Macromolecules **1994,** *27,* 1093-1098

End-Functionalized Polymers of Styrene and *p*-Methylstyrene by Living Cationic Polymerization with Functionalized Initiators[1]

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Received September 20, 1993; Revised Manuscript Received November 29, 1993[●]

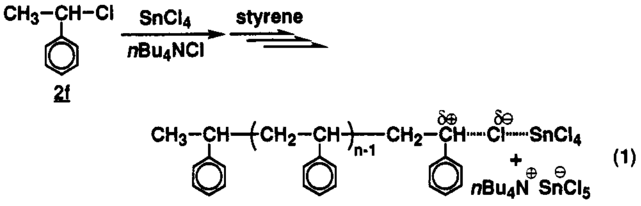
ABSTRACT: A series of α-end-functionalized polymers of styrene and *p*-methylstyrene were synthesized by living cationic polymerizations in CH_2Cl_2 at −15 °C initiated with the HCl adducts [**2**; $CH_3CH(OCH_2CH_2X)Cl$; X = chloride, benzoate, acetate, phthalimide, methacrylate] of vinyl ethers carrying pendant substituents X that serve as the terminal functionalities in the products. When coupled with $SnCl_4$ (activator) in the presence of nBu$_4$NCl, these functionalized initiators (**2**) quantitatively initiated living polymerizations, where the carbon–chlorine bond of **2** was activated by $SnCl_4$. The number-average molecular weights ($\bar{M}_n$) of the polymers increased in direct proportion to monomer conversion, and the molecular weight distributions were narrow ($\bar{M}_w/\bar{M}_n < 1.2$). ^{1}H NMR analysis showed all the polymers to possess controlled molecular weights ($\overline{DP}_n = [M]_0/[\mathbf{2}]_0$) and end functionalities close to unity (i.e., $\bar{F}_n \cong 1$; one terminal functionality X per chain).

Introduction

Polymers with terminal functional groups, or "end-functionalized polymers", may be synthesized most effectively by living polymerizations via initiators that carry functionalities to be incorporated into the polymer terminals (as head or α-end groups). In addition to the classical examples in anionic living processes, this "functionalized initiator method" is equally available in recently developed living cationic polymerizations of vinyl monomers. However, the monomers currently applicable to these cationic syntheses are confined to vinyl ethers, isobutylene, and alkoxystyrenes, most of which possess electron-donating substituents and, accordingly, are relatively reactive or form stable growing carbocations.[2] For example, a series of end-functionalized polymers of vinyl ethers[3] and *p*-alkoxystyrenes (methoxy and *tert*-butoxy)[4,5] have been obtained with the binary initiating systems consisting of an iodoether-type initiator (adducts of hydrogen iodide and vinyl ethers) and a mild Lewis acid (as activator or coinitiator) such as zinc iodide.

The synthesis via the initiating systems established for vinyl ethers, however, cannot directly be extended to styrene and *p*-alkylstyrenes, which are far less reactive in cationic polymerization and give much less stable growing cations than do vinyl ethers and *p*-alkoxystyrenes. In most cases these initiating systems are simply ineffective for polymerizing styrene and its alkyl derivatives, or in other cases the initiator/activator concentrations to effect their polymerizations are so high that the extreme reaction conditions render the produced polymers poorly controlled. It is therefore readily understood that relatively few end-functionalized polymers have been available thus far for these less reactive vinyl monomers in cationic polymerization.

Despite the paucity of end-functionalized polymer synthesis, on the other hand, we have recently achieved the living cationic polymerizations of styrene,[6] α-methylstyrene,[7] and vinyl ethers[8] by employing stronger Lewis acids as activators, such as tin tetrachloride and tetrabromide. The living cationic polymerization of styrene, for example, can be effected in a polar solvent (methylene chloride) by an initiator/activator combination of 1-phenylethyl chloride and tin tetrachloride (eq 1); another key to this process is the simultaneous use of an added halide salt, typically, tetra-*n*-butylammonium chloride (nBu$_4$NCl), that is considered to suppress the dissociation of the growing carbocation. This finding suggests that the favorable factors for the living styrene polymerization may be the uses of an alkyl chloride-type initiator, a strong Lewis acid activator, an externally added halide salt, and a polar polymerization solvent.



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This study is to apply this proposition to the synthesis of end-functionalized polymers of styrene and *p*-methylstyrene (*p*MeSt). Namely, as illustrated in Scheme 1, we employed a series of adducts (**2a**–**2e**) of hydrogen chloride with vinyl ethers (**1a**–**1e**, respectively) as the alkyl chloride (or chloroether) type initiators to be coupled with a strong Lewis acid (tin tetrachloride; $SnCl_4$) and an externally added salt (nBu$_4$NCl) in CH_2Cl_2 solvent. To introduce α-end functional groups (see products **4**; R = H), the initiators **2a**–**2e** are accordingly designed to carry pendant functionalities (X) derived from the vinyl ether precursors (**1a**–**1e**). The functional groups X include chloroethyl (**2a**), carboxylate esters (**2b** and **2c**), phthalimide (**2d**), and methacrylate (**2e**). As readily seen, the alkyl chloride in **2a** provides a versatile starting point for further functional group transformations; the esters and the imide in **2b**–**2d** can be converted afterward into a hydroxy (alcohol) and an alkylamine, respectively; and the unsaturated ester in **2e** is for macromonomers (**4e**) polymerizable by radical and anionic mechanisms.

