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Controlled Cationic Polymerization of *p*-(Chloromethyl)styrene: BF_3-Catalyzed Selective Activation of a C−O Terminal from Alcohol

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ABSTRACT: Controlled cationic polymerization of *p*-(chloromethyl)styrene (CMS) was achieved with an alcohol [$CH_3CH(Ph)OH$] as an initiator and a highly oxophilic Lewis acid, $BF_3{\cdot}OEt_2$, as an activator/catalyst. The polymerization is initiated by the BF_3-mediated selective activation of the C−O bond of the alcohol and proceeds via a similar activation of the resulting ∼∼C−OH dormant polymer terminal to give linear polymers without branched structures that would form via reactions of the chloromethyl pendent groups. Addition of a small amount of water retarded the polymerization to give controlled molecular weights that increased with conversion and were close to the calculated values for living polymers. Additional use of tetrabutylammonium hydroxide (n-Bu_4NOH) as a hydroxide anion source further narrowed the molecular weight distribution ($M_w/M_n = 1.5-1.8$). Copolymerization of CMS and styrene or *p*-chlorostyrene with the BF_3-based system also gave copolymers with controlled molecular weights. This is the first example of *controlled cationic* polymerization of CMS without concurrent side reactions of the chloromethyl functional groups. The success owes to the use of highly oxophilic $BF_3{\cdot}OEt_2$ in conjunction with an appropriate alcoholic initiator.

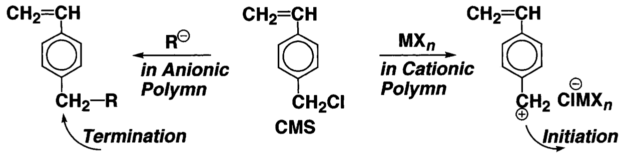
Introduction

p-(Chloromethyl)styrene (CMS) or *p*-vinylbenzyl chloride is a functional styrene with a reactive pendent benzyl group susceptible to Lewis acid-assisted cation formation, nucleophilic substitution, etc. (Scheme 1). CMS is thus usually polymerized not via ionic but via radical pathway for keeping the benzyl moiety intact,[1] although the control of molecular weights has been difficult. Linear poly(CMS) with controlled molecular weights has been obtained only by living anionic polymerization of protected CMS followed by deprotection.[2,3]

Direct and controlled radical polymerization of CMS, on the other hand, was recently achieved with nitroxide to give linear polymers without undesirable reactions of the chloromethyl groups.[4,5] Another effective way is the use of reversible addition−fragmentation chain transfer (RAFT) agents.[6] In contrast, metal-catalyzed living radical polymerization, based on reversible activation of a dormant carbon−halogen terminal, is not suited for linear poly(CMS) but leads to branched or hyperbranched polymers via generation of multiple growing ends from both of the alkene and the chloromethyl groups in CMS.[7−9]

CMS can also be polymerized via a cationic mechanism.[1] For example, the $CH_3CH(Ph)Cl/SnCl_4$-initiating system, which is effective in living cationic polymerization of styrene,[10] was employed but resulted in polymers with uncontrolled molecular weights due to inevitable initiation from the pendent benzyl chloride.[11] A similar monomer, *m*-(1-chloroethyl)styrene [3-(1-chloroethyl)ethenylbenzene], was also polymerized with $SnCl_4$ into hyperbranched polymers.[12] Thus, no linear poly(CMS) with controlled molecular weights has yet been obtained in cationic polymerization.

Scheme 1



Quite recently, we have developed a novel controlled cationic polymerization of unprotected *p*-hydroxystyrene[13] with combinations of an alcohol as an initiator and boron trifluoride etherate ($BF_3{\cdot}OEt_2$) as an activator or a catalyst. In sharp contrast to usual cationic polymerization, it cleanly proceeds without protection of the phenolic pendent function, and the BF_3 system can also be applied to styrene[14] and *p*-alkoxystyrenes.[15] The initiating system is based on the BF_3-mediated reversible dissociation of carbon−oxygen bond and clearly differs from others based on the dissociation of carbon−halogen bonds with metal halides in the following points: (1) The most effective initiators for the BF_3-based systems are not halides but alcohols with a potentially active C−O bond for a carbocation formation. (2) The polymerization proceeds via a similar reversible C−O bond activation at polymer terminal. (3) The polymerization proceeds even in the presence of water, which in turn helps fine reaction control. These features stem from the high oxophilicity of $BF_3{\cdot}OEt_2$ and its tolerance to water.[16]

This study was thus aimed to a challenge to make linear and controlled polymers from unprotected CMS by the BF_3-mediated cationic polymerization based on the selective activation of C−O terminals (Scheme 2). To the best of our knowledge, there have been no examples for selective cation formation from CMS and similar compounds with two different cationogen sites both in polymerization and in organic reactions.

