Living Cationic Polymerization of *p*-Chlorostyrene and Related Para-Substituted Styrene Derivatives at Room Temperature[1]

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ABSTRACT: Cationic polymerizations of *p*-chlorostyrene (pClSt), *p*-(chloromethyl)styrene (pCMS), and *p*-(acetoxymethyl)styrene (pAcOMS) were examined with HCl−vinyl monomer adduct (**1**; $CH_3CH(R)Cl$; **1a**: R = Ph, **1b**: R = OCH_2CH_2Cl)/SnX_4 initiating systems in the presence or absence of an ammonium salt. Living polymers were obtained from pClSt using the 1-phenylethyl chloride (**1a**)/$SnCl_4$/$n Bu_4NCl$ initiating system in CH_2Cl_2 at 0 °C. Thus, without the ammonium salt, the **1a**/$SnCl_4$ system led to a conventional cationic polymerization to give polymers with bimodal molecular weight distributions (MWDs), but in the presence of $n Bu_4NCl$, polymers with unimodal and very narrow MWDs ($\bar{M}_w/\bar{M}_n \approx 1.1$) were obtained. The number-average molecular weight ($\bar{M}_n$; by ^{1}H NMR) of the polymers increased in direct proportion to conversion, agreed with the calculated value assuming that one polymer chain forms per molecule of **1a**, and further increased on addition of a fresh pClSt feed into a completely polymerized solution. More important, living poly(pClSt) with narrow MWDs were also obtained even at +25 °C, where the corresponding polymerization of styrene is not living. This is the first example of living polymerization of pClSt at room temperature. Living polymers were also obtained by initiating the polymerization with the vinyl ether adduct (**1b**), and end-functionalized polymers of pClSt could be prepared by a functionalized vinyl ether adduct in a similar way. In contrast to pClSt, neither pCMS nor pAcOMS was polymerized in a living fashion.

Introduction

Among cationically polymerizable vinyl monomers, styrene derivatives, vinyl ethers, and isobutene are the most common for living polymerization.[2] A characteristic of living cationic polymerization of vinyl ethers is that polar functional groups can readily be incorporated into the pendant groups without deteriorative reaction control.[2] This advantage thus led to many functionalized poly(vinyl ethers) with well-controlled structures, including block or end-functionalized.[2] In contrast, there are few functionalized polystyrene derivatives synthesized by either conventional or living cationic polymerization. Most of them were polymers of protected *p*-hydroxystyrene derivatives which can be converted into poly(vinylphenol).[3−7] Because polystyrenes have, in general, better mechanical properties relative to poly(vinyl ethers), functionalized polystyrenes would be interesting as new materials.

In cationic polymerization when a strongly electron-donating group is present, it enhances the reactivity of monomers and stabilizes the growing carbocation, and *p*-alkoxystyrenes are closer in reactivity to vinyl ethers than other styrenes without any electron-donating group. In fact, living cationic polymerizations of alkoxy- or alkyl-substituted styrenes[7−9] are possible with initiating systems that were originally developed for alkyl vinyl ethers,[10] whereas styrene, which lacks an electron-donating substituent, requires special initiating systems to achieve living cationic polymerization. Such systems include 1-phenylethyl chloride (**1a**)/$SnCl_4$/$n Bu_4NCl$, which yields polystyrene with a narrow molecular weight distribution (MWD).[11]

Table 1. Initiating Systems Based on Vinyl Monomer−HX Adducts for Living Cationic Polymerization of Styrene Derivatives and Their ^{13}C NMR Chemical Shifts for *β*-Carbon

monomer	initiating system	$\delta(C^\beta)$, ppm
p-methoxystyrene[7a,c,d]	HI/ZnI_2	111.1
p-tert-butoxystyrene[7b]	HI/ZnI_2	112.1
α-methylstyrene[12,13]	$CH_3CH(OR)Cl/SnBr_4$	112.3
p-methylstyrene[14,15]	$CH_3CH(OR)Cl/SnCl_4/n Bu_4NCl$	112.5
styrene[11]	$CH_3CH(Ph)Cl/SnCl_4/n Bu_4NCl$	113.8
p-chlorostyrene	present study	114.4
p-(chloromethyl)styrene	present study	114.6
p-(acetoxymethyl)styrene	present study	114.1

Since that system was introduced, the initiating systems have been developed in our group for living cationic polymerization of styrene derivatives (Table 1)[12−15] less reactive than *p*-alkoxystyrenes, from which block[13] or end-functionalized[14,15] polymers have been prepared. However, living polymerization of less reactive styrene derivatives still appears beyond reach. Kennedy successfully carried out the living cationic polymerization of pClSt, but the MWDs of the products were not narrow even at very low temperature.[16] Recent development of initiating systems encouraged us to study living cationic polymerization of less reactive styrenes, where an electron-withdrawing functional group is attached to the phenyl ring.