A spin-off of this study was that the **2**/$SnCl_4$ initiating systems with nBu$_4$NCl turned out to induce living cationic polymerization of *p*MeSt that is better controlled than those previously developed, in terms of molecular weight control and the narrowness in molecular weight distri-

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[●] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

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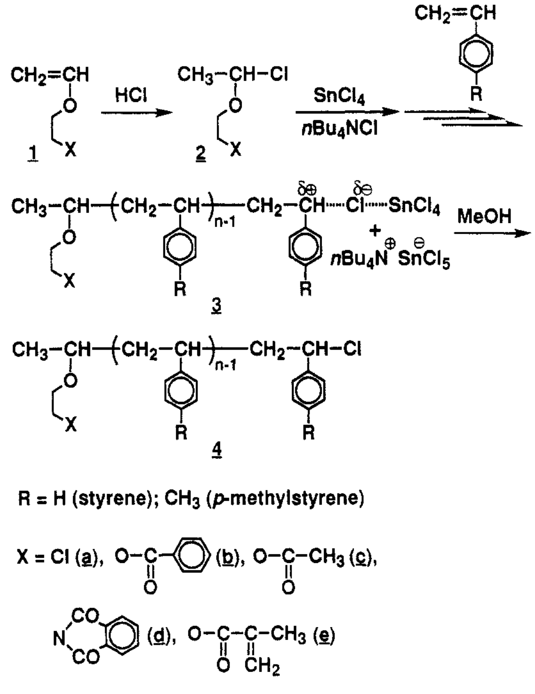
Scheme 1



butions (MWDs). These systems thus led to another series of end-functionalized polymers of an alkylstyrene (**4a**–**4e**; R = CH_3).

Results and Discussion

1. End-Functionalized Polystyrene. 1-1. Living Cationic Polymerization. As illustrated in Scheme 1, a series of end-functionalized polystyrenes (**4a**–**4e**; R = H) were prepared with the use of functionalized initiators (**2a**–**2e**), which were the adducts of hydrogen chloride with vinyl ethers (**1a**–**1e**) carrying functional pendant groups X. The polymerizations were carried out in CH_2Cl_2 at −15 °C with these initiators (**2**) in conjunction with $SnCl_4$ in the presence of $n\mathrm{Bu}_4\mathrm{NCl}$. As will be shown later, preliminary experiments revealed that $SnCl_4$ should be added last to a mixture of styrene, initiator **2**, and $n\mathrm{Bu}_4\mathrm{NCl}$ at −78 °C, immediately followed by warming the solution to −15 °C. If the mixing was carried out at −15 °C, living polystyrene still forms, but its end functionality is below unity. Accordingly, unless otherwise specified, all the experiments were carried out via the "low temperature mixing" procedures.

Figure 1 shows the representative time–conversion curves for the polymerizations with the **2**/$SnCl_4$/$n\mathrm{Bu}_4\mathrm{NCl}$ systems. First, the polymerization with **2a** (X = Cl) (open triangles in Figure 1) was compared with the previously reported living process with 1-phenylethyl chloride (**2f**; filled triangles) under the same conditions ($[\mathrm{M}]_0/[\mathbf{2}]_0/[\mathrm{SnCl}_4]_0/[n\mathrm{Bu}_4\mathrm{NCl}]_0$ = 1000/20/100/40 mM).[6] The initiating system with **2a** induced a quantitative polymerization without an induction phase, where the overall rate was almost identical to that with **2f**. Although these reactions were carried out at rather high concentrations of $SnCl_4$ and $n\mathrm{Bu}_4\mathrm{NCl}$, which would not be practical and might cause undesirable reactions, it was also found that the polymerization with **2a** is possible at low concentrations (open circles), where the overall rate was reduced accordingly. On the other hand, at the identical reagent concentrations, the reaction rate was virtually independent of the functional groups X of the initiators, as indicated by the results for **2a** and **2b** (open and filled circles, respectively). These facts are consistent with the polymerization pathway shown in Scheme 1. Namely, once the initiation has been completed, all the initiating systems should lead to the identical growing active sites, regardless of the structure of the initiators. For all initiating systems, the polymerizations were first order with respect to monomer, as evidenced by linear plots of the logarithmic conversion data $\log([\mathrm{M}]_0/[\mathrm{M}]_t)$ against time t, where $[\mathrm{M}]_t$ and $[\mathrm{M}]_0$ are the monomer concentrations at time t and 0.

