Living Cationic Polymerization of α-Methylstyrene Initiated with a Vinyl Ether–Hydrogen Chloride Adduct in Conjunction with Tin Tetrabromide[1]

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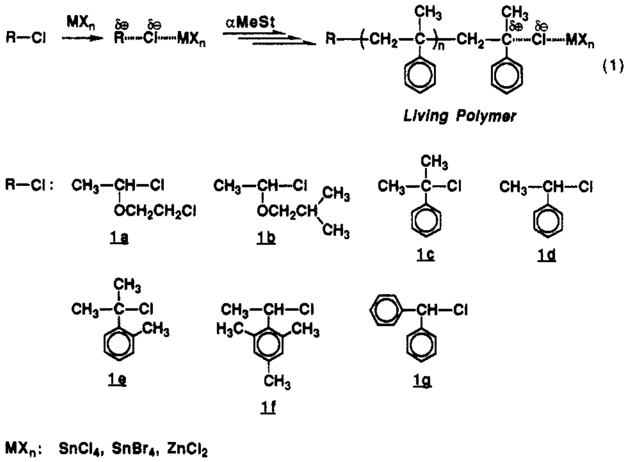
ABSTRACT: The first example of living cationic polymerization of α-methylstyrene was achieved with an initiating system that consists of the HCl–adduct of 2-chloroethyl vinyl ether [**1a**: $CH_3CH(OCH_2CH_2Cl)Cl$] and tin tetrabromide ($SnBr_4$) in CH_2Cl_2 at −78 °C. The number-average molecular weight of the polymers increased in direct proportion to monomer conversion up to 110 000 ($\overline{DP}_n$ = 1000) and agreed with the calculated values assuming that one polymer chain forms per **1a** molecule. Throughout the reaction, the molecular weight distribution of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n \sim 1.1$). The living nature of the polymerization was further demonstrated by monomer-addition experiments. ^{1}H NMR analysis of the polymers obtained with **1a**/$SnBr_4$ has shown that **1a** indeed serves as an initiator (the fragment of **1a** attached to the α-end) while $SnBr_4$ serves as an activator.

Introduction

In cationic polymerization, α-methylstyrene (αMeSt) is a reactive monomer that generates a stable propagating end of a tertiary benzyl cation. Despite this advantage, however, the α-methyl group in αMeSt also causes chain-transfer reactions by increasing the number of the acidic β-protons (from two in simple vinyl monomers $CH_2{=}CHR$ to five), thus rendering the control of polymer molecular weights difficult.[2] Furthermore, the steric hindrance imposed by the α-substituent leads to the ceiling temperature (T_c) of the monomer as low as room temperature; its polymerization should accordingly be carried out at low temperature, often at −78 °C, to obtain poly(αMeSt) of reasonably high molecular weights. In contrast to the well-known anionic counterparts,[3] living cationic polymerization of αMeSt has not yet been achieved. Previous papers describe the preparation of long-lived poly(αMeSt) by the so-called quasiliving technique[4,5] and, more recently, by the αMeSt polymerization with iodine in SO_2-based solvents,[6] but these examples fail to give well-controlled living polymers with narrow molecular weight distributions (MWD).

In contrast, there is a recent extensive development of living cationic polymerizations of vinyl ethers, isobutene, and styrene derivatives.[7] Most of the initiating systems for these living cationic processes consist of a protonic acid–monomer adduct (as an initiator) and a Lewis acid (as an activator or coinitiator). The development encouraged us to examine the possibility of the living cationic polymerization of αMeSt by a series of two-component initiating systems (R–Cl/MX_n), where the initiator (R–Cl) is the hydrogen chloride adduct of a vinyl or related compound, while the activator (MX_n) is a metal halide. In this paper, we report the first example of living cationic polymerization of αMeSt in methylene chloride (CH_2Cl_2) solvent at −78 °C. The best initiating system consists of the adduct (**1a**; initiator) of hydrogen chloride and 2-chloroethyl vinyl ether ($CH_2{=}CHOCH_2CH_2Cl$) coupled *with tin tetrabromide* ($SnBr_4$), a relatively mild Lewis acid.