Although living polymers can be prepared anionically from a variety of styrenes with an electron-withdrawing group,[17] it has so far been very difficult to polymerize some monomers in a living fashion. For example, side reactions accompany polymerization of *p*-chlorostyrene (pClSt), and *p*-(chloromethyl)styrene (pCMS) terminates anionic polymerization to give a macromonomer. In this

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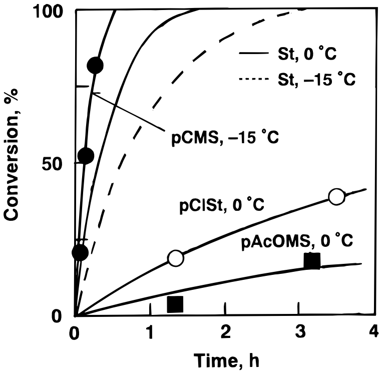
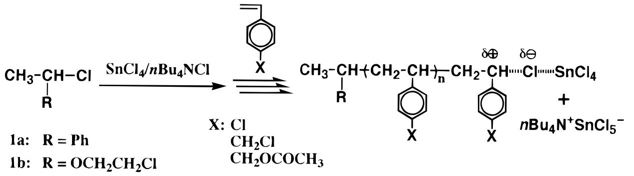


Figure 1. Time−conversion curves for polymerization of styrene derivatives with **1a**/$SnCl_4$/nBu_4NCl in CH_2Cl_2: $[M]_0 = 1.0$ M, $[\mathbf{1a}]_0 = 20$ mM, $[SnCl_4]_0 = 100$ mM, $[nBu_4NCl]_0 = 40$ mM. Monomer and reaction temperature: (●) pCMS, −15 °C; (○) pClSt, 0 °C; (■) pAcOMS, 0 °C.

Scheme 1



study, therefore, we have selected these two monomers to examine their cationic polymerization. In addition to these monomers, we also examined the polymerization of *p*-(acetoxymethyl)styrene (pAcOMS), which was readily prepared from pCMS and sodium acetate.

As shown in Table 1, the initiating systems developed in our group[7,11−15] for living cationic polymerization of styrene derivatives invariably contain an adduct of a vinyl monomer with hydrogen halide and a Lewis acid, and less reactive monomers (*p*-methylstyrene[14] and styrene[11]) require a stronger Lewis acid. When such a Lewis acid is employed, an ammonium salt is also essential to achieve living polymerization. In this study, we examined the cationic polymerization of pClSt, pCMS, and pAcOMS using the HCl−adduct (**1**)/SnX_4 (X = Br, Cl) initiating systems either in the presence or absence of nBu_4NCl (Scheme 1). We also examined the synthesis of end-functionalized polymers of pClSt using a functional initiator derived from a vinyl ether.[12,14]

Results and Discussion

Cationic Polymerization of pClSt, pCMS, and pAcOMS with 1a/$SnCl_4$/nBu_4NCl. In analogy to styrene polymerization,[11] pClSt, pCMS, and pAcOMS were polymerized with the **1a**/$SnCl_4$/nBu_4NCl (20/100/40 mM) system in CH_2Cl_2 at −15 or 0 °C.[18] In all cases, quantitative polymerizations occurred without an induction phase (Figure 1). Among the three monomers, pCMS polymerized fastest, even at temperatures lower than those for the other two. Polymerization rates decreased in the order pCMS > styrene > pClSt > pAcOMS, although the chemical shifts of their β-carbons, which is an index of π-electron density, are very close to each another (Table 1).