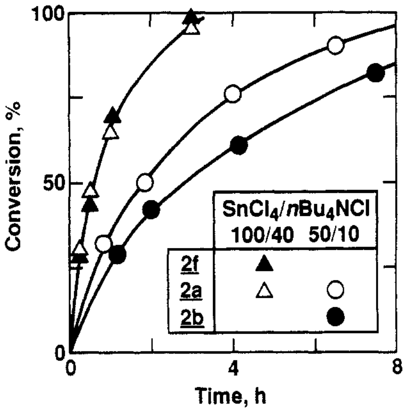


Figure 1. Polymerization of styrene by **2**/$SnCl_4$/$n\mathrm{Bu}_4\mathrm{NCl}$ in CH_2Cl_2 at −15 °C: $[\mathrm{M}]_0$ = 1.0 M; $[\mathbf{2}]_0$ = 20 mM; $[\mathrm{SnCl}_4]_0/[n\mathrm{Bu}_4\mathrm{NCl}]_0$ = 100/40 [(▲) with **2f** (PhEtCl); (△) with **2a** (X = Cl)], 50/10 [(○) with **2a** (X = Cl); (●) with **2b** (X = benzoate)] mM. See the inset table.

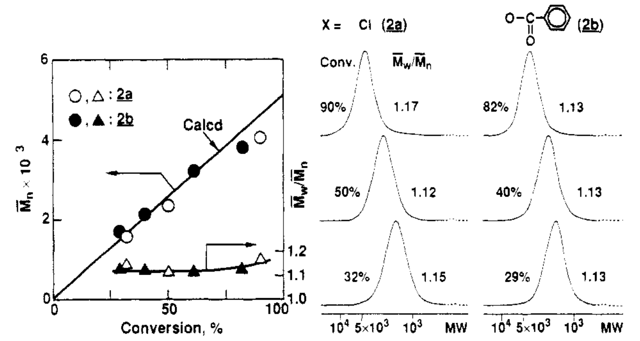


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of polystyrenes obtained with **2**/$SnCl_4$/$n\mathrm{Bu}_4\mathrm{NCl}$ in CH_2Cl_2 at −15 °C: $[\mathrm{M}]_0$ = 1.0 M; $[\mathbf{2}]_0$ = 20 mM; $[\mathrm{SnCl}_4]_0$ = 50 mM; $[n\mathrm{Bu}_4\mathrm{NCl}]_0$ = 10 mM. Initiator: **2a** (X = Cl) (○, △); **2b** (X = benzoate) (●, ▲). Line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **2** molecule.

Figure 2 shows the number-average molecular weights ($\bar{M}_n$) and the MWDs of the polymers thus obtained with the **2**/$SnCl_4$ systems. The $\bar{M}_n$ increased in direct proportion to monomer conversion and agreed with the calculated values assuming that one polymer chain forms per molecule of the initiator. The MWDs stayed narrow throughout the reactions ($\bar{M}_w/\bar{M}_n < 1.2$). These results indicate that the vinyl ether adducts in conjunction with $SnCl_4$ and $n\mathrm{Bu}_4\mathrm{NCl}$ lead to living cationic polymerization of styrene. However, small amounts of oligomers (MW ~ 300; the dashed lines in the MWD curves) were formed during the early stages of the polymerizations. On the analogy of the αMeSt polymerization with **2**/$SnBr_4$,[7] they are probably the oligomers with an indanyl ring that are formed after two styrene units have been attached to **2** during the very early stages of the propagation.

Figure 3 shows the MWDs of the polymers obtained with **2a**–**2e**/$SnCl_4$/$n\mathrm{Bu}_4\mathrm{NCl}$ at 30–50% conversion of styrene, which demonstrate that not only **2a** and **2b** but also the other HCl adducts of functionalized vinyl ethers (**2c**–**2e**; X = acetate, phthalimide, methacrylate) also give

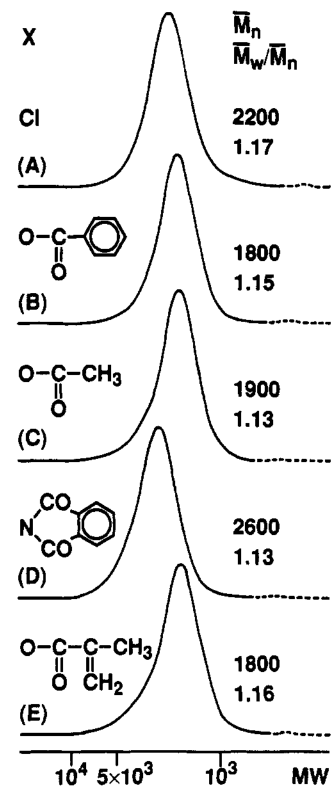


Figure 3. MWD curves of end-functionalized polystyrenes obtained with $2/SnCl_4/nBu_4NCl$ in CH_2Cl_2 at -15 °C: $[M]_0 = 1.0$ M; $[2]_0 = 20$ mM; $[SnCl_4]_0 = 50$ mM; $[nBu_4NCl]_0 = 10$ mM. Conversion = 30–50%.

polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.2$). Thus, living polystyrenes are obtainable with the $2/SnCl_4/nBu_4NCl$ initiating system, despite the polar functional group X therein.

