Macromolecules **1996,** *29,* 6061−6067

Living Carbocationic Polymerization of α-Methylstyrene Using Tin Halides as Coinitiators

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Received February 2, 1996; Revised Manuscript Received June 10, 1996[⊗]

ABSTRACT: The polymerization of α−methylstyrene (αMeSt) was studied in conjunction with the $(CH_3)_3CCH_2C(CH_3)_2CH_2C(Ph)_2Cl$ (1,1-diphenylethylene-capped 2,4,4-trimethyl-2-chloropentane)/$SnBr_4$ or $SnCl_4$ initiating systems. Using $SnBr_4$, living polymerization was obtained in methyl chloride (MeCl)/hexane (Hex) 60/40 to 40/60 v/v at −80 or −60 °C. The polymers exhibited theoretical molecular weights and narrow molecular weight distributions ($M_w/M_n \sim 1.1$). The low polymerization rate obtained in MeCl/Hex 40/60 v/v more than doubled when the solvent polarity was increased to 60/40 v/v. A similar ca. twofold increase in rate was also observed when the temperature was raised from −80 to −60 °C. Living polymerization and high rates were obtained using $SnCl_4$; however, theoretical molecular weight and therefore 100% initiator efficiency were only achieved at $[SnCl_4] \sim 0.5$[chain end]. Mechanistic studies indicated that the initiator is fully ionized at this ratio, giving rise to $SnCl_6^{2-}$ counteranions. The polymer chain end, however, is not fully ionized, and propagation involves $SnCl_5^-$ counteranions.

Introduction

The living polymerization of αMeSt was first demonstrated with the $CH_3CH(OCH_2CH_2Cl)Cl/SnBr_4$ initiating system in CH_2Cl_2 at −78 °C.[1] We recently reported the living polymerization of αMeSt in conjunction with $TiCl_n(OR)_{4-n}$ (R = ethyl, isopropyl, butyl) in hexane/methyl chloride (Hex/MeCl) 60/40 v/v at −80 °C.[2] The living sequential block copolymerization of isobutylene (IB) with αMeSt was also reported by us using a general scheme developed for the synthesis of block copolymers by living carbocationic sequential block copolymerization when the second monomer is more reactive than the first one. It involves capping with a highly reactive but nonhomopolymerizable monomer such as 1,1-diphenylethylene (DPE), followed by tailoring the Lewis acidity to the reactivity of the second monomer. Accordingly, PIB-*b*-PαMeSt diblock[2] and PαMeSt-*b*-PIB-*b*-PαMeSt triblock[3] copolymers were prepared by first polymerizing IB followed by capping with DPE using $TiCl_4$ and then replacing $TiCl_4$ with $SnBr_4$, a weaker Lewis acid, before the addition of αMeSt.

While in CH_2Cl_2 fast polymerization of αMeSt occurs,[1] using nonpolar solvents or solvent mixtures in conjunction with $SnBr_4$, the polymerization is rather slow.[1−3] In the sequential block copolymerization of αMeSt with IB, a Hex/MeCl 60/40 v/v solvent mixture and low temperature (−80 °C) were used to ensure solubility of both polymer segments and to avoid inter- and intramolecular alkylation in the polymerization of αMeSt. Under these conditions however complete conversion was only reached in ∼20 h. The polymerization rate may be increased by increasing solvent polarity, raising the temperature, and by using a stronger Lewis acid. When selecting a Lewis acid, it is important however to consider the reactivity of the monomer. A Lewis acid that is too strong may induce a rapid, but uncontrolled polymerization and possible side reactions (chain transfer etc.) may prevent control of molecular weight and molecular weight distribution. For example, $TiCl_4$ induces an instantaneous polymerization of αMeSt; however, the products exhibited indanyl end groups, uncontrolled molecular weights, and a broad molecular weight distribution.[2] In contrast, the use of a milder $TiCl_n(OR)_{4-n}$ resulted in controlled molecular weights, narrow molecular weight distribution and prevented intra- and intermolecular alkylation.[2] Similarly, in CH_2Cl_2 at −78 °C living polymerization was reported with $SnBr_4$; $SnCl_4$ however induced a rapid polymerization that resulted in lower than expected molecular weights and broad molecular weight distributions.[1]

Results of studies on the effects of solvent polarity, temperature, and Lewis acidity on the polymerization rate and the livingness of αMeSt are reported in this paper.

Experimental Section

Materials and Procedures. Tin tetrachloride (99%, Aldrich) and tin tetrabromide (1 M solution in CH_2Cl_2) were used as received. Cumyl chloride was prepared by the hydrochlorination of α-methylstyrene in CH_2Cl_2. ^1H NMR (ppm) 2.10 (s, 6H), 7.25−7.45 (m, 3H), 7.60−7.70 (m, 2H).

Decapping experiments were carried out on preformed PIB−DPE−OMe polymers of $M_n = 1300$ in Hex/MeCl 60/40 v/v at −80 °C. The preformed polymers were mixed with $SnCl_4$ at different ratios $[SnCl_4]/[\text{chain ends}] = 0.25$, 0.5, 1.0, and 2.0. Upon mixing, a yellow to orange color developed that persisted during the reaction time and disappeared upon quenching with precooled methanol after 30, 60, and 180 min. The polymers were purified and analyzed by ^1H NMR. All other materials have been described.[3,4]

Conductivity measurements were carried out using a YSI Model 35 conductance meter equipped with a cell of 0.1 cm^{-1} cell constant and a BBC Goertz Metrawatt SE 120 plotter. Since the total volume of the 0.005 M solutions titrated with $SnCl_4$ (0.54 M in hexane) or $SnBr_4$ (1 M in CH_2Cl_2) was relatively large (900 mL), dilution and solvent polarity change upon addition of the tin halides was considered minimal. After the addition of each $SnCl_4$ or $SnBr_4$ increment, equilibrium (i.e., constant) conductivity was reached before the addition of the next increment.