Figures 2 and 3, respectively, show the ^{1}H NMR spectra and the MWDs (GPC curves) of the products thus obtained from pCMS (A), pAcOMS (B), and pClSt (C). Spectra A and B exhibit signals (the hatched peaks in Figure 2) at 2.8 ppm, which are derived neither from monomers nor from the repeat units expected to form through vinyl addition reactions, whereas spectrum C

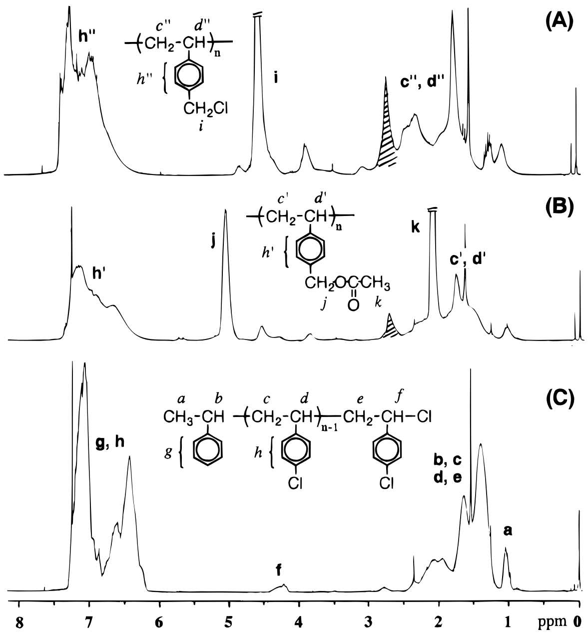


Figure 2. ^{1}H NMR spectra (in $CDCl_3$) of the polymers obtained from pCMS (A), pAcOMS (B), and pClSt (C) by **1a**/$SnCl_4$/nBu_4NCl. See Figure 1 for the reaction conditions.

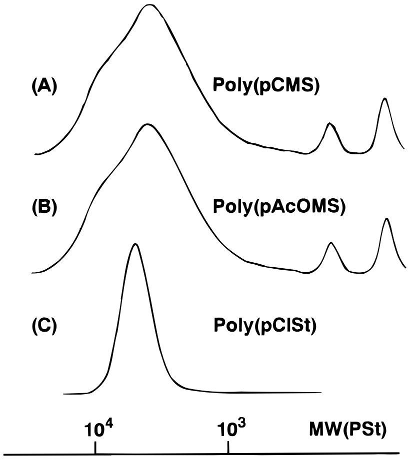


Figure 3. MWD curves of the product polymers obtained from polymerization of styrene derivatives with **1a**/$SnCl_4$/nBu_4NCl in CH_2Cl_2. See Figure 1 for the reaction conditions.

shows no major peak in the same region. This signal appears assignable to the methylene protons between a phenyl ring and an alkyl substituent, not the benzyl protons of the monomer repeat units [peaks *i* (A) and *j* (B)]. The appearance of such units along with the low molecular weights and broad MWDs of the products (Figure 3A,B) indicates the undesirable initiation with, and/or the chain transfer to, the benzyl moieties in the polymerization of pCMS and pAcOMS. The undesirable initiation may accelerate polymerization rate of pCMS relative to that of pClSt. On the other hand, the polymerization of pAcOMS is much slower than that of pClSt: possibly the effective concentration of $SnCl_4$ is decreased due to its complexation with the acetoxy groups and/or because the acetoxy groups might coordinate with growing chain ends. In contrast to pCMS and pAcOMS, a polymer with a very narrow MWD was obtained from pClSt (Figure 3C, $\bar{M}_w/\bar{M}_n = 1.09$, $\bar{M}_n = 4480$) under similar conditions. The following section discusses this system in more detail.

***p*-Chlorostyrene Polymerization. (a) 1a/$SnCl_4$.** As shown above, the pendant chlorine of pClSt was

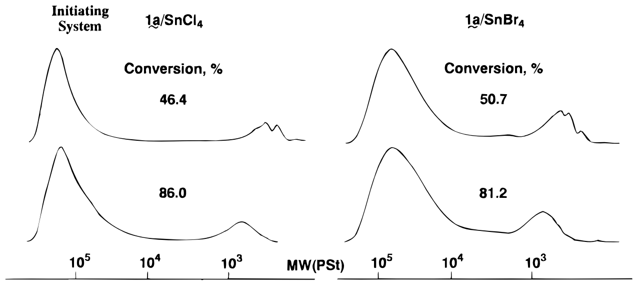


Figure 4. MWD curves of the product polymers obtained from polymerization of pClSt with **1a**/SnX_4 (X = Cl, Br) in CH_2Cl_2 at 0 °C: $[M]_0 = 1.0$ M, $[\mathbf{1a}]_0 = 20$ mM, $[SnX_4]_0 = 100$ mM.