1-2. End-Group Analysis. The end-group structure of the polymers thus obtained was then determined by ^{1}H NMR spectroscopy. All the samples for ^{1}H NMR analysis were fractionated by preparative size-exclusion chromatography to be free from the low molecular weight products (the dashed lines in Figure 3). For example, Figure 4A shows the ^{1}H NMR spectrum of a typical sample of the end-functionalized polystyrene obtained with the **2a** (X = Cl)/$SnCl_4/nBu_4NCl$ initiating system. The spectrum exhibits all key absorptions of the polystyrene main chain (*e*–*g*), the chloroethyl group of the initiator fragment (*a*–*d*), and the chlorinated terminal (*h*) that is originated from the chlorine in the initiator, $SnCl_4$, or nBu_4NCl.[9]

The number-average degree of polymerization ($\overline{DP}_n$) of the polymers obtained with **2a** was determined from the peak intensity ratio of the main-chain phenyl group *g* to the ω-end group *h* (*g*/5*h*). As shown in Table 1, the $\overline{DP}_n$ was in good agreement with the calculated value ($\overline{DP}_n = [M]_0 \cdot (\%\ \text{conversion}/100)/[\mathbf{2a}]_0$) which was based on the assumption that one living polymer chain is formed from one molecule of **2a**. The number-average end functionality ($\bar{F}_n$) of the terminal (α-end) chloroethyl group, also determined from the ^{1}H NMR peak ratio $(c + d)/4h$, was close to unity, indicating the formation of the polystyrene that has almost one chloroethyl group per chain. Similar results were obtained for the polymers prepared with the other initiators **2b**–**2e** (Figures 4B–E; entries 2–5 in Table 1).

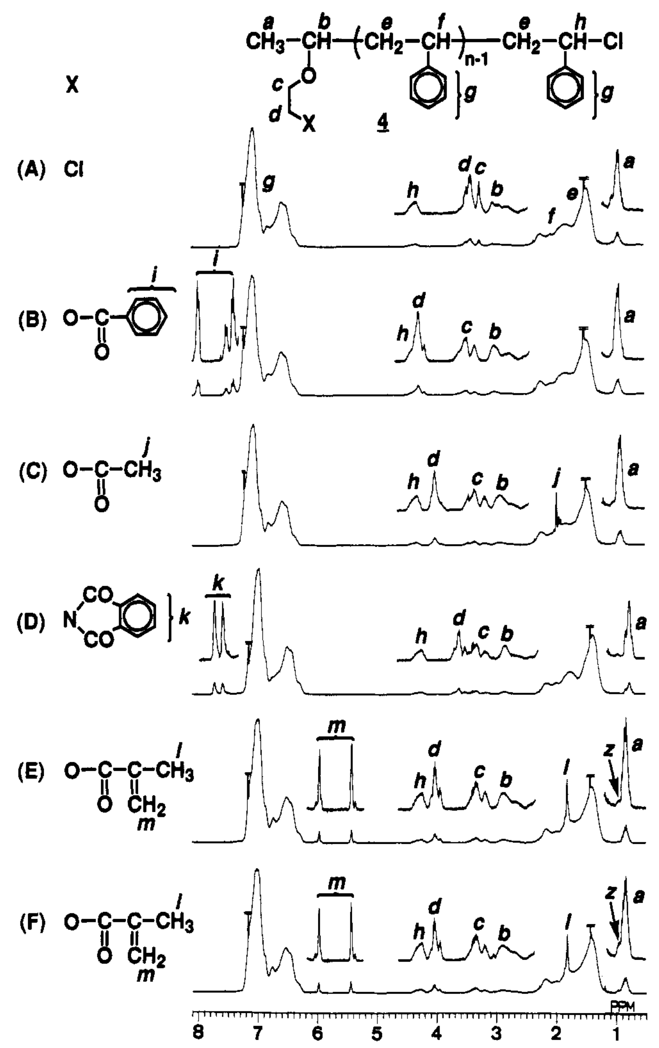


Figure 4. ^{1}H NMR spectra of end-functionalized polystyrenes obtained with $2/SnCl_4/nBu_4NCl$ in CH_2Cl_2 at -15 °C: $[M]_0 = 1.0$ M; $[2]_0 = 20$ mM; $[SnCl_4]_0 = 50$ mM; $[nBu_4NCl]_0 = 10$ mM. Conversion = 30–50%. The sample for spectrum F was obtained without the "low temperature mixing" (see text).

Table 1. Synthesis of End-Functionalized Polystyrene with $2/SnCl_4/nBu_4NCl$[a]

entry	X (initiator)	$\overline{DP}_n$(calcd)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\overline{DP}_n$(obsd)[d]	$\bar{F}_n$[e]
1	chloride (**2a**)	21	2200	1.17	21	0.95
2	benzoate (**2b**)	16	1800	1.15	17	0.93
3	acetate (**2c**)	18	1900	1.13	17	0.86
4	phthalimide (**2d**)	24	2600	1.13	24	1.00
5	methacrylate (**2e**)	18	1800	1.16	18	0.94
6[f]	methacrylate (**2e**)	16	1600	1.12	15	0.77

[a] $[M]_0/[2]_0/[SnCl_4]_0/[nBu_4NCl]_0 = 1000/20/50/10$ mM; in CH_2Cl_2, at -15 °C; mixing $SnCl_4$ with a monomer solution containing **2** and nBu_4NCl was carried out at -78 °C. [b] $([M]_0/[2]_0) \times$ conversion (by gas chromatography). [c] Measured by SEC. [d] Determined from the ^{1}H NMR peak intensity ratio *g*/5*h* (see Figure 4). [e] Determined from the ^{1}H NMR peak intensity ratio of the functional "head" group to the "tail" chloride group; $(c + d)/4h$ (entry 1); $c/2(d + h - c)$ (entry 2); $d/2h$ (entry 3); $k/4h$ (entry 4); $m/2h$ (entries 5 and 6) (see Figure 4). [f] The mixing was carried out at -15 °C; $[M]_0/[2]_0/[SnCl_4]_0/[nBu_4NCl]_0 = 1000/20/100/40$ mM.

