Direct Living Cationic Polymerization of *p*-Hydroxystyrene with Boron Trifluoride Etherate in the Presence of Water[1]

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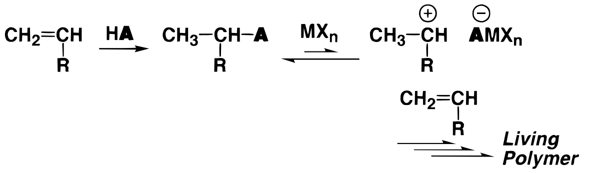
ABSTRACT: Direct living cationic polymerization of *p*-hydroxystyrene (pHS) has been developed in the presence of a fairly large amount of water using BF_3OEt_2 as a Lewis acid catalyst and the adducts (**1**−**4**) of *p*-methoxystyrene (pMOS) and a series of protonic compounds as initiators. In contrast to most living cationic polymerizations, the water and the alcohol adducts (**3** and **4**, respectively) produced polymers with number-average molecular weights (M_n) close to the calculated values from the monomer/initiator mole ratios. With **4**/BF_3OEt_2, the M_n increased with monomer conversion, and the living nature of the chains was confirmed by sequential monomer addition experiments. The polymerization proceeded even in the presence of a large amount water to afford polymers whose M_n increased in direct proportion to monomer conversion with fairly narrow MWDs ($M_w/M_n < 1.4$). This initiating system was also effective at or above ambient temperature (from −15 to +60 °C). The success of this controlled cationic polymerization of unprotected pHS is due to the stability of BF_3OEt_2 and to its tolerance of the hydroxy groups in the monomer and water and the proper selection of the initiator. This initiator contains a covalent C−O bond that is preferentially dissociated by an oxophilic Lewis acid, BF_3. This is the first example of a direct living polymerization of pHS, by any mechanism, without protecting the hydroxy groups.

Introduction

p-Hydroxystyrene (pHS) is an interesting monomer because its polymer is used in photoresists, epoxy-curing agents, adhesives, etc.[2] Obviously, however, the hydroxy group often induces side reactions, which complicates its direct polymerization, and for reaction control the phenol group must be protected in most cases. Protected versions of pHS such as *p-tert*-butoxystyrene,[3] *p*-acetoxystyrene,[4,5] and *p*-(*tert*-butyldimethylsilyloxy)styrene[6] can be polymerized by living anionic, cationic, and radical polymerizations into polymers with controlled molecular weights and narrow molecular weight distributions (MWDs). Even in radical polymerizations, in which the neutral radicals are usually stable toward ionic functional groups, the phenol must be protected to avoid side reactions.[4,5]

We have been investigating living cationic polymerizations of vinyl ethers and styrenes using initiating systems that consist of a protonic acid or its adduct as initiator and a Lewis acid as activator or catalyst (eq 1).[7−9] In these living polymerizations, there is a fast interconversion between the dormant covalent species and the growing species therefrom. The equilibrium is shifted to the dormant species, thereby maintaining a very low concentration of the cationic species, if both components of the initiating system are properly selected.



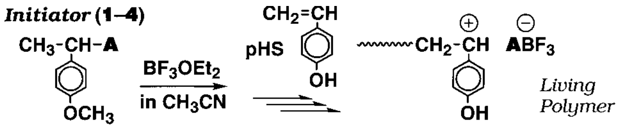
(1)

A: Cl, I, OAc, etc.

MX_n: $ZnCl_2$, $SnCl_4$, $EtAlCl_2$, $TiCl_m(OR)_{4-m}$, etc.

R: OR', Ph, etc.

Scheme 1



−**A**: −Cl (**1**), −OCOCH3 (**2**), −OCH2CH3 (**3**), −OH (**4**)

Despite the accepted notion that cationic polymerizations of vinyl monomers must be done under stringently dry conditions, we have recently reported that a water-tolerant Lewis acid, $Yb(OTf)_3$ ($OTf = OSO_2CF_3$), leads to controlled cationic polymerization of *p*-methoxystyrene (pMOS) *in aqueous media* using pMOS−HCl adduct as the initiator.[10] This polymerization presumably proceeds via reversible activation of the C−Cl bond at the dormant polymer terminus in the presence of water. This suggests that the use of water-tolerant compounds may lead to living/controlled cationic polymerizations of phenol-containing monomers such as pHS.