stable during cationic polymerization using $SnCl_4$ to give a polymer with a narrow MWD. To search optimum initiating systems and reaction conditions for living pClSt polymerization, the monomer was polymerized with **1a**/$SnCl_4$ or $SnBr_4$ in CH_2Cl_2 at 0 °C in the presence or absence of $n$$Bu_4NCl$. The typical reagent concentrations were as follows: $[\text{pClSt}]_0 = 1.0$ M, $[\mathbf{1a}]_0 = 20$ mM, $[SnX_4]_0 = 100$ mM (X = Cl, Br). With $SnCl_4$ but without the salt, pClSt conversion reached 80% in 2 h, whereas a much slower polymerization occurred with $SnBr_4$ (81% conversion in 28 days).[19] In both cases, the product polymers had bimodal MWDs (Figure 4). The higher polymer fraction had a broad MWD whose peak molecular weight stayed virtually unchanged throughout the reaction, whereas the lower polymer fraction shifted toward higher molecular weight with increasing conversion as shown in Figure 4, indicating that it had a long-lived growing end. In this aspect, the polymerization is similar to that of styrene with **1a**/$SnCl_4$.[11] A polymerization with $SnBr_4$ is judged too slow; thus we employed $SnCl_4$ for further experiments in this study.

In the presence of $n$$Bu_4NCl$ (10 and 40 mM), the salt retarded the polymerization reaction, which reached ca. 100% monomer conversion in 1 day. The product polymers had unimodal and very narrow MWDs ($\bar{M}_w/\bar{M}_n \approx 1.1$) regardless of the amount of $n$$Bu_4NCl$ (cf. Figure 3). The $\bar{M}_n$ increased in direct proportion to monomer conversion, and the MWDs of these polymers stayed very narrow ($\bar{M}_w/\bar{M}_n \approx 1.1$) throughout the reaction (see below).

Quite recently, our group found that HCl–vinyl ether adducts [$CH_3CH(OR)Cl$, R; CH_2CH_2Cl, etc.] induce living polymerizations of α-methylstyrene[12,13] and p-methylstyrene.[14,15] We thus examined the pClSt polymerization with an adduct (**1b**) of 2-chloroethyl vinyl ether (CEVE), instead of **1a**, in the presence of $n$$Bu_4NCl$. With **1b**/$SnCl_4$, pClSt was smoothly polymerized at nearly the same rate as with **1a**/$SnCl_4$ (Figure 5). In both cases, the relationship between $\bar{M}_n$ and monomer conversion is linear, and the $\bar{M}_w/\bar{M}_n$ values were as low as 1.1 throughout the polymerization (Figure 6). When **1b** was employed, the product polymer is accompanied by a small amount of low molecular weight byproducts (Figure 6), whose ^{1}H NMR spectrum shows peaks due to both CEVE and pClSt units. These oligomers formed at the early stage of the polymerization, and their amount remained unchanged while the product polymers increased.

(b) $\bar{M}_n$(SEC) vs $\bar{M}_n$(NMR). As shown in Figure 6, the $\bar{M}_n$ values determined by size-exclusion chromatography (SEC) deviated from the calculated values assuming that one polymer chain forms per molecule of **1a**. The deviation of the $\bar{M}_n$ is likely because it was calculated on the basis of a polystyrene calibration. The absolute $\bar{M}_n$ of the product polymers was then determined by ^{1}H NMR.

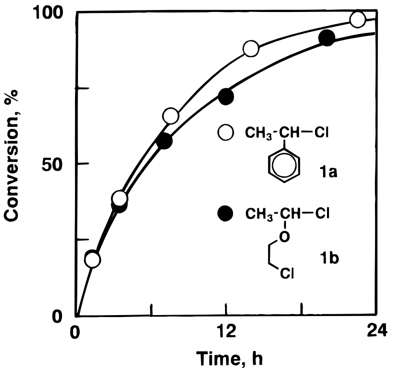


Figure 5. Time–conversion curves for the polymerization of pClSt with **1**/$SnCl_4$/$n$$Bu_4NCl$ in CH_2Cl_2 at 0 °C: $[M]_0 = 1.0$ M, $[\mathbf{1}]_0 = 20$ mM, $[SnCl_4]_0 = 100$ mM, $[n\text{Bu}_4\text{NCl}]_0 = 40$ mM. Initiator: (○) **1a**; (●) **1b**.