Experimental Section

Materials. CMS (Seimi Chemical, >95%, *p*-/*m*-isomer = 95/5) was washed with 20% NaOH aqueous solution and saturated brine, dried overnight with anhydrous sodium sulfate, and distilled twice over calcium hydride under reduced pressure (2.0 mmHg, 56 °C) before use. Styrene (Wako Chemicals,

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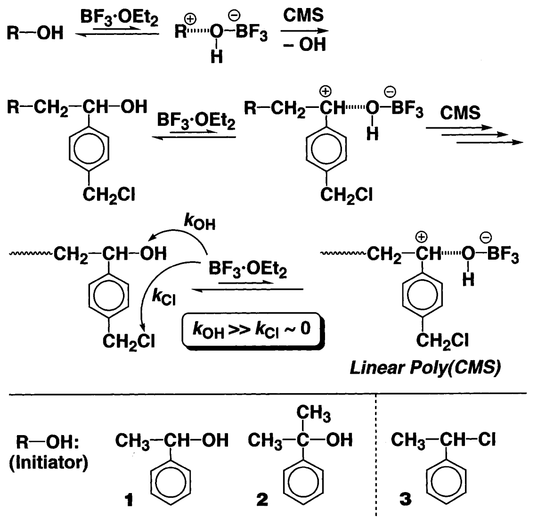
Scheme 2



>99%) and *p*-chlorostyrene (Hokko Chemicals, 99%) were dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. 1-Phenylethyl alcohol (**1**) (>98%), α-cumyl alcohol (**2**) (>98%), and 1-phenylethyl chloride (**3**) (>97%), all from Tokyo Kasei, were distilled from the best commercial products over calcium hydride under reduced pressure before use. $BF_3{\cdot}OEt_2$ (Aldrich, purified and redistilled), $SnCl_4$ (Aldrich, 99.995%), 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 and doubly distilled from phosphorus pentoxide and then from calcium hydride before use. Nitroethane was doubly distilled over calcium hydride. Distilled deionized water was used as a form of saturated solution in CH_2Cl_2 ($[H_2O]$ = 125 mM at 25 °C).[17]

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 a solution of $BF_3{\cdot}OEt_2$ (0.15 mmol; 0.30 mL of 500 mM in CH_2Cl_2) into a monomer solution (2.7 mL), containing CMS (1.5 mmol; 0.21 mL), bromobenzene (0.21 mL), **1** (30 μmol; 3.6 μL), and water (0.12 mmol; 2.2 μL), in CH_2Cl_2 at 0 °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 13 standard polystyrene samples (Tosoh; M_n = 500–3 840 000; M_w/M_n = 1.01–1.14) as well as 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. Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

Results and Discussion

Cationic Polymerization with Alcohol/$BF_3{\cdot}OEt_2$: Formation of Linear Polymers. Cationic polymerization of CMS was examined with $BF_3{\cdot}OEt_2$ in the presence or absence of cationogens in CH_2Cl_2 at −15 °C (Figure 1). The boron Lewis acid alone led to slow polymerization of CMS to reach almost quantitative conversion (96%) in 140 h. Water, which is believed to be a protogen or co-initiator in BF_3-mediated cationic polymerization, adversely affected the rate of polymerization. In contrast, alcohol with a potentially active site for cation formation, 1-phenylethyl alcohol (**1**) and cumyl alcohol (**2**),[14] led to remarkable rate enhancements, where both the polymerizations ensued within 1 h. Addition of 1-phenylethyl chloride (**3**), which is a good initiator for $SnCl_4$-mediated living cationic polymerization, did not affect the rate to result in a similar slow polymerization.

