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Living Cationic Polymerization of α-Methylstyrene. 2. Synthesis of Block and Random Copolymers with 2-Chloroethyl Vinyl Ether and End-Functionauzed Polymers†

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LIVING CATIONIC POLYMERIZATION OF α-METHYLSTYRENE. 2. SYNTHESIS OF BLOCK AND RANDOM COPOLYMERS WITH 2-CHLOROETHYL VINYL ETHER AND END-FUNCTIONALIZED POLYMERS†

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ABSTRACT

Both AB and BA block copolymers of α-methylstyrene (αMeSt) and 2-chloroethyl vinyl ether (CEVE) were synthesized by the sequential living cationic polymerization initiated with the HCl-CEVE adduct (**1a**)/$SnBr_4$ system in CH_2Cl_2 at −78°C. αMeSt-CEVE (AB) block copolymers with narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n \sim 1.15$) were obtained when αMeSt was polymerized first, followed by addition of CEVE to the resulting αMeSt living polymer solution. The reverse order of monomer addition, from CEVE to αMeSt, also led to a BA-type block copolymer. In the polymerization of a mixture of the two monomers, almost random copolymers were obtained. Living polymerizations of αMeSt were also induced with functional initiating systems, HCl-functionalized vinyl ether adducts (**1b**–**1d**)/$SnBr_4$, to give end-functionalized poly(αMeSt)s with a methacrylate, an acetate, or a phthalimide terminal.

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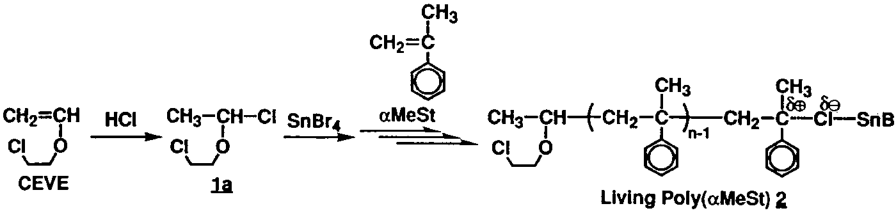
INTRODUCTION

In addition to those for vinyl ethers [1], isobutene [2], and others [3–5], we have recently found the living cationic polymerization of α-methylstyrene (αMeSt) with an initiating system that consists of the HCl-adduct of 2-chloroethyl vinyl ether (CEVE) [**1a**: $CH_3CH(OCH_2CH_2Cl)Cl$] and tin tetrabromide ($SnBr_4$) (Eq. 1) [6]. The polymer molecular weight is controlled by the ratio of the monomer to the initiator **1a**, and the molecular weight distribution (MWD) is very narrow ($\overline{M}_w/\overline{M}_n \sim 1.1$). Thus, well-defined living poly(αMeSt) can now be obtained cationically as well as anionically [7].



(1)

This finding prompted us to synthesize well-controlled block and end-functionalized polymers of αMeSt by our cationic processes. In this work we first examined block and random copolymerizations of αMeSt with CEVE, where poly(αMeSt) is a hard segment with a relatively high T_g (168°C) as hydrocarbon polymers [8] and the poly(vinyl ether) a soft segment with a low T_g (below 0°C) [9]. In the previously reported block copolymerizations of vinyl ethers and *p*-alkoxystyrenes with the HI/ZnI_2 initiating system [10, 11], it is known that the addition sequence of monomers greatly affects blocking efficiency. Namely, more reactive monomers, vinyl ethers, should be polymerized first for attaining a high blocking efficiency, probably due to the difference in the reactivity of the two monomers. However, the relationship between the blocking efficiency and the reactivity of monomers in the living cationic polymerization has not been clarified. The fact that the HCl-adduct of CEVE (**1a**) is an excellent initiator for the living cationic polymerization of αMeSt [6] suggests the possibility of the formation of block and random copolymers of αMeSt with CEVE.

Second, the HCl-adducts of functionalized vinyl ethers with methacrylate, acetate, and phthalimide were employed as the initiators for end-functionalized poly(αMeSt)s. In anionic polymerization it is difficult to introduce these polar functional groups into polymer chains because of side reactions imposed by them. Poly(vinyl ether)s and poly(*p*-alkoxystyrene)s with these functional groups have been obtained by living cationic polymerization [12–16]; however, poly(αMeSt)s with functional groups have not been obtained.

EXPERIMENTAL

Materials

α-Methylstyrene (Wako Chemicals, purity > 98%) and 2-chloroethyl vinyl ether (Nisso Maruzen Chemical, purity > 99%) were washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight with anhydrous sodium sulfate, and distilled twice over calcium hydride before use. 2-Vinyloxyethyl methacrylate (VEM), 2-acetoxyethyl vinyl ether (AcOVE), and 2-vinyloxyethyl phthalimide (VEP) were prepared by the reaction of CEVE with sodium methacrylate [17], sodium acetate [18], and potassium phthalimide [19], respectively. $SnBr_4$ (Aldrich, 1.0 M solution in methylene chloride) was 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), tetralin, and *n*-octane (the internal standards for gas chromatography) were purified by the usual methods and distilled over calcium hydride before use [1].