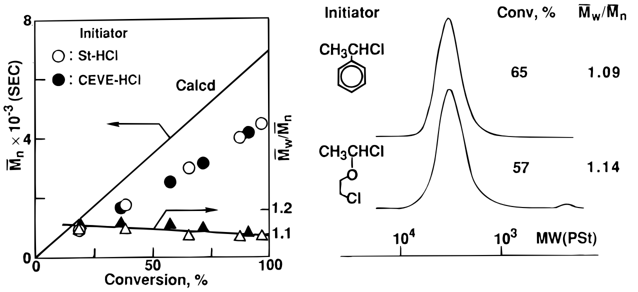


Figure 6. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(pClSt) obtained with **1**/$SnCl_4$/$n$$Bu_4NCl$ in CH_2Cl_2 at 0 °C. See Figure 5 for the reaction conditions. Initiator: (○,△) **1a**; (●,▲) **1b**. The diagonal solid line indicates the $\bar{M}_n$ calculated from the feed ratio of pClSt to **1** and monomer conversion.

Figure 2C shows ^{1}H NMR spectrum of poly(pClSt) obtained after quenching the polymerization with methanol. In addition to the signals of the pClSt repeat units (e.g., peaks c–e, h), a small broad peak f appeared at 4.1–4.4 ppm, which is assignable to the methine proton of the chlorine terminal [$-CH_2\underline{CH}(p\text{-}C_6H_4Cl)Cl$].[11b,14] The degree of polymerization ($\overline{DP}_n$) and $\bar{M}_n$ for the polymer were determined from the ^{1}H NMR peak intensity ratio of the aromatic protons (peak h) of the pClSt units to the methine proton (peak f) of the chlorine terminal, assuming that one polymer chain forms per **1a** molecule. The observed values [$\bar{M}_n$(NMR)] increased proportionally to monomer conversion and were in good agreement with the calculated counterparts for living polymers (Figure 7A). Figure 7B plots the $\bar{M}_n$(NMR) of the polymers as a function of the $\bar{M}_n$(SEC) in the molecular weight range from 10^3 to 10^4. Their relationship is linear, and on the basis of this calibration, the $\bar{M}_n$(NMR) values of the other samples were calculated from the relation

$$\bar{M}_n(\text{NMR}) = 1.43 \times \bar{M}_n(\text{SEC})$$

(c) Monomer-Addition Experiments. In the pClSt polymerization with **1a**/$SnCl_4$/$n$$Bu_4NCl$, a fresh feed of pClSt was added to the reaction mixtures just before the initial charge of the monomer had completely been polymerized. The second-stage polymerization immediately ensued, and the polymerization rate in the second stage was nearly the same as in the initial stage (Figure 8A). The $\bar{M}_n$ of the polymers further increased in direct proportion to monomer conversion and agreed with the calculated values for living polymers (Figure

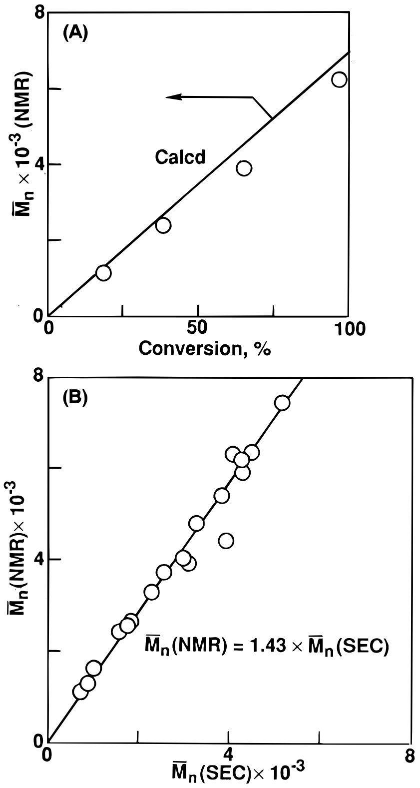


Figure 7. (A) $\bar{M}_n$ values determined by ^{1}H NMR plotted as a function of monomer conversion. The solid line indicates the $\bar{M}_n$ calculated from the feed ratio of pClSt to **1a** and monomer conversion. (B) Comparison between the $\bar{M}_n$ values by ^{1}H NMR and those by size-exclusion chromatography.