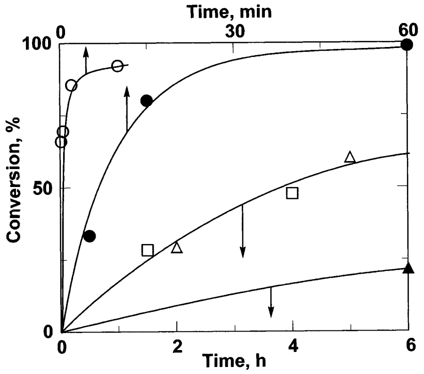


Figure 1. Polymerization of CMS with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at −15 °C: $[CMS]_0$ = 0.50 M; $[initiator]_0$ = 10 mM; $[BF_3{\cdot}OEt_2]_0$ = 50 mM. Initiator: (●) **1**; (○) **2**; (△) **3**; (□) none; (▲) H_2O.

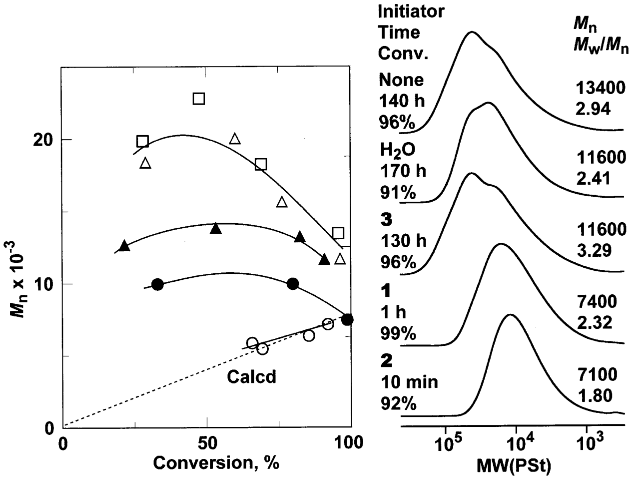


Figure 2. M_n, M_w/M_n, and SEC curves of poly(CMS) obtained with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at −15 °C: $[CMS]_0$ = 0.50 M; $[initiator]_0$ = 10 mM; $[BF_3{\cdot}OEt_2]_0$ = 50 mM. Initiator: (●) **1**; (○) **2**; (△) **3**; (□) none; (▲) H_2O. The diagonal dashed line indicates the calculated M_n assuming the formation of one living polymer per initiator molecule.

Figure 2 shows the number-average molecular weights (M_n), molecular weight distributions (MWDs), and size-exclusion chromatograms (SEC) of the polymers. The polymers obtained in the absence of intentionally added initiators had relatively high ((1−2) × 10^4) and uncontrolled molecular weights. The polymers with **3** had similar molecular weights and MWDs. Addition of water slightly decreased molecular weights. In contrast, there were clear effects of **1** and **2** on molecular weights. The M_n became smaller and close to the calculated values assuming that one initiator generates one polymer chain. The MWDs were unimodal and narrower especially with **2**. This is primarily due to the fast initiation

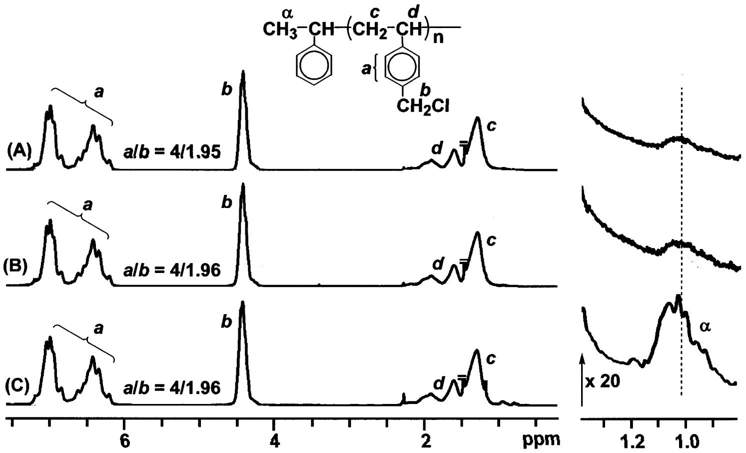


Figure 3. ^{1}H NMR spectra of poly(CMS) obtained with (A) $BF_3 \cdot OEt_2$ (M_n = 13 400, M_w/M_n = 2.94), (B) $H_2O/BF_3 \cdot OEt_2$ (M_n = 11 600, M_w/M_n = 2.41), and (C) **1**/$BF_3 \cdot OEt_2$ (M_n = 7400, M_w/M_n = 2.32) in CH_2Cl_2 at −15 °C: $[CMS]_0$ = 0.50 M; $[H_2O]_0$ = $[\mathbf{1}]_0$ = 10 mM; $[BF_3 \cdot OEt_2]_0$ = 50 mM.

from these secondary or tertiary alcohols on activation of the C−O bonds.