Comparison of entries 5 and 6 in Table 1 (initiator **2e**) shows how the temperature for mixing the initiating system and the monomer affects the end functionality (see section 1-1 and above). The sample obtained without the low temperature mixing had apparently a low $\bar{F}_n$ value (entry 6 in Table 1). This means that the sample has an α-end other than the methacrylate. Close inspection of the ^{1}H NMR spectrum (Figure 4F) revealed that there was a small absorption (*z*) near the large α-end methyl signals, *a*; virtually none of such peaks is observed for the sample obtained via the low temperature mixing (entry 5; Figure 4E). The absorption *z* is attributed to the methyl group of the α-end of the polymers [$CH_3CHPh\sim\sim\sim$] initiated

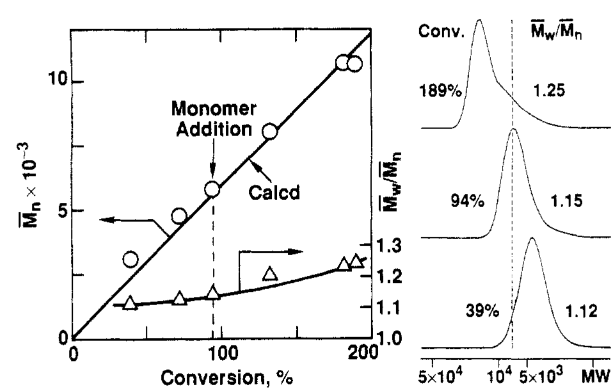


Figure 5. Monomer-addition experiments in the polymerization of *p*MeSt with **2a** (X = Cl)/$SnCl_4$/$n$$Bu_4NCl$ in CH_2Cl_2 at −15 °C: $[M]_0 = [M]_{add}$ = 1.0 M; $[\mathbf{2a}]_0$ = 20 mM; $[SnCl_4]_0$ = 25 mM; $[nBu_4NCl]_0$ = 20 mM. Line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **2a** molecule.

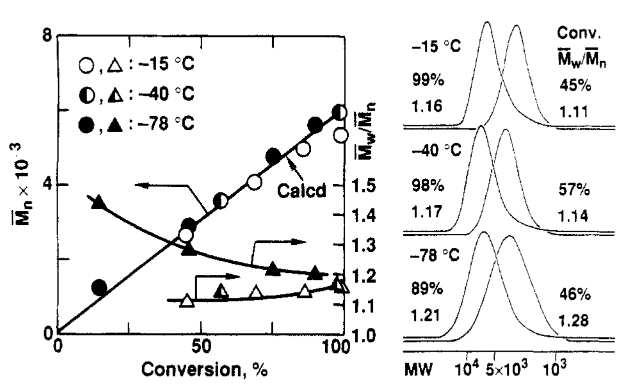


Figure 6. Effects of temperature on the polymerization of *p*MeSt with **2a**/$SnCl_4$/$n$$Bu_4NCl$ in CH_2Cl_2: $[M]_0$ = 1.0 M; $[\mathbf{2a}]_0$ = 20 mM; $[SnCl_4]_0$ = 25 mM; $[nBu_4NCl]_0$ = 20 mM. Temperature: −15 °C (○, △); −40 °C (◐, ▲); −78 °C; (●, ▲). Line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **2a** molecule.

by protons, generated along with the formation of the low molecular weight oligomers during the early stages of the polymerization (see above). The amount of the oligomers was in fact higher in the products obtained without the low temperature mixing. If the proton transfer, another possibility to give the protonated α-end, occurred throughout the polymerization, ω-ends of polymers other than the chloride would arise, and thus the peak intensity ratio of the α-ends ($a + z$) to the ω-end (the chloride h) must be larger than 3. However, other ω-ends are not observed, and the α/ω end-group ratio value is 3.09, close to 3, for the sample of Figure 4F. The methyl protons z were observed even for the samples via the low temperature mixing (Figures 4A–E), but the amounts were quite small, which corresponds to the much smaller amount of the low molecular weight oligomers.

Thus, the vinyl ether-based initiators **2a**–**2e** provided a versatile method to synthesize a series of end-functionalized polystyrenes (Scheme 1).