Polymerization. αMeSt polymerization experiments were carried out in 75 mL test tubes. Scheme 1 describes the polymerizations. $TiCl_4$ solution (1/3 v/v) in hexane was added to a Hex/MeCl mixture containing 2,4,4-trimethyl-2-chloropentane (TMPCl) and the proton trap 2,6-di-*tert*-butylpyridine (DTBP) precooled to −80 °C, followed by the addition of DPE ([DPE]/[TMPCl] = 2). When capping was complete,[5] $Ti(OR)_4$ was added to deactivate $TiCl_4$, followed by the addition of

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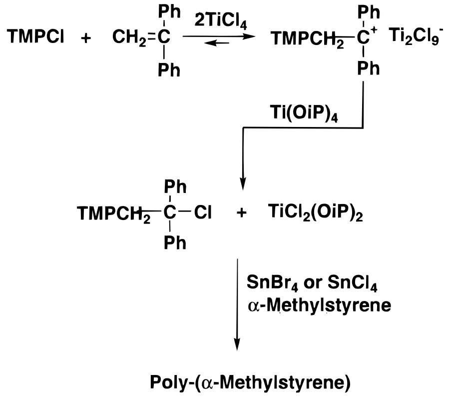
[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

S0024-9297(96)00168-4 CCC: $12.00

Scheme 1



$SnBr_4$.[2] The αMeSt solution in Hex/MeCl was added last. At predetermined time intervals, the polymerizations were terminated by adding prechilled methanol. The polymers were purified by dissolution−precipitation in dichloromethane/methanol and dried under vacuum prior to GPC measurements.

When the polymerization was carried out at −60 °C, after complete capping was achieved at −80 °C, the reaction mixture was warmed to −60 °C in 5 min. $Ti(OR)_4$, $SnBr_4$, and αMeSt were then added as above.

In the polymerization of αMeSt using $SnCl_4$ as coinitiator, the capping reaction with DPE was carried out in a 500 mL three-neck round-bottom flask equipped with an overhead mechanical stirrer. It was followed by the addition of $Ti(OIp)_4$ in slight stoichiometric excess over $TiCl_4$, and $SnCl_4$ was introduced to regenerate the active species. Then appropriate amounts of reaction mixture were delivered to 75 mL culture tubes followed by the addition of αMeSt. The total volume in the culture tube was 25 mL.

Using $n\mathrm{Bu_4NCl}$ to deactivate $TiCl_4$, the capping reaction was carried out in a Hex/MeCl 60/40 v/v solution (total volume 30 mL) containing 0.1487 g of TMPCl, 0.35 g of DPE, and 0.36 g of DTBP with $[TiCl_4]$:[TMPCl] = 3 at −80 °C for 2 h. After 2 h, 0.38 g of $n\mathrm{Bu_4NCl}$ ($[n\mathrm{Bu_4NCl}]:[TiCl_4] = 0.6$) was added followed by the addition of 235 mL precooled hexane to precipitate the salt. The $[n\mathrm{Bu_4NCl}]:[TiCl_4] = 0.6$ ratio was used to ensure complete removal of $TiCl_4$ (precipitated either as $n\mathrm{Bu_4N^+TiCl_5^-}$ or $n\mathrm{Bu_4N^+Ti_2Cl_9^-}$). The precipitate was filtered, MeCl was added to adjust the Hex/MeCl ratio to 60/40 v/v, and $SnCl_4$ was added to regenerate the active species. The reaction mixture was colorless prior to the addition of $SnCl_4$, and it turned light orange after the addition of $SnCl_4$. Then appropriate amounts of reaction mixtures were delivered to 75 mL culture tubes followed by the addition of αMeSt. Interestingly, after the addition of αMeSt, the polymerization solution remained colorless when high I_{eff}s were obtained, while a slight orange color was observed when I_{eff}s were low. Conversions were determined gravimetrically.

Characterization. Molecular weights were measured using a Waters HPLC system equipped with a Model 510 HPLC pump, a Model 410 differential refractometer, a Model 486 tunable UV−vis detector, an on-line multiangle laser light scattering detector (MiniDawn, Wyatt Technology Inc.), a Model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The flow rate of the mobile phase (THF) was 1.0 mL/min. The absolute molecular weights and molecular weight distributions were determined using the ASTRette software. Refractive index increment (d*n*/d*c*) of PαMeSt was measured by a laser interferometer (Optilab, Wyatt Technology Inc.).

Results and Discussion

1. Effect of Solvent Polarity. Three different Hex/MeCl mixtures (60/40, 50/50, 40/60 v/v) were utilized to investigate the effect of solvent polarity on the living polymerization of αMeSt using $SnBr_4$ at −80 °C. According to the first-order plots (Figure 1), the polymerization rate increases with increasing polarity. For example, ∼100% conversion was reached in 6 h with Hex/MeCl 40/60 v/v, while only 80 and 65% were obtained with the Hex/MeCl 50/50 v/v and Hex/MeCl 60/40 v/v solvent mixtures, respectively. These results are in line with a general observation in cationic polymerization that polymerization rates increase with increasing solvent polarity. Polar solvents solvate the active species better, yielding a higher concentration of cations, thus increasing the propagation rate.

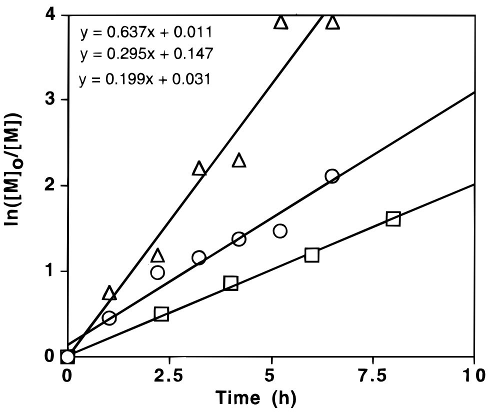


Figure 1. $\ln([M]_0/[M])$ vs time plot in the polymerization of αMeSt in different solvents with $TMPCl/TiCl_4/DPE/Ti(OIp)_4/SnBr_4$/−80 °C system. Hex/MeCl: (□) 60/40; (○) 50/50; (△) 40/60. $[TiCl_4] = 0.0364$ M, [DTBP] = 0.004 M, [TMPCl] = 0.002 M, [DPE]/[TMPCl] = 2, $[SnBr_4] = 0.04$ M.