Results and Discussion

1. Search of Initiating Systems. (a) Lewis Acid Activator. A series of polymerizations were carried out with the use of adduct **1a** coupled with various Lewis acids (MX_n). As shown in Figure 1, the overall polymerization rate apparently followed the order of the Lewis acidity of MX_n ($SnCl_4 > SnBr_4 > ZnCl_2$). Namely, tin tetrachloride induced an almost instantaneous rapid polymerization. In contrast, its zinc counterpart led to a slow reaction, which appeared to stop at a conversion around 30%, although the amount of the Lewis acid was 5 times as large as that of the other Lewis acids. Tin tetrabromide also induced a rapid and quantitative polymerization. More important, the system with $SnBr_4$ gave polymers with very narrow molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n \sim 1.1$), which suggests the occurrence of living polymerization. In contrast, the **1a**/$SnCl_4$ and **1a**/$ZnCl_2$ systems resulted in polymers with broad MWDs. These results suggest that $SnBr_4$ is suited for controlled polymerization of αMeSt.

(b) Initiator (R–Cl). To search for the best initiator for the living cationic polymerization of αMeSt, then, a variety of organic chlorides (**1a–g**), mostly HCl–vinyl monomer adducts, were employed in conjunction with $SnBr_4$. As shown in Figure 2, the polymerization rate depended on the structure of the initiator: **1a** > **1b** > **1c** > **1d**. For example, the styrene adduct (**1d**) resulted in a very slow polymerization that was completed in about 1 day (93% conversion in 21 h), whereas the reaction by the αMeSt counterpart (**1c**) was much faster but involved

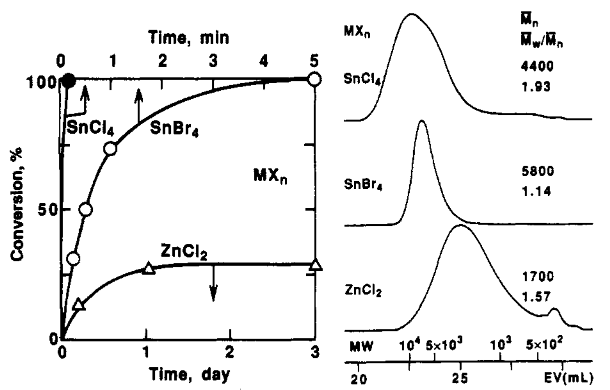


Figure 1. Polymerization of αMeSt by **1a**/MX_n in CH_2Cl_2 at −78 °C: $[M]_0 = 0.50$ M; $[\mathbf{1a}]_0 = 10$ mM; $[MX_n]_0 = 20$ (for $SnCl_4$ and $SnBr_4$) or 100 (only for $ZnCl_2$) mM. MX_n: $SnCl_4$ (●); $SnBr_4$ (○); $ZnCl_2$ (△).

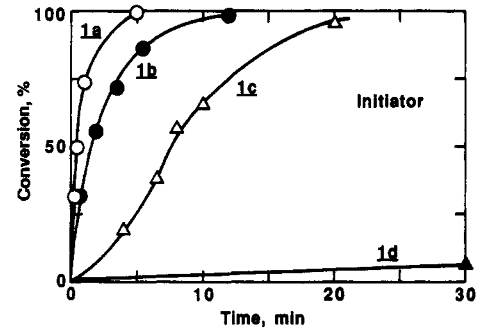


Figure 2. Polymerization of αMeSt by **1**/$SnBr_4$ in CH_2Cl_2 at −78 °C: $[M]_0 = 0.50$ M; $[\mathbf{1}]_0 = 10$ mM; $[SnBr_4]_0 = 20$ mM. Initiator: **1a** (○); **1b** (●); **1c** (△); **1d** (▲).

