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Novel BF_3OEt_2/R−OH Initiating System for Controlled Cationic Polymerization of Styrene in the Presence of Water

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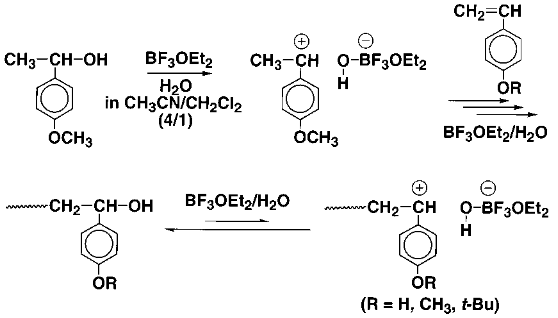
ABSTRACT: A controlled cationic polymerization of styrene was achieved with an alcohol [water−vinyl monomer adduct: $CH_3CR(Ph)OH$; −R = −H (**2**), $-CH_3$ (**3**)] as an initiator coupled with BF_3OEt_2. In the presence of a fairly large amount of water, the polymerization gave polymers with molecular weights that increased in direct proportion to monomer conversion and agreed well with the calculated values, assuming that one initiator molecule generates one polymer chain, although the molecular weight distributions (MWDs) were broad ($M_w/M_n \sim 2$). 2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP) and tetrabutylammounium hydroxide (n-Bu_4NOH) retarded the polymerization and narrowed the MWDs. ^1H NMR and MALDI−TOF−MS analysis supported the polymerization mechanism where BF_3OEt_2 selectively and reversibly activates the terminal C−OH bond derived from the initiator to generate the growing cationic species. Similar controlled polymerizations of *p*-chlorostyrene (pClSt) and *p*-methylstyrene (pMS) were also achieved by the R−OH/BF_3OEt_2 system with a proper ratio of water and DTBMP. This is the first example of a controlled cationic polymerization of styrene via reversible activation of the C−OH bond mediated by BF_3OEt_2 in the presence of water.

Introduction

Boron trifluoride (BF_3) or its etherate (BF_3OEt_2) is one of the representative Lewis acids that are effective in cationic polymerizations of styrene and other monomers.[1,2] In general, Lewis acids play an important role in controlling cationic vinyl polymerization, usually as catalysts (co-initiators) to be coupled with protogens or cationogens as initiators; these initiator/Lewis acid combinations are usually called initiating systems. Rather surprisingly, BF_3OEt_2 or BF_3 has rarely been used, probably due to the lack of suitable initiators. Most of the conventional systems employ adventitious or intentionally added water as an initiator/protogen, and thus the initiation and the propagation processes are ill-defined. However, we have recently found that BF_3OEt_2, coupled with a suitable alcohol [e.g., water−monomer adduct: $CH_3CH(Ph$-p-$OCH_3)OH$], can induce living cationic polymerization of *p*-alkoxystyrenes and even unprotected *p*-hydroxystyrene, both of which possess strong electron-donating groups (eq 1).[3,4] In this living polymerization, BF_3OEt_2 activates the C−OH bond of the adduct to form the initiating cationic species. The subsequent propagation regenerates a similar C−OH bond at the polymer terminal that is reversibly activated by BF_3OEt_2 to dissociate into the growing cation, thus achieving the dormant (covalent)−cation equilibrium as in other living cationic polymerizations.



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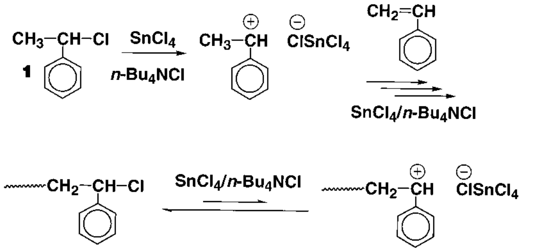
Contrary to the long held belief that cationic polymerization does not proceed in the presence of water, these living polymerizations of alkoxystyrenes proceed even in an aqueous solvent (100 molar excess over BF_3), and it is not necessary to protect the phenolic group in *p*-hydroxystyrene monomer. The reason for the success in such a unique polymerization is that, different from BCl_3 and other halogenated boron compounds, BF_3 is hardly decomposed by water and is a strong oxophilic Lewis acid.[5] Thus, BF_3 can selectively and reversibly activate the C−OH bond at a polymer terminal into a cation, even in the presence of water.

This study extends the scope of our R−OH/BF_3OEt_2 initiating systems to styrene, a common vinyl monomer[6] that lacks a cation-stabilizing, electron-donating substituent. We have already achieved its living cationic polymerization with an initiating system that consists of the hydrogen chloride adduct of styrene (**1**) as an initiator and a strong Lewis acid, $SnCl_4$, as an activator in the presence of tetrabutylammonium chloride (n-Bu_4NCl) (eq 2).[7−12] $SnCl_4$ reversibly activates the dormant C−Cl bond originated from **1**, to generate the cationic species. The added ammonium salt most probably provides the chlorine anion that can interact with $SnCl_4$ or regenerate the dormant C−Cl species via the reaction with the carbocationic growing terminal. Similar polymerizations have been developed with other metal chlorides such as BCl_3,[13] $TiCl_4$,[14,15] and $TiCl_3(Oi$-$Pr)$,[16] again coupled with the dormant C−Cl terminus.