2. End-Functionalized Poly(*p*-methylstyrene).

2-1. Living Cationic Polymerization. Prompted by the efficient initiation of the living polymerizations of styrene by the vinyl ether-based initiating systems (**2**/$SnCl_4$/$n$$Bu_4NCl$), we extended this finding to the synthesis of end-functionalized poly(*p*MeSt) (Scheme 1, R = CH_3). To determine the feasibility of the synthesis, *p*MeSt was polymerized with **2a**/$SnCl_4$/$n$$Bu_4NCl$ in CH_2Cl_2 at −15 °C ($[M]_0/[\mathbf{2a}]_0/[SnCl_4]_0/[nBu_4NCl]_0$ = 1000/20/25/20 mM). As with styrene, the polymerization was initiated by the initial mixing of $SnCl_4$ with a monomer solution containing **2** and $n$$Bu_4NCl$ at −78 °C and then immediately raising the temperature to −15 °C. Monomer consumption occurred smoothly without an induction phase and was complete in 15 min. The overall polymerization rate was much larger than that of styrene at the same reagent concentrations. As shown in Figure 5, the $\bar{M}_n$'s of the polymers were directly proportional to monomer conversion and in good agreement with the calculated values, assuming that one polymer chain forms per **2a** molecule, though they were based on a polystyrene calibration.

To demonstrate further the living nature of the polymerization, a fresh feed of monomer was added to the reaction mixture just before the initial charge of the monomer was consumed. The $\bar{M}_n$ further increased in direct proportion to monomer conversion and agreed with the calculated value. The MWDs were narrow throughout the reaction, particularly in the first-phase polymerization where the $\bar{M}_w/\bar{M}_n$ ratios were 1.1–1.15, though they became broader after the monomer addition ($\bar{M}_w/\bar{M}_n \sim 1.3$). These results indicate that **2a**/$SnCl_4$/$n$$Bu_4NCl$ also induces living cationic polymerization of *p*MeSt. Equally important, the poly(*p*MeSt) thus obtained had narrower MWDs than those previously reported.[10–12]

According to a separate series of experiments, where the initial molar ratio of monomer to initiator was varied ($[M]_0/[\mathbf{2a}]_0$ = 50–200) while the concentrations of $SnCl_4$ and $n$$Bu_4NCl$ were constant, poly(*p*MeSt) with controlled molecular weights and narrow MWDs ($\bar{M}_w/\bar{M}_n \leq 1.2$) can be obtained with initiator **2a**.

The effects of polymerization temperature were also investigated to optimize the reaction conditions (Figure 6). The polymerization with **2a**/$SnCl_4$ in the presence of $n$$Bu_4NCl$ occurred quantitatively in the temperature range −15 to −78 °C, and the rate was smaller at lower temperatures [time for 90% conversion: 8 min (−15 °C); 15 min (−40 °C); 40 min (−78 °C)]. The $\bar{M}_n$ values of the polymers were in good agreement with the calculated values irrespective of the temperature. The MWDs of the polymers obtained at −40 °C were as narrow as those at −15 °C ($\bar{M}_w/\bar{M}_n \sim 1.15$). At −78 °C, however, this system gave broader MWDs, but they became narrower as the polymerization proceeded. Thus, the broadening in MWD is not due to chain transfer but due to the slower interconversion between the dormant and activated species.[6,8] Lowering temperature is, therefore, not adequate for the synthesis of poly(*p*MeSt) with narrow MWDs, and we decided to investigate the synthesis of end-functionalized poly(*p*MeSt) with the **2**/$SnCl_4$/Bu_4NCl initiating systems at −15 °C.

2-2. Polymerizations with Functional Initiators. A series of the HCl adducts of functionalized vinyl ether (**2a**, **2c**–**2e**) were employed for the *p*MeSt polymerization coupled with $SnCl_4$ and $n$$Bu_4NCl$ in CH_2Cl_2 at −15 °C. As shown in Figure 7A, all of the initiating systems induced quantitative polymerization, though the acetate-type initiator **2c** gave a rate smaller than did the other initiators, for which the rates were virtually independent of the pendant functionalities X.[13] For all of the initiating systems, the $\bar{M}_n$ values increased in direct proportion to monomer conversion and agreed with the calculated values (Figure 7B). The MWDs stayed narrow throughout the reactions ($\bar{M}_w/\bar{M}_n < 1.2$). These results indicate that the **2**/$SnCl_4$/$n$$Bu_4NCl$ initiating systems induce the living cationic polymerizations of not only styrene and but also *p*MeSt.

2-3. End-Group Analysis. Figure 8 shows the ^{1}H NMR spectra of the polymers obtained with **2**/$SnCl_4$/$n$$Bu_4NCl$ at 40–60% monomer conversions. For example, a typical spectrum of the polymers obtained with **2a** (X =

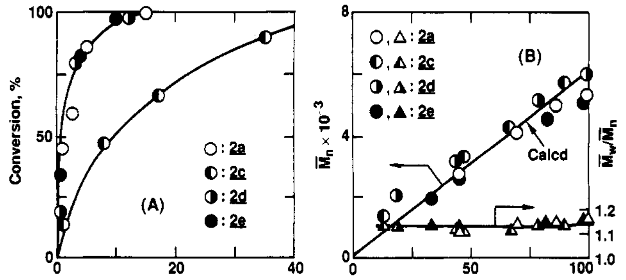


Figure 7. Polymerization of *p*MeSt with the functional initiating systems in CH_2Cl_2 at −15 °C: $[M]_0$ = 1.0 M; $[2]_0$ = 20 mM; $[SnCl_4]_0$ = 25 mM; $[nBu_4NCl]_0$ = 20 mM. **2a** (X = Cl) (○, △); **2c** (X = acetate) (◐, △); **2d** (X = phthalimide) (◑, △); **2e** (X = methacrylate) (●, ▲). Line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per **2** molecule.