Synthesis of HCl-Vinyl Ether Adducts (*1a–1d*)

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 minutes 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-VEM (**1b**), HCl-AcOVE (**1c**), and HCl-VEP (**1d**), were synthesized by similar methods; specifically for **1d**, the solvent was CH_2Cl_2 because VEP is insoluble in *n*-hexane.

Polymerization Procedures

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the AB (αMeSt → CEVE) block copolymerization is given below. The reaction was initiated by adding, via dry syringes, solutions of **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 αMeSt (0.33 mL) and tetralin (0.08 mL) in CH_2Cl_2 at -78°C. A mixture of CEVE (0.51 mL) and *n*-octane (0.49 mL) was added to the preformed living poly(αMeSt) solution immediately after the end of the first-phase polymerization. After a certain period the polymerization was quenched with prechilled methanol (2 mL). Monomer conversions were determined from the concentrations of residual αMeSt and CEVE measured by gas chromatography with tetralin and *n*-octane, respectively, as internal standards.

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, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform on three polystyrene gel columns (Shodex K-802 + K-803 + K-804) that were connected to a Jasco Trirotar-V precision pump, a Jasco UV-970 UV/VIS detector set at 256 nm, and a Jasco 830-RI refractive index detector. The columns were calibrated against eight standard poly(αMeSt) samples (Polymer Laboratories, $\overline{M}_n$ = 3,500–300,000, $\overline{M}_w/\overline{M}_n$ = 1.03–1.08) as well as αMeSt trimer, dimer, and monomer. The columns were also calibrated against 10 standard polystyrene samples ($\overline{M}_n$ = 800–300,000, $\overline{M}_w/\overline{M}_n$ = 1.03–1.10) as well as styrene oligomers (tetramer, trimer, and dimer) and monomer. The former calibration curve was used for poly(αMeSt), and the latter for poly(CEVE) and αMeSt-CEVE copolymers. ^{1}H-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 (**10**) for ^{1}H-NMR analysis were fractionated by preparative SEC (column: Shodex K-2002 and H-2001, respectively).

RESULTS AND DISCUSSION

Living Polymerization of CEVE

Prior to copolymerization of αMeSt with CEVE, the homopolymerization of the latter with the **1a**/$SnBr_4$ initiating system was investigated in CH_2Cl_2 at −78°C (Eq. 2). The polymerization occurred smoothly (conversion = 91% for 10 minutes) without an induction phase. As shown in Fig. 1, the number-average molecular weights ($\overline{M}_n$) of the polymers were directly proportional to monomer conversion and in good agreement with the calculated values assuming that one polymer chain forms per adduct **1a** molecule. Throughout the reaction the MWD was very narrow ($\overline{M}_w/\overline{M}_n$ < 1.1). Thus, CEVE was also polymerized in a living fashion by **1a**/$SnBr_4$ as αMeSt was.

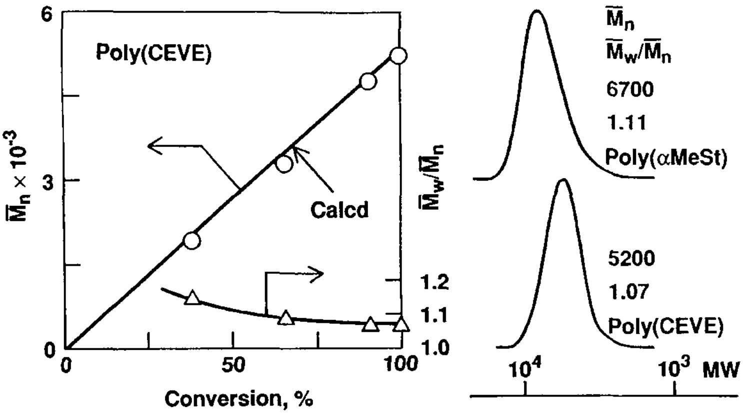
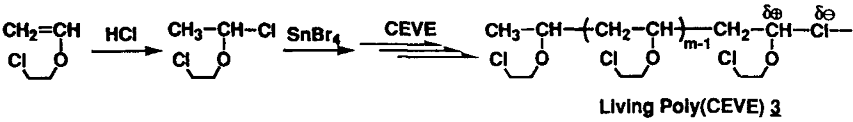


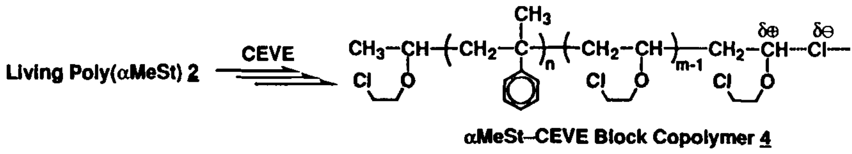
FIG. 1. $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and MWD curves of poly(CEVE) and poly(αMeSt) obtained with **1a**/$SnBr_4$ in CH_2Cl_2 at −78°C. $[M]_0$ = 0.50 M; $[\mathbf{1a}]_0$ = 10 mM; $[SnBr_4]_0$ = 20 mM. The "Calcd" solid line indicates the calculated $\overline{M}_n$ assuming the formation of one living polymer per **1a** molecule. Conversion for MWD curves ~ 100%.