This paper reports the direct living cationic polymerization of unprotected pHS in aqueous CH_3CN using BF_3OEt_2 as the Lewis acid and a series of protonic adducts (**1**−**4**) of pMOS as the initiator (Scheme 1). Boron trifluoride etherate (BF_3OEt_2) has been widely used for conventional and uncontrolled cationic polymerizations of various monomers.[11] Though not frequently noted, BF_3OEt_2 is highly tolerant of water,[12] similar to $Yb(OTf)_3$, whereas other boron halides such as BCl_3 easily react with protonic compounds. Furthermore, BF_3OEt_2 reportedly induces the direct cationic polymerization of pHS without protection of the phenol group,[13] although no details were given. Herein, we report that the proper selection of the initiator, to be coupled with BF_3OEt_2, leads to the living cationic polymerization of pHS in the presence of a large amount of water. To our knowledge, this is the first example of

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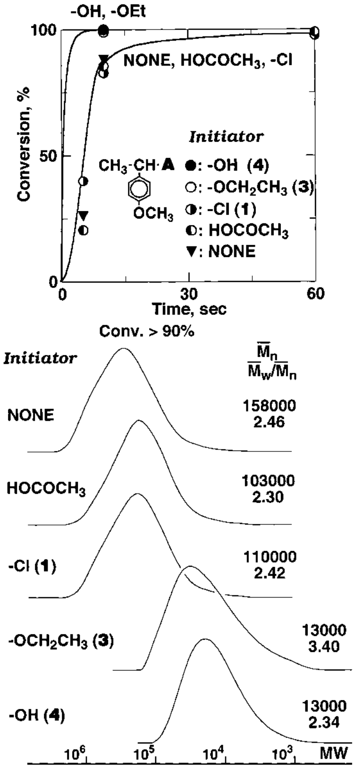


Figure 1. Time−conversion and MWDs curves for the polymerization of pHS with BF_3OEt_2 at −15 °C in acetonitrile. $[pHS]_0 = 0.20$ M; $[initiator]_0 = 4.0$ mM; $[BF_3OEt_2]_0 = 2.0$ mM.

a direct living cationic polymerization of unprotected pHS.

Results and Discussion

Direct Cationic Polymerization of pHS. Unprotected pHS was polymerized by BF_3OEt_2 in both the presence and absence of acetic acid or a series of initiators (**1**, **3**, or **4**) in acetonitrile at −15 °C without protection of the phenol group. Acetonitrile is an ideal solvent since it dissolves pHS monomer and polymer. As shown in Figure 1, BF_3OEt_2 quantitatively polymerizes pHS in both the absence and presence of initiator. Acetic acid and the hydrogen chloride adduct (**1**), which are effective initiators for living cationic polymerizations of styrene in the presence of $SnCl_4$, afforded polymers with number-average molecular weights (M_n) that were much higher ($M_n > 10^5$) than the calculated values [M_n(calcd) = 6150 at 100% conversion], assuming that one initiator molecule generates one polymer chain. In contrast, the alcohol (**3**) and water adducts (**4**), which are not effective in the usual metal chloride-mediated living cationic polymerization due to the strong C−O bond, induce faster polymerizations, and the M_n's of the resulting polymers are closer ($M_n \sim 10^4$) to the calculated value. This is due to the strongly oxophilic nature of boron trifluoride,[12] which easily activates C−O bonds to generate cationic species. The polymerization also proceeds in the absence of an initiator, although the results are less reproducible. This is probably due to the highly hygroscopic nature of pHS.

Controlled Polymerization of pHS. pHS was also polymerized using adducts **1**−**4** in the presence of BF_3OEt_2 in acetonitrile at −15 °C in the presence of a fairly large amount of water ($[H_2O]_0 = 12$ mM). The polymerizations proceed even in the presence of water, although they are all retarded by water (Figure 2). As in the water-free polymerizations, the hydrogen chloride adduct (**1**) polymerizes pHS slower than the alkoxide (**3**) or hydroxide (**4**) adducts. The polymerization with acetic acid adduct (**2**) was slightly slower than with **3** and **4**.

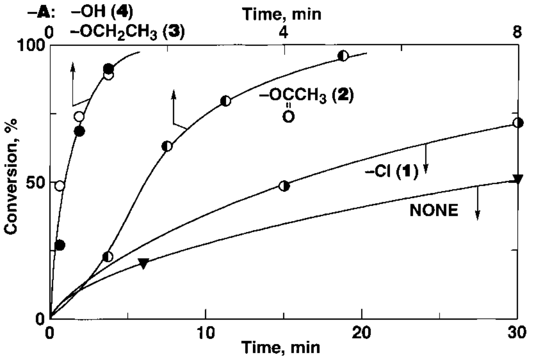


Figure 2. Time−conversion curves for the polymerization of pMOS with $CH_3CH(p\text{-}MeOPh)A/BF_3OEt_2$ in the presence of water at −15 °C in acetonitrile: $[pHS]_0 = 0.20$ M; $[initiator]_0 = 4.0$ mM; $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 12.0$ mM. A = Cl (◑), $OCOCH_3$ (◐), OCH_2CH_3 (○), OH (●); without initiator (▼).