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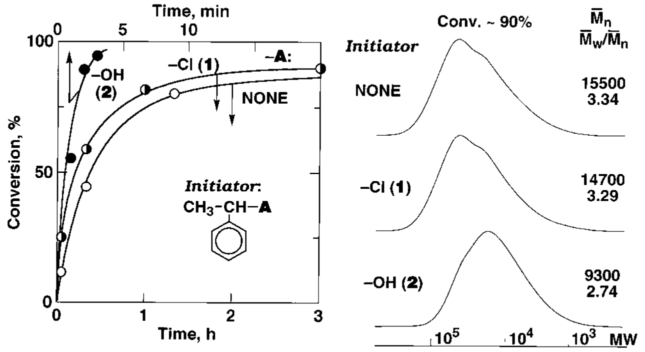
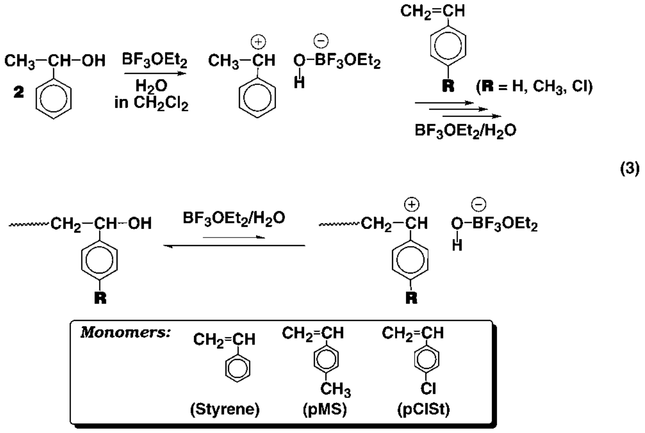


Figure 1. Time–conversion, M_n, and M_w/M_n curves for the polymerization of styrene with BF_3OEt_2 at 0 °C in CH_2Cl_2: $[styrene]_0 = 1.0$ M; $[initiator]_0 = 10$ mM; $[BF_3OEt_2]_0 = 50$ mM. Initiator: (◑) **1**; (●) **2**; (○) none.

These polymerizations should be done in highly purified and anhydrous solvents because the ionic intermediates and the strong Lewis acids are readily decomposed or hydrolyzed by even a trace of water. In addition, the polymers thus obtained possess a halogen at the ω-end, which lowers the thermal stability of the product[17] and generates halogen compounds on decomposition. Polystyrenes obtained even in metal-catalyzed and TEMPO-mediated living radical polymerizations also possess less stable C–halogen[18] and C–ON[19] termini, respectively.

In this paper, we report that the BF_3-based initiating system (R–OH/BF_3OEt_2 + H_2O; eq 3) polymerizes styrene to give polymers with controlled molecular weights and terminal groups. In addition, we investigated the related polymerizations of p-substituted styrene derivatives with an electron-donating p-methyl and a withdrawing p-chloro group.



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Results and Discussion

1. Controlled Polymerization in the Presence of Water. 1-Phenylethyl chloride (**1**) and its alcohol analogue (**2**) were employed as initiators for the cationic polymerization of styrene coupled with BF_3OEt_2 in CH_2Cl_2 at 0 °C (Figure 1). The relatively slow polymerization by BF_3OEt_2 and adventitious water (open circles) was accelerated by addition of **1** (half-filled circles) or **2** (filled circles), where **2** induced a much faster polymerization. The number-average molecular weights (M_n) of the polymers obtained with **2**/BF_3OEt_2 were close to the calculated values assuming that one initiator molecule generates one polymer chain [M_n(calcd) = 9500 at 90% monomer conversion], whereas **1**/BF_3OEt_2 or BF_3OEt_2 alone gave polymers with higher M_n. The molecular weight distributions (MWDs) with **2** were narrower than those with **1** or in the absence of these initiators. Thus, BF_3OEt_2, a highly oxophilic Lewis acid,[5] preferentially activates the C–O bond in **2** to generate cationic species, which result in the fast cationic polymerization of styrene similar to more reactive p-alkoxy- and p-hydroxystyrenes.[3,4]

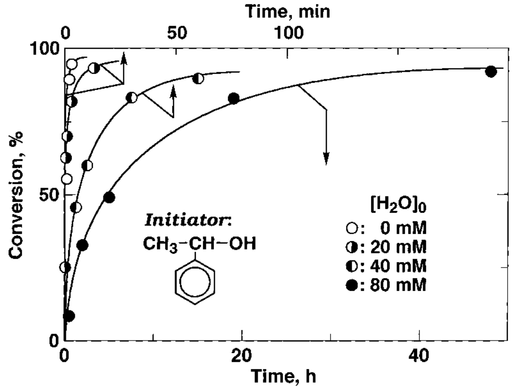


Figure 2. Time–conversion curves for the polymerization of styrene with **2**/BF_3OEt_2 in the presence of water at 0 °C in CH_2Cl_2: $[styrene]_0 = 1.0$ M; $[\mathbf{2}]_0 = 10$ mM; $[BF_3OEt_2]_0 = 50$ mM; $[H_2O]_0 = 0$ (○), 20 (◑), 40 (◐), and 80 (●) mM.

