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THE LIVING CATIONIC POLYMERIZATION OF α -METHYLSTYRENE WITH BCl_3 AS COINITIATOR

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ABSTRACT

The cationic polymerization of α -methylstyrene (αMeSt) was studied using the cumyl chloride (CumCl), $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{Ph})_2-\text{OCH}_3$ (TMPDPEOMe) or $(\text{CH}_3)_2\text{C}(\text{Ph})\text{CH}_2\text{C}(\text{CH}_3)(\text{Ph})\text{Cl}$ (the HCl adduct of αMeSt dimer, $\text{Di}\alpha\text{MeStHCl}$)/ BCl_3 initiator/coinitiator systems in the presence of proton trap in methyl chloride:hexanes (MeCl:Hex) or MeCl :methylcyclohexane (MeCl:MeChx) mixtures at -80 and -60°C . While CumCl is not an efficient initiator in conjunction with BCl_3 , TMPDPEOMe and $\text{Di}\alpha\text{MeStHCl}$ were found to be very efficient initiators. The polymerization was much faster in the MeCl:Hex mixture than in MeCl:MeChx . The polymerization rate was also higher at -80°C than at -60°C in the same solvent. The polymerization was found to be living at -80°C , as well as at -60°C , giving rise to poly(α -methylstyrene) ($\text{P}\alpha\text{MeSt}$) with controlled molecular weight and narrow molecular weight distribution ($M_w/M_n \sim 1.1\text{--}1.2$). The chain ends remained living for up to 40 minutes under monomer starved conditions at -80°C , but they rapidly decomposed at -60°C .

INTRODUCTION

The first examples of living carbocationic polymerization were reported over a decade ago [1, 2]. Curiously, the living polymerization of αMeSt , a very

reactive and inexpensive monomer, has remained unsolved until recently. Although several attempts have been made to attain controlled cationic polymerization of α MeSt, early results were less than satisfactory [3-7].

Higashimura and coworkers [8] reported the first living polymerization of α MeSt, with the HCl-adduct of 2-chloroethyl vinyl ether $\text{CH}_3\text{CH}(\text{OCH}_2\text{CH}_2\text{Cl})\text{Cl}/\text{SnBr}_4$ initiating system at -78°C in dichloromethane (CH_2Cl_2). The obtained M_n s were in good agreement with the calculated ones assuming that one polymer chain is formed per initiator. Polymers with M_n s up to 110,000 were obtained with narrow molecular weight distributions (MWDs) ($M_w/M_n \sim 1.1-1.2$).

The living polymerization of α MeSt initiated by CumCl in conjunction with BCl_3 in a CH_2Cl_2 :toluene 1:7 (v:v) solvent mixture at -78°C in the presence of tetra-*n*-butylammonium chloride (nBu_4NCl) was also claimed by Matyjaszewski *et al.* [9]. However, diagnostic plots were not shown to prove the absence of chain transfer and termination. In the absence of nBu_4NCl , lower than theoretical M_n and broad MWD ($M_w/M_n = 3.4$) were obtained. The polymerization in the presence of nBu_4NCl was reportedly slow, but P α MeSt with controlled M_n and narrow MWD was produced at low (0.005M) initiator concentration. With 0.02M CumCl concentration, however, poor molecular weight control and broad MWDs were obtained.

We recently reported the living polymerization of α MeSt with $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{Ph})_2-\text{Cl}$ (1,1-diphenylethylene capped 2,4,4-trimethyl-2-chloropentane) as initiator in conjunction with $\text{TiCl}_n(\text{OR})_{4-n}$ (R= ethyl, isopropyl, butyl) [10] and SnBr_4 or SnCl_4 in Hex/MeCl, 60:40 - 40:60 (v:v) at -80°C [11]. The polymerization with SnCl_4 seemed especially attractive because of the high rates even at low SnCl_4 concentration, however theoretical molecular weights and thus 100% initiator efficiencies were only achieved at $[\text{SnCl}_4]/[\text{chain end}] \sim 0.5$.

We continued our search for a new and efficient living system and in this paper describe the living polymerization of α MeSt using BCl_3 at low concentrations.

EXPERIMENTAL

Materials

Sources and purification of MeCl, Hex, and MeChx have been described [12]. α MeSt (Aldrich, 99%) was purified by the same method reported for styrene [13].

The synthesis of (TMPDPEOMe) has already been published [14]. The olefinic dimer of α MeSt (DiaMeSt) was synthesized by us, or after it became

available in 1997, was purchased from Aldrich (exo olefinic dimer $\geq 97\%$, endo olefinic dimer $\leq 3.0\%$, indanyl dimer $\leq 0.1\%$, α MeSt $\leq 0.1\%$) and used as received.

For the synthesis of Di α MeSt, Rosen's method [15], originally developed for the dimerization of styrene, was first evaluated. The method yielded 54.4 mol% indanyl dimer and 45.5 mol% olefinic dimer (29.0 mol% endo double bonds, and 16.5 mol% exo double bonds) under the conditions suggested for styrene (53 wt% H₂SO₄ 1:1 v:v, 120°C, 4 hours).

The above process was slightly modified by using 43 wt% H₂SO₄ and keeping the temperature between 100 and 110°C. Other experimental conditions were unchanged. The product contained 4 mol% α MeSt, 12.6 mol% of indanyl dimer, and 87.4 mol% olefin (60.9 mol% exo olefin, and 26.5 mol% endo olefin). The dried crude material was distilled *in vacuo*. The forecut and the first cut were not used. The fraction (second cut) collected between 148.5°C/3.75Hgmm and 150°C/3.90Hgmm was used for the hydrochlorination. This fraction contained 2.0 mol% indanyl dimer, and 98 mol% olefinic dimer (54.2 mol% exo double bonds, and 43.8 mol% endo double bonds).

To obtain the initiator Di α MeStHCl, 25mL Di α MeSt was dissolved in 100mL olefin free dry Hex in a two neck flask and under stirring dry HCl gas was bubbled through it at -78°C for 24 hours. Di α MeStHCl formed a white precipitate. After 24 hours, dry N₂ was bubbled through the reaction mixture for 1 hour to remove HCl, then the flask was lifted from the dry ice/acetone bath and was allowed to warm up to nearly ambient temperature under N₂ stream. Since Di α MeStHCl is not stable at room temperature, the flask was placed as quickly as possible into the -80°C heptane bath in the glove box. The product was filtered at -80°C on a glass filter and was washed with prechilled (-80°C), dry, olefin free Hex and cold nitrogen gas was drawn through it for a few minutes. The ¹H NMR spectrum recorded in CD₂Cl₂ at -80°C showed that the product was essentially pure Di α MeStHCl containing traces of Hex. Since it decomposes rapidly at room temperature especially when in solution, it was stored at temperatures $\leq -40^\circ\text{C}$.