The polymers obtained with the BF_3-based systems were analyzed by ^{1}H NMR. Figure 3A shows the spectrum of the polymers with $BF_3 \cdot OEt_2$ alone. It showed each characteristic signal of the monomer unit, chlorobenzyl (*b*) at 4.2−4.5 ppm, phenyl (*a*) at 6.2−7.3 ppm, and main-chain methylene (*c*) and methine (*d*) protons at 1.2−2.2 ppm. The peak intensity ratio of the phenyl to the benzyl groups was 4/1.95, close to the calculated values (4/2) assuming that the benzyl chloride moiety was kept intact. A similar spectrum was obtained for the polymers produced in the presence of H_2O (Figure 3B). The polymers obtained with **1** and $BF_3 \cdot OEt_2$ had a similar phenyl/benzyl ratio (4/1.96), which also confirms formation of the linear polymers (Figure 3C). Thus, BF_3 did not activate the C−Cl bond in the monomer and resulted in the linear polymers with or without cationogens.

It is noteworthy that the methyl groups originating from **1** at the α-end can be clearly seen in Figure 3C. This indicates that **1** serves as an initiator in the presence of $BF_3 \cdot OEt_2$ to generate the 1-phenylethyl cation as an initiating species. It is of interest that, specifically with the boron-based Lewis acid, alcohols such as **1** can now serve as effective initiators, rather than chain transfer agents and terminates commonly perceived in conventional cationic polymerization, except for few examples in BCl_3-catalyzed isobutylene processes.[18] In contrast, the polymers obtained with $BF_3 \cdot OEt_2$ alone or $BF_3 \cdot OEt_2/H_2O$ showed only a very small absorption at 1.1 ppm to be attributed to the methyl proton of $CH_3CH(PhCH_2Cl)-$ generated by proton initiation. However, the peak intensity was too weak, which indicates unidentified initiation in the absence of alcoholic initiators. Thus, an alcohol such as **1** and **2** facilitates the formation of initiating species in the BF_3-meidated cationic polymerization and induces well-defined initiation.

Controlled Cationic Polymerization with 1/$BF_3 \cdot OEt_2$: Molecular Weight Control and Additives. For further controlling polymer molecular weights, with alcohols as initiators, an additive that can supply a hydroxide anion was investigated in the polymerization with **1**/$BF_3 \cdot OEt_2$ in CH_2Cl_2 at 0 °C (Figure 4). Such additives were effective in styrene polymerization where the MWDs became narrower most probably due to fast interconversion of cationic species into the C−OH dormant counterpart in comparison with propagation.[14]

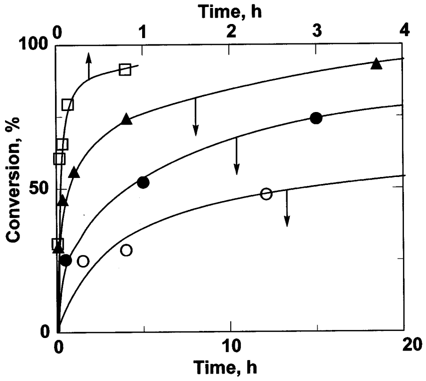


Figure 4. Effects of additives on the polymerization of CMS with **1**/$BF_3 \cdot OEt_2$ in CH_2Cl_2 at 0 °C: $[CMS]_0$ = 0.50 M; $[\mathbf{1}]_0$ = 10 mM; $[BF_3 \cdot OEt_2]_0$ = 50 mM; $[H_2O]_0$ = 0 or 40 mM; $[n\text{-}Bu_4NOH]_0$ 0−1.5 mM. Additive: (□) none; (▲) H_2O (40 mM); (●) $H_2O/n\text{-}Bu_4NOH$ (40/0.7 mM); (○) $H_2O/n\text{-}Bu_4NOH$ (40/1.5 mM).

In the presence of purposefully added water, the polymerization became slower and reached almost quantitative conversion in 20 h (filled triangles in Figure 4; cf. 91% in 48 min in the corresponding system without added water). Additional use of a hydroxide anion source such as $n\text{-}Bu_4NOH$ drastically slowed the polymerization (filled and open circles in Figure 4).

