Direct Synthesis of Amphiphilic Random and Block Copolymers of *p*-Hydroxystyrene and *p*-Methoxystyrene via Living Cationic Polymerization with BF_3OEt_2/ROH Systems[1]

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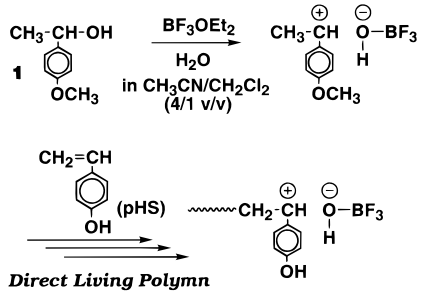
ABSTRACT: This study shows that BF_3OEt_2 induces living cationic polymerization of *p*-alkoxystyrenes and their living copolymerization with *p*-hydroxystyrene (pHS) without protection of the phenolic group. Similar to pHS, controlled cationic polymerizations of *p*-methoxystyrene (pMOS) and *p*-*tert*-butoxystyrene (tBOS) were achieved by combination of the water adduct of pMOS [**1**; $CH_3CH(C_6H_4$-*p*-$OCH_3)OH$] and BF_3OEt_2 in the presence of a fairly large amount of water (equimolar to the monomer or 100 molar excess over BF_3OEt_2) in a CH_3CN/CH_2Cl_2 mixture solvent (4/1 v/v) at 0 °C. The **1**/BF_3OEt_2 initiating system also induced living random copolymerization of pHS and pMOS, where the M_n of the products increased in direct proportion to polymer yield with relatively narrow molecular weight distribution (MWDs) ($M_w/M_n \sim 1.4$). The copolymer compositions agreed with the calculated values from the monomer feed ratios and the conversion of each monomer. MALDI-TOF-MS analysis revealed that each monomer unit was distributed almost randomly. Sequential block copolymerization of unprotected pHS and pMOS with **1**/BF_3OEt_2 gave well-defined amphiphilic diblock copolymers with controlled molecular weight and relatively narrow MWDs ($M_w/M_n \sim 1.3$).

Introduction

Recently, we have found that *p*-hydroxystyrene (pHS; *p*-vinylphenol) is polymerized directly into living polymers with borontrifluoride etherate (BF_3OEt_2) coupled with an alcohol as an initiator [$CH_3CH(C_6H_4$-*p*-$OCH_3)$-OH (**1**); the adduct of water and *p*-methoxystyrene] (Scheme 1).[2] Obviously, this new living cationic polymerization is unique in several aspects relative to conventional cationic polymerizations and even to more recently developed other living cationic processes.[3−5] First, pHS does not need any protection of its phenolic group, which often induces chain transfer or termination reactions in cationic polymerization. Second, a fairly large amount of water (100 molar excess over BF_3OEt_2) is required for the living polymerization to occur, in contrast to the "common knowledge" in cationic polymerization that water must be removed rigorously from reaction media.[6] Third, the polymerization solvent of choice is acetonitrile, which is a highly polar and strongly coordinating solvent not often employed in cationic polymerization.[6] We have concluded[2] that all these unique features originate from the characteristics of BF_3OEt_2 as a Lewis acid (co-initiator or catalyst).[7] As illustrated in Scheme 1, the boron compound apparently generates a carbocationic species by dissociation of the aliphatic C−OH bond in the initiator **1**, with the phenolic group intact.[8] The factors contributing to this selective dissociation include the high oxophilicity of BF_3 and the highly polar medium consisting of CH_3CN and water. In addition, BF_3OEt_2 seems water-tolerant, without undergoing decomposition or deactivation even in the presence of water and phenolic groups.[7] Thus, the **1**/BF_3OEt_2 is a novel initiating system for unprotected pHS in the presence of excess water.