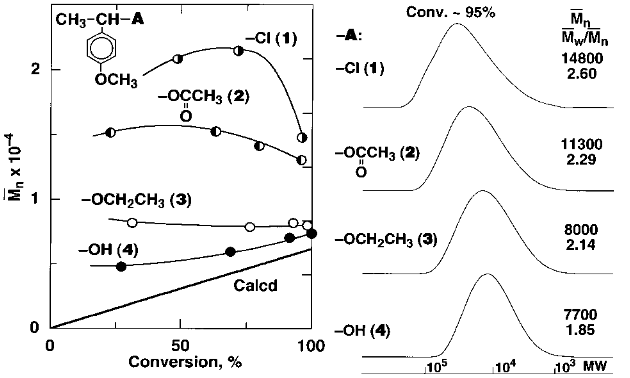


Figure 3. M_n, M_w/M_n, and MWD curves of poly(pHS) obtained with $CH_3CH(p\text{-}MeOPh)A/BF_3OEt_2$ in the presence of water at −15 °C in acetonitrile: $[pHS]_0 = 0.20$ M; $[initiator]_0 = 4.0$ mM; $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 12.0$ mM. B = Cl (◑), $OCOCH_3$ (◐), OCH_2CH_3 (○), OH (●). The diagonal bold line indicates the calculated M_n assuming each initiator molecule generates one living polymer.

As shown in Figure 3, the M_n's of the polymers obtained with **1** and **2** were still higher than the calculated values but much lower than in the absence of water. The molecular weight distributions (MWDs) were broad for all of the polymerizations. The higher and almost constant M_n's are probably due to slow initiation forms **1** and **2** when coupled with BF_3OEt_2 as an activator. On the other hand, **3** and **4** gave polymers whose M_n values were relatively close to the calculated values at the later stage of the polymerization. These results indicate that the polymer chains were generated not from the added water but from the adducts. The M_n increased slightly with monomer conversion when **4**/BF_3OEt_2 was used, and all of the MWDs were unimodal and narrower than those produced in the absence of added water ($M_w/M_n < 2$).

To investigate the possible controlled nature of the BF_3OEt_2-meditated pHS direct polymerizations with **3** or **4**, a fresh feed of pHS was added to the reaction mixture just before the initial charge of monomer had completely polymerized. As shown in Figure 4, the M_n values of the polymers increased in direct proportion to monomer conversion and were close to the calculated values even with **3**/BF_3OEt_2. The MWDs were almost

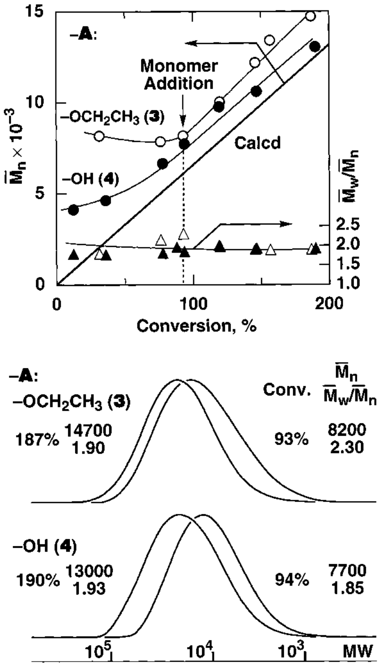


Figure 4. Monomer addition experiments for the pHS polymerization with **3** (○, △) or **4** (●, ▲)/BF_3OEt_2 in the presence of water in acetonitrile at −15 °C: $[pHS]_0 = [pHS]_{add} = 0.20$ M; [**3** or **4**]$_0$ = 4.0 mM; $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 12.0$ mM. The diagonal bold line indicates the calculated M_n assuming each initiator molecule generates one living polymer.