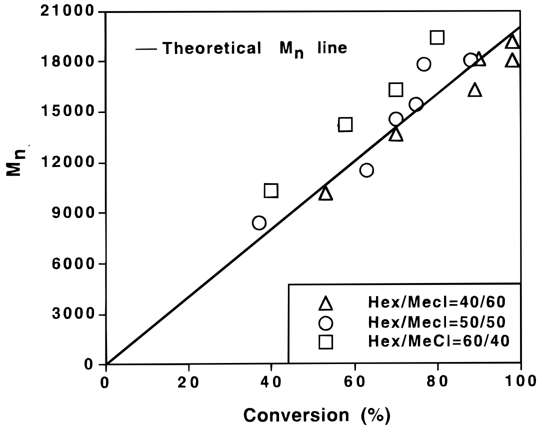


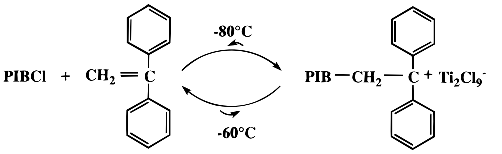
Figure 2. M_n vs conversion in the polymerization of αMeSt with the $TMPCl/TiCl_4/DPE/Ti(OIp)_4/SnBr_4$/−80 °C system. $[TiCl_4] = 0.0364$ M, [DTBP] = 0.004 M, [TMPCl] = 0.002 M, [DPE]/[TMPCl] = 2, $[SnBr_4] = 0.04$ M.

The M_n versus conversion plots for all three solvent systems (Figure 2) are linear starting at the origin, which together with the linear first-order plots indicate that the polymerization is living in all three solvent systems. The obtained M_ns are close to the theoretical M_n, demonstrating close to 100% initiator efficiency (I_{eff}).

Although the use of a higher polarity Hex/MeCl 40/60 v/v solvent mixture resulted in faster αMeSt polymerization, in the triblock synthesis, the solvent employed must also dissolve both PIB and PαMeSt segments. It was found that high molecular weight PIB (∼80 000 g/mole, typical in the triblock synthesis) is insoluble in Hex/MeCl 40/60 v/v at −80 °C; therefore this solvent mixture is not appropriate for triblock synthesis.

2. Effect of Temperature. To examine the effect of temperature on αMeSt polymerization the polymerization was also carried out at −60 °C. After the

Scheme 2



completion of the capping reaction at −80 °C, the temperature was increased to −60°C, and $Ti(OIp)_4$, $SnBr_4$, and αMeSt were then added in this order.

Similarly to the results obtained at −80 °C, higher solvent polarity resulted in higher polymerization rates. At constant solvent composition, the rates were higher at the higher temperature; for instance, 55% conversion was reached in 2 h while the conversion was only 40% at −80 °C using the Hex/MeCl 60/40 v/v solvent mixture.

The M_n vs conversion plots (not shown) were linear and narrow molecular weight distributions ($M_w/M_n < 1.1$) were obtained; however, the obtained M_ns were higher than the theoretical M_ns, indicating about 70% I_{eff}s. Since it pointed toward decomposition of the poly(isobutenyldiphenylcarbenium) ions at −60°C, the DPE capping was studied using low molecular weight PIB ($M_n \sim 2000$ g/mol). The polymerization of IB was carried out at −80 °C, and after complete IB conversion was reached (1 h polymerization time), DPE was added. After capping (1 h), a sample was taken and the temperature was raised to −60 °C during 5 min. After 30 min, the reaction mixture was quenched by ammonical methanol. The capping efficiency was examined by ^{1}H NMR spectroscopy. The complete disappearance of the peaks at 1.7 ($-CH_2C(C\mathbf{H}_3)_2Cl$) and 1.9 ppm ($-C\mathbf{H}_2C(CH_3)_2Cl$) and the appearance of new peaks at 2.5 ($-C\mathbf{H}_2C(Ph)_2OCH_3$) and 3.0 ppm ($-CH_2C(Ph)_2OC\mathbf{H}_3$) verified that the sample quenched at −80 °C was completely capped with DPE. However, the sample quenched at −60 °C carried ~80 mol % $CH_2C(CH_3)_2Cl$ and ~20 mol % DPE capped chain ends. This was the first indication that the capping reaction is reversible and that the equilibrium constant of capping is highly dependent on the temperature (Scheme 2).

Since the original observation, a systematic investigation has been carried out with DPE, substituted DPEs, and different Lewis acids at varying temperature and solvent polarity.[6] Furthermore it has been shown[6] that decapping is relatively slow which explains that the I_{eff} (~70%) is higher than the theoretical 20%, the percentage of capped chain ends at equilibrium.

Importantly, decapping was absent at −60 °C in 30 min when $Ti(OIp)_4$ was added before raising the temperature. With the deactivation of $TiCl_4$ at −80°C, chain end ionization and therefore decapping are suppressed (Scheme 2). Thus, the polymerization of αMeSt was repeated at −60 °C with the TMPCl/$TiCl_4$/DPE/$Ti(OIp)_4$/$SnBr_4$ system. However, the temperature was maintained at −80 °C until αMeSt was added, and then it was increased to −60 °C in a 5 min period.

The PαMeSt obtained exhibited close to theoretical M_ns and narrow molecular weight distributions. The linear M_n versus conversion (Figure 3) and first-order plots (Figure 4) indicates that the polymerization of αMeSt is living.

The apparent rate constants, $k_{p,a}$s ($=k_p[P^+]/[I]_0$), of αMeSt polymerization at −80 and −60 °C were calculated from the first-order plots and are summarized in Table 1. $k_{p,a}$ increases with increasing solvent polarity and temperature. The rate constant more than doubled by increasing solvent polarity from Hex/MeCl 60/40 to Hex/MeCl 40/60. A similar ca. twofold increase of $k_{p,a}$ was also observed when the temperature was raised from −80 to −60 °C.

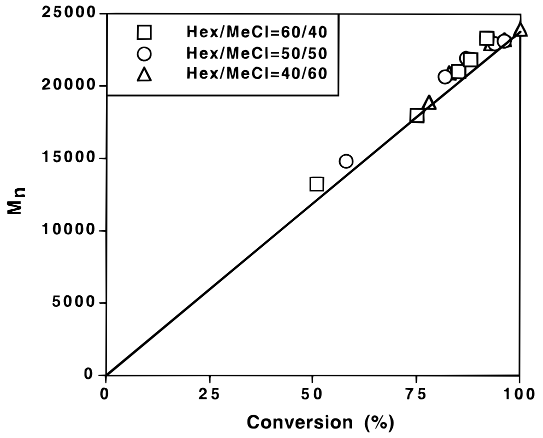


Figure 3. M_n vs conversion in the polymerization of αMeSt with TMPCl/$TiCl_4$/DPE/$Ti(OIp)_4$/$SnBr_4$/−60 °C system. The temperature was increased from −80 to −60 °C upon the addition of αMeSt in a 5 min period. $[TiCl_4] = 0.0364$ M, [DTBP] = 0.004 M, [TMPCl] = 0.002 M, [DPE]/[TMPCl] = 2, $[SnBr_4] = 0.04$ M.