The success in the direct living cationic polymerization of pHS prompted us to apply the **1**/BF_3OEt_2 initiating system for other cationically polymerizable monomers. Among them, *p*-alkoxystyrenes are suited for the living cationic polymerization because of the electron-donating alkoxy groups similar to the hydroxyl group in pHS.[9,10] This paper reports the living cationic polymerization of *p*-methoxystyrene (pMOS) and *p*-*tert*-butoxystyrene (tBOS) with the **1**/BF_3OEt_2 initiating system and the random and block copolymerizations of the two monomers. The latter part thus provides a new method for the synthesis of pHS-based amphiphilic polymers[11,12] without protection and deprotection procedures.

Scheme 1. Direct Living Cationic Polymerization of Unprotected *p*-Hydroxystyrene (pHS) with BF_3OEt_2



Results and Discussion

Homopolymerizations of *p*-Alkoxystyrenes. Prior to the random and block copolymerizations with unprotected pHS, we examined living cationic polymerizations of pMOS and tBOS with BF_3OEt_2 in conjunction with **1** in a mixture of acetonitrile and dichloromethane (4/1 v/v) at 0 °C in the presence of excess water (**1**/BF_3OEt_2/H_2O = 4/2/200 mM) (Scheme 2). CH_2Cl_2 was required as cosolvent because polymers of pMOS and tBOS were not very soluble in CH_3CN.

As with pHS, polymerizations of both monomers occurred smoothly without an induction phase (Figure 1A). The polymerization rate remarkably depends on

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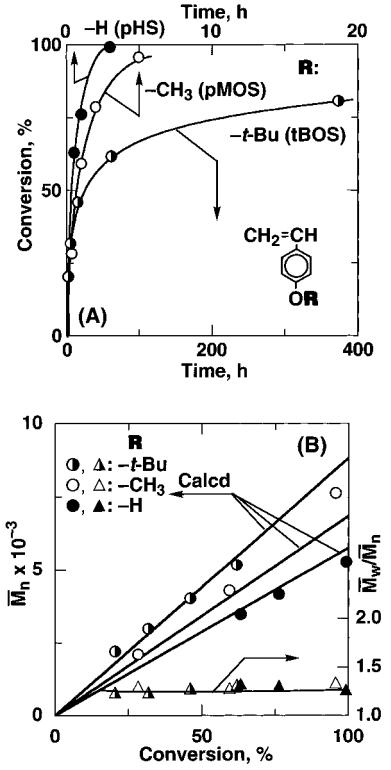
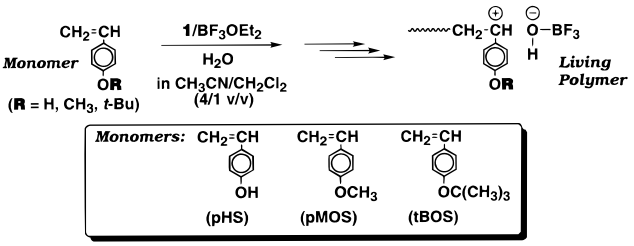


Figure 1. Time−conversion, M_n, and M_w/M_n curves of the polymerization of pHS (●, ▲), pMOS (○, △), and tBOS (◑, ▲) with **1**/BF_3OEt_2 in the presence of water at 0 °C in acetonitrile (including 20 vol % of CH_2Cl_2 for pMOS and tBOS): [monomer]$_0$ = 0.20 M; [**1**]$_0$ = 4.0 mM; [BF_3OEt_2]$_0$ = 2.0 (for pHS) or 10 (for pMOS and tBOS) mM; [H_2O]$_0$ = 200 mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **1** molecule.

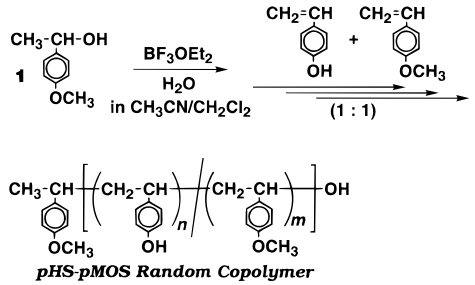
the substituents in the monomer (rate: pHS > pMOS > tBOS).[13] The polymerization of tBOS became slower in the later stage. Independent of the para substituents, in contrast, the number-average molecular weights (M_n) of the polymers increased in direct proportion to monomer conversion and were close to the respective calculated values on the assumption that one initiator molecule generates one polymer chain (Figure 1B).