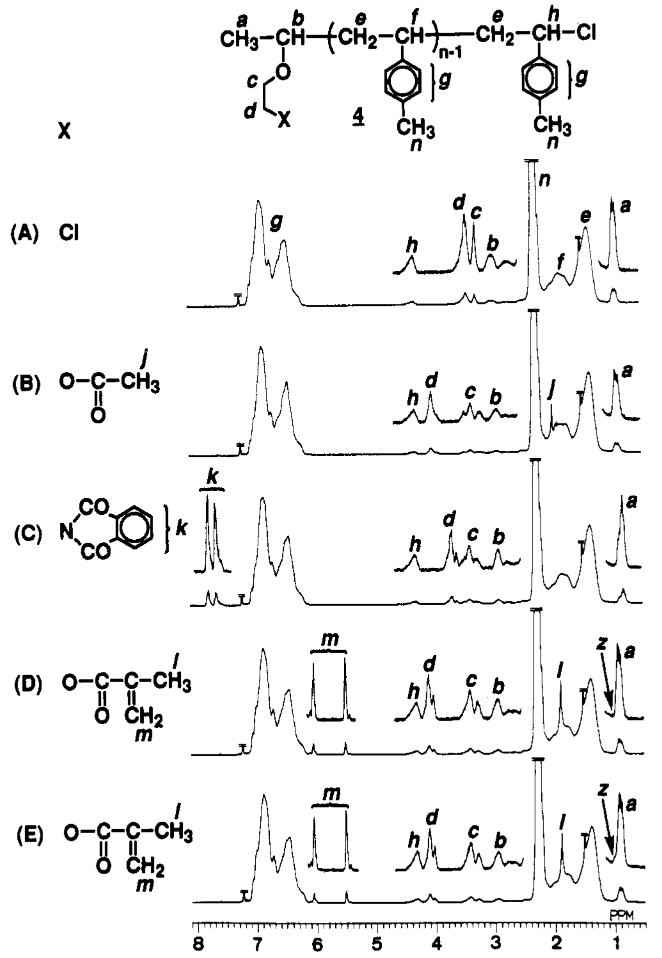


Figure 8. ^1H NMR spectra of end-functionalized poly(*p*MeSt)s obtained with $2/SnCl_4/nBu_4NCl$ in CH_2Cl_2 at −15 °C; $[M]_0$ = 1.0 M; $[2]_0$ = 20 mM; $[SnCl_4]_0$ = 25 mM; $[nBu_4NCl]_0$ = 20 mM. Conversion = 40–60%. The sample for spectrum E was obtained without the "low temperature mixing" (see text).

Cl) is given in Figure 8A. Analogously to the end-functionalized polystyrenes (Figure 4A), all key absorptions are seen; the poly(*p*MeSt) main chain (*e*–*g*, *n*), the chloroethyl group of the initiator fragment (*a*–*d*), and the chlorinated terminal (*h*). Despite the quenching with methanol, the ω-end was the chloride as in the corresponding polystyrenes. The ratio of the "tail" methine protons *h* to the main-chain phenyl groups *g* (*g*/4*h*) gave the observed $\overline{DP}_n$, which proved almost equal to the value calculated from the *p*MeSt/**2a** feed ratio (entry 1 in Table 2). The $\bar{F}_n$, obtained from the ratio of the "head" chloroethyl protons *c* + *d* to the "tail" methine protons *h* [(*c* + *d*)/4*h*], was very close to unity, confirming the near quantitative attachement of the functional group X to the α-end.

Table 2. Synthesis of End-Functionalized Poly(*p*-methylstyrene) with $2/SnCl_4/nBu_4NCl$[a]

entry	X (initiator)	$\overline{DP}_n$(calcd)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\overline{DP}_n$(obsd)[d]	$\bar{F}_n$[e]
1	chloride (**2a**)	26	2700	1.18	24	1.01
2	acetate (**2c**)	31	3800	1.14	33	0.92
3	phthalimide (**2d**)	29	3100	1.13	27	0.98
4	methacrylate (**2e**)	24	2800	1.14	23	0.97
5[f]	methacrylate (**2e**)	20	2600	1.13	22	0.89

[a] $[M]_0/[2]_0/[SnCl_4]_0/[nBu_4NCl]_0$ = 1000/20/25/20 mM; in CH_2Cl_2, at −15 °C; mixing $SnCl_4$ with a monomer solution containing **2** and nBu_4NCl was carried out at −78 °C. [b] ($[M]_0/[2]_0$) × conversion (by gas chromatography). [c] Measured by SEC. [d] Determined from the ^1H NMR peak intensity ratio *g*/4*h* (see Figure 8). [e] Determined from the ^1H NMR peak intensity ratio of the functional "head" group to the "tail" chloride group; (*c* + *d*)/4*h* (entry 1); *d*/2*h* (entry 2); *k*/4*h* (entry 3); *m*/2*h* (entries 4 and 5) (see Figure 8). [f] The mixing was carried out at −15 °C.