The Di α MeStHCl stock solution was prepared as follows: Di α MeStHCl was placed into a culture tube. Its weight was measured roughly on a balance and a calculated amount of MeCl was added. In order to determine the concentration of the stock solution 2.0mL was placed into a weighted vial. White crystals appeared on the wall of the vial when the MeCl evaporated. The moisture was wiped off from the vial and its weight was quickly measured. Then the vial was left under the hood to let Di α MeStHCl decompose to Di α MeSt and HCl. When an indicator paper

indicated the absence of HCl, the weight of Di α MeSt was measured. The concentrations based on the above two methods agreed well.

BCl_3 (99.9%) and the proton trap 2,6-di-*tert*-butylpyridine (DTBP) (99.4%) were purchased from Aldrich Chemical Co. and used as received.

Procedures

Polymerization

The polymerizations were carried out under dry N_2 atmosphere in 75mL test tubes equipped with teflon-faced rubber-lined screw caps in a stainless steel glove box [12]. The order of addition was Hex or MeChx, stock solutions of initiator and proton trap, MeCl, and BCl_3 stock solution. This was followed immediately by the addition of α MeSt stock solution. (With Di α MeStHCl the proton trap was added just before the addition of α MeSt.) All ingredients were chilled to -80°C before addition. The reactions were quenched with prechilled (-80°C) methanol. The samples were air dried and then dried under vacuo at $\sim 50^\circ\text{C}$. Blank samples were prepared by combining all the reactants with the exception of monomer. The weight of blank was then deducted from the weights of the polymer samples to calculate monomer conversion.

The apparent first order rate constants were calculated from the slopes of the $\ln([M]_0/[M])$ vs. time plots.

Characterization

M_n s and M_w/M_n s were measured by GPC (already described [14]) using either a conventional calibration curve obtained with P α MeSt standards of narrow MWD (Polymer Laboratories and Pressure Chemical) and Viscotek TriSEC GPC software or using a multi-angle laser light scattering (MALLS) detector [16] and ASTRA software. In the latter calculations, $dn/dc = 0.225 \text{ mL/g}$ (THF, 25°C) was used. Generally, the M_n s were somewhat higher and the M_w/M_n ratios somewhat lower based on MALLS. ^1H NMR experiments were performed on a Bruker 250 MHz spectrometer equipped with a variable temperature controller.

RESULTS AND DISCUSSION

Compared to styrene, which can be polymerized by living cationic polymerization with a variety of initiator-coinitiator pairs, α MeSt is more reactive because poly α MeSt $^+$ is a tertiary benzylic carbocation stabilized by the α -methyl substituent. Due to the α -methyl substituent, however poly α MeSt $^+$ also readily undergoes side

TABLE 1. The Polymerization of α MeSt with the CumCl/ BCl_3 Initiating System in MeCl:MeChx 40:60 (v:v) Solvent Mixture at -80°C . $[\text{I}]_0 = [\text{CumCl}]_0 = 0.00226\text{M}$, $[\alpha\text{MeSt}]_0 = 0.384\text{M}$, $[\text{DTBP}] = 0.0038\text{M}$

$[\text{I}]_0:[\text{BCl}_3]$	Reaction Time, min	Conversion, %	M_n	M_w/M_n	I_{eff} , %
1:2	4	35.4	36,400	1.26	4.9
1:2	32	100	64,600	1.27	32.7
1:3	2	31.9	33,800	1.22	19.3
1:3	9.3	100	60,900	1.25	33.5

reactions such as β -proton elimination and chain transfer to monomer by indanyl ring formation, that must be avoided in order to obtain living polymerization. These reactions may be eliminated at low temperature and by the use of non-polar solvent mixtures. Termination is reportedly absent using BCl_3 [5], and thus this Lewis acid is a candidate to induce living polymerization.

An important consideration is the structure of the initiator. In order to obtain polymers with controlled molecular weight and narrow (Poisson) molecular weight distribution, the rate of initiation should be comparable to and preferably higher than the rate of propagation. It was reported that CumCl, which thought to have nearly the same terminal structure as that of the chain end, is not an efficient initiator in conjunction with SnBr_4 [8]. With CumCl as well as with a variety of other organic chlorides, (for example, 1-phenyl ethyl chloride and benzhydryl chloride) much higher than theoretical M_n s were obtained, apparently the rate of initiation with these initiators is much lower than the rate of propagation [8]. Our polymerization experiments with CumCl in conjunction with BCl_3 in MeCl:MeChx 40:60 v:v solvent mixture at -80°C confirmed that initiation is much slower than propagation. Representative results are shown in Table 1.

As indicated by the low initiator efficiencies, CumCl is an inefficient initiator for the polymerization of α MeSt. For this reason, in our initial studies TMPDPEOMe was selected as initiator due to the high initiator efficiency (I_{eff}) reported previously [9, 10], and because of our interest in block copolymerization of isobutylene with α MeSt. It is postulated that, that similarly to its reaction with TiCl_4 [17], TMPDPEOMe is rapidly converted to the corresponding chloride in a reaction with BCl_3 , according to the following equation [18]:

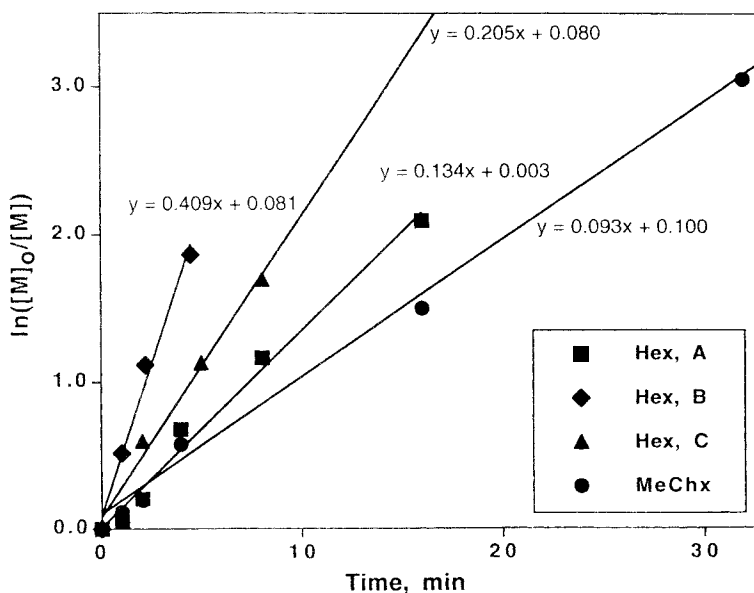
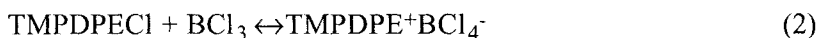


Figure 1. The first order plot in the polymerization of α MeSt in MeCl:Hex or MeChx 40:60 (v:v) solvent mixture at -80°C . Exp. conditions: Hex: [DTBP] = 0.003M, $[M]_0 = [\alpha\text{MeSt}]_0 = 0.35\text{M}$; MeCl:Hex 40:60 (v:v) solvent mixture; A: $[\text{TMPDPEOMe}]_0 = 0.002\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.002\text{M}$; B: $[\text{TMPDPEOMe}]_0 = 0.00245\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.00245\text{M}$; C: $[\text{TMPDPEOMe}]_0 = 0.002\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.002\text{M}$. MeChx: $[\text{TMPDPEOMe}]_0 = 0.0022\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.0022\text{M}$



TMPDPECl is then ionized by the excess BCl_3 :



It is assumed that BCl_2OMe is inert under the polymerization conditions. This is supported by the observation that polymerization is absent when $[\text{TMPDPEOMe}]_0 = [\text{BCl}_3]_0$, i.e., BCl_2OMe is too weak to coinitiate.