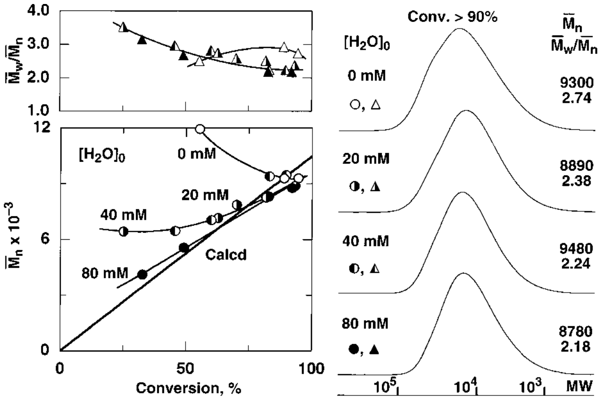


Figure 3. M_n and M_w/M_n curves of the polystyrene obtained with **2**/BF_3OEt_2 in the presence of water at 0 °C in CH_2Cl_2: $[styrene]_0 = 1.0$ M; $[\mathbf{2}]_0 = 10$ mM; $[BF_3OEt_2]_0 = 50$ mM; $[H_2O]_0 = 0$ (○, △), 20 (◑, ▲), 40 (◐, ▲), and 80 (●, ▲) mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **2** molecule.

Water, intentionally added in excess to an initiator, is necessary for the living cationic polymerization of alkoxy- and hydroxystyrenes with BF_3OEt_2.[3,4] The addition of water at varying concentrations (0–80 mM) was also investigated for the styrene polymerization with **2**/BF_3OEt_2 in CH_2Cl_2. At high water concentrations, the reaction mixtures became turbid. However, as shown in Figure 2, the polymerizations actually proceeded, and their rates clearly depended on its concentration: the larger amount of water, the slower the polymerizations.

Figure 3 shows the M_n and MWDs of the polystyrenes thus obtained. In the absence of water, the polymers had broad MWDs (M_w/M_n = 2.5–2.9), whereas the M_n was close to the calculated values at the later stage of the polymerization, indicating a slow initiation or a slow interconversion between the dormant and the active species relative to propagation. As a larger amount of water was added, the M_n of the polymers became closer to the calculated values even from the beginning and

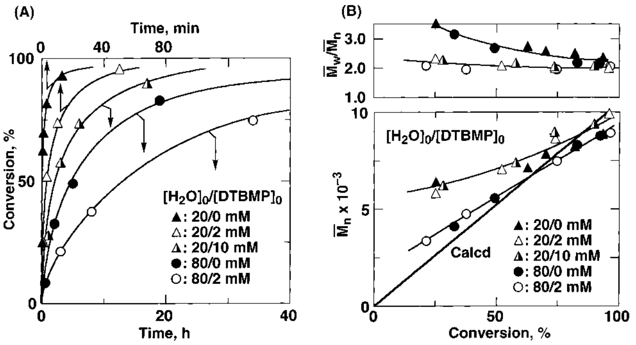


Figure 4. Effects of DTBMP on the polymerization of styrene with **2**/BF_3OEt_2 at 0 °C in CH_2Cl_2 in the presence of water: $[\text{styrene}]_0 = 1.0$ M; $[\mathbf{2}]_0 = 10$ mM; $[BF_3OEt_2]_0 = 50$ mM; $[H_2O]_0 = 20$ (for ▲, ▲, and △) and 80 (for ○ and ●) mM; $[\text{DTBMP}]_0 = 0$ (for ▲ and ●), 2.0 (for △ and ○), and 10 (for ▲). The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **2** molecule.

increased with monomer conversion. In addition, the MWDs became narrower as polymerization proceeded.

These results suggest that the added water accelerates the interconversion of the active (cationic) species into the dormant C−OH species by providing hydroxide anion (see below). Uniquely in the BF_3OEt_2-mediated polymerization, the C−OH terminus thus formed is not dead but dormant due to the highly oxophilic nature of BF_3OEt_2. In contrast, water acts as an irreversible chain transfer agent in usual cationic polymerizations with metal chlorides and strong protonic acids to generate the substantially dead chain end with C−OH terminus, which is difficult to activate in these systems.