As shown in Figure 5, the M_n of the polymers obtained with **1**/$BF_3 \cdot OEt_2$ and combinations of $H_2O/n\text{-}Bu_4NOH$ were all close to the calculated values and increased with conversion. The addition of water slightly narrowed the MWDs. On further addition of $n\text{-}Bu_4NOH$, the MWDs became narrower particularly at low conversions. However, the MWDs were still broader than those of poly(*p*-alkoxystyrene)s[13,15] due to the less reactive −C−OH poly(CMS) terminal bearing an electron-withdrawing chloromethyl pendent group. The SEC peak molecular weights clearly increased with conversion. Thus, control of molecular weights can be achieved with **1**/$BF_3 \cdot OEt_2$ in the presence of water and a hydroxide anion source as additives.

Figure 6 compares ^{1}H NMR spectra of the polymers obtained with **1**/$BF_3 \cdot OEt_2$ in the presence of water (A) and those with $CH_3CH(Ph)Cl/SnCl_4$ with $n\text{-}Bu_4NCl$ (B). The polymers with the R−OH/BF_3-based system again quantitatively carried the chloromethyl groups (*a*/*b* =

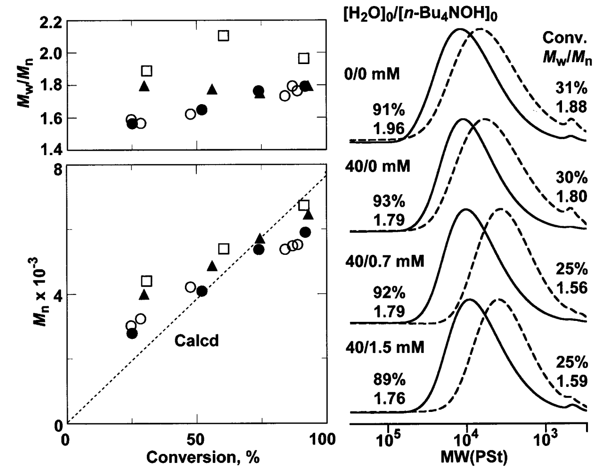


Figure 5. M_n, M_w/M_n, and SEC curves of poly(CMS) obtained with $BF_3·OEt_2$ in CH_2Cl_2 at 0 °C: $[CMS]_0 = 0.50$ M; $[\mathbf{1}]_0 = 10$ mM; $[BF_3·OEt_2]_0 = 50$ mM; $[H_2O]_0 = 0$ or 40 mM; $[n\text{-}Bu_4NOH]_0$ 0−1.5 mM. Additive: (□) none; (▲) H_2O (40 mM); (●) $H_2O/n\text{-}Bu_4NOH$ (40/0.7 mM); (○) $H_2O/n\text{-}Bu_4NOH$ (40/1.5 mM). The diagonal dashed line indicates the calculated M_n assuming the formation of one living polymer per **1** molecule.

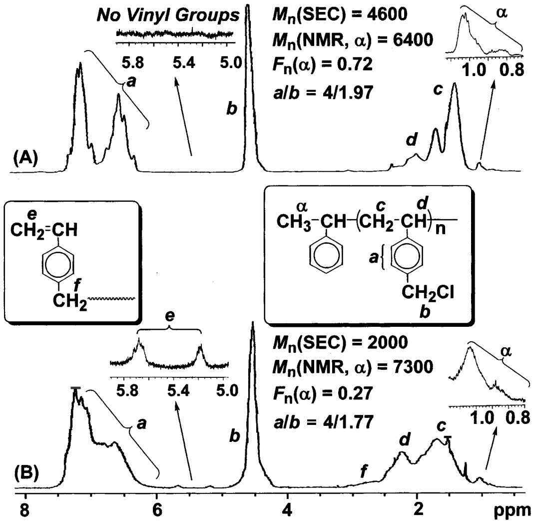


Figure 6. ^{1}H NMR spectra of poly(CMS) obtained with (A) $\mathbf{1}/BF_3·OEt_2/H_2O$ (10/50/40 mM) ($M_n = 4600$, $M_w/M_n = 1.84$) and (B) $\mathbf{3}/SnCl_4/n\text{-}Bu_4NCl$ (10/50/20 mM) ($M_n = 2000$, $M_w/M_n = 1.87$) in nitroethane at −15 °C: $[CMS]_0 = 0.50$ M.

