere to the polymerization to precipitate polystyrene from the reaction medium. The polystyrene was filtered from the catalyst residues most of which remained in the solvent phase. Finally the polymer sample was dried to constant weight in a vacuum oven at 40 °C.

3.3.3 Sampling using Schlenk technique

A polymerization was carried out using the method described in Section 3.3.1. To extract a sample of the polymerization, the main tap of the reaction flask was removed whilst argon purged through. A syringe was used to take sample from the reaction system under the atmosphere of argon. The sample was then immediately quenched in methanol. In order to eliminate the risk of introducing impurities with the syringe

needle, the syringe was first dried at 240 °C for two hours to remove all traces of water and was then allowed to cool in argon and stored until to be used.

3.3.4 Sampling using Omnifit fittings

Another vessel was developed to enable the removal of samples during the course of a polymerization (**Fig. 3.8**). The components of the vessel were purchased from Omnifit, and half of a 10mm glass chromatography column was attached to the side of the sampling equipment. The column was connected to a 3-way column bleed valve equipped with Luerlock syringe adaptor.

The polymerization procedure was the same as described in section 3.3.1. The sampling vessel was re-attached to the vacuum line under inert gas once the polymerization was initiated. A desired quantity of the polymer solution was drawn out into the dry syringe after the three way valve was opened. The sample was then injected into methanol immediately by turning the 3-way valve to the correct position. The syringe was then washed with dry solvent in preparation for the next sample without removing the syringe. In this way samples could be taken from a polymerization without contaminating the polymerization mixture.

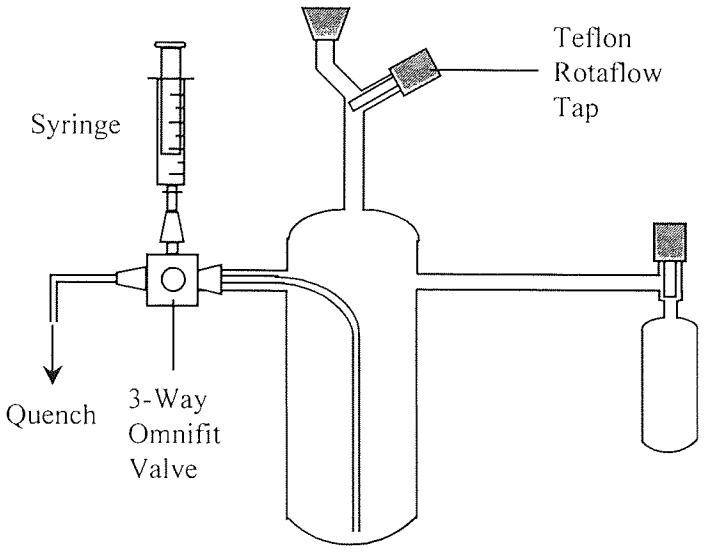


Fig. 3. 8 The polymerization vessel for sampling.

3.4 Analysis of polymer products

3.4.1 Gel Permeation Chromatography

Gel Permeation Chromatography (GPC), also known as Size Exclusion Chromatography (SEC), was used to determine the molecular weight and molecular weight distribution of polymers. The technique is dependent upon fractionation of polymer molecules in the sample according to their sizes. When a solution of the polymer sample passed through a series of columns containing a stationary phase, cross-linked beads possessing pores of different sizes, the polymers with small chains (hydrodynamic volume) entered the relatively small pores and their passage was then slow down. In contrast, large polymer chains eluted more rapidly as they entered fewer pores than molecules with smaller volumes. Therefore the high molecular polymers leave the column first followed by the low molecular weight polymers.

3.4.1.1 Apparatus

Fig. 3.9 shows a schematic of the GPC apparent used. It mainly consists of a series of columns, detectors, a pump and reservoirs. The elutant used for GPC in the project was HPLC grade THF, which was pumped at a rate of 1 ml/min by a Knauer high performance liquid chromatography pump. A 0.5% w/v solution of polymer made up in THF was introduced into the system using a Rheodyne injector in conjunction with a 100 μL loop. Before entering the main columns, the polymer sample was passed first through a 0.5 μm in-line filter and followed by a 5 μm guard column (Polymer Laboratories), in order to remove any particles and prevent blockage in the rest of system. The main gel columns comprised a single bead 10^3 Å μ-PL and a mixed B column. The eluted polymer from the columns was analysed by a Knauer differential refractometer and a ultra-violet detector (UV) in series. The refractometer detects the difference in refractive index between the eluted polymer solution and the eluent, i.e. THF, which is proportional to the concentration of the eluting polymer. Polymers with a chromophoric group (e.g. polystyrene) absorb at a wavelength in the UV region. A data collecting unit (DCU) was used to recorded the outputs from the detectors, and

the data was finally introduced to a personal PC for analysis using PL Caliber® software.

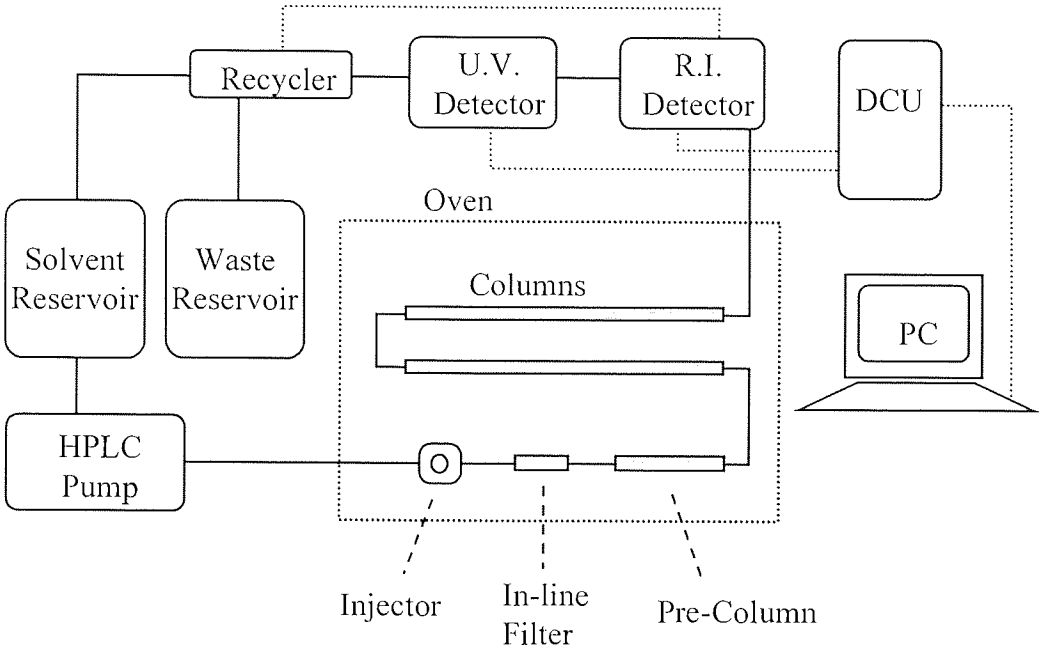


Fig. 3. 9 Schematic of GPC.

3.4.1.2 A sample GPC trace

A typical GPC trace is shown in **Fig. 3.10**, obtained using a differential refractometer as a detector. Since the refractometer detector responds to the difference in refractive index between the eluted polymer solution and the eluent, the height of the trace is proportional to their difference. Assuming the refractive index depends upon the concentration of the polymer only, the weight fraction (W) or concentration of the eluting polymer is related to the difference in refractive index (Δn), and then to the height of the trace (h), given by

$$W \propto \Delta n \propto h \qquad (1)$$

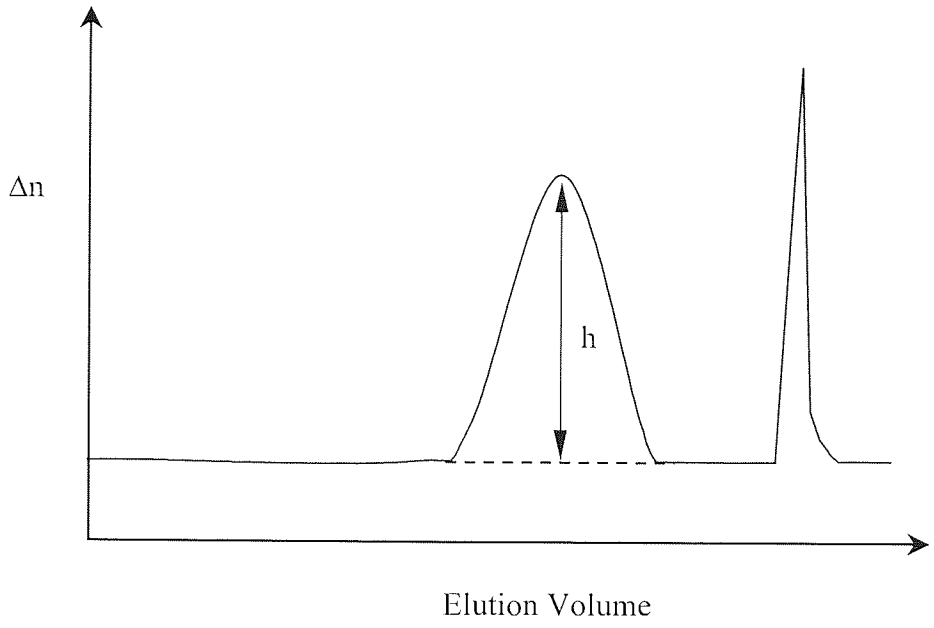


Fig. 3. 10 A typical GPC trace.

3.4.1.3 Determination of molecular weight averages

The number average molecular weight ($\overline{M_n}$) and the weight average molecular weight ($\overline{M_w}$) are defined as

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i} \qquad \overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{2}$$

where N_i is the number of molecules of molecular weight M_i, which can be related to the mass (W_i)of the polymer with molecular weight M_i in the following

$$W_i = \frac{N_i M_i}{N_A} \tag{3}$$

where N_A is the Avogadro constant.

Subsituting Equation (3) into (2), one obtains

$$\overline{M_n} = \frac{\sum W_i}{\sum W_i / M_i} \qquad \overline{M_w} = \frac{\sum W_i M_i}{\sum W_i} \tag{4}$$

Combining Equation (1) into (4) yield

$$\overline{M_n} = \frac{\sum h_i}{\sum h_i / M_i} \qquad \overline{M_w} = \frac{\sum h_i M_i}{\sum h_i} \tag{5}$$

As a consequence, the molecular weights of polymers can be calculated from the height of the GPC trace.

Table 3. 1 Retention times for standard samples with different molecular weights.

M_i	Time (mins)	Log M	Fit ratio
135000	10.79	5.130	1.002
70600	11.13	4.849	0.994
50400	11.45	4.702	1.003
20650	12.29	4.315	1.003
10850	12.97	4.035	0.999
9680	13.08	3.986	0.997
4950	13.85	3.695	0.999
2960	14.41	3.471	1.002
580	15.92	2.763	0.999
162	17.10	2.210	1.000

3.4.1.4 Calibrations of the GPC column

In order to determine molecular weight M_i at any particular volume or time, the columns were calibrated using polystyrene standards of known peak molecular weight (M) ranging from 162 to 135000. The retention times for the different standard samples with various molecular weights are listed in **Table 3.1**, and the calibration curve is shown in **Fig. 3.11**. Toluene is the marker for the GPC. The data were fitted with a curve and the fit ratios are presented in the table as well.

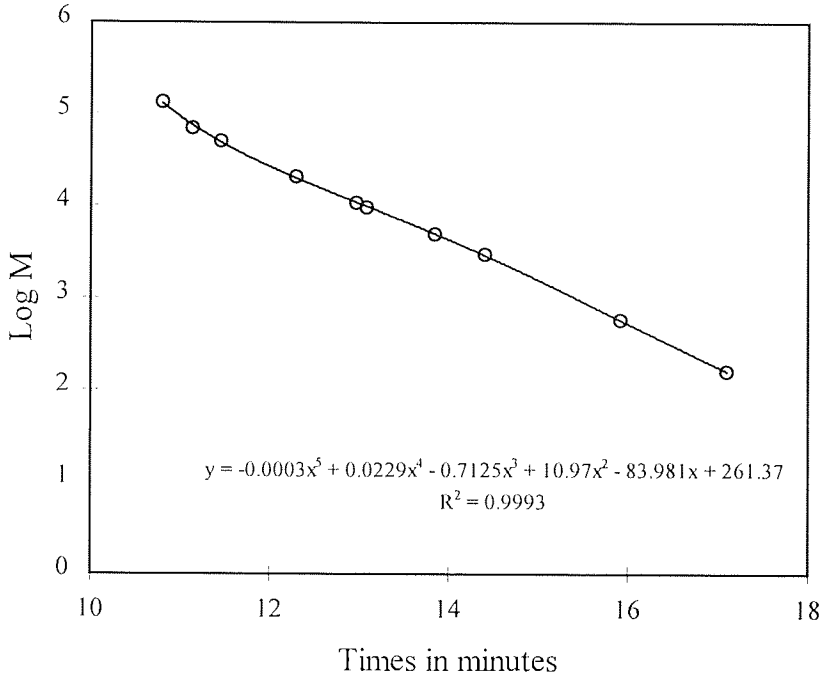


Fig. 3. 11 A calibration curve for GPC.

3.4.2 Nuclear Magnetic Resonance (NMR) spectrometry

A Bruker AC300 spectrometer was employed to characterise the ^{13}C and ^{1}H spectra. Sample solutions were made by dissolving the polymer in deuterated chloroform ($CDCl_3$) with a small quantity of tetramethyl silane (TMS) as reference.

A pulse technique, P.E.N.D.A.N.T ^{13}C spectroscopy, was employed for ^{13}C analysis. There exist some noticeable differences on the conventional ^{13}C spectrum. The signals

corresponding to the carbon atoms are edited positively or negatively, depending on their types of substitution. For example, peaks from the methyl and methine carbons appear as positive peaks, whilst those from methylene and quaternary carbons appear as negative peaks.

The S.P.E.E.D. technique was the another pulsing technique that was used for ^{13}C analysis. During the analysis, the signals corresponding to carbonyl and quaternary carbons were enhanced, and signals from methine, methylene and methyl carbons were decoupled.

Both ^{1}H and ^{13}C spectra were edited on a personal computer using WinNMR software from Bruker.

CHAPTER 4

OPTIMISATION OF POLYMERIZATION OF STYRENE MONOMERS (SCHLENK TECHNIQUE)

4.1 Introduction

Cationic polymerization of styrene monomers has been studied by many authors **[3, 4, 48-51]** using different initiators (BCl_3 **[3, 48]**, $SnCl_4$ **[4, 49-51]**) and solvents (e.g. trichloromethane $CHCl_3$ **[3, 52]**, dichloromethane CH_2Cl_2 **[4, 48-50]**). A living polymerization of styrene has also been reported to be feasible if the initial system and reaction condition were chosen carefully.

In the studies described in this chapter, styrene was chosen as a monomer, 1-phenyl ethylchloride (1-PEC) as an initiator and tin tetrachloride ($SnCl_4$) as a catalyst (activator) in initial experiments on conventional cationic polymerization. A living polymerization of styrene with 1-PEC / $SnCl_4$ initiation systems in the presence of tetra-*n*-butylammonium chloride (nBu$_4$NCl) was then examined. The further aims of the chapter were systematically to study the effects of solvent polarity, temperature, the initial concentrations of salt and catalyst, and initiator initial concentration on the cationic polymerization of styrene monomers with respect to polydispersity, molecular weight distribution (MWD) and initiator efficiency, etc, optimising the conditions under which a living cationic polymerization of styrene could be achieved.

4.2 Cationic polymerization of styrene monomers (St / 1-PEC / $SnCl_4$ / DCM)

Cationic polymerization of styrene (initial concentration 1 M) was carried out with 0.02 M 1-phenyl ethylchloride (1-PEC) and 0.2 M $SnCl_4$ initiating system in a total volume of 50 ml using dichloromethane CH_2Cl_2 (DCM) solvent at a low temperature of -15 °C. A low temperature was chosen in the initial experiments as it is thought to facilitate the maximising of the rate of propagation over the rates of termination and transfer, and hence living nature of conventional cationic polymerization. The reaction time was three hours.

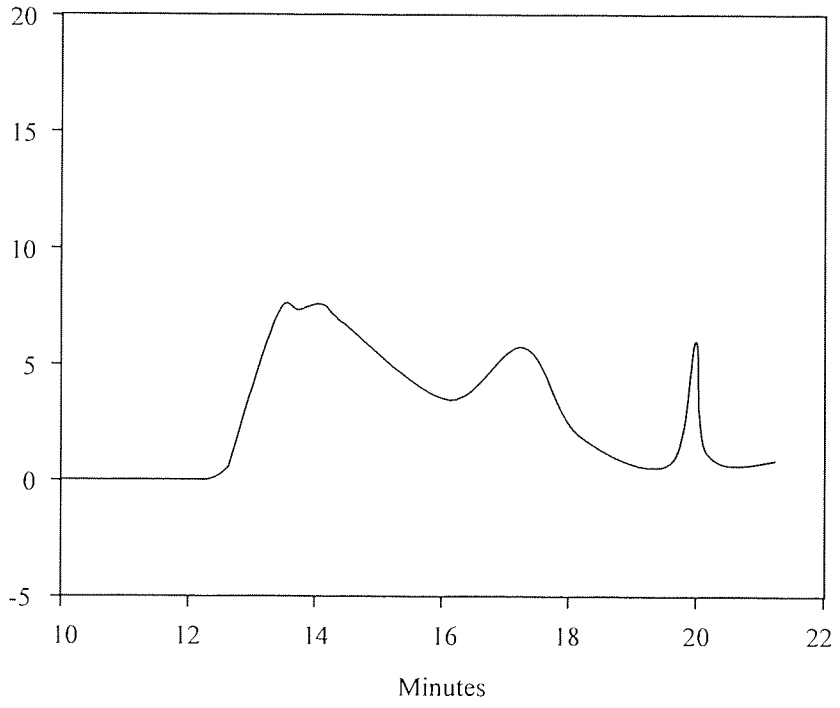


Fig. 4. 1. A GPC trace of polystyrene obtained from the polymerization initiated with 1-PEC / $SnCl_4$ initiating system in DCM at -15 °C.

Fig. 4.1 shows the GPC trace of the polymer obtained with the 1-PEC / $SnCl_4$ initiating system. The peaks before 20 minutes elution time correspond to the polystyrene; the peak at 19.8 minute represents THF solvent. As can be seen from the trace, the molecular weight molecular (MWD) was bimodal with a high polydispersity

($\overline{M_w}/\overline{M_n}$ = 4.059), and consisted of a broad population of high molecular weight polymers and a relatively narrow fraction of low molecular weight polymers. Neither of the fractions appeared to be narrow enough to be considered to from a living system.

It is clear that the polymerization of styrene monomer with 1-PEC / $SnCl_4$ initiating system in DCM solvent at -15 °C shows a typical transfer dominated conventional cationic polymerization, indicated by the high polydispersity (P.D. = $\overline{M_w}/\overline{M_n}$). Such cationic polymerizations have been observed in the polymerizations of styrene initiated with acetyl perchlorate **[37]**, perchloride acid **[101]**, and other oxygen-containing protonic acids **[103]**. The bimodal MWD has been attributed to the coexistence of two growing species (**Fig. 4.2**) that propagate simultaneously but independently of each other **[81]**, of which one results in a high molecular weight (MW) polymer and the other polymers with low MWs.

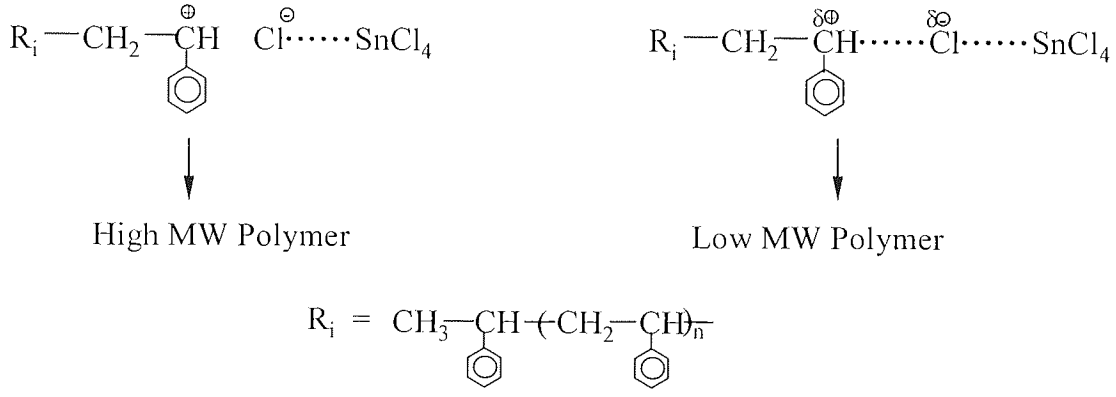


Fig. 4. 2. Coexistence of two growing species for cationic polymerisation of styrene monomer.

4.3 Living polymerization systems (St / 1-PEC / $SnCl_4$ / nBu_4NCl / DCM)

Reports in the literature have shown that living polymerizations can be achieved by the addition of a chloride salt to provide a sufficient concentration of anion ions, which exerts an additional carbocation stabilisation by way of a common ion effect [4]. In the preliminary experiments, 0.005M tetra-*n*-butylammonium chloride, equal to 0.5 per cent of the amount of the styrene monomer, was introduced into the cationic polymerization of styrene monomer system, to determine whether a living styrene polymerization occurs.

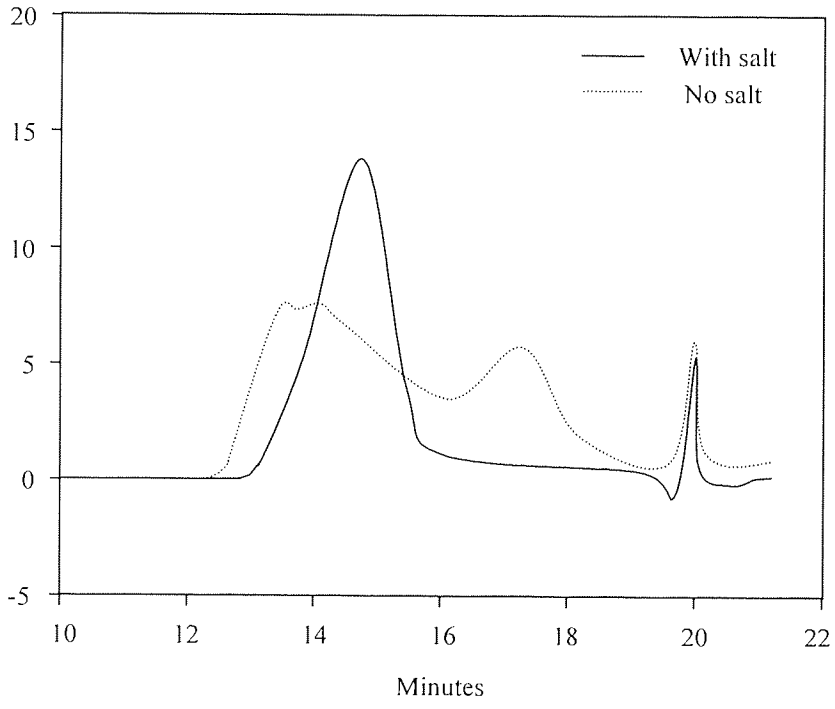


Fig. 4. 3. A GPC trace of polystyrene obtained from the polymerization initiated with 1-PEC / $SnCl_4$ initiating system in DCM at -15 °C in the presence of nBu_4NCl.

Fig. 4.3 shows the GPC traces of the polymer obtained from the polymerization of styrene monomer (initial concentration 1 M) initiated with 0.02M 1-PEC / 0.2M $SnCl_4$ initiating system in dichloromethane at - 15 °C in the presence of 0.005M of nBu_4NCl. As can be seen from the trace, the addition of the salt dramatically

suppressed the formation of the broad population of high molecular weight polymer in the case of polymerization without the salt (**Fig. 4.1**), and resulted in a nearly mono-disperse. The polystyrene obtained had a narrow polydispersity ($\overline{M_w}/\overline{M_n}$ = 1.21), which is indicative of a living styrene polymerization. Due to the experimental difficulties, a value of $\overline{M_w}/\overline{M_n} \leq 1.2$ or 1.3 could be agreed on as a criterion for a 'narrow' molecular weight distribution (Poisson distribution) for a living cationic polymerization **[31]**.

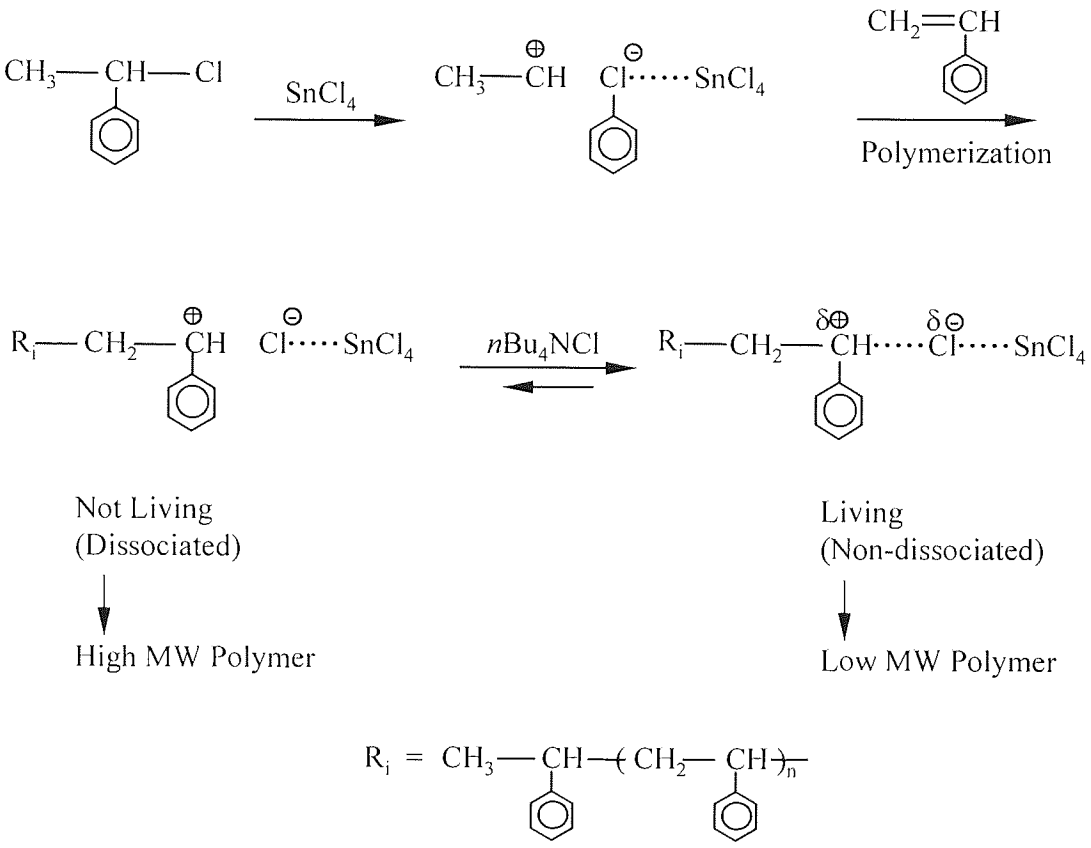


Fig. 4. 4. Reaction scheme for the living cationic polymerization of styrene.

The salt induced living polymerization of styrene can be explained as the nucleophilic stabilisation of the reactive growing carbocation. The reaction scheme for the living cationic polymerization of styrene in the presence of the salt is shown in **Fig. 4.4**. The chloride anion from the initiator (1-PEC) provides a highly nucleophilic counter anion to ensure an effective nucleophilic stabilisation of the growing styryl carbocation. A strong Lewis acid ($SnCl_4$) induces the efficient initiation of a relatively non-reactive

styrene monomer with 1-PEC. In the polymerization the active centre can be presented in several forms as described in section 2.3.2.2. 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 will leads to a broad and possible multi-modal molecular weight distribution.

The added salt capable of complexing with the catalyst produced a sufficient concentration of the chloride anion, which suppressed the formation of the free ionic form in the equilibrium. So that the non-dissociated growing species (in the form of ion pairs) predominated in the presence of the added common ion salt, a neutral salt that has the same anion as that association with the growing carbocation, where the ionic dissociation of carbocationic species is suppressed. Living polymers with a high MW were, therefore, produced.

4.4 Factors affecting styrene living polymerization

4.4.1 Solvent polarity (DCM + C. hex)

As described in section 2.3.2.2 of Chapter 2, the growing species in cationic polymerization are in equilibrium among various dissociation states, and the dissociation of the growing chain end (carbocation ion pairs) depends upon the dielectric permittiving of solvent. Solvent polarity will remarkably affect the rates of cationic polymerization and the molecular weight distribution MWD of the polymers. It is generally recognised that less polar solvents are easier to induce a living polymerization than polar solvents, because of their favouring the less ionised species of the growing chains that lead to a living polymer **[55, 101]**.

Results of the section 4.3 show a living styrene polymerization can be achieved in the presence of a tetra-butylammonium salt in a polar solvent, dichloromethane CH_2Cl_2 (DCM). Less polar solvents, mixtures of dichloromethane and cyclohexane (C.hex),

were used as polymerization solvents, to test the above hypothesis that less polar solvent favour living polymerization. In the presence of 0.005 M of tetra-*n*-butylammonium chloride (nBu$_4$NCl), the polymerizations of styrene monomers (initial concentration 1M) with 0.02 M 1-phenyl ethylchloride (1-PEC) / 0.2 M tin tetrachloride ($SnCl_4$) system were carried out in various solvent mixtures of DCM and C.hex at -15 °C. The main results on the polymerization are summarised in **Table 4.1**, and the reaction time was three hours.

Table 4. 1 Styrene polymerization in mixtures of DCM and C.hex. $[Styrene]_0 = 1M$, $[1\text{-PEC}]_0 = 0.02M$, $[SnCl_4]_0 = 0.2M$, $[n\text{Bu}_4\text{NCl}]_0 = 0.005M$, -15 °C, 3 hours.

CH_2Cl_2 : C.hex (v : v)	M_n	M_w	M_w / M_n (P.D.)	M_n (Calculated)	I_{eff}	Conversion (%)
50 : 0	4770	5777	1.21	4943	1.03	98
40 : 10	3658	4221	1.15	3744	1.02	82.3
30 : 20	2836	3280	1.16	3095	1.09	54.7
20 : 30	1321	1595	1.21	297	0.23	5.7
10 : 40	2351	3419	1.45	131	0.06	2.5
0 : 50	-	-	-	-	-	-

The polydispersity of polymers, P.D. = M_w / M_n, was calculated as the ratio of weight- to number-average molecular weights determined relative to standard polystyrene samples by means of gel-permeation chromatography (GPC). As can be seen from **Table 4.1**, the polydispersities of the product polymers were less than or equal to 1.21 until the ratio of DCM and C.hex was 20 : 30 (v : v), indicating that living polymerizations were still achieved at mixtures of less polar solvent, cyclohexane (C.hex), and DCM. During the polymerization in the mixed solvent with the composition of CH_2Cl_2 and C.hex being 10 : 40 (v : v), solvents appeared non-

transparent or 'cloudy'. This could be the consequence of the formation of deposits in the solvent, because of the low solubility of the initiator, monomer and salt in the less polar solvent mixture. No polymer was produced when the polymerization was carried out in the non-polar solvent, cyclohexane.

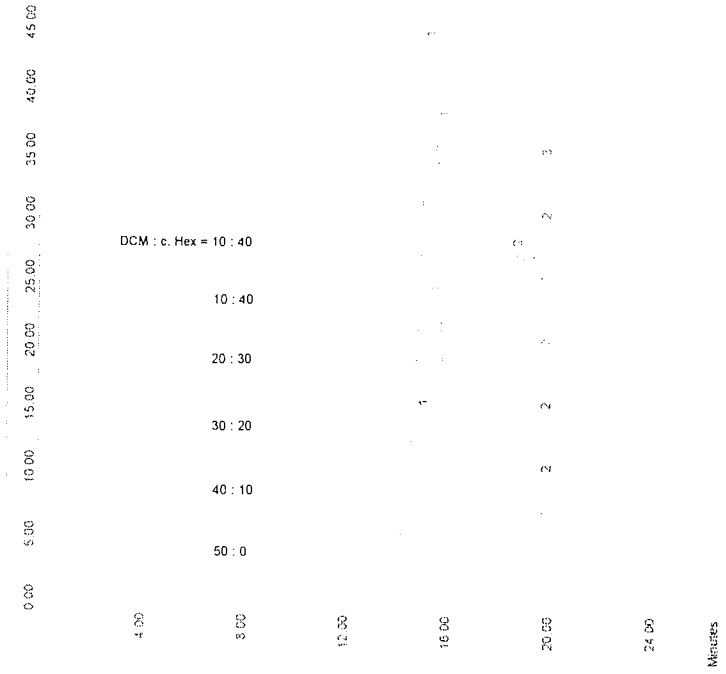


Fig. 4. 5 GPC traces of polystyrenes obtained from the polymerizations initiated with 0.02 M 1-PEC / 0.2 M $SnCl_4$ initiating system at mixtures of DCM and C.hex in the presence of nBu$_4$NCl (0.005M) at -15 °C, reaction time = 3 hrs.

Fig. 4.5 shows the GPC traces of polystyrenes obtained from the polymerizations whose results are given in **Table 4.1**. The peaks between 19 and 22 minute elution time correspond to THF solvent. Polymers had narrow mono-modal molecular weight distributions, provide that ratio of DCM and C.hex was not more than 20 : 30 (v : v), corresponding to the values of polymer polydispersity listed in the **Table 4.1**. A broad molecular weight distribution, probably bimodal indicated by the other small peak close to the solvent peak, was observed for the polymerization in the mix solvent of DCM and C.hex of 10 : 40 (v : v), and the polydispersity was determined using GPC to be 1.45 shown in **Table 4.1**, which is indicative of a non-living polymerization.

The calculation of M_n was based on the assumption that the initiation reaction is rapid and one initiator molecule leads to one propagating active site, so the M_n (Cal.) was calculated by the following expression:

$$\overline{M_n} = \frac{[M]_0}{[I]_0} \times 104.15 \qquad (1)$$

where $[M]_0$ and $[I]_0$ are the initial concentration of the monomer and initiator, respectively, and 104.15 is the molecular weight of styrene. **Fig. 4.6** shows comparison of number average molecular weight (M_n) of polymers, measured with GPC and calculated for the polymerization systems described in the above in solvent mixtures of DCM and C.hex. Both measured and calculated results show that a decrease in solvent polarity by addition of less polar C.hex into DCM reduced M_n for the given reaction period of 3 hours. The reduced M_n can be attributed to the decrease in the rate of polymerization in a less polar solvent. The measured M_n and calculated M_n compared well except for the polymerizations in mixtures of DCM and C.hex with their mix ratios being 20 : 30 and 10 : 40 (v : v). The discrepancies between measured and calculated M_n may be due to measurement errors, since the magnitude of the calculated Mn relied on the weight of the polymer, which was very small for the polymerizations at mixtures of DCM and C.hex of 20 : 30 and 10 : 40 (v : v), respectively.

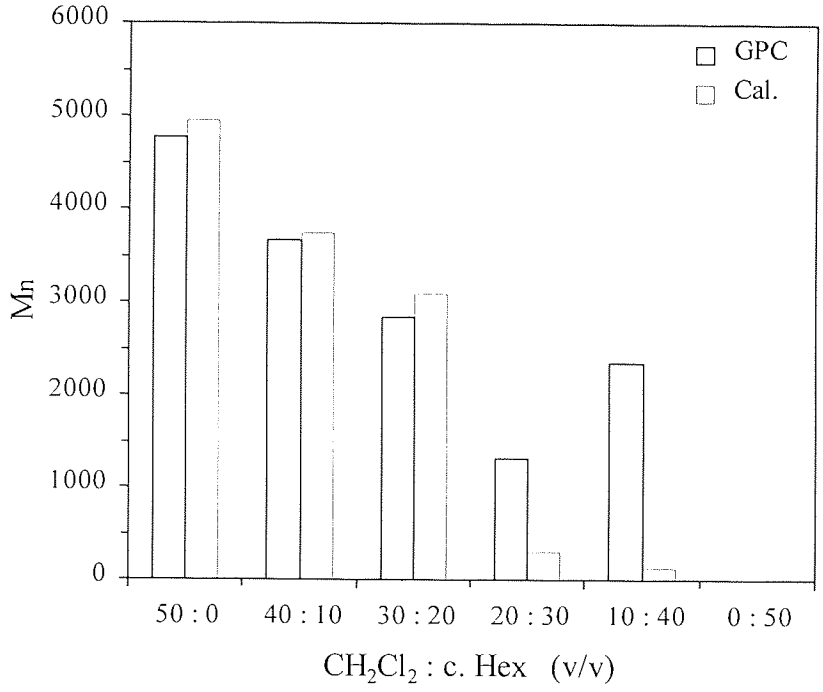


Fig. 4. 6 Number average molecular weights of polystyrenes obtained from the polymerizations initiated with 0.02 M 1-PEC / 0.2 M $SnCl_4$ initiating system at mixtures of DCM and C.hex in the presence of nBu$_4$NCl (0.005M) at -15 °C, reaction time = 3 hrs.

For cationic polymerizations, the conversion can be defined as the weight of the polymer produced divided by the monomer initial weight multiplied by 100. **Fig. 4.7** shows the conversions of the polymerizations in solvent mixtures of DCM and C.hex; and the reaction conditions were described in the second paragraph in this section. The conversions decreased with decreasing the polarity of the solvent, i.e. addition of less polar C.hex. This means the rate of propagation is slow for the polymerizations in less polar solvent. The conversions were observed to be less than 6% when the ratios of DCM and C.hex were 20 : 30 or 10 : 40, indicating a very slow polymerization reaction.

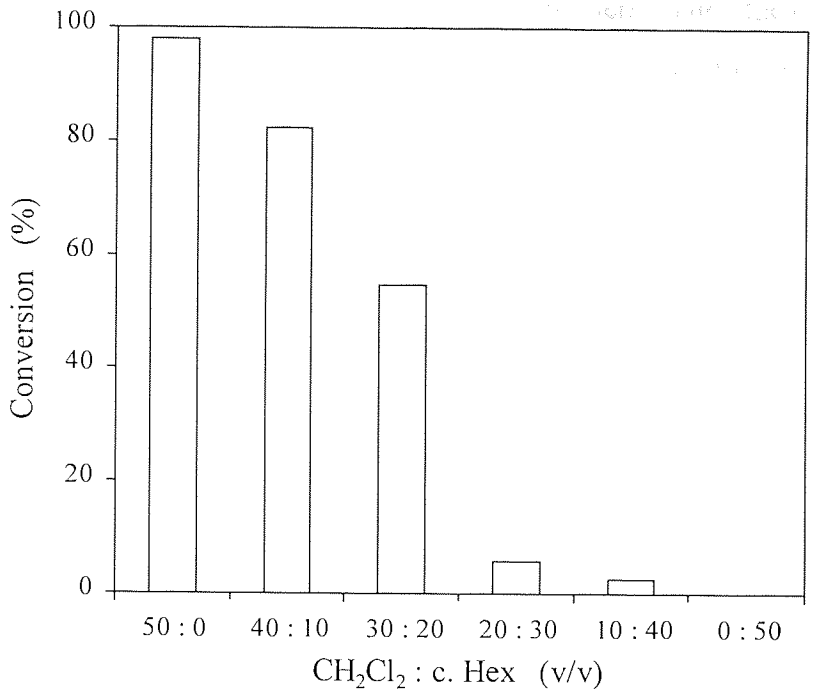


Fig. 4. 7 Conversions of the polymerizations initiated with 0.02 M 1-PEC / 0.2 M $SnCl_4$ initiating system at mixtures of DCM and C.hex in the presence of nBu$_4$NCl (0.005M) at -15 °C, reaction time = 3 hrs.

The efficiency of the cationic polymerization, I_{eff}, was measured as the ratio of the number of polymer molecules generated to the initial concentration of the initiator multiplied by 100. For a living cationic polymerization with one initiator molecule being assumed to lead to one polymer active site or molecule, the initiator efficiency can then be obtained form the ratio of calculated number average molecular weight, M_n (Cal.) to experimental number average molecular weight, M_n (GPC), measured using GPC, as follows:

$$I_{eff} = \frac{M_n(Cal.)}{M_n(GPC)} \qquad (2)$$

Fig. 4.8 shows the dependence of initiator efficiencies of the polymerizations in solvent mixtures of DCM and C.hex. For polymerizations conducted in the mixture solvents with the ratio of DCM and C.hex being not less than 30 : 20 (v : v), the efficiencies of the initiator were observed to be very close to 1, further proved the

living character of the polymerizations of styrene monomers. When the content of less polar C.hex in the solvent mixtures were 60%, the efficiency of the initiator was reduced to about 23%, owing to the experimental errors as the calculated M_n was based on the polymer weight that was very low due to the very low conversion (5.7%). Further reduced solvent polarity resulted in a polymerization with an even lower efficiency of the initiator. This may be related to the non-living characteristics of the polymerization because of a high P.D. (1.45).

Obviously the polarities of solvents had a significant effect on the polymerizations.

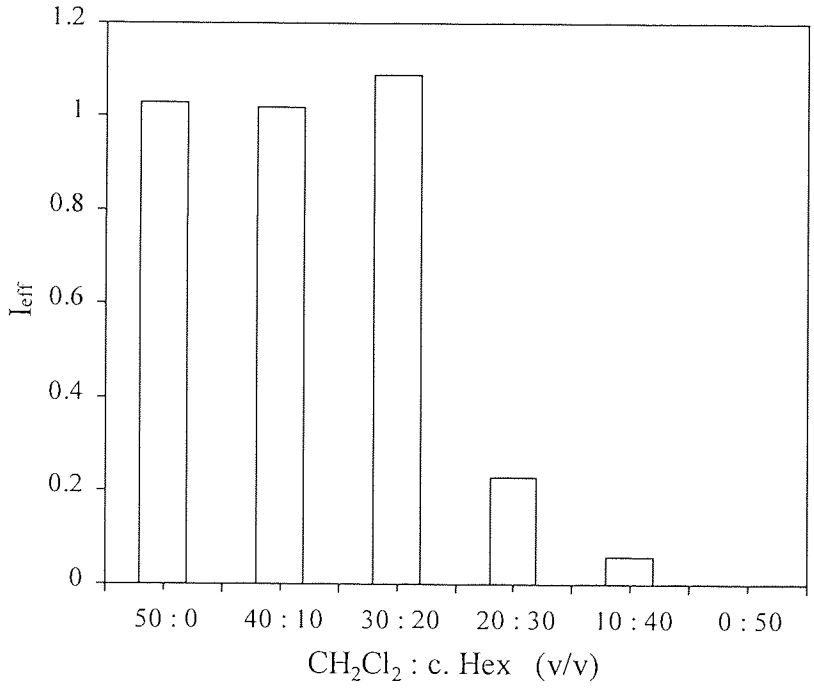


Fig. 4. 8 Initiator efficiencies of the polymerizations initiated with 0.02 M 1-PEC / 0.2 M $SnCl_4$ initiating system at mixtures of DCM and C.hex in the presence of nBu$_4$NCl (0.005M) at -15 °C, reaction time = 3 hrs.