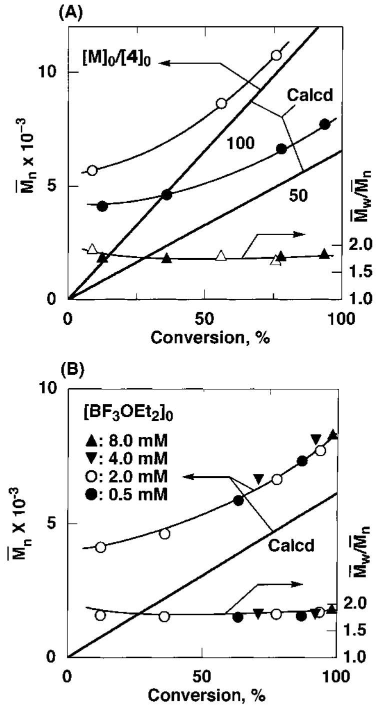


Figure 5. M_n and M_w/M_n values of poly(pHS) obtained with **4**/BF_3OEt_2 in the presence of water in acetonitrile at −15 °C at varying **4** (A) or BF_3OEt_2 (B) concentrations: (A) $[pHS]_0 = 0.20$ M; [**4**]$_0$ = 2.0 (○, △) or 4.0 mM (●, ▲); $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 12.0$ mM, (B) $[pHS]_0 = 0.20$ M; [**4**]$_0$ = 4.0 mM; $[BF_3OEt_2]_0 = 0.5$ (●), 2.0 (○), 4.0 (▼), 8.0 mM (▲); $[H_2O]_0 = 12.0$ mM. The diagonal bold line indicates the calculated M_n assuming each **4** molecule generates one living polymer.

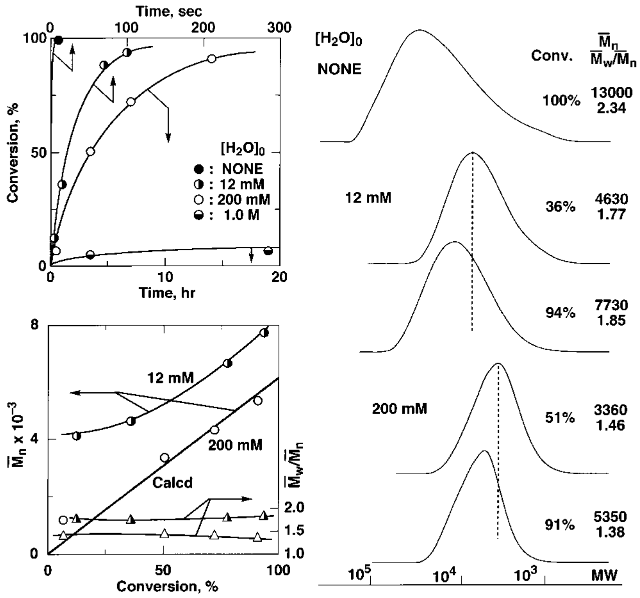
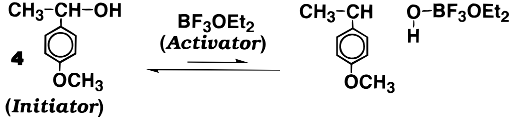


Figure 6. Effects of water on the pHS polymerization with **4**/BF_3OEt_2 in acetonitrile at −15 °C: $[pHS]_0 = 0.20$ M; [**4**]$_0$ = 4.0 mM; $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 0$ (●), 12 (◑, ▲), 200 (○, △), 1000 M (⊖). The diagonal bold line indicates the calculated M_n assuming each **4** molecule generates one living polymer.

unchanged after the monomer addition or narrowed somewhat. These results indicate that the growing chains are long-lived. However, the initiation and/or exchange between the dormant and propagating species may be slower than propagation under these conditions.[15]

Effect of the Concentration of 4 and BF_3OEt_2. Two polymerization series (A and B) were performed in acetonitrile at −15 °C to determine the effect of the concentrations of **4** and BF_3OEt_2 on the polymerization rate and M_n in the presence of a fairly large amount of water. In series A, the initial concentration of the monomer ($[M]_0$) and boron trifluoride etherate ($[BF_3OEt_2]_0$) were kept constant, whereas that of the adduct ([**4**]$_0$) was varied. In series B, $[M]_0$ and [**4**]$_0$ were constant, and $[BF_3OEt_2]_0$ was varied.

The polymerizations were quantitative at all concentrations, and the rate increased with increasing [**4**]$_0$ (series A) or $[BF_3OEt_2]_0$ (series B). Figure 5 shows the M_n and M_w/M_n values of the polymers obtained with **4**/BF_3OEt_2 at varying concentrations. In both series, the M_n of the polymers increased with monomer conversion irrespective of the variations in [**4**]$_0$ (series A) and $[BF_3OEt_2]_0$ (series B). The M_n values are inversely proportional to [**4**]$_0$ and somewhat close to the calculated values assuming that one polymer forms per **4** molecule (diagonal solid lines, Figure 5A,B). The M_n values were independent of $[BF_3OEt_2]_0$ (Figure 5B). These results show that **4** plays the role of the initiator, whereas BF_3OEt_2 activates the stable C−O bond in **4** to form a carbocation (eq 2).