The molecular weight distributions (MWDs) invariably remained relatively narrow throughout the reactions ($M_w/M_n \sim 1.3$) (Figure 2). However, the pMOS polymers obtained at high conversion (>90%) showed

Scheme 2. Living Cationic Polymerization of *p*-Alkoxystyrenes with 1/BF_3OEt_2



Scheme 3. Random and Living Copolymerization of Unprotected pHS with PMOS



a shoulder in the higher molecular weight region, which suggests a chain-coupling reaction via Friedel−Crafts alkylation of the polymer chain ends onto the phenyl groups of poly(pMOS) in the later stage of the polymerization. Despite this limitation, these results indicate that the **1**/BF_3OEt_2 initiating system (with excess H_2O) is effective in controlling cationic polymerization of not only pHS but also pMOS and tBOS, to give polymers with controlled molecular weights and narrow MWDs.

Random Copolymerization of pHS and pMOS. For random copolymerization (Scheme 3), an equimolar mixture of pHS and pMOS was polymerized with **1**/BF_3OEt_2 in the presence of water in CH_3CN/CH_2Cl_2 (4/1 v/v) at 0 °C (Figure 3). Both monomers polymerized smoothly, pHS slightly faster than pMOS, in accordance with their close homopolymerization rates. The M_n of the copolymer increased in direct proportion to the consumption of monomers and agreed well with the calculated values. The MWDs were relatively narrow. These results show that a random and living copolymerization of unprotected pHS and pMOS is possible with **1**/BF_3OEt_2 where copolymer composition is close

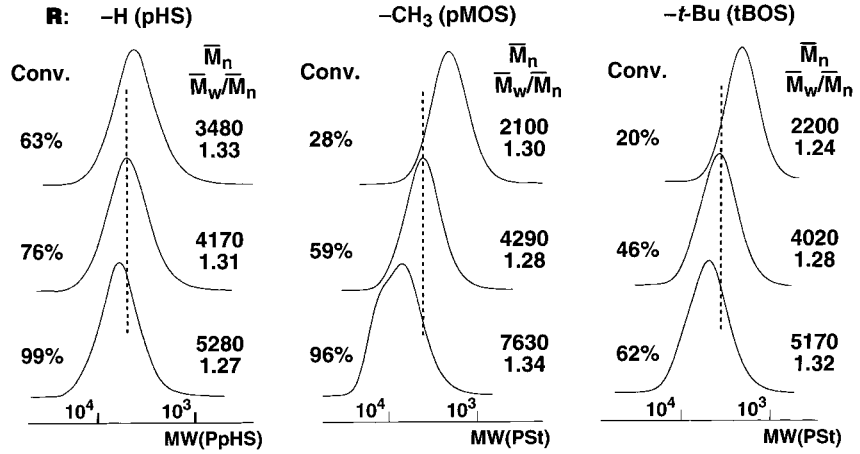


Figure 2. Molecular weight distribution curves of poly(pHS), poly(pMOS), and poly(tBOS) obtained in the same experiments as in Figure 1.