4.4.2 Effect of temperature on cationic polymerization of styrene

Analogous to the polarity of the solvent, the reaction temperature is another factor that can profoundly affect the equilibrium among various dissociation states of the growing species in the cationic polymerization, as described in section 2.3.2.2 of Chapter 2. Low temperatures have been considered to facilitate suppressing of side reactions and render living cationic polymerization possible. This is the reason that the cationic polymerizations of styrene monomers reported in the previous sections were conducted at -15 °C.

Table 4. 2 Dependence of initiator efficiency at various temperatures for styrene polymerization. $[Styrene]_0$ = 1M, $[1\text{-PEC}]_0$ = 0.02M, $[SnCl_4]_0$ = 0.2M, $[n Bu_4NCl]_0$ = 0.005M, DCM : C.hex = 40 : 10 (v : v).

T °C	M_n	M_w	M_w / M_n (P.D.)	M_n (Calculated)	I_{eff}	Conversion (%)
-60	828	2714	1.48	176	0.1	3.1
-45	2072	2515	1.21	1508	0.73	31.4
-30	3193	3701	1.16	2774	0.87	51.9
-15	4818	5476	1.13	4728	0.98	86
0	5202	6134	1.18	5052	0.97	91.2
20	4232	5530	1.31	2939	0.82	60.2

Experiments in the section 4.3 showed a living styrene polymerization can still be achieved in less polar solvents, mixtures of dichloromethane (DCM) and cyclohexane (C.hex) at -15 °C. The reaction temperature was varied to elucidate the effects of temperature on the polymerization of styrene. Polymerizations of styrene, initial concentration 1M, were carried out with the use of 0.02 M 1-PEC / 0.2 M $SnCl_4$ initiating system in the presence of 0.005 M tetra-*n*-butylammonium chloride in the

mixture of DCM and C.hex of 40 : 10 (v : v). Some results are summarised in **Table 4.2** and the GPC traces of polystyrenes obtained from the polymerizations are shown in **Fig. 4.9**. The reaction time was fixed to three hours.

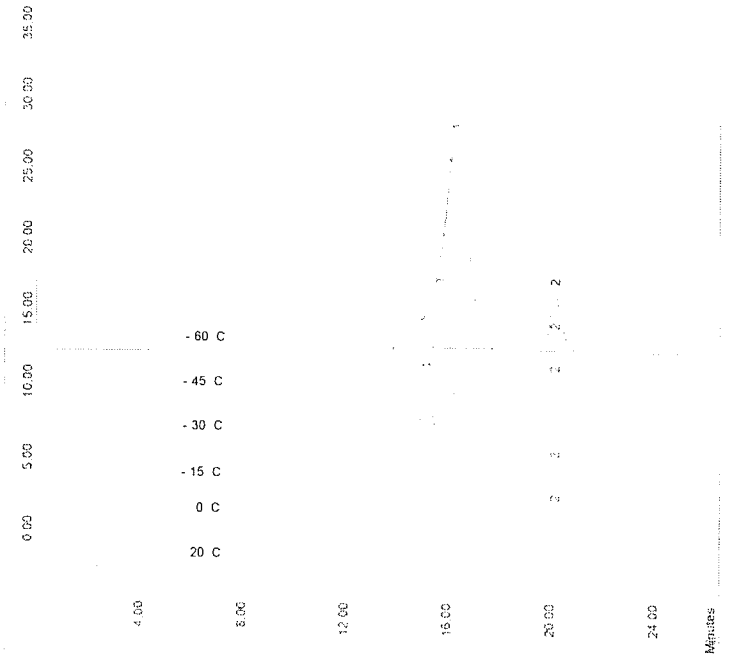


Fig. 4. 9 GPC traces of polystyrenes obtained from the polymerizations initiated with 0.02 M 1-PEC / 0.2M $SnCl_4$ initiating system in the mixture of DCM and C.hex of 40 : 10 (v : v) at different temperatures; $[n\text{Bu}_4\text{NCl}]_0$ = 0.05 M, time = 3 hrs.

At room temperature (20 °C), the polymerization initiated 1-PEC / $SnCl_4$ system with $n\text{Bu}_4\text{NCl}$ in the solvent mixture was shown to be a conventional polymerization with side reactions by the high polydispersity of 1.31. The polymers obtained at temperatures between -45 and 0 °C had very low polydispersities, the values of M_w / $M_n \leq 1.2$, are indicative of a living polymerization. A further lower temperature of -60 °C led to an increase in the polydispersity of polymers (P.D. = 1.48), which is not consistent with the former expectation that low temperatures favour living polymerizations **[33]**. This may possibly have been associated with slow initiation in this case.

As shown in **Fig. 4.9**, narrow mono-modal molecular weight distributions were observed for the polystyrenes obtained from the polymerizations at temperatures from + 20 to - 45 °C, which are another evidence of living polymerization. At - 60 and 20 °C, the polymers had broad MWDS ($\overline{M_w} / \overline{M_n}$ > 1.3), indicating cationic polymerizations with side reactions.

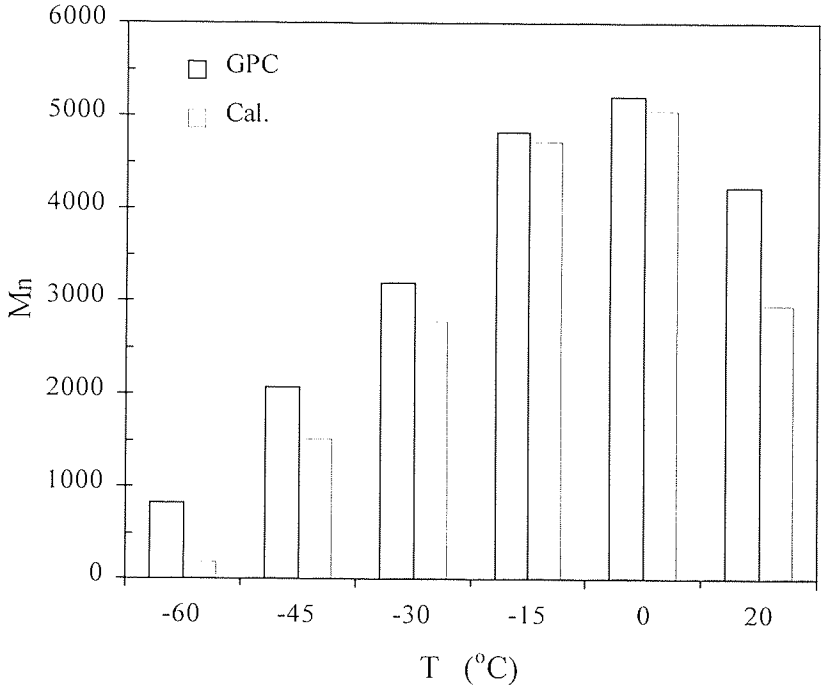


Fig. 4. 10 Number average molecular weights of polymers obtained from the polymerizations at different temperatures: $[Styrene]_0$ = 1M, $[1\text{-PEC}]_0$ = 0.02 M, $[SnCl_4]_0$ = 0.2 M, $[n Bu_4NCl]_0$ = 0.05 M, DCM : C.hex = 40 : 10 (v : v), time = 3 hrs.

Fig. 4.10 shows calculated (Cal.) and experimental (GPC) number average molecular weights (M_n) of polystyrenes obtained from the polymerizations at different temperatures, initiated with 0.02 M 1-PEC / 0.2M $SnCl_4$ initiating system in the mixture of DCM and C.hex of 20 : 30 (v : v); $[n Bu_4NCl]$ = 0.05 M, time = 3 hrs. The number average molecular weights decreased with decreasing temperature except for the temperature of 20 °C. The calculated M_n were fairly comparable to experimental M_n for the temperatures between -45 and 0 °C at which living polymerization occurs; whilst measured M_n differs from calculated M_n when the polymerization was not

living at 20 or – 60 °C. Such difference in M_n may be linked to measurement errors and non-living characters.

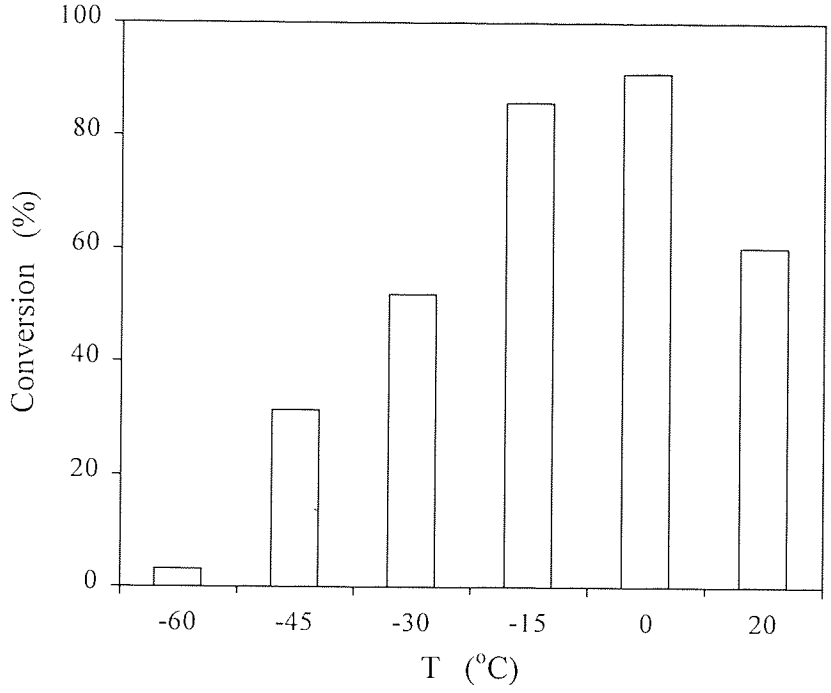


Fig. 4. 11 Conversions of the polymerizations at different temperatures: $[1\text{-PEC}]_0$ = 0.02 M, $[SnCl_4]_0$ = 0.2 M, $[n Bu_4NCl]_0$ = 0.05 M, DCM : C.hex = 40 : 10 (v : v), time = 3 hrs.

Fig. 4.11 shows the conversions of the polymerizations initiated with 0.02 M 1-PEC / 0.2M $SnCl_4$ initiating system in the mixture of DCM and C.hex of 20 : 30 (v : v) at different temperatures; $[n Bu_4NCl]$ = 0.05 M, time = 3 hrs. The conversions for the same reaction times (3 hours) decreased dramatically with the decrease in temperature except at room temperature of 20 °C, which is consistent with the expectation that reducing temperature slows the chain propagation.

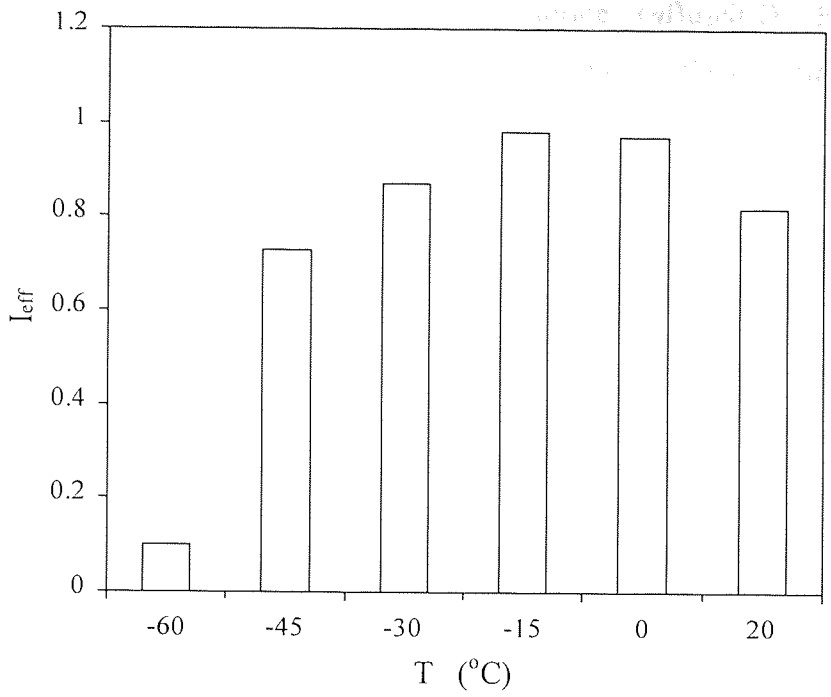


Fig. 4. 12 Initiator efficiencies of the polymerizations at different temperatures: [1-PEC]$_0$ = 0.02 M, [$SnCl_4$]$_0$ = 0.2 M, [nBu$_4$NCl]$_0$ = 0.05 M, DCM : C.hex = 40 : 10 (v : v), time = 3 hrs.

Fig. 4.12 shows the initiator efficiencies of the polymerizations initiated with 0.02 M 1-PEC / 0.2M $SnCl_4$ initiating system in the mixture of DCM and C.hex of 20 : 30 (v : v) at different temperatures; [nBu$_4$NCl] = 0.05 M, time = 3 hrs. For temperatures between -45 and 0 °C, the efficiencies of the initiator were higher than 0.73 but less than one, the theoretical value for a living polymerization; the discrepancies may be results from the experimental errors. A very low efficiency of the initiator was obtained for the non-living polymerization at -60 °C.

As a conclusion, a living polymerization could be achieved in less polar solvent mixtures at temperatures -45 and 0 °C.

4.4.3 The effect of added salt concentration [nBu$_4$NCl] on polymerization

Investigations shows that a living polymerization of styrene can be achieved using 1-phenyl ethylchloride (1-PEC) as an initiator and tin tetrachloride ($SnCl_4$) as a catalyst

in the presence of tetra-*n*-butylammonium chloride (nBu$_4$NCl). For further clarification of the effect of the concentration of the added salt, the polymerizations of styrene (initial concentration 1 M) with 0.02 M 1-PEC / 0.2 M $SnCl_4$ system were carried out in 50 ml of the mixture of dichloromethane (DCM) and cyclohexane (C.hex) with a ratio of 40 : 10 (v : v) at -15 °C in the presence of different concentrations of nBu$_4$NCl. The results for these polymerizations are summarised in **Table 4.3**, for reactions carried out for three hours.

Table 4. 3 Results for styrene polymerization in the presence of nBu$_4$NCl of various concentrations. $[Styrene]_0$ = 1M, $[1\text{-PEC}]_0$ = 0.02 M, $[SnCl_4]_0$ = 0.2 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, time = 3 hrs.

[nBu$_4$NCl] (M)	M_n	M_w	M_w / M_n (P.D.)	M_n (Calculated)	I_{eff}	Conversion (%)
0.001	4199	5040	1.2	3625	0.86	73.5
0.003	4273	5132	1.2	4205	0.98	83
0.008	3496	4090	1.17	3559	1.02	87.3
0.01	4096	4878	1.19	4553	1.11	79.4
0.02	4397	5000	1.13	4202	0.96	80.5
0.03	5009	5860	1.17	4370	0.87	74.6
0.05	5494	6367	1.15	5495	1	84.7
0.06	2725	3241	1.19	3080	1.13	95.6
0.07	3479	4091	1.18	3052	0.88	89.5
0.1	4287	4991	1.16	3906	0.91	88.7

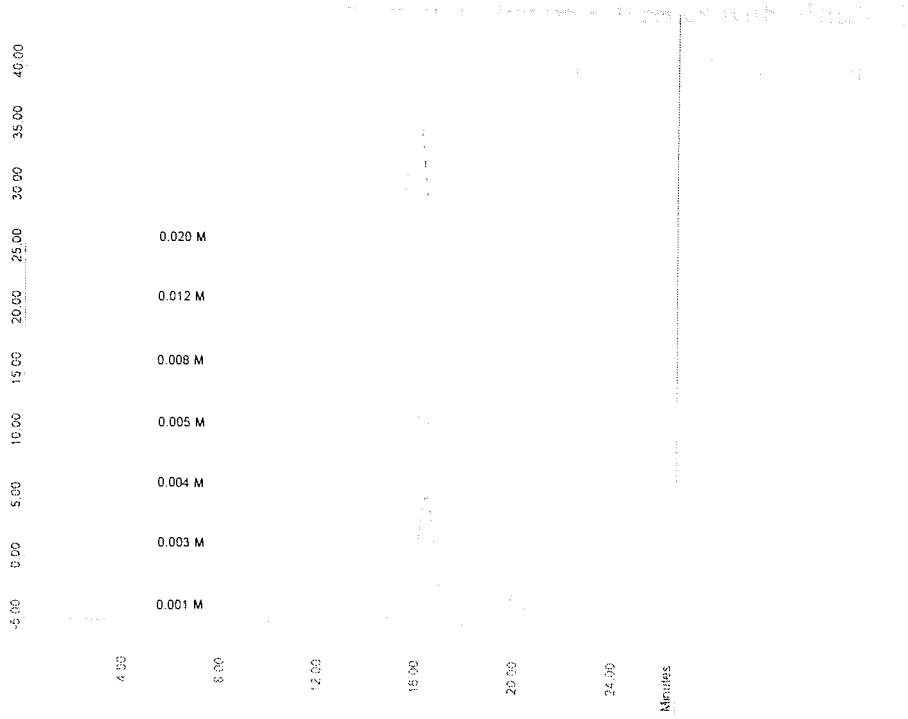


Fig. 4. 13 GPC traces of polystyrene obtained from the polymerizations in the presence of different concentrations of nBu$_4$NCl: [1-PEC]$_0$ = 0.02 M, [SnCl$_4$]$_0$ = 0.2 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, time = 3 hrs.

For all polymerizations listed in Table 4.3 of which the concentrations of nBu$_4$NCl were in the range from 0.001 M to 0.1 M, the polymers obtained had very narrow polydispersities, M_w / M_n ≤ 1.2, which are indicative of a living polymerization. It appears that addition of nBu$_4$NCl renders a living cationic polymerization in the solvent mixture, regardless of the concentrations of the added salt; a trace of the salt e.g. 0.001 M is enough for a living polymerization to be achieved, and the highest concentration used, 0.1 M, did not reach the overdose amount at which the living polymerization could be damped.

Fig. 4.13 shows the GPC traces of the polymer obtained from the polymerization initiated with 1-PEC / SnCl$_4$ initiating system in the mix of DCM and C.hex at -15 °C in the presence of different concentrations of nBu$_4$NCl. Some results are not included in **Table 4.3**. Addition of a small amount of the salt dramatically suppressed the formation of the broad population of high molecular weight polymer in the case of polymerization without the salt (**Fig. 4.1**). Nearly monodisperse, narrow molecular

weight distribution polymers were observed for all of the polystyrenes with nBu$_4$NCl ranging from 0.001 M to 0.2 M, further provide evidence of a living polymerization.

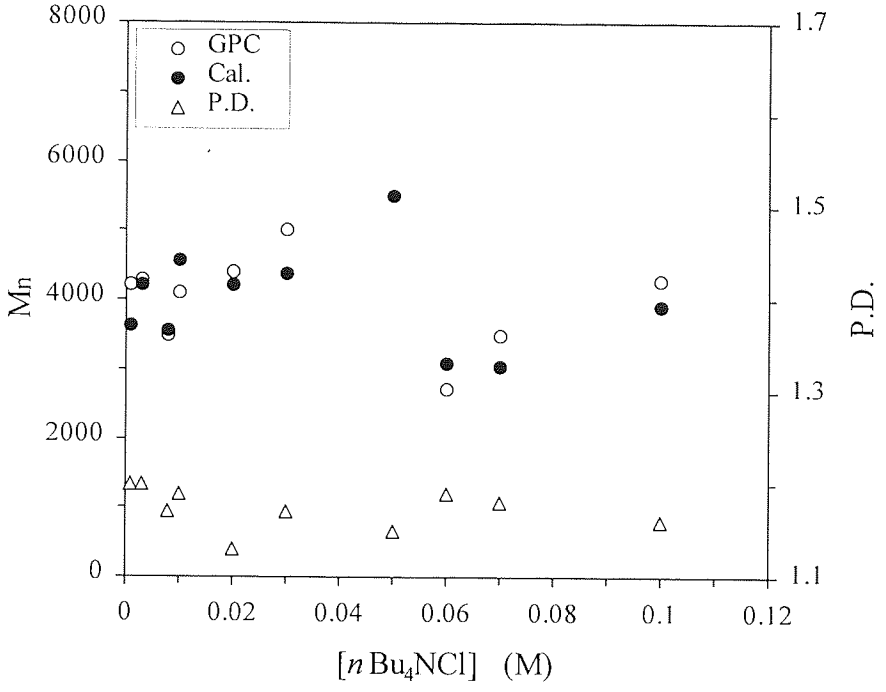


Fig. 4. 14 Number average molecular weights and polydispersity (P.D.) of polymers obtained from the polymerizations in the presence of different concentrations of nBu$_4$NCl: [1-PEC]$_0$ = 0.02 M, [SnCl$_4$]$_0$ = 0.2 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, time = 3 hrs.

Fig. 4.14 shows calculated (Cal.) and experimental (GPC) number average molecular weights (M_n) and the polydispersities (P.D.) of polystyrenes obtained from the polymerizations at different concentrations of nBu$_4$NCl; the polymerization conditions were described in the first paragraph of this section. The calculated M_n was in good agreement with experimental M_n for all polymerizations; although the differences between the M_n's were noticeable.

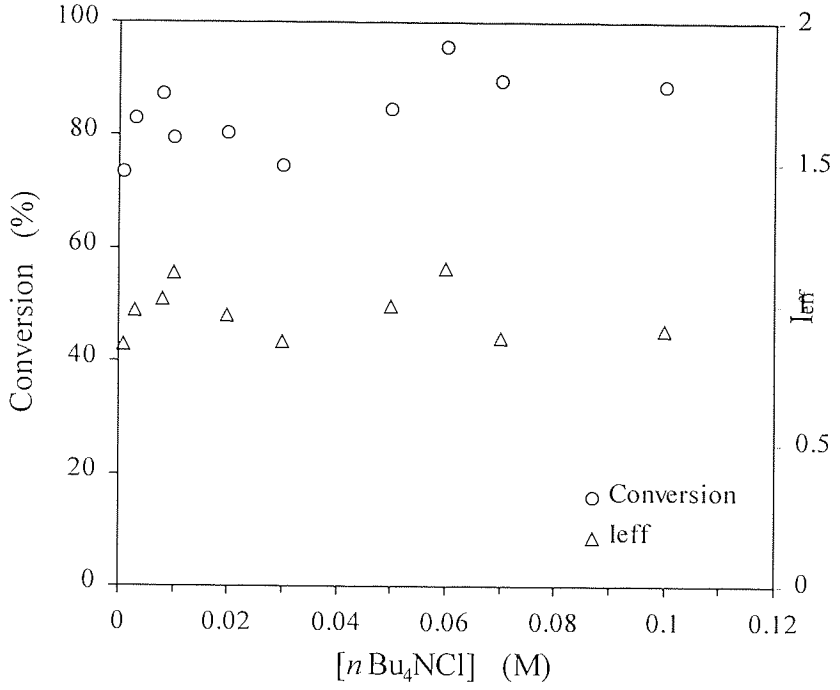


Fig. 4. 15 Conversions and initiator efficiencies of the polymerizations in the presence of different concentrations of nBu$_4$NCl: [1-PEC]$_0$ = 0.02 M, [SnCl$_4$]$_0$ = 0.2 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, time = 3 hrs.

The conversions and the initiator efficiencies of the polymerizations initiated with 0.02 M 1-PEC / 0.2M $SnCl_4$ initiating system in the mixture of DCM and C.hex of 40 : 10 (v : v) in the presence of different concentration of nBu$_4$NCl are shown in **Fig. 4.15**. The conversions for the same reaction times (3 hours) levelled off over the whole range of the concentration of nBu$_4$NCl investigated, indicating that the further excess addition of the salt had no noticeable influence on the rate of polymerization and the salt did not participate in the reaction.

The efficiencies of the initiator were scattered between 0.8 and 1.2 for all of the polymerizations. The discrepancies from the theoretical values, for an ideal living polymerization, may be attributed to experimental errors or the presence of the impurities such as moisture and oxygen for the magnitudes greater than 1.0 **[27]**. However, the possibility of the existence of impurities could be excluded because a number of techniques were employed in this work to prevent the system from contamination, in comparison to the polymerizations reported in the literature **[27]**.

4.4.4 Role of catalyst ($SnCl_4$)

As living polymerizations were achieved in the presence of tetra-*n*-butylammonium chloride (nBu_4NCl) with concentrations ranging from 0.001 M to 0.1 M, an approximately mean concentration i.e. [nBu_4NCl] = 0.02 M was chosen for the remaining experiments. Polymerizations of styrene monomers (initial concentration 1 M) initiating with 0.02 M 1-PEC and different initial concentrations of tin tetrachloride ($SnCl_4$) were conducted in 50 ml of the mixture of DCM and C.hex (40 : 10 (v : v)) at -15 °C for 3 hours; the main results are summarised in **Table 4.4**, and the GPC traces for the polymers obtained from the polymerizations are shown in **Fig. 4.16**.

Table 4. 4 Styrene polymerizations initiated with various concentrations of the catalyst. $[Styrene]_0$ = 1M, $[1\text{-PEC}]_0$ = 0.02 M, $[nBu_4NCl]_0$ = 0.02 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, 3 hrs.

$[SnCl_4]$ (M)	M_n	M_w	M_w / M_n (P.D.)	M_n (Calculated)	I_{eff}	Conversion (%)
0.05	1662	1947	1.17	1118	0.67	20.8
0.1	3408	3931	1.15	3176	0.85	49.3
0.15	4149	4837	1.16	4201	1.01	73.9
0.2	4397	5000	1.13	4202	0.96	80.5
0.3	5404	6203	1.15	4965	0.92	89.7
0.4	7060	8132	1.15	5624	0.8	93.9

All polymerizations produced polymers with very narrow polydispersities, $M_w / M_n < 1.2$, corresponding to the near mono-dispersity narrow molecular weight distributions MWDs observed for different concentrations of the catalyst (**Fig 4.16**). It would seem

that the polymerizations were living independent of the concentration of $SnCl_4$. This would suggest that the catalyst did not affect the nature of the products.

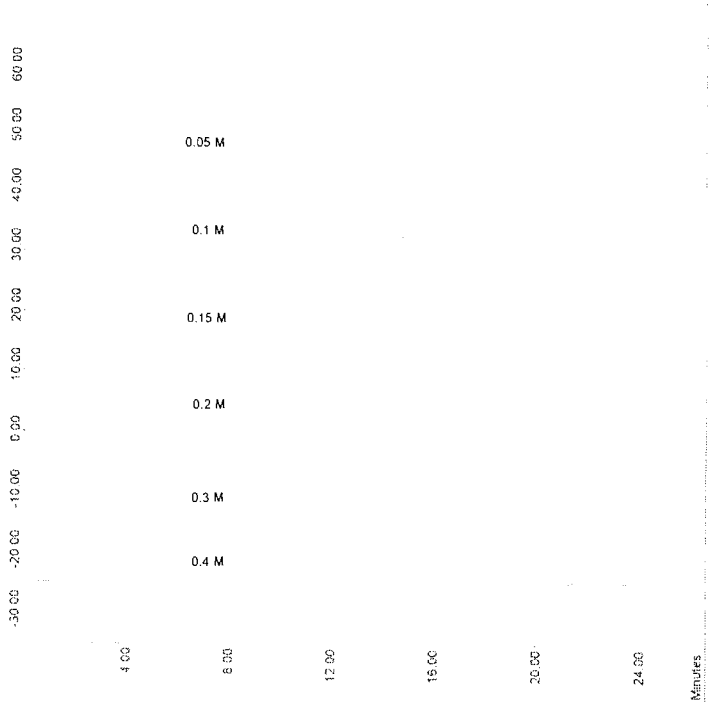


Fig. 4. 16 GPC traces of polymers obtained from the polymerizations initiated with various concentrations of $SnCl_4$: $[1\text{-PEC}]_0$ = 0.02 M, $[n\text{Bu}_4\text{NCl}]_0$ = 0.02 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, 3 hrs.

The calculated (Cal.) and experimental (GPC) number average molecular weights, the polydispersities and conversions for the polymerizations initiated with $SnCl_4$ of various concentrations are shown in **Figs. 4.17** and **4.18**, respectively. The experimental values of M_n agreed well with calculated values of M_n, especially at higher concentrations of $SnCl_4$. The molecular weights and the conversion increased gradually with increasing catalyst concentration. This is consistent with the expectation that an increase in catalyst concentration would accelerate polymerization and result in an increase in conversion for a specific period.

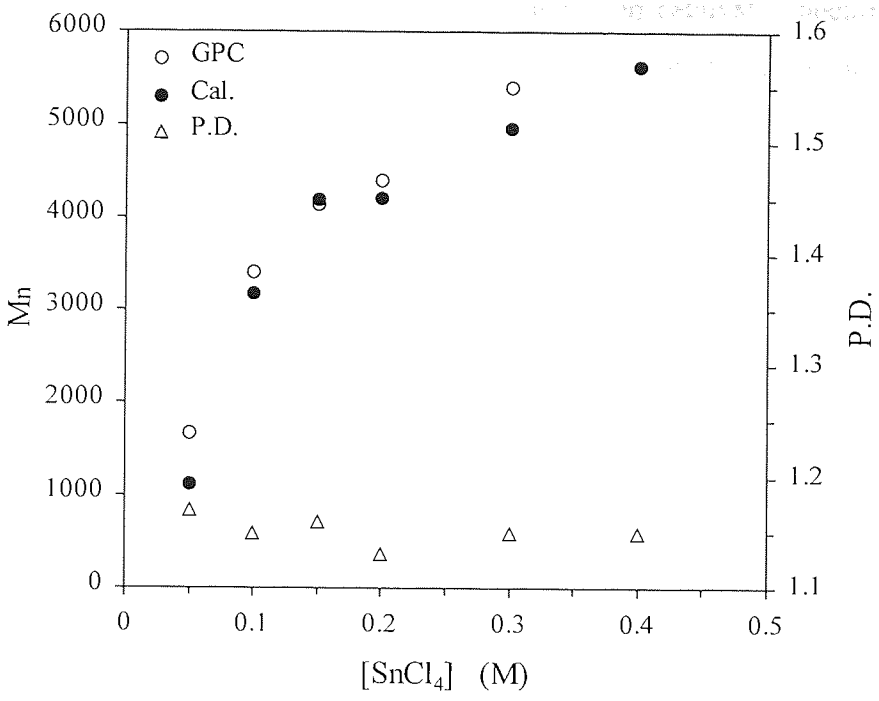


Fig. 4. 17 M_n's and P.D. of polymers obtained from the polymerizations initiated with various concentrations of $SnCl_4$: $[1\text{-PEC}]_0$ = 0.02 M, $[n\text{Bu}_4\text{NCl}]_0$ = 0.02 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, 3 hrs.

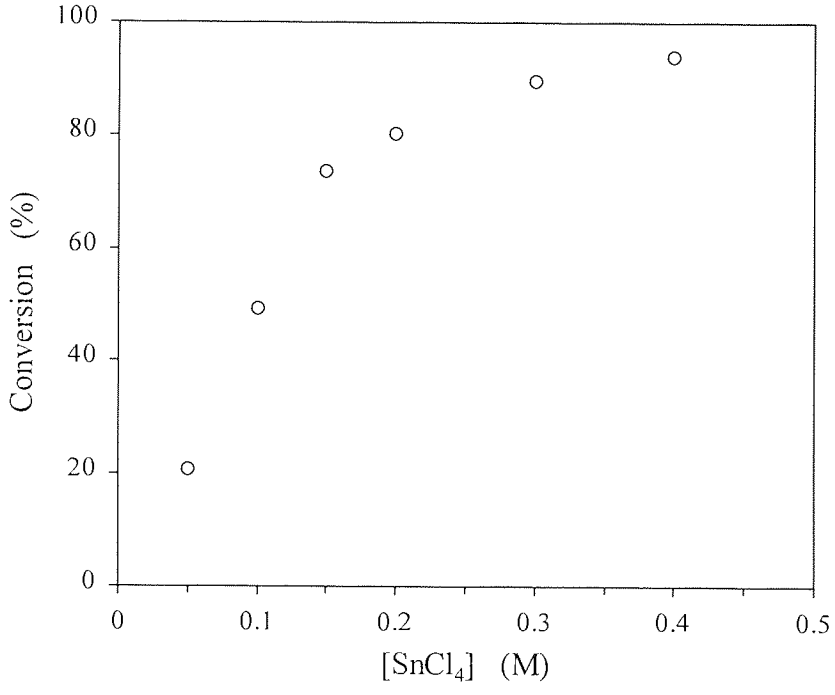


Fig. 4. 18 Conversions of the polymerizations with the same conditions as **Fig. 4.17**.

Fig. 4.19 shows the dependence of initiator efficiency on catalyst concentration. No clear dependence of the efficiencies of the initiator on catalyst concentration was found, the efficiencies were in the range of 0.6 to 1.0.

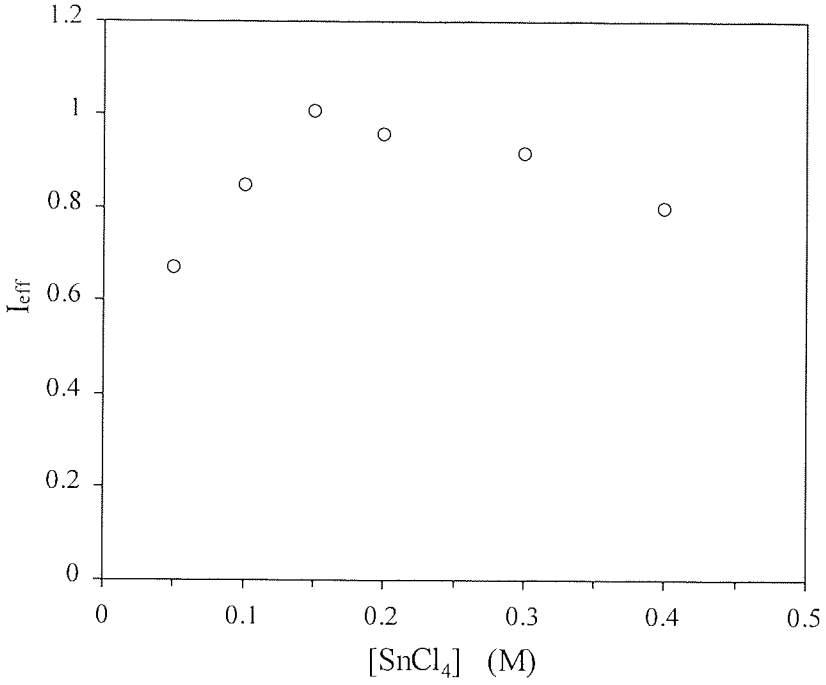


Fig. 4. 19 Initiator efficiencies of the polymerizations with the same conditions as **Fig. 4.18.**

Similar results (**Table 4.5**) and trends with respect to number average molecular weights, conversion, polydispersity and initiator efficiency were found for the styrene polymerizations conducted under the same conditions as the above except for the ratio of DCM to C.hex in which was chosen as 30 : 20 (v : v). It was indicated living polymerizations for the various catalyst concentration. It can be concluded that the catalyst plays a role in accelerating polymerization without affecting the characteristics of the polymers.

Table 4. 5 Styrene polymerizations initiated with various concentrations of the catalyst at mixtures of DCM and C.hex (30 : 20 (v : v)). $[Styrene]_0$ = 1M, $[1\text{-PEC}]_0$ = 0.02 M, $[n\text{Bu}_4\text{NCl}]_0$ = 0.02 M, -15 °C, 3 hrs.

$[SnCl_4]$ (M)	M_n	M_w	M_w / M_n (P.D.)	M_n (Calculated)	I_{eff}	Conversion (%)
0.05	1417	1700	1.2	112	0.08	3.6
0.1	1680	1930	1.15	833	0.5	15.3
0.2	2836	3280	1.16	3095	1.09	54.7
0.3	2678	3091	1.15	2192	0.82	36.6
0.4	4350	4984	1.15	3020	0.69	56

Table 4. 6 Styrene polymerizations initiated with various concentrations of the 1-PEC. $[SnCl_4]_0$ = 0.2 M, $[n\text{Bu}_4\text{NCl}]_0$ = 0.02 M, DCM : C.hex = 30 : 20 (v : v), -15 °C, 3 hrs.

[1-PEC] (M)	DP_n	M_n	M_w	M_w / M_n (P.D.)	M_n (Calculated)	I_{eff}	Conversion (%)
0.007	142	3549	4039	1.14	3712	1.05	25
0.01	99.9	3393	3856	1.14	2993	0.88	28.8
0.02	54	2836	3280	1.16	3095	1.09	54.7
0.04	33.7	2589	3031	1.17	2651	1.02	75.4
0.05	22.3	2116	2445	1.16	2167	1.02	93.5

4.4.5 Effect of concentration of initiator [1-PEC]

In cationic polymerization initiation, initiation plays a very important role in determining if the polymerization will be living. To investigate the effect of the initial concentration of the initiator, polymerizations of styrene monomers (1M) initiated with different concentrations of 1-phenyl ethylchloride (1-PEC) and 0.2 M $SnCl_4$ were then examined; $[n\text{Bu}_4\text{NCl}]_0$ = 0.02 M, DCM : C.hex = 30 : 20 (v : v), -15 °C, 3 hours. The results are summarised in **Table 4.6**, and the GPC traces for the polymers obtained from the polymerizations are shown in **Fig. 4.20**.

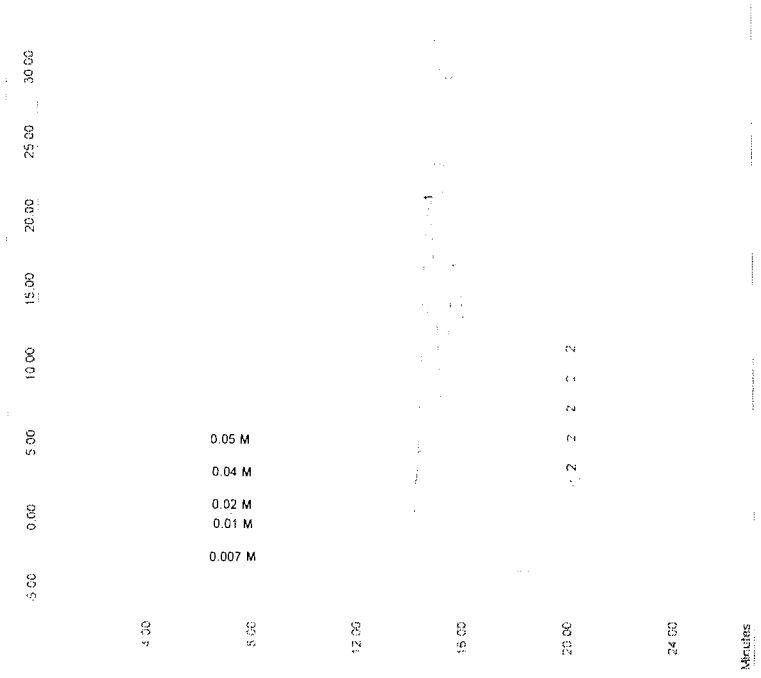


Fig. 4. 20 GPC traces of polymers obtained from the polymerizations initiated with various concentrations of 1-PEC: $[SnCl_4]_0$ = 0.2 M, $[n\text{Bu}_4\text{NCl}]_0$ = 0.02 M, DCM : C.hex = 30 : 20 (v : v), -15 °C, 3 hrs.

In spite of different concentration of the initiator, the induced polymers had very narrow polydispersities, $M_w / M_n < 1.2$, which is indicative of a living polymerization process. The corresponding GPC showed near mono-dispersity and narrow molecular weight distributions MWDs for all reactions (**Fig 4.20**).

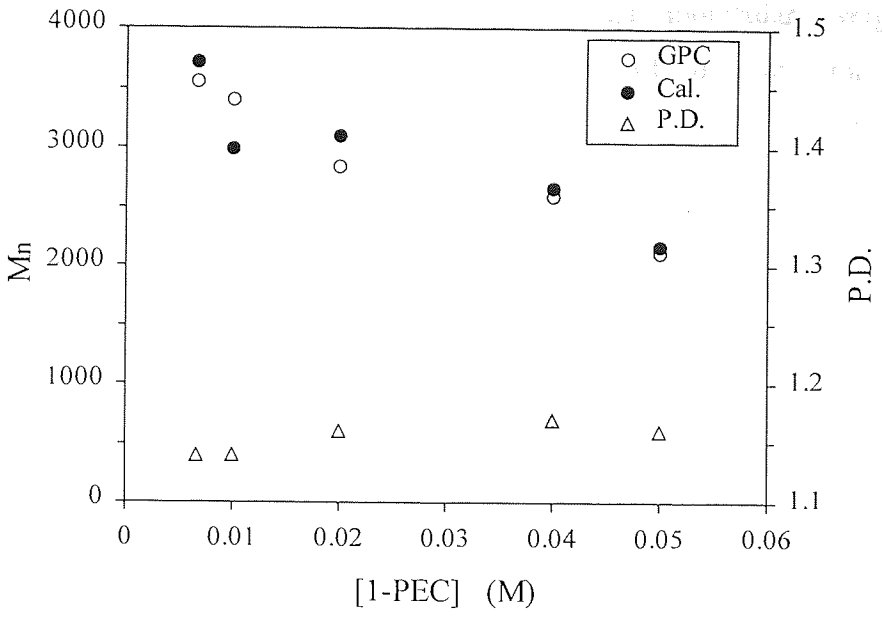


Fig. 4. 21 Number average molecular weights and polydispersity (P.D.) of polymers obtained from the polymerizations initiated with various concentrations of 1-PEC: $[SnCl_4]_0$ = 0.2 M, $[nBu_4NCl]_0$ = 0.02 M, DCM : C.hex = 30 : 20 (v : v), -15 °C, 3 hrs.

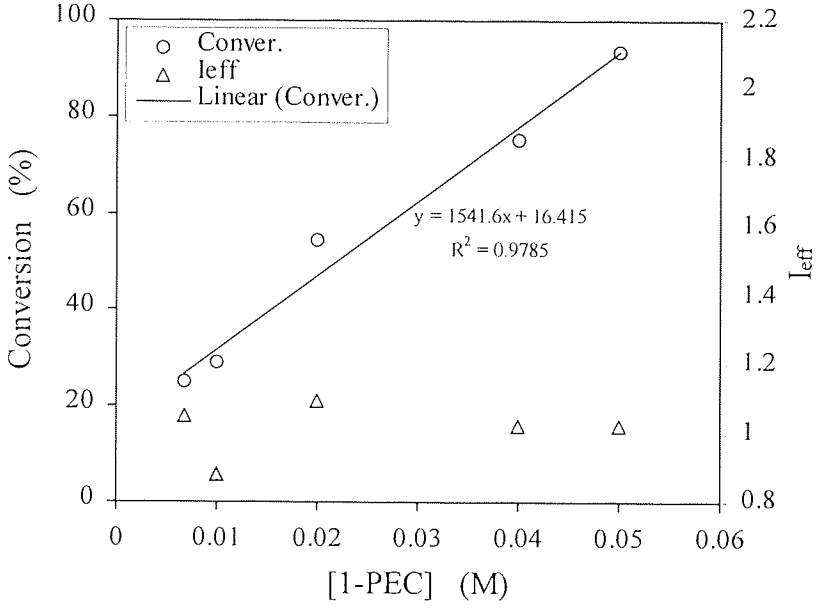


Fig. 4. 22 Conversions of the polymerizations initiated with various concentrations of 1-PEC: $[SnCl_4]_0$ = 0.2 M, $[nBu_4NCl]_0$ = 0.02 M, DCM : C.hex = 30 : 20 (v : v), -15 °C, 3 hrs.