The polymerization of α MeSt was first studied in MeCl:MeChx or Hex 40:60 (v:v) solvent mixture at -80°C . Immediately after the addition of BCl_3 to the initiator solution, the color of the reaction mixture turned yellow, indicating ionization of the initiator. Upon addition of α MeSt, a white, powder-like precipitate appeared, which did not settle during the studied reaction time.

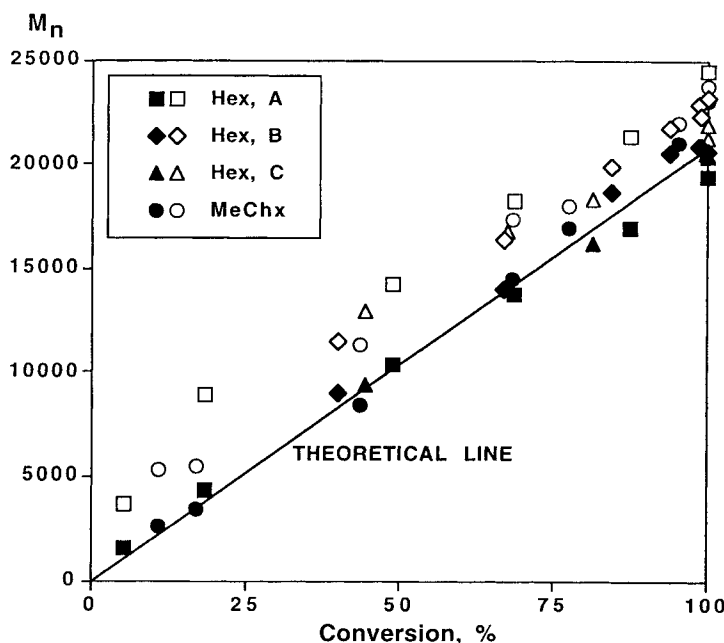


Figure 2. The M_n vs. conversion plot in the polymerization of α MeSt in MeCl:Hex or MeChx 40:60 (v:v) solvent mixture at -80°C . Exp. Hex: conditions: $[\text{DTBP}] = 0.003\text{M}$, $[\text{M}]_0 = [\alpha\text{MeSt}]_0 = 0.35\text{M}$; A: $[\text{TMPDPEOMe}]_0 = 0.002\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.002\text{M}$; B: $[\text{TMPDPEOMe}]_0 = 0.00245\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.00245\text{M}$; C: $[\text{TMPDPEOMe}]_0 = 0.002\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.002\text{M}$. MeChx: $[\text{TMPDPEOMe}]_0 = 0.0022\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.0022\text{M}$ Open symbols: MALLS, solid symbols: conventional calibration.

The first order plots of several experiments are shown in Figure 1. The corresponding M_n s and polydispersity ratios (M_w/M_n) are plotted against conversion in Figures 2 and 3, respectively. Although some reaction conditions were varied, the $[\text{initiator}]:[\text{BCl}_3]_0$ ratio was kept constant at 1:2. Interestingly, as Figure 1 shows that the first order plots are linear indicating that the concentration of the active centers remained constant during the polymerization, in spite of the heterogeneous nature of the polymerization. It is noted that the rate is somewhat higher when Hex is used instead of MeChx.

The M_n vs. conversion plot is shown in Figure 2. The M_n s linearly increase with the conversion, indicating the absence of chain transfer to monomer. For comparison, M_n s based on linear calibration and absolute M_n s obtained from

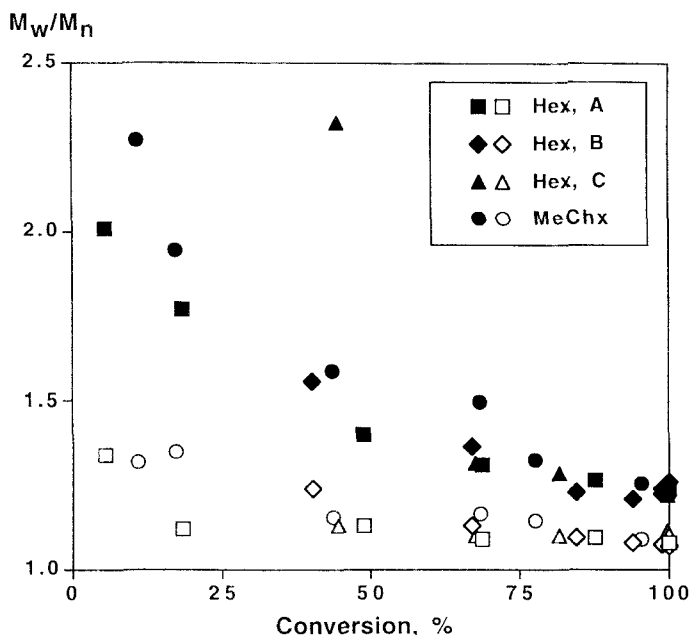


Figure 3. The polydispersity ratio vs. conversion plot in the polymerization of α -MeSt in MeCl:Hex or MeChx 40:60 (v:v) solvent mixture at -80°C . Exp. conditions: Hex: [DTBP] = 0.003M, $[M]_0 = [\alpha\text{MeSt}]_0 = 0.35\text{M}$; A: $[\text{TMPDPEOMe}]_0 = 0.002\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.002\text{M}$; B: $[\text{TMPDPEOMe}]_0 = 0.00245\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.00245\text{M}$; C: $[\text{TMPDPEOMe}]_0 = 0.002\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.002\text{M}$. MeChx: $[\text{TMPDPEOMe}]_0 = 0.0022\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.0022\text{M}$ Open symbols: MALLS, solid symbols: conventional calibration.

MALLS are also plotted. The experimental M_n s are close to the theoretical value calculated based on 100% I_{eff} , i.e., that one polymer chain was started from one initiator molecule. The M_n s obtained by MALLS are somewhat higher, especially at lower molecular weights, than the M_n s calculated based on linear calibration. (It is well known that the polydispersity index is underestimated by MALLS at low molecular weights, see also Figure 3). Thus, Figures 1 and 2 show that the polymerization is living under these conditions. The monotonous decrease of the M_w/M_n ratios with the conversion (Figure 3) is a consequence of the slow continuous exchange between the active cations and the dormant chloro ends [19].