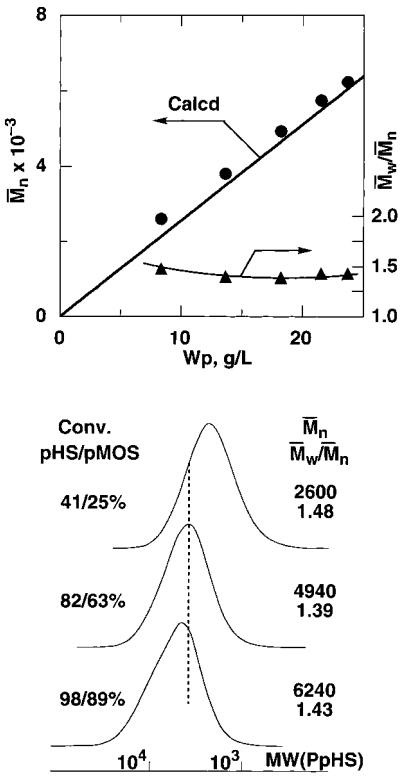


Figure 3. M_n, M_w/M_n, and MWD curves of pHS−pMOS random copolymers obtained with **1**/BF_3OEt_2 in the presence of water in acetonitrile (including 20 vol % of CH_2Cl_2) at 0 °C: $[pHS]_0 = [pMOS]_0 = 0.10$ M; $[\mathbf{1}]_0 = 4.0$ mM; $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 200$ mM. The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **1** molecule.

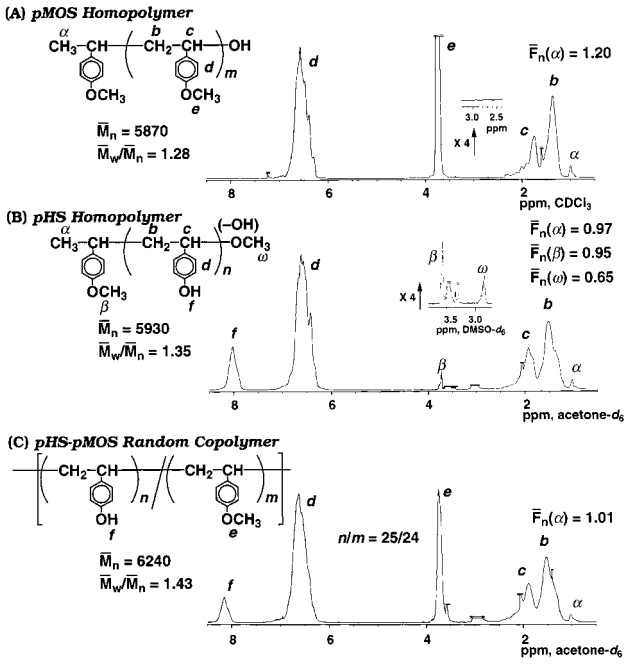


Figure 4. ^{1}H NMR spectra of (A) poly(pMOS) (M_n = 5930, M_w/M_n = 1.35), (B) poly(pHS) (M_n = 5870, M_w/M_n = 1.28), and (C) pHS−pMOS random copolymer (M_n = 6240, M_w/M_n = 1.43) obtained with **1**/BF_3OEt_2 at 0 °C.

to the initial mole ratio of the monomers.

The terminal structures of the poly(pMOS), poly(pHS), and poly(pHS-*random*-pMOS) obtained with **1**/BF_3OEt_2 were examined by ^{1}H NMR spectroscopy (Figure 4, A−C, respectively). All these polymers gave characteristic signals of the main-chain units, i.e., hydroxy groups (f), phenyl groups (d), methoxy groups (e), and main-chain aliphatic protons (b and c). In addition to those, a small signal appeared in all spectra, due to the α-end CH_3 group (α; 1.0 ppm) derived from the initiator (**1**). The α-end functionality was close to unity [$F_n(\alpha) \sim 1.0$]. The spectrum of the poly(pHS) clearly showed the *p*-methoxyphenyl group (β at 3.7 ppm) originated from the initiator, where the functionality was also close to unity [$F_n(\beta) = 0.95$].[2] These results indicate that one polymer was generated from one initiator. For the poly(pMOS) and the random copolymer, the initiator fragment cannot be seen due to overlapping of the peak with the main-chain pMOS segments.

The poly(pHS) (Figure 4B) exhibits a signal assigned to the −CH−OCH_3 group (ω; 2.85 ppm) at the ω-end due to quenching the polymerization with methanol.[14] The ω-end functionality [$F_n(\omega) = 0.6$] was lower than the unity, probably due to the existence of the terminal hydroxy group derived from the initiator.[2] In contrast, the poly(pMOS) was free from such a methoxy ω-end[15] (Figure 4A), which suggests that all chain ends of poly(pMOS) are capped with C−OH bonds, not quenched with methanol, probably because of the lower electron donation from the *p*-methoxy group than from the *p*-hydroxyl group in the dormant terminal. It will be supported by MALDI-TOF-MS analysis (see below) although the hydroxy terminal cannot be seen in the ^{1}H NMR spectrum due to overlapping or broadening of the peaks.