Figs. 4.21 and **4.22** shows the number average molecular weights, the polydispersities, conversions and the efficiencies of the initiator for the polymerizations initiated with 1-PEC at various concentrations respectively. The molecular weights decreased linearly with increasing initiator concentration, which would suggest that the initiation is rapid compared to chain propagation and high initial concentration of 1-PEC would lead to a greater number of active sites and lower MW. The % conversions observed after the 3 hours increased linearly with the concentration of 1-PEC, and fit a linear relation with a very high fitness (R^2 = 0.98). The efficiencies of the initiator were found to be nearly close to unity, the theoretical value except for [1-PEC] = 0.01 M in which I_{eff} was 0.88 (seems error).

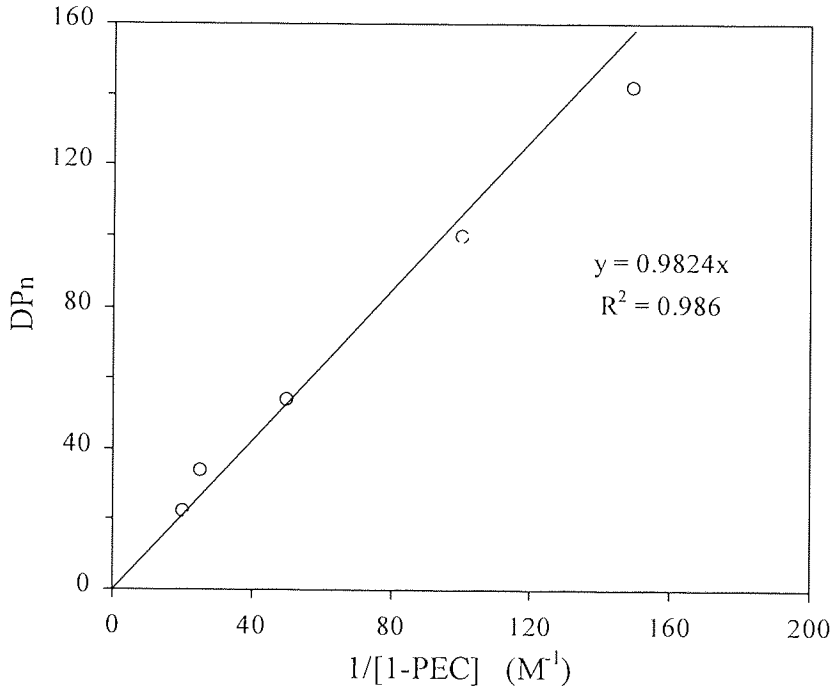


Fig. 4. 23 The degree of polymerization for the polymerizations initiated with various concentrations of 1-PEC: $[SnCl_4]_0$ = 0.2 M, $[nBu_4NCl]_0$ = 0.02 M, DCM : C.hex = 30 : 20 (v : v), -15 °C, 3 hrs.

If a polymerization is to be described as living, the number average degree of polymerization (DP_n) should be proportional to the inverse of the initial concentration of the initiator, as represented by Equation (13) in section 2.3.3.2 of Chapter 2. A linear dependency of DP_n on the initiator concentration was found for the

polymerizations studied above (**Fig. 4.23**), and the plot of DP_n against 1/[1-PEC] passed through the origin. Such findings further proved that the polymerizations were living.

Table 4. 7 Styrene polymerizations initiated with various concentrations of the 1-PEC with [nBu$_4$NCl] = 0.005 M at mixtures of DCM and C.hex (40 : 10). $[SnCl_4]_0$ = 0.2 M, -15 °C, 3 hrs.

[1-PEC] (M)	DP_n	M_n	M_w	M_w / M_n (P.D.)	M_n (Calculated)	I_{eff}	Conversion (%)
0.005	209.7	6371	7223	1.13	6739	1.06	30.9
0.01	86.6	4933	5535	1.12	5343	1.03	59.3
0.02	50	4818	5476	1.13	4728	0.98	86
0.03	31.7	3405	3931	1.15	3020	0.89	91.5
0.04	25	2730	3274	1.2	2682	0.98	100

Table 4.7 lists the results for the polymerizations conducted on the similar conditions as **Table 4.6** except for the ratio of DCM to C.hex in which was chosen as 40 : 10 (v : v) and [nBu$_4$NCl]$_0$ = 0.005 M. The similar influences of the initiator concentration on the polymerization were found.

4.4.6 Monomer initial concentration

The effect of varying the initial concentration of monomer was studied using 1-phenyl ethylchloride (1-PEC) as an initiator and tin tetrachloride ($SnCl_4$) as a catalyst in the presence of tetra-n-butylammonium chloride (nBu$_4$NCl) in the mixture of DCM and C.hex at -15 °C for 3 hours. The initial conditions were: $[1\text{-PEC}]_0$ = 0.01 M, $[SnCl_4]_0$ = 0.3 M, [nBu$_4$NCl]$_0$ = 0.005 M, DCM : C.hex = 40 : 10 (v : v). The results of these studies are given in **Table 4.8**, **Figs. 4.24** and **4.25**.

Table 4. 8 Polymerizations of styrene monomers of varying concentrations. [1-PEC]$_0$ = 0.01 M, [$SnCl_4$]$_0$ = 0.3 M, [nBu$_4$NCl]$_0$ = 0.005 M, DCM : C.hex = 40 : 10 (v : v), , -15 °C, 3 hrs.

[Styrene] (M)	M_n	M_w	M_w / M_n (P.D.)	M_n (Calculated)	I_{eff}	Conversion (%)
0.75	6057	6843	1.13	7113	1.17	87.3
1	7532	8660	1.15	8228	1.09	79
1.5	9887	11339	1.15	12498	1.26	86.8
2	10686	12336	1.16	13019	1.22	70

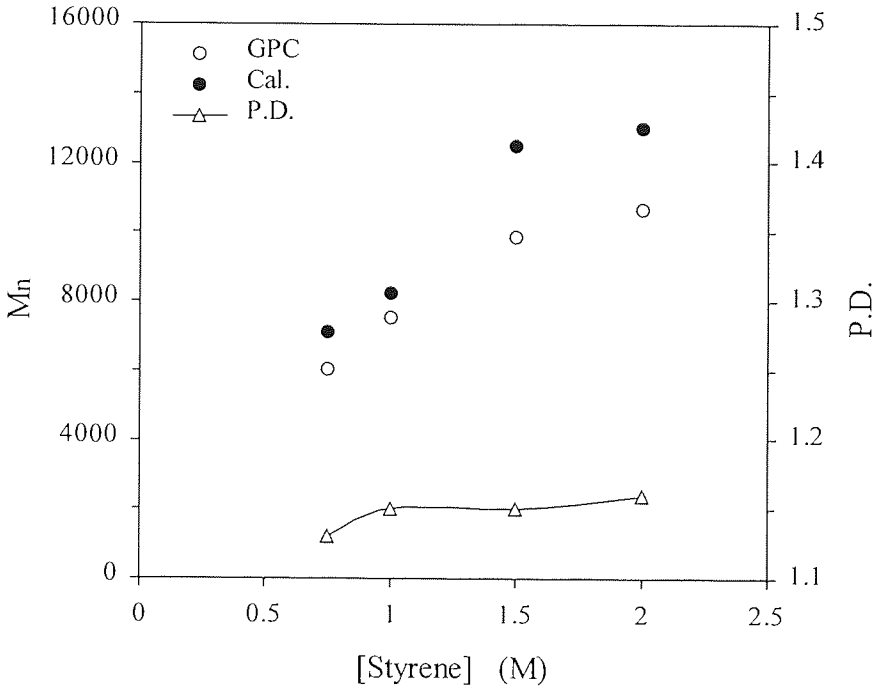


Fig. 4. 24 Number average molecular weights and polydispersities for the polymerizations of styrene of varying concentrations: [1-PEC]$_0$ = 0.01, [$SnCl_4$]$_0$ = 0.3 M, [nBu$_4$NCl]$_0$ = 0.005 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, 3 hrs.

According to the reaction scheme, an increase in the monomer initial concentration accelerates propagation, resulting in an increase in molecular weight, as demonstrated by the trend of M_n against styrene initial concentration. At various monomer initial concentrations, the polymers obtained still had a narrow polydispersities with P.D. ≤ 1.16, indicating a living polymerization. No dependence of conversion on styrene initial concentration was found. The efficiencies of the initiator were higher than 1, the theoretical value, and less than 1.27. This would suggest that more than one polymer chains per one initiator molecule was formed. Since impurities were not likely to be introduced into the system because of the employment of special sample handling techniques described in Chapter 3, the possible reason for the higher initiator efficiencies may be due to the mechanisms involved themselves, such as irreversible transfer.

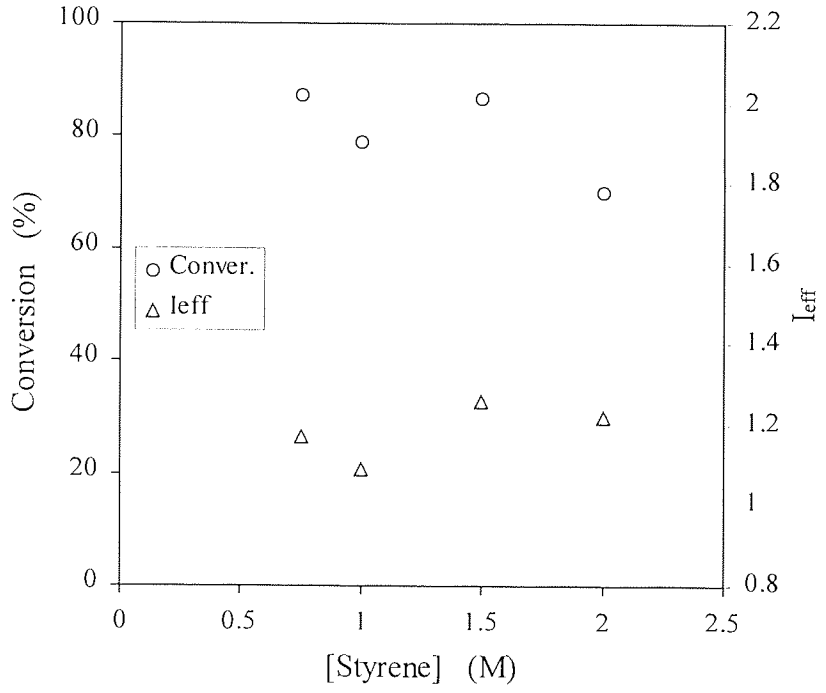


Fig. 4. 25 Conversions for the polymerizations of styrene monomers of varying concentrations: $[1\text{-PEC}]_0 = 0.01$, $[SnCl_4]_0 = 0.3$ M, $[n\text{Bu}_4\text{NCl}]_0 = 0.005$ M, DCM : C.hex = 40 : 10 (v : v), -15 °C, 3 hrs.

4.5 Optimum conditions for styrene living polymerizations

Based on the above systematic studies on the polymerizations of styrene monomers with varying the solvent polarity, temperature, the initial concentrations of the salt, initiator, catalyst and monomer, the conditions required for a living cationic polymerization can be summarised as following:

Monomer:	Styrene (St)	0.75 – 2 M
Initiator:	1-phenyl ethylchloride (1-PEC)	0.005 – 0.05 M
Catalyst:	tin tetrachloride ($SnCl_4$)	0.05 – 0.4 M
Salt:	tetra-*n*-butylammonium chloride (nBu$_4$NCl)	0.001 – 0.1 M
Solvent:	dichloromethane (DCM) : cyclohexane (C.hex)	50 : 0 – 20 : 30
Temperature:	(T)	0 to -45 °C
Reaction time:		3 hours

4.6 Error analysis for the Schlenk technique

To access the reproducibility of the polymerization, repeat experiments were designed to carry out in the presence of tetra-*n*-butylammonium chloride (nBu$_4$NCl) of varying concentrations under the initial conditions: $[\text{Styrene}]_0$ = 1 M, $[\text{1-PEC}]_0$ = 0.02 M, $[SnCl_4]_0$ = 0.2 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, 3 hrs. The results are shown in **Table 4.9**.

The precision of the measurements using GPC was estimated by the accuracy of the results relative to the mean value, which is defined as the difference between the measured (X_i) and the mean ($\overline{X_i}$) values divided by the mean, as follows:

$$Accuracy = \frac{(X_i - \overline{X})}{\overline{X}} \qquad (3)$$

Results in **Table 4.9** show that the measurements of average molecular weights using GPC and the efficiency of the initiator had an accuracy of about 10%, whilst the relative high accuracy was observed for the polydispersity and conversion (< 4%). As the calculation of the initiator efficiency involves the measured M_n, hence the polymerization experiments had errors of at least 10% regarding to molecular weights. Clearly it will be appropriate if the interpretation of results takes the measurement errors into account.

Table 4. 9 Results for styrene polymerizations in the presence of nBu$_4$NCl of various concentrations. [Styrene]$_0$ = 1 M, [1-PEC]$_0$ = 0.02 M, [SnCl$_4$]$_0$ = 0.2 M, DCM : C.hex = 40 : 10 (v : v), -15 °C, 3 hrs.

	[nBu$_4$NCl]	M_n	M_w	M_w/M_n (P.D.)	M_n (Cal.)	I_{eff}	Conver. (%)
	0.02	4397	5000	1.13	4202	0.96	80.5
	0.02	3658	4346	1.19	4411	1.21	86.7
Mean		4028	4673	1.16	4307	1.09	83.6
Accuracy (%)		9.2	7.0	2.6	2.4	11.5	3.7
	0.1	3394	4038	1.19	4156	1.23	85.8
	0.1	4994	6203	1.24	5809	1.16	84.3
	0.1	4287	4991	1.16	3906	0.91	88.7
Mean		4225	5077	1.20	4624	1.10	86
Accuracy (%)		13.1	14.8	2.4	17.1	11.5	1.9

CHAPTER 5

KINETIC STUDIES OF POLYMERIZATION OF STYRENE USING OMNIFIT SAMPLING

5.1 Introduction

The optimal conditions required for a living cationic polymerization have been established for styrene monomers for a fixed polymerization time (3 hours) using 1-phenyl ethylchloride (1-PEC) as an initiator and tin tetrachloride ($SnCl_4$) as a catalyst in dichloromethane (DCM) / cyclohexane (C.hex) cosolvents in the presence of tetra-*n*-butylammonium chloride (nBu$_4$NCl), as described in Chapter 4. Polymerizations were studied in terms of average molecular weights, monomer conversion and initiator efficiency with respect to several factors, but the detail of the mechanism was still not clear. Then, the development of a complete understanding of the mechanisms of the living cationic polymerization of styrene was of great interest in the following studies.

This chapter focuses on the investigations into the rate of polymerization for styrene with 1-PEC / $SnCl_4$ initiation systems in the presence of nBu$_4$NCl at mixtures of DCM and C.hex. A modified sampling method was developed to take samples at regular intervals with the benefits of its preventing the system from impurities. The orders of reaction with respect to monomer, initiator and catalyst were then derived form the

experimental data. Comparison was made to prediction of the rate of polymerization by the proposed mechanisms for polymerization.

5.2 Investigations into the rate of polymerization

The kinetic experiments were conducted using a unique sampling device constructed from Omnifit parts to clarify the dependence of the rate of polymerization on the concentration of the various reactants, such as initiator, catalyst, salt, and monomer, and on the solvent polarity and reaction temperature, to identify the mechanisms of cationic polymerization of styrene monomers.

For a living polymerization with fast initiation, the polymerization is generally considered as first order with respect to the monomer concentration, then the rate of polymerization depends on the propagation stage. During the polymerization, the number of active centres (growing species) is constant and the rate of polymerization (r_p) can be expressed as

$$r_p = -\frac{d[M]}{dt} = k_p[P^+][M] = k_{app}[M] \qquad (1)$$

Where $[M]$ represents the concentration of monomer, t is the time in seconds, k_p is the second-order rate constant for propagation **[104-106, 27]**, $[P^+]$ is the concentration of instantaneously actively growing species (constant) and k_{app} is the apparent first-order constant for propagation and is a function of temperature only. Integrating equation (1) yields

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_{app}t \qquad (2)$$

Obviously there is a linear dependency of $\ln([M]_0/[M])$ on time for a living polymerization with fast initiation, which will be used as a criterion to test the livingness of cationic polymerizations of styrene monomers.

5.2.1 Effect of salt

Experiments were conducted to elucidate the effect of the concentration of tetra-*n*-butylammonium chloride (nBu$_4$NCl) on the rate of polymerization. Number average molecular weights of the polymers, sampled using the Ominifit technique, were determined by GPC. The initial concentrations of styrene monomer, initiator (1-phenyl ethylchloride) and catalyst (tin tetrachloride) were 1 M, 0.02 M and 0.2 M respectively. A mixture of dichloromethane CH_2Cl_2 (DCM) and C.hex (30:20 in volume) was used as solvent in the polymerization and the reactions were kept at - 15 °C. The extent of conversions of each polymerization was determined by gravimetry.

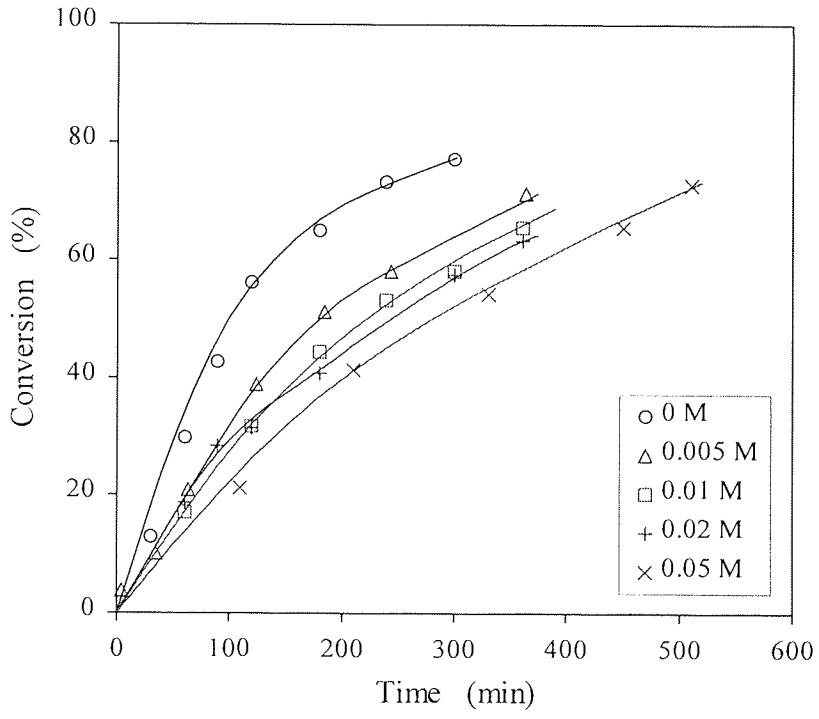


Fig. 5. 1 Conversion vs time curves for styrene polymerizations at -15°C with varying nBu$_4$NCl concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Fig. 5.1 shows the conversion versus time curves for the styrene polymerizations over a range of concentrations of nBu$_4$NCl. The polymerizations were not completed within 8.5 hours under the reaction conditions. The time of eight hours is probably the limit for practical experimental operations since it normally took one to two hours to handle the last polymer sample and the reaction system. Monomer conversions increased gradually with time as expected.

The first-order kinetic plots of $\ln([M]_0/[M])$ as a function of time for the polymerizations with vary nBu$_4$NCl concentrations are shown in **Fig. 5.2,** in which [M] is the concentration of monomer. After the addition of the salt the curved plots became straight lines; a slight curve was observed when nBu$_4$NCl concentration was quite low (0.005 M) indicating consumption of catalyst in this case. The linearity of $\ln([M]_0/[M])$ versus time demonstrates that essentially no termination occurred within the studied lifetimes of the polymerizations.

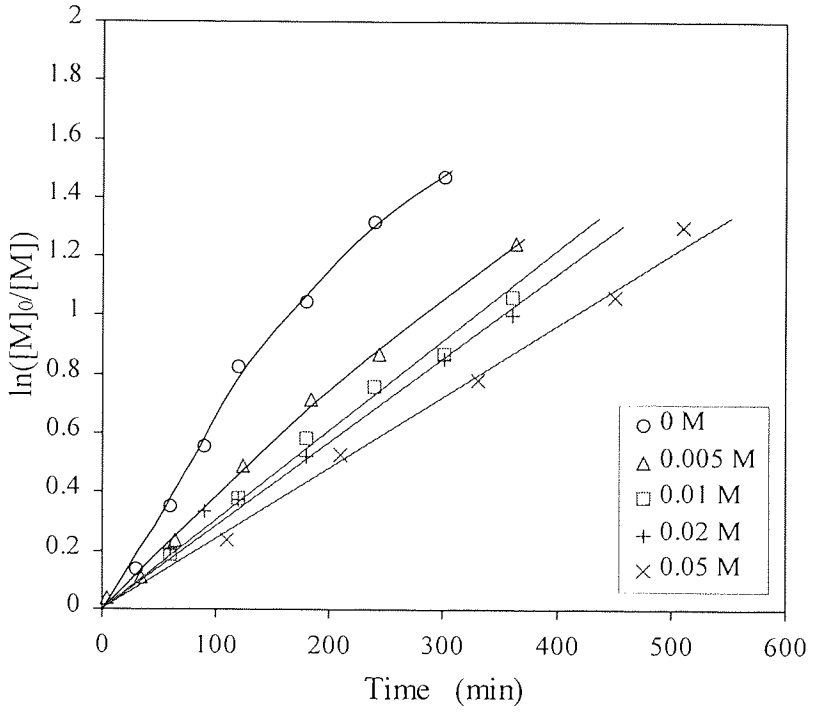


Fig. 5. 2 Graph of $\ln([M]_0/[M])$ against time for polymerizations at -15°C with varying nBu$_4$NCl concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

According to the equation (2) the apparent rate constant can be extracted form the slopes of the plots of $\ln([M]_0/[M])$ against time. The slope of the lines decreased when the salt concentration increased. **Fig. 5.3** shows the apparent rate constants as a function of the initial concentration of tetra-*n*-butylammonium chloride. The curve graph of k_{app} against [nBu$_4$NCl] would suggest that the rate of polymerization does not have a simple order dependence on the initial concentration of tetrabutylammonium chloride. This may be because salt involved in some equilibrium and so not expect simple. As shown in **Fig. 5.3**, the rate of polymerization decreased as the initial concentration of the salt increased, which has been observed by other workers **[2, 4]** and is believed to be associated with the suppression of the formation of the non-living, dissociated polymer chain ends with high MW by the high concentration of counter anions provide by the added salt. The dissociation equilibrium of the propagation centres (P^+X^-) may be expressed as

$$P^+X^- \rightleftharpoons P^+ + X^- \tag{3}$$

The equilibrium constant is then given by

$$K = \frac{[P^+][X^-]}{[P^+X^-]} \tag{4}$$

It is expected that the apparent rate constant of polymerization (k_{app}) depends upon the concentration of active propagating sites (centres), and then

$$k_{app} \propto [P^+] = \frac{K[P^+X^-]}{[X^-]} \tag{5}$$

Although $[X^-]$ may be related to the initial concentration of nBu$_4$NCl, equation (5) shows that the apparent rate constant does not have a direct correlation with the initial concentration of nBu$_4$NCl.

M_n against conversion was constructed for the same polymerizations (as shown in **Fig. 5.2**) to establish the absence of chain transfer and thus provide evidence for livingness of the polymerizations. The M_n of polymers increased in direct proportion to monomer conversion and agreed well with the theoretical number-average MW expected from the concentration ratios of monomer to initiator in the presence of salts (**Fig. 5.4**). This linear relationship indicates that the polymerization is living. The plots of M_n vs conversion were independent of the initial concentration of the salt. Some deviation at low conversions in **Fig. 5.4** may be due to the poor accuracy of finding % conversion.

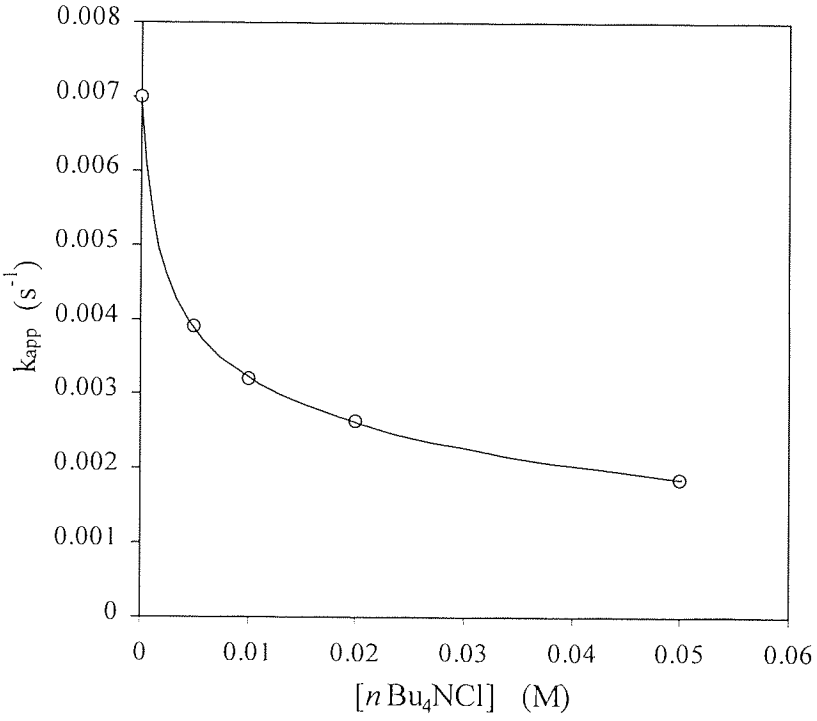


Fig. 5. 3 Effect of nBu$_4$NCl concentration on the apparent rate constant of styrene polymerization at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

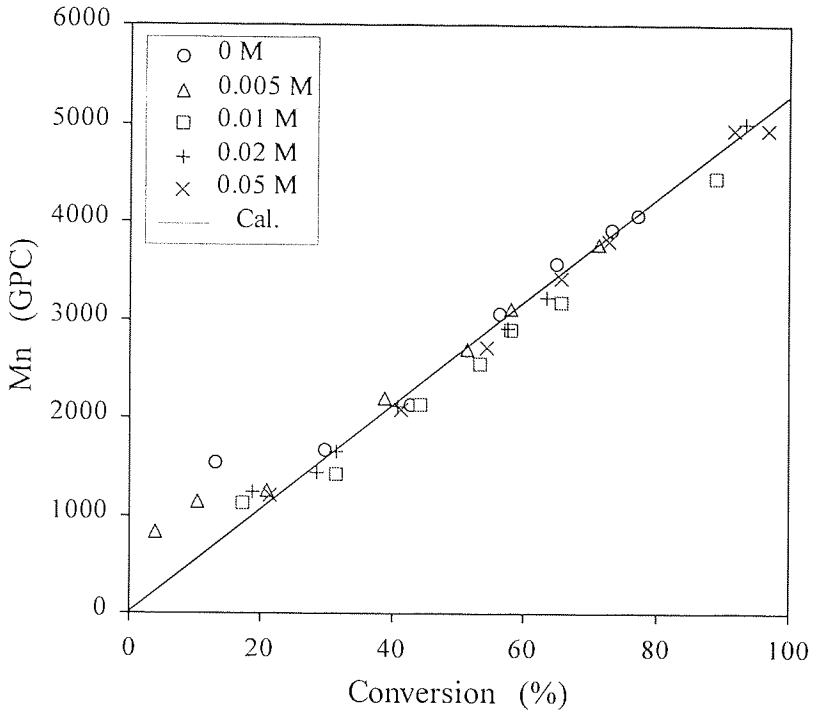


Fig. 5. 4 M_n vs conversion plots for styrene polymerizations at -15°C with varying nBu$_4$NCl concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

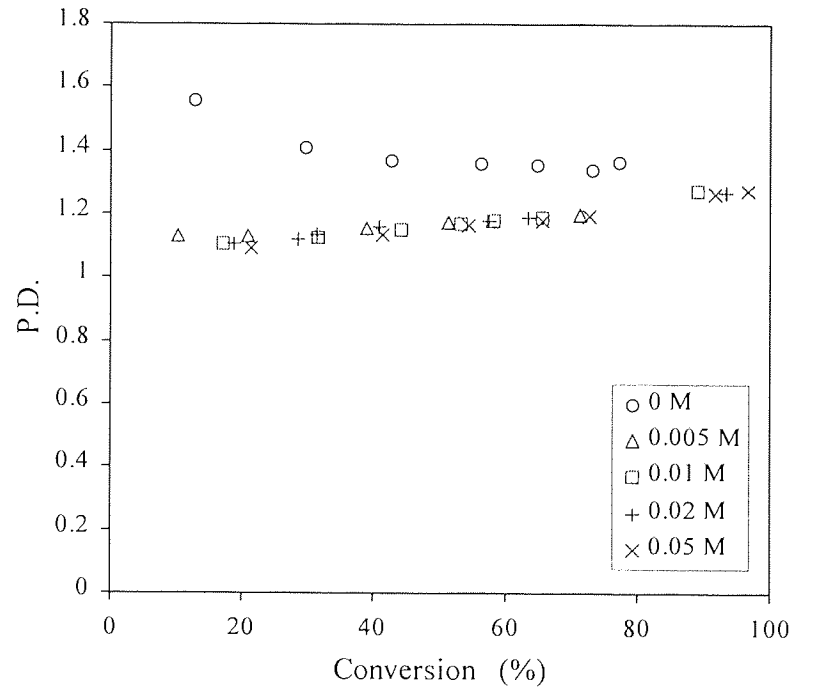


Fig. 5. 5 Polydispersities of the polymers obtained at interval during styrene polymerizations at -15°C with varying nBu$_4$NCl concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v/v).

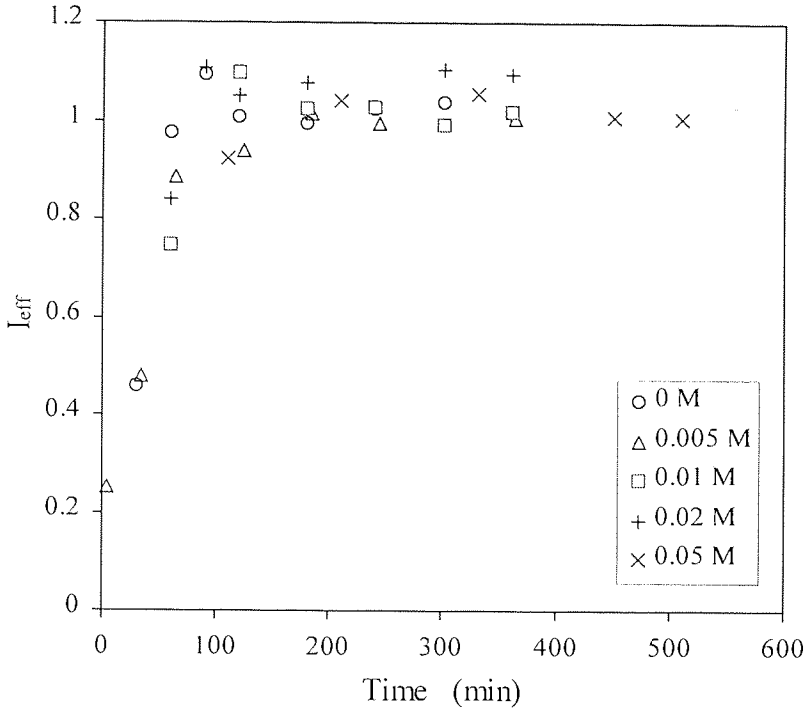


Fig. 5. 6 Efficiencies of the initiator for styrene polymerizations at -15°C with varying nBu$_4$NCl concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Fig. 5.5 shows the dependence of polydispersity of the polymers obtained on conversion. The molecular weight distributions were bimodal when high polydispersities ($\overline{M_w}/\overline{M_n}$ > 1.3) were obtained. In the presence of nBu$_4$NCl, the polymers had very narrow, monomodal MWDs with $\overline{M_w}/\overline{M_n}$ < 1.2. Such observations confirmed the absence of transfer reaction during polymerization, because these reactions would have broadened the distribution.

Fig. 5.6 shows the plots of initiation efficiencies vs time for the same styrene polymerizations. In the initial stage the efficiency increased gradually with time and reached a plateau around 1, close to the theoretical initiator efficiency assuming one initiator molecule leads to one active polymer centre. After about 100 minutes, corresponding to a conversion of about 30%. This may be evidence of slow build up of the propagation species (P^+X^-) or slow initiation, which has been observed in the isobutylene polymerization with benzyl halides as initiators **[107]**. The increase in efficiency was slightly slower in the presence of the salt.

5.2.2 Effect of initiator concentration

Reactions were carried out to study what effect varying the initial concentration of the initiator, 1-phenyl ethylchloride (1-PEC) would have on the rate of polymerization. The polymerizations were performed in mixtures of dichloromethane / C.hex (30/20 v/v) at - 15 °C. The Ominifit sampling technique was used to take polymer samples at interval for the GPC analysis and weight analysis. The initial concentrations of styrene monomer, catalyst and salt were 1 M, 0.2 M and 0.02 M respectively, and the initial concentration of 1-PEC varied.

Plots of $\ln([M]_0/[M])$ against time were made for each experiment, as shown in **Fig. 5.7,** and the apparent rate constants for each experiment were obtained from the gradients of the lines over the first few points. It is clear that all of the plots were linear and passed through the origin, thereby demonstrating the absence of irreversible termination within the lifetimes of the polymerizations on varying initiator initial concentrations. Increasing initiator initial concentration resulted in an increase in the slope of the line and then a greater apparent rate constant.

The order of reaction with respect to initiator was estimated from the plot of log k_{app} versus log [1-PEC], shown in **Fig. 5.8**. The slope of the straight line through the points yields an order of 1.28 with a very good fit (R^2 = 0.99), indicating that the apparent rate constant has an order dependence of 1 on the initial concentration of initiator unless the fractional order has some significance in terms of association of propagating centres.

Fig. 5.9 shows plots of M_n as a function of conversion which resulted from the same polymerizations whose kinetic runs were plotted in **Fig. 5.7**. The plots of M_n vs conversion depended on the initial concentration of initiator. When the initial concentrations of initiator were not less than 0.01 mol dm^{-3}, the plots were found to be linear and to fall on the theoretical lines (solid lines), indicating the absence of chain transfer in the polymerizations. This is consistent with indication of living polymerization by the very narrow and nearly uniform MWDs ($\overline{M_w}/\overline{M_n}$ < 1.2)

observed for the polymers obtained as shown in **Fig. 5.10**. The curve of M_n vs conversion for the lowest concentration of 1-PEC (0.004 M) was evidence of the presence of irreversible transfer reaction, surprisingly in contrast to the lower polydispersities being less than 1.2 (**Fig. 5.10**).

Fig. 5.11 shows the plots of initiation efficiencies against time for the same polymerizations. The initiation efficiencies were found to be close to the theoretical value (one), except for the initial concentration of 1-PEC was 0.004 M. The high efficiencies greater than one observed for [1-PEC] being 0.004 M, indicating that more polymer chains are being formed than expected, are in agreement with the findings of Endsor **[27]**, which were attributed to the presence of impurities or undergoing transfer reactions. However this would appear unlikely because many techniques were used to prevent the ingress of impurities into the polymerization. The most possible reason for the higher efficiencies might be due to the measurement errors in weighting polymers since polymerizations were very slow at $[1\text{-PEC}]_0$ = 0.004 M.

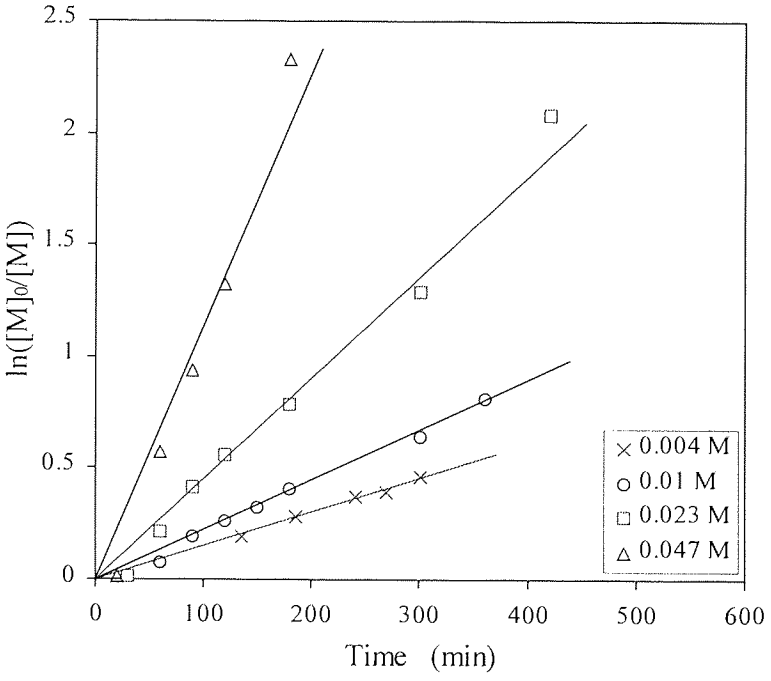


Fig. 5. 7 Graph of $\ln([M]_0/[M])$ against time for polymerizations at -15°C with varying initiator concentrations. $[St]_0$ = 1M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

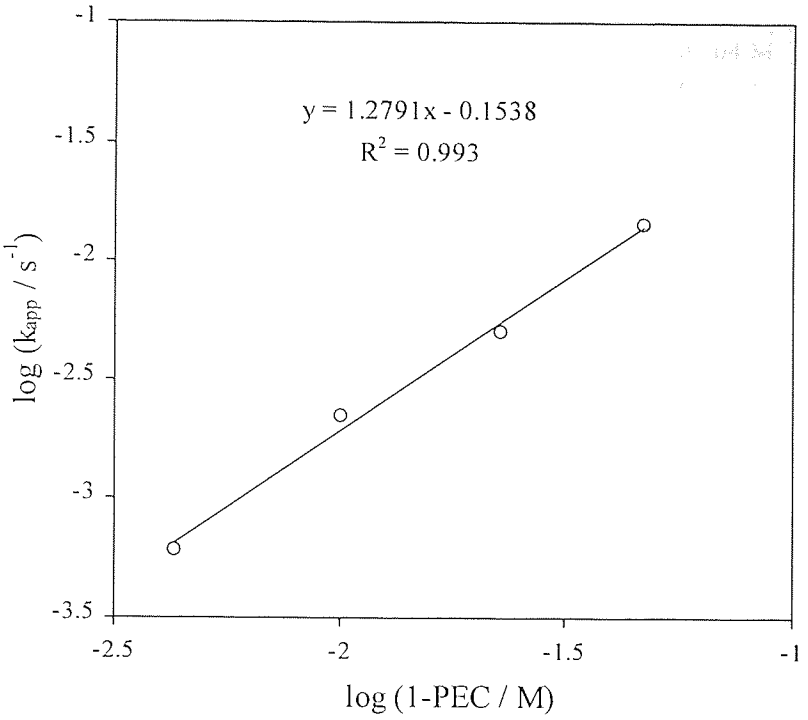


Fig. 5. 8 Effect of initiator concentration on the rate of styrene polymerization at -15°C with varying initiator concentrations. $[St]_0$ = 1M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

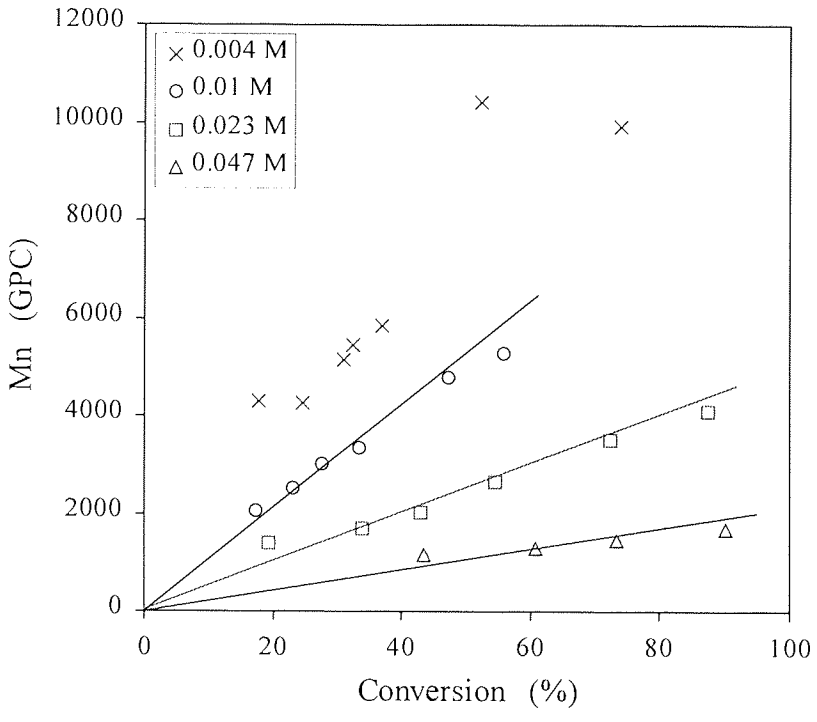


Fig. 5. 9 M_n vs conversion plots for styrene polymerizations at -15°C with varying initiator concentrations. $[St]_0$ = 1M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

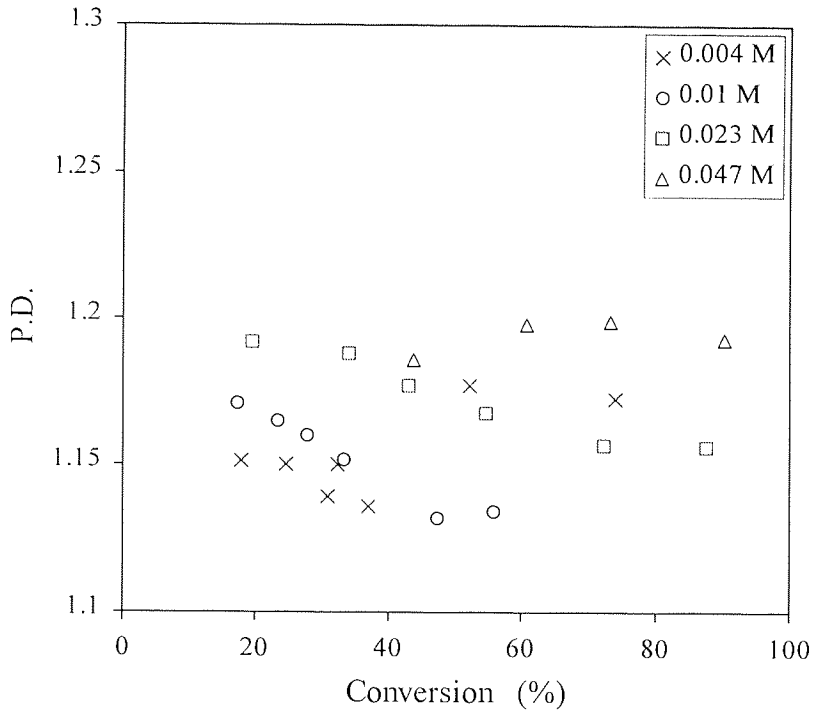


Fig. 5. 10 Polydispersities of the polymers obtained during styrene polymerizations at -15°C with varying initiator concentrations. $[St]_0$ = 1M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

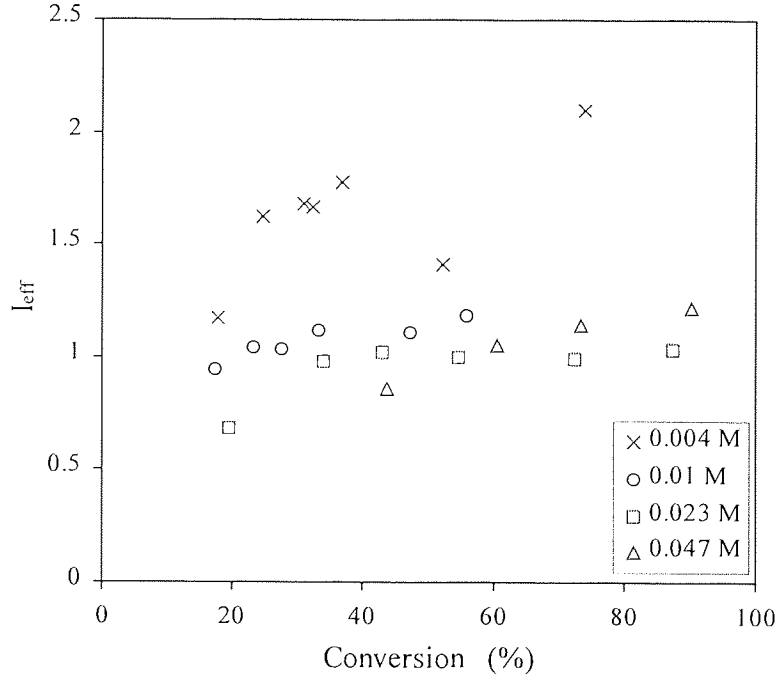


Fig. 5. 11 Efficiencies of the initiator for the same polymerizations as in **Fig. 5.7**.