(2)

Effects of Water Concentration. The role of water in the pHS polymerization with **4**/BF_3OEt_2 was investigated further by varying the water concentration (0−1.0 M). As shown in Figure 6, the polymerization proceeded even when the concentration of water was equal to that of monomer ($[H_2O]_0 = [pHS]_0 = 200$ mM).

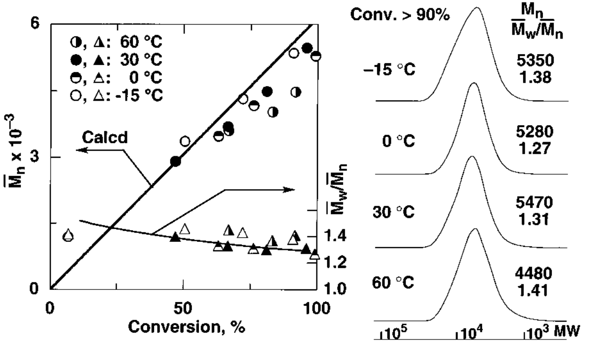


Figure 7. M_n, M_w/M_n, and MWD curves of poly(pHS) obtained with **4**/BF_3OEt_2 in the presence of water in acetonitrile at high temperatures: $[pHS]_0 = 0.20$ M; $[\mathbf{4}]_0 = 4.0$ mM; $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 200$ mM. (◑, ▲) 60 °C, (●, ▲) 30 °C, (◒, ▲) 0 °C, and (○, △) −15 °C. The diagonal bold line indicates the calculated M_n assuming each **4** molecule generates one living polymer.

In this case, M_n increased in direct proportion to monomer conversion with relatively narrow MWDs ($M_w/M_n \sim 1.4$). Although the polymerization was slower at such a high water concentration, the M_n was closer to the calculated values with narrower MWDs. This indicates that water interacts with BF_3OEt_2 to modify its Lewis acidity via coordination. A significant amount of new polymer chains was not generated directly from water because boron trifluoride is not hydrolyzed easily into the required fluoroboric acid.[12] This is also supported by the fact that the polymerization was very slow without the initiator but in the presence of water (see Figure 2). The added water may also produce hydroxide anion, which is a common anion of the polymerization initiated with **4**. This may suppress dissociation of the growing end by similar mechanism as added *n*-Bu_4NCl in the HCl/$SnCl_4$-mediated living cationic polymerization of styrene in CH_2Cl_2.[16] Along with the hydroxide anion, water may generate H_3O^+ or more complex cationic species under such high water concentration, but it may not act as an effective initiator, in contrast to free proton, under vigorously dry conditions for usual cationic polymerizations. Although the role of water has not been clarified yet, this initiating system requires added water to control the polymerization, rather than for initiation.

Polymerizations were also investigated using **4**/BF_3OEt_2 in the presence of water (200 mM) at higher temperature. As shown in Figure 7, similar polymers were obtained at or above ambient temperature, which usually produces lower molecular weight polymers due to chain transfer in cationic polymerizations. At all temperatures, M_n increased in direct proportion to monomer conversion, and the MWDs were fairly narrow ($M_w/M_n = 1.2-1.4$), especially those obtained at 0 °C ($M_w/M_n \sim 1.2$). The success of such living polymerizations at higher temperatures is probably due to the stability of the terminal C−O bond or to stabilization of the growing carbocation by nucleophilic acetonitrile.

Living Polymerization. In the pHS polymerization using **4**/BF_3OEt_2 in the presence of a large amount of water at 0 °C, a fresh feed of pHS was added to the reaction mixture just before the initial charge of the monomer had completely 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 M_n of the polymers increased in direct proportion to monomer conversion and agreed well with the calculated values for living polymers (Figure 8B). The MWDs stayed relatively narrow even after the monomer addition. Thus, the living polymerization of unprotected pHS is accomplished using **4**/BF_3OEt_2 as the initiating system in the presence of a fairly large amount of water.