(2)

Block Copolymerization

With use of the **1a**/SnBr$_4$ initiating system, the sequential block copolymerization from αMeSt to CEVE was examined in CH_2Cl_2 at −78°C (Eq. 3). As shown in Fig. 2(A), the first-stage polymerization of αMeSt led to a living polymer with narrow MWD ($\bar{M}_w/\bar{M}_n$ ~ 1.15). On addition of CEVE of the living poly(αMeSt) solution (conversion ~ 100%), CEVE was polymerized smoothly (85% for 13 minutes) at almost the same rate as in its homopolymerization (91% for 10 minutes). The MWD stayed very narrow ($\bar{M}_w/\bar{M}_n$ ~ 1.15), and the peak top of the MWD curve (both ultraviolet and refractive-index detection) clearly shifted toward higher molecular weight (Fig. 2B).



(3)

Figure 3 shows the ^{1}H-NMR spectrum of the polymers with peak assignments. In addition to the signals of αMeSt (*g*) and the CEVE (*i*–*k*) repeat units, the spectrum consists of the resonances of the methyl proton *a* at the α-end and the methine proton *l* at the ω-end arising on quenching the polymerization with methanol. The

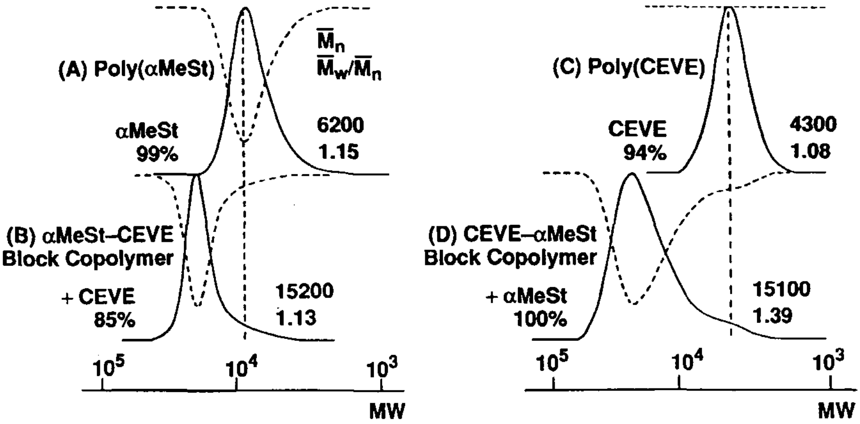


FIG. 2. MWD curves of poly(αMeSt) (A), poly(CEVE) (C), and the polymers obtained after the addition of CEVE (B) and αMeSt (D) to Samples A and C, respectively, with **1a**/SnBr$_4$ in CH_2Cl_2 at −78°C. (A and B): $[\alpha MeSt]_0$ = 0.50 M; $[\mathbf{1a}]_0$ = 10 mM; $[SnBr_4]_0$ = 20 mM; $[CEVE]_{add}$ = 1.0 M. (C and D): $[CEVE]_0$ = 0.50 M; $[\mathbf{1a}]_0$ = 10 mM; $[SnBr_4]_0$ = 20 mM; $[\alpha MeSt]_{add}$ = 1.0 M. (——) RI detection; (- - -) UV detection at 256 nm.

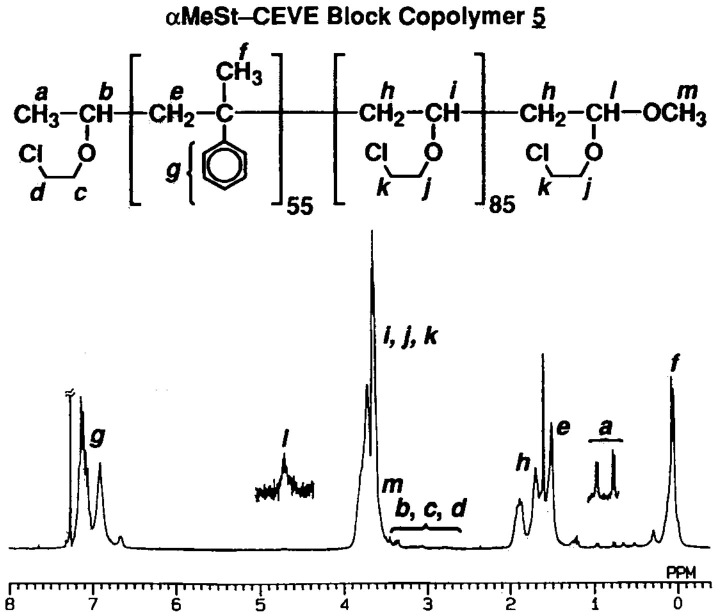
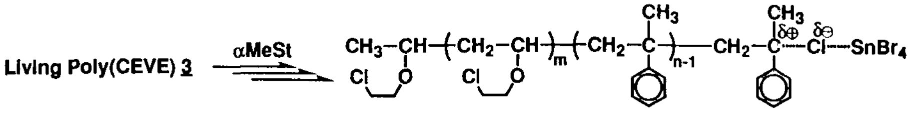


FIG. 3. ^{1}H-NMR spectrum of αMeSt-CEVE block copolymers: αMeSt/CEVE = 55/86 ($\overline{DP}_n$ measured by ^{1}H NMR), Sample B in Fig. 2.

integrated peak intensity ratio of *a* (head) to *l* (tail) was 3.0, which agreed with the calculated value, 3. This indicates that all living poly(αMeSt) ends initiate polymerization of CEVE. The number-average degrees of polymerization ($\overline{DP}_n$) of the αMeSt and the CEVE segments can be obtained from the peak intensity ratio *g* to *a* and ($i + j + k$) to *a*, respectively. The values were 55 for αMeSt and 86 for CEVE, which are in good agreement with the calculated values ($[M]_0/[\mathbf{1a}]_0 \times$ conversion), 50 (αMeSt) and 85 (CEVE), respectively. These results show that AB block copolymers of αMeSt and CEVE were synthesized by **1a**/$SnBr_4$ with nearly perfect blocking efficiency. This is the first example of success in blocking from styrenic monomers to vinyl ethers.