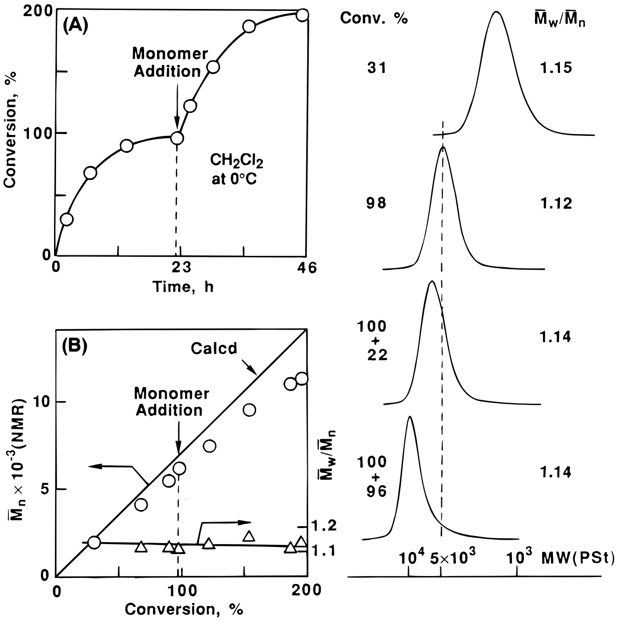


Figure 8. Time–conversion curve and $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(pClSt) obtained in a monomer-addition experiment in the polymerization with **1a**/SnCl$_4$/*n*Bu$_4$NCl in CH$_2$Cl$_2$ at 0 °C: $[M]_0 = [M]_{add} = 1.0$ M, $[\mathbf{1a}]_0 = 20$ mM, $[SnCl_4]_0 = 100$ mM, $[n\mathrm{Bu}_4\mathrm{NCl}]_0 = 40$ mM.

8B). The MWDs even after the monomer addition stayed very narrow ($\bar{M}_w/\bar{M}_n = 1.1-1.2$). Thus, the living nature of the polymerization with **1a**/SnCl$_4$/*n*Bu$_4$NCl was demonstrated.

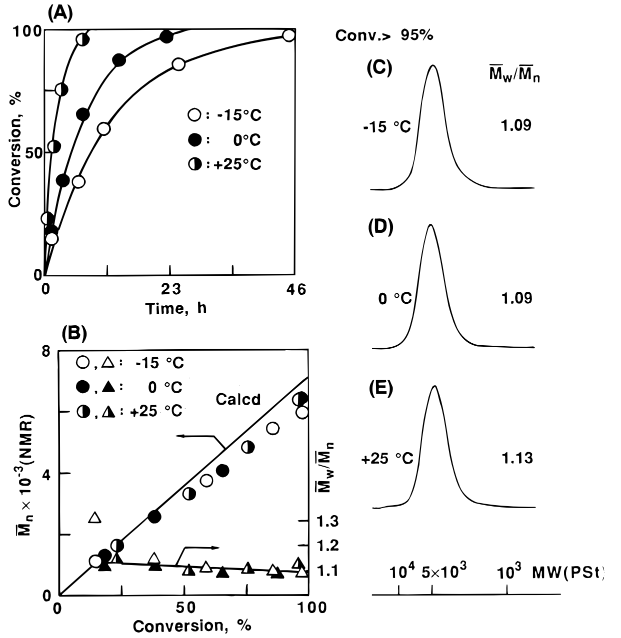


Figure 9. Time conversion curves and $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(pClSt) obtained with **1a**/SnCl$_4$/*n*Bu$_4$NCl in CH$_2$Cl$_2$ at varying temperature: $[M]_0 = 1.0$ M, $[\mathbf{1a}]_0 = 20$ mM, $[SnCl_4]_0 = 100$ mM, $[n\mathrm{Bu}_4\mathrm{NCl}]_0 = 40$ mM. Reaction temperature: (○,△, C) −15 °C; (●,▲, D) 0 °C; (◐,▲, E) +25 °C.

Living Cationic Polymerization of pClSt at Room Temperature. pClSt was polymerized with the **1a**/SnCl$_4$/*n*Bu$_4$NCl initiating system in CH$_2$Cl$_2$ at −15, 0, and +25 °C. As Figure 9A shows, induction-free quantitative polymerizations occurred at all temperatures, which proved to be of first order with respect to monomer. The polymerization even at +25 °C was much slower (96% in 7 h) than that of styrene at 0 °C (95% in 70 min).