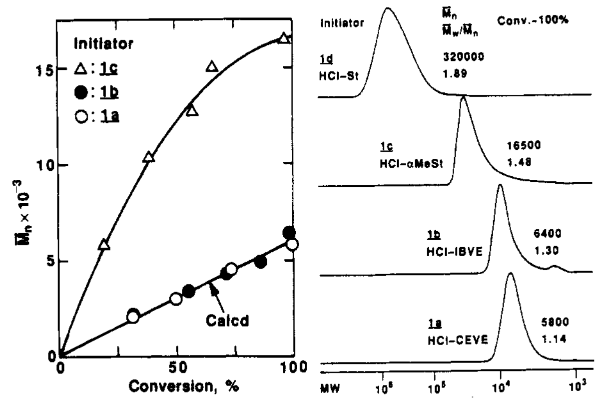


Figure 3. $\bar{M}_n$ and MWD curves of poly(αMeSt) obtained with **1**/$SnBr_4$ in CH_2Cl_2 at −78 °C: $[M]_0 = 0.50$ M; $[\mathbf{1}]_0 = 10$ mM; $[SnBr_4]_0 = 20$ mM. Initiator: **1a** (○); **1b** (●); **1c** (△). The line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1** molecule.

an initiation slower than the propagation, as indicated by the S-shaped conversion profile. In sharp contrast, the two vinyl ether adducts (**1a** and **1b**) led to even faster and smooth polymerizations of first order with respect to the monomer [straight $\log([M]_t/[M]_0)$ versus plots, where $[M]_t$ and $[M]_0$ are the monomer concentrations at time t and 0].

Figure 3 shows the number-average molecular weights ($\bar{M}_n$) and MWDs of the polymers thus obtained, where the $\bar{M}_n$ was measured by size-exclusion chromatography calibrated against standard poly(αMeSt) samples (see the Experimental Section). With **1a** as the initiator, $\bar{M}_n$ increased in direct proportion to monomer conversion and agreed with the calculated value assuming that one polymer chain forms per molecule of adduct **1a**. The MWDs of these polymers stayed very narrow ($\bar{M}_w/\bar{M}_n \sim 1.1$) throughout the reaction. These results showed that **1a**/$SnBr_4$ led to living cationic polymerization of αMeSt.

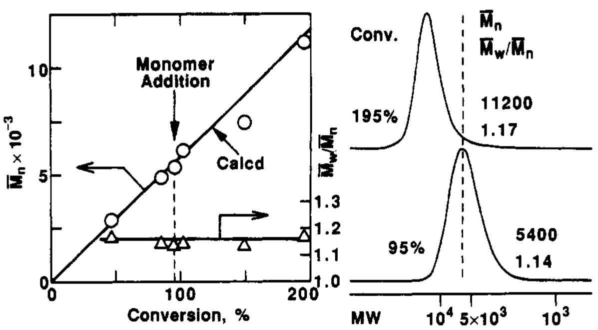


Figure 4. Monomer-addition experiments in the polymerization of αMeSt with **1a**/$SnBr_4$ in CH_2Cl_2 at −78 °C: $[M]_0 = [M]_{add} = 0.50$ M; $[\mathbf{1a}]_0 = 10$ mM; $[SnBr_4]_0 = 20$ mM. The line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1a** molecule.

The $\bar{M}_n$'s of the polymers obtained with **1b**/$SnBr_4$ were also directly proportional to monomer conversion and in good agreement with the calculated values. However, as shown in the size-exclusion chromatogram, this system resulted in a small fraction of the polymers with MW(peak) of ca. 2000, in addition to a main fraction of higher molecular weights with fairly narrow MWDs. The minor fraction was formed only during the early stage of the polymerization, and neither amount nor molecular weight changed with monomer conversion, which is in contrast to the main fraction. Therefore, long-lived polymers indeed form from **1b**/$SnBr_4$, but a side reaction occurs in the initiation step or during the early stage of the polymerization.