Alternatively, the added water may serve as a reversible chain transfer agent in the BF_3OEt_2-mediated polymerization, and the possibility of proton initiation via water cannot fully be excluded. However, water is not a good initiator for the polymerization,[3] as also indicated by the MALDI−TOF−MS analysis of the obtained polymers (see below).

Another feature of BF_3OEt_2 is its tolerance to water, which also contributes to the effects of water in the polymerization. Metal chlorides that are usually employed in cationic polymerization are easily hydrolyzed by water to form proton or hydrogen chloride that can initiate polymerization. However, BF_3OEt_2 is difficult to hydrolyze into fluoroboric acid and thereby preferentially activates the −C−OH bond in the initiator or at the polymer terminal, in comparison to the H−OH bond in water.

2. Effects of a Sterically Hindered Pyridine and a Hydroxide Anion Source. To clarify the role of the added water, we examined the addition of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), which is a proton scavenger and has been used for living cationic polymerization of vinyl monomers to prevent uncontrolled initiation from adventitious water.[9−12,20,21] The effects of DTBMP were then investigated in the styrene polymerization with **2**/BF_3OEt_2 at varying H_2O/DTBMP ratios (Figure 4). The addition of DTBMP remarkably retarded the polymerization, and when the ratio was 20/10 mM, in particular, the reaction mixtures remained transparent throughout the reaction, probably due to the ionization of water into the pyridinium salt that is highly soluble in CH_2Cl_2 (eq 4). Figure 4B shows the M_n and M_w/M_n values of the polymers thus obtained. With even a small amount of DTBMP, the MWDs became narrower than in its absence, whereas the M_n was independent of the concentration of DTBMP.

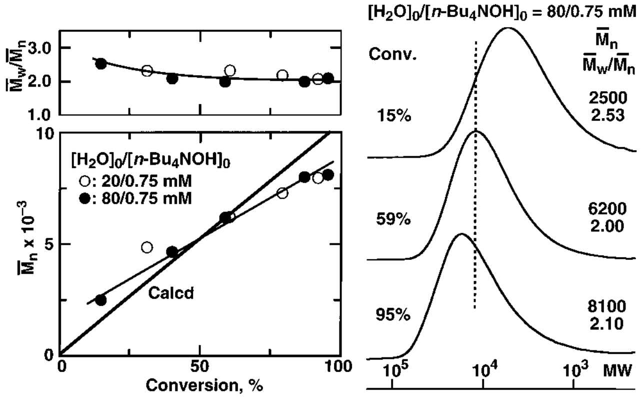
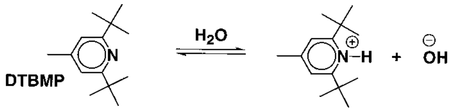


Figure 5. M_n and M_w/M_n curves of the polystyrene obtained with **2**/BF_3OEt_2 in the presence of water and n-Bu_4NOH at 0 °C in CH_2Cl_2: $[\text{styrene}]_0 = 1.0$ M; $[\mathbf{2}]_0 = 10$ mM; $[BF_3OEt_2]_0 = 50$ mM; $[H_2O]_0 = 20$ (○) or 80 (●) mM, $[n\text{-}Bu_4NOH]_0 = 0.75$ mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **2** molecule.



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These results again show that the added water serves as a reservoir of hydroxide anion that may decrease the concentration of the growing cationic species similar to n-Bu_4NCl in the R−Cl/$SnCl_4$-mediated living cationic polymerization of styrene in CH_2Cl_2.[7,8] This was also supported by the decrease of polymerization rate by addition of water and further by DTBMP as described above. In particular, the sterically hindered pyridine increases the concentration of hydroxide anion, which results in faster deactivation of the cationic species into the dormant species and then narrower MWDs.

We further examined addition of a potentially more effective and direct hydroxide anion source, n-Bu_4NOH. The ammonium salt can act in just the same way as n-Bu_4NCl in the R−Cl/$SnCl_4$-mediated living cationic polymerization[7,8] because both salts generate common anions in each polymerization. Water was also added as a solvent for n-Bu_4NOH. As shown in Figure 5, the addition of n-Bu_4NOH indeed narrowed the MWDs ($M_w/M_n \sim 2.0$), as with DTBMP. As the polymerization proceeded, the size-exclusion chromatography (SEC) curves shifted to high molecular weights and the M_n increased. Thus, R−OH/BF_3OEt_2-mediated cationic polymerization can be controlled by the increase of the concentration of hydroxide anion

3. Initiation Mechanism. The choice of initiators is one of the most important keys to the living cationic polymerization of vinyl monomers.[10−12] We herein employed α-cumyl alcohol (**3**: the water adduct of α-methylstyrene) as an initiator, in place of the water−styrene adduct (**2**), for the long-lived cationic polymerization of styrene with BF_3OEt_2. Styrene was then polymerized with **3**/BF_3OEt_2 in CH_2Cl_2 at −15 °C in the presence of water and DTBMP (40 and 2.0 mM, respectively) (Figure 6). The M_n of the polymers obtained with **3** increased in direct proportion to monomer conversion and was close to the calculated values throughout the reaction, and the MWDs were narrower ($M_w/M_n = 1.86$) than those with **2**. Under these conditions, **2** gave polymers with M_n higher than the calculated values at