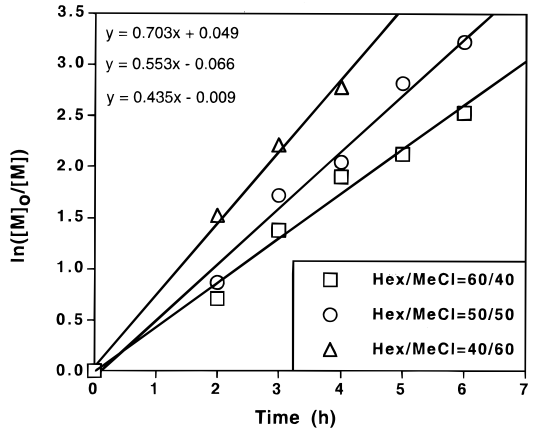


Figure 4. First-order plot in the polymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/$Ti(OIp)_4$/$SnBr_4$/−60 °C system. The temperature was increased from −80 to −60 °C upon the addition of αMeSt in a 5 min period. $[TiCl_4] = 0.0364$ M, [DTBP] = 0.004 M, [TMPCl] = 0.002 M, [DPE]/[TMPCl] = 2, $[SnBr_4] = 0.04$ M.

Table 1. Apparent Rate Constants (L/mol·s) of αMeSt Polymerization in Different Solvents at Different Temperatures Using $SnBr_4$

Hex/MeCl	$k_{p,a-80°C}$	$k_{p,a-60°C}{}^a$	$k_{p,a-60°C}/k_{p,a-80°C}$
40/60	0.088	0.128	1.5
50/50	0.041	0.098	2.4
60/40	0.028	0.067	2.4

[a] Average of two series of experiments.

3. $SnCl_4$ Coinitiation. We recently used a new concept in the living polymerization of isobutyl vinyl ether, accomplished using $TiCl_4$ coinitiator when $[TiCl_4]$ < [chain end]. It was proposed that under these conditions the gegen ion is $TiCl_5^-$, a much stronger nucleophile compared to the $Ti_2Cl_9^-$ dimeric gegenion, which dominates at $[TiCl_4]_{free}$/[chain end] ≥ 2. In general, a Friedel−Crafts acid may be a weak Lewis acid when the monomeric counteranions arise, but a strong acid when it forms dimeric gegenions. Accordingly, the coinitiator/initiator molar ratio is very im-

Table 2. Results of αMeSt Polymerization Using Low Relative Concentrations of SnCl$_4$ As Coinitiator[a]

no.	SnCl$_4$/TMPCl	conv (%)	M_n	MWD	I_{eff} (%)
1	0.2	0			
2	0.5	0			
3	1.0	0			
4	2.0	100	26100	1.07	79
5	3.0	100	32700	1.09	66
6	4.0	100	43600	1.09	48

[a] [TiCl$_4$] = 0.036 M, [DTBP] = 0.004 M, [TMPCl] = 0.002 M, [DPE]/[TMPCl] = 2.0, [Ti(OIp)$_4$]/[TiCl$_4$] = 1.07, polymerization time 30 min.

portant and may determine the outcome of the polymerization.

Thus, although SnCl$_4$ reportedly leads to nonliving behavior in CH$_2$Cl$_2$ at −78 °C,[1] we investigated the polymerization of αMeSt using SnCl$_4$ in Hex/MeCl 60/40 v/v at −80 °C system, varying the SnCl$_4$/TMP-CH$_2$C(Ph)$_2$Cl molar ratio from 0.2 to 4.0. No polymer formed in 30 min with SnCl$_4$/TMP-CH$_2$C(Ph)$_2$Cl < 1.0. With SnCl$_4$/TMP-CH$_2$C(Ph)$_2$Cl ≥ 2, the polymerizations were rapid, and 100% conversions were reached in 30 min. Table 2 lists the monomer conversions, the obtained M_ns, and the MWDs. The obtained M_ns are higher than the theoretical M_n ($M_{n,theo}$ = 20650 g/mol), but interestingly the MWDs are narrow ($M_w/M_n < 1.1$). The M_ns decreased and approached the theoretical M_n with decreasing SnCl$_4$/TMPCl ratio. The highest I_{eff} (79%) was obtained at SnCl$_4$/TMPCl = 2. These results suggested living polymerization with slow initiation and that 100% initiator efficiency might be obtained by further decreasing the SnCl$_4$/TMPCl ratio.

In the living polymerization of αMeSt initiated by the TMPCl/TiCl$_4$/DPE/Ti(OIp)$_4$/SnBr$_4$/−80 °C system, ~7 mol % excess Ti(OIp)$_4$ over TiCl$_4$ was used to deactivate TiCl$_4$. Since high concentrations of SnBr$_4$ were used, the excess Ti(OIp)$_4$ was found to have a negligible effect on the living polymerization with this specific system. However, in the present experiments using low concentrations of SnCl$_4$ as coinitiator, it was found that the excess Ti(OIp)$_4$ had a profound effect on the conversion and the molecular weight of PαMeSt. The excess Ti(OIp)$_4$ most probably reacts with SnCl$_4$, and the resulting decrease of SnCl$_4$ concentration will be reflected in the lowered polymerization rate.

To examine the effect of excess Ti(OIp)$_4$ on the polymerization of αMeSt, experiments were carried out using Ti(OIp)$_4$/TiCl$_4$ = 1.02 and 1.16, varying the SnCl$_4$/TMPCl ratio from 1.0 to 4.0. With Ti(OIp)$_4$/TiCl$_4$ = 1.16, no polymerization was observed at SnCl$_4$/TMPCl ≤ 1.8. At SnCl$_4$/TMPCl = 2.1, 90% conversion was obtained in 30 min and 100% in 60 min. Conversions of 100% were achieved in 30 min when the SnCl$_4$/TMPCl ratio was above 2.1.