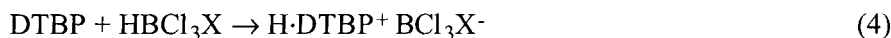
The apparent first order rate constants were calculated by assuming Reaction Schemes 1 and 2. These calculated rate constants are given in Table 2 for

TABLE 2. The Apparent First Order Rate Constants ($k_{p,app}=k_p[P^+]$) in the Polymerization of α MeSt at -80°C Under Different Conditions. $[\alpha\text{MeSt}]_0 = 0.35\text{M}$, $[\text{DTBP}] = 0.003\text{M}$, $[\text{I}]_0 = [\text{TMPDPEOMe}]_0$.

Experiment	Solvent, (v:v)	$[\text{BCl}_3]_0$, 10^3M	$[\text{I}]_0$, 10^3M	$k_{p,app}$ $\times 10^3, \text{s}^{-1}$	$k_{p,app}/([\text{I}]_0[\text{BCl}_3]_{\text{eff}})$, $\text{s}^{-1}\text{M}^{-2}$
A	MeCl:Hex (40:60)	4.0	2.0	2.23	558
B	MeCl:Hex (40:60)	4.9	2.45	6.82	1350
C	MeCl:Hex (40:60)	4.0	2.0	3.42	855
D	MeCl:Hex (40:60)	4.4	2.2	4.82	996
E	MeCl:Hex (40:60)	4.4	2.2	2.30	475
MeChx	MeCl:MeChx (40:60)	4.4	2.2	1.55	320

the experiments in which the $[\text{initiator}]:[\text{BCl}_3]_0$ ratio was 1:2. Assuming that the polymerization is first order in initiator and coinitiator concentration, the rates at different initiator and coinitiator concentrations can be compared by dividing the apparent first order rate constants by initiator and $[\text{BCl}_3]_{\text{eff}}$ concentration ($[\text{BCl}_3]_{\text{eff}} = [\text{BCl}_3]_0 - [\text{TMPDPEOMe}]$).

Table 2 indicates large differences in $k_{p,app}/([\text{I}]_0[\text{BCl}_3]_{\text{eff}})$ values even under the same conditions (cf. Experiments A and C as well as D and E). The differences in the rates are most probably due to the presence of different amount of protic impurities. Protic impurities decrease the effective BCl_3 concentration according to reactions 3 and 4. Since their concentration is about $1\text{--}2 \times 10^{-3} \text{M}$ and cannot be controlled, the reproducibility is poor.



In Reaction Scheme 3, HX represents protic impurities (e.g. H_2O , HCl). Thus, if the $[\text{BCl}_3]$ is only slightly higher than the concentration of the impurities, a small change in $[\text{HX}]$ can cause large relative changes in the actual $[\text{BCl}_3]_{\text{eff}}$ and consequently in the polymerization rates.

In a control experiment, α MeSt was polymerized in the absence of TMPDPEOMe initiator to determine the contribution of direct initiation. At $[\text{BCl}_3]_0 = 0.004\text{M}$, $[\alpha\text{MeSt}]_0 = 0.35\text{M}$, and $[\text{DTBP}] = 0.003\text{M}$, after 64 minutes, 6.9%

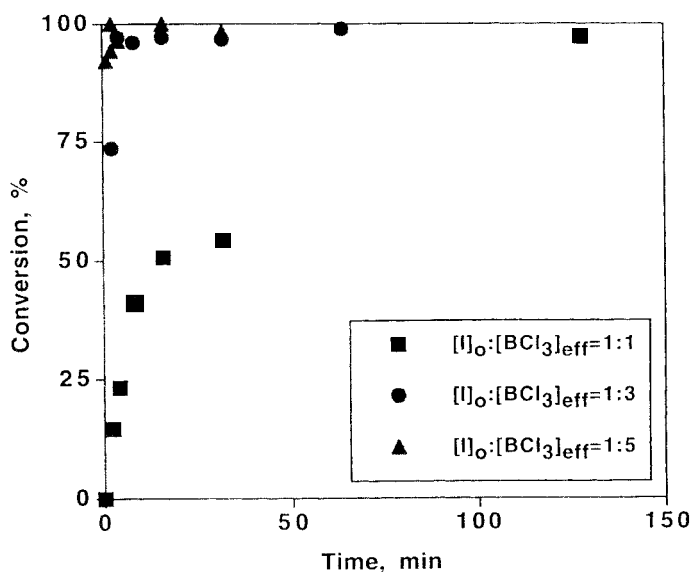


Figure 4. The conversion vs. time plot in the polymerization of α MeSt using MeCl:MeChx 40:60 solvent mixture at -80°C . $[\text{M}]_0 = [\alpha\text{MeSt}]_0 = 0.384\text{M}$, $[\text{I}]_0 = [\text{TMPDPEOMe}]_0 = 0.00226\text{M}$, $[\text{DTDP}] = 0.0038\text{M}$.

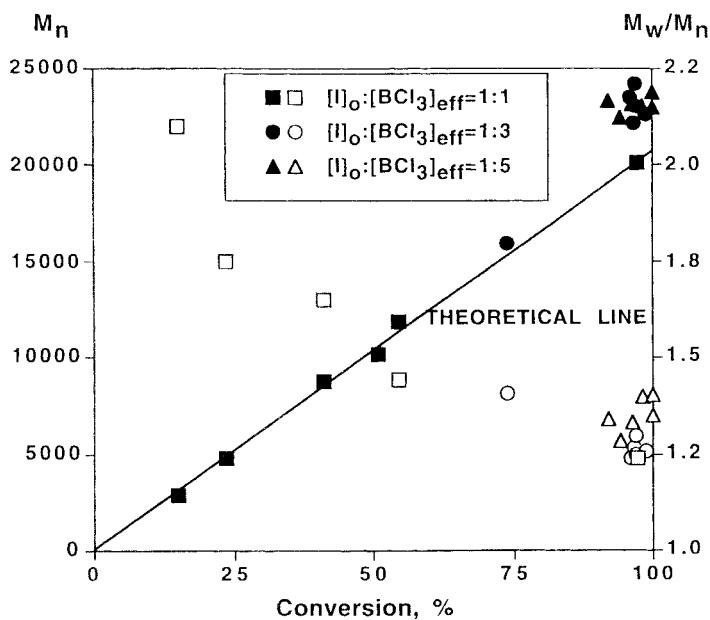


Figure 5. The M_n and M_w/M_n vs. conversion plots in the polymerization of α MeSt using MeCl:MeChx 40:60 (v:v) solvent mixture at -80°C . $[\alpha\text{MeSt}]_0 = 0.384\text{M}$, $[\text{I}]_0 = [\text{TMPDPEOMe}]_0 = 0.00226\text{M}$, $[\text{DTBP}] = 0.0038\text{M}$. Solid symbols: M_n , open symbols: M_w/M_n , conventional calibration.

TABLE 3. α MeSt Polymerization in the Absence of Initiators at -80°C in MeCl:MeChx 40:60 v:v Solvent Mixture. Other Exp. Conditions: $[\alpha\text{MeSt}]_0 = 0.384\text{M}$, $[\text{DTBP}] = 0.0038\text{M}$. $[\text{P}]$ is the Concentration of the Polymer Molecules.