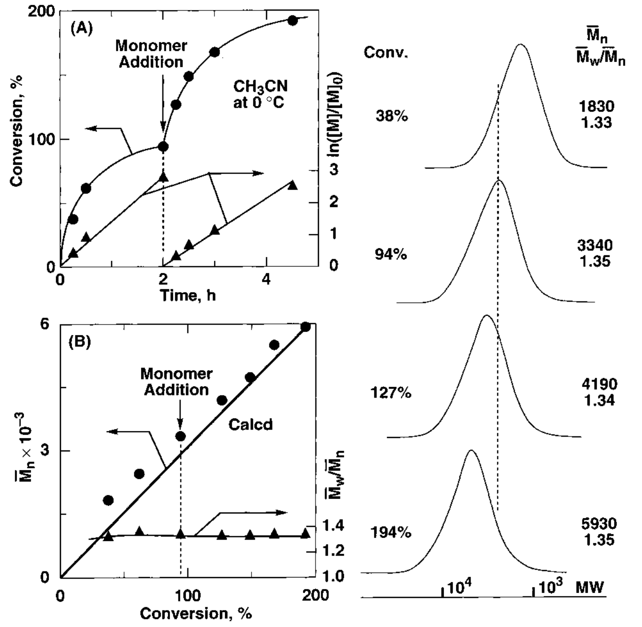


Figure 8. Time−conversion curve and M_n, M_w/M_n, and MWD curves of poly(pHS) obtained in a monomer-addition experiment in the polymerization with **4**/BF_3OEt_2 in the presence of water in acetonitrile at 0 °C: $[pHS]_0 = [pHS]_{add} = 0.10$ M; $[\mathbf{4}]_0 = 4.0$ mM; $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 200$ mM. The diagonal bold line indicates the calculated M_n assuming each **4** molecule generates one living polymer.

Polymer Analysis. The terminal structure of the poly(pHS) obtained using **4** and BF_3OEt_2 in acetonitrile was examined by ^1H NMR spectroscopy. Figure 9A shows the ^1H NMR spectrum of the polymer obtained by quenching the polymerization with excess methanol. The spectrum is characteristic of poly(*p*-vinylphenol) with resonances due to the hydroxy groups (e), phenyl groups (d), and main-chain aliphatic protons (b and c). In addition to these large resonances, small signals due to the end groups are visible. They are the CH_3 (α; 1.0 ppm) and *p*-CH_3O group (β; 3.7 ppm) at the α-end, which are derived from the pMOS water adduct (**4**) initiator, and the −C(Ar)*H*−OCH_3 group (ω; 2.85 ppm) at the ω-end due to quenching the polymerization with methanol. The functionalities of α and β ($F_n = 1.0$) show that one polymer was generated from one initiator, whereas the functionality of the ω-end was less than unity. This is probably due to the formation of hydroxy terminal group derived from the initiator, which was not quenched with methanol.

The polymers after the reaction with acetic anhydride exhibit signals typical of poly(*p*-acetoxystyrene) (Figure 9B). This indicates that the polymerization operates by normal vinyl addition polymerization and does not undergo polyaddition by reaction of the pendant phenol groups with the carbon−carbon double bond.

Figure 10 shows the corresponding matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra of the poly(pHS) obtained using **4**/BF_3OEt_2 as the initiating system and the poly(*p*-acetoxystyrene) generated by reaction of poly-