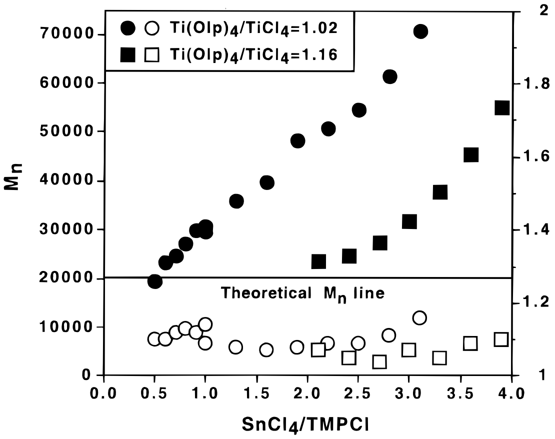
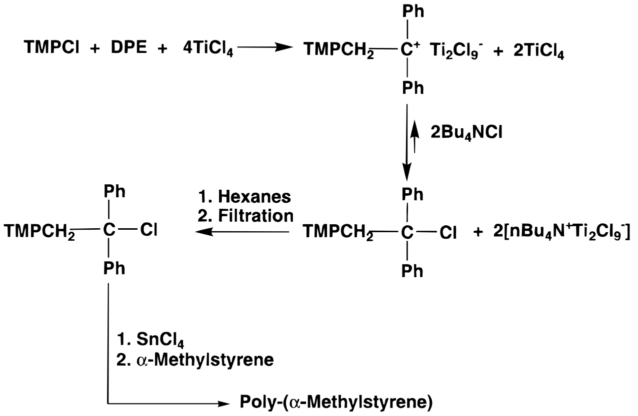


Figure 5. M_n (filled symbols) and MWD (open symbols) vs SnCl$_4$/TMPCl in the polymerization of αMeSt at −80 °C. [TiCl$_4$] = 0.036M, [DTBP] = 0.004M, [TMPCl] = 0.002M, [DPE]/[TMPCl] = 2.0, polymerization time 30 min for [Ti(OIp)$_4$]/[TiCl$_4$] = 1.02, 30 min for SnCl$_4$/TMPCl = 0.9 and 1.0, 60 min for SnCl$_4$/TMPCl = 0.7 and 0.8, and 90 min for SnCl$_4$/TMPCl = 0.5 and 0.6. The theoretical M_n line is based on 100% monomer conversion.

Scheme 3



With Ti(OIp)$_4$/TiCl$_4$ = 1.02, i.e., with very small excess Ti(OIp)$_4$, 100% conversions were obtained in 30 min at SnCl$_4$/TMPCl ≥ 1.0. Interestingly, αMeSt smoothly polymerized even at SnCl$_4$/TMPCl < 1.0. Conversions of 100% were reached in 60 min for SnCl$_4$/TMPCl ≥ 0.7 and 90 min for SnCl$_4$/TMPCl=0.6. However, only 90% conversion was obtained in 90 min for SnCl$_4$/TMPCl = 0.5. No polymerization was observed with SnCl$_4$/TMPCl ≤ 0.4. Figure 5 shows the obtained M_ns and the M_w/M_ns as a function of SnCl$_4$/TMPCl ratio. The obtained M_ns approach the theoretical M_n with decreasing SnCl$_4$ concentration. As high as 96% I_{eff} was achieved at SnCl$_4$/TMPCl = 0.5. Interestingly, narrow MWDs were obtained in all cases, suggesting fast exchange between living and dormant centers. These results confirmed that the polymerization is influenced by the excess Ti(OIp)$_4$.

To completely eliminate the effect of Ti(OIp)$_4$, the polymerization was also carried out in a Ti(OIp)$_4$-free system. TMPCl was capped with DPE in the presence of TiCl$_4$, which was followed by the addition of nBu$_4$NCl to deactivate TiCl$_4$. The formed salt was precipitated in nonpolar solvent and was filtered out from the system (Scheme 3).

The polarity of the solutions was readjusted to Hex/MeCl 60/40 v/v, and the polymerizations were induced by the addition of SnCl$_4$ followed by αMeSt and were quenched after 2 h. (The complete removal of TiCl$_4$ was corroborated by the fact that polymerization was absent in the absence of SnCl$_4$.) Conversions of 100% were obtained when SnCl$_4$/TMPCl ≥ 0.5, while 81% was obtained at SnCl$_4$/TMPCl = 0.4. All polymers exhibited narrow MWDs ($M_w/M_n \leq 1.1$). No polymerization was observed at SnCl$_4$/TMPCl < 0.4.

Figure 6 shows a plot of the obtained M_ns and I_{eff}s versus SnCl$_4$/TMPCl. For comparison, results obtained with the Ti(OIp)$_4$/TiCl$_4$ = 1.02 ratio are also plotted. Reassuringly, the two plots are virtually identical. The obtained M_ns approached the theoretical M_ns with decreasing SnCl$_4$/TMPCl, and the highest I_{eff} = 94% was achieved at SnCl$_4$/TMPCl = 0.4. Interestingly, although slight tailing toward lower molecular weights is ob-

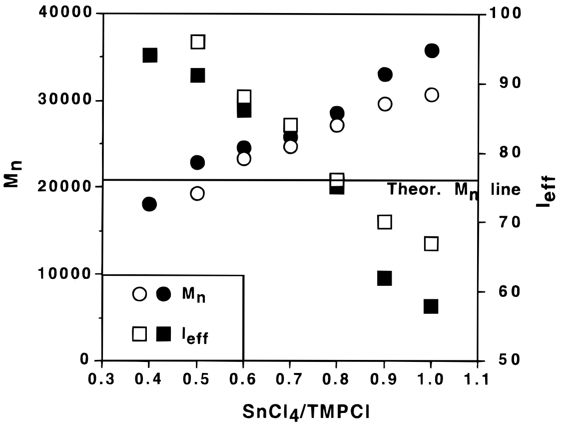


Figure 6. M_n and I_{eff} vs $SnCl_4$/TMPCl in the polymerization of αMeSt. [$TiCl_4$] = 0.036M, [DTBP] = 0.004M, [TMPCl] = 0.002M, [DPE]/[TMPCl] = 2.0, [Bu_4NCl]/[$TiCl_4$] = 0.6 (filled symbols), polymerization time 2 h. The open symbols represent data obtained with [Ti(OIp)$_4$]/[$TiCl_4$] = 1.02 (see Figure 5).