Figure 9B plots the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the polymers thus obtained. The $\bar{M}_n$'s for −15 °C as well as 0 °C were directly proportional to monomer conversion and in good agreement with the calculated values assuming that one polymer chain forms per **1a** molecule. The polymers exhibited narrow MWDs, maintaining the $\bar{M}_w/\bar{M}_n$ ratio near 1.1 over the whole conversion range. The lower polymerization temperature did not induce termination reactions but just retarded the polymerization rate.

The polymerization at +25 °C also gave the polymers with narrow MWDs, and the $\bar{M}_n$ increased in proportion to monomer conversion while the MWD remained narrow. We believe that this is the first example of living polymerization of pClSt at room temperature. It should be noted that the corresponding polymerization of styrene is not living at +25 °C. For example, when styrene was polymerized with **1a**/SnCl$_4$/*n*Bu$_4$NCl (20/100/40 mM) at 0 °C in CH$_2$Cl$_2$, the product polymers had a relatively narrow MWD ($\bar{M}_w/\bar{M}_n = 1.28$) but the MWD curve showed both a tailing and an additional peak in the higher molecular weight region. Because of the lower electron density on the phenyl ring of pClSt, no growing carbocations attack the phenyl groups intramolecularly to form indanyl end structures,[16a] which is the major uncontrollable side reaction in the styrene polymerization. Intermolecular attack of carbocations to phenyl rings to form higher molecular weight polymers was also suppressed due to deactivated phenyl rings and/or the steric hindrance of the chlorine group.

End Group Analysis and Synthesis of End-Functionalized Polymers. The terminal structure of the polymer prepared by **1b**/SnCl$_4$/*n*Bu$_4$NCl was analyzed by ^{1}H NMR spectroscopy (Figure 10). The spec-

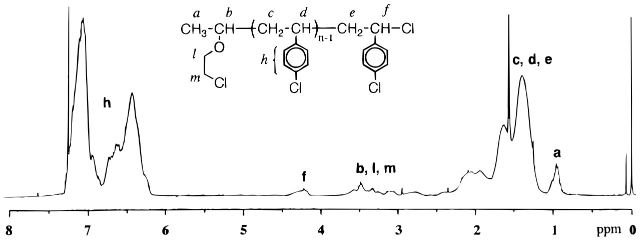


Figure 10. ^{1}H NMR spectrum (in $CDCl_3$) of poly(pClSt) obtained with **1b**/$SnCl_4$/$n$$Bu_4NCl$ in CH_2Cl_2 at 0 °C: $[M]_0 = 1.0$ M, $[\mathbf{1b}]_0 = 20$ mM, $[SnCl_4]_0 = 100$ mM, $[nBu_4NCl]_0 = 40$ mM.

trum shows peaks (a, b, l, and m) assignable to the CEVE unit, in addition to those of pClSt. The signal (a) of the methyl protons at the head group appears below 1 ppm, which is a typical absorption of the methyl protons at the head group derived from a vinyl ether, not from a styrene derivative (the methyl at the head group > 1 ppm; see Figure 2C).[14] These results show that **1b** initiated the polymerization of pClSt and that no side reactions occurred, such as a chain transfer or elimination of HCl from **1b** at the initial stage of the polymerization.

The small broad peak f at 4.1−4.4 ppm is assignable to the methine proton of the chlorine terminal (see above). The end-functionality $\bar{F}_n$ was thereby determined from the NMR peak intensity ratio of the methyl (a) of the **1b** unit to the methine of the terminal end (f). The observed $\bar{F}_n$ (0.92) shows that there is nearly one **1b** moiety per polymer chain; i.e., one polymer forms per **1b** molecule (see Figure 2C). The nearly quantitative attachment of the CEVE unit (or **1b**) shows that a variety of end-functionalized poly(pClSt) may be synthesized with HCl−vinyl ether adducts containing an ester or a phthalimide group, etc. as in the polymerization of vinyl ethers.

Regardless of initiator, poly(pClSt) by **1**/$SnCl_4$/$n$$Bu_4NCl$ has the chlorine end group, and no resonance was detected for other possible end groups such as an indan, an olefin, or a methoxide.[20] Polystyrene by **1**/$SnCl_4$/$n$$Bu_4NCl$[11b,14] and poly(pClSt) by Kennedy's system[16] also have a similar chlorine end group.

In conclusion, we have demonstrated that the living cationic polymerization of pClSt can be induced with **1**/$SnCl_4$/$n$$Bu_4NCl$ even at room temperature. The HCl−vinyl ether adduct **1b** also gave living polymers with narrow MWDs, which are a kind of end-functionalized polymers. A variety of vinyl ethers would lead to end-functionalized poly(pClSt).