The reverse order of monomer addition (i.e., from CEVE to αMeSt) was also examined for the BA block copolymerization with the **1a**/$SnBr_4$ system (Eq. 4). The first stage gave a homopolymer of CEVE with a narrow MWD, as shown in Fig. 2(C). On the subsequent addition of αMeSt to the living poly(CEVE), it was consumed slower than in its homopolymerization under the same conditions [time for 99%: 50 minutes (block copolymerization); 5 minutes (homopolymerization)]. This is attributable to the complexation of $SnBr_4$ by the ether oxygens in the preformed CEVE units, which decreases the effective concentration of $SnBr_4$ available to the activation of the growing end. The MWD curve of the resultant polymers in the second stage (Fig. 2D) had ultraviolet absorption due to the αMeSt units, the ultraviolet and refractive-index traces were almost identical, and the peak top of the MWD curve shifted toward higher molecular weight. These indicate the incorporation of αMeSt units over the entire molecular weight range and the formation of the BA block polymers.

However, the slight tailing observed in both ultraviolet and refractive-index traces indicates that a small amount of propagating end lost the activity after the addition of αMeSt. As described later and also in a previous paper [6], the propagating ends with two and/or three αMeSt units were susceptible to indanyl ring formation. In contrast, the growing ends with more than three αMeSt units did not undergo indan formation. This is probably due to the rigid main chain of poly(αMeSt) and to the high syndiotacticity of the generated poly(αMeSt) ($rr > 90\%$). Thus, the tailing is probably due to the polymers with CEVE units and two and/or three αMeSt units with a terminal indanyl ring. These results indicate that BA block copolymers are obtainable, though less controlled than the corresponding AB block.



(4)

CEVE–αMeSt Block Copolymer 6

Random Copolymerization

For random copolymerization of αMeSt and CEVE, their equimolar mixture (0.50 M each) was polymerized with **1a**/$SnBr_4$ in CH_2Cl_2 at −78°C (Eq. 5). As shown in Fig. 4, αMeSt and CEVE were consumed almost simultaneously, and the consumption rate of CEVE was slightly larger than that of αMeSt. In the homopolymerizations, however, αMeSt was polymerized faster than CEVE. As pointed out already, the smaller rate of CEVE is due to the complexation of $SnBr_4$ by the vinyl ether monomer and/or polymers via their ether oxygens.

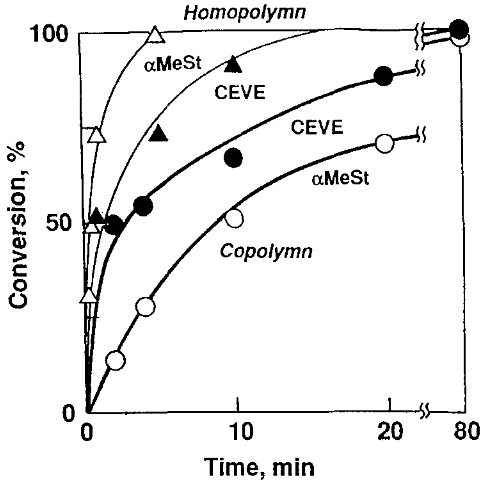
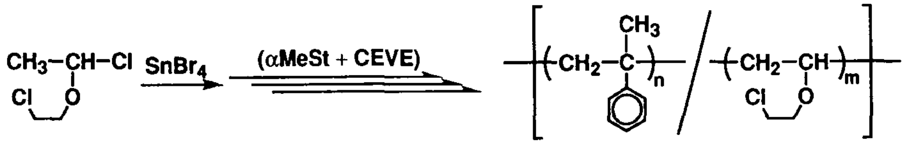


FIG. 4. Time-conversion curves for the copolymerization of αMeSt (○) and CEVE (●), and the homopolymerizations of αMeSt (△) and CEVE (▲) with **1a**/$SnBr_4$ in CH_2Cl_2 at −78°C. $[\alpha MeSt]_0 = [CEVE]_0 = 0.50$ M; $[\mathbf{1a}]_0 = 10$ mM; $[SnBr_4]_0 = 20$ mM.



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(5)

Figure 5 plots the $\overline{M}_n$ of the polymers obtained against the total yield of the monomers. The $\overline{M}_n$ values increased in direct proportion to the yield and agreed with the calculated values, assuming that one polymer chain is formed per **1a** molecule. The MWD was unimodal, and the ultraviolet and refractive-index traces were almost identical. These results suggest that long-lived random copolymers of αMeSt and CEVE were generated. The deviation from linearity in the $\overline{M}_n$-yield plot at higher conversion and tailing in the MWD curves indicate that some transfer reaction occurs in the copolymerization. This is due to indanyl ring formation followed by proton transfer, mostly to CEVE monomer (see above).