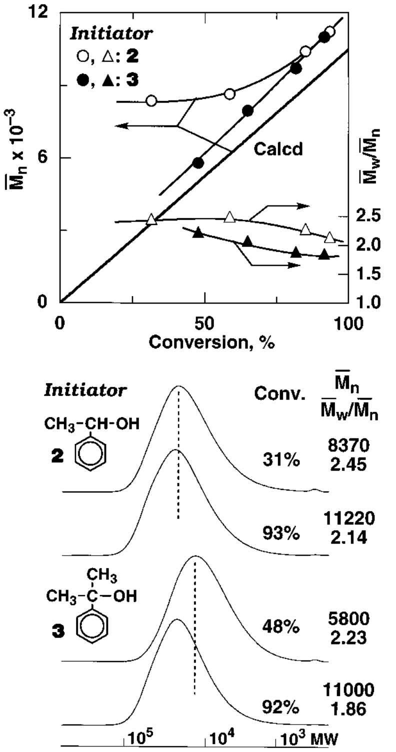

Figure 6. M_n and M_w/M_n curves of the polystyrene obtained with **2** or **3**/BF$_3$OEt$_2$ in the presence of water at −15 °C in CH$_2$Cl$_2$: [styrene]$_0$ = 1.0 M; [initiator]$_0$ = 10 mM; [BF$_3$OEt$_2$]$_0$ = 50 mM; [H$_2$O]$_0$ = 40 mM; [DTBMP]$_0$ = 2.0 mM. Initiator: (○, △) **2**; (●, ▲) **3**. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per an initiator molecule.

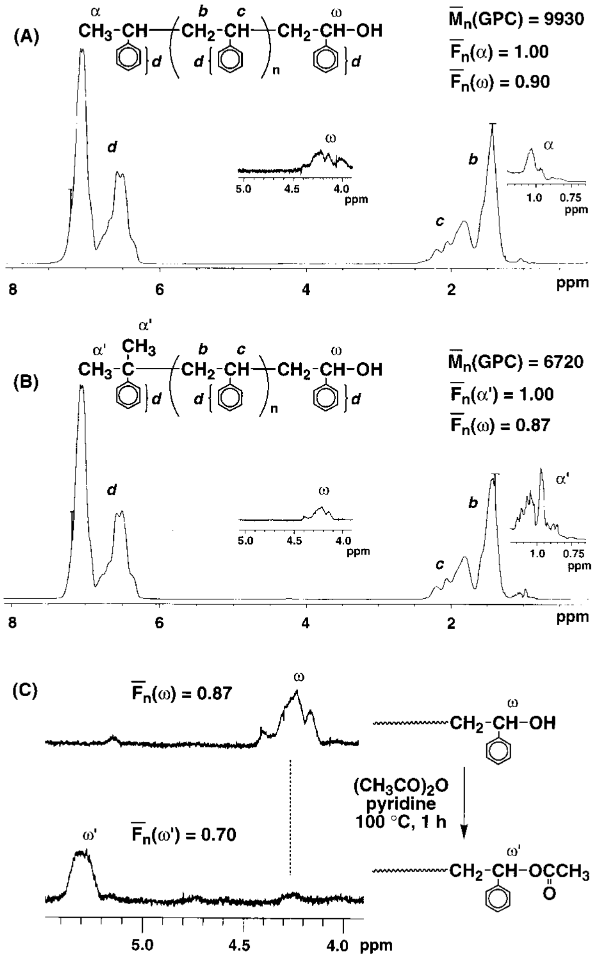

Figure 7. ^{1}H NMR spectra of polystyrene obtained at −15 °C in CH$_2$Cl$_2$ in the presence of water and DTBMP (A) with **2**/BF$_3$OEt$_2$ (M_n = 9930, M_w/M_n = 2.17) and (B) with **3**/BF$_3$OEt$_2$ (M_n = 6720, M_w/M_n = 1.97) and (C) the same polymer after the reaction with acetic anhydride as in part B.

the early stage of the polymerization due to the slow initiation. This indicates that **3** induced faster initiation to give polymers with more controlled molecular weights and narrower MWDs.