For the random copolymers (Figure 4C), the pHS/pMOS composition, obtained from the peak intensity ratio (d/e), was in good agreement with the calculated values from the monomer feed ratios and conversion of each monomer. Furthermore, the aromatic peak (d) was broader in the copolymers than in the two homopolymers (Figure 4A,B), supporting the random sequence.

These polymers were analyzed by matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Figure 5 shows the spectra of poly(pMOS), poly(pHS), and poly(pHS-*random*-pMOS) obtained with **1**/BF_3OEt_2 (Figure 5, A−C, respectively). The spectra of the poly(pMOS) and the poly(pHS) consist of the sharp peaks separated by 134 Da (Figure 5A) and 120 Da (Figure 5B), which correspond to the molecular weights of pMOS and pHS monomers, respectively. The molecular weight of each peak for the poly(pMOS) was very close to the calculated value for H−(pMOS)$_{n+1}$−OH + Na^+, the chain structure expected from the reaction mechanism (see below). In contrast, the observed peak molecular weights for the poly(pHS) agreed well with those of the polymers having the initiator moiety at the α-end but without a methoxy or hydroxy group at the ω-end, due to elimination induced by laser ionization. This indicates the lower stability of these C−O bonds adjacent to the pHS unit. These results also indicate that the pMOS and pHS homopolymerizations with **1**/BF_3OEt_2 give living polymers without significant side reactions.

On the other hand, the spectrum of the random copolymer exhibited complicated peaks; on close inspection, however, the spectrum gave quite valuable information. Each signal was separated by about 14 Da interval, which corresponds to the difference in molecular weights between pMOS and pHS monomer units.

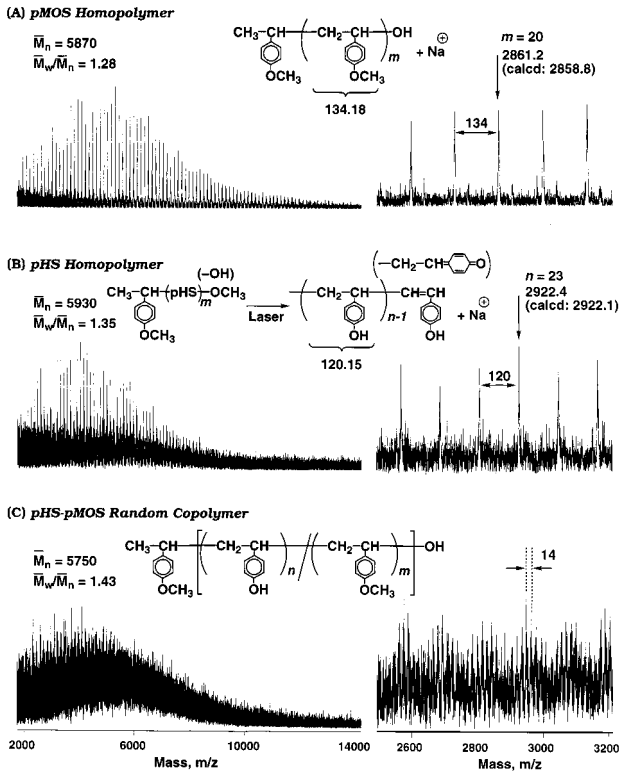


Figure 5. MALDI-TOF-MS spectra of (A) poly(pMOS) (M_n = 5930, M_w/M_n = 1.35), (B) poly(pHS) (M_n = 5870, M_w/M_n = 1.28), and (C) pHS−pMOS random copolymer (M_n = 5750, M_w/M_n = 1.43) obtained with **1**/BF_3OEt_2 at 0 °C.

The spectrum was also free from peaks of the corresponding homopolymers (Figure 5C). These results suggest that the polymers were not mixtures of the homopolymers but random copolymers.