As shown in Fig. 6, the ^{1}H-NMR spectrum of the random copolymers thus obtained (A) was quite different from those of the block copolymer (B) and a blend of the homopolymers (C). Figure 6(A) shows that all the peaks broadened, and absorptions *a* and *b* appeared; the latter were assignable to the methyl protons of αMeSt units adjacent to CEVE units and the methylene protons of CEVE units adjacent to αMeSt units, respectively. Samples of the random copolymers and the block copolymers cast from a toluene solution were transparent, whereas a sample of the homopolymer blend was opaque because of macrophase separation. These results also demonstrate the formation of almost random copolymers.

As described above, it is unique that both AB and BA block copolymers can be obtained in sequential living cationic copolymerization among different types of

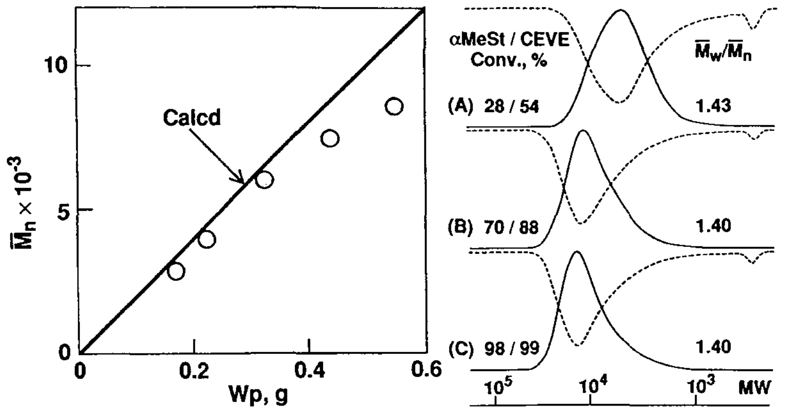


FIG. 5. $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and MWD curves of the copolymers of αMeSt and CEVE obtained with **1a**/$SnBr_4$ in CH_2Cl_2 at −78°C. $[\alpha MeSt]_0 = [CEVE]_0 = 0.50$ M; $[\mathbf{1a}]_0 = 10$ mM; $[SnBr_4]_0 = 20$ mM. The "Calcd" solid line indicates the calculated $\overline{M}_n$ assuming the formation of one living polymer per **1a** molecule. (——) RI detection; (- - -) UV detection at 256 nm.

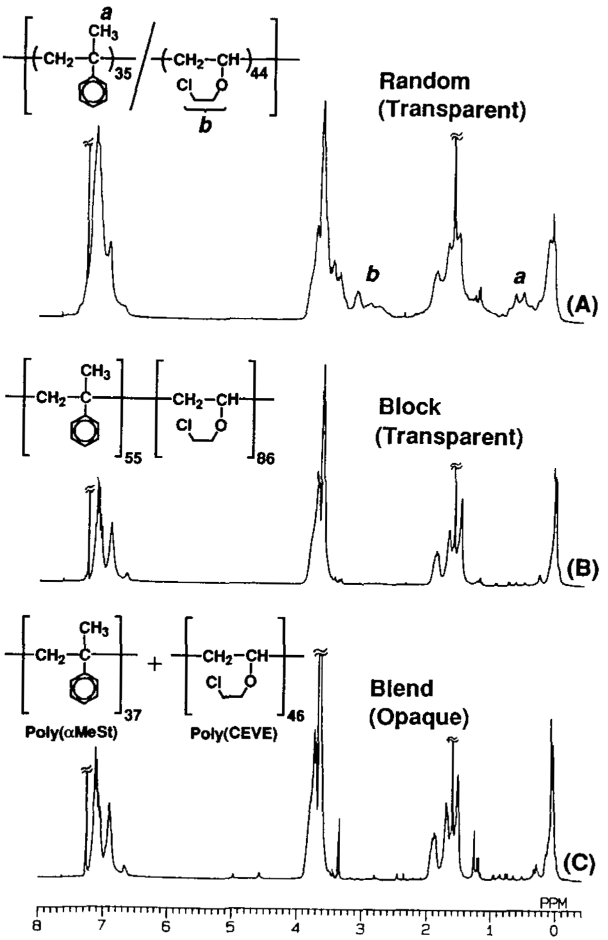
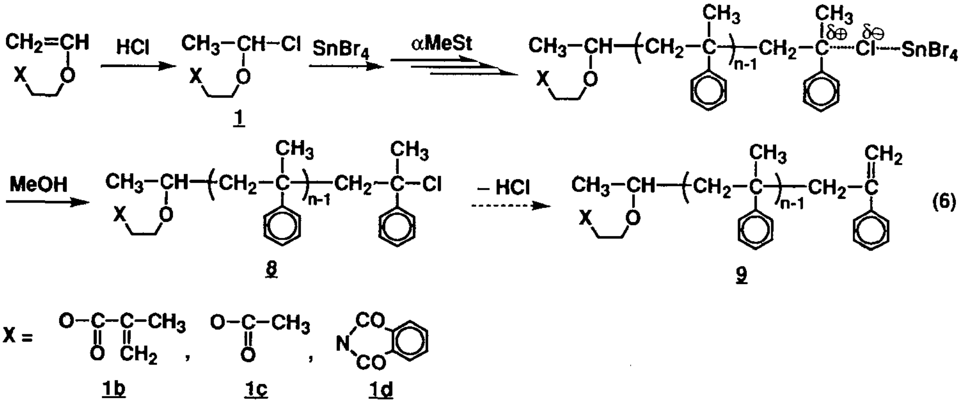