5.2.3 Effect of catalyst

Polymerizations were conducted in mixtures of DCM / C.hex (30 / 20 v / v) at - 15 °C to determine the rate of polymerization with different initial concentrations of catalyst. Polymer samples were taken at intervals using the Ominifit sampling technique. The initial concentrations of styrene monomer, initiator and salt were 1 M, 0.02 M and 0.02 M respectively. In a series of experiments the initial concentration of $SnCl_4$ was varied.

Fig. 5.12 shows plots of $\ln([M]_0/[M])$ vs time were made for each experiment and the apparent rate constants for each experiment were extracted from the slopes of the lines over the first few points. The linearity of the plots except for $[SnCl_4]_0$ = 0.6 M demonstrates the absence of irreversible termination within the lifetimes of the polymerizations, and increasing catalyst concentration accelerated polymerization.

The plot of log k_{app} versus log $[SnCl_4]$, shown in **Fig. 5.13**, was used to estimate the order of reaction with respect to catalyst. The straight line through the points had a gradient of 0.73 with R^2 = 0.99, which indicates that the apparent rate constant has a first order dependence on the initial concentration of catalyst.

Plots of log k_{app} versus the initial concentrations of initiator and catalyst in **Figs. 5.8** and **5.13** proved that the apparent rate constant are directly proportional to both initial concentrations of 1-PEC and $SnCl_4$, $[1\text{-PEC}]_0$ or $[SnCl_4]_0$, indicating the first order rate dependence on $[1\text{-PEC}]_0$ or $[SnCl_4]_0$. Based on the equation (1), the rate of polymerization (r_p) can then be expressed as

$$r_p \propto [M]^1[1-PEC]^1[SnCl_4]^1 \qquad (5)$$

Fig. 5.14 shows plots of M_n against conversion for the polymerizations. The plots were independent of the initial concentration of $SnCl_4$. The M_n of the polymers increased in direct proportion to conversion and agreed well with the theoretical

number-average MW (solid line) expected from the concentration ratios of monomer to initiator for $SnCl_4$ varying from 0.1 to 0.6 M, indicating the absence of irreversible chain transfer. That the points all lie on one line indicates that [$SnCl_4$] does not influence the overall number of propagating sites.

The polymers, obtained from the same polymerizations whose kinetic runs were plotted in **Fig. 5.12**, had very narrow, monomodal MWDs with $\overline{M_w}/\overline{M_n}$'s around 1.2 (**Fig. 5.15**), which are indicative of a living polymerization.

Fig. 5.16 shows the efficiencies of initiator as a function of conversion for the same polymerizations of styrene. The gradual build-up of the initiation efficiencies was evidence that rapid initiation did not take place in the initial stages, i.e. slow initiation, corresponding to conversions less than ~ 30%.

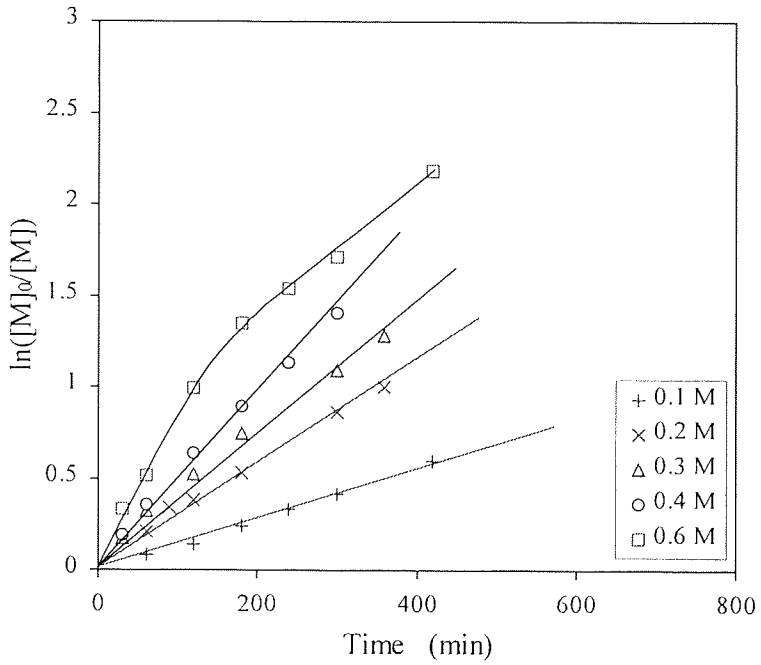


Fig. 5. 12 Graph of $\ln([M]_0/[M])$ against time for polymerizations at -15°C with varying $SnCl_4$ concentrations.

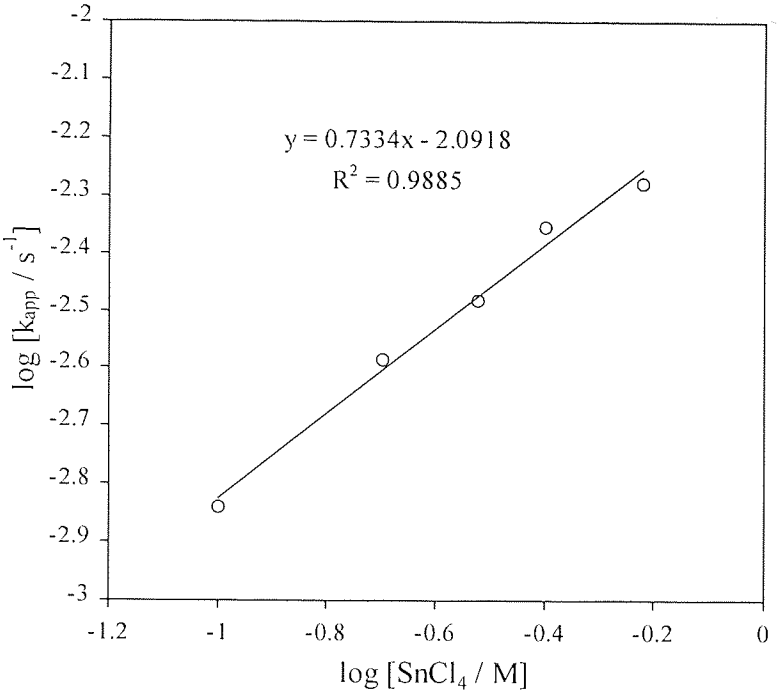


Fig. 5. 13 Effect of $SnCl_4$ concentration on the rate of styrene polymerization at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[n\text{Bu}_4\text{NCl}]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

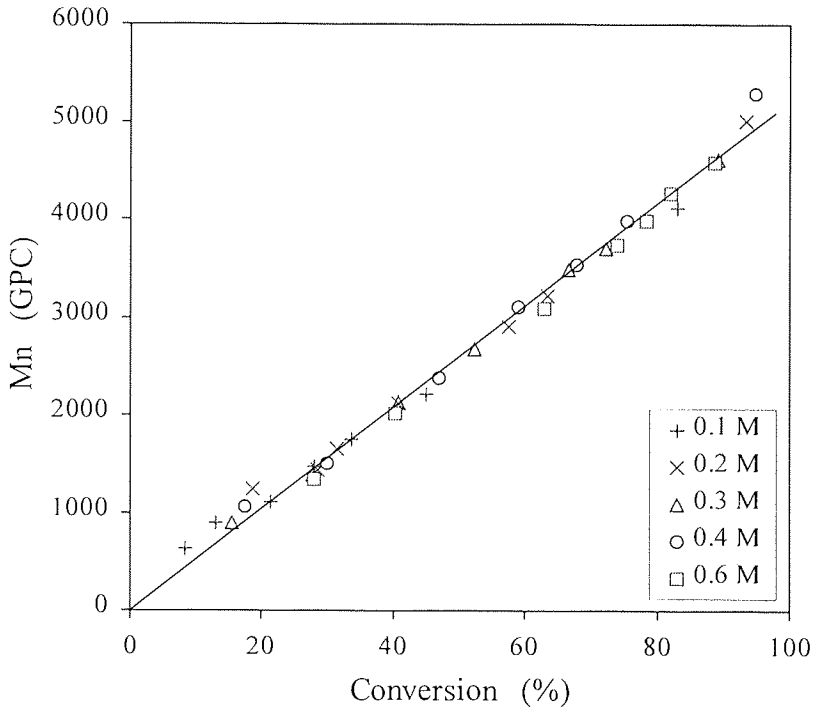


Fig. 5. 14 M_n vs conversion plots for styrene polymerizations at -15°C with varying $SnCl_4$ concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[n\text{Bu}_4\text{NCl}]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

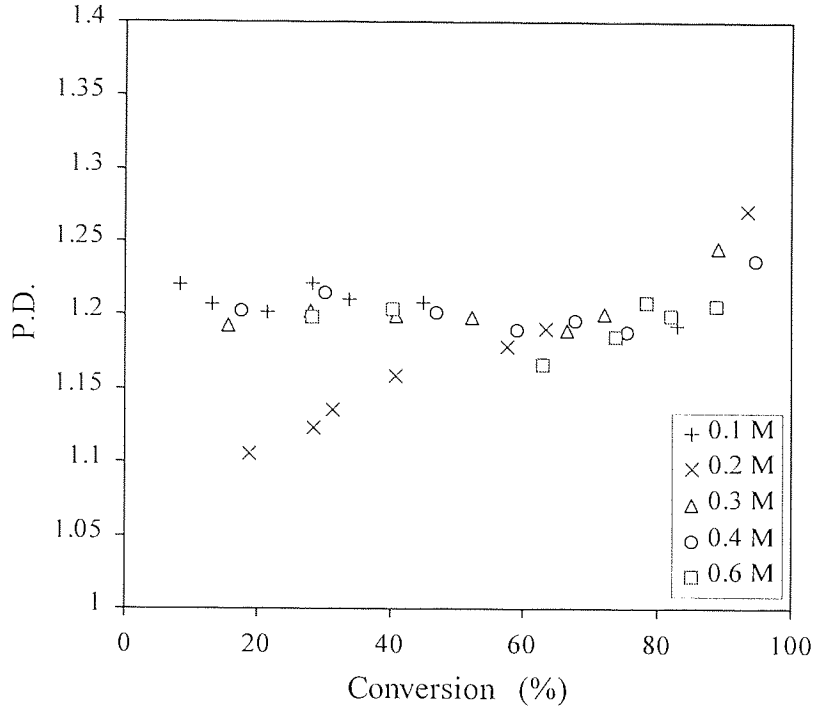


Fig. 5. 15 Polydispersities of the polymers obtained during styrene polymerizations at -15°C with varying $SnCl_4$ concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[n\text{Bu}_4\text{NCl}]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

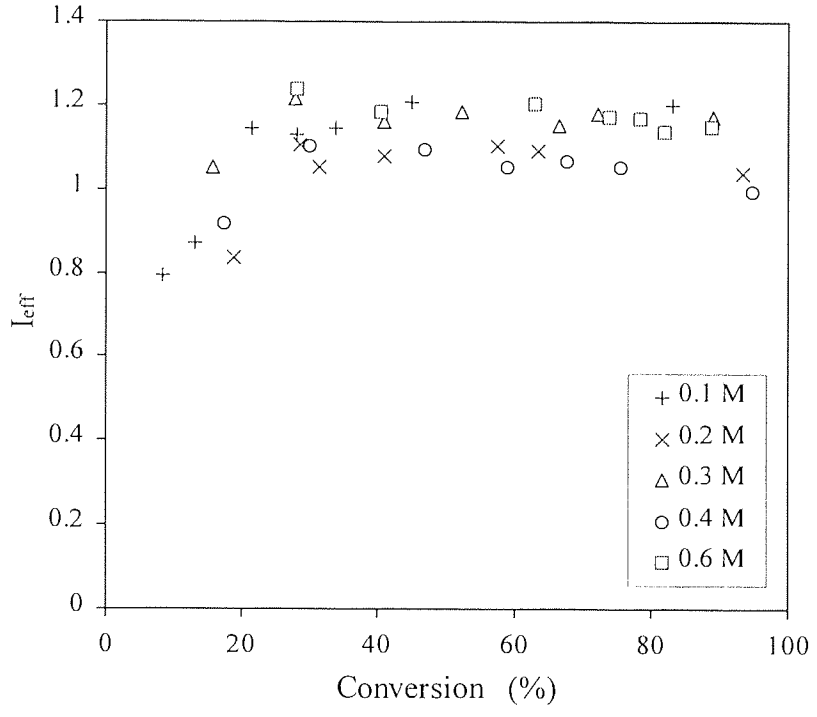


Fig. 5. 16 Efficiencies of the initiator for styrene polymerizations at -15°C with varying $SnCl_4$ concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[n\text{Bu}_4\text{NCl}]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

5.2.4 Effect of solvent polarity

Reactions were conducted to study the effect on polymerization of varying the polarity of solvent, which was achieved by mix DCM with C.hex at different ratios. The initial concentrations of styrene monomer, initiator, catalyst and salt were 1 M, 0.02 M, 0.2 M and 0.02 M respectively, and the reaction temperature was - 15 °C.

Plots of $\ln([M]_0/[M])$ against time were made for each experiment, as shown in **Fig. 5.17,** and the apparent rate constant for each experiment was obtained from the gradients of the lines for the first few points, which are listed in **Table 5.1**. The plots were linear for the polymerizations in mixtures of DCM / C.hex with 30 / 20 and 20 / 30, indicating the absence of irreversible termination within the lifetimes of the polymerizations. The non linearity of the plots for the other polymerizations are of indicative of the presence of irreversible termination. Decreasing solvent polarity led to a reduction in the apparent rate constant and a reduction in the rate of polymerization.

Table 5. 1 The dependence of apparent rate constant on the solvent polarity.

DCM : C.hex	50 : 0	40 : 10	30 : 20	20 : 30	10 : 40
k_{app} (s^{-1})	16.07×10^{-3}	5.33×10^{-3}	4.77×10^{-3}	1.08×10^{-3}	0.80×10^{-3}

The dependence of M_n on conversion for the polymerizations is shown in **Fig. 5.18**. For the polymerizations at middle polarity solvents, DCM / C.hex = 30 / 20 or 20 / 30, the plots of M_n vs conversion were observed to be linear and to agree well with the theoretical line (solid line), demonstrating the absence of chain transfer in the polymerizations. The discrepancies of M_n from the theoretical lines for other ratios of DCM / C.hex indicate some evidence of transfer. The low polydispersities ($\overline{M_w} / \overline{M_n}$ ~ 1.2) were also found for the polymerizations at middle polarity solvents (**Fig. 5.19**).

As shown in **Fig. 5.20**, most of initiation efficiencies scattered around the theoretical value (one), except for DCM / C.hex 10 / 40 in which the abnormal higher efficiencies might be associated with the characteristics of conventional cationic polymerization.

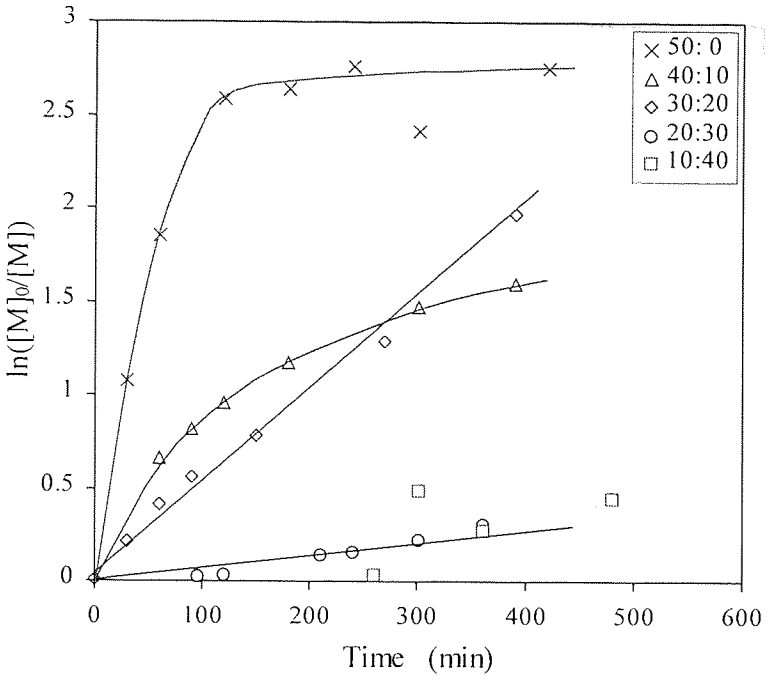


Fig. 5. 17 Graph of $\ln([M]_0/[M])$ against time for styrene polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n Bu_4NCl]_0$ = 0.02M.

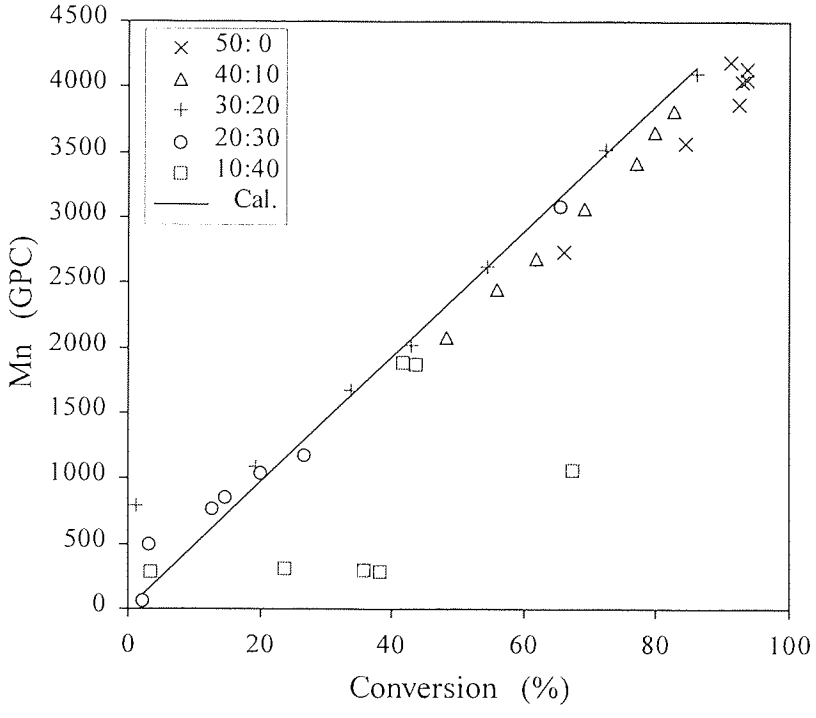


Fig. 5. 18 M_n vs conversion plots for styrene polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n Bu_4NCl]_0$ = 0.02M.

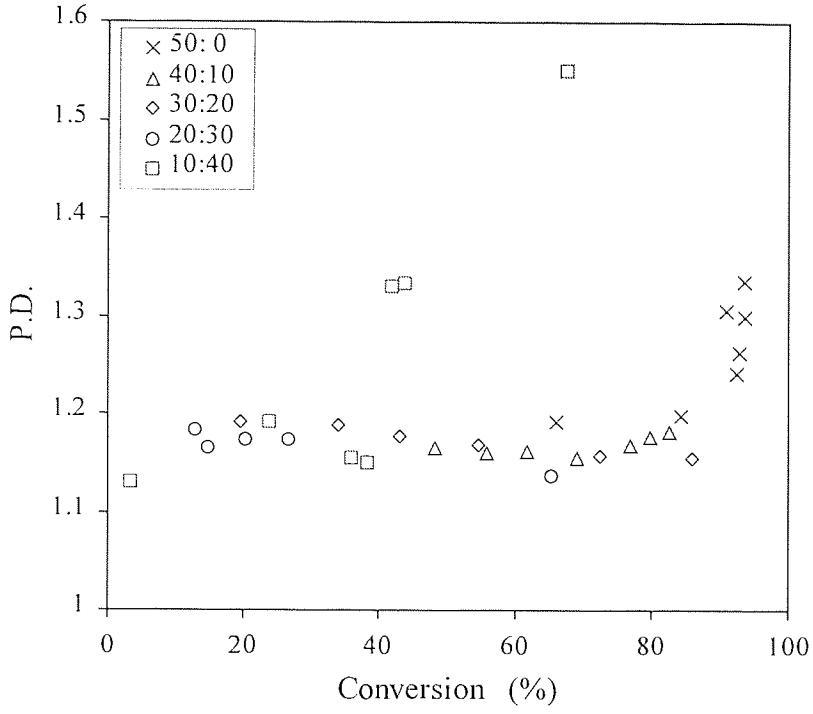


Fig. 5. 19 Polydispersities of the polymers obtained from polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n Bu_4NCl]_0$ = 0.02M.

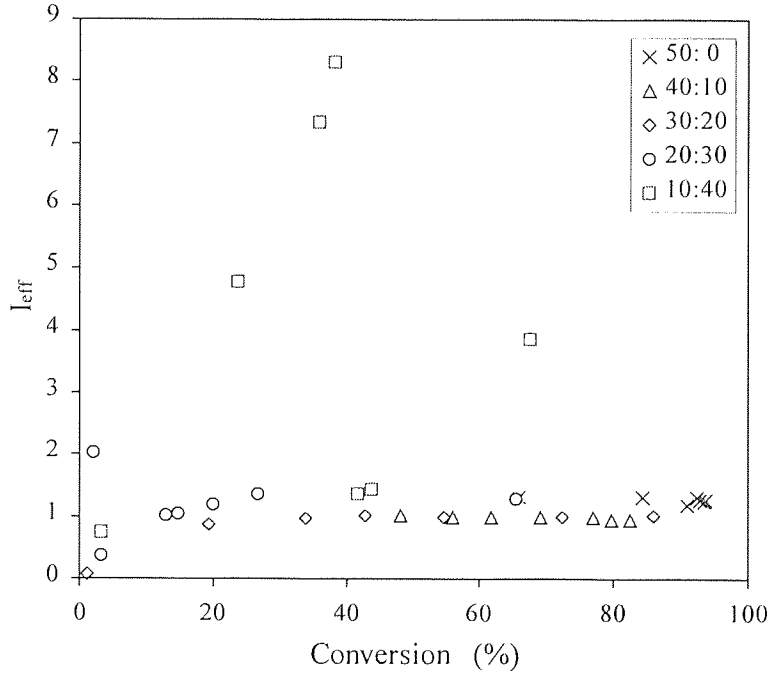


Fig. 5. 20 Efficiencies of the initiator for styrene polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n Bu_4NCl]_0$ = 0.02M.

5.2.5 Effect of temperature

Experiments were conducted to study the effect of temperature on the rate of polymerization. The initial concentrations of styrene monomer, initiator, catalyst and salt were kept constants; [Styrene] = 1 M, [1-PEC] = 0.02 M, [$SnCl_4$] = 0.2 M, [$n$$Bu_4NCl$] = 0.02 M and DCM / C.hex = 30 / 20 (v / v).

Plots of $\ln([M]_0/[M])$ against time were made for each experiment, as shown in **Fig. 5.21,** and the apparent rate constants for each experiment, obtained in the normal way, are listed in **Table 5.2**. Linear plots were observed for polymerizations at temperatures below 0°C, indicating the absence of irreversible termination and constant concentration of propagating species. The non linearity of the plots for the other polymerizations are indicative of the presence of irreversible termination at higher temperatures. The apparent rate constants decreased with a reduce in temperature, which indicates that polymerization slows down at lower temperatures.

Table 5. 2 The dependence of apparent rate constant on temperature.

T (K)	228	243	258	273	293
k_{app} (s^{-1})	0.99×10^{-3}	1.15×10^{-3}	2.60×10^{-3}	5.34×10^{-3}	7.07×10^{-3}

Fig. 5.22 shows the plot of ln (k_{app}) against the reciprocal of the absolute temperature for the styrene polymerization. A straight line with $R^2 = 0.95$ was obtained, and so the dependence of the apparent rate constant on temperature can be expressed as

$$\ln k_{app} = -2265.3\frac{1}{T} + 2.8485$$

Fig. 5.23 shows plots of M_n vs conversion for the polymerizations. The linearity of the plots were observed for temperatures of -15 °C and -30 °C, and M_n to agree well with the theoretical line, demonstrating the absence of chain transfer in the polymerizations. The discrepancies of M_n from the theoretical lines for other

temperatures are some evidence of transfer. The polymers obtained at temperatures below 0 °C had very low polydispersities ($\overline{M_w}/\overline{M_n} \leq 1.2$) which was indicative of the absence of transfer (**Fig. 5.24**).

As shown in **Fig. 5.25**, at lower temperatures the initiation efficiencies gradually increases to the theoretical value, which is some evidence of a slow build-up of propagating active centres.

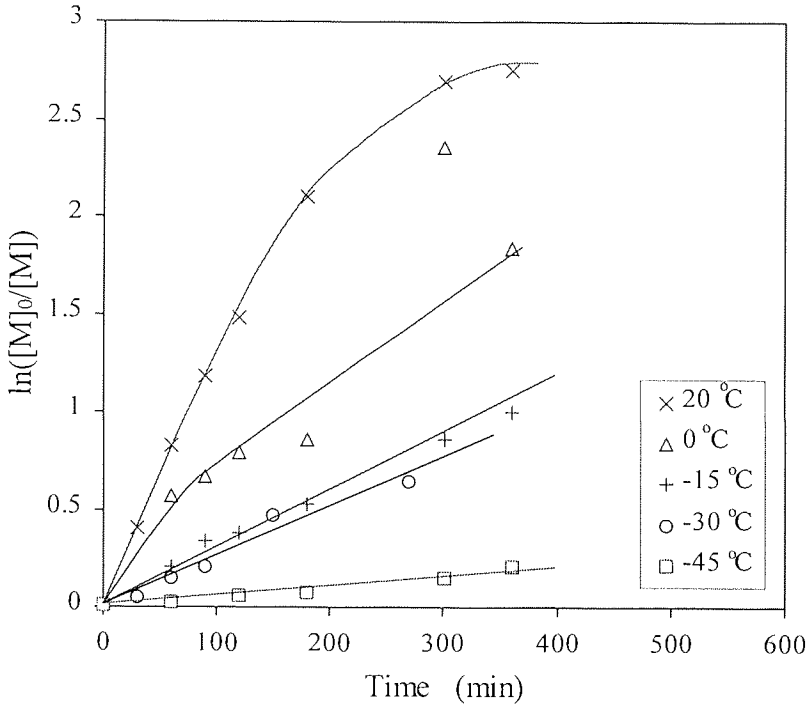


Fig. 5. 21 Graph of $\ln([M]_0/[M])$ against time for styrene polymerizations at various temperatures. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n Bu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

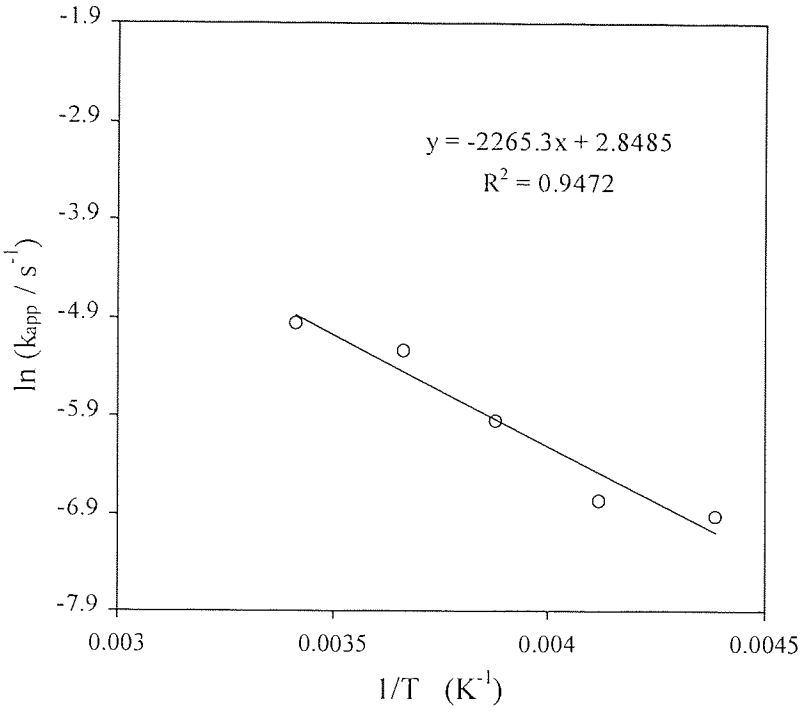


Fig. 5. 22 Effect of temperature on the apparent rate constant of styrene polymerization. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

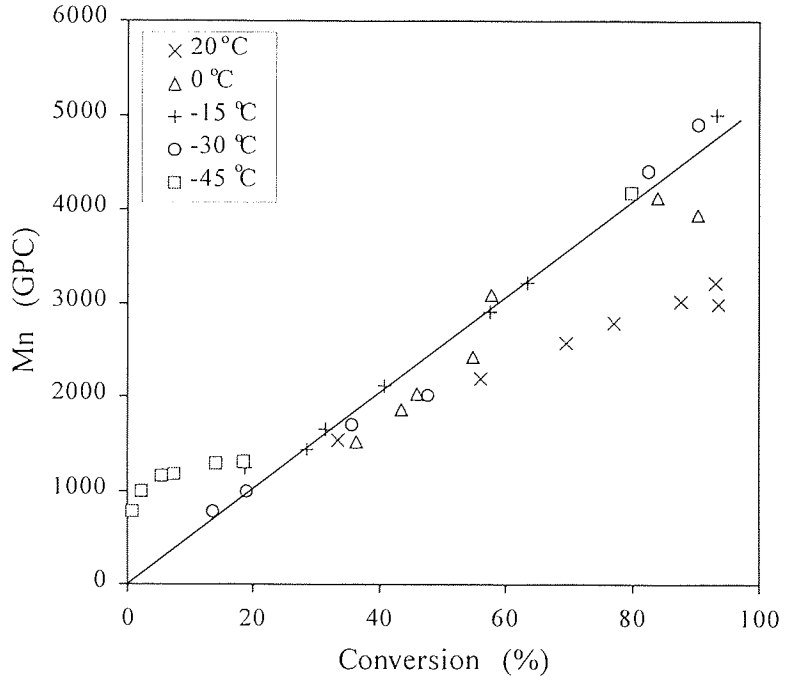


Fig. 5. 23 M_n vs conversion plots for styrene polymerizations at various temperatures. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

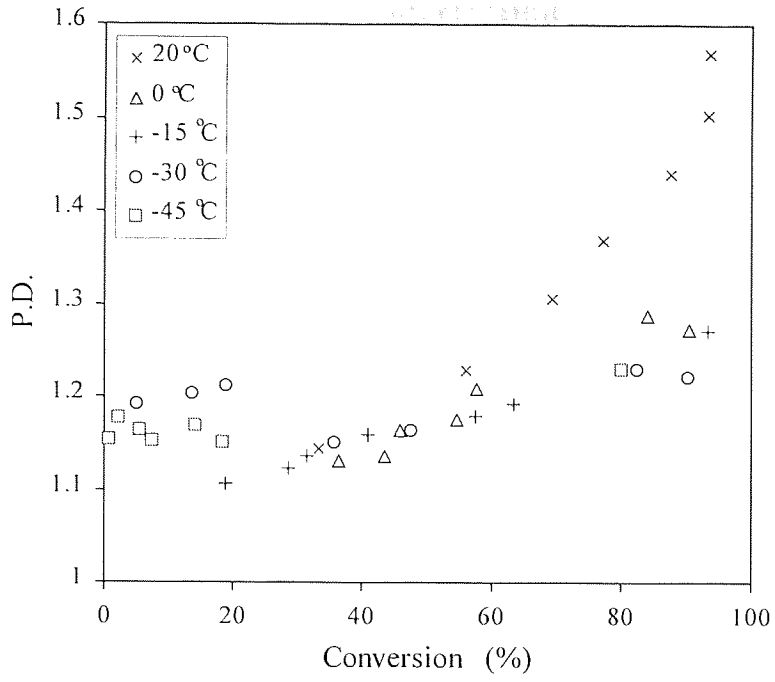


Fig. 5. 24 Polydispersities of the polymers obtained from the polymerizations at various temperatures. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.02M; $[nBu_4NCl]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

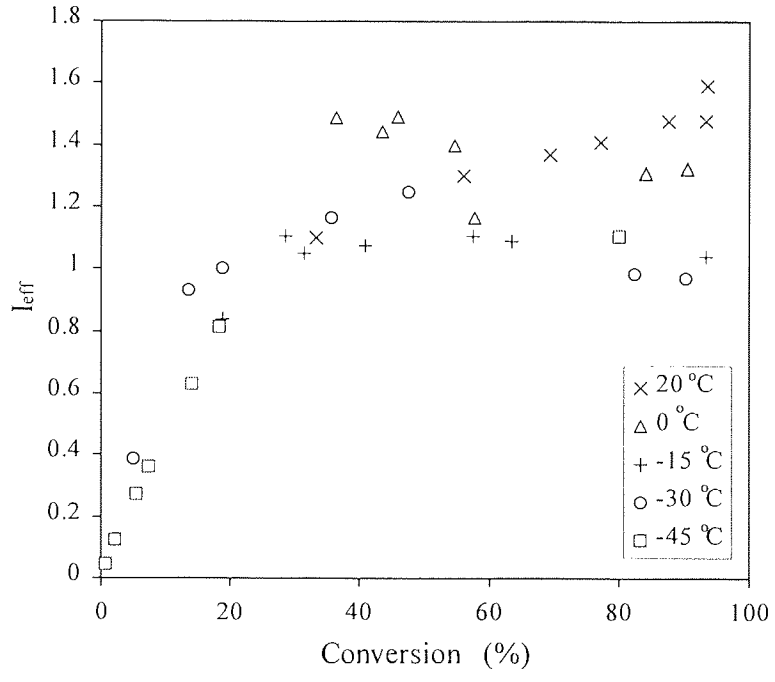


Fig. 5. 25 Efficiencies of the initiator for styrene polymerizations at various temperatures. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v).

5.3 Kinetics of living styrene polymerization

The rate of polymerization was also studied by measuring the number average degree of polymerization of the polymer after different time periods, which had been employed by Endsor **[27]**.

5.3.1 Degree of polymerization

For a living polymerization, assuming one initiator molecular leads to one discreet polymer chain, the number average degree of polymerization (DP_n) is expressed as:

$$DP_n = \frac{[M]_0 - [M]}{[I]_0} \tag{6}$$

where $[M]_0$ is the initial monomer concentration (mol l^{-1}),

$[M]$ is the instantaneous monomer concentration (mol l^{-1}), and

$[I]_0$ is the initial initiator concentration (mol l^{-1}).

The kinetics of chain propagation are generally regarded as first-order and the monomer concentration can then be given by:

$$[M] = [M]_0 e^{-k_{app}t} \tag{7}$$

where t is the time (seconds), and

k_{app} is the apparent rate constant (seconds^{-1}).

Combining equations (6) and (7) yields

$$DP_n = \frac{[M]_0\left(1 - e^{-k_{app}t}\right)}{[I]_0} \quad (8)$$

At the end of polymerization, the final number average degree of polymerization can be defined as

$$DP_{n\infty} = \frac{[M]_0}{[I]_0} \quad (9)$$

Substituting equation (9) into (8) yields

$$DP_n = DP_{n\infty}\left(1 - e^{-k_{app}t}\right) \quad (10)$$

Rearranging this expression

$$\ln\left(1 - \frac{DP_n}{DP_{n\infty}}\right) = -k_{app}t \quad (11)$$

Rewriting equation (11):

$$\ln\left(DP_{n\infty} - DP_n\right) = \ln DP_{n\infty} - k_{app}t \quad (12)$$

Obviously the apparent rate constant of the reaction can be obtained from the slope of the plot of $\ln(DP_{n\infty}-DP_n)$ against time.

5.3.2 Comparison of the measured and estimated rates of polymerization

To test the application of equation (12), a typical experiment was conducted as described in **Fig. 5.7** with $[\text{Styrene}]_0$ = 1M; $[\text{1-PEC}]_0$ = 0.023M; $[SnCl_4]_0$ = 0.2M; $[n\text{Bu}_4\text{NCl}]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v); T = -15 °C. Polymer samples were taken using Omnifit techniques at desired intervals and the resultant polymers

were analysed by GPC. The molecular weights and degree of polymerization are listed in **Table 5.3**.

Table 5. 3 Dependence of molecular weight and degree of polymerization on time.

Time (min)	$\ln[M]_0/[M]$	Conversion (%)	M_n (GPC)	P.D.	DP_n	$\ln(DP_{n\infty}-DP_n)$*
30	0.01	1	797	1.239	0.6	3.82
60	0.22	19	1377	1.192	9.0	3.62
90	0.41	34	1671	1.188	15.7	3.42
120	0.56	43	2026	1.177	19.9	3.27
180	0.79	55	2629	1.168	25.3	3.05
300	1.29	72	3515	1.157	33.5	2.55
420	2.08	88	4099	1.156	40.5	1.76

* $DP_{n\infty}$ (cal.) = 46.3

Based on equation (9), the final (expected) number average degree of polymerization ($DP_{n\infty}$) was calculated to be 46.3, which was used in the calculation of $\ln(DP_{n\infty}-DP_n)$ listed in the final column in **Table 5.3**. A plot of $\ln(DP_{n\infty}-DP_n)$ versus time is shown in **Fig. 5.26**, which presented a linear plot with a slope of -0.005, an intercept of 3.928 and R^2 = 0.99. According to equation (12), a value of $DP_{n\infty}$ was obtained from the intercept to be 50.8, which agrees well with the expected final number average degree of polymerization ($DP_{n\infty}$ = 46.3) with an error of 8.9%. The apparent rate constant of 0.005 s^{-1}, estimated from the slop of the plot of $\ln(DP_{n\infty}-DP_n)$ against time, is identical to the apparent rate obtained from the gradient of the graph of $\ln\{[M]_0/[M]\}$ versus time as shown in **Fig. 5.7**. The good agreement in degree of polymerization or rate constant between the calculated and the estimated from the plot in **Fig. 5.26** implies the suitability of equation (12) describing the living polymerization.

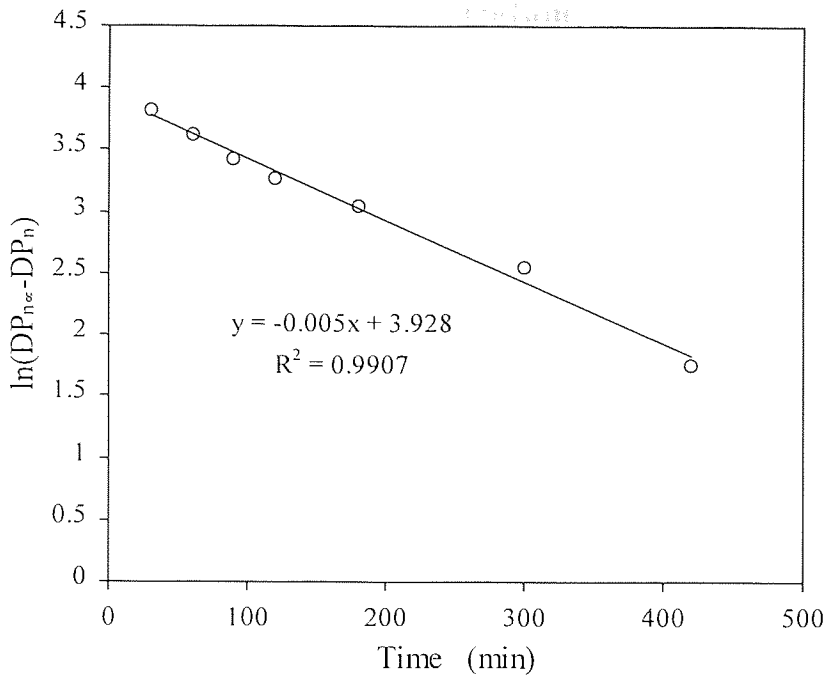


Fig. 5. 26 Plot of $\ln(DP_{n\infty}-DP_n)$ against time for styrene polymerizations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.023M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v); T = -15 °C.

Table 5. 4 Comparison of $DP_{n\infty}$ or k_{app} between measured (or used) and intercept values.

	$DP_{n\infty}$	k_{app}
Calculated (or measured)	46.3	0.005
Intercept	50.8	0.005
Difference	4.5	0
Errors (%)	8.9	0

5.4 Mechanisms for styrene polymerization

As the living polymerizations exclude transfer and termination, their mechanisms depend on the propagation process. The following two propagation mechanisms have been proposed in terms of the number of active centres.

5.4.1 Propagation by a single species

A mechanism similar to Michaelis-Menten kinetics [27] can be considered for styrene polymerization initiated with a 1-PEC/$SnCl_4$ system in the presence of tetra-*n*-butylammonium chloride. Michaelis-Menten kinetics applies to enzyme catalysed reactions, as shown in **Fig. 5.27**, 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. The reaction between enzyme and the inhibitor reduces the rate of enzyme catalysis. The rate of reaction (r_c) for the Michaelis-Menten kinetics can be expressed as

$$r_c = \frac{d[P]}{dt} = k_p[ES] = k_p[E]_0\left(1+\frac{K}{[S]}\left(1+\frac{[I]}{K_2}\right)\right)^{-1} \qquad (13)$$

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

Where K is the Michaelis-Menten constant and K_2 the equilibrium constant for the reaction between enzyme and inhibitor.

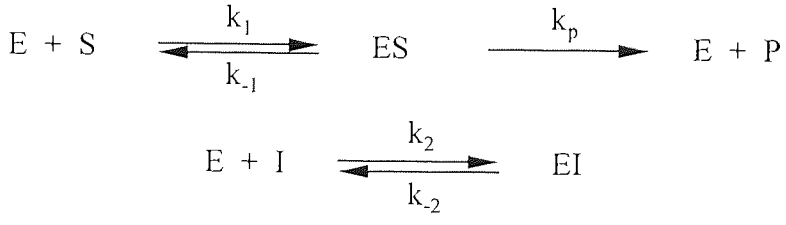


Fig. 5. 27 Reaction scheme for Michaelis-Menten kinetics.