4/1.97) even in the presence of water. The initiating α-end group was detected; the M_n determined from the peak intensity ratio of the initiator moiety to the main chain [M_n(NMR, α) = 152.62 × 3*a*/4α + 122.16] was 6400, slightly larger than that obtained by SEC with a standard polystyrene calibration [M_n(SEC) = 4600]. We have already employed the same initiating system for styrene polymerization, where the M_n(NMR, α) of the polystyrene obtained by a similar calculation agreed well with M_n(SEC).[14] The smaller value for M_n(SEC) of poly(CMS) is partly due to difference in hydrodynamic volume between poly(CMS) and polystyrene.

For ω-end groups, the methine proton of −C*H*−OH would appear around 4.5 ppm, based on a similar proton for the OH-terminal polystyrene obtained by the same system.[14] This peak probably overlapped with the large absorptions (*b*) of the chloromethyl groups of poly(CMS).

In contrast, the polymers obtained with the $SnCl_4$-based system showed broader NMR peaks than those with the BF_3. The relative intensity of the chloromethyl

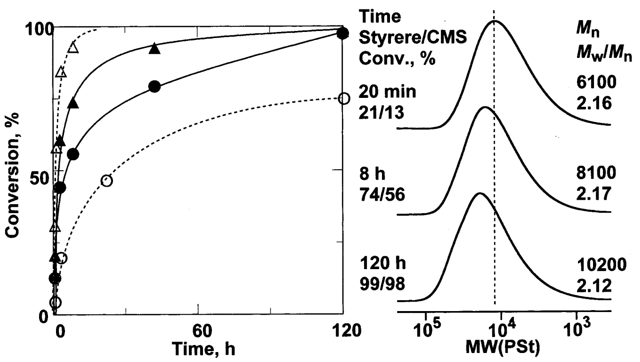


Figure 7. Copolymerization of CMS (●) and styrene (▲) and homopolymerization of CMS (○) or styrene (△) with $\mathbf{1}/BF_3·OEt_2/H_2O$/2,6-di-*tert*-butyl-4-methylpyridine in CH_2Cl_2 at −15 °C: $[CMS]_0 = [styrene]_0 = 0.50$ M (for copolymerization); $[CMS]_0 = [styrene]_0 = 1.0$ M (for homopolymerization); $[\mathbf{1}]_0 = 10$ mM; $[BF_3·OEt_2]_0 = 50$ mM; $[H_2O]_0 = 40$ mM; [2,6-di-*tert*-butyl-4-methylpyridine]$_0$ = 2.0 mM.

to the phenyl protons was apparently lower (*a*/*b* = 4/1.77) than the calculated values (4/2) for poly(CMS). In addition, the vinyl protons of styrene units (*e*) were detected along with a broad peak (*f*) around 3 ppm. This indicates that a part of the chloromethyl group in CMS initiated cationic polymerization in the presence of $SnCl_4$. Furthermore, low molecular weights based on SEC and broad NMR absorptions suggest a branched structure.

These results indicate that $BF_3·OEt_2$ selectively activates the covalent C−O terminal originating from R−OH to afford linear polymers with controlled molecular weights. This system thus enabled the first controlled cationic polymerization of CMS with preserving the chloromethyl moiety.

Copolymerization of CMS and Styrene Derivatives with $\mathbf{1}/BF_3·OEt_2$. The $\mathbf{1}/BF_3·OEt_2$-initating system was then employed for copolymerization of CMS with other styrene monomers. The copolymerization was directed to the analysis of reactivity of CMS in cationic polymerization while excluding the possibility of initiation from the chloromethyl group and to the synthesis of linear styrene-based polymers with reactive chloromethyl groups.[2] With the electron-withdrawing pendent group, the reactivity of CMS seems lower than styrene as indicated by the ^{13}C chemical shift of the β-carbon at a lower field than for styrene [$\delta(C^\beta)$: 114.6 (CMS) vs 113.8 (styrene) ppm].[11] In fact, homopolymerization with $\mathbf{1}/BF_3·OEt_2$ proceeded much faster with styrene than with CMS, as shown in Figure 7 (open triangles and circles for styrene and CMS, respectively). This is in sharp contrast to that CMS was consumed faster than styrene with $CH_3CH(Ph)Cl/SnCl_4$ because of undesirable initiation from the chloromethyl moiety. In copolymerization of an equimolar mixture of the two monomers, the difference became smaller than in the respective homopolymerizations (filled triangles and circles for styrene and CMS, respectively).