FIG. 6. ^{1}H-NMR spectra: (A) random copolymers of αMeSt and CEVE, αMeSt/CEVE = 35/44 ($\overline{DP}_n$ calculated from conversion), Sample B in Fig. 5; (B) αMeSt-CEVE block copolymers, αMeSt/CEVE = 55/86 ($\overline{DP}_n$ measured by ^{1}H NMR), Sample B in Fig. 2; (C) blend of poly(αMeSt) ($\overline{DP}_n$ = 37) and poly(CEVE) ($\overline{DP}_n$ = 46), αMeSt/CEVE = 1/1 (repeat units ratio).

vinyl monomers. It has been reported that αMeSt readily copolymerizes with CEVE in conventional cationic polymerizations [20]. This probably stems from the fact that the reactivity of CEVE is comparable to αMeSt, as seen from Fig. 4.

End-Functionalized Poly(αMeSt)

Noting the facile and quantitative initiation of αMeSt polymerization from the HCl-vinyl ether adduct **1a**, we extended this finding to the synthesis of end-functionalized polymers. Thus, as illustrated in Eq. (6), a series of functional initiators (**1b**–**1d**), which were the adducts of HCl with vinyl ethers carrying functional pendant groups X, were prepared. The functional group X included a methacryloyloxy (**1b**), acetoxy (**1c**), or imide (**1d**). From **1b**, a macromonomer with an anionic or radical polymerizable group will be obtained; initiators **1c** and **1d** have the protected forms of hydroxy and amino groups, respectively. As Eq. (6) implies, these functional groups will be attached to the head (α-end) of the resulting polymers, provided that the initiation from **1b–1d** is quantitative and that the ensuing propagation is free from chain transfer (or undergoes living polymerization).



According to the route given in Eq. (6), αMeSt was polymerized with initiators **1b–1d**, in conjunction with $SnBr_4$ in CH_2Cl_2 at −78°C. The polymerizations occurred without an induction phase and completed in ~10 minutes, where the reaction rate was virtually independent of the functional groups X of the initiator **1**. The $\overline{M}_n$ of the polymers increased in direct proportion to monomer conversion (Fig. 7). The $\overline{M}_n$'s with **1d** were in good agreement with the calculated values, assuming that one polymer chain forms per **1d** molecule. Those with **1b** and **1c**

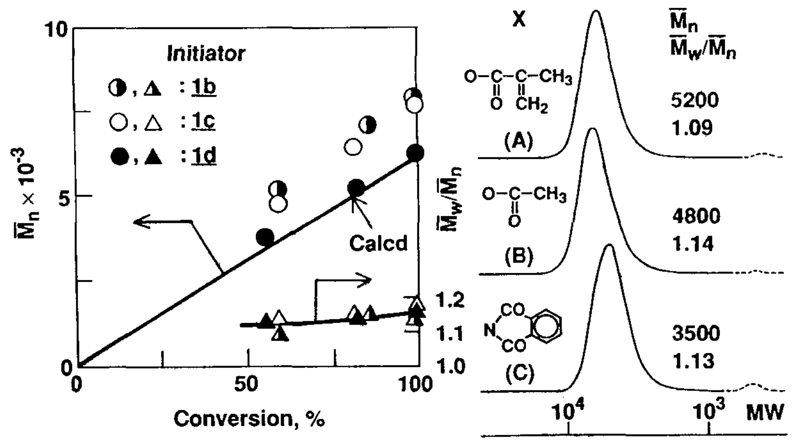


FIG. 7. $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and MWD curves of end-functionalized poly(αMeSt) obtained with $1/SnBr_4$ in CH_2Cl_2 at −78°C. $[\alpha MeSt]_0$ = 0.50 M; $[1]_0$ = 10 mM; $[SnBr_4]_0$ = 20 mM. The "Calcd" solid line indicates the calculated $\overline{M}_n$ assuming the formation of one living polymer per 1 molecule. Conversion for MWD curves ~ 60%.