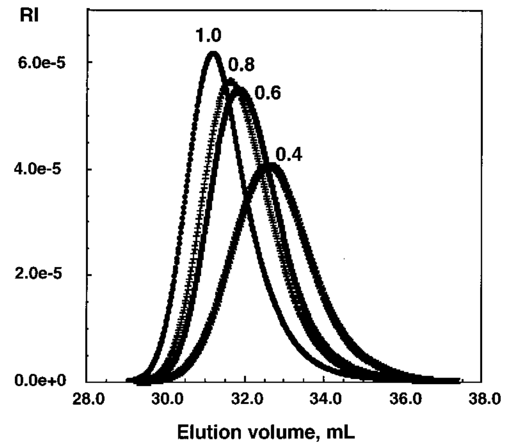


Figure 7. SEC RI traces of PαMeSt obtained at different $SnCl_4$/TMPCl ratios (noted on the figure). $SnCl_4$/TMPCl = 0.4 (M_n = 18000, M_w/M_n = 1.1), 0.6 (M_n = 24600, M_w/M_n = 1.1), 0.8 (M_n = 28200, M_w/M_n = 1.1), and 1.0 (M_n = 35700, M_w/M_n = 1.1).

served in the SEC of PαMeSt obtained at higher $SnCl_4$/TMPCl ratios (Figure 7), the M_w/M_ns remained virtually constant at ~1.1.

In conclusion, the living polymerization of αMeSt with ~100% I_{eff}s can be achieved at $SnCl_4$/TMPCl ~ 0.5.

4. Kinetic and Mechanistic Studies. The dependence of the molecular weight on [$SnCl_4$] implies that the reaction orders of initiation and propagation in [$SnCl_4$] are different. The use of $SnCl_4$ as Lewis acid in the polymerization of styrene in a polar solvent such as CH_2Cl_2 has been studied[7-9] and a first-order dependence of the polymerization rate on [$SnCl_4$] was also reported.[8,9] Since solvent polarity may affect the reaction order, we attempted to determine the reaction order in [$SnCl_4$] for our Hex/MeCl 60/40 v/v solvent system. Figure 8 shows the plot of ln([M]$_0$/[M]) versus time at three different concentrations of $SnCl_4$ (2.5 × 10^{-3}, 4.5 × 10^{-3}, and 8.5 × 10^{-3} M). Sampling was difficult using the highest concentration, since the polymerization was very fast and essentially complete in less than 2 min. This also limited the $SnCl_4$ concentration range where data could be collected. Although all polymers exhibited narrow MWDs (M_w/M_n ~ 1.1), the I_{eff}s were less than 100%, decreasing with increasing $SnCl_4$ concentration (~80, ~65, and ~46%, respectively, slightly increasing with increasing conversions). Experiments carried out with preformed PIB−DPE−OMe and excess $SnCl_4$ indicated that no decapping of the PIB chain ends occurred after 3 h of reaction. Thus the less than 100% I_{eff}s are due to the high rates of propagation relative to initiation. The slope of the first-order plot gives $k_p[P^+]$, where [P^+] is the concentration of the growing centers. It is more useful to calculate $k_p[P^+]/[P]$, where [P] is the total polymer concentration, and usually equals [I]$_0$ when I_{eff} is 100%. This allows the comparison of data obtained at different [I]$_0$. In our case, however, I_{eff}s are not 100%; therefore the plot of ln($k_p[P^+]/[P]$) vs ln[$SnCl_4$] must be used to determine the reaction order (Figure 9). From Figure 9, a slope of ~1.9 was obtained, which may indicate second-order [$SnCl_4$] dependence and thus the presence of $Sn_2Cl_9^-$ gegenions. However, the actual concentration of $SnCl_4$ especially at the lowest level is questionable and may be substantially lower than 2.5 × 10^{-3} M due to reaction with protic impurities (~0.001 M) in the system. If the lowest concentration point is neglected, a slope of 1 is obtained, suggesting a first-order dependence and the presence of $SnCl_5^-$ counterions.

Therefore to determine the nature of counterions and elucidate the observed differences in polymerization behavior between $SnBr_4$ and $SnCl_4$, we decided to carry out conductance studies. In these studies, three compounds, nBu$_4$NCl (shown in Figure 10), TMP-CH$_2$C(Ph)$_2$-Cl (shown in Figure 11), and cumyl chloride (shown in Figure 12), were titrated with $SnCl_4$ or $SnBr_4$, and the conductances of the solutions were followed.

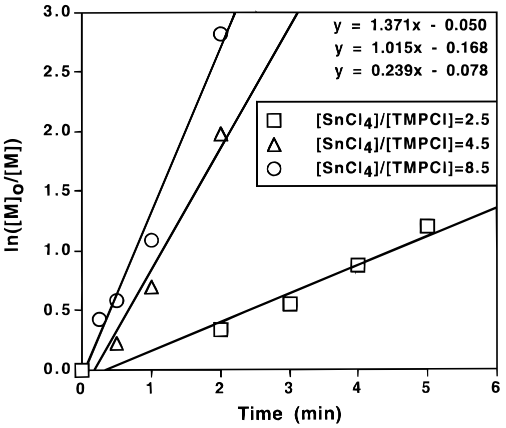


Figure 8. First-order plots in the polymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/Ti(OIp)$_4$/$SnCl_4$/−80 °C system. [$TiCl_4$] = 0.0364 M, [DTBP] = 0.004 M, [TMPCl] = 0.001 M, [DPE]/[TMPCl] = 2.

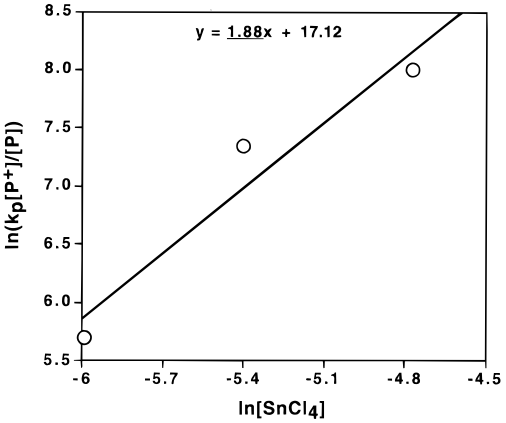


Figure 9. ln k_p vs −ln[$SnCl_4$] in the polymerization of αMeSt with the TMPCl/$TiCl_4$/DPE/Ti(OIp)$_4$/$SnCl_4$/−80 °C system. [$TiCl_4$] = 0.0364 M, [DTBP] = 0.004 M, [TMPCl] = 0.001 M, [DPE]/[TMPCl] = 2, [$SnCl_4$] = 0.04 M.