The terminal structure of the polymers obtained with **2** or **3**/BF$_3$OEt$_2$ in CH$_2$Cl$_2$ was examined by ^{1}H NMR spectroscopy (Figure 7). These polymers give characteristic signals; i.e., phenyl groups (d) and main-chain aliphatic protons (b and c). In addition to these large absorptions, the signals due to the end groups appeared, namely, CH$_3$− (α or α′; 1.0 ppm) at the α-end and −CH−OH (ω; 4.2 ppm) at the ω-end, where the former originated from the alcohols (**2** and **3**) as initiators and the latter from the alcohols or added water. The shape of these α-end signals clearly differs from each other. The hydroxy ω-terminal was confirmed by reaction with acetic anhydride, which eliminated the ω-end absorption (ω) and produced a new absorption (5.3 ppm) of the methine proton (ω': −CH−OCOCH$_3$) adjacent to an acetoxy group (Figure 7C). The absence of the methoxy terminus originating from methanol on quenching is due to the strong covalent nature of the C−OH dormant terminus as well as a low concentration of the active species. Similar results were obtained in the polymerization styrene with the R−Cl/SnCl$_4$ system[8] and *p*-methoxystyrene with R−OH/BF$_3$OEt$_2$.[4] The functionalities of the α and α′ ends [$F_n(\alpha) = F_n(\alpha') = 1.0$] show that one polymer was generated from one initiator, and the added water did not generate new polymer chains. In contrast, those of the methine groups were slightly lower than unity [$F_n(\omega) \sim 0.9$], which suggests some loss of living growing polymer terminal (∼∼C−OH). These results indicate that the polymerization proceeds via the reversible activation of the terminal C−OH bond by BF$_3$OEt$_2$ even in the presence of water to give long-lived polymers. The Lewis acid breaks the terminal ∼∼C−OH bond into ∼∼C$^+$ + $^-$OH, rather than into ∼∼C−O$^-$ + H$^+$.

Figure 8 shows the matrix-assisted laser-desorption−ionization time-of-flight mass (MALDI−TOF−MS) spectra of the polystyrene samples obtained with **2** and **3**. Each spectrum consists of a series of sharp peaks each separated by a 104.2 Da interval, which corresponds to the molecular weight of styrene monomer. The molecular weight of each individual peak was very close to the calculated value for CH$_3$−CHR−(−CH$_2$−CHPh−)$_n$−OH + Na$^+$, [R = Ph or Ph−CH$_3$(*p*)], i.e., polystyrene with the initiator moiety at the α-end and the hydroxyl group at the ω-end, along with the sodium cation from the MALDI matrix component. This shows that the HO-capped polystyrenes produced with R−OH/BF$_3$OEt$_2$ are stable toward the laser ionization, in contrast to the corresponding Cl-capped polystyrene synthesized via living cationic or transition metal-mediated living radical polymerization, which completely loses the halogen at the ω-end during the MS analysis.[22] However, both spectra in Figure 8 exhibit a minor series of peaks, shifted by 17 Da from the major series, which suggests some loss of the C−OH bond at the ω-end during the polymerization or the laser-induced ionization.

The difference in molecular weight between the main peak series with **2** and with **3** is 14 Da, which corre-

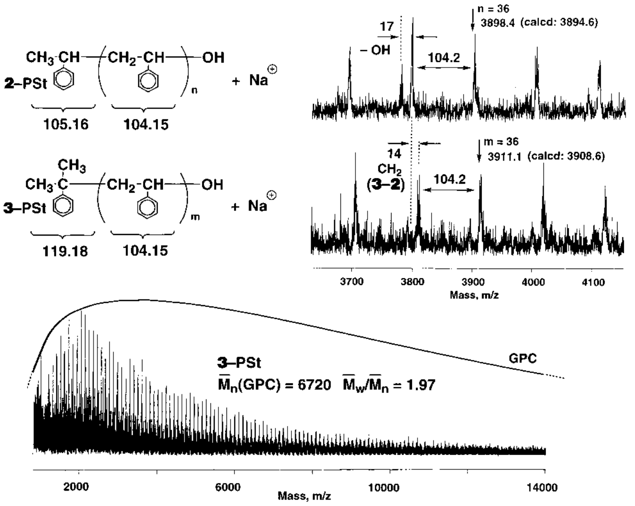

Figure 8. MALDI–TOF–MS spectra of the polymers that were analyzed by ^{1}H NMR in Figure 6, parts A and B, respectively. The curve indicated as GPC was obtained by converting the SEC traces into the corresponding number fraction on the assumption that the peak intensity in SEC curves is proportional to the molecular weight fraction of the polymers.

sponds to the molecular weight difference between the initiators. In particular, the spectrum of the polymer produced by **3** was free from the peaks observed with **2**, which have the same structure as that of the polymers initiated by water. These results also support the polymerization mechanism where BF_3OEt_2 activates the C–O bond of the initiator selectively to form the carbocationic species, rather than generating a proton form water. Thus, water is less reactive as an initiator than **2** and **3** in the BF_3-mediated polymerization. This can be explained by the concept of hard and soft acids and bases (HSAB).[2,23] BF_3, a hard Lewis acid, preferentially interacts with the hydroxyl group, a hard base, whereas a proton as a harder acid attracts hydroxide anion more strongly than BF_3. On the other hand, a carbocation is softer than proton, and thus the C–OH species can generate cationic species more easily than H_2O can.