Similar results were obtained for the polymers prepared with the functional initiators (**2c**–**2e**) with other functional groups (Figure 8B–D; Table 2, entries 2–4).

The sample of Figure 8E (entry 5 in Table 2), which was obtained without being cooled at −78 °C on mixing $SnCl_4$ with a monomer solution, shows an $\bar{F}_n$ lower than that of the sample via such a low temperature mixing (Figure 8D and entry 4). The low $\bar{F}_n$ was due to the existence of small amounts of the proton-initiated polymers that possess a $CH_3CH(pMePh)$∼∼∼ group (peak *z*) at the α-end. In contrast, the signals *z* were too small to be seen in the sample with the $\bar{F}_n$ very close to unity (Figure 8D). These results indicate that the mixing should be carried out at −78 °C also for the better-controlled synthesis of end-functionalized poly(*p*MeSt).

In conclusion, well-defined α-end-functionalized polystyrenes and poly(*p*MeSt)s were synthesized with the initiating systems that consist of the HCl adduct of functional vinyl ethers (**2**), $SnCl_4$, and nBu_4NCl in CH_2Cl_2 at −15 °C. The success in the synthesis is due to the fact that (1) a combination of HCl, $SnCl_4$, and nBu_4NCl is effective in living cationic polymerizations of styrene and *p*MeSt as well as vinyl ethers[6,8] and (2) the C–Cl bond of the HCl adducts of vinyl ethers (initiator) is more reactive than that of the growing terminals of polystyrene and poly(*p*MeSt), which permits a quantitative and fast initiation and, in turn, a narrow MWD. The α-end functional groups included esters (protected hydroxyl), phthalimide (protected amine), and methacrylate (for macromonomers).

Experimental Section

Materials. Styrene (Wako Chemicals; purity >98%), *p*-methylstyrene (Tokyo Kasei; purity >95%), and 2-chloroethyl vinyl ether (CEVE; **1a**) (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 under reduced pressure over calcium hydride before use. The functionalized vinyl ethers for the initiator synthesis, 2-(benzoyloxy)ethyl vinyl ether (**1b**),[14] 2-acetoxyethyl vinyl ether (**1c**),[15] [2-(vinyloxy)ethyl]phthalimide (**1d**),[16] and 2-(vinyloxy)ethyl methacrylate (**1e**),[17] were prepared by the reactions of CEVE with sodium benzoate, sodium acetate, potassium phthalimide, and sodium methacrylate, respectively. $SnCl_4$ (Aldrich, 1.0 M solution in CH_2Cl_2) and nBu_4NCl (Tokyo Kasei; purity >98%) 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), phenyl bromide, and tetralin (the internal standards for gas chromatography) were purified by the usual methods and distilled over calcium hydride before use.[6] 1-Phenylethyl chloride (**2f**; Wako Chemicals; purity >97%) was distilled twice under reduced pressure.

Synthesis of HCl-Vinyl Ether Adducts (2a–2e). The HCl–CEVE adduct **2a** was synthesized by bubbling dry HCl gas through a solution of CEVE (in 50 mL of *n*-hexane; 1.00 M) for 30 min at 0 °C.[7,8] The gas was generated by dropping concentrated sulfuric acid into powdery sodium chloride and subsequently 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 **2a** was confirmed by ^{1}H NMR spectroscopy. The solution was sealed into brown ampules under dry nitrogen and stored in a freezer. The concentration of **2a** was determined by titrating the labile chloride in **2a** by the Volhard method; the observed value (1.06 M; calcd 1.00 M) further confirmed the quantitative formation of **2a** from CEVE. The other adducts (**2b**–**2e**) were synthesized by similar methods; specifically for **2d**, however, the solvent for the HCl bubbling was CH_2Cl_2, because the precursor **1d** 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 is given below. The reaction was initiated by adding, via dry syringes, solutions of **2a** (in *n*-hexane; 0.50 mL) and $SnCl_4$ (in methylene chloride; 0.50 mL) sequentially in this order into a mixture (4.0 mL) of styrene (0.58 mL), phenyl bromide (0.12 mL), and nBu$_4$NCl in CH_2Cl_2 at −78 °C. Immediately after the mixing, the tube was placed in the bath kept at −15 °C. The reaction was quenched with prechilled methanol (2 mL). Monomer conversions were determined from the concentrations of residual monomers measured by gas chromatography with phenyl bromide and tetralin (for styrene and *p*MeSt, 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, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ 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 and a Jasco 830-RI refractive index detector. The columns were calibrated against ten standard polystyrene samples ($\bar{M}_n$ = 800–300 000; $\bar{M}_w/\bar{M}_n$ = 1.03–1.10) as well as styrene oligomers (tetramer, trimer, and dimer) and monomer. ^{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 for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

Acknowledgment. With gratitude M.S. acknowledges the partial support of this work by a Grant-in-Aid for Scientific Research (No. 05650898) from the Ministry of Education, Science, and Culture, Japan, and the Tokuyama Science Foundation.

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