$[\text{BCl}_3]_0$, M	Time, min	Conversion, %	M_n	M_w/M_n	$[\text{P}]$, M
0.00226	128	2.2	36,400	1.18	2.84×10^{-5}
0.00678	64	9.3	431,000	1.57	9.92×10^{-5}
0.0113	32	86.2	487,000	1.63	8.16×10^{-5}

conversion ($M_n = 180000$) was obtained. Apparently, direct initiation is negligible compared to controlled initiation in these systems.

The polymerization was also studied at varied $[\text{TMPDPEOMe}]:[\text{BCl}_3]_0 = 1:2, 1:4$ and $1:6$ ratios. The conversion vs. time plots are shown in Figure 4. The M_n s and the polydispersity ratios are plotted against the conversion in Figure 5.

With increasing $[\text{BCl}_3]_0$ the rate increases, and with $[\text{TMPDPEOMe}]:[\text{BCl}_3]_0 = 1:6$ complete conversion is reached in less than 4 minutes. Due to the high rate of the polymerization, only two-two data points could be used to measure apparent rate constants for the two higher BCl_3 concentration, thus $k_{p,\text{app}} = 2.4 \times 10^{-2}, 1.4 \times 10^{-2}$ and $1.1 \times 10^{-3} \text{ s}^{-1}$ obtained for the $[\text{BCl}_3]_0:[\text{TMPDPEOMe}] = 6, 4$ and 2 ratios can only be considered as approximate. For similar reasons, the polymerization order in $[\text{BCl}_3]$ could not be calculated. The apparent rate constants obtained for the two higher BCl_3 concentrations are consistent with the presumed first order, but the rate constant obtained with the lowest $[\text{BCl}_3]$ (which is similar to the $k_{p,\text{app}} = 1.5 \times 10^{-3} \text{ s}^{-1}$ in Table 2, obtained from Figure 1) is much lower. This is due to the fact that all $[\text{BCl}_3]_{\text{eff}}$ should be lowered by the concentration of protic impurities to obtain the actual concentration of BCl_3 . With this correction, all three apparent rate constants are consistent with the estimated $\sim 1\text{-}2 \times 10^{-3} \text{M}$ concentration of protic impurities. In spite of the rate deviation due to uncontrolled and varied levels of protic impurities, the initiator:coinitiator ratio does not have any influence on the M_n vs. conversion plot. The experimental M_n values are close to the theoretical ones, indicating $\sim 100\%$ I_{eff} and the virtual absence of chain transfer to monomer.

Table 3 shows the results of control experiments obtained in the absence of TMPDPEOMe . Though with increased $[\text{BCl}_3]$ the polymerization rate by direct initiation is higher, the polymerization is apparently still much slower than controlled polymerization.

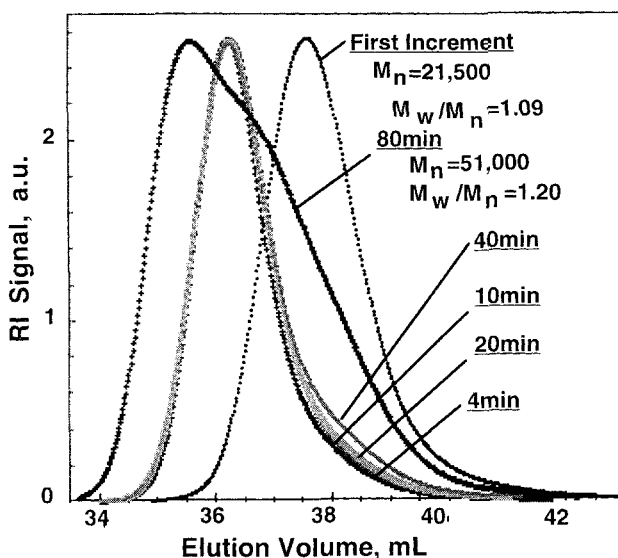


Figure 6. The RI GPC traces of P α MeSt samples prepared with incremental monomer addition in MeCl:MeChx 40:60 (v:v) at -80°C . First increment: $[\text{TMPDPEOMe}]_0 = 0.0022\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.0066\text{M}$, $[\alpha\text{MeSt}]_0 = 0.38\text{M}$ (1mL), $[\text{DTBP}] = 0.0031\text{M}$, $V = 20\text{mL}$. Second increment: 1mL αMeSt in 3.6mL solution. 4 min: $M_n = 40,500$, $M_w/M_n = 1.15$; 10 min: $M_n = 42,200$, $M_w/M_n = 1.09$; 20 min: $M_n = 41,300$, $M_w/M_n = 1.13$; 40 min: $M_n = 42,300$, $M_w/M_n = 1.10$.

The lifetime of the active centers was studied in a series of experiments using the $[\text{initiator}]:[\text{BCl}_3]_{\text{eff}} = 1:3$ ratio, where a second increment of αMeSt was added to the reaction mixture after the conversion of the first increment reached $\sim 100\%$ (4 minutes). The time of the second addition was then varied. The polymerization was quenched 16 minutes (100% conversion in all cases) after the addition of the second increment. The GPC traces of the products can be seen in Figure 6.

As can be seen in Figure 6, the chain ends remain living up to 40 minutes, about 10 times longer than the 3-4 minute time necessary to reach practically complete monomer conversion. (While the absolute times depend on the actual $[\text{BCl}_3]$, the ratio should be similar.) The peaks moved smoothly to higher molecular weights without tailing after the polymerization of the second monomer increment, and the M_n s approximately doubled. After 80 minutes, however, a substantial fraction of the active centers were dead, as evident from the low molecular weight shoulder on the GPC trace (cf. Curve 80 minutes in Figure 6). Thus, polymer

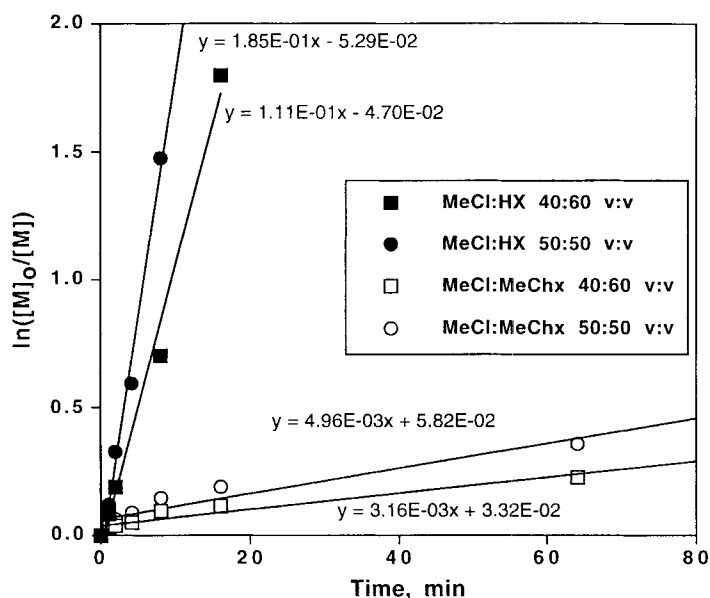


Figure 7. The $\ln([M]_0/[M])$ vs. time plot in the polymerization of α MeSt at -60°C . Other exp. conditions: $[\text{TMPDPEOMe}]_0 = 0.00226\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.00226\text{M}$, $[M]_0 = [\alpha\text{MeSt}]_0 = 0.39\text{M}$, $[\text{DTBP}] = 0.00364\text{M}$

chains whose ends remained living grow longer as illustrated by the shift of the peak position to lower elution volume, i.e. to higher molecular weight.