4. Polymerization of *p*-Substituted Styrene Derivatives. The R–OH/BF_3OEt_2 initiating systems were used to polymerize *p*-methyl- (pMS) and *p*-chlorostyrene (pClSt) in CH_2Cl_2 at 0 °C (eq 3). Since electron-donating substituents enhance the reactivity of monomers in cationic polymerization, larger amounts of H_2O and DTBMP were employed for the more reactive pMS: $[H_2O]_0/[DTBMP]_0$ = 80/10 (for pMS) and 40/2 (for pClSt). (The ratio is 40/2 or 80/2 for styrene.)

For both monomers, polymerizations proceeded smoothly and quantitatively. Figure 9 shows the M_n, M_w/M_n, and MWD curves for the poly(pMS) and the poly(pClSt) obtained with **2** or **3**/BF_3OEt_2. The M_n values of the latter polymer were calculated using the following relationship between the M_n(NMR) and M_n(SEC) calibrated against polystyrene: $M_n(NMR) = 1.43M_n(SEC)$.[24]

The M_n values of the poly(pMS) obtained with **2**, were higher than the calculated values even at a high water concentration ($[H_2O]_0$ = 80 mM), due to the slow initiation from **2**. The C–O bond of **2** is less reactive than that derived from pMS because styrene is less reactive than pMS in cationic polymerization. In contrast, M_n increased with **3** in direct proportion to monomer conversion. For the less reactive pClSt, the M_n with both **2** and **3** increased in direct proportion to monomer conversion even at a low water concentration ($[H_2O]_0$ = 40 mM). Thus, with the proper selection of the initiator and the H_2O/DTBMP ratio, the R–OH/BF_3OEt_2 initiating systems induced the controlled cationic polymerization of not only styrene but also *p*-substituted styrene derivatives.[3,4]

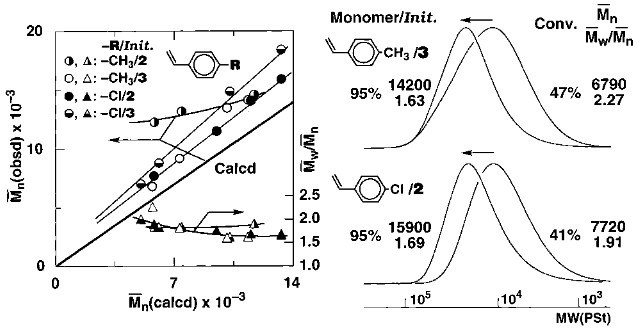

Figure 9. M_n and M_w/M_n curves of the poly(pMS) and poly(pClSt) obtained with **2** or **3**/BF_3OEt_2 in the presence of water at 0 °C in CH_2Cl_2: $[monomer]_0 = 1.0$ M; $[initiator]_0 = 10$ mM; $[BF_3OEt_2]_0 = 50$ mM; $[H_2O]_0/[DTBMP]_0 = 80/10$ (for pMS) and 40/2 (for pClSt) mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per an initiator molecule. The M_n(obsd) of the poly(pClSt) was obtained by the following relationship, $M_n(NMR) = 1.43 \times M_n(SEC)$, as described in the text. $M_n(calcd)$ = ($[monomer]_0/[initiator]_0$) × (conversion by GC) × (formula weight of monomer).

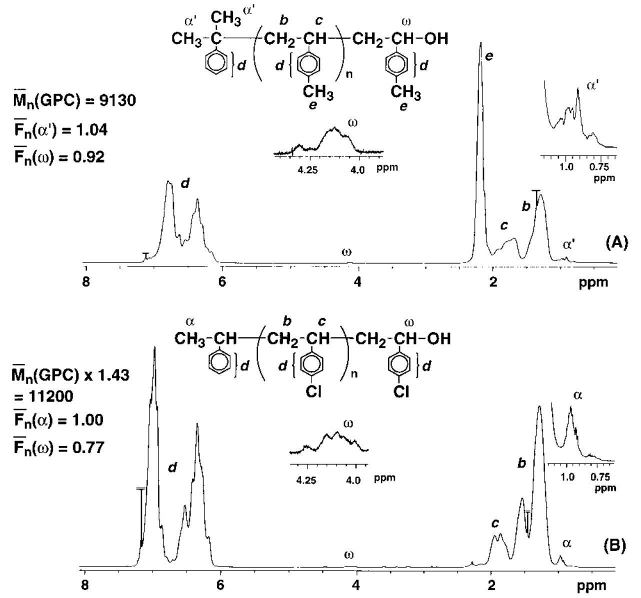

Figure 10. ^{1}H NMR spectra of poly(pMS) (M_n = 9130, M_w/M_n = 1.82) obtained with **3**/BF_3OEt_2 and poly(pClSt) (M_n = 11 200, M_w/M_n = 1.77) with **2**/BF_3OEt_2 at 0 °C.