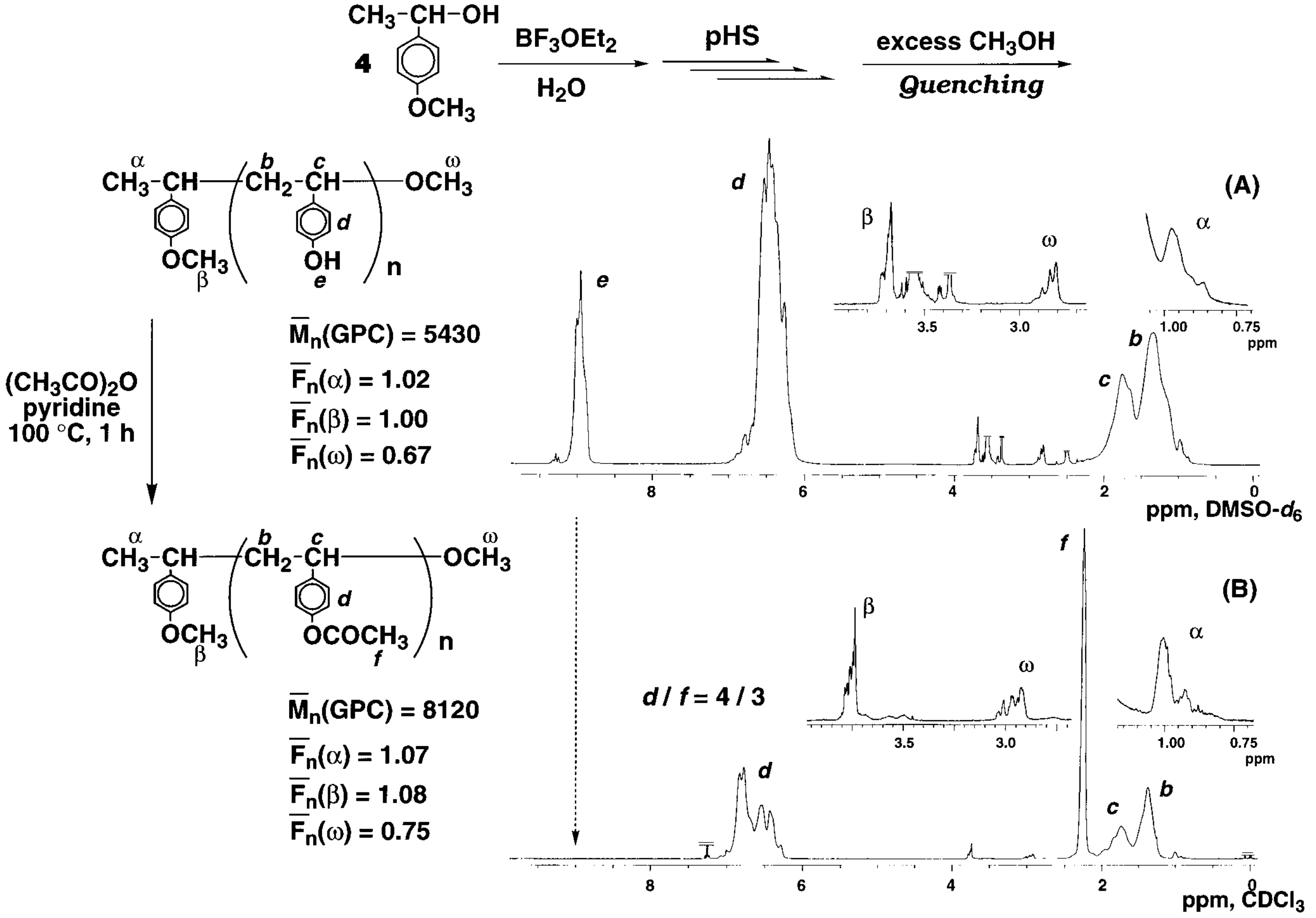


Figure 9. ^{1}H NMR spectra of poly(pHS) ($M_n = 5430$, $M_w/M_n = 1.27$) obtained with **4**/BF$_3$OEt$_2$ in the presence of water in acetonitrile at 0 °C (A) and the polymer after the reaction with acetic anhydride (B).

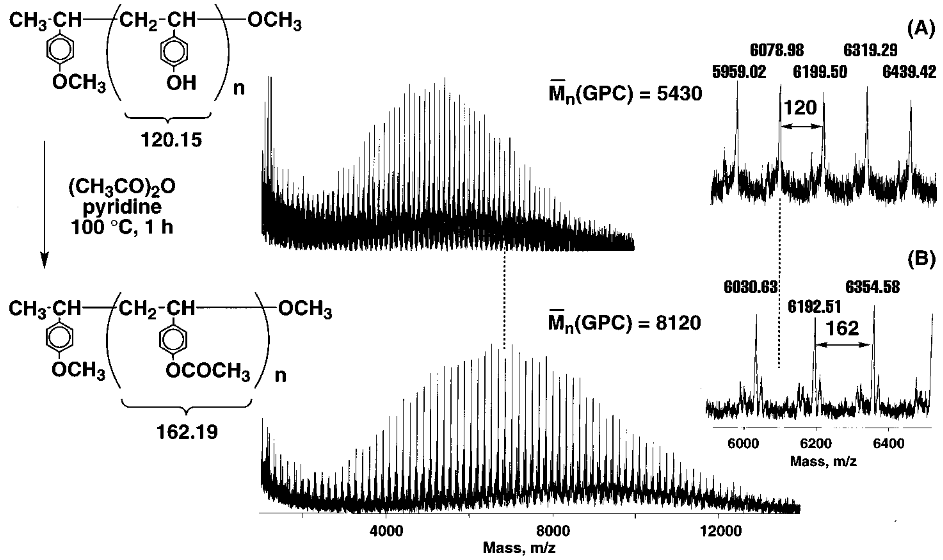


Figure 10. MALDI-TOF-MS spectra of the polymers that were analyzed by ^{1}H NMR in Figure 9.