The $\bar{M}_n$'s of the polymers with **1c**/$SnBr_4$ increased with conversion, while they were higher than the calculated values. The MWDs were broader ($\bar{M}_w/\bar{M}_n \sim 1.3$) than those with **1a**/$SnBr_4$. The higher $\bar{M}_n$ and the S-shaped time–conversion curve (cf. Figure 2) indicate the slow initiation from **1c**. It seems somewhat strange that the reactivity of **1c** is lower than that of the polymer end, because they have nearly the same terminal structure [$CH_3C(CH_3)(Ph)–Cl$ vs $\sim\sim\sim CH_2C(CH_3)(Ph)–Cl$]. This point should be further investigated.

The HCl–styrene adduct (**1d**)/$SnBr_4$ system gave high molecular weight polymers ($\bar{M}_n = 320\,000$) with broad MWDs ($\bar{M}_w/\bar{M}_n \sim 2$). This shows that **1d** is apparently a less effective initiator for αMeSt polymerization, which is anticipated from the fact that styrene is less reactive than αMeSt in cationic polymerization.

Other chlorides (**1e–g**) also gave polymers in the presence of $SnBr_4$; however, the molecular weights are higher than the calculated values ($\bar{M}_n = 10\,000–45\,000$).

From these results, the HCl–CEVE adduct (**1a**) proved to be the best initiator for living cationic polymerization of αMeSt when coupled with $SnBr_4$. It is probably attributed to the fact that CEVE is slightly more reactive than αMeSt.[8]

2. Monomer-Addition Experiment. To investigate the living nature of the αMeSt polymerization with the **1a**/$SnBr_4$ initiating system, a fresh feed of αMeSt was added to the reaction mixture just before the initial charge of the monomer had been consumed (conversion > 95%). The added αMeSt feed was smoothly polymerized at nearly the same rate as in the first stage. As shown in Figure 4, even after the monomer addition, the polymer molecular weight further increased in direct proportion to monomer conversion, and the MWD stayed very narrow ($\bar{M}_w/\bar{M}_n \sim$

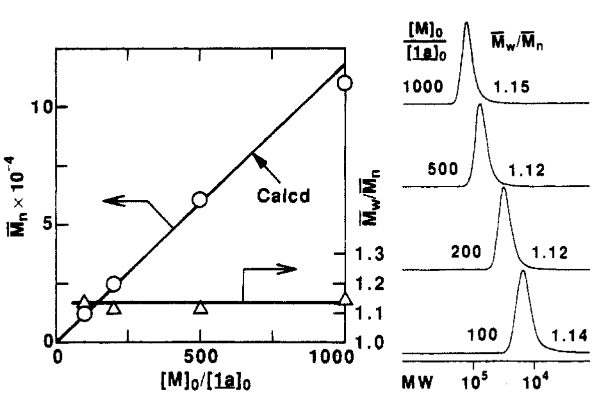


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(αMeSt) obtained with **1a**/SnBr$_4$ in CH$_2$Cl$_2$ at −78 °C with varying initial molar ratio of monomer to **1a**: $[M]_0$ = 0.50–2.5 M; $[\mathbf{1a}]_0$ = 2.5–5.0 mM; $[\mathrm{SnBr_4}]_0$ = 20 mM. The line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1a** molecule.

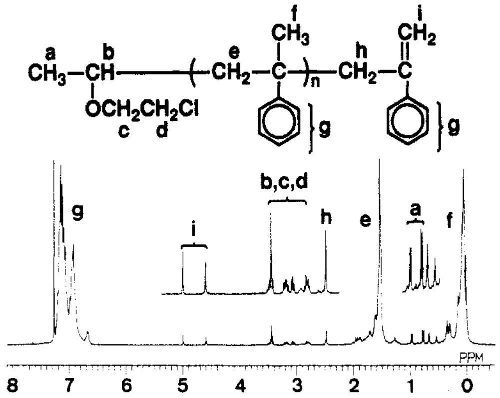


Figure 6. ^{1}H NMR spectrum of poly(αMeSt) obtained with **1a**/SnBr$_4$ in CH$_2$Cl$_2$ at −78 °C. $[M]_0$ = 0.50 M; $[\mathbf{1a}]_0$ = 10 mM; $[\mathrm{SnBr_4}]_0$ = 20 mM; conversion = 47%; $\bar{M}_n$(SEC) = 2900; $\bar{M}_w/\bar{M}_n$ = 1.17.