To clarify the randomness of the copolymers, statistical analysis was carried out by simulation. Figure 6 compares the observed MALDI-TOF-MS spectrum of the random copolymer (A) and the simulated spectrum of the hypothetical copolymer (B) that was constructed assuming the following: (1) The copolymer has the same number-average degree of polymerization ($\overline{n+m}$) and the same polydispersity ratio (P_w/P_n) as those of the real copolymer shown in Figure 6A. (2) The distribution obeys the Schulz−Zimm exponential distribution (n_{n+m}).[16,17] (3) Each monomer unit is distributed randomly, where the probability of each unit is the same as that of the copolymer composition (pMOS/pHS ratio) obtained by the initial monomer feed and the two monomers' conversion. These assumptions lead to the probability ($P_{k,n+m-k}$) or fraction of the copolymer that has k units of pHS and ($n + m - k$) units of pMOS:

$$P_{k,n+m-k} = n_{n+m}({}_{n+m}C_k P_n{}^k P_m{}^{n+m-k}) \quad (1)$$

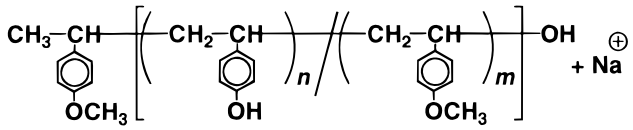
where n_{n+m} is defined as

$$n_{n+m} = [\rho^b \exp(-\rho)]/b! \quad (2)$$

$$\rho = (b+1)(n+m)/(\overline{n+m}) \quad (3)$$

$$P_w/P_n = 1 + 1/(b+1) \quad (4)$$

For the copolymer in Figure 6A, $\overline{n+m} = ([\text{pHS}]_0/[\mathbf{1}]_0) \times \text{conv(pHS)} + ([\text{pMOS}]_0/[\mathbf{1}]_0) \times \text{conv(pMOS)} = 25 \times 0.92 + 25 \times 0.79 = 42.25$; $P_w/P_n = 1.43$. Figure 6B plotted $P_{k,n+m-k}$ against the molecular masses on the assumption that the copolymer has the following structure (ionized with Na^+):



The simulated mass spectrum (Figure 6B) consists of a series of clustered peaks, where each of which is for copolymers with the same $n + m$ values but different compositions. The observed and simulated spectra are very similar to each other, which indicates that the pHS and the pMOS units were distributed almost randomly or statistically. Although the simulation is based on the simple hypothesis that the molecular weight distribution obeys the Schulz−Zimm distribution with the isotope effects neglected, the MALDI-TOF-MS analysis supports that the **1**/BF_3OEt_2 system induced cationic random copolymerization of pHS and pMOS.

Block Copolymerization. Sequential block copolymerization of unprotected pHS and pMOS was also investigated with the BF_3OEt_2-based initiating system. pHS was first polymerized with **1**/BF_3OEt_2 in the presence of water in acetonitrile at 0 °C (Figure 7). After a nearly complete consumption of pHS, a feed of pMOS, equimolar to the former, and CH_2Cl_2 as a cosolvent were added into the living poly(pHS) solution. The second monomer was smoothly polymerized. As shown in Figure 7, the MWD curves shifted to higher molecular weights upon pMOS addition. Thus, the **1**/BF_3OEt_2/H_2O system was effective in block copolymerization of pMOS and pHS without protection of the phenolic groups.

Figure 8 shows the ^{1}H NMR spectrum of a typical product thus obtained. Similar to the homopolymers and the random copolymers, the block copolymers show characteristic signals of the main-chain units and the CH_3 group (α; 1.0 ppm) at the α-end that originated from the initiator (**1**), and the functionality of the methyl group is almost unity [$F_n(\alpha) = 1.04$]. In addition, there was no absorption at 2.85 ppm for the methoxy group due to the methanol quenching (cf. Figure 4B). This indicates a complete cross-propagation; i.e., the growing poly(pHS) terminal was virtually converted into the poly(pMOS) terminal after addition of pMOS.