The effects of temperature and solvent composition were studied in the next series of experiments. As anticipated, at -60°C the $\text{P}\alpha\text{MeSt}$ appeared to be more soluble.

The first order plots for four solvent mixtures are shown in Figure 7.

The polymerization is faster in the more polar MeCl:Hex (or MeChx) 50:50 v:v solvent mixture compared to the less polar 40:60 v/v mixture. The faster polymerization may be due to a higher ionization of the dormant chain ends in the more polar medium. Somewhat unexpectedly, the polymerization rate is much lower using MeChx compared to Hex. This suggests that the concentration of protic impurities is much higher in MeChx compared to Hex, which lowers the actual concentration of BCl_3 according to Equations 3 and 4. A similar observation has been reported in the polymerization of isobutylene in MeCl:MeChx solvent mixture. [12]

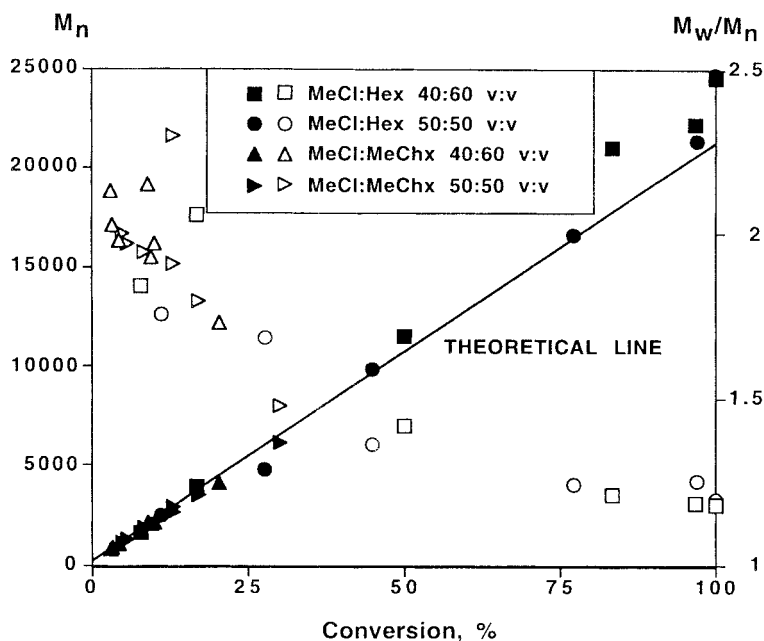


Figure 8. The M_n and M_w/M_n vs. conversion plots in the polymerization of α -MeSt at -60°C . Other exp. conditions: $[\text{TMPDPEOMe}]_0 = 0.00226\text{M}$, effective $[\text{BCl}_3] = 0.00226\text{M}$, $[\alpha\text{MeSt}]_0 = 0.39\text{M}$, $[\text{DTBP}] = 0.00364\text{M}$. Solid symbols: M_n , open symbols: M_w/M_n (conventional calibration).

In Figure 8, the M_n s and polydispersity ratios are plotted against the conversion. The M_n s follow the theoretical line and the M_w/M_n ratios decrease with increasing conversion, as observed at -80°C .

In a new series of experiments, higher BCl_3 concentrations were used to compensate for the diminished BCl_3 concentration due to reaction with protic impurities. The data are shown in Figure 9, where the conversions are plotted against time.

The polymerizations with $[\text{I}]_0:[\text{BCl}_3]_{\text{eff}} = 1:10$ were very fast, and thus, the first order plots were calculated only for the $[\text{I}]_0:[\text{BCl}_3]_{\text{eff}} = 1:5$ ratio in this series of experiments. From the first order plot (not shown) the apparent rate constant was calculated to be $k_{p,\text{app}} = 1 \times 10^{-2}\text{s}^{-1}$. This is less than half of what was obtained at -80°C , indicating a negative apparent activation energy for the rate of polymerization. The calculated apparent activation energy of $-3.5\text{ kcal mol}^{-1}$ is similar to values reported for cationic polymerization of monomers such as isobutylene,

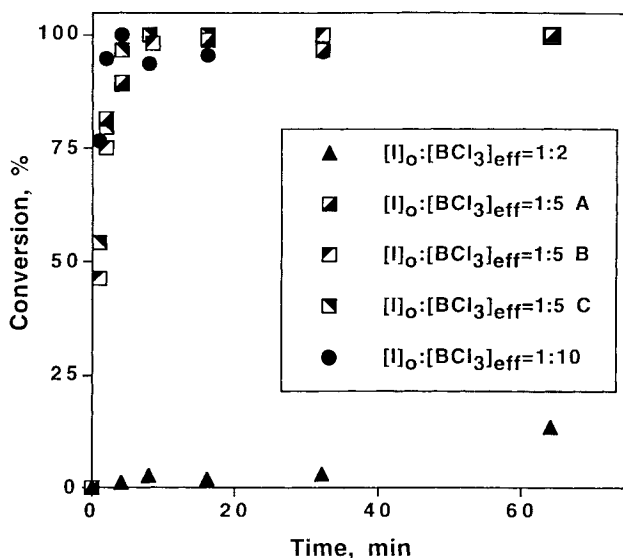


Figure 9. The conversion vs. time plot in the polymerization of α MeSt at -60°C using MeCl:MeChx 40:60 (v:v) solvent mixture. Other exp. conditions: $[I]_0 = [\text{TMPDPEOME}]_0 = 0.00223\text{M}$, $[\alpha\text{MeSt}]_0 = 0.39\text{M}$, $[\text{DTBP}] = 0.0038\text{M}$. A, B, and C are parallel experiments

α MeSt and indene, recently compiled by Sigwalt [20]. The generally accepted view is, that higher ionization of the chain ends at lower temperature may explain the negative apparent activation energy. The M_n s and M_w/M_n s are plotted against conversion in Figure 10. The molecular weights are close to the theoretical values except at high conversion where they are about 10% higher. The deviation at high conversions may be due to interchain alkylation.

Chain extension experiments were also carried out at -60°C to determine the lifetime of the active centers. Similarly to the corresponding experiments carried out at -80°C , a second increment of α MeSt was added after complete monomer conversion was reached. The corresponding GPC traces (Figure 11) indicate that about 60% of the chain ends underwent irreversible termination in less than 30 minutes under monomer starved conditions.