For the styrene living polymerization with 1-PEC/$SnCl_4$ as a initiation system in the presence of tetra-*n*-butylammonium chloride, a single active propagation species was assumed to be in dynamic equilibrium with the dormant polymer chains. The likely reaction between butylammonium chloride and $SnCl_4$ results in a decrease in the effective concentration of catalyst, turn slowing down initiation and propagation. Corresponding to Michaelis-Menten kinetics for enzyme catalysis, tin (IV) chloride can be considered as the enzyme, a polymer chain of n and n+1 repeat units the substrate and the product, respectively, a chloride anion from the butylammonium chloride the inhibitor, and the active propagating polymer chain, ES. The substrate concentration then equals the initial concentration of initiator, provided that initiation is rapid. According to equation (13), the rate of polymerization can be expressed as

$$\frac{-d[M]}{dt} = k_p[SnCl_4]_0[M]\left(1+\frac{K}{[1-PEC]_0}\left(1+\frac{[nBu_4NCl]_0}{K_2}\right)\right)^{-1} \qquad (14)$$

and the apparent rate constant k_{app} as

$$k_{app} = k_p[SnCl_4]_0\left(1+\frac{K}{[1-PEC]_0}\left(1+\frac{[nBu_4NCl]_0}{K_2}\right)\right)^{-1} \qquad (15)$$

Rewriting equation (15) yields

$$\frac{1}{k_{app}} = \frac{1}{k_p[SnCl_4]_0}\left(1+\frac{K}{[1-PEC]_0}\right)+\frac{K}{k_pK_2[SnCl_4]_0[1-PEC]_0}[nBu_4NCl]_0 \qquad (16)$$

Therefore based on the proposed mechanism, there will be a linear relationship between the reciprocal of the apparent rate constant and the concentration of butylammonium chloride when the initial concentrations of catalyst and initiator are kept constant.

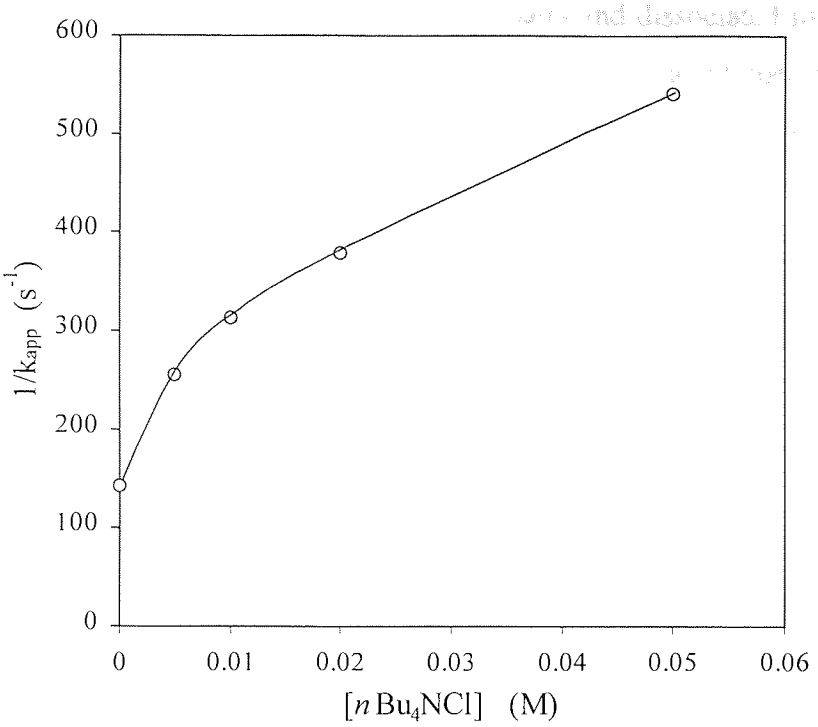


Fig. 5. 28 Plot of the reciprocal of k_{app} versus initial concentration of nBu$_4$NCl.

Fig. 5.28 shows the reciprocal of the apparent rate constant against the initial concentration of butylammonium chloride for polymerizations with [Styrene]$_0$ = 1M; [1-PEC]$_0$ = 0.023M; [$SnCl_4$]$_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v); T = -15 °C. Although the plot of $1/k_{app}$ against [nBu$_4$NCl] is not linear at low concentrations of nBu$_4$NCl it does tend to show linearity above 0.15 mol dm^{-3}. It is possible therefore to explain this dependence in terms of two sets of conditions, and hence two species, operating. One of these species is present at low concentrations of nBu$_4$NCl, probably equivalent to the conventional species, and the other at higher concentrations of nBu$_4$NCl. This is perhaps tenuous evidence for the existence of two types of propagating species.

5.4.2 Propagation by two species

The mechanism for styrene polymerization initiated with the 1-PEC / $SnCl_4$ system in the presence of butylammonium chloride is proposed in terms of two active species based on Winstein ionicity spectrum **[21]**. The propagating chain end can exist in

various forms: covalent species, close contact ion-pairs and dissociated ions with the three types in equilibrium with each other. Assuming the covalent species does not contribute significantly to the rate of polymerization, the apparent rate constant for the polymerization can be given by

$$k_{app} = k_1[P^+SnCl_5^-] + k_2[P^+] \qquad (17)$$

where k_1 and k_2 are the rate constants of propagation for the chain ends present as close contact ion pairs and free ions respectively; $[P^+SnCl_5^-]$ and $[P^+]$ are concentrations of chain ends present as close contact ion pairs and free ions respectively, shown in **Fig. 5.29**.

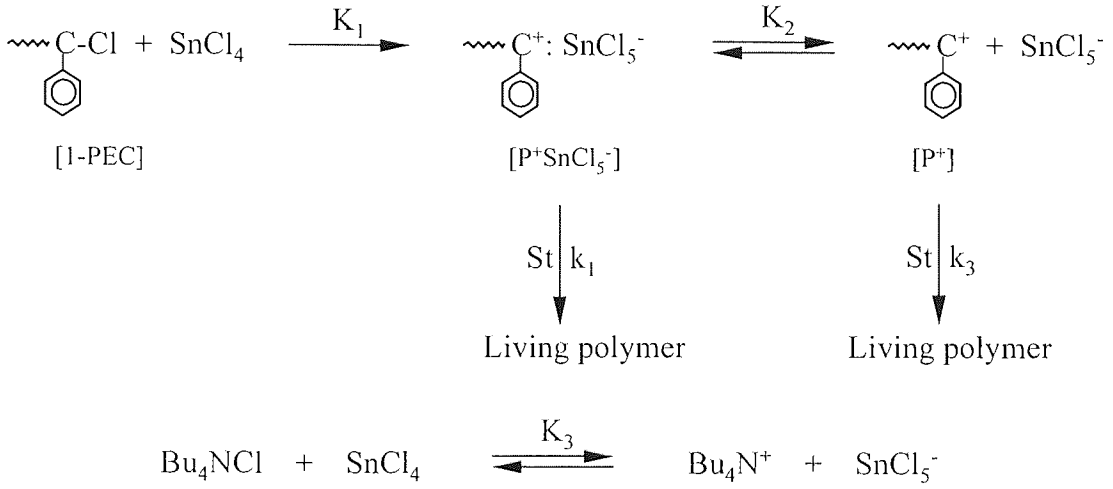


Fig. 5. 29 Proposed mechanism for styrene polymerization with the 1-PEC / $SnCl_4$ / $n$$Bu_4NCl$ system.

The equilibrium constants for the formation of the propagating species shown in **Fig. 5.29** can be expressed as

$$K_1 = \frac{[P^+SnCl_5^-]}{[1-PEC][SnCl_4]} \qquad (18)$$

and

$$K_2 = \frac{[P^+][SnCl_5^-]}{[P^+SnCl_5^-]} \tag{19}$$

Substituting equations (18) and (19) into (17) yields

$$k_{app} = \left(k_1 K_1 + \frac{k_2 K_1 K_2}{[SnCl_5^-]} \right) [SnCl_4][1 - PEC] \tag{20}$$

The concentration of $SnCl_5^-$ can be given by

$$[SnCl_5^-] = [nBu_4NCl]_0 - [Cl^-] + [P^+] \tag{21}$$

where $[Cl^-]$ is the concentration of free chloride anions, and $[n\text{Bu}_4\text{NCl}]_0$ the initial concentration of $n\text{Bu}_4\text{NCl}$. The $[Cl^-]$ and $[P^+]$ are assumed to be small in comparison with $[n\text{Bu}_4\text{NCl}]_0$, as almost all the $SnCl_5^-$ is formed by reaction of $SnCl_4$ and $n\text{Bu}_4\text{NCl}$, and equation (21) may be simplified to

$$[SnCl_5^-] = [nBu_4NCl]_0 \tag{22}$$

Substituting equation (22) into equation (20) gives

$$k_{app} = \left(k_1 K_1 + \frac{k_2 K_1 K_2}{[nBu_4NCl]_0} \right) [SnCl_4][1 - PEC] \tag{23}$$

As the concentration of close contact ion pairs is likely to be small compared to the concentration of covalent species, the [1-PEC] and $[SnCl_4]$ can be given by

$$[1 - PEC] = [1 - PEC]_0 - [P^+SnCl_5^-] - [P^+] \approx [1 - PEC]_0 \tag{24}$$

and

$$[SnCl_4] = [SnCl_4]_0 - [P^+SnCl_5^-] - [SnCl_5^-] \approx [SnCl_4]_0 - [nBu_4NCl]_0 \quad (25)$$

Substituting equations (24) and (25) into equation (23) yields

$$\frac{k_{app}}{[SnCl_4]_0 - [nBu_4NCl]_0} = k_1K_1[1-PEC]_0 + \frac{k_2K_1K_2[1-PEC]_0}{[nBu_4NCl]_0} \quad (26)$$

where [1-PEC]$_0$ is the initial concentration of the initiator, 1-PEC. If [I]$_0$ is kept constant, the plot of k_{app}/([SnCl$_4$]$_0$-[nBu$_4$NCl]$_0$) against 1/[nBu$_4$NCl]$_0$ will be a straight line.

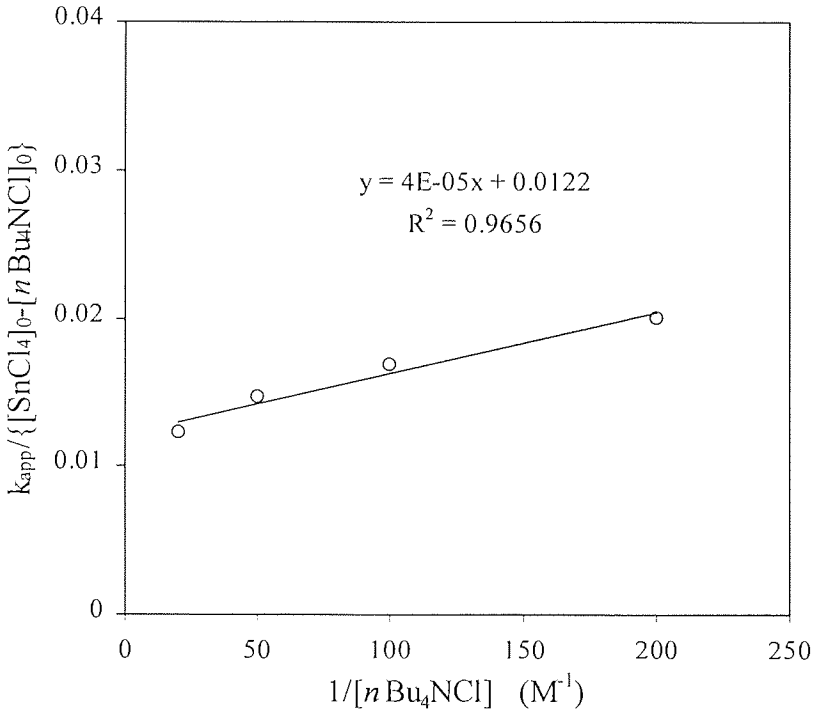


Fig. 5. 30 Plot of k_{app}/{[SnCl$_4$]$_0$-[nBu$_4$NCl]$_0$} against 1/[nBu$_4$NCl]$_0$.

Fig. 5.30 shows the plot of $k_{app}/([SnCl_4]_0\text{-}[n Bu_4NCl]_0)$ versus $1/[n Bu_4NCl]_0$ for styrene polymerizations in the presence of a series of $n Bu_4NCl$ concentrations with $[Styrene]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.023M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v); T = -15 °C. A straight line with R^2 = 0.97 was obtained, indicating that the two species mechanism can apply for the styrene polymerization in the presence of butylammonium chloride.

5.5 Polymer characterisation

5.5.1 ^{1}H NMR analysis of polystyrene

The terminal structure of the living polymers, obtained from the polymerization of styrene using 1-phenyl ethylchloride as an initiator and tin tetrachloride as a catalyst in DCM / C.hex cosolvents in the presence of tetra-*n*-butylammonium chloride, was examined by ^{1}H NMR spectroscopy. **Fig. 5.31** shows the spectrum of the polymers obtained with 1-PEC / $SnCl_4$ / $n Bu_4NCl$ in DCM / C.hex 30 / 20 v / v at –15 °C, following by quenching with methanol at monomer conversion equal to 60%.

The ^{1}H NMR analysis of the polymer sample did not reveal any peaks in the 4.7 – 6.7 ppm range, indicating the absence of unsaturated end groups which may result from chain transfer or termination. This is extra evidence for the absence of chain transfer and termination in addition to the linearities of the plots of $\ln([M]_0/[M])$ against time and M_n against conversion as discussed in section 5.2.1.

The resonance at 1.6 ppm (a) was assigned to the residual protons of water in methanol. The strong resonances at 6.7 – 7.3 ppm are from the phenyl protons (b) of the styrene units, i.e. the aromatic absorption. The absorption of the methyl protons (c) at the α-end of the polystyrene was observed at 1.1 ppm. The signal at 1.4 ppm was ascribed to the methine protons (d), and the signals in the 2 – 2.5 ppm range to

the methine protons (e) adjacent to phenyl. The absorption assigned to the chlorinated ω-terminal methine proton (f) was fond at 4.6 ppm although the peak intensity is small. This would suggest that the living polymerization proceeds via activation of the carbon-chlorine bond (C-Cl) and that the chlorine atom is attached to the terminal even after the quenching with methanol, which was observed by other researchers **[33, 93]**.

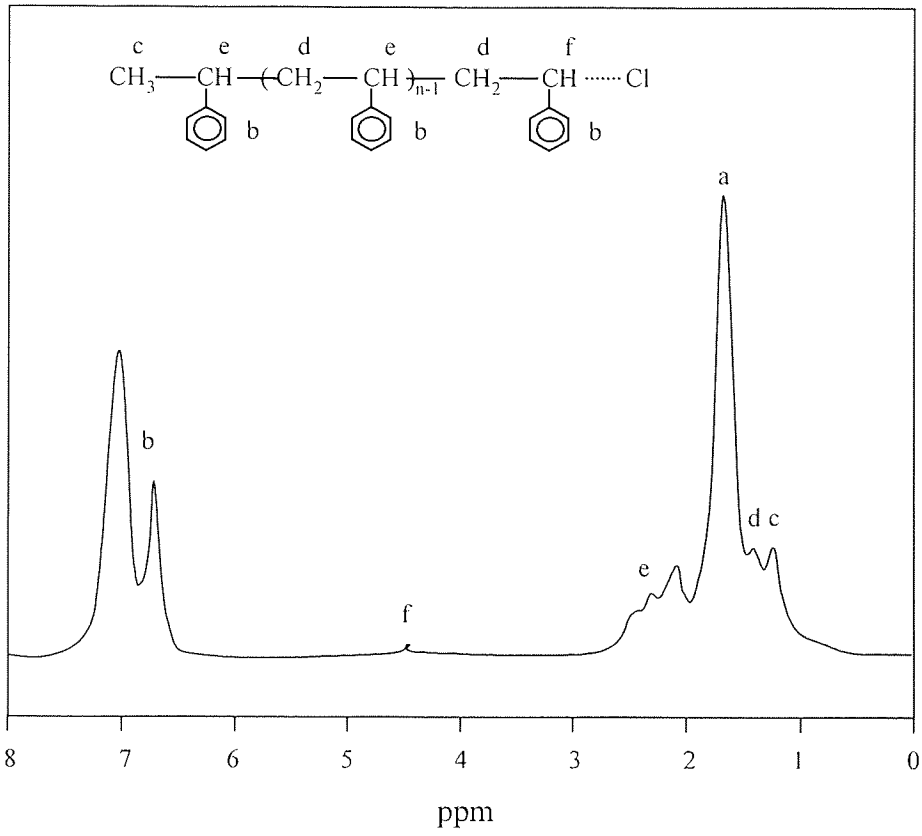


Fig. 5. 31 ^{1}H NMR spectrum of polystyrene obtained with 1-PEC/$SnCl_4$/nBu_4NCl in DCM/C.hex 30/20 v/v at -15 °C after quenching the polymerization with methanol at monomer conversion equal to 60%. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M.

5.5.2 ^{13}C NMR analysis of polystyrene

Fig. 5.32 shows the ^{13}C NMR spectrum of the polymers obtained with 1-PEC/$SnCl_4$/nBu_4NCl in DCM/ C.hex 30/20 v/v at -15 °C after quenching with

methanol at monomer conversion equal to 60%. The negative peaks at about 77 ppm were due to the absorption of the deuterated chloroform solvent used. The signals at 125 - 129 ppm were ascribed to the aromatic carbon atoms (g) of the polystyrene. The absorptions of the aliphatic carbon atoms (h) of the polystyrene were observed at about 40 ppm.

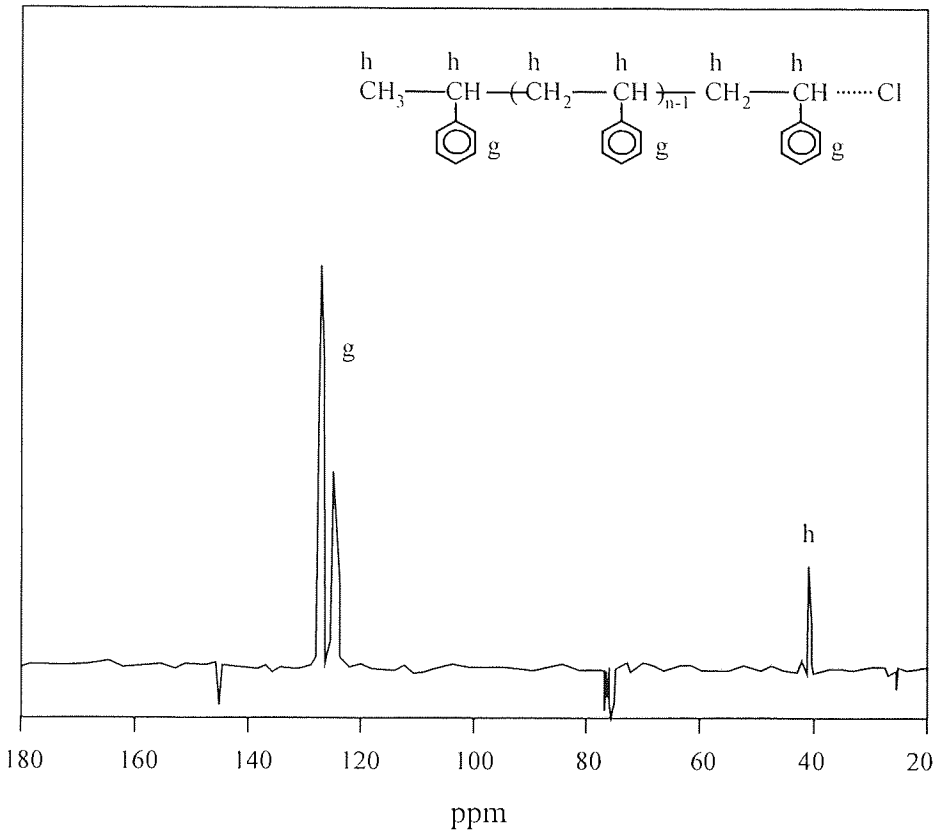


Fig. 5. 32 ^{13}C NMR spectrum of polystyrene obtained with 1-PEC/$SnCl_4$/nBu_4NCl in DCM/C.hex 30/20 v/v at -15 °C after quenching the polymerization with methanol at monomer conversion equal to 60%. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NCl]_0$ = 0.02M.

CHAPTER 6

DEVELOPMENT OF POLYMERIZATION SYSTEMS IN THE PRESENCE OF BROMIDE SALTS ($R_{4n}NBr_4$)

6.1 Introduction

The kinetics of styrene polymerization with 1-phenyl ethylchloride / tin (IV) tetrachloride initiation systems in the presence of tetra-*n*-butylammonium chloride in mixtures of DCM and C.hex were described in Chapter 5. The high initiation efficiencies shown in **Figs. 5.11**, **5.20** and **5.24** are evidence of more polymer chains are being formed than expected. These values were attributed to the presence of impurities, transfer reactions **[27]**, or measurement errors. As the presence of impurities or transfer reactions would appear unlikely because many techniques were used to prevent polymerization from impurities, the measurement error on weighing polymers was then ascribed to be the most possible reason for the higher efficiencies.

However, other possible explanations could be made to explain the higher initiation efficiencies. If the added salt (i.e. nBu$_4$NCl) was involved in the reaction, more polymer chains could be formed than expected. To test this hypothesis styrene polymerizations in the presence of ammonium chlorides with different alkyl groups (CH_3-) had to be carried out. As bromide salts having various alkyl groups were commercially available, polymerizations were conducted in the presence of different

bromide salts. The structure of the polystyrenes were also determined by ^{1}H and ^{13}C NMR spectroscopy.

6.2 Reactions in the presence of bromide salts with various alkyl groups

The kinetic experiments using a unique sampling device constructed from Omnifit parts were conducted to study the polymerization of styrene monomers initiated with the 1-phenyl ethylchloride / tin (IV) tetrachloride system in the presence of various ammonium bromides.

6.2.1 The ratio of [monomer] to [initiator] being 50 : 1

Experiments were conducted to elucidate the effect of the type of the bromide salt on the rate of polymerization, which was determined using gel permeation chromatography (GPC) with THF as solvent. Polymer samples were taken at interval using the Ominifit sampling technique. The initial concentrations of styrene monomer, initiator (1-phenyl ethylchloride) and catalyst (tin tetrachloride) were constant; $[Styrene]_0$ = 1 M, $[1\text{-PEC}]_0$ = 0.02 M and $[SnCl_4]_0$ = 0.2 M. A mixture of dichloromethane CH_2Cl_2 (DCM) and C.hex (30:20 in volume) was used as solvent and the reactions were kept at - 15 °C.

Fig. 6.1 shows the monomer conversion against time curves for the styrene polymerizations in the presence of 0.02M solutions of different bromide salts: tetra-*n*-butylammonium bromide, tetra-*n*-pentylammonium bromide, tetra-*n*-heptylammonium bromide, and tetra-*n*-octylammonium bromide. The polymerizations were not completed within 7 hours under the reaction conditions. Monomer conversions increased gradually with time as expected. Clearly the trends of the plots of conversion versus time are quite similar for polymerizations in the

bromide salts with different alkyl groups, indicating that the nature of the alkyl group of the added bromide salt has no effect on the rate of polymerization.

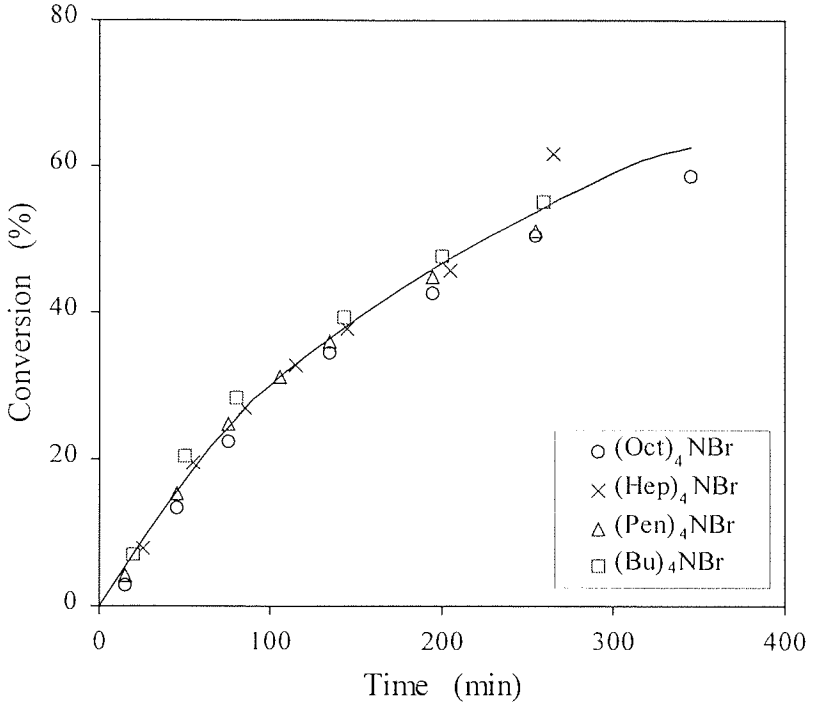


Fig. 6. 1 Conversion vs time curves for styrene polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

To test whether the polymerizations were free of termination, $\ln([M]_0/[M])$ was plotted against time for the polymerizations in the presence of 0.02M solutions of different bromide salts is shown in **Fig. 6.2.** A series of straight lines were observed although there were some deviations from the line at high conversions, this may be attributed to the measurement errors in weighing polymers since small variations in the measurement of [M] under these conditions leads to large variations in $\ln [M]_0/[M]$. The linearity of $\ln([M]_0/[M])$ versus time demonstrates that essentially no termination occurred within the studied lifetimes of the polymerizations.

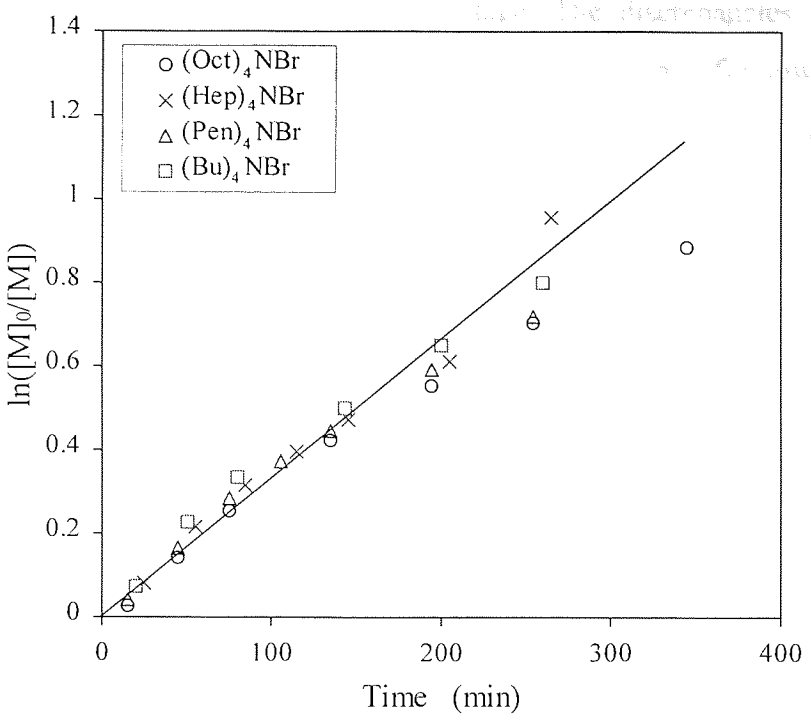


Fig. 6. 2 Graph of $\ln([M]_0/[M])$ against time for polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Based on the Equation (2) in chapter 5 and assuming first order kinetics, the pseudo first order rate constant of polymerization can be extracted from the slopes of the plots of $\ln([M]_0/[M])$ against time. It can be seen from the **Fig. 6.2** the slopes of the lines can be thought to be the same regardless of the different bromide salts. Then the pseudo first order rate constant for all polymerizations can be estimated from the slope as 0.0034 s^{-1}, and its magnitude is independent of the type of the bromide salts present in the polymerization.

The number average molecular weight against conversion was constructed for the same polymerizations (as shown in **Fig. 6.2**) to testify the absence of chain transfer and thus provide evidence for livingness of the polymerizations. **Fig. 6.3** shows the number average molecular weight M_n as a function of monomer conversion. M_n increased in direct proportion to monomer conversion and agreed fairly with the theoretical number-average MW expected from the concentration ratios of monomer

to initiator (solid line) except in the initial stage. The discrepancies in the low conversions may be ascribed to be the GPC measurement error for low molecular weight polymers or slow initiation explained in section 5.2.1 of chapter 5. No significant effect of the type of bromide salts was found on the number average molecular weight of the polymer obtained.

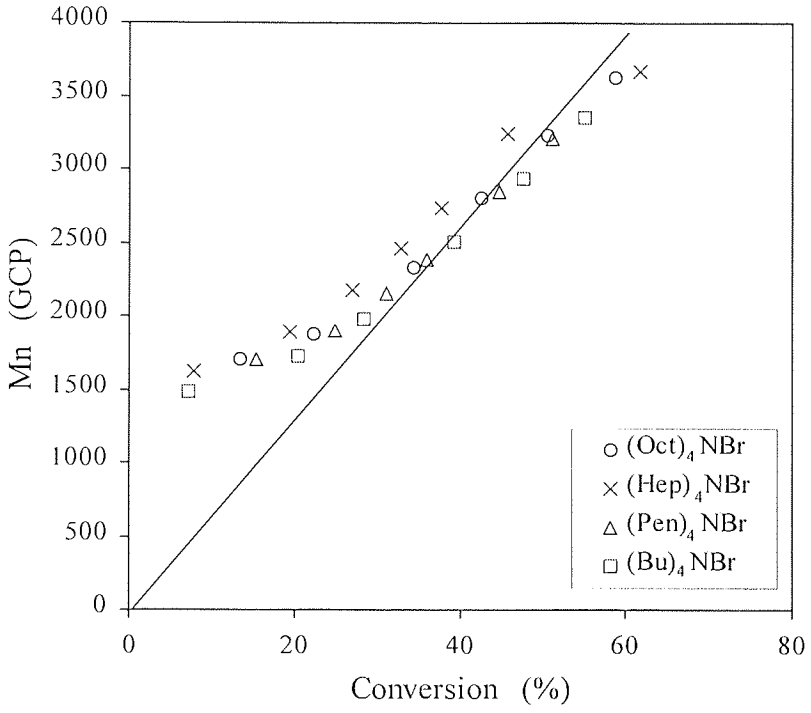


Fig. 6. 3 M_n vs conversion plots for styrene polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Fig. 6.4 shows the polydispersities (P.D.) of the polymers obtained in the presence of 0.02M solutions of various bromide salts. The molecular weight distributions were mono-modal with very low polydispersities ($\overline{M_w} / \overline{M_n}$ < 1.15), which are indicative of living polymerization. Such observations confirmed again the absence of transfer reactions during polymerization.

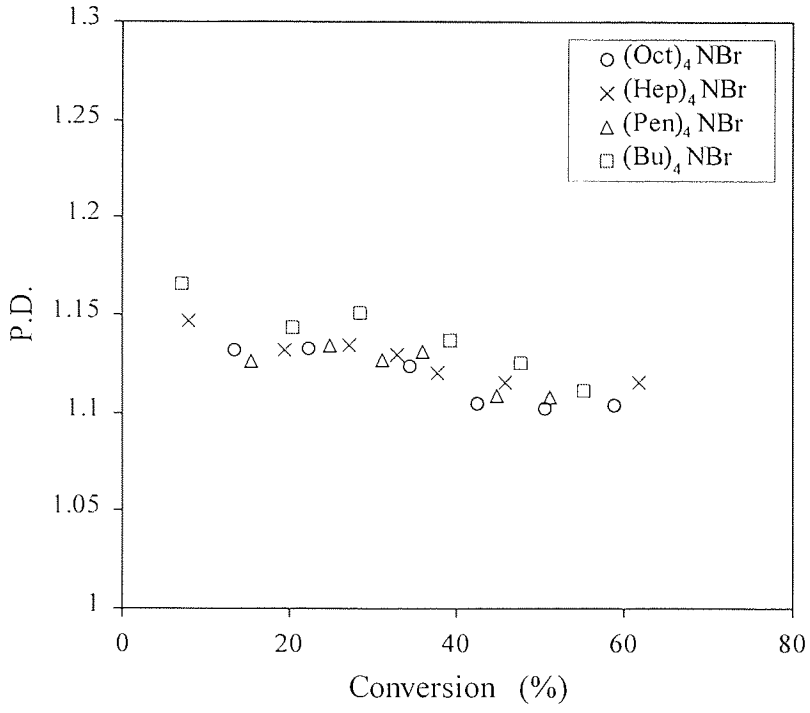


Fig. 6. 4 Polydispersities of the polymers obtained during styrene polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Fig. 6.5 shows the initiator efficiencies as a function of monomer conversion for the same styrene polymerizations in the presence of different bromide salts. In the initial stage, i.e. conversion less than 30%, the initiating efficiencies increased gradually with conversion and reached a plateau around 0.9, which is close to the theoretical initiator efficiency assuming one initiator molecule leads to one polymer active centre. This would suggest slow initiation or slow build up of the propagation species, as described in section 5.2.1 in chapter 5.

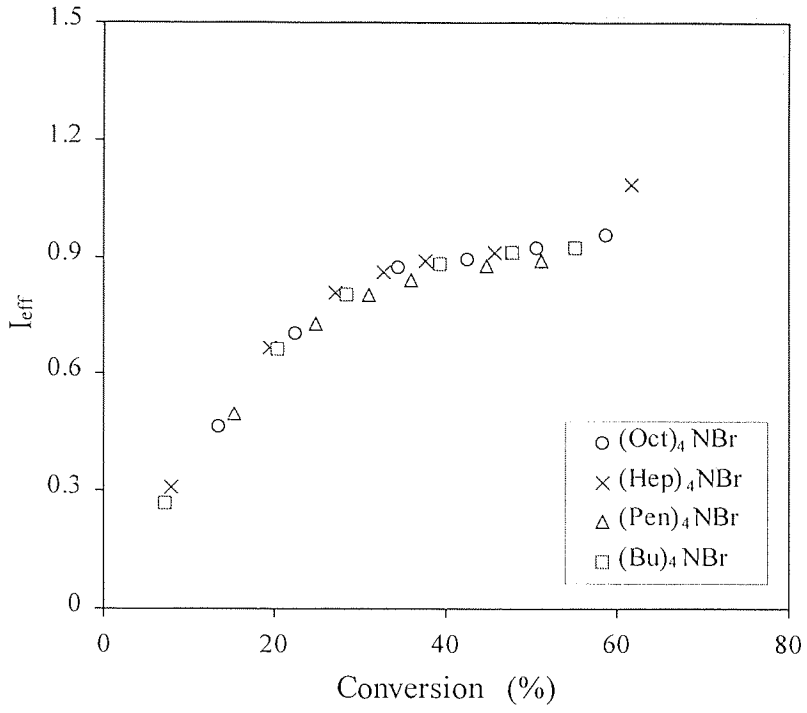


Fig. 6. 5 Efficiencies of the initiator for styrene polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

6.2.2 The ratio of [monomer] to [initiator] being 100 : 1

In order to confirm the findings described in the previous section, a series of experiments was carried out with different ratios of the initial concentration of monomer to the initial concentration of initiator, i.e. the initial concentration of 1-PEC was reduced to half that used in the experiments described in the previous section.

Reactions were conducted to study the effect of the type and molar ratios of the bromide salts on the styrene polymerization. The polymerizations occurred at mixtures of dichloromethane / C.hex (30/20 v/v) at - 15 °C. The Ominifit sampling technique was used to take polymer samples at intervals for the GPC and weight analyse. The initial concentrations of styrene monomer, 1-phenyl ethylchloride and tin (IV) tetrachloride were kept constants; $[Styrene]_0$ = 1 M, $[1\text{-PEC}]_0$ = 0.01 M and $[SnCl_4]_0$ = 0.2 M.

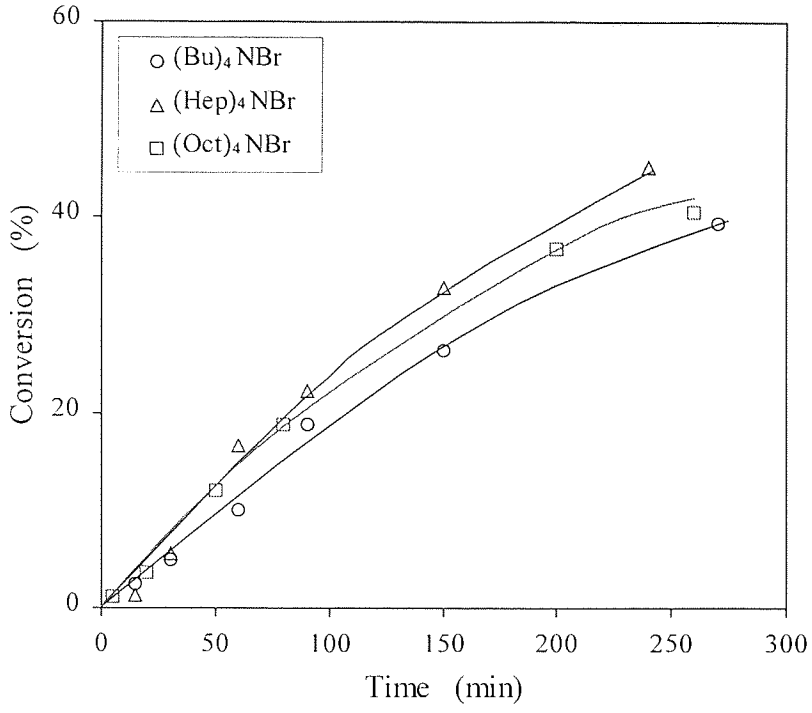


Fig. 6. 6 Conversion vs time curves for styrene polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.01M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Fig. 6.6 shows the plots of monomer conversion against time for the styrene polymerizations initiates with 0.01M 1-PEC / 0.2M $SnCl_4$ in the presence of 0.02M solutions of different bromide salts: tetra-*n*-butylammonium bromide, tetra-*n*-ammonium bromide, and tetra-*n*- ammonium bromide. As the initial concentration of the initiator was reduced to 0.01M, the reactions slowed down compared to those described in section 6.2.1. Monomer conversions increased gradually with time as expected, and reached 40% only after four hours. Unlike the polymerizations with $[1\text{-PEC}]_0$ = 0.02M, the monomer converted more slowly in the presence of $(Bu)_4NBr$ than those with $(Hep)_4NBr$ and $(Oct)_4NBr$.

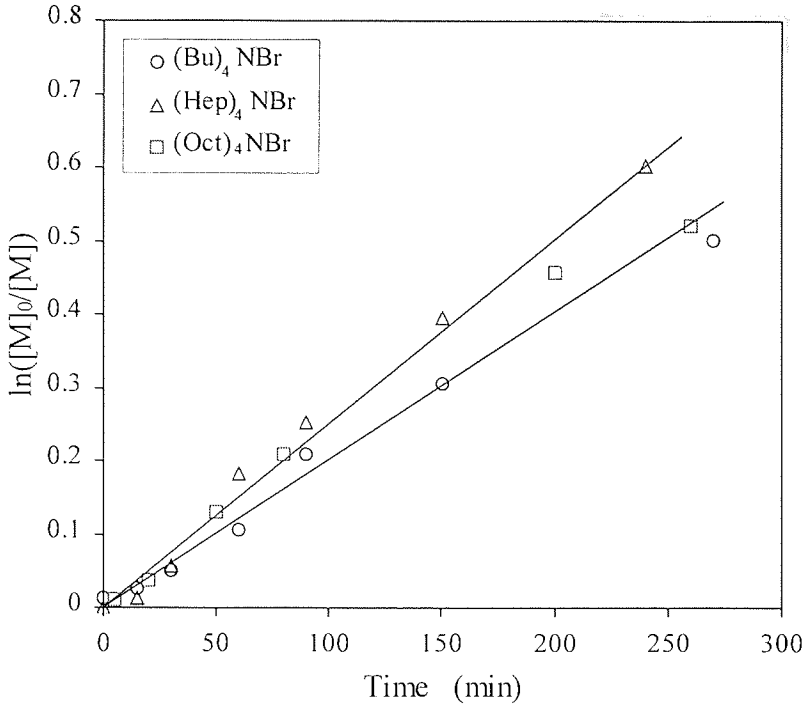


Fig. 6. 7 $\ln([M]_0/[M])$ against time for polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.01M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Fig. 6.7 shows the plots of $\ln([M]_0/[M])$ against time for styrene polymerizations in the presence of 0.02M solutions of three bromide salts with various alkyl group. Clearly all the plots were linear and passed through the origin, indicating the absence of irreversible termination within the lifetimes of the polymerizations. The apparent rate constants for the polymerizations can be obtained from the gradients of the plots for the first few points. It can be seen from the slopes of the lines that the polymerization under nBu$_4$NBr was slower than that in the presence of other bromide salts.

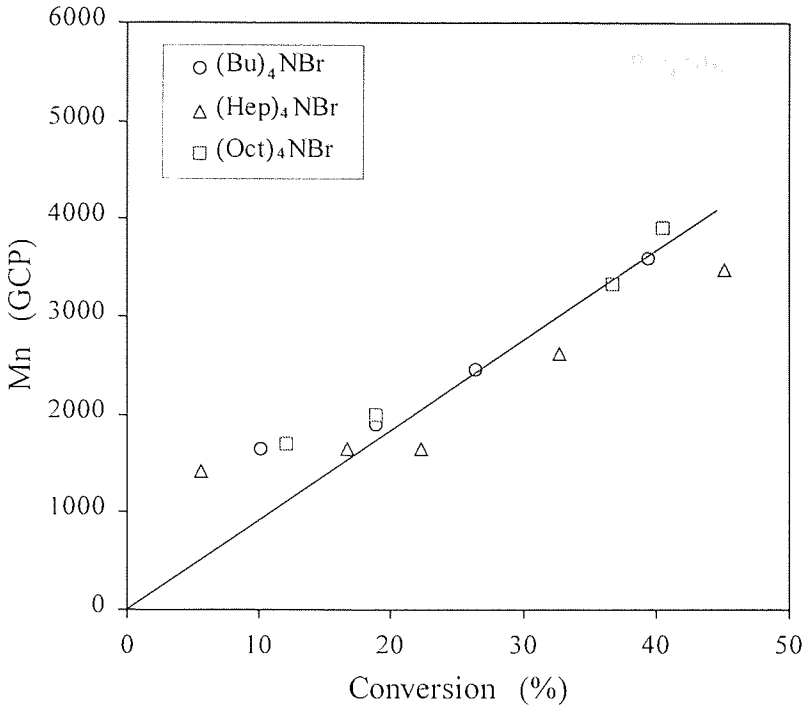


Fig. 6. 8 M_n vs conversion plots for styrene polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.01M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Fig. 6.8 shows plots of M_n as a function of conversion which resulted from the same polymerizations whose kinetic runs were plotted in **Fig. 6.7**. For polymerizations in the presence of 0.02M solutions of $(Bu)_4NBr$ or $(Oct)_4NBr$, the graphs were found to be linear and to fall on the theoretical line (solid) except for the first points, evidence of the absence of chain transfer in the polymerizations. However, the experimental data slightly differed from the theoretical line for the polymerization in the presence of $(Hep)_4NBr$. It could not be accounted for the presence of irreversible transfer reaction, since the polymers obtained had very narrow and nearly uniform MWDs with $\overline{M_w} / \overline{M_n} < 1.17$, as shown in **Fig. 6.9**.