Parts A and B of Figure 10 show the ^{1}H NMR spectra of the poly(pMS) and poly(pClSt), respectively, used for end group analysis. As in the spectra of polystyrene (Figure 7), the terminal CH_3– groups (α or α′; 1.0 ppm) at the α-end and the –CH–OH (*ω*; 4.2 ppm) at the *ω*-end were observed. This also indicates that the polymerizations of *p*-substituted styrenes proceeded in a controlled fashion.

In conclusion, the alcohol/BF_3OEt_2 initiating system is applicable for controlled cationic polymerization of styrene in the presence of a fairly large amount of water. The BF_3-mediated controlled cationic polymerization of styrene and its derivatives is unique from the following viewpoints. (1) The polymerization proceeds via the reversible activation of the stable C−O terminus. Most of the reported cationic polymerizations (e.g., with R−OR′/BCl_3) proceed via the reversible activation of the carbon−halogen terminal even with the use of the initiator with a C−O bond, because most of the metal halides (Lewis acids) convert the C−O bond into a C−halogen via an anion-exchange reaction.[11] (2) The controlled cationic polymerization can be achieved even in the presence of a fairly large amount of water that should be strictly removed in the usual cationic polymerization. Furthermore, the added water contributes to the control of the polymerization most probably by providing a reservoir of hydroxide anion as with a common-ion salt. (3) The produced polymers possess a stable hydroxy group at the ω-end as a functional group. This system opened a new way for controlled cationic polymerization via selective activation of C−O terminal with an oxophilic Lewis acid, BF_3, and can be applied for other functionalized monomers such as chloromethylstyrene, which is now under investigation in our laboratory.

Experimental Section

Materials. Styrene (Wako Chemicals, >99%), *p*-methylstyrene (Aldrich, 96%), and *p*-chlorostyrene (Hokko Chemicals, 99%) were dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. The water adducts [1-phenylethyl alcohol (**2**) (Tokyo Kasei, >98%) and α-cumyl alcohol (**3**) (Tokyo Kasei, >98%)] were distilled from calcium hydride (1 Torr, 56 and 75 °C, respectively) before use. BF_3OEt_2 (Aldrich, purified and redistilled), 2,6-di-*tert*-butyl-4-methylpyridine (Aldrich, 98%), and tetrabutylammonium hydroxide (Aldrich, 1.0 M solution in water, ACS reagent) were used as received. CH_2Cl_2 as a solvent and bromobenzene as an internal standard for gas chromatography were dried overnight over calcium chloride, doubly distilled from phosphorus pentoxide and then from calcium hydride before use. Distilled deionized water was used as a form of saturated solution in CH_2Cl_2 ($[H_2O] = 125$ mM at 25 °C).[25]

Polymerization Procedures. The polymerizations were carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for styrene polymerization is given below. The polymerization was initiated by adding solutions of BF_3OEt_2 (0.15 mmol; 0.30 mL of 500 mM in CH_2Cl_2) into a monomer solution (2.7 mL) containing styrene (3.0 mmol; 0.34 mL), **2** (30 μmol; 3.6 μL), DTBMP (6.0 μmol; 1.2 mg), and water (0.12 mmol; 2.2 μL), in CH_2Cl_2 at −15 °C. The total volume of the reaction mixture was thus 3.0 mL. After a predetermined time, the polymerization was terminated with prechilled methanol (1.0 mL). Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with bromobenzene as an internal standard. The quenched reaction mixture was washed with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymer.

Measurements. The MWD, M_n, and M_w/M_n values of polymers were measured in chloroform at 40 °C on three polystyrene gel linear columns [Shodex K-805L; (pore size 20−1000 Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU-980 precision pump and Jasco 930-RI refractive index and 970-UV ultraviolet detectors. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; $M_n = 580{-}1547\,000$; $M_w/M_n < 1.1$) as well as the styrene monomer.

^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA 500 spectrometer, operating at 500.16 MHz.

MALDI−TOF−MS was performed on PerSeptive Biosystems Voyager DE-STR spectrometer with a 3-m reflector flight tube and a 337 nm nitrogen laser, having a pulse width of 3 ns, along with a delayed extraction capability. All experiments were done at an accelerating potential of 20 kV. In general, mass spectra from 256 spectra shots were accumulated to produce a final spectrum. Angiotensin I (human; MW = 1296.5) (BACHEM) and insulin (bovine pancreas 28.3; MW = 5733.50) (nacalai) were used as internal standards to calibrate the mass scale. Sample solutions were prepared by dissolving the polymer, matrix (dithranol), and cationizing agent (sodium trifluoroacetate) in THF. Typically, 10 μL of a polymer solution (10 mg/mL), 80 μL of a matrix solution (30 mg/mL), and 10 μL of a cationizing agent solution (10 mg/mL) were mixed in a glass vial. Immediately after mixing, 0.5-μL portions of the mixed solution were deposited onto the gold-plated wells of the sample plate and dried under air at room temperature. The plate was inserted into the apparatus under high vacuum ($\sim 10^{-7}$ Torr) for measurements.

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