An important finding of the present study is that, CumCl is not an efficient initiator for the polymerization of α MeSt in conjunction with BCl_3 . Thus, CumCl, which formerly thought to have nearly the same terminal structure as that of the chain end, is a poor model of the growing end. This is presumably due to the lack

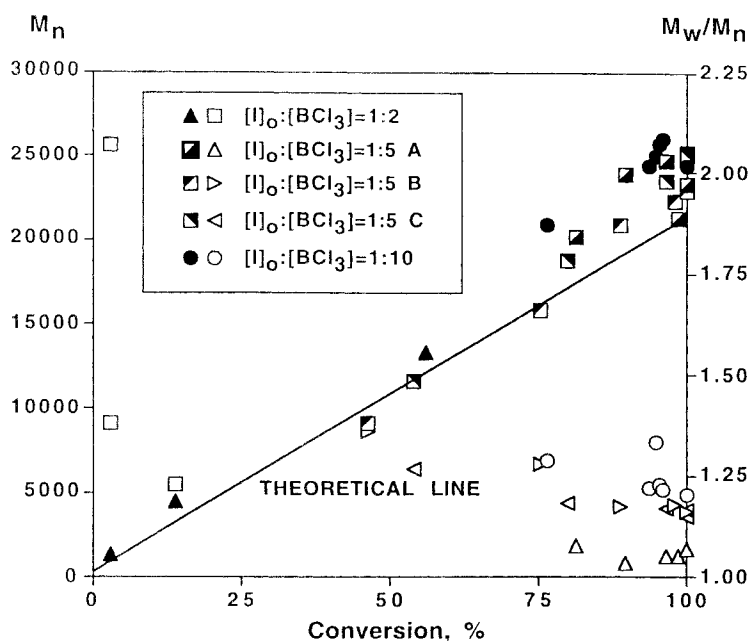


Figure 10. The M_n vs. conversion plot in the polymerization of α MeSt at -60°C using MeCl:MeChx 40:60 (v:v) solvent mixture. Other exp. conditions: $[I]_0 = [\text{TMPDPEOMe}]_0 = 0.00223\text{M}$, $[\alpha\text{MeSt}]_0 = 0.39\text{M}$, $[\text{DTBP}] = 0.0038\text{M}$. A, B, and C are parallel experiments. Solid symbols M_n , open symbols: M_w/M_n (conventional calibration).

of steric strain, which is present in the dormant polymer end and results in higher ionization equilibrium constant. This concept is well known in the polymerization of isobutylene and has been used to explain the differences in initiating efficiencies of *t*BuCl and TMPCl. Namely, *tert*-BuCl is a very inefficient, but 2-chloro-2,4,4-trimethylpentane (TMPCl) is a very efficient initiator for the polymerization of isobutylene in conjunction with a variety of Lewis acids (BCl_3 , TiCl_4 , etc).

To demonstrate the significance of steric strain, $\text{Di}\alpha\text{MeStHCl}$ was synthesized and for the first time, used as initiator for the living polymerization of αMeSt in conjunction with BCl_3 ($[\text{Di}\alpha\text{MeStHCl}]:[\text{BCl}_3]_0 = 1:3$) at -80°C , in MeCl:MeChx 40:60 (v:v). The first order plot, as shown in Figure 12 is linear, and the obtained $k_{p,\text{app}} = 1.5 \times 10^{-2}\text{s}^{-1}$ apparent propagation rate constant is in good agreement with $k_{p,\text{app}} = 1.4 \times 10^{-2}\text{s}^{-1}$ calculated from the results of Figure 4. for $[\text{TMPDPEOMe}]:[\text{BCl}_3]_0 = 1:4$. More importantly, the M_n vs. conversion plot,

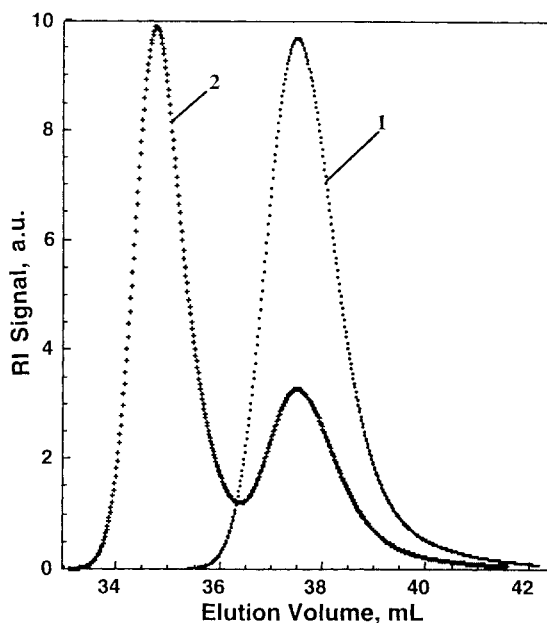


Figure 11. The GPC RI traces of P α MeSt samples prepared with incremental monomer addition in MeCl:MeChx 40:60 (v:v) at -60°C . 1: First increment: $[\text{TMPDPEOMe}]_0 = 0.00225\text{M}$, $[\text{BCl}_3]_{\text{eff}} = 0.0109\text{M}$, $[\alpha\text{MeSt}]_0 = 0.38\text{M}$ (1mL), $[\text{DTBP}] = 0.0038\text{M}$, $V = 20\text{mL}$, 100% conversion after ~ 10 min, $M_n = 22,900$, $M_w/M_n = 1.16$. 2: Second increment: 1mL α MeSt in 3.6mL solution, added 34 min after the first increment, 100% conversion, $M_n = 45,000$, $M_w/M_n = 1.59$ (conventional calibration).

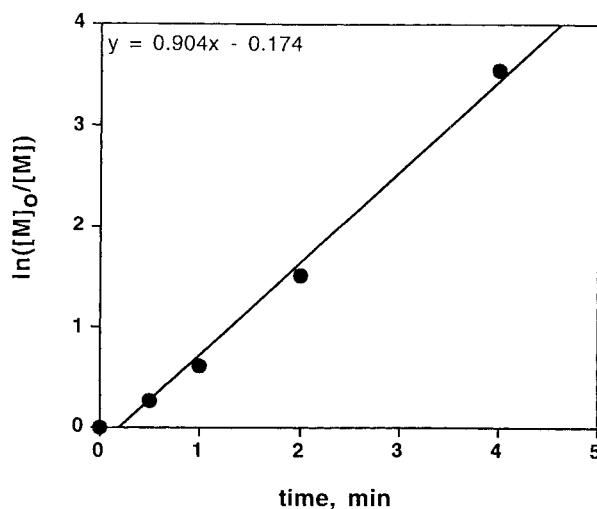


Figure 12. First order plot for the polymerization of α MeSt by the Di α MeStHCl/BCl₃/MeCl:MeChx 40:60 (v:v)/ -80°C system $[\text{Di}\alpha\text{MeStHCl}]_0 = 0.002\text{M}$, $[\text{BCl}_3]_0 = 0.006\text{M}$, $[\alpha\text{MeSt}]_0 = 0.35\text{M}$, $[\text{DTBP}] = 0.003\text{M}$.