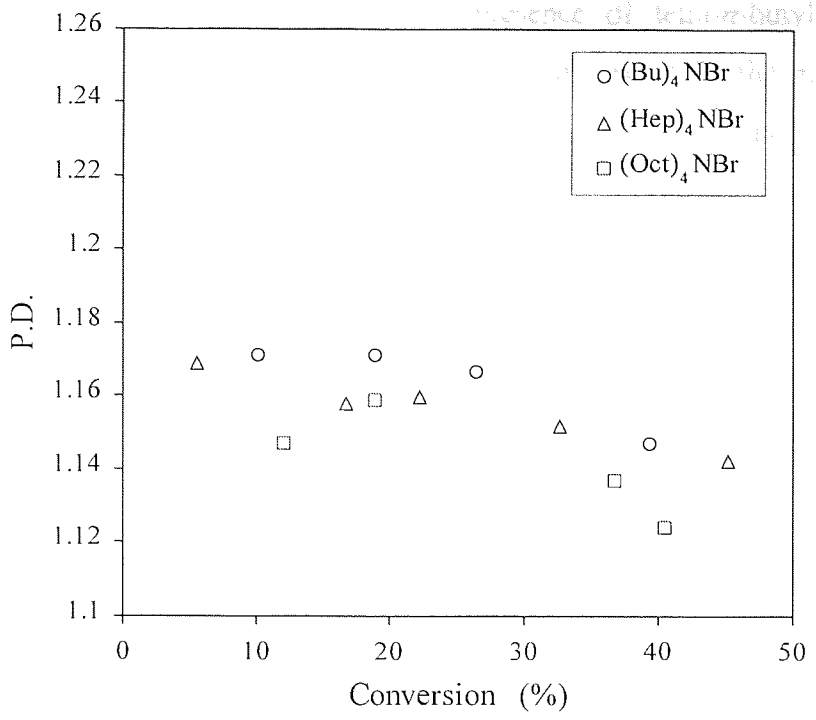


Fig. 6. 9 Polydispersities of the polymers obtained during styrene polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.01M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

Fig. 6.9 shows the polydispersities (P.D.) of the polymers obtained in the presence of 0.02M solutions of various bromide salts. For all polymer samples analysed, molecular weight distributions MWDs were mono-modal and polydispersities ($\overline{M_w} / \overline{M_n}$) were less than 1.15, indicating that all polymerizations in the presence of different bromide salts are living with fairly rapid initiation.

Fig. 6.10 shows the plots of initiating efficiencies against conversion for the same polymerizations. The initiating efficiencies increased gradually when monomer conversion increased, implying slow initiation. When conversions were high than 20%, the initiating efficiencies were found to level around 1.2. These high initiating efficiencies, greater than the theoretical value estimated from the initial concentration of 1-PEC assuming one initiator molecule leads to one polymer chain end, implies that more polymer chains were formed than expected. The same findings have been

observed for styrene polymerization in the presence of tetra-*n*-butylammonium chloride. This may be attributed to the presence of impurities, or the measurement errors in weighting polymers or the added bromide salts participating into the propagation reaction. However the latter appears unlikely. If bromide salts involved in the reaction, different bromide salts should result in polymers with different number average molecular weights, since the bromide salts would be expected to have different number of alkyl groups. Based on the findings described above, the type of the bromide salts had found to have no significant effects on styrene polymerization.

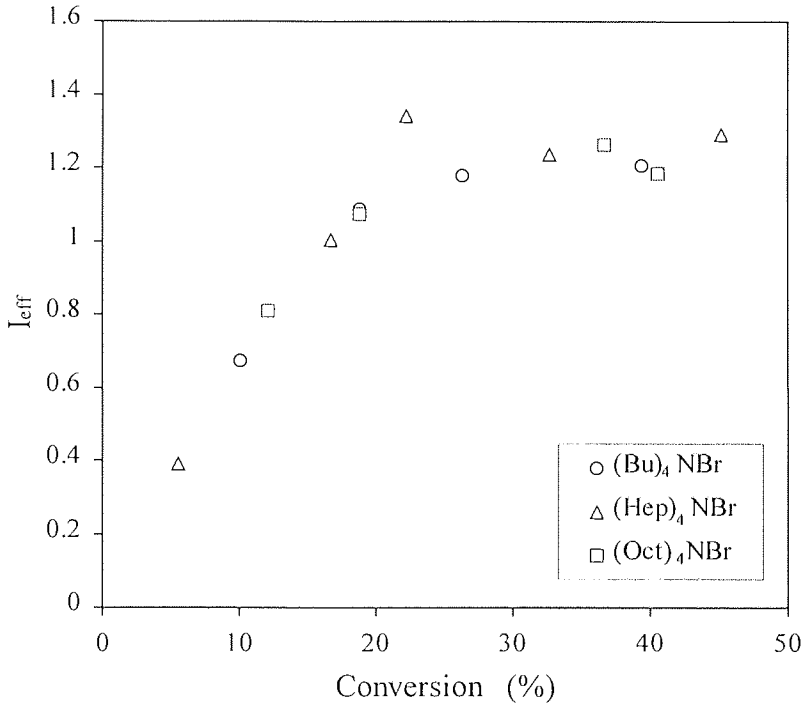


Fig. 6. 10 Efficiencies of the initiator for styrene polymerizations at -15°C in the presence of 0.02M solutions of different bromide salts. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.01M; $[SnCl_4]_0$ = 0.2M; DCM / C.hex = 30 / 20 (v / v).

6.3 Kinetics of styrene polymerization with bromide salts

As described in section 5.3, for a living polymerization, the apparent rate constant of the polymerization (k_{app}) can be obtained from the slope of the plot of $\ln(DP_{n\infty} - DP_n)$ against time t, given by

$$\ln\left(DP_{n\infty} - DP_n\right) = \ln DP_{n\infty} - k_{app}t \qquad (1)$$

where $DP_{n\infty}$ and DP_n are the final number average degree of polymerization and number average degree of polymerization, respectively.

An experiment was conducted with $[Styrene]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n Bu_4NBr]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v/v); T = -15 °C. Polymer samples were taken using Omnifit techniques at desired time intervals and the resultant polymers were analysed by GPC. **Table 6.1** shows the number average molecular weights, polydispersities and degree of polymerization on time for the polymerizations.

Table 6. 1 Dependence of molecular weight and degree of polymerization on time.

Time (min)	$\ln[M]_0/[M]$	Conversion (%)	M_n (GPC)	P.D.	DP_n
20	0.07	7	1483	1.166	3.8
50	0.23	20	1723	1.143	11.0
80	0.33	28	1981	1.151	15.3
143	0.50	39	2502	1.137	21.2
200	0.65	48	2939	1.125	25.7
260	0.80	55	3349	1.111	29.7

Table 6. 2 Dependence of $\ln(DP_{n\infty}-DP_n)$ on time for a range of values of $DP_{n\infty}$.

Time (min)	$\ln(30-DP_n)$	$\ln(40-DP_n)$	$\ln(50-DP_n)$	$\ln(60-DP_n)$
20	3.26	3.59	3.83	4.03
50	2.95	3.37	3.67	3.89
80	2.69	3.21	3.55	3.80
143	2.18	2.94	3.36	3.66
200	1.45	2.66	3.19	3.54
260	-1.12	2.34	3.01	3.41

For a living polymerization, the final number average degree of polymerization ($DP_{n\infty}$) can be estimated from the initial concentrations of monomer and initiator, assuming one initiator molecular leads to one discreet polymer chain, given by

$$DP_{n\infty} = \frac{[M]_0}{[I]_0} \qquad (2)$$

For the polymerization with $[Styrene]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n Bu_4NBr]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v/v); T = -15 °C, the final number average degree of polymerization can then be estimated to be 50.

The final degree of polymerization (50), the DP_n of the final sample (30), and the intervals between them were used to calculate the $\ln(DP_{n\infty}-DP_n)$ in Eq. (1). **Table 6.2** shows the dependence of $\ln(DP_{n\infty}-DP_n)$ on time for a range of values of $DP_{n\infty}$ used, so as to estimate the most appropriate value of $DP_{n\infty}$.

Fig. 6.11 shows the plots of $\ln(DP_{n\infty}-DP_n)$ against time for a range values of $DP_{n\infty}$ between 30 – 60. It can be seen that linear plots were obtained except for $DP_{n\infty}$ used being 30. When $DP_{n\infty}$ used equal to the calculated final degree of polymerization, i.e. 50, a linear plot was obtained with a slope of -0.0033, an intercept of 3.848 and R^2 = 0.99. Therefore the apparent rate constant of polymerization can be obtained from the slope of the plot of $\ln(DP_{n\infty}-DP_n)$ against time as 0.0024 s^{-1}. This value agreed well with the apparent rate constant, 0.0029 s^{-1}, obtained from the gradient of the plot of $\ln\{[M]_0/[M]\}$ versus time.

Table 6.3 shows the value of $DP_{n\infty}$ used and that calculated from the plot of $\ln(DP_{n\infty}-DP_n)$ against time, and the difference between them. When using 50 as the value of $DP_{n\infty}$, the percentage error for the intercept $DP_{n\infty}$ was about 15.6%. Taking into rate constant and $DP_{n\infty}$ used into account, a good agreement was achieved for the value of $DP_{n\infty}$ used 50.

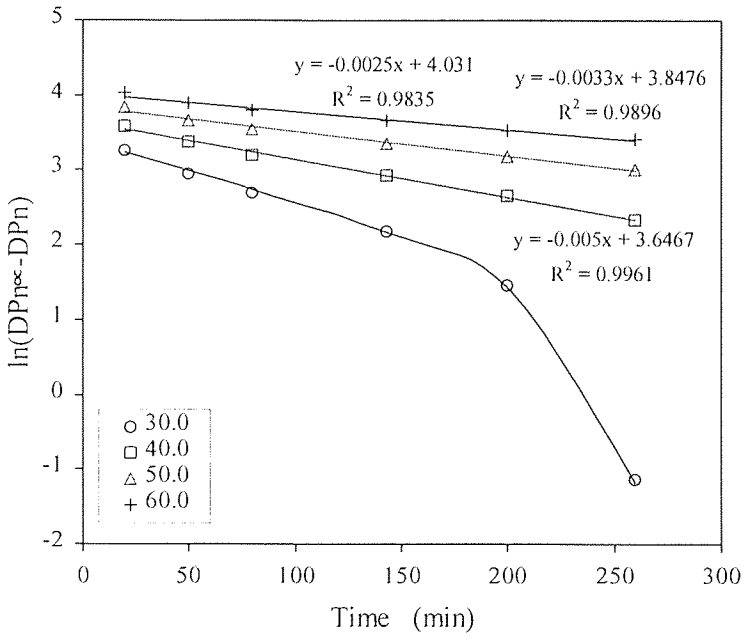


Fig. 6. 11 Plot of $\ln(DP_{n\infty}-DP_n)$ against time for styrene polymerizations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.023M; $[SnCl_4]_0$ = 0.2M; $[nBu_4NBr]_0$ = 0.02M; DCM / C.hex = 30 / 20 (v / v); T = -15 °C.

Table 6. 3 Comparison of $DP_{n\infty}$ between used and intercept values.

$DP_{n\infty}$ (used)	30	40	50	60
$DP_{n\infty}$ (Intercept)	36.1	33	42.2	51.9
Difference	6.1	-7.0	-7.8	-8.1
Errors (%)	20.3	17.5	15.6	13.5

6.4 Polymer characterisation by NMR spectroscopy

Analogue to the polymerization in the presence of tetrabutylammonium chloride, a mechanism was proposed for the styrene polymerization in the presence of bromide salts, as shown in **Fig. 6.12**. The terminal structure of the living polymer was also examined by ^{1}H and ^{13}C NMR spectroscopy.

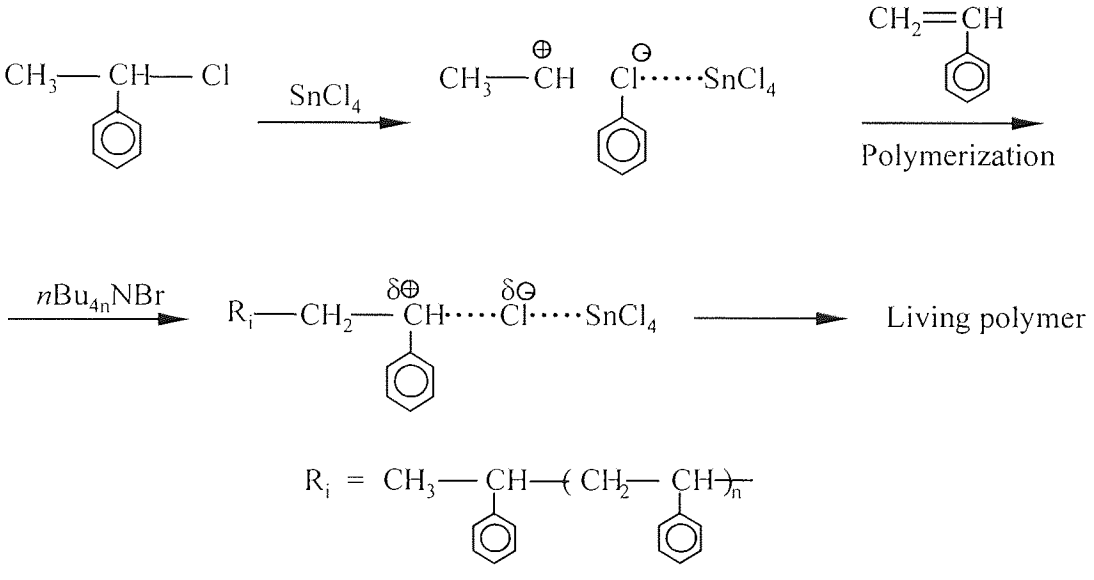


Fig. 6. 12 A proposed mechanism for styrene polymerization in the presence of bromide salts.

6.4.1 ^{1}H NMR

Fig. 6.13 shows the ^{1}H NMR spectrum of the polymers obtained from the styrene polymerization using 1-phenyl ethylchloride (0.02M) as an initiator and tin tetrachloride (0.2M) as a catalyst in DCM/C.hex 30/20 v/v cosolvents at -15 °C in the presence of 0.02M solutions of tetra-*n*-butylammonium bromide (nBu$_4$NBr) after quenching with methanol. **Table 6.4** shows the resonances and their assignment.

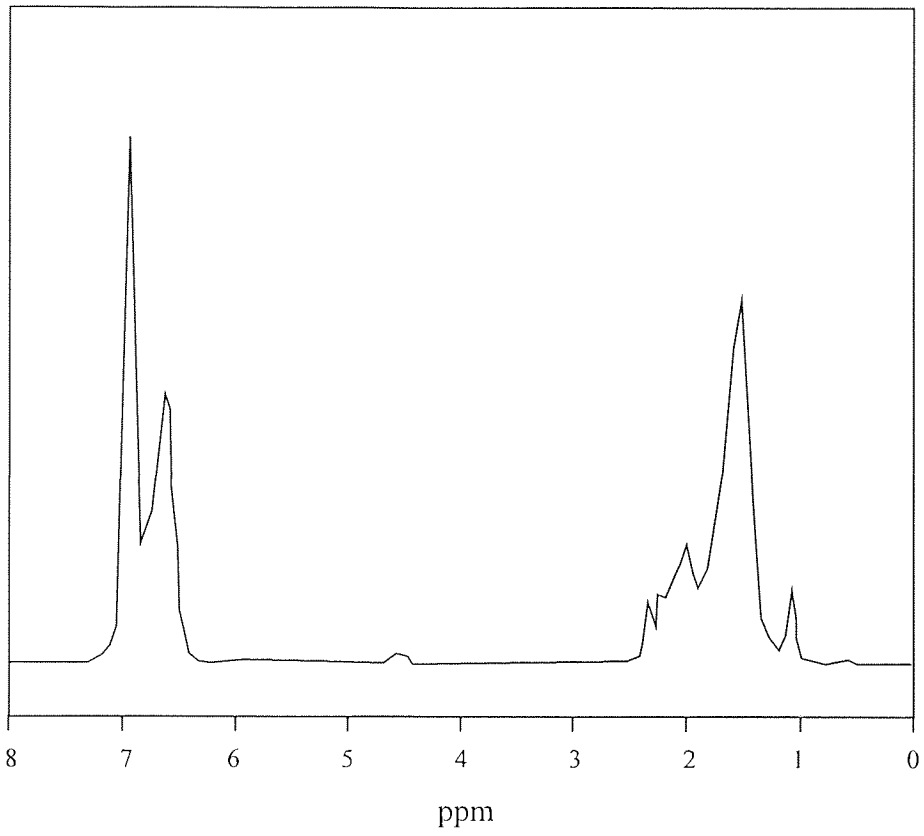
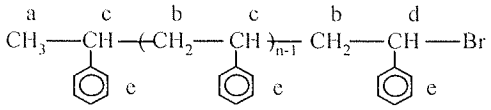


Fig. 6. 13 ^{1}H NMR spectrum of polystyrene obtained with 1-PEC/$SnCl_4$/nBu$_4$NBr in DCM/C.hex 30/20 v/v at -15 °C after quenching the polymerization with methanol at monomer conversion equal to 60%. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n\text{Bu}_4\text{NBr}]_0$ = 0.02M.

Table 6. 4 ^{1}H NMR results for styrene polymerization under nBu$_4$NBr.

ppm	Assignment	Terminal structure
1.15	CH_3- (a)	
1.58	from solvent	
1.96 2.19 2.35	-CH_2- (b) -CH- (c)	
4.47	-CH-Br (d)	
6.68 7.17	aromatic (e)	

^{1}H NMR analysis of the polymer sample failed to reveal any peaks in the 4.5 – 6.7 ppm range, which is evidence of the absence of unsaturation at the chain ends results from chain transfer or termination.

The strong resonance at 1.58 ppm was from the residual protons of water in methanol. The peak at 1.15 ppm was assigned to the methyl protons at the α-end of the polystyrene. Signals at 1.96 – 2.35 ppm were ascribed to the methylene and methine protons –CH_2 and –CH respectively. The resonances of the phenyl protons of the styrene units were observed at 6.68 – 7.17 ppm. The weak peak at 4.47 ppm was from the brominated ω-terminal methine proton, which suggest that the living polymerization proceeds via activation of the carbon-bromide bond (C-Br) and that the bromide atom is attached to the terminal even after the quenching with methanol.

6.4.2 ^{13}C NMR

Fig. 6.14 shows the ^{13}C NMR spectrum of the polymers obtained with 0.02M 1-PEC / 0.2M $SnCl_4$ / 0.02M nBu$_4$NBr in DCM/C.hex 30/20 v/v at -15 °C after quenching with methanol. The negative signal at about 77 ppm were from the deuterated chloroform solvent used. The absorptions at 125 - 129 ppm were ascribed to the aromatic carbon atoms of the polystyrene. The signal at about 40 ppm was from the aliphatic carbon atoms of the polystyrene.

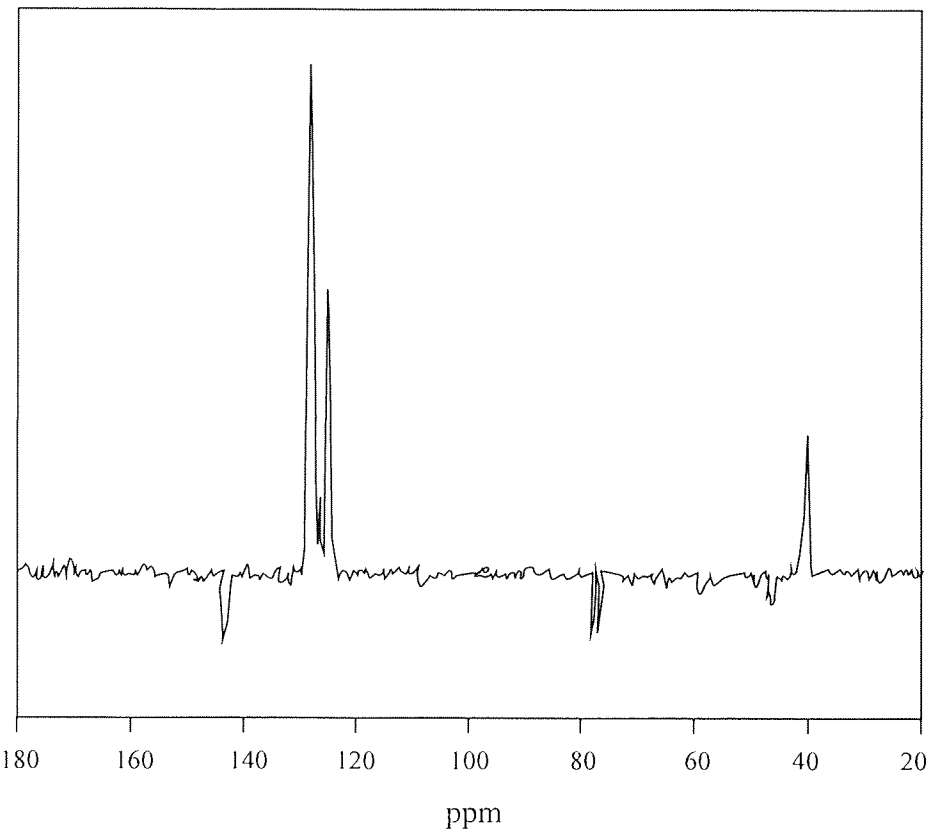


Fig. 6. 14 ^{13}C NMR spectrum of polystyrene obtained with 1-PEC/$SnCl_4$/nBu$_4$NBr in DCM/C.hex 30/20 v/v at -15 °C after quenching the polymerization with methanol at monomer conversion equal to 60%. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.02M; $[SnCl_4]_0$ = 0.2M; $[n\text{Bu}_4\text{NBr}]_0$ = 0.02M.

CHAPTER 7

POLYMERIZATION OF STYRENE USING $TiCl_4$ AS CATALYST IN THE PRESENCE OF PYRIDINE

7.1 Introduction

The results described in chapters 4-6 showed that living cationic polymerizations of styrene monomers take place when using 1-phenyl ethylchloride (1-PEC) as an initiator and tin tetrachloride ($SnCl_4$) as a catalyst in DCM / C.hex mixtures in the presence of tetra-*n*-butylammonium chloride (nBu_4NCl), under certain conditions. Exploration of potential living conditions for styrene polymerization by using another catalyst or salt was then undertaken.

Titanium tetrachloride ($TiCl_4$) has been used as a catalyst in living polymerizations of isobutylene **[77, 104, 108]** and vinyl monomers **[69]**. This chapter focuses on the investigations into styrene polymerization with 1-PEC / $TiCl_4$ initiation systems in mixtures of DCM and C.hex in the presence of pyridine instead of halide salts. An Omnifit sampling method was used to prevent the ingress of impurities into the system. The orders of reaction were obtained from the kinetic study.

7.2 Styrene polymerization with 1-PEC / $TiCl_4$ / nBu_4NCl

Polymerization of styrene monomer with initial concentration 1 M was conducted with 0.02 M 1-PEC and 0.05 M $TiCl_4$ initiating system in DCM / C.hex 30/20 v/v mixture at -15 °C in the presence of 0.02M nBu$_4$NCl. Orange precipitates were observed during the reaction, and no polymer was obtained. The formation of the precipitate may be due to the 'salting out' of $TiCl_4$ in the presence of nBu$_4$NCl.

Table 7. 1 Styrene polymerization with 1-PEC / $TiCl_4$ as the initial system

Time (min)	M_n	M_n (Calculated)	M_n / M_w (P.D.)	I_{eff}	Conversion (%)
2	3073	2476	3.493	0.81	46
4	3373	3508	2.717	1.04	65
6	3668	4277	2.596	1.17	80
8	3768	4718	2.473	1.25	88
10	3936	4997	2.414	1.27	93
15	4391	5392	2.181	1.23	100

A further polymerization was carried out with the absence of nBu$_4$NCl. The initial concentrations of styrene monomer, initiator, catalyst and salt were set at $[Styrene]_0$ = 1 M, $[1\text{-PEC}]_0$ = 0.02 M, $[TiCl_4]_0$ = 0.1 M, DCM / C.hex 20/30 v/v, and T = - 15 °C. The main results are listed in **Table 7.1**. The polymerization finished within 15 minutes. The polymers obtained had high polydispersities ($\overline{M_w} / \overline{M_n} > 2$), indicating that the polymerization was not living.

7.3 Styrene polymerization with 1-PEC / $TiCl_4$ / DTBP

It is well known that 2,6-di-*tert*-butylpyridine (DTBP) is incapable of complexation with carbocations (electrophiles) due to steric hindrance, but has highly specific reactivity toward protons **[109]**. Thus, DTBP was used in the polymerization system, styrene / 1-PEC / $TiCl_4$ / DCM / C.hex, so as to capture protons from the systems and suppress side reactions. A series of experiments was conducted to study the dependence of the rate of polymerization on the initial concentration of the various reactants, such as 1-PEC, $TiCl_4$, DTBP, and monomer, and on the solvent polarity and reaction temperature.

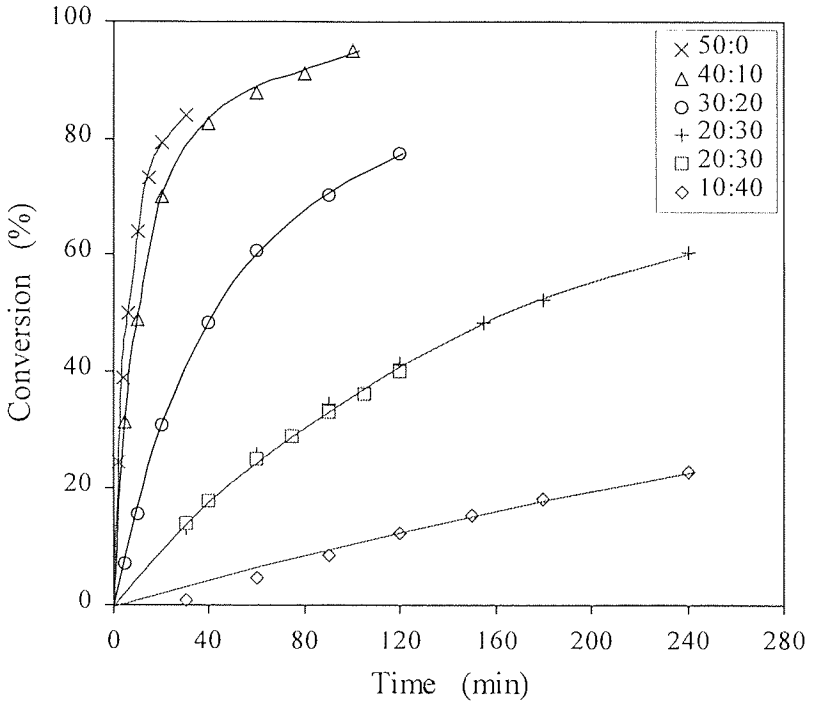


Fig. 7. 1 Conversion against time for styrene polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M.

7.3.1 Effect of solvent polarity

Experiments were conducted to study the effect on polymerization of varying the polarity of the solvent, which was achieved by mixing DCM with C.hex in different ratios. The initial concentrations of styrene monomer, initiator, catalyst and salt were identical in all polymerizations; $[Styrene]_0$ = 1 M, $[1\text{-PEC}]_0$ = 0.005 M, $[TiCl_4]_0$ = 0.05 M, $[DTBP]_0$ = 0.02 M and T = - 15 °C.

Plots of monomer conversion against time for styrene polymerizations under different solvent polarity are shown in **Fig. 7.1**. Monomer conversions increased gradually with time as expected. As the solvent polarity decreased the rate of monomer conversion decreased, i.e. the polymerizations were fast in polar solvents. When the ratio of DCM : C.hex was 10:40 the rate of polymerization was very slow.

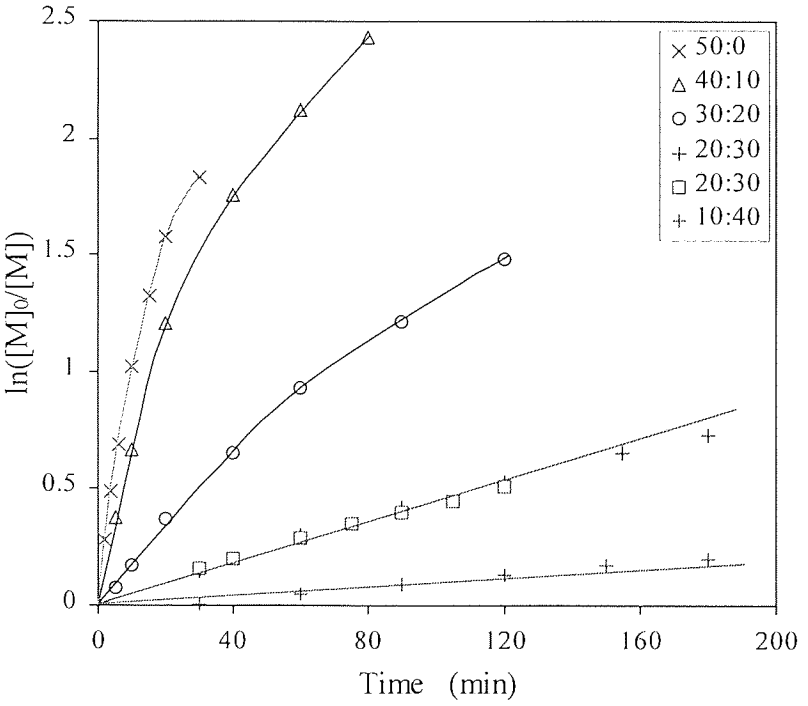


Fig. 7. 2 Plots of $\ln([M]_0/[M])$ against time for styrene polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M.

Fig. 7.2 shows the plots of $\ln([M]_0/[M])$ against time for styrene polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. For the polymerizations in solvents with lower polarities such as mixtures of DCM / C.hex with 20/30 and 10/40 in volume, the plots were linear, which is indicative of the absence of irreversible termination within the lifetimes of the polymerizations. Decreasing solvent polarity resulted in the decrease in the gradients of the plots and in turn the decrease in the apparent rate constant of the polymerization.

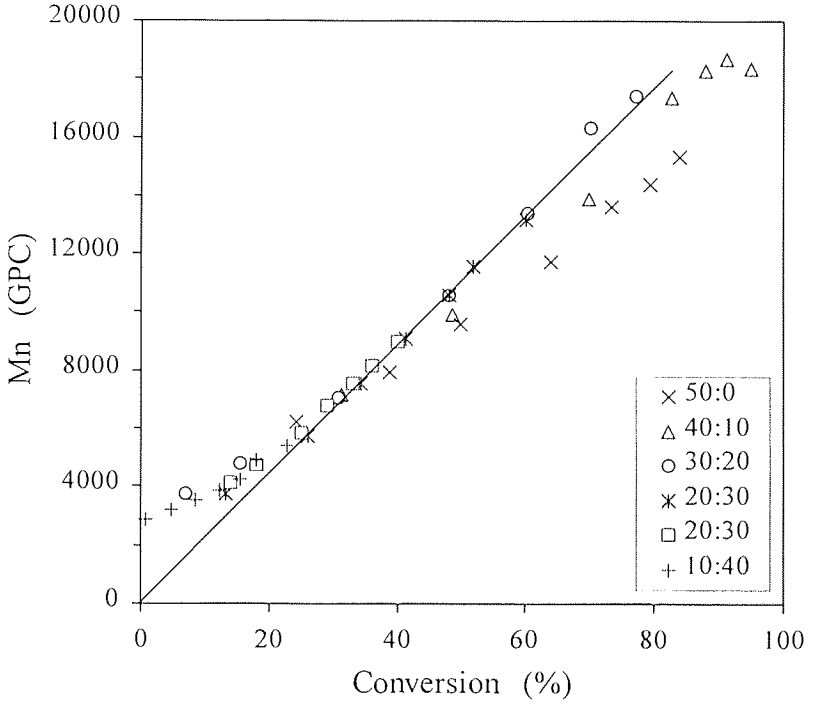


Fig. 7. 3 M_n vs conversion plots for styrene polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M.

Fig. 7.3 shows the plots of number average molecular weight against monomer conversion for the polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. In case of DCM / C.hex 20/30 v/v, the plots were found to be linear and to agree well with the theoretical line (solid), indicating the probable absence of chain transfer in the polymerizations. The discrepancies of M_n from the theoretical line for

the polymerizations in higher polarity solvents are evidence of transfer under such conditions.

Fig. 7.4 shows the polydispersities of the polymers obtained. The low polydispersities ($\overline{M_w}/\overline{M_n}$ ~ 1.2) were found for the polymerizations at lower polarity solvents. Thus the mixture of DCM and C.hex (20/30, v/v) was chosen as the solvent for the further polymerizations.

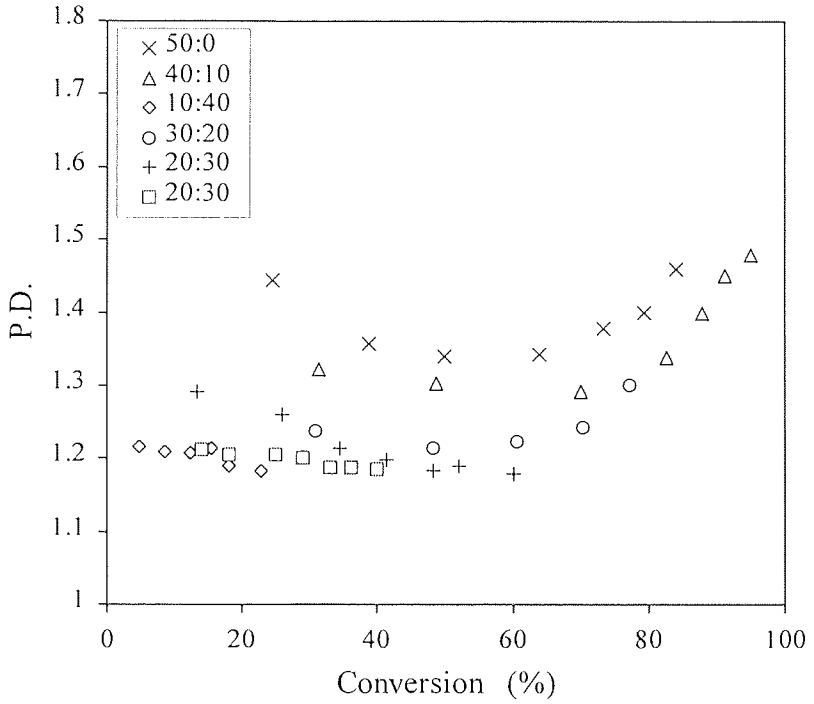


Fig. 7. 4 Polydispersities of the polymers obtained from polymerizations in mixtures of DCM and C.hex with varying ratios at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M.

7.3.2 Effect of temperature

Reactions were conducted to study the effect of reaction temperature on the rate of polymerization. The initial concentrations of styrene monomer, initiator, catalyst and

salt were kept constant at $[Styrene]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

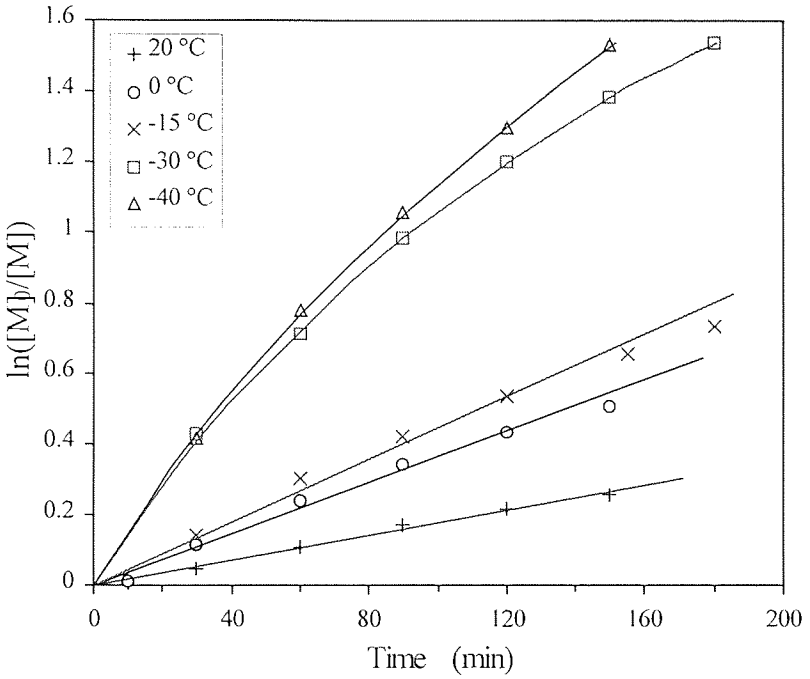


Fig. 7. 5 Plots of $\ln([M]_0/[M])$ against time for styrene polymerizations at various temperatures. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

Fig. 7. 5 shows the plots of $\ln([M]_0/[M])$ against time for styrene polymerizations at different temperatures. Based on the first order kinetic assumption, the apparent rate constants for each polymerization were obtained from the gradients of the lines for the first few points (see **Table 7.2**). For temperatures not less than -15°C, the plots are linear, indicating the absence of irreversible termination for the polymerizations at higher temperatures.

Table 7. 2 The dependence of apparent rate constant on temperature.

T (K)	228	243	258	273	293
k_{app} (s^{-1})	8.67×10^{-3}	7.42×10^{-3}	3.88×10^{-3}	3.51×10^{-3}	1.84×10^{-3}

Fig. 7.6 shows the plot of ln (k_{app}) against the reciprocal of the absolute temperature for the styrene polymerization. A straight line with $R^2 = 0.97$ was obtained, and so the dependence of the apparent rate constant on temperature can be expressed as

$$\ln k_{app} = -1751.5\frac{1}{T} - 12.212 \qquad (1)$$

Obviously the rate constant increased with decreasing temperature, which is common in ionic polymerizations. The change of temperature not only affects the rate constant of polymerization (k_p) but also changes the equilibrium constant for the following equilibrium:

$$PSt\text{-}Cl \cdots MCl_x \rightleftharpoons PSt^+MCl_x^-$$

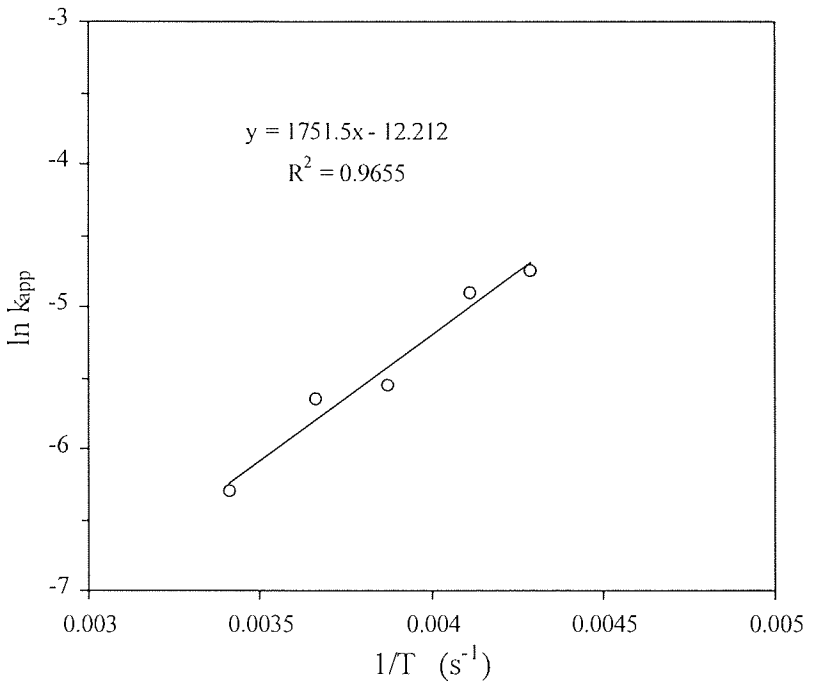


Fig. 7. 6 Effect of temperature on the apparent rate constant of styrene polymerization. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

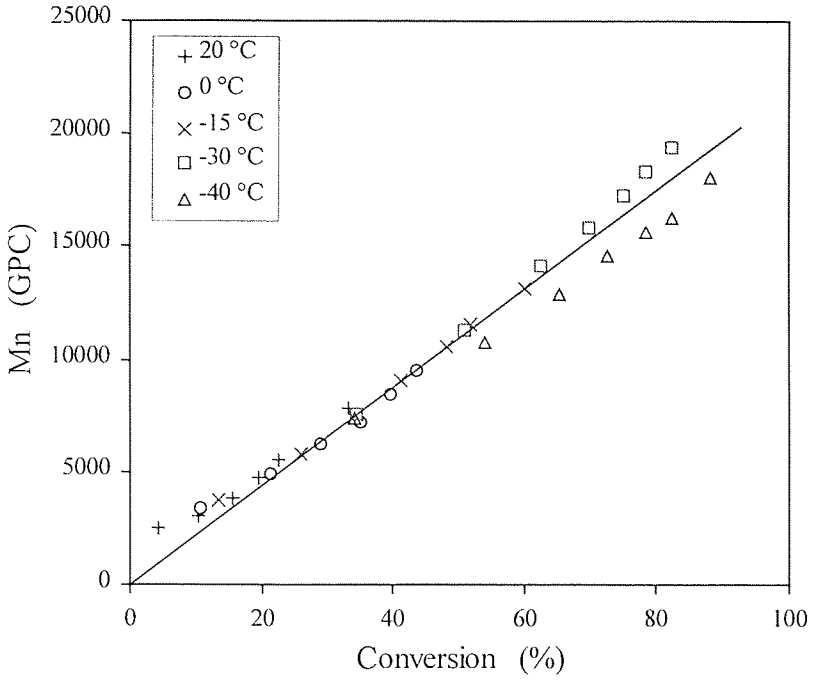


Fig. 7. 7 M_n vs conversion plots for styrene polymerizations at various temperatures. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

Plots of M_n against conversion for the polymerizations are shown in **Fig. 7. 7**. The plots were linear, indicating the absence of chain transfer, and M_n agreed well with the theoretical line except for –30°C and –40°C. The discrepancies at the lower temperatures were some evidence of transfer. The polymers obtained from the polymerizations occurred at temperatures below -15°C had high polydispersities with $\overline{M_w} / \overline{M_n} > 1.2$ (**Fig. 7. 8**), which implies the polymerizations are not living at lower temperatures. This would agree with the displacement of equilibrium.

Fig. 7.9 shows the polydispersities of the polymers obtained from the polymerizations. The gradually increased initiating efficiencies at the initial stage is some evidence of slow build-up of propagating active centre or slow initiation, which has been revealed for the styrene polymerization with 1-PEC / SnCl4 / halide salts, described in the previous chapters.