1.1). Thus, the living nature of the polymerization with **1a**/SnBr$_4$ was further demonstrated.

3. Polymer Molecular Weight Control. After establishing the living nature of the polymerization with **1a**/SnBr$_4$, another series of experiments were carried out, where the initial molar ratio of monomer to initiator was varied ($[M]_0/[\mathbf{1a}]_0$ = 100–1000) while the concentration of SnBr$_4$ was constant ($[\mathrm{SnBr_4}]_0$ = 20 mM). As shown in Figure 5, the polymer molecular weight at 100% conversion were directly proportional to the feed ratio ($[M]_0/[\mathbf{1a}]_0$) of αMeSt to **1a**. The $\bar{M}_n$ values were in good agreement with those calculated with the assumption that each molecule of the adduct **1a** forms one polymer chain.[9] In addition, the MWD of the polymers remained very narrow ($\bar{M}_w/\bar{M}_n \sim 1.1$) over the whole range of the $[M]_0/[\mathbf{1a}]_0$ ratio (or the degree of polymerization) up to 1000 ($\bar{M}_n \sim$ 110 000). Thus, the **1a**/SnBr$_4$ system effectively generates high molecular weight poly(αMeSt) with very narrow MWD, and **1a** serves as an initiator as shown in eq 1.

4. End-Group Analysis. The terminal structure of the polymers obtained with **1a**/SnBr$_4$ in CH$_2$Cl$_2$ was then analysed by ^{1}H NMR spectroscopy. Figure 6 shows the spectrum of a typical poly(αMeSt) sample.[10] Besides the signals due to the αMeSt repeat unit (e–g), there appeared characteristic signals a–d which are assignable to the initiator moiety. Signals of other α-ends, such as the α-methyl (δ 1.1) from the proton initiator, were absent. The two peaks for the terminal methyl (a) most likely result from stereoisomers.

The absorption i is attributed to the methylene proton of the olefin at the ω-end. The generation of the olefin is explained as below: The polymerization proceeds via the activation of the C–Cl bond of the polymer terminal by SnBr$_4$, and the chloride at the terminal remains unchanged without being substituted with methoxide even after the reaction was quenched with methanol, as in the living cationic polymerization of styrene with the CH$_3$CH(Ph)Cl/SnCl$_4$/nBu$_4$NCl system.[11] In some cases, the remaining chloride terminal is indeed detected in our poly(αMeSt) samples along with the olefin by ^{1}H NMR spectroscopy. Thus, the olefin is generated by the elimination of hydrogen chloride from the C–Cl terminal during the workup of the product (see the Experimental Section). In fact, the integrated peak intensity ratio of b–d at the α-end to i at the ω-end is 2.4, which agrees with the calculated value, 2.5. In view of the absence of the other α- and ω-end signals, the agreement indicates the attachment of a nearly one initiator fragment per chain.

These results demonstrate not only that the polymerization is living but also that it in fact proceeds as depicted in eq 1, where the hydrogen chloride–vinyl ether adduct (**1a**) serves as an initiator that generates the growing end and SnBr$_4$ activates the C–Cl bond of **1a** to trigger the living propagation of αMeSt.

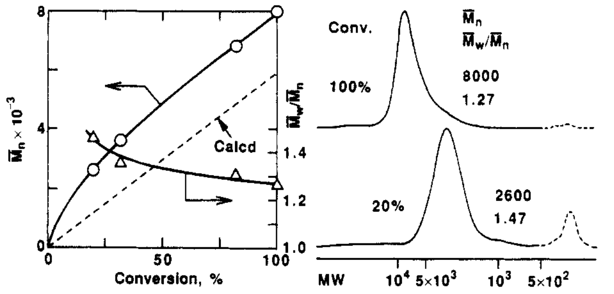
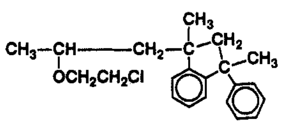


Figure 7. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(αMeSt) obtained with **1a**/SnBr$_4$ in toluene at −78 °C: $[M]_0$ = 0.50 M; $[\mathbf{1a}]_0$ = 10 mM; $[\mathrm{SnBr_4}]_0$ = 20 mM. The line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **1a** molecule.