The obtained polymers showed unimodal SEC curves moving to high molecular weights with conversions. Thus, the $\mathbf{1}/BF_3·OEt_2$ system gave styrene/CMS copolymers that have controlled molecular weights and probably somewhat gradient sequences rather than random.

The same initiating system was also applied to copolymerization of *p*-chlorostyrene (pClSt) and CMS in CH_2Cl_2 at 0 °C (Figure 8). The β-carbon chemical shift of pClSt was similar but slightly higher fielded than

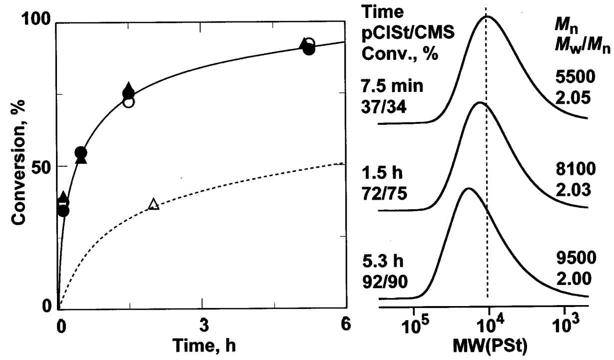


Figure 8. Copolymerization of CMS (●) and pClSt (▲) and homopolymerization of CMS (○) or pClSt (△) with **1**/$BF_3 \cdot OEt_2$/H_2O/2,6-di-*tert*-butyl-4-methylpyridine in CH_2Cl_2 at −0 °C: $[CMS]_0 = [styrene]_0 = 0.50$ M (for copolymerization); $[CMS]_0 = [styrene]_0 = 1.0$ M (for homopolymerization); $[\mathbf{1}]_0 = 10$ mM; $[BF_3 \cdot OEt_2]_0 = 50$ mM; $[H_2O]_0 = 40$ mM; [2,6-di-*tert*-butyl-4-methylpyridine]$_0$ = 2.0 mM.

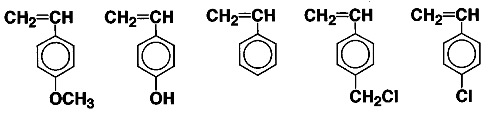
that of CMS [$\delta(C^{\beta})$: 114.4 ppm (pClSt)].[11] Although pClSt polymerized slower than CMS (open triangles and circles for pClSt and CMS, respectively), both monomers were polymerized at almost the same rate in the corresponding copolymerization. The MWDs were unimodal, and the molecular weights increased with conversions as with the styrene/CMS pair.

Conclusions

The R−OH/$BF_3 \cdot OEt_2$ initiating system proved effective in giving linear poly(CMS) with controlled molecular weights even via a cationic mechanism, where $BF_3 \cdot OEt_2$ is necessary for providing linear polymers without a branched structure while R−OH for controlling molecular weights by generating definite initiating species on activation by $BF_3 \cdot OEt_2$. The key to this is that the boron catalyst is an oxophilic Lewis acid and thus selectively cleaves the terminal C−OH group into a carbocation without generating a similar benzyl carbocation from the pendent chloromethyl group.

Chart 1 summarizes cationic polymerizations of CMS and other styrenes with the R−Cl/$SnCl_4$[10,11] and R−OH/$BF_3 \cdot OEt_2$ systems.[12−15] The BF_3-based systems are highly tolerant to functional groups to give linear and controlled polymers of these monomers despite intervention of carbocationic growing species. However, the control of molecular weights for styrenes without functional groups was inferior to that with the $SnCl_4$-based systems. This may be due to a relatively slow interconversion between the dormant and the active species for the BF_3-based systems. Further tuning of the initiating systems should be needed for more fine control.

Chart 1



	CH_2=CH OCH_3	CH_2=CH OH	CH_2=CH	CH_2=CH CH_2Cl	CH_2=CH Cl
R–Cl/$SnCl_4$ (M_w/M_n)	○ (1.1–1.2)	No Polymer	○ (1.1–1.2)	Branched	○ (1.1–1.2)
R–OH/$BF_3 \cdot OEt_2$ (M_w/M_n)	○ (1.2–1.3)	○ (1.2–1.3)	○ (1.8–2.5)	○ (1.5–2.0)	○ (1.5–2.0)

○ : Living or Controlled Cationic Polymerization

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