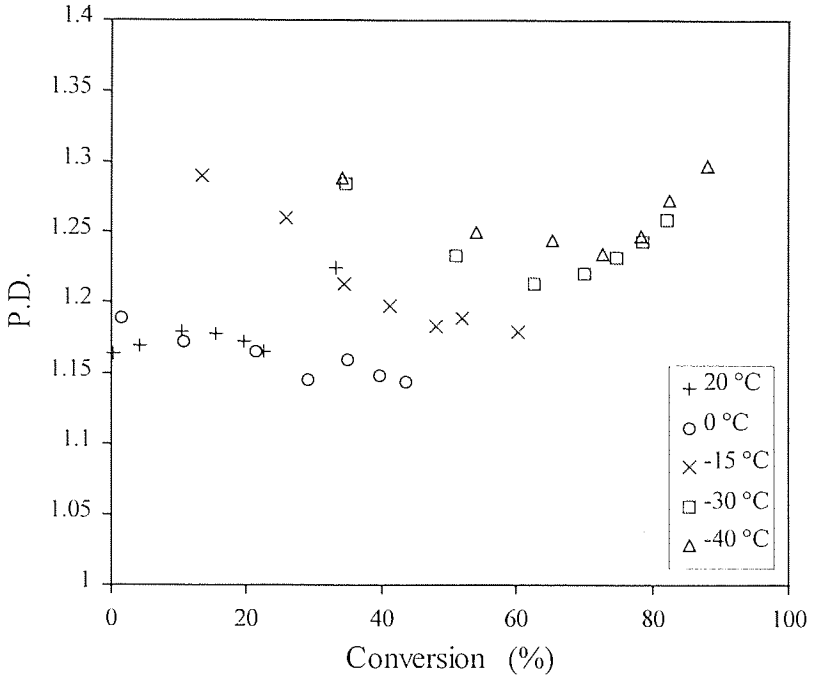


Fig. 7. 8 Polydispersities of the polymers obtained from the polymerizations at various temperatures. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

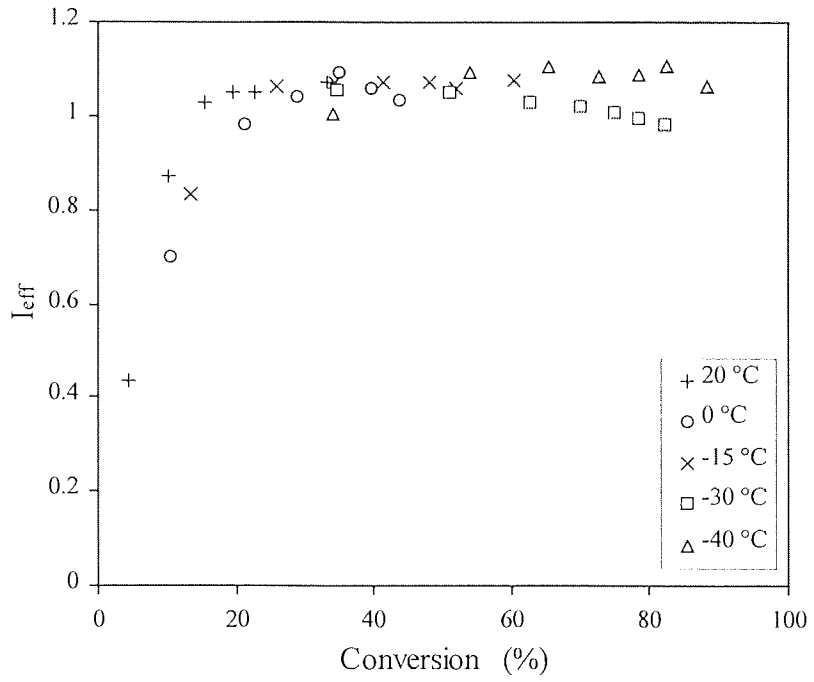


Fig. 7. 9 Efficiencies of the initiator for styrene polymerizations at various temperatures. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

7.3.3 Effect of DTBP initial concentration

Polymerizations were carried out in mixtures of DCM / C.hex (30/20 v/v) at - 15 °C to determine the rate of polymerization for styrene polymerizations in the presence of 2,6-di-*tert*-butylpyridine (DTBP) of varying initial concentrations. The initial concentrations of monomer, initiator and catalyst were constants; $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M, and in a series of experiments the initial concentration of DTBP was varied.

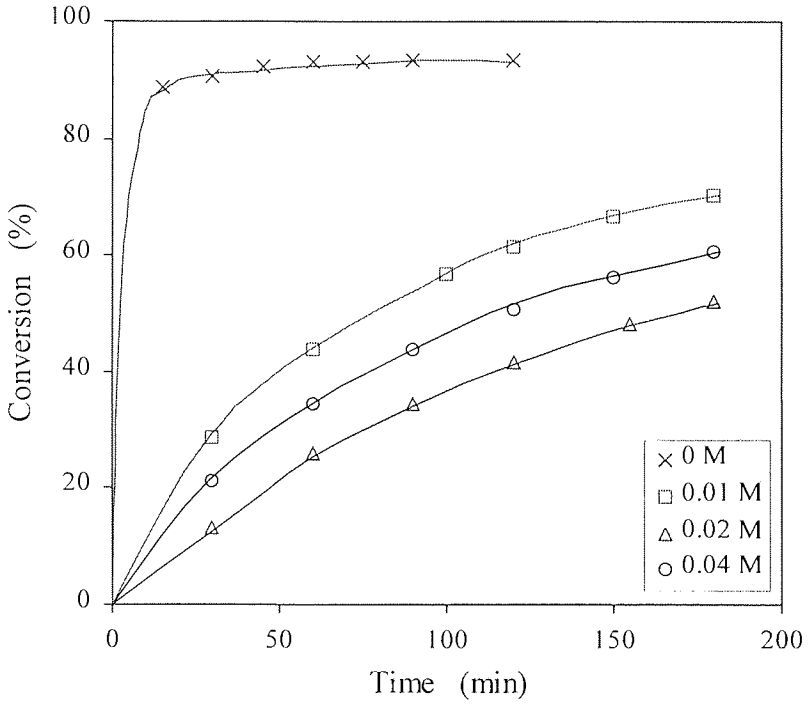


Fig. 7. 10 Monomer conversion vs time curves for styrene polymerizations at -15°C with varying DTBP concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; DCM / C.hex = 20/30 (v/v).

Plots of monomer conversion against time for the styrene polymerizations over a range of initial concentrations of DTBP are shown in **Fig. 7.10**. Without DTBP the polymerization was completed within 10 minutes. Addition of DTBP led to a decrease in the rate of monomer conversion.

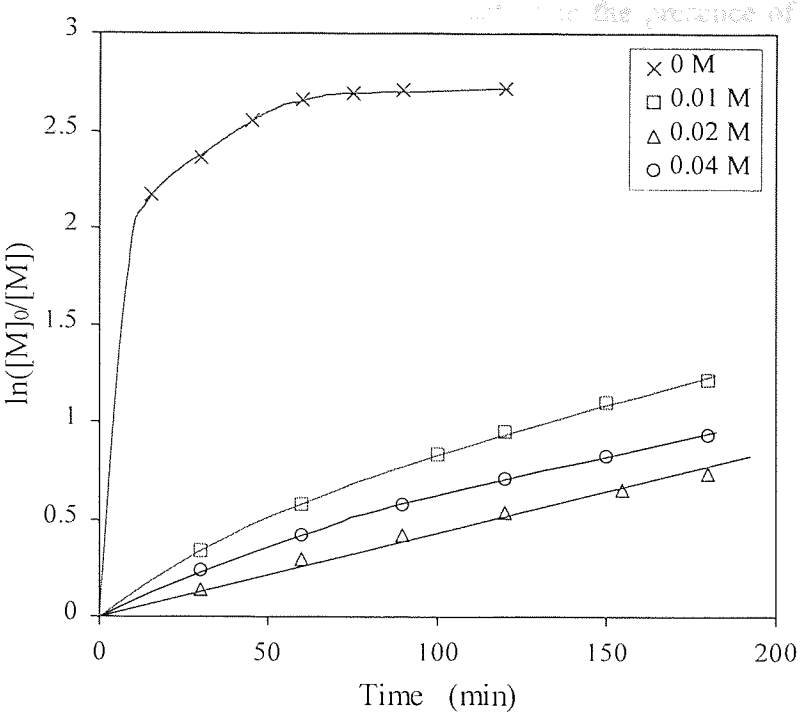


Fig. 7. 11 Plots of $\ln([M]_0/[M])$ against time for polymerizations at -15°C with varying DTBP concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; DCM / C.hex = 20/30 (v/v).

$Ln([M]_0/[M])$ was plotted against time for the polymerizations for the range of DTBP initial concentrations used as shown in **Fig. 7. 11**. The curve plot for the polymerization in the absence of DTBP indicates a conventional cationic polymerization. In the case of DTBP initial concentration being 0.02 M, the plot was a straight line, demonstrating essentially no termination occurred within the studied lifetimes of the polymerizations.

As described in section 5.2 in chapter 5, the rate constant can be extracted from the slopes of the plots of $\ln([M]_0/[M])$ against time assuming first order kinetic. **Fig. 7.12** shows the plot of the rate of polymerization against the initial concentration of DTBP. This no linearity plot would suggest that the rate of polymerization does not have a simple order dependence on the initial concentration of DTBP. The results shown in **Fig. 7.12** may fit a scheme that when the [DTBP] increases to 0.02M conventional catalyst is being complexed out of the system. The increase of [DTBP] above ~0.02M

may have little effect because rates of polymerization in the presence of 0.02M and 0.04M DTBP are identical within the experimental error.

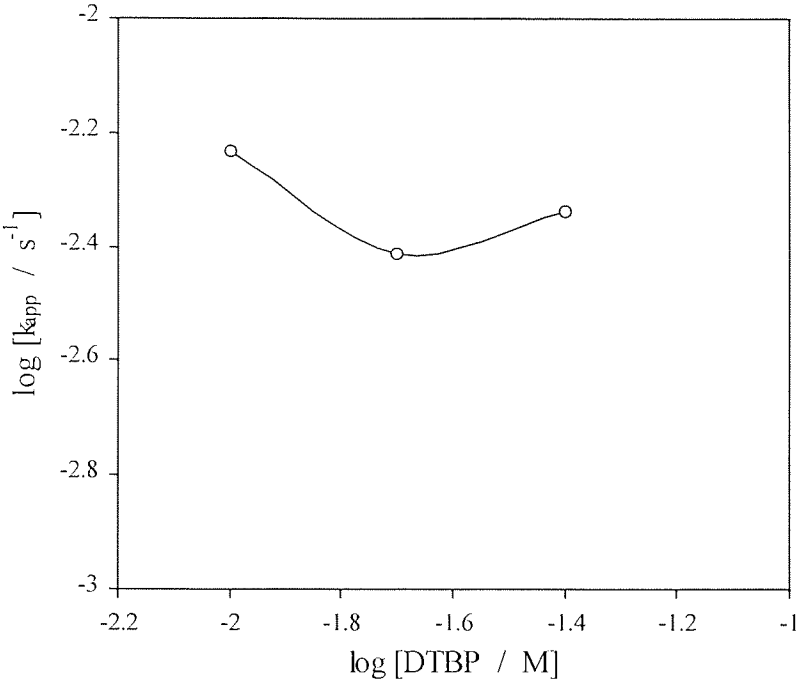


Fig. 7. 12 Effect of DTBP concentration on the rate of styrene polymerization at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; DCM / C.hex = 20/30 (v/v).

In **Fig. 7. 13**, plots of M_n against monomer conversion were constructed for the same polymerizations to establish the absence of chain transfer. The number average molecular weight of the polymers obtained was found to increase in direct proportion to monomer conversion, and agree well with the theoretical M_n expected from the concentration ratios of monomer to initiator when the initial concentrations of DTBP were 0.01M and 0.02 M respectively. In the cases of the initial concentrations of DTBP being 0 M or 0.04 M, the discrepancies from the theoretical values (solid line) were some evidence of the presence of transfer.

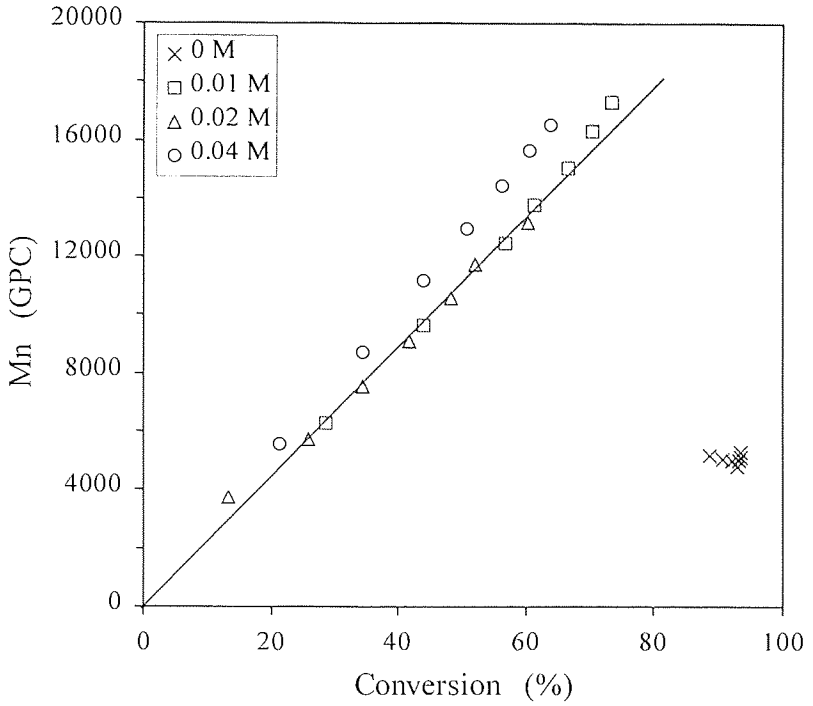


Fig. 7. 13 M_n vs monomer conversion plots for styrene polymerizations at -15°C with varying DTBP concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; DCM / C.hex = 20/30 (v/v).

Fig. 7.14 shows the polydispersities of the polymers obtained. Without DTBP the molecular weight molecular MWDs were bimodal with high polydispersities ($\overline{M_w}/\overline{M_n}$ > 3). After addition of DTBP, the polymers had uniform MWDs with $\overline{M_w}/\overline{M_n}$ ~ 1.25, which is indicative of a living polymerization.

Fig. 7.15 shows the initiator efficiencies as a function of conversion for the same polymerizations. As expected the efficiencies were very high (~ 4.5) without addition of DTBP. In the presence of DTBP the efficiencies were around 1, close to the theoretical initiator efficiency assuming one initiator molecule leads to one polymer active centre.

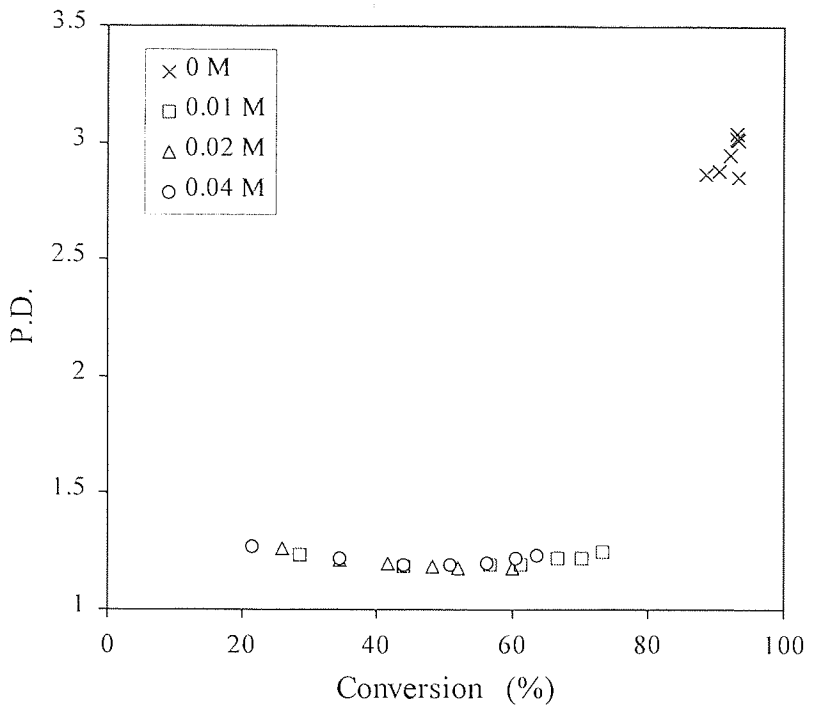


Fig. 7. 14 Polydispersities of the polymers obtained during styrene polymerizations at -15°C with varying DTBP concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; DCM / C.hex = 20/30 (v/v).

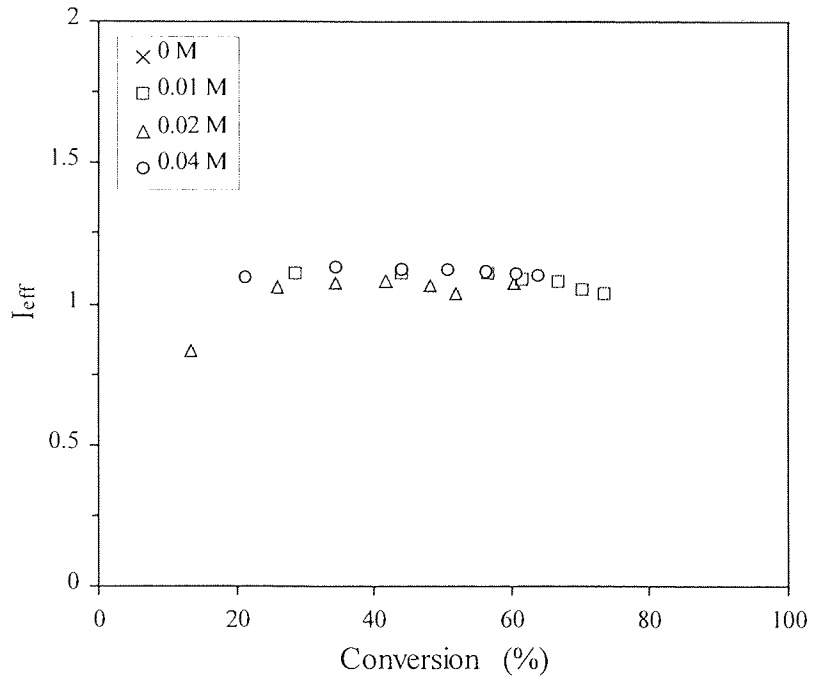


Fig. 7. 15 Efficiencies of the initiator for styrene polymerizations at -15°C with varying DTBP concentrations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; DCM / C.hex = 20/30 (v/v).

7.3.4 Effect of $TiCl_4$ initial concentration

Experiments were conducted to elucidate the effect of the initial concentration of titanium tetrachloride on the rate of polymerization. The initial concentrations of monomer, initiator and salt were constant; $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[DTBP]_0$ = 0.02M. Mixtures of DCM / C.hex 20/30 (v/v) were used as solvent and the reactions were kept at - 15 °C.

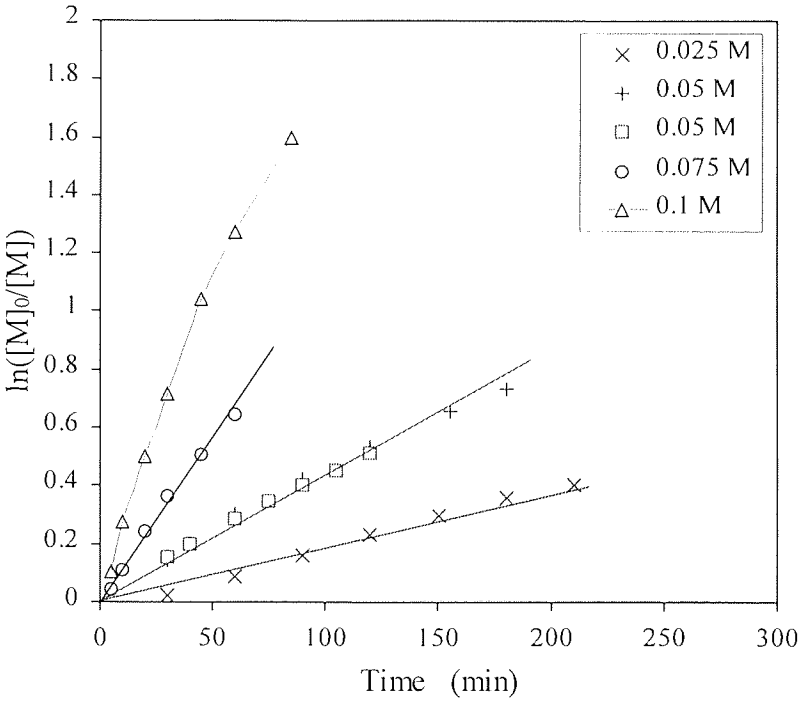


Fig. 7. 16 Plots of $\ln([M]_0/[M])$ against time for polymerizations with varying $TiCl_4$ concentrations at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

Fig. 7. 16 shows the plots of $\ln([M]_0/[M])$ against time for the polymerization with varying initial $TiCl_4$ concentrations. The initial linearity of the plots demonstrates the absence of irreversible termination within the lifetimes of the polymerizations except for $[TiCl_4]_0$ = 0.1M. Increasing $TiCl_4$ initial concentration resulted in the increase in the slope of the plot, in turn the rate constant of polymerization.

The apparent rate constant for each experiment was obtained from the slope of the straight line respectively. **Fig. 7.17** shows the plot of k_{app} versus $[TiCl_4]^2$, from which the order of reaction with respect to catalyst was estimated. The straight line through the points with a gradient of 2.93 and $R^2 = 0.97$ shows that under these conditions the order of the reaction relative to $TiCl_4$ is 2. This differs from the order with respect to $SnCl_4$ of 1.0 reported in section 5.2.3 in chapter 5, which means $TiCl_4$ did not perform in the same way as $SnCl_4$ as an initiator, obviously there were reactions involving $TiCl_4$. These mechanisms may be the subject of further studies.

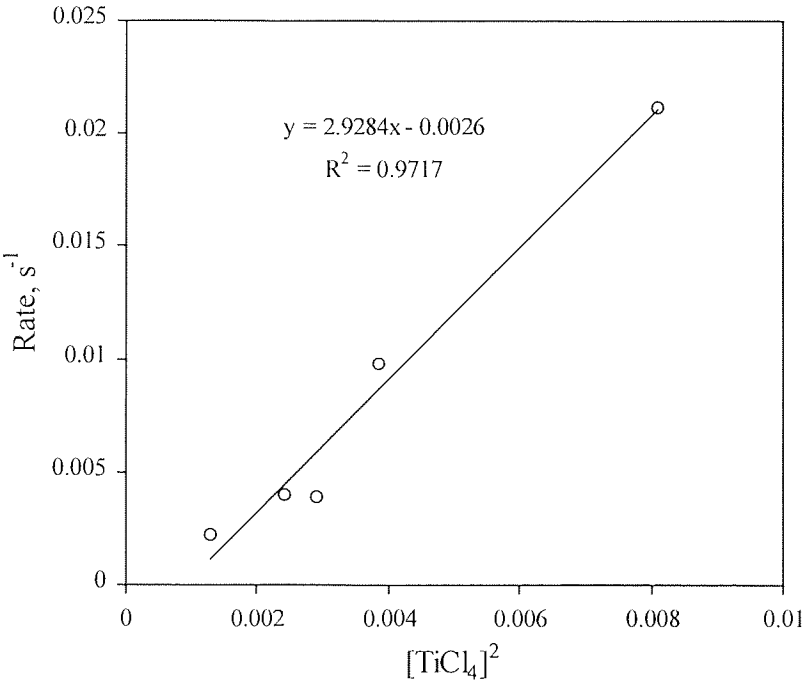


Fig. 7. 17 Effect of $TiCl_4$ concentration on the rate of styrene polymerization at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

The M_n vs conversion plots (**Fig. 5.18**) shows that the number average molecular weight of the polymers increased in direct proportion to conversion and agreed well with the theoretical number-average MW (solid line) expected from the concentration ratios of monomer to initiator for $TiCl_4$ varying from 0.05 to 0.075 M, indicating the absence of irreversible chain transfer. The discrepancies that occurred at $[TiCl_4]_0$ =

0.025 and 0.1 M are unlikely to be due to the presence of chain transfer, as the polymers obtained from the same polymerizations whose kinetic runs were plotted in **Fig. 7.16** had narrow and nearly uniform MWDs with $\overline{M_w}/\overline{M_n}$'s around 1.25 (**Fig. 7.19**), which demonstrates living polymerization. The reasons for these discrepancies may be considered for further studies.

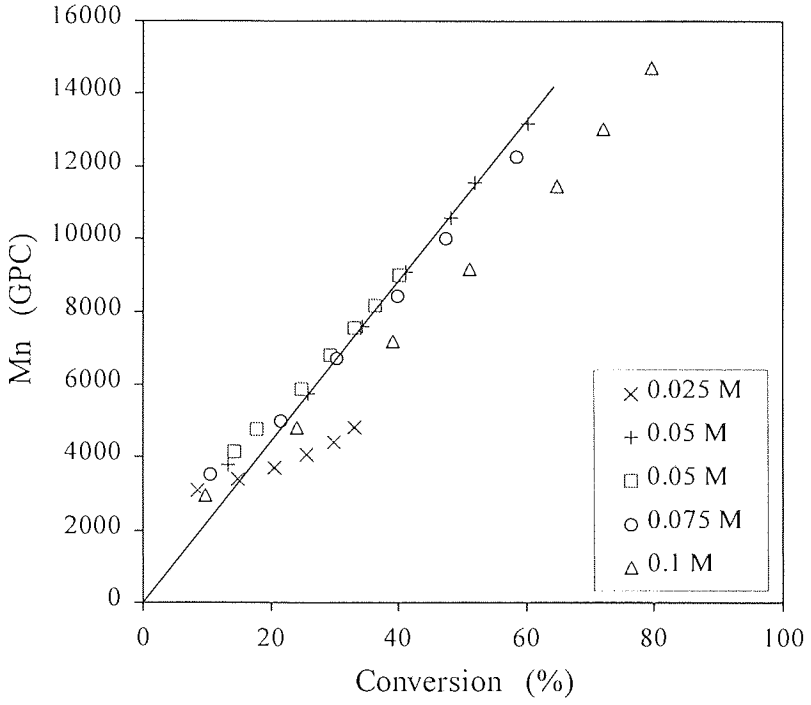


Fig. 7. 18 M_n vs conversion plots for styrene polymerizations at -15°C with varying $TiCl_4$ concentrations at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

Fig. 7.20 shows the efficiencies of initiator as a function of conversion for the same polymerizations. The initiating efficiencies increased gradually with conversion before reached a plateau, which may be evidence of slow build up of active species at the initial stages. Such slow initiation has been observed for isobutylene polymerization **[109]**.

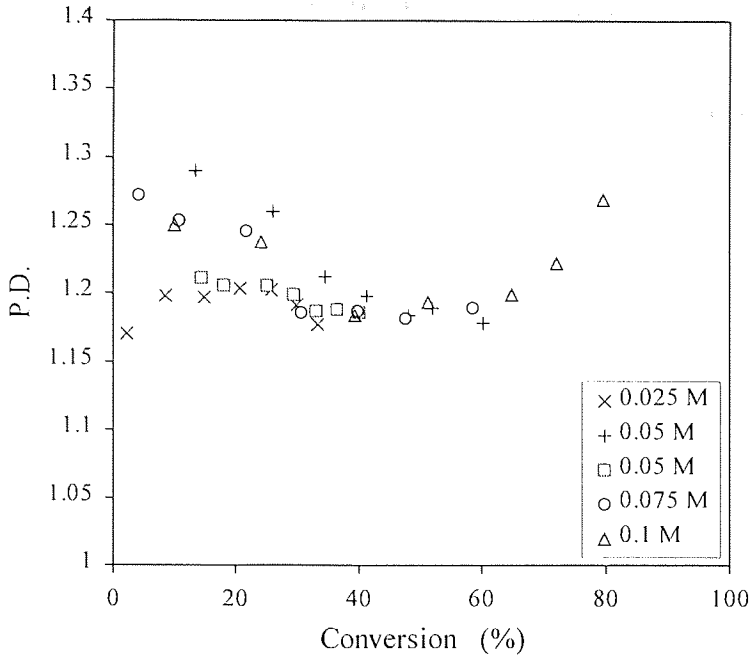


Fig. 7. 19 Polydispersities of the polymers obtained during styrene polymerizations at -15°C with varying $TiCl_4$ concentrations at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[DTBP]_0$ = 0.02M; DCM/C.hex = 20/30 (v/v).

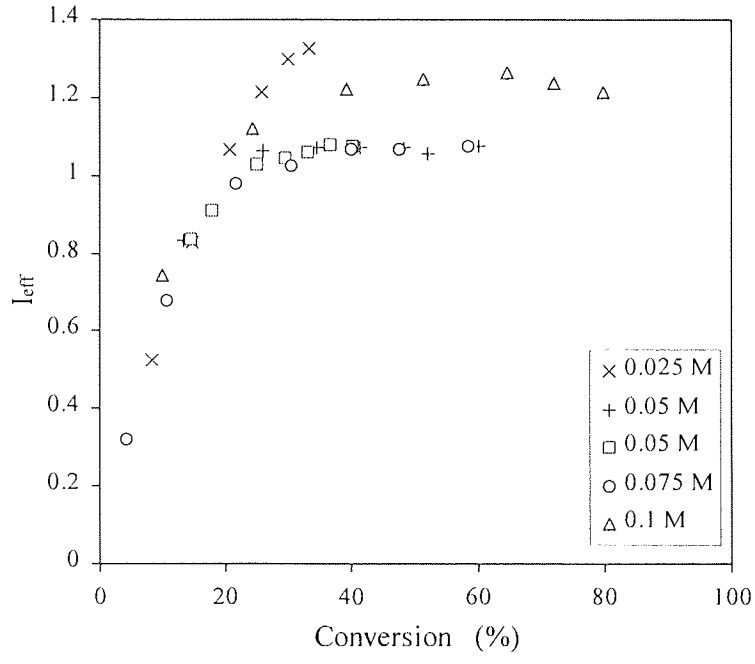


Fig. 7. 20 Efficiencies of the initiator for styrene polymerizations at -15°C with varying $TiCl_4$ concentrations at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

7.3.5 Effect of 1-PEC initial concentration

Reactions were conducted to study the effect varying the initial concentration of the initiator, 1-phenyl ethylchloride, on the rate of styrene polymerization. The initial concentrations of styrene monomer, catalyst and salt were constants; $[Styrene]_0$ = 1M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM/C.hex = 20 / 30 (v/v), T = - 15 °C.

Fig. 7. 21 shows the plots of $\ln([M]_0/[M])$ against time for the polymerizations. The plots were linear and passed through the origin, demonstrating the absence of irreversible termination. An increase in the initial 1-PEC concentration led to an increase in the gradients of the plots.

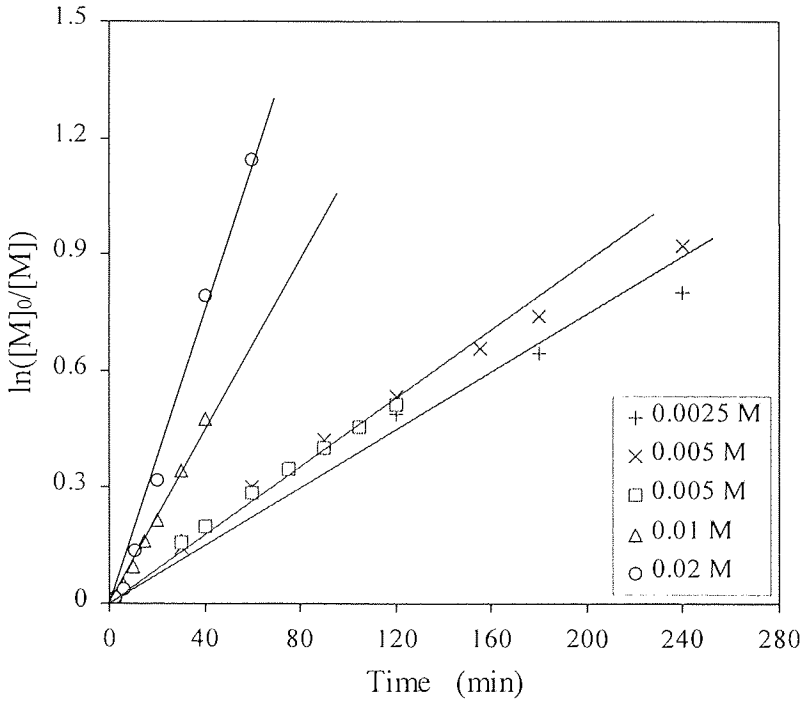


Fig. 7. 21 Plots of $\ln([M]_0/[M])$ against time for styrene polymerizations with varying 1-PEC concentrations at -15°C. $[St]_0$ = 1M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

Assuming first order kinetics, the apparent rate constants for each experiment were obtained from the gradients of the plots. The order of reaction with respect to 1-PEC

was estimated from the plot of log k_{app} versus log [1-PEC] (**Fig. 7. 22**). The slope of the straight line through the points yields an order of 1.03 with $R^2 = 0.94$, implying that the apparent rate constant has a first order dependence on the initial concentration of the initiator.

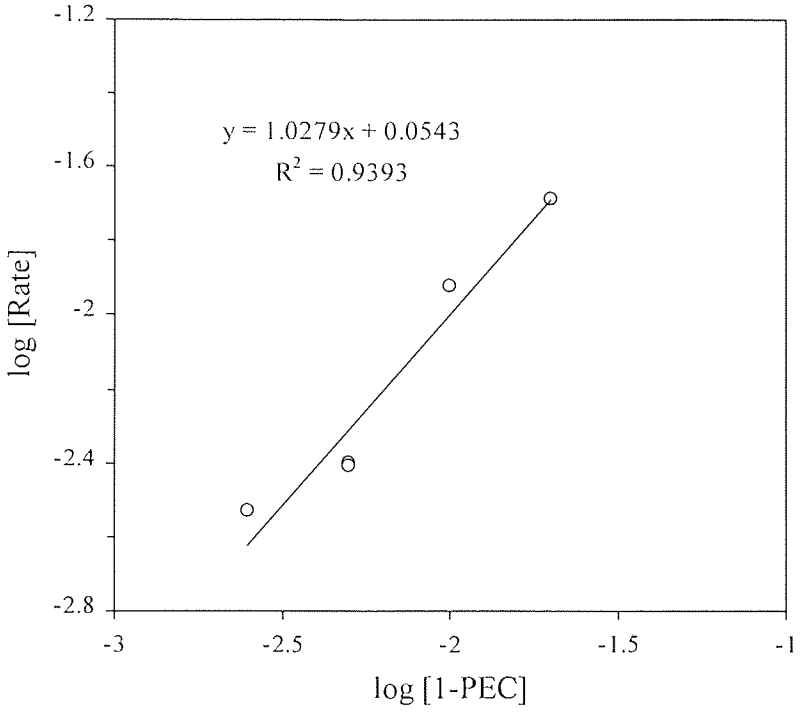


Fig. 7. 22 Effect of 1-PEC initial concentration on the rate of styrene polymerizations at -15°C. $[St]_0$ = 1M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

Fig. 7. 23 shows M_n vs. conversion plots for the polymerizations whose kinetic runs were plotted in **Fig. 5.7**. The plots differed for the different initial concentrations of 1-PEC. The plots were of linear and agreed with the theoretical line (solid) when $[1\text{-PEC}]_0$ not greater than 0.005 M, demonstrating the absence of chain transfer. This is consistent with the system being a living polymerization, producing narrow and nearly uniform MWDs ($\overline{M_w}/\overline{M_n} < 1.25$) found for the polymers obtained (**Fig. 7.24**).

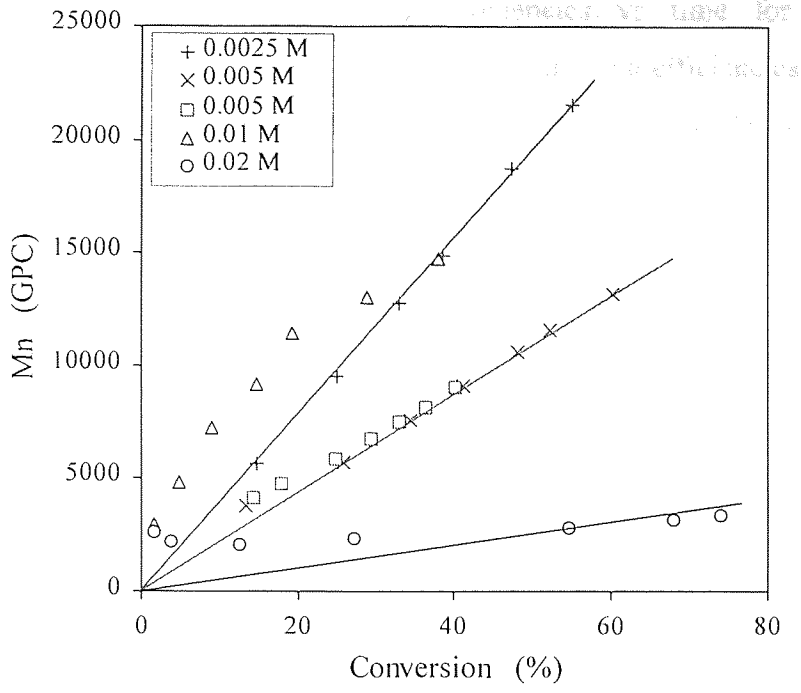


Fig. 7. 23 M_n vs conversion plots for styrene polymerizations with varying 1-PEC concentrations at -15°C. $[St]_0$ = 1M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

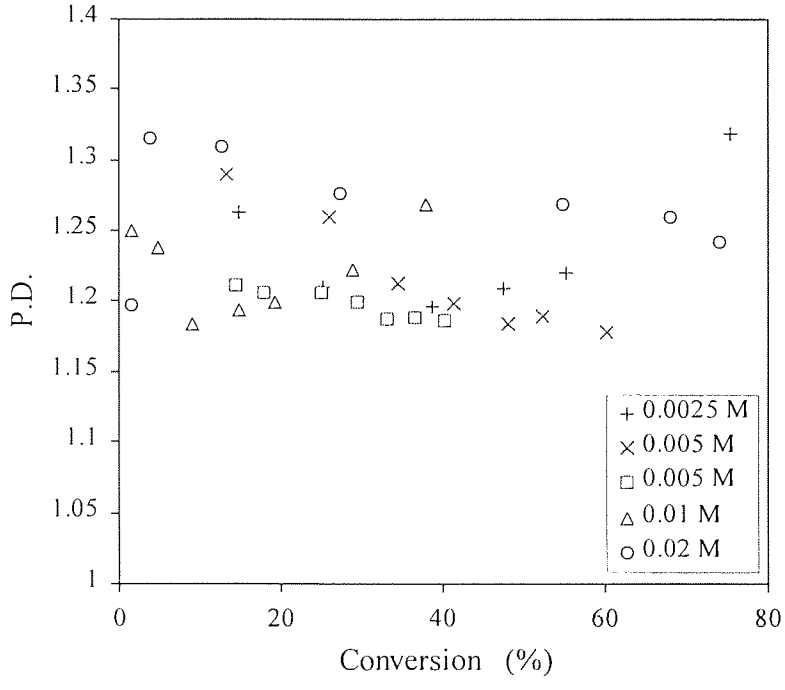


Fig. 7. 24 Polydispersities of the polymers obtained during styrene polymerizations with varying 1-PEC concentrations at -15°C. $[St]_0$ = 1M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

Fig. 7.25 shows the plots of initiating efficiencies vs time for the same polymerizations. For $[1\text{-PEC}]_0$ equal to 0.005 M, the initiating efficiencies were close to the theoretical value. The gradual build up of the efficiencies under higher initial concentrations of 1-PEC was some evidence of slow initiation.

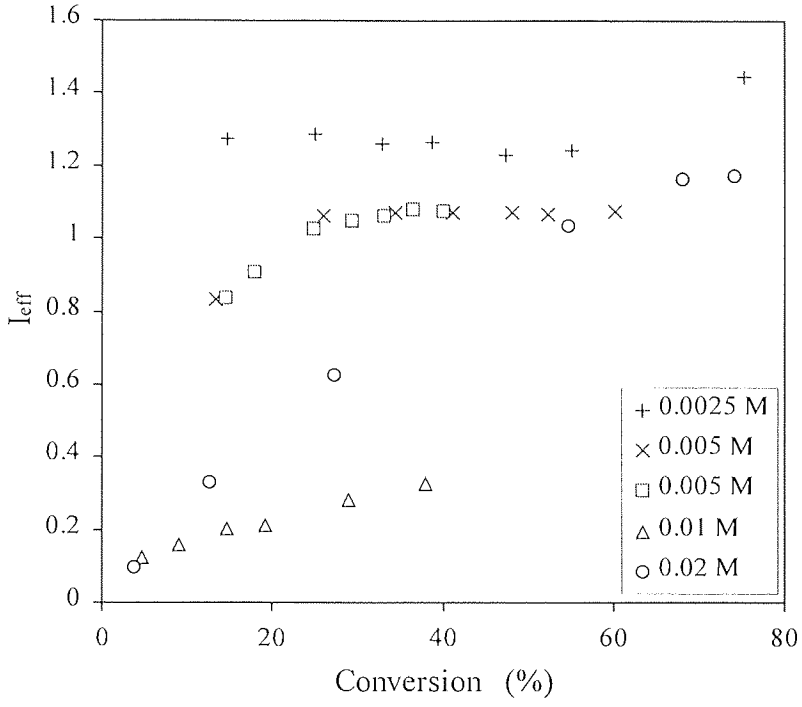


Fig. 7. 25 Efficiencies of the initiator for the same polymerizations as in **Fig. 7.20**.

7.3.6 Effect of secondary addition of monomer to a polymerization

Styrene polymerizations were carried out with $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v); T = -15°C. The initial concentration of styrene monomer was varied. **Fig. 7.26** shows M_n vs conversion plots for the polymerizations. As expected the high initial monomer concentration resulted in polymers with high number average molecular weights. The agreement between the experimental and theoretical values (solid lines) demonstrate living polymerization.

The livingness of the polymerizations was further examined by adding sequentially styrene monomer to a polymerized reaction mixture (denotes as (1+1) M in **Fig. 7.26**).

The added 1 M styrene (equivalent to the first stage) polymerized at nearly the same rate as in the first stage. This would suggest that the concentration of propagating species remained constant through the living polymerization and there was no terminative transfer reaction. The polymers obtained had narrow and nearly uniform MWDs with (P.D. < 1.3), as shown in **Fig. 7.27**, which is of indicative of a living polymerization.

Fig. 7.28 shows the initiating efficiencies of 1-PEC for the polymerizations. The initiating efficiencies were found to close to the theoretical value of 1 based on the assumption that one initiator molecule leads to one active polymer chain end.