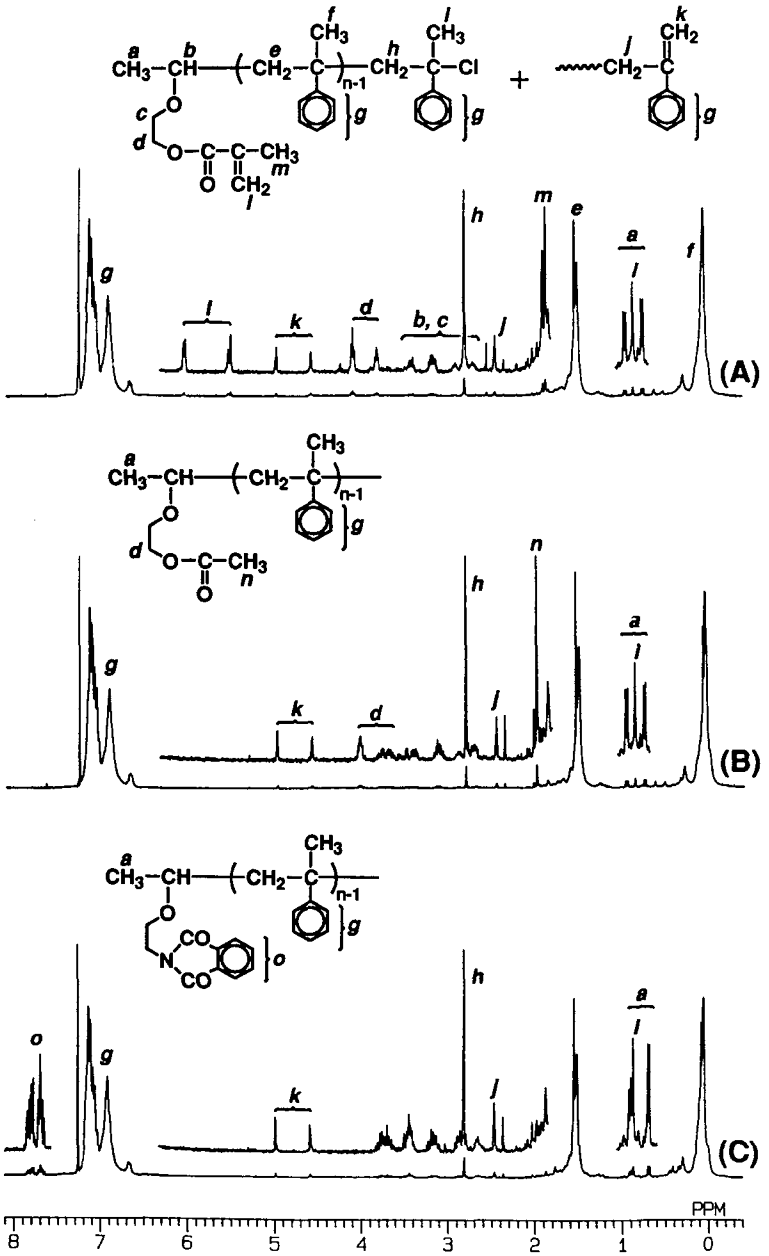
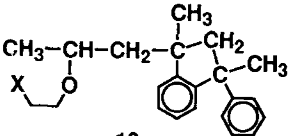


FIG. 8. ^{1}H-NMR spectra of end-functionalized poly(αMeSt) obtained with **1b** (A), **1c** (B), and **1d** (C). See Fig. 7 for reaction conditions.

were, however, slightly higher than the calculated values. The MWDs were narrow in all cases ($\overline{M}_w/\overline{M}_n \sim 1.15$). These facts show the living nature of the polymerization of αMeSt initiated by the **1**/$SnBr_4$ system, despite the polar functional group X therein. However, low molecular weight oligomers (the dashed lines in the MWD curves) were formed during the early stage of the polymerizations. The oligomer was proved to be **10**, having an indanyl ring that is formed after the dimerization of αMeSt with **1**, and this may account for the higher $\overline{M}_n$'s of the polymers obtained with **1b** and **1c** (see below).



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The end-group structure of the polymers was determined by ^{1}H-NMR spectroscopy. Figure 8(A) shows the ^{1}H-NMR spectrum of a typical sample of the methacryloyloxy-capped poly(αMeSt) obtained with the **1b**/$SnBr_4$ initiating system. The spectrum exhibits all key absorptions of the poly(αMeSt) main-chain (*e*–*g*) and methacryloyloxy group of the initiator fragment (*a*–*d*, *l*, and *m*).

The $\overline{DP}_n$ for the methacryloyloxy-capped polymers was determined from the peak intensity ratio of the phenyl group *g* to the methacryloyloxy group *l* ($2g/5l$). As shown in Table 1, $\overline{DP}_n$'s were in good agreement with the values from size-exclusion chromatography (SEC) calibrated against standard poly(αMeSt) samples. The number-average end-functionality ($\overline{F}_n$) of the terminal methacrylate for the produced polymers was determined from $\overline{DP}_n$(SEC)/$\overline{DP}_n$(NMR). The value was close to unity, indicating that the polymers obtained possess almost one methacryloyloxy group per chain.

Very similar results were obtained for the polymers synthesized with the initiator that carries an acetoxy (**1c**) or a phthalimide (**1d**) pendant group. The ^{1}H-NMR

TABLE 1. Synthesis of End-Functionalized Poly(αMeSt) with **1**/$SnBr_4$[a]

	$\overline{DP}_n$			
Initiator	GC[b]	SEC[c]	NMR[d]	$\overline{F}_n$[e]
1b	30	43	44	0.96
1c	30	40	41	0.98
1d	28	30	33	0.92

[a] $[\alpha MeSt]_0/[\mathbf{1}]_0/[SnBr_4]_0$ = 500/10/20 mM; in CH_2Cl_2, at −78°C; see Eq. (6).

[b] $[\alpha MeSt]_0/[\mathbf{1}]_0$ × conversion (by gas chromatography).