In conclusion, the **1**/BF_3OEt_2 initiated the living polymerization of *p*-alkoxystyrenes in the presence of a fairly large amount of water. Well-defined random and block copolymers of pHS and pMOS were directly synthesized with the **1**/BF_3OEt_2 system without protection of the phenolic groups in pHS monomer. These copolymers may be interesting as amphiphilic polymers directly derived from pHS.

Experimental Section

Materials. pHS was prepared as reported,[18] recrystallized from *n*-hexane, stored as methanol solution at −20 °C, and further purified by azeotropic drying with toluene just before use. pMOS (Aldrich, 97%) was dried overnight over calcium chloride, distilled from calcium hydride under reduced pressure, and stored at −80 °C. tBOS (Hokko Chemicals, 99%) was distilled twice from calcium hydride under reduced pressure and stored at −80 °C. BF_3OEt_2 (Aldrich; purified, redistilled) was used as received. The water adduct of pMOS [**4**: 4-methoxy-α-methylbenzyl alcohol (Aldrich, 99%)] was distilled from calcium hydride (2 Torr, 110 °C) before use. CH_3CN (Wako,

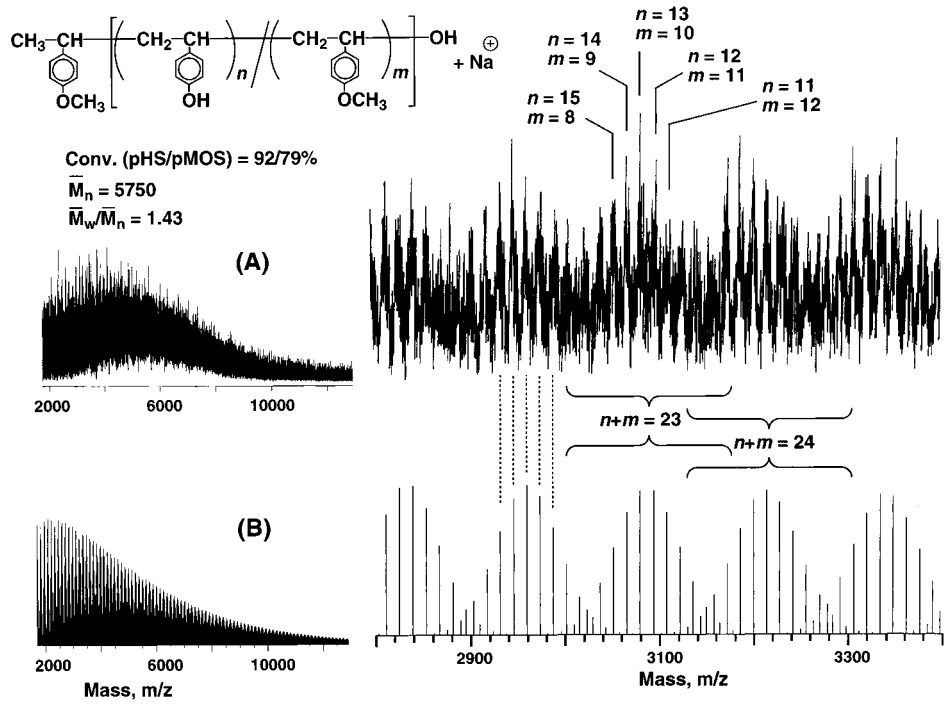


Figure 6. Comparison between (A) MALDI-TOF-MS spectrum of the random copolymer (monomer conversions: pHS, 92%; pMOS, 79%) and (B) the statistically simulated molar masses.