Experimental Section

Materials. p-Chlorostyrene (Hokko Chemical), p-(chloromethyl)styrene (Hokko Chemical), and bromobenzene (Aldrich; internal standard for gas chromatography) were of commercial sources and purified by double distillation over calcium hydride under reduced pressure. Commercial **1a** and $SnCl_4$ were distilled twice over phosphorus pentoxide under reduced pressure. The HCl−CEVE adduct (**1b**) was prepared as reported previously.[12] These materials were sealed into brown ampules under dry nitrogen and stored in a freezer; gas chromatographic purity (except for $SnCl_4$) > 99%. $n$$Bu_4NCl$ (Tokyo Kasei, purity > 98%) was used without further purification after drying in vacuo. Methylene chloride (polymerization solvent) was washed by the usual methods and distilled over calcium hydride at least twice before use.

Preparation of *p*-(Acetoxymethyl)styrene (pAcOMS). A 500-mL three-necked round bottom flask equipped with a mechanical stirrer was charged with anhydrous sodium acetate (117.6 g, 1.43 mol), n-tetrabutylammonium iodide (1.0 g, 2.71 mmol), and 150 mL of DMF. To this suspension was added pCMS (100 mL, 0.598 mol) using a syringe, then this mixture was stirred for 13 h at 50 °C. The reaction mixture was poured into 300 mL of water and was extracted with 150 mL of diethyl ether three times. After the combined ether solution was washed with water three times, it was dried over Na_2SO_4 overnight, and the ether was removed. The crude product was purified by double distillation over calcium hydride under reduced pressure to give pure pAcOMS as a colorless oil; the monomer was identified by ^{1}H NMR ($CDCl_3$).

Polymerization Procedures. Polymerization was carried out under dry nitrogen in a baked glass tube equipped with a three-way stopcock. The reaction was initiated by adding a solution of $SnCl_4$ in CH_2Cl_2 (0.50 mL) to a mixture (4.50 mL) of a monomer, **1**, $n$$Bu_4NCl$, and bromobenzene in the same solvent and was quenched with prechilled methanol (2 mL) containing a small amount of ammonia. Conversion was determined from the residual concentration of pClSt by gas chromatography with bromobenzene as an internal standard. The quenched reaction mixtures were washed with 2% hydrochloric acid and then with deionized water to remove the tin-containing residues, evaporated to dryness under reduced pressure, and dried in vacuo overnight to give the product polymers.

In a typical polymerization, pClSt (0.64 mL), **1a** (0.50 mL of a 200 mM CH_2Cl_2 solution), bromobenzene (0.17 mL), and $n$$Bu_4NCl$ (0.40 mL of a 500 mM CH_2Cl_2 solution) were added to 2.79 mL of CH_2Cl_2. The reaction was initiated by adding 0.5 mL of an $SnCl_4$ solution (1.0 M in CH_2Cl_2). The reaction was quenched with prechilled methanol (2 mL) containing a small amount of ammonia. The quenched reaction mixtures were diluted with toluene to 20−30 mL, and it was washed sequentially with 2% hydrochloric acid three times, aqueous 1% sodium hydroxide solution once, and deionized water three times. After the solvents were removed by evaporation under reduced pressure, the polymers were dried under vacuum overnight.

Measurements. The MWDs of polymers were measured by size-exclusion chromatography (SEC) in chloroform on three polystyrene gel columns (Shodex K-802, K-803, and K-804) that were connected to a Jasco 880-PU pump and a Jasco 830-RI refractive index detector. The same chromatograph was employed to determine the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratio of the polymers on the basis of a polystyrene calibration (10 standard samples in the molecular weight range from 10^2 to 3×10^5). ^{1}H NMR spectra of the polymers were recorded at 270 MHz in $CDCl_3$ at 25 °C on a JEOL JNM-GSX 270 spectrometer. The $\bar{M}_n$ was also determined from ^{1}H NMR peak intensity ratio of the aromatic protons of the pClSt units to the methine proton adjacent to the terminal chlorine (see the text).

References and Notes

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(19) The polymerization rate followed the order of the Lewis acidity of two tin halides. A similar trend was observed with polymerization of isobutyl vinyl ether (IBVE) using the IBVE−HCl adduct/Lewis acid initiating system. Kamigaito, M.; Maeda, Y.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 1643.

(20) The polymerization reactions were terminated with methanol containing a small amount of ammonia.

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