(pHS) with acetic anhydride. These spectra consist of sharp peaks separated by 120 Da (for Figure 10A) and 162 Da (for Figure 10B), which correspond to the molecular weight of pHS and acetoxystyrene monomer, respectively. A set of peaks due to a homologous series polymers (Figure 10A) shifted to higher molecular weight regions without significant formation of another set of peaks (Figure 10B) after the reaction with acetic anhydride. These results also indicate that the pHS polymerization with **4**/BF$_3$OEt$_2$ in the presence of water proceeds in a controlled fashion to give living polymers without significant side reactions.

In conclusion, we have demonstrated that pHS can be polymerized directly by a cationic polymerization using a combination of the water adduct (**4**) and BF$_3$ in the presence of water. To the best of our knowledge, this is the first example of the controlled polymerization of unprotected pHS.

Experimental Section

Materials. pHS was prepared as reported previously[17] and then recrystallized from *n*-hexane, stored as methanol solution at −20 °C, and further purified by azeotropic drying with toluene just before use. BF_3OEt_2 (Aldrich; purified, redistilled) was used as received. The pMOS−HCl adduct (**1**) was prepared by bubbling dry HCl gas into a 1.0 M solution of pMOS in CCl_4 at 0 °C, and then dry nitrogen was bubbled to remove excess HCl.[18] The water adduct of pMOS [**4**: 4-methoxy-α-methylbenzyl alcohol (Aldrich, 99%)] was distilled from calcium hydride (2 mmHg, 110 °C) before use. The adduct of acetic acid and pMOS (**2**) was prepared by the reaction of **4** and acetic anhydride in pyridine at 100 °C for 1 h, extracted with Et_2O, and purified by distillation (2 mmHg, 110 °C). The ethanol adduct (**3**) was prepared by the reaction of **1** (20 mL of 1.0 M solution in CCl_4) and ethanol (100 mL) at room temperature overnight, extracted with Et_2O, and purified by distillation (2 mmHg, 110 °C). CH_3CN (Wako Pure Chemical Industries, Ltd.; $H_2O < 50$ ppm) was used as received. Distilled deionized water was used for the polymerizations without degassing.

Measurements. The MWD, M_n, and M_w/M_n ratios of the polymers were measured by size-exclusion chromatography (SEC) in DMF containing 10 mM LiBr at 40 °C on three hydrophilic polymer gel columns [TOSOH α-M (pore size: 1000 Å) × 2 + α-3000 (pore size: 250 Å); each 7.8 mm i.d. × 30 cm; flow rate 1.0 mL/min; at 40 °C] that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index and 970-UV ultraviolet detectors. The columns were calibrated against six standard poly(pHS) samples synthesized via living cationic polymerization of *p-tert*-butoxystyrene[3] followed by deprotection ($M_n = 4.0 \times 10^3 - 1.1 \times 10^5$, $M_w/M_n = 1.1 - 1.2$).

^{1}H NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ 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.

Polymerization Procedures. The polymerizations were carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. In a typical example, BF_3OEt_2 (0.006 mmol; 0.30 mL of 20 mM solution in CH_3CN) was added to a solution of pHS (0.6 mmol; 0.073 g), **4** (0.012 mmol; 1.68 μL), and water (0.6 mmol; 10.8 μL) in CH_3CN (2.7 mL). The total volume of the reaction mixture was 3.0 mL. The polymerization was terminated with prechilled methanol (1.0 mL). Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR using the peak intensity ratio between the peaks around 5.5−7.5 ppm (area A) and those at 5.1 ppm (area B) of the methylene protons of the vinyl group in monomer. The former peaks consist of the aromatic protons of monomer and polymer and the methine proton of the vinyl group in monomer. Conversion of monomer was thus calculated according to the following equation: conversion (%) = $(1 - [B/(A - B)]/[B_0/(A_0 - B_0)]) \times 100$, where A_0 and B_0 mean those before addition of BF_3OEt_2. The polymer was isolated by precipitation into *n*-hexane and toluene mixture (1:1; 200 mL). The filtrated precipitate was dissolved in methanol and evaporated to dryness under reduced pressure and vacuum-dried to give the product polymer.

References and Notes

(1) This work was presented in part at (a) the 48th Annual Meeting of the Society of Polymer Science, Kyoto, Japan, May 1999; paper IPf046: Satoh, K.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1999**, *48* (2), 173. (b) IUPAC International Symposium on Ionic Polymerization, Kyoto, Japan, July 1999; paper C1-212 (Satoh, K.; Kamigaito, M.; Sawamoto, M. IP'99 *Preprints*, p 58). (c) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 895.

(2) For example: Fréchet, J. M.; Tessier, T. G.; Willson, C. G.; Ito, H. *Macromolecules* **1985**, *18*, 317.

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