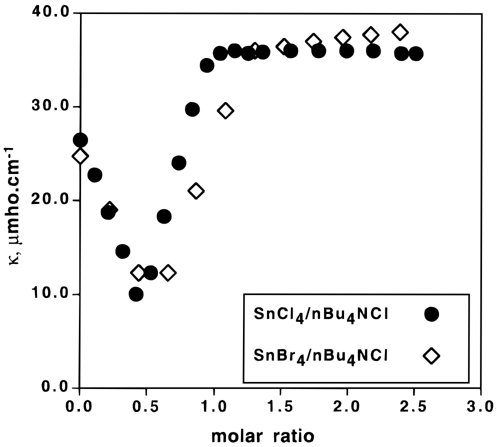


Figure 10. Conductometric titration of $n\mathrm{Bu_4NCl}$ with $\mathrm{SnCl_4}$ and $\mathrm{SnBr_4}$ in $\mathrm{CH_2Cl_2}$ at −80 °C. Total volume of titration 900 mL, [DTBP] = 4×10^{-3} M, [$n\mathrm{Bu_4NCl}$] = 5×10^{-3} M.

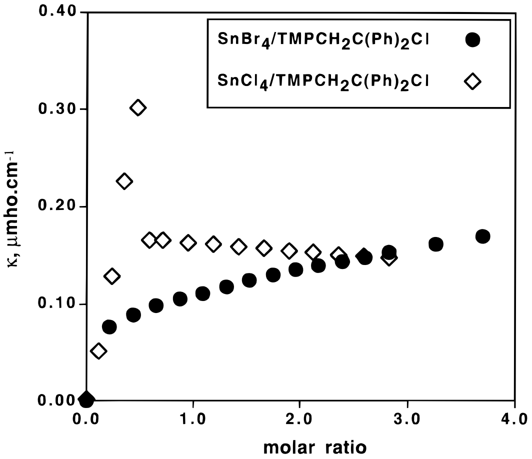


Figure 11. Conductometric titration of $\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$ with $\mathrm{SnCl_4}$ and $\mathrm{SnBr_4}$ in Hex/MeCl 60/40 v/v at −80 °C. Total volume of titration 900 mL, [DTBP] = 4×10^{-3} M, [$\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$] = 5×10^{-3} M. Conductivity = 0.22 μmho·cm^{-1} at $\mathrm{SnBr_4/TMP\text{-}CH_2C(Ph)_2Cl} = 8$.

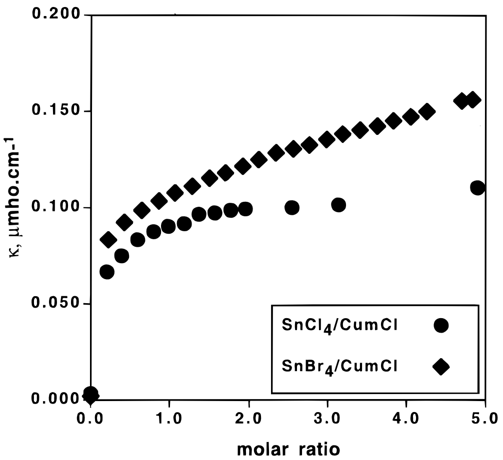


Figure 12. Conductometric titration of cumyl chloride with $\mathrm{SnCl_4}$ and $\mathrm{SnBr_4}$ in Hex/MeCl 60/40 v/v at −80 °C. Total volume of titration 900 mL, [DTBP] = 4×10^{-3} M, [cumyl chloride] = 5×10^{-3} M.

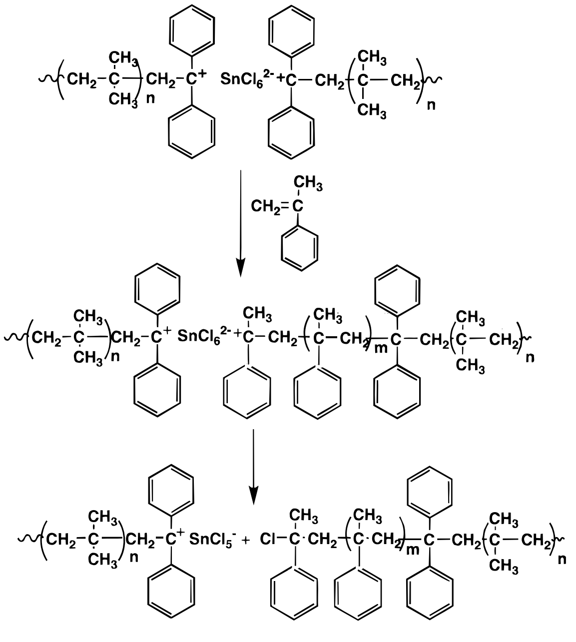
The reaction between $n\mathrm{Bu_4NCl}$ and $\mathrm{SnCl_4}$ has already been studied by ^{119}Sn NMR spectroscopy[10] in $\mathrm{CD_2Cl_2}$. At [$\mathrm{SnCl_4}$]/[$n\mathrm{Bu_4NCl}$] = 0.5, a sharp signal was found at −732 ppm, indicating the presence of $\mathrm{SnCl_6}^{2-}$ counteranions. Thus, the $\mathrm{SnCl_5}^-$ anion is still a strong enough Lewis acid to ionize $n\mathrm{Bu_4NCl}$. At 0.5 < [$\mathrm{SnCl_4}$]/[$n\mathrm{Bu_4NCl}$] < 1, broad signals indicating slow exchange between tin species arose. When [$\mathrm{SnCl_4}$]/[$n\mathrm{Bu_4NCl}$] > 1, one sharp average signal was observed, indicating the presence of $\mathrm{SnCl_5}^-$ counterions. Our conductance study is in line with these observations. The relatively high conductivity of the $n\mathrm{Bu_4NCl}$ solution in $\mathrm{CH_2Cl_2}$ decreases upon the addition of $\mathrm{SnCl_4}$ (Figure 10) and reaches a minimum at [$\mathrm{SnCl_4}$]/[$n\mathrm{Bu_4NCl}$] = 0.5. By increasing the $\mathrm{SnCl_4}$ concentration beyond this ratio, the conductivity increases and levels off at [$\mathrm{SnCl_4}$]/[$n\mathrm{Bu_4NCl}$] = 1, and remains unchanged upon further increase in [$\mathrm{SnCl_4}$]. Thus the salt $n\mathrm{Bu_4N^+SnCl_5^-}$ is fully ionized and $\mathrm{Sn_2Cl_9}^-$ counterions do not arise. The minimum conductivity at [$\mathrm{SnCl_4}$]/[$n\mathrm{Bu_4NCl}$] = 0.5 suggests that although ionization is complete, the dissociation constant of $(n\mathrm{Bu_4N^+})_2\mathrm{SnCl_6}^{2-}$ is much lower than that of $n\mathrm{Bu_4N^+SnCl_5^-}$, and if it is higher than that of $n\mathrm{Bu_4NCl}$ at all, it is not high enough to compensate for the decreased mobility of the anion compared to the much smaller $\mathrm{Cl^-}$. Almost identical plots were obtained using $\mathrm{SnBr_4}$, indicating that the $\mathrm{SnBr_4Cl^-}$ anion is also a strong enough Lewis acid to ionize $n\mathrm{Bu_4NCl}$. (The slight increase at [$\mathrm{SnBr_4}$]/[$n\mathrm{Bu_4NCl}$] > 1.5 may be due to a small increase in the solvent polarity upon addition of $\mathrm{SnCl_4}$ solution in $\mathrm{CH_2Cl_2}$.)