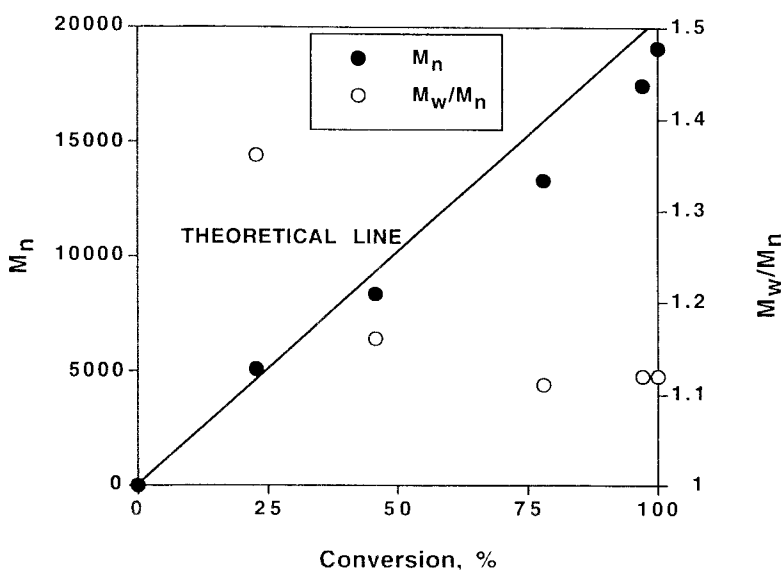


Figure 13. M_n and M_w/M_n vs. conversion plots for the polymerization of α MeSt by the $\text{Di}\alpha\text{MeStHCl}/\text{BCl}_3/\text{MeCl}:\text{MeChx}$ 40:60 (v:v)/ -80°C system. $[\text{Di}\alpha\text{MeStHCl}]_0=0.002\text{M}$, $[\text{BCl}_3]_0=0.006\text{M}$, $[\alpha\text{MeSt}]_0=0.35\text{M}$, $[\text{DTBP}]=0.003\text{M}$.

shown in Figure 13, is linear and very close to the theoretical line, apparently, $\text{Di}\alpha\text{MeStHCl}$ is an efficient initiator. This suggests that the rate of initiation is similar to the rate of propagation, i.e., $\text{Di}\alpha\text{MeStHCl}$ is a satisfactory model of the dormant $\text{P}\alpha\text{MeSt}$ end.

Using the model compound $\text{Di}\alpha\text{MeStHCl}$, we also attempted to identify the side reaction responsible for the slow destruction of the living $\text{P}\alpha\text{MeSt}^+$ chain end at -80°C . When $\text{Di}\alpha\text{MeStHCl}$ (0.002M) was mixed with BCl_3 (0.006M) in the presence of DTBP (0.0035M) in $\text{MeCl}:\text{MeChx}$ 40:60 (v:v) at -80°C and quenched after 4 hours, the only product isolated at room temperature was the exo-olefinic dimer. Although $\text{Di}\alpha\text{MeStHCl}$ also undergoes spontaneous elimination at room temperature, and therefore, the extent of elimination at -80°C could not be determined, indanyl cyclization is apparently absent. To determine the extent of elimination at -80°C , in a separate experiment, the above reaction mixture was aged for 4 hours and then αMeSt was added and polymerized for 10 minutes. To our surprise, $\text{P}\alpha\text{MeSt}$ with close to theoretical M_n ($=21000$), and narrow MWD ($M_w/M_n=1.07$) was obtained indicating the absence of decomposition of the $\text{Di}\alpha\text{MeSt}^+$ cation. This unexpected finding suggesting a difference in the stability of $\text{P}\alpha\text{MeSt}^+$ and $\text{Di}\alpha\text{MeSt}^+$ cation is under investigation.

CONCLUSIONS

The living cationic polymerization of α MeSt was accomplished with the TMPDPEOMe or Di α MeStHCl/BCl₃/MeCl:Hex or MeCl:MeChx 40:60 v:v system, at -80 and -60°C. Under monomer starved condition, the chain ends retain their living character for up to 40 minutes at -80°C. At -60°C, however, the chain ends undergo rapid decomposition. The large differences in initiating efficiencies of CumCl, which is very inefficient, and Di α MeStHCl, which was found to be very efficient, are explained by differences in the ionization equilibrium constant, brought about by different back strain in the two molecules.

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REFERENCES

- [1] M. Miyamoto, M. Sawamoto, and T. Higashimura, *Macromolecules*, **17**, 265 (1984).
- [2] R. Faust and J. P. Kennedy, *Polymer Bulletin*, **15**, 317 (1986).
- [3] J. P. Kennedy and R. A. Smith, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1539 (1980).
- [4] S. C. Guhaniyogi and J. P. Kennedy, *J. Macromol. Sci., Chem. A18*, 77 (1982).
- [5] R. Faust, A. Fehérvári, and J. P. Kennedy, *J. Macromol. Sci., Chem.*, **A18**, 1209 (1982).
- [6] J. E. Puskás, G. Kaszás, J. P. Kennedy, and W. G. Hager, *J. Polym. Sci., Pt. A, Polym. Chem.*, **30**, 41 (1992).
- [7] Y. Tsunogae and J. P. Kennedy, *J. Polym. Sci., Pt. A Polym. Chem.*, **32**, 403 (1994).
- [8] T. Higashimura, M. Kamigaito, M. Kato, T. Hasebe, and M. Sawamoto, *Macromolecules*, **26**, 2670 (1993).
- [9] K. Matyjaszewski, A. Bon, Ch.-H. Lin, and J. S. Xiang, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **34(1)**, 487 (1993).
- [10] D. Li and R. Faust, *Macromolecules*, **28**, 1383 (1995).

- [11] D. Li, S. Hadjikyriacou, and R. Faust, *Macromolecules*, *29*, 6061 (1996).
- [12] M. Györ, H.-Ch. Wang, and R. Faust, *J. Macromol. Sci., Pure Appl. Chem.*, *A29*, 639 (1992).
- [13] Zs. Fodor, M. Györ, and R. Faust, *J. Macromol. Sci., Pure & Appl. Chem.*, *A30*, 349 (1993).
- [14] S. Hadjikyriacou, Zs. Fodor, and R. Faust, *J. Macromol. Sci., Pure & Appl. Chem.*, *A32*, 1137 (1995).
- [15] M. J. Rosen, *J. Org. Chem.*, *18* 1701 1953.
- [16] Zs. Fodor and R. Faust, *J. Macromol. Sci., Pure & Appl. Chem.*, *A31*, 1985 (1994).
- [17] B. Charleux, M. Moreau, J.-P. Vairon, S. Hadjikyriacou, and R. Faust, *Macromol. Symp.* in press.
- [18] Y. C. Bae, Zs. Fodor, and R. Faust, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, *37(1)*, 801 (1996).
- [19] A. H. E. Müller, R. Zhuang, D. Yan, and G. Litvinenko, *Macromolecules* *28*, 4326 (1995).
- [20] P. Sigwalt, *Macromol. Symp.*, in press.

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