[c] [$\overline{M}_n$(SEC) − MW(initiator moiety)]/MW(αMeSt).

[d] From ^{1}H-NMR peak intensity ratio; $2g/5l$ (**1b**), $2g/5d$ (**1c**), $4g/5o$ (**1d**).

[e] $\overline{DP}_n$(SEC)/$\overline{DP}_n$(NMR).

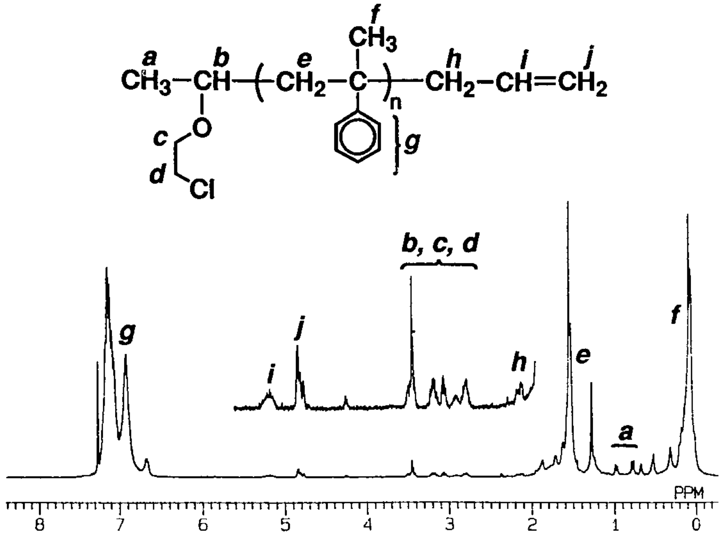

FIG. 9. ^{1}H-NMR spectrum of poly(αMeSt) obtained with **1a**/SnBr$_4$ in CH$_2$Cl$_2$ at −78°C after quenching the reaction with allyltrimethylsilane at αMeSt conversion = 48%; $\overline{M}_n$ = 2800, $\overline{M}_w/\overline{M}_n$ = 1.30. [αMeSt]$_0$ = 0.50 M; [**1a**]$_0$ = 10 mM; [SnBr$_4$]$_0$ = 20 mM; [CH$_2$=CHCH$_2$SiMe$_3$]$_0$ = 0.50 M.

spectra are shown in Figs. 8(B) and 8(C). Table 1 shows the $\overline{DP}_n$ and the $\overline{F}_n$ of these polymers. As with the polymer initiated by **1b**, the α-end groups from **1c** and **1d** were clearly observed (Fig. 8B, peaks *d* and *n*; Fig. 8C, peak *o*).

It seems strange that all the polymers had almost one unit of the functional group, though low molecular weight oligomers with an indanyl ring also formed. The proton transfer to αMeSt monomer may follow the indan formation to produce polymers with an α-methyl end [(CH$_3$)$_2$C(Ph)—]. If this type of polymer was produced, the α-methyl signal would appear at 1.1 ppm. However, no such signals were observed. This indicates that the initiation by proton is absent or negligible under our reaction conditions. In fact, according to a previous study [6], initiation from the HCl-adduct of αMeSt (cumyl chloride) is very slow, even in the presence of SnBr$_4$. Accordingly, the polymerization initiated by proton (HCl)/SnBr$_4$ hardly occurred during the fast polymerization with **1**/SnBr$_4$.

As shown in Figs. 8(A–C), two types of ω-ends were observed: a chloride (*h* and *i*) and an olefin (*j* and *k*). No methoxide group was detected, despite the quenching with methanol at the end of the synthesis. This is in sharp contrast to the quantitative attachment of the methoxide to the poly(CEVE) end (Fig. 3). If the living polymerization with **1**/SnBr$_4$ proceeds via the activation of the terminal C—Cl bond by SnBr$_4$ (Eq. 6), these terminal structures indicate that the chloride end remains unchanged without being substituted with a methoxide, even after the quenching with methanol. On the other hand, the terminal olefin would be generated by the elimination of HCl from the chloride terminal during the polymerization (i.e., chain transfer) or the workup of the product.

The absence of HCl elimination during the polymerization has been shown by the following experiments. It is known that allyltrimethylsilane (CH$_2$=CHCH$_2$-

$SiMe_3$) reacts with alkyl chlorides in the presence of Lewis acid [21, 22]. This compound was also used for allylation of poly(isobutene) generated by cationic processes [23–25]. When the αMeSt polymerization with **1a**/$SnBr_4$ was quenched with excess allyltrimethylsilane, the ω-end of the polymers proved to be the allyl group (*h–j* in Fig. 9). There were neither signals of the olefin (4.6 and 5.0 ppm) nor of the chloride. The peak intensity ratio of $(i + j)$ to $(b + c + d)$ was 0.57, which agreed with the calculated value, 0.6. This indicates that the growing polymer end is not killed by proton transfer during the polymerization, but that it can be effectively quenched by allyltrimethylsilane.

CONCLUSIONS

Initiating systems consisting of the adduct of hydrogen chloride with vinyl ether (**1**) and $SnBr_4$ are effective in the synthesis of not only AB and BA block and random copolymers of αMeSt with CEVE but also end-functionalized poly(αMeSt) with polar functional groups.

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