To determine the nature of counterions during initiation and propagation of αMeSt, $\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$, and cumyl chloride (mimicking the growing chain end) were titrated with $\mathrm{SnCl_4}$, and $\mathrm{SnBr_4}$, using the Hex/MeCl 60/40 v/v solvent system. Contrary to the high conductance obtained with $n\mathrm{Bu_4NCl}$ in $\mathrm{CH_2Cl_2}$, the $\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$ solution exhibited negligible conductance, indicating negligible ionization in the absence of tin halides. Upon addition of $\mathrm{SnCl_4}$, the conductivity sharply increased, reaching a maximum at [$\mathrm{SnCl_4}$]/[$\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$] = 0.5 (Figure 11). With further increase of the [$\mathrm{SnCl_4}$]/[$\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$] ratio, the conductivity decreased abruptly at [$\mathrm{SnCl_4}$]/[$\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$] = 0.6 and remained unchanged. Thus similarly to the [$\mathrm{SnCl_4}$]/[$n\mathrm{Bu_4NCl}$] system, at [$\mathrm{SnCl_4}$]/[$\mathrm{TMP\text{-}CH_2(Ph)_2Cl}$] ≤ 0.5, $\mathrm{SnCl_6}^{2-}$ anions, and at [$\mathrm{SnCl_4}$]/[$\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$] ≥ 1, $\mathrm{SnCl_5}^-$ anions, exist. The maximum conductivity at [$\mathrm{SnCl_4}$]/[$\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$] = 0.5 suggests that the dissociation constant of $\mathrm{TMP\text{-}CH_2C(Ph)_2{}^+SnCl_5{}^-}$ salt is at least comparable to the dissociation constant of $(\mathrm{TMP\text{-}CH_2C(Ph)_2{}^+})_2\mathrm{SnCl_6}^{2-}$, in which case the higher conductivity is the result of the increased mobility of the double-charged $\mathrm{SnCl_6}^{2-}$ anion compared to the similarly-sized, but single-charged $\mathrm{SnCl_5}^-$. Importantly, titration with $\mathrm{SnBr_4}$ resulted in a continuously increasing conductivity. Thus $\mathrm{SnBr_4Cl^-}$ is too weak to ionize $\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$, and $\mathrm{SnBr_4}$ is not strong enough to fully ionize $\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$ when a stoichiometric amount is used.

In the titration of CumCl with $\mathrm{SnCl_4}$ or $\mathrm{SnBr_4}$, increasing the concentration of tin halides resulted in a continuously increasing conductance (Figure 12), suggesting incomplete ionization and thus the presence of $\mathrm{SnCl_5}^-$ and $\mathrm{SnBr_4Cl^-}$ anions at all [CumCl]/[tin halide] ratios.

Based on the above results, the following conclusions can be reached. The polymerization of αMeSt is living and involves single-charged counteranions. However, initiation relative to propagation is slow with $\mathrm{SnCl_4}$, when [$\mathrm{SnCl_4}$]/[$\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$] ≥ 0.5. It is apparent from the conductivity studies that the reactivity of $\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$ is higher in conjunction with $\mathrm{SnBr_4}$ compared to $\mathrm{SnCl_4}$.[11] Since ionization of $\mathrm{TMP\text{-}CH_2C(Ph)_2Cl}$

Scheme 4



is complete at $[SnCl_4]/[TMP\text{-}CH_2C(Ph)_2Cl] = 0.5$, a further increase in $[SnCl_4]$ only increases the rate of αMeSt propagation. At $[SnCl_4]/[TMP\text{-}CH_2C(Ph)_2Cl] \leq 0.5$, the initiating species is $\{TMP\text{-}CH_2C(Ph)_2^+\}_2\text{-}SnCl_6^{2-}$. After cationation of αMeSt, however, termination by chlorination occurs since $SnCl_5^-$ is no longer strong enough to keep the $-C(CH_3)(Ph)Cl$ end ionized (Scheme 4). Thus, initiation must be essentially complete before propagation via the living−dormant (chloro) chain end equilibrium takes place.

Conclusion

The living polymerization of αMeSt was accomplished in conjunction with the $(CH_3)_3CCH_2C(CH_3)_2CH_2C(Ph)_2\text{-}Cl/SnBr_4$ or $SnCl_4$ initiating systems. Using $SnBr_4$ living polymerization is obtained in methyl chloride (MeCl)/hexane (Hex) 60/40 to 40/60 v/v at −80 or −60 °C. The polymers exhibited theoretical molecular weights and narrow molecular weight distributions ($M_w/M_n \sim 1.1$); however the polymerization rate is low. Living polymerization and high rates were obtained using the stronger Lewis acid $SnCl_4$ even at low concentrations. Theoretical molecular weight and therefore 100% initiator efficiency, however, was only achieved at $[SnCl_4] \sim 0.5$[chain end]. Mechanistic studies indicated that the initiator is fully ionized at this ratio, giving rise to $SnCl_6^{2-}$ counteranions. The polymer chain end, however, is not fully ionized and propagation involves $SnCl_5^-$ counteranions. Since the rate-determining step of initiation is cationation of the monomer (zero order in $[SnCl_4]$), further increase in $[SnCl_4]$ only increases the rate of propagation (first order in $[SnCl_4]$) and results in less than 100% I_{eff}.

Acknowledgment. This work was supported by the National Science Foundation (Grant DMR-9502777).

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MA960168Y