5. Polymerization in Toluene. Polymerization with **1a**/SnBr$_4$ was also carried out in a less polar solvent, toluene, under conditions similar to those in CH$_2$Cl$_2$ ($[M]_0/[\mathbf{1a}]_0/[\mathrm{SnBr_4}]_0$ = 500/10/20 mM). The polymerization rate in toluene was much smaller than that in CH$_2$Cl$_2$ (time for 99%; 72 h vs 3 min).

Figure 7 plots the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values against conversion. The $\bar{M}_n$ values increased with conversion; however, they were consistently higher than the calculated values. The MWDs were slightly broader ($\bar{M}_w/\bar{M}_n \sim 1.3$) than those of the polymers obtained in CH$_2$Cl$_2$. Close inspection of size-exclusion chromatograms of the products showed that low molecular weight oligomers (dashed line in Figure 6) are formed during the early stage of the polymerization. The main fraction of the oligomers (peak molecular weight = 320) was separated by preparative size-exclusion chromatography. Characterization by ^{1}H NMR spectroscopy showed the compound to be **2**, having



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an indanyl ring that is formed after the dimerization of αMeSt with **1a**. A similar indane-capped structure was detected in the trimer fraction. This indicates that a part of the propagating end is dead at the early stage of polymerization in toluene. However, the terminal group of higher molecular weight polymers is the olefin, as in the (living) polymers obtained in CH_2Cl_2. These results suggest that, even in toluene, the polymers with high molecular weight (above tetramer) are long-lived but that the lower oligomers (dimer and trimer) are subject to side reactions like indane ring formation.

Concluding Remarks. Thus, the ideal living cationic polymerization of αMeSt is feasible with the **1a**/$SnBr_4$ initiating system in CH_2Cl_2 at −78 °C. It is worth noting that well-defined living poly(αMeSt) can be obtained with a type of vinyl ether adduct **1a** as an initiator, which obviously differs in structure, stability, and reactivity from the propagating end derived from αMeSt. Another feature of this polymerization is the use of $SnBr_4$, a metal halide whose Lewis acidity may be moderate, falling in between those of $SnCl_4$ and $ZnCl_2$.

Experimental Section

Materials. α-Methylstyrene (Wako Chemicals; purity >98%) was washed with 10% aqueous sodium hydroxide solution and then with water to be free from an inhibitor, dried overnight with anhydrous sodium sulfate, and distilled twice over calcium hydride before use. $SnBr_4$, $SnCl_4$, and $ZnCl_2$ (all Aldrich, 1.0 M solution in methylene chloride for $SnBr_4$ and $SnCl_4$ or in diethyl ether for $ZnCl_2$) were used as received. Methylene chloride (solvent) was washed with 10% aqueous sodium hydroxide and then with water, dried overnight with calcium chloride, and doubly distilled over phosphorus pentoxide and then over calcium hydride before use. *n*-Hexane (the solvent for initiator) and tetralin (the internal standard for gas chromatography) were purified by the usual methods and distilled over calcium hydride before use. 1-Phenylethyl chloride (**1d**: Wako Chemicals; purity >97%) was distilled twice under reduced pressure. Benzhydryl chloride (**1g**: Tokyo Kasei; purity >99%) was used as received.