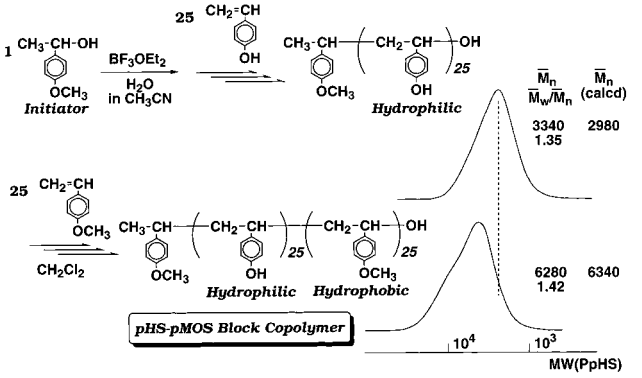


Figure 7. Molecular weight distribution curves of poly(pHS) and pHS−pMOS block copolymers obtained with **1**/BF_3OEt_2 in the presence of water in acetonitrile at 0 °C: $[pHS]_0 = [pMOS]_{add} = 0.10$ M; $[\mathbf{1}]_0 = 4.0$ mM; $[BF_3OEt_2]_0 = 2.0$ mM; $[H_2O]_0 = 200$ mM. 20 vol % of CH_2Cl_2 was added along with pMOS. Conversions are over 95% for both monomers.

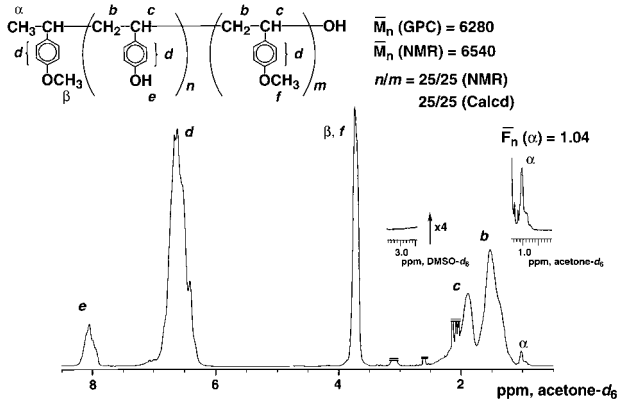


Figure 8. ^{1}H NMR spectrum of pHS−pMOS block copolymer ($M_n = 6280$, $M_w/M_n = 1.42$) obtained with **1**/BF_3OEt_2 at 0 °C.

$H_2O < 50$ ppm) was used as received. Distilled water (Wako) was used for the polymerizations without degassing. CH_2Cl_2 (Wako, >99%) as a solvent and bromobenzene (Wako, >98%) as an internal standard for gas chromatography (for *p*-alkoxystyrenes in homopolymerizations) were dried overnight over calcium chloride and doubly distilled from phosphorus pentoxide and then from calcium hydride before use.

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: 100 nm) × 2 + α-3000 (pore size: 25 nm); each 7.8 mm i.d. × 30 cm; flow rate 1.0 mL/min] 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 tBOS[10] followed by deprotection ($M_n = 4.0 \times 10^3 - 1.1 \times 10^5$, $M_w/M_n = 1.1-1.2$). The MWD, M_n, and M_w/M_n values of poly(pMOS) and poly(tBOS) were measured in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: $1-10^4$ nm; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] connected to the same pump/detector combination as above. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; $M_n = 580-1\,547\,000$; $M_w/M_n < 1.1$) as well as the styrene monomer.

^{1}H NMR spectra were recorded in acetone-d_6, 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 a 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 laser 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. A typical example for pMOS polymerization is given below. The copolymerization was initiated by adding solutions of BF_3OEt_2 (0.006 mmmol; 0.30 mL of 20 mM in CH_3CN) into a monomer solution (2.7 mL) containing pMOS (0.6 mmol, 0.08 mL) **1** (0.012 mmol, 1.68 μL), water (0.6 mmol, 10.8 μL), and bromobenzene (0.04 mL) in a CH_3CN/CH_2Cl_2 mixture (2.0/0.5 mL) at 0 °C. The total volume of the reaction mixture was 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 the residual monomers measured by ^{1}H NMR. The quenched solutions were diluted with ethyl acetate ($\sim$25 mL), washed with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymer. For example, conversion for the mixture run for 2 h was 59% by gas chromatography, and polymer yield was 57%. The M_n and M_w/M_n values for the obtained polymer were 4290 and 1.28, respectively (see Figure 2).

References and Notes

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