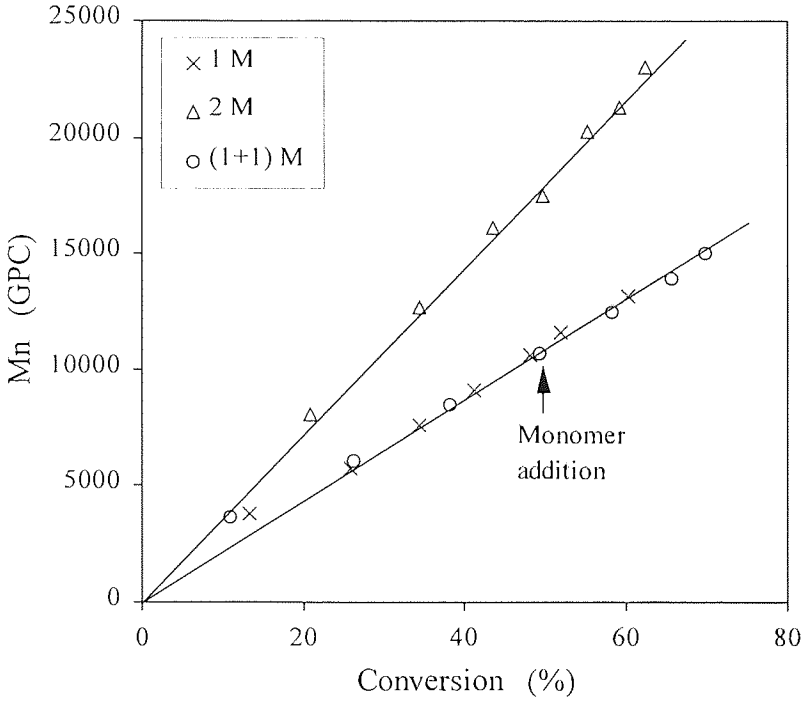


Fig. 7. 26 M_n vs conversion plots for styrene polymerizations at -15°C. $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

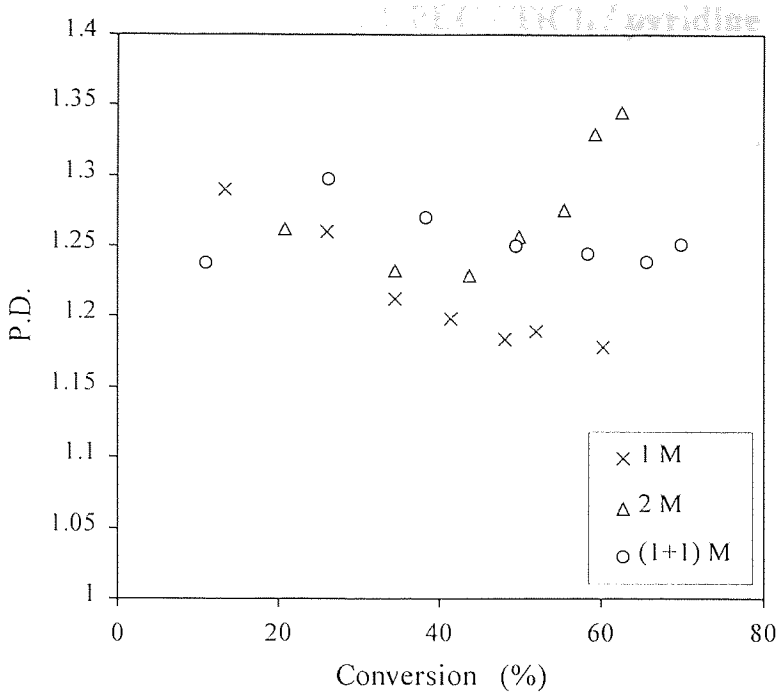


Fig. 7. 27 Polydispersities of the polymers obtained from the polymerizations at -15°C. $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v).

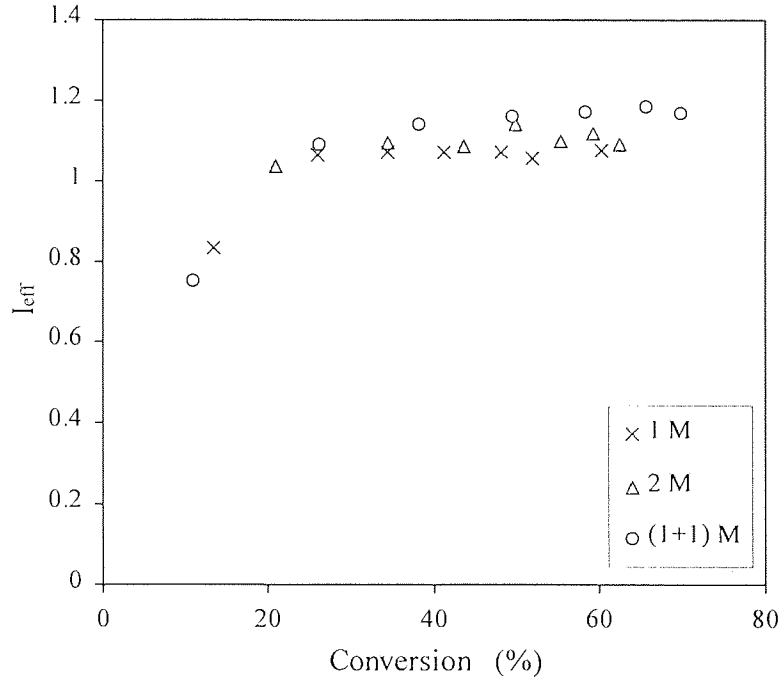


Fig. 7. 28 Efficiencies of the initiator for styrene polymerizations at -15°C. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM/C.hex = 20/30 (v/v).

7.4 Styrene polymerization with 1-PEC / $TiCl_4$ / pyridine

Styrene polymerizations were also conducted in the presence of pyridine instead of 2,6-di-*tert*-butylpridine with $[Styrene]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[pyridine]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v), T = -15°C. Comparison between pyridine and DTBP was made.

Linear plots of $\ln([M]_0/[M])$ vs time (**Fig. 7. 29**) demonstrate living polymerization, i.e. the absence of irreversible termination. The apparent rate constants were obtained from the slopes of the lines to be 0.003 and 0.0043 s^{-1} for pyridine and DTBP respectively. The polymerization was slow in the presence of pyridine compared to DTBP for the same conditions. These observations indicate areas requiring further study.

Fig. 7. 30 shows plots of M_n vs conversion for the polymerizations. The linearity of the plots were observed for both pyridine and DTBP, and M_n agreed well with the theoretical line, indicating the absence of chain transfer in the polymerizations. Such livingness of polymerization was further established by the low polydispersities ($\overline{M_w} / \overline{M_n} \leq 1.3$), which was found for the polymers obtained (**Fig. 7. 31**).

The initiator efficiencies vs conversion plots (**Fig. 7. 32**) shows some evidence of slow built up of propagating active species at the initial stages for pyridine before the initiating efficiencies reached the theoretical value.

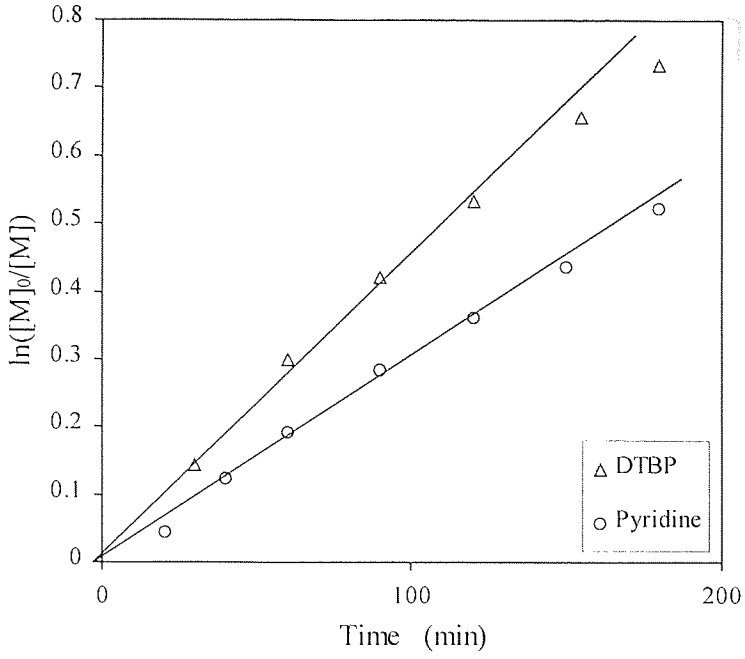


Fig. 7. 29 Plots of $\ln([M]_0/[M])$ against time for styrene polymerizations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[salt]_0$ = 0.02M; DCM/C.hex = 20/30 (v/v) ; T = -15°C.

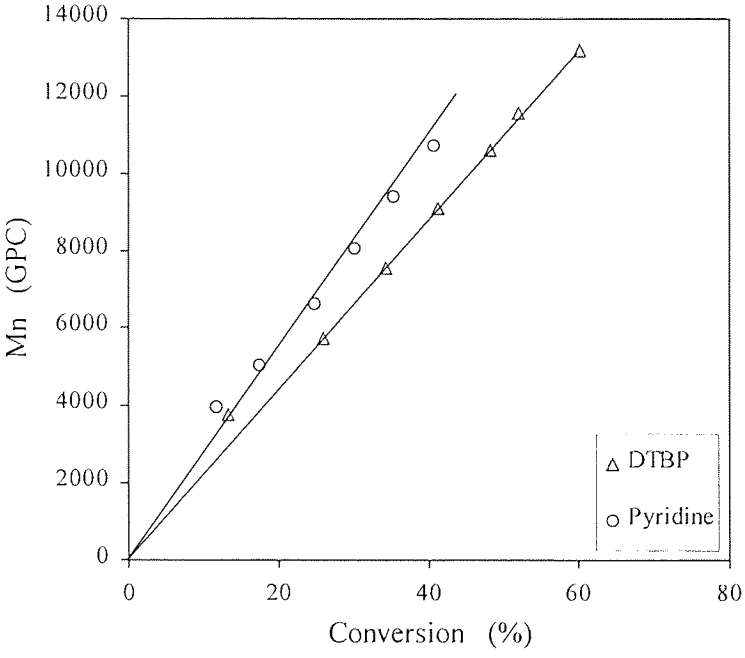


Fig. 7. 30 M_n vs conversion plots for styrene polymerizations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[salt]_0$ = 0.02M; DCM/C.hex = 20/30 (v/v); T = -15°C.

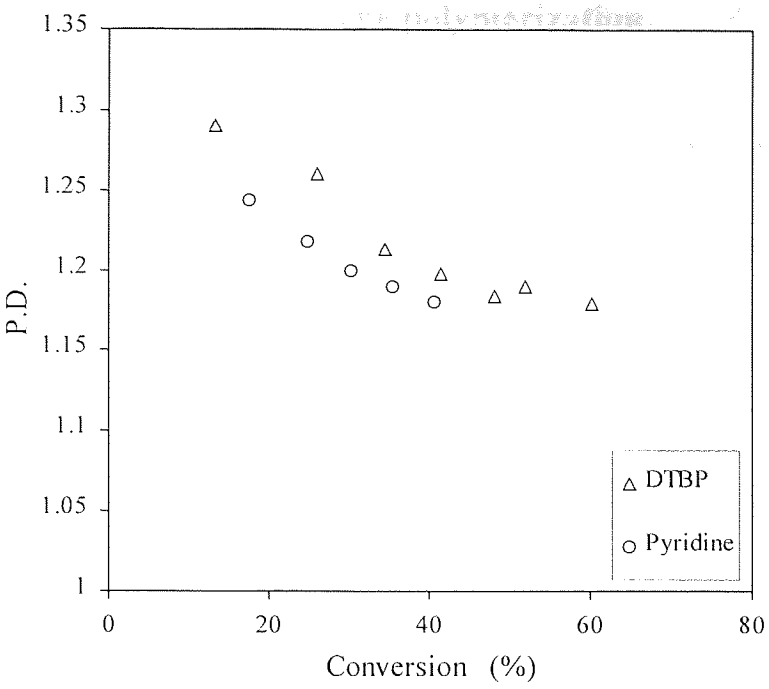


Fig. 7. 31 Polydispersities of the polymers obtained from the polymerizations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[salt]_0$ = 0.02M; DCM/C.hex = 20/30 (v/v) ; T = -15°C.

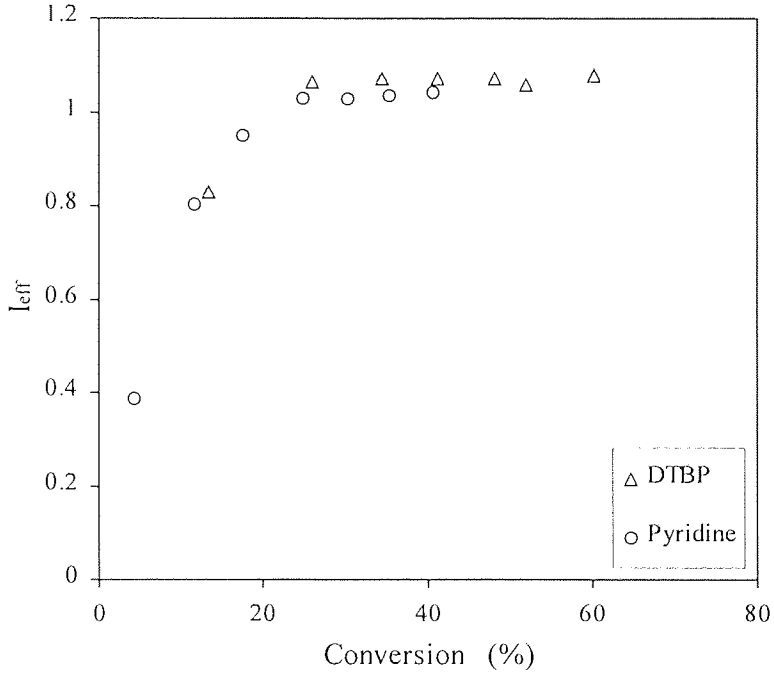


Fig. 7. 32 Efficiencies of the initiator for styrene polymerizations. $[St]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[salt]_0$ = 0.02M; DCM/C.hex = 20/30 (v/v) ; T = -15°C.

7.5 Initiator efficiencies of styrene polymerization

If the initiation is a first-order reaction, the rate of initiation can then be expressed as:

$$-\frac{d[I]}{dt} = k_1[I] \tag{2}$$

where $[I]$ represents the concentration of initiator, t is the time in seconds, k_1 is the rate constant for initiation. Integrating equation (2), the initiator concentration can then be given by

$$[I] = [I]_0 e^{-k_1 t} \tag{3}$$

Rearranging equation (3) yields

$$\ln\left(\frac{[I]_0}{[I]}\right) = k_1 t \tag{4}$$

The initiator efficiency can be expressed as

$$I_{eff} = \frac{[I]_0 - [I]}{[I]_0} = 1 - \frac{[I]}{[I]_0} \tag{5}$$

Combining equations (4) and (5) yields

$$\ln(1 - I_{eff}) = k_1 t \tag{6}$$

Obviously there is a linear dependency of $\ln(1-I_{eff})$ on time for the first order initiation.

If the initiation is regarded as a second order reaction, the rate of initiation can then be expressed as:

$$-\frac{d[I]}{dt} = k_2[I]^2 \tag{7}$$

where k_2 is the rate constant for initiation. Integrating equation (7) yields

$$\frac{1}{[I]} = k_2 t + c_1 \tag{8}$$

where c_1 is a constant. Substituting equations (5) into (8), one yields

$$\frac{1}{1-I_{eff}} = k_2[I]_0 t + c_1[I]_0 \tag{9}$$

Since k_2, c_1 and $[I]_0$ are constants plotting $1/(1-I_{eff})$ against time should produce a straight line for the second order reaction. Therefore equations (6) and (9) can then be used to determine the order with respect to the initiator.

Fig. 7.33 shows the plots of $\ln(1-I_{eff})$ and $1/(1-I_{eff})$ against time respectively for styrene polymerizations with $[Styrene]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.075M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20 / 30 (v / v) ; T = -15°C. There is no linear dependence of $1/(1-I_{eff})$ on time, which is indicative of the second order kinetics. A straight line with R^2 = 0.97 was obtained for the plot of $\ln(1-I_{eff})$ versus time, indicating that the styrene polymerization is a first-order reaction with respect to initiator.

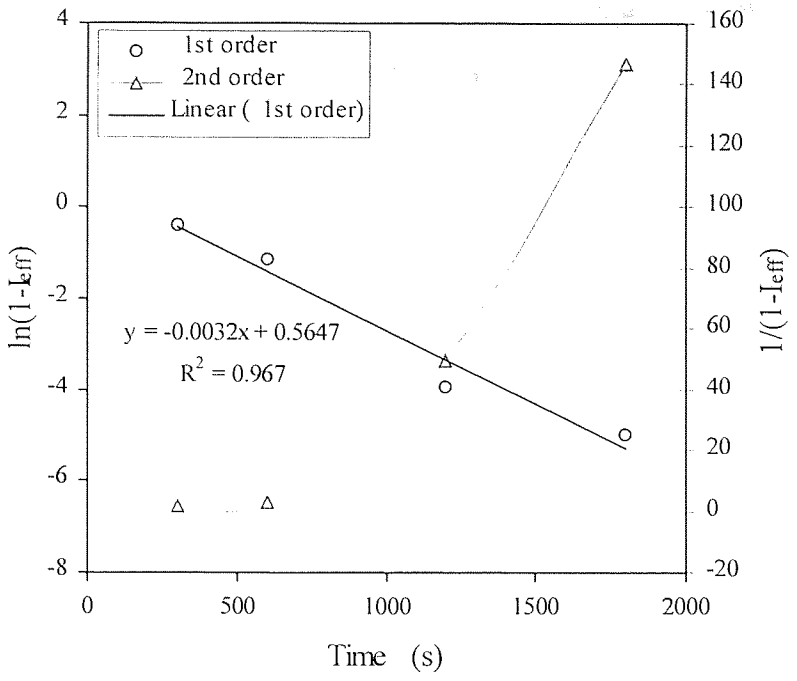


Fig. 7. 33 Plots of $\ln(1-I_{eff})$ and $1/(1-I_{eff})$ against time.

CHAPTER 8

CONCLUSIONS AND FURTHER WORK

Styrene chosen as a monomer in this work is a commercially available vinyl monomer. A conventional cationic polymerization of styrene was carried out with 1-phenyl ethylchloride (1-PEC) as an initiator and tin tetrachloride ($SnCl_4$) as a catalyst (activator) in dichloromethane (DCM) as solvent at a low temperature, -15°C. Such a transfer dominated cationic polymerization was indicated by the high polydispersity (P.D. = 4.06) with a bimodal MWD, which has been attributed to the coexistence of two growing species that propagate simultaneously but independently of each other **[81]**. One of these species results in a high molecular weight (MW) polymer and the other polymers with low MWs.

Addition of a small amount of a salt (nBu$_4$NCl) dramatically suppressed the formation of the broad population of high molecular weight polymer, and resulted in polymers with very narrow molecular weight distribution MWD (P.D. $\leq$ 1.2), which is indicative of a living polymerization when taken in conjunction with other observations. The salt induced living polymerization of styrene can be explained as the nucleophilic stabilisation of the reactive growing carbocation. nBu$_4$NCl is capable of complexing with the $SnCl_4$ to produce a sufficient concentration of the chloride anions which suppress the formation of the free ionic form in the equilibrium. Consequently, the non-dissociated growing species (in the form of ion pairs) predominated.

Effects of solvent polarity, reaction temperature, concentrations of catalyst, initiator and salt on the polymerization of styrene monomers were investigated using the

Schlenk technique in terms of polydispersity, molecular weight and initiator efficiency etc, in order to optimise the condition under which a living cationic polymerization of styrene is obtained. The conditions required for a living polymerization are summarised as: $[styrene]_0 \sim 0.75 - 2$ M; $[1\text{-PEC}]_0 \sim 0.005 - 0.05$ M; $[SnCl_4]_0 \sim 0.05 - 0.4$ M; $[n Bu_4NCl]_0 \sim 0.001 - 0.1$ M; DCM/C.hex ~ 50/0 – 20/30 v/v; T ~ 0 to -45°C.

Solvent polarity will remarkably affect the rates of cationic polymerization and the molecular weight distribution MWD of the polymers, since the growing species in cationic polymerization are in equilibrium among various dissociated states, and the dissociation of the growing chain end (carbocation ion pairs) depends upon the dielectric permitivity of solvent. Less polar solvents are generally recognised to be easier to induce a living polymerization than polar solvents, because of their favouring the less ionised species of the growing chains that lead to a living polymer **[55, 101]**. Living polymerization of styrene was still achieved in this project at mixtures of DCM and less polar solvent, cyclohexane (C.hex), until the ratio of DCM and C.hex was 10:40 (in volume) at which ratio a deposit was observed. Decreasing solvent polarity led to a decrease in number average molecular weigh (M_n). The deposit formed in the solvents appeared 'cloudy', which could be the consequence of the low solubility of the initiator, monomer and salt in the less polar solvent mixture. No polymer was produced when the polymerization was carried out in the non-polar solvent, cyclohexane.

The reaction temperature is another factor that can profoundly affect the equilibrium among various dissociation states of the growing species in the cationic polymerization, and low temperatures have been considered to facilitate suppressing of side reactions and render living cationic polymerization possible. The polystyrenes obtained with 1-PEC / $SnCl_4$ / Bu_4NCl / DCM : C.hex 40:10 at temperatures of -45 and 0°C had very low polydispersities (P.D. ≤ 1.2) which are indicative of a living polymerization. As expected, the polydispersities of the polystyrenes increased with increasing reaction temperatures (> 0°C). Polymerization at a lower temperature of -60 °C led to an increase in the polydispersity of polymers (P.D. = 1.48), which is not consistent with the former expectation that low temperatures favour living

polymerizations **[33]**. This may possibly have been associated with slow initiation in this case.

As expected, increasing catalyst $SnCl_4$ concentration accelerated polymerization and resulted in an increase in M_n; living polymerization was maintained until catalyst concentration less than 0.6M. Polymers with lower M_n were obtained at a high initiator concentration and all the polymerizations showed indications of being living up to an initiator concentration of 0.05M. The results would suggest that the polymerizations were living independent of the concentration of $SnCl_4$, and the catalyst plays a role in accelerating polymerization without affecting the characteristics of the polymerization itself.

Initiation plays a very important role in determining if the polymerization will be living in cationic polymerization. Polymerizations of styrene monomers (1M) initiated with different concentrations of 1-phenyl ethylchloride (1-PEC) and 0.2 M $SnCl_4$ were then examined; $[n\text{Bu}_4\text{NCl}]_0$ = 0.02 M, DCM : C.hex = 30 : 20 (v : v), -15 °C, 3 hours. All induced polymers had very narrow polydispersities, M_w / M_n < 1.2. The linear decrease in molecular weights with increasing initiator concentration would suggest that the initiation is rapid compared to chain propagation and high initial concentration of 1-PEC would lead to a greater number of active sites and lower MW.

Static investigations on polymerizations of styrene described in Chapter 4 using the Schlenk technique were unable to monitor the polymerization course and got insight into the detail of the polymerization mechanism although the conditions for a living polymerization were optimised. This was because sampling using the Schlenk technique could not take place during polymerization without explosion of the reaction systems to air, which could contaminate polymerization. In order to identify the mechanisms of cationic polymerization of styrene, an Omnifit sampling method was used to take samples regularly with the benefits of its preventing the system from impurities. This novel sampling method consists a sampling vessel which was re-attached to the vacuum line under inert gas once the polymerization was initiated, and so a desired quantity of the polymer solution was drawn out into the dry syringe after

the three way valve was opened. In this way samples could be taken from a polymerization without contaminating the polymerization mixture.

Kinetic experiments were carried out using the Omnifit sampling method to clarify the dependence of the rate of polymerization on the concentration of the various reactants, such as initiator, catalyst, salt, and monomer, and on the solvent polarity and reaction temperature to identify the mechanisms for styrene polymerization with 1-PEC/$SnCl_4$/nBu$_4$NCl at mixtures of DCM and C.hex. For a living polymerization with fast initiation, the polymerization is generally considered as first order with respect to the monomer concentration, then the rate of polymerization depends on the propagation stage. There is a linear dependency of $\ln([M]_0/[M])$ on time for a living polymerization with fast initiation, which will be used as a criterion to test the livingness of cationic polymerizations of styrene monomers.

Kinetic studies of styrene polymerization with $[St]_0$ = 1M, $[1\text{-PEC}]_0$ = 0.02M, $[SnCl_4]_0$ = 0.2M, DCM / C.hex = 30 / 20 (v / v) over a range of concentrations of nBu$_4$NCl showed that monomer conversions increased gradually with time as expected. With the addition of the salt, the linearity of $\ln([M]_0/[M])$ versus time demonstrates that essentially no termination occurred within the studied lifetimes of the polymerizations. The slight curve observed at [nBu$_4$NCl] = 0.005 M indicated consumption of catalyst in this case. The M_n of the obtained polymers increased in direct proportion to monomer conversion and agreed well with the theoretical number-average MW expected from the concentration ratios of monomer to initiator, which demonstrated the absence of chain transfer and thus provide evidence for livingness of the polymerizations. The gradual increase in the initiator efficiency in the initial stage may be evidence of slow build up of the propagation species or slow initiation.

Experiments were carried out to study what effect varying the initial concentration of the initiator, 1-phenyl ethylchloride (1-PEC) would have on the rate of polymerization. Linear plots of $\ln([M]_0/[M])$ against time passed through the origin demonstrated the absence of irreversible termination within the lifetimes of the polymerizations on varying initiator initial concentrations. The apparent rate constants

for each experiment obtained from the gradients of the lines over the first few points suggested that increasing initiator initial concentration resulted in an increase in the slope of the line and then a greater apparent rate constant. For the initial concentrations of initiator not less than 0.01 mol dm^{-3}, the absence of chain transfer in the polymerizations was demonstrated by the linear plots of M_n against conversion, which is consistent with indication of living polymerization by the very narrow and nearly uniform MWDs ($\overline{M_w} / \overline{M_n} < 1.2$) observed for the polymers obtained.

The role of $SnCl_4$ on the rate of styrene polymerization was studied by conducting polymerizations under varying initial concentration of $SnCl_4$ in mixtures of DCM / C.hex (30 / 20 v / v) at - 15 °C. The plots of $\ln([M]_0/[M])$ vs time except for $[SnCl_4]_0$ = 0.6 M demonstrate the absence of irreversible termination within the lifetimes of the polymerizations, and increasing catalyst concentration accelerated polymerization. The plots were independent of the initial concentration of $SnCl_4$. The M_n of the polymers increased in direct proportion to monomer conversion and agreed well with the theoretical number-average MW (solid line) expected from the concentration ratios of monomer to initiator for $SnCl_4$ varying from 0.1 to 0.6 M, indicating the absence of irreversible chain transfer, and the points all lie on one line indicates that $[SnCl_4]$ does not influence the overall number of propagating sites.

The linearities of both the $\ln([M]_0/[M])$ vs. time plot and the M_n vs. monomer conversion plot, and the narrow MWD measured using GPC demonstrated the livingness of the polymerizations for the polymerizations in mixtures of DCM / C.hex with 30 / 20 and 20 / 30, indicating the absence of irreversible termination within the lifetimes of the polymerizations. Reducing reaction temperature resulted in the decrease in the apparent rate constants, i.e. polymerization slows down at lower temperatures. Plotting ln (k_{app}) against the reciprocal of the absolute temperature for the polymerization produced a straight line, which is consistent with the theoretical expectation.

The orders of reaction with respect to monomer, initiator and catalyst were derived form the kinetic studies. The plots of log k_{app} versus the initial concentrations of initiator and catalyst were used to estimate the order of reaction with respect to

initiator and catalyst. The straight lines plots obtained, with gradients around unity, proved that the apparent rate constant has a first order dependence on the initial concentration of initiator and catalyst, $[1\text{-PEC}]_0$ or $[SnCl_4]_0$, respectively. Accordingly, the rate of polymerization (r_p) can then be expressed as

$$r_p \propto [M]^1[1-PEC]^1[SnCl_4]^1$$

Based on the assumption of first-order kinetics, $\ln(DP_{n\infty}-DP_n)$ is proportional to the reaction time. The apparent rate constant was then estimated from the slope of the plot of $\ln(DP_{n\infty}-DP_n)$ against time, which is identical to the apparent rate obtained from the gradient of the graph of $\ln\{[M]_0/[M]\}$ versus time.

Two propagation mechanisms have been proposed in terms of the number of the active centre, propagation by a single species and by two species, to describe the polymerization of styrene. The linear relationship between $k_{app}/([SnCl_4]_0\text{-}[n\text{Bu}_4\text{NCl}]_0)$ and $1/[n\text{Bu}_4\text{NCl}]_0$ calculated based on the experimental data would suggest that the 'two species' propagation mechanism applies for the styrene polymerization with 1-PEC/$SnCl_4$ in the presence of butylammonium chloride.

The high initiation efficiencies shown in **Figs. 5.11**, **5.20** and **5.24** in Chapter 5 implied than more polymer chains are being formed than expected. These values might arise from the presence of impurities, transfer reactions **[27]**, or measurement errors; the last would appear unlikely because many techniques were used in this project to prevent polymerization from impurities. In addition, the involvement of the added salt (i.e. $n\text{Bu}_4\text{NCl}$) in the reaction means more polymer chains could be formed than expected, which might result in the higher initiation efficiencies. Then styrene polymerizations in the presence of ammonium chlorides with different alkyl groups (CH_3-) were carried out so as to clarify the assumption. Different bromide salts having various alkyl groups were used instead of $n\text{Bu}_4\text{NCl}$, as they were commercially available.

Kinetic studies from the plots of the $\ln([M]_0/[M])$ vs. time and the M_n vs. monomer conversion, and the P.D. measurements using GPC indicated that living styrene

polymerizations were achieved using the 1-PEC/$SnCl_4$ initiating system in mixtures of DCM/C.hex 30/20 v/v at -15°C in the presence of various bromide salts, tetra-*n*-butylammonium bromide $C_{16}H_{36}NBr$, Tetra-*n*-pentylammonium bromide $C_{20}H_{44}NBr$, Tetra-*n*-heptylammonium bromide $C_{28}H_{60}NBr$, and Tetra-*n*-octylammonium bromide $C_{32}H_{68}NBr$, respectively. The types of the bromide salts were found to have no significant effect on monomer conversion, M_n, polydispersity and initiating efficiency. ^1H and ^{13}C NMR analysis of the resultant polystyrene indicated that the end-functionality of the obtained polystyrene is chlorine rather than bromide. Those findings imply that the added bromide salts do not affect the structure of the polymer obtained, and the higher initiator efficiencies were not the consequence of the involvement of the added salts in polymerization reaction.

After successful synthesis of living cationic polymerizations of styrene monomers using 1-phenyl ethylchloride (1-PEC) as an initiator and tin tetrachloride ($SnCl_4$) as a catalyst in DCM / C.hex mixtures in the presence of nBu_4NCl or bromide salts under certain conditions, the last stage of this project was to explore the potential living conditions for styrene polymerization by using another catalyst or salt. As titanium tetrachloride ($TiCl_4$) is a stronger Lewis acid than $SnCl_4$, the former has been used as a catalyst in living polymerizations of isobutylene **[77, 104, 108]** and vinyl monomers **[69]**, and so it was used as catalyst instead of $SnCl_4$ in the last stage of this project.

No polymer was obtained from the polymerization of styrene (initial concentration 1 M) with 0.02 M 1-PEC and 0.05 M $TiCl_4$ initiating system in DCM / C.hex 30/20 v/v mixture at -15 °C in the presence of 0.02M nBu_4NCl. The formation of the orange precipitates were attributed to the 'salting out' of $TiCl_4$ in the presence of nBu_4NCl.

As 2,6-di-*tert*-butylpyridine (DTBP) is incapable of complexation with carbocations (electrophiles) due to steric hindrance, but has highly specific reactivity toward protons **[109]**. DTBP was used instead of nBu_4NCl in the polymerization system, styrene / 1-PEC / $TiCl_4$ / DCM / C.hex, so as to capture protons from the systems and suppress side reactions. A series of experiments on polymerization of styrene were conducted using titanium tetrachloride ($TiCl_4$) as a catalyst and 1-PEC as an initiator in mixtures of DCM and C.hex at -15°C in the presence of 2,6-di-*tert*-butylpyridine

(DTBP) or pyridine, studying the dependence of the rate of polymerization on the initial concentration of the various reactants, such as 1-PEC, $TiCl_4$, DTBP, and monomer, and on the solvent polarity and reaction temperature.

The livingness of the polymerizations was examined by GPC analysis, which showed that the polymers obtained had narrow polydispersities (P.D. < 1.3), the linearities of both the $\ln([M]_0/[M])$ vs. time plot and the M_n vs. monomer conversion plot also demonstrated that the polymerizations are living, when the ratio of DCM and C.hex was less than 40 : 10 and the reaction temperature was not lower than -15°C. Investigations into the rate of polymerization showed that the rate of polymerization does not have a simple order dependence on the initial concentration of DTBP. The reaction order relative to $TiCl_4$ was estimated as 2.56, which is different from the order with respect to $SnCl_4$ of 1.0. Similar to the polymerizations using $SnCl_4$ as a catalyst, the rate constant of polymerization was found to have a first order dependence on the initial concentration of 1-PEC.

The livingness of the styrene polymerizations, carried out with $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.05M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20/30 (v/v); T = -15°C, was further examined by adding sequentially styrene monomer to the polymerized reaction mixture. The added 1M styrene (equivalent to the first stage) polymerized at nearly the same rate as in the first stage, indicating that the concentration of propagating species remained constant through the living polymerization and there was no terminative transfer reaction.

Two equations were derived for the styrene polymerization in the presence of pyridine with the first order kinetic initiation and second order initiation respectively, as follows:

For 1st order $$\ln\left(1 - I_{eff}\right) = k_1 t$$

For 2nd order $$\frac{1}{1 - I_{eff}} = k_2[I]_0 t + c_1[I]_0$$

Obviously there is a linear dependency of $\ln(1-I_{eff})$ on time for the first order initiation, and $1/(1-I_{eff})$ is proportional to the time since k_2, c_1 and $[I]_0$ are constants. Based on the experimental results from the styrene polymerizations with $[Styrene]_0$ = 1M; $[1\text{-PEC}]_0$ = 0.005M; $[TiCl_4]_0$ = 0.075M; $[DTBP]_0$ = 0.02M; DCM / C.hex = 20 / 30 (v / v) ; T = -15°C, no linear dependence of $1/(1-I_{eff})$ on time was observed, and plotting $\ln(1-I_{eff})$ against time produced a straight line with R^2 = 0.97, which would suggest that the styrene polymerization in the presence of DTBP is first order reaction with respect to initiator.

^1H and ^{13}C NMR analysis of the resultant polystyrene revealed the absorption assigned to the chlorinated ω-terminal methine proton although the peak intensity is small. This would suggest that the living polymerization proceeds via activation of the carbon-chlorine bone (C-Cl) and that the chlorine atom is attached to the terminal even after the quenching with methanol.

Further work is required to explore the potential living conditions for styrene polymerization by using a new initiator, so that more complex polymers such as block copolymers can be synthesised. This type of polymer has found wide applications in industries.

The mechanism for the styrene polymerization with 1-PEC/$TiCl_4$ in the presence of DTBP or pyridine is to be elucidated. The changes of the terminal structure can be monitored by NMR analysis. A Ti NMR may be used to identify the role of $TiCl_4$ during the polymerization.

Urgent future work is to improve the accuracy of using GPC on the determination of molecular weights of polymers, especially for the polystyrene with low molecular weights. As a fitting procedure is involved in the calibration for GPC and most of the standards have molecular weights greater than several thousands, the determination of low molecular weight was then lack of confidence. Other methods that can be used to determine low molecular weight are to seek.

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APPENDIX A MS EXCEL SPREADSHEET

The spreadsheet was used to calculate kinetic results for styrene polymerizations, such as theoretical molecular weights, the degree of polymerization (DP_n), monomer conversion and initiator efficiency. Comparisons of the measured and estimated rates of polymerization were also included in the spreadsheet. The formulae used are based on equations (1) – (12) in Chapter 5.

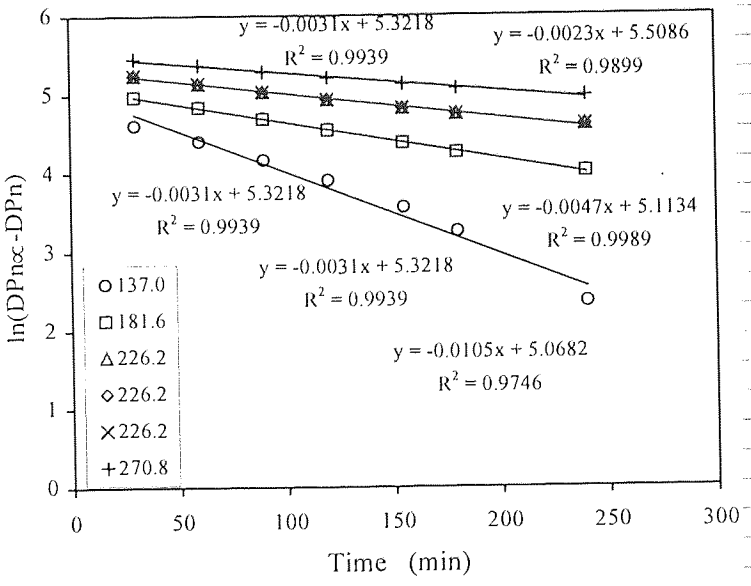
Date		Styrene	1-PEC	$TiCl_4$	2,6pyridine	CH_2Cl_2	c.Hex	cata.
13/06/1999		100	0.5	5	2	20	30	
		100	0.4	3.5	2.0			0.05 M
Flask, g	249.62	g		ml		M		
TiCl4	249.98	0.36		0.21		0.04		
CH_2Cl_2	271.59	21.61		16.31				
c.Hex	290.25	18.66		24.20				
Transfer (1-PEC)	292.21	1.96		1.48		0.005		
(2,6pyridine)						0.005		
Styrene	297.92	5.71		6.28	48.48	1.13		
		48.3			46.294			
Time	Minute	W_0	W_1	W_2	W_3	W_4	W_P	W_P (actual)
00:30								
01:00	30	11.028	11.492	17.71	6.218	11.13	0.102	0.76
01:30	60	11.29	11.816	18.004	6.188	11.488	0.198	1.48
02:00	90	11.078	11.757	17.999	6.242	11.343	0.265	1.97
02:30	120	11.296	11.739	18.004	6.265	11.615	0.319	2.36
03:05	155	11.151	11.667	18.15	6.483	11.536	0.385	2.75
03:30	180	10.847	11.533	17.853	6.32	11.252	0.405	2.97
04:30	240	11.098	11.678	20.256	8.578	11.735	0.637	3.44

$$\ln(DP_{n\infty} - DP_n) = \ln(DP_{n\infty}) - k\,t$$

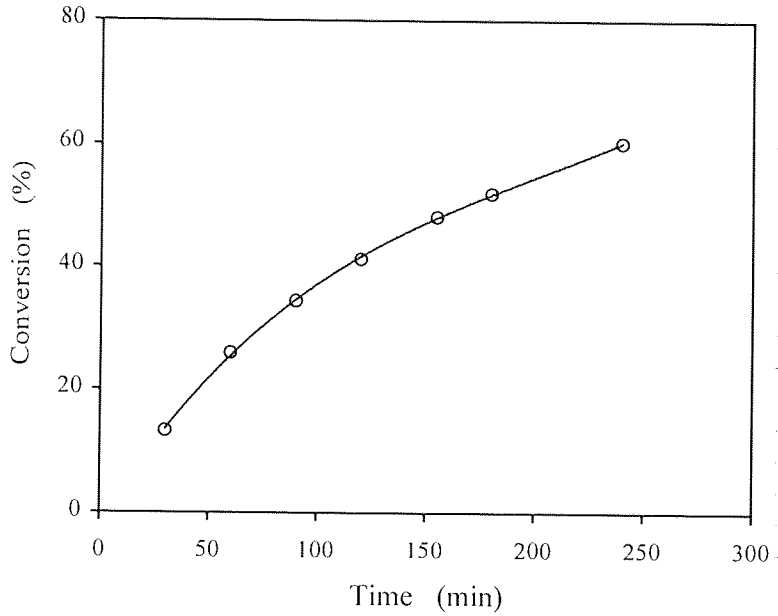
DPn∞ (cal.	226.2
From the plot of ln(DPn∞-DPn) vs. time (t)	
ln(DPn∞)	5.34133
k	0.003342
DPn∞ (inte	208.8

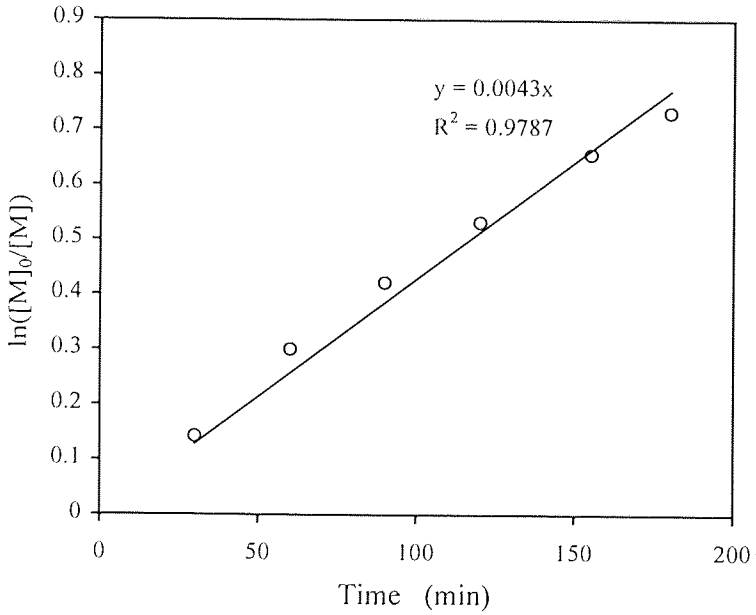
				ln(DPn∞-DPn)				
		DPn∞ (max)	(cal.)	(intercept)				
		137.0	226.2	208.8				
	Minute	137.0	181.6	226.2	226.2	226.2	270.8	
	30							
	60	4.61	4.98	5.25	5.25	5.25	5.46	
	90	4.40	4.84	5.14	5.14	5.14	5.37	
	120	4.16	4.69	5.03	5.03	5.03	5.29	
	155	3.91	4.55	4.93	4.93	4.93	5.21	
	180	3.56	4.38	4.82	4.82	4.82	5.13	
	240	3.25	4.26	4.75	4.75	4.75	5.07	
		2.35	4.01	4.60	4.60	4.60	4.97	
	ln(DPn∞)							
	DPn∞ (inter	5.068233	5.113407	5.321819	5.321819	5.321819	5.508554	
	Δ DPn∞	158.9	166.2	204.8	204.8	204.8	246.8	
	k	21.9	-15.3	-21.4	-21.4	-21.4	-24.0	
	k (from the	0.010535	0.004677	0.003114	0.003114	0.003114	0.002346	
	Δ k				0.003649			
		188.7	28.2	14.6	14.6	14.6	35.7	

Date		Styrene	1-PEC	TiCl4	2,6pyridine	CH2Cl2	c.Hex		
13/06/1999		100	0.5	5	2	20	30		
DPn∝	226.2								
Mn∝	23556								
[polymer]	[M]	DPn	Mn (cal.)	**Mn (GPC)**	Ieff	Conver.(%)	$\ln[M]_0/[M]$	**P.D.**	ln(DPn∝
			Cal.	GPC	Ieff			P.D.	-DPn)
0.15	0.98	30.1	3133	**3769**	0.83	13	0.14	**1.29**	5.25
0.29	0.84	58.7	6111	**5748**	1.06	26	0.30	**1.26**	5.14
0.39	0.74	77.8	8108	**7567**	1.07	34	0.42	**1.213**	5.03
0.47	0.66	93.4	9724	**9083**	1.07	41	0.53	**1.198**	4.93
0.54	0.59	108.9	11341	**10595**	1.07	48	0.66	**1.184**	4.82
0.59	0.54	117.5	12238	**11570**	1.06	52	0.73	**1.19**	4.75
0.68	0.45	136.2	14182	**13174**	1.08	60	0.92	**1.179**	4.60



Date	Styrene	1-PEC	TiCl4	2,6pyridine	CH2Cl2	c.Hex
13/06/1999	100	0.5	5	2	20	30





Date	Styrene	1-PEC	TiCl4	2,6pyridine	CH2Cl2	c.Hex
13/06/1999	100	0.5	5	2	20	30