Synthesis of HCl–Vinyl Monomer Adducts (1a–f). The HCl–CEVE adduct **1a** was synthesized by bubbling dry HCl gas through a solution of CEVE (in *n*-hexane; 1.00 M) at 0 °C. The gas was generated by dropping concentrated sulfuric acid into powdery sodium chloride and dried by passing it through a column packed with calcium chloride. After 30 min, the excess HCl in the reaction mixture was removed by bubbling dry nitrogen gas, and the clean and quantitative formation of adduct **1a** was confirmed by ^1H NMR spectroscopy. The solution was sealed into ampules under dry nitrogen and stored in a freezer. The concentration of **1a** was determined by titrating the chloride by the Volhard method; the observed value (1.06 M) further confirmed the quantitative formation of **1a** from CEVE. The other adducts, HCl–IBVE (**1b**), HCl–αMeSt (**1c**), HCl–*o*-methyl-αMeSt (**1e**), and HCl–2,4,6-trimethylstyrene (**1f**), were synthesized by similar methods.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example is given below. The reaction was initiated by adding, via dry syringes, solutions of HCl–CEVE **1a** (in *n*-hexane; 0.50 mL) and $SnBr_4$ (in methylene chloride; 0.50 mL) sequentially in this order into a mixture (4.0 mL) of α-methylstyrene (0.33 mL) and tetralin (0.08 mL) in CH_2Cl_2 at −78 °C and was quenched with prechilled methanol (2 mL). Monomer conversion was determined from its residual concentration of αMeSt measured by gas chromatography with tetralin as an internal standard.

The quenched reaction mixtures were diluted with toluene (20 mL), washed sequentially with 2% hydrochloric acid, aqueous 1% sodium hydroxide solution, and water to remove the tin-containing residues, evaporated to dryness under reduced pressure, and dried in vacuo overnight to give the product polymers.

Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography in chloroform on three or four polystyrene gel columns [Shodex K-802 + K-803 + K-804 (or + K-805)] that were connected to a Jasco Trirotar-V precision pump and a Jasco 830-RI refractive index detector; the four-column set was used specifically for high polymers ($\bar{M}_n > 2 \times 10^5$). The columns were calibrated against 10 standard poly(αMeSt) samples (Polymer Laboratories; $\bar{M}_n$ = 3500–773 000; $\bar{M}_w/\bar{M}_n$ = 1.03–1.08) as well as αMeSt dimer and trimer separately prepared in this work. The weight-average molecular weight ($\bar{M}_w$) was also measured by static laser light scattering in toluene at 25 °C on an Otsuka Electronics SLS-802 photometer (λ = 633 nm; four-point measurements; $c = 7.6 \times 10^{-4}$–3.1×10^{-3} g/mL). The refractive index increment (dn/dc) was measured in toluene at 25 °C on an Otsuka Electronics DRM-1020 double-beam differential refractometer [λ = 633 nm; four-point measurements; $c = 7.6 \times 10^{-4}$–3.1×10^{-3} g/mL; dn/dc = 0.11 mL/g for the sample obtained at $[M]_0/[\mathbf{1a}]_0 = 1000$ (Figure 5)]. ^1H NMR spectra of the polymers were recorded at 270 MHz in $CDCl_3$ at 25 °C on a JEOL GSX-270 spectrometer. Polymers and lower molecular weight oligomers (**2**) for ^1H NMR analysis were fractionated by preparative SEC (Shodex K-2002 and H-2001, respectively).

References and Notes

(1) This work was presented in part at: (a) The 41st Annual Meeting of the Society of Polymer Science, Yokohama, Japan, May 1992; Paper ID08. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Polym. Prepr. Jpn., Engl. Ed.* **1992**, *41* (1), E64. (b) The 4th SPSJ International Polymer Conference, the Society of Polymer Science, Yokohama, Japan, Nov–Dec 1992; Paper 30A27.

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(9) The $\bar{M}_w$ values were also measured by static light scattering (SLS). The value measured by SEC is in good agreement with that by SLS. For example, with the sample obtained at $[M]_0/[\mathbf{1a}]_0 = 1000$ (Figure 5), $\bar{M}_w$(SEC) = 126 000 and $\bar{M}_w$(SLS) = 123 000.

(10) The obtained polymers are syndiotactic rich (>90%).

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