Synthesis of Amphiphilic Block Copolymers of 4-Substituted Styrene and Cyclohexene Oxide Utilizing Radical/Cation Transformation Polymerization

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Introduction

Radical polymerization is most commonly used in industry for polymer formation from vinyl and diene compounds. Free-radical polymerization techniques have been well-documented in a large volume of papers and patents and have been well-systematized.[1−3] It is difficult to synthesize block copolymers by conventional free-radical polymerization because of bimolecular termination and chain transfer. In the past decade, however, block copolymers of several vinyl monomers were synthesized to a significant extent by controlled radical polymerization.[4]

In the course of our ESR studies on propagating radicals of vinyl compounds, we found that propagating radicals were transformed into the corresponding cations through electron transfer to an electron acceptor. Using this finding, we previously synthesized block copolymers of 4-methoxystyrene (MOS) and cyclohexene oxide (CHO) using 2,2′-azobis(isobutyronitrile) (AIBN) in the presence of diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$), an electron acceptor, without the formation of telechelic polymers.[5−7] This radical/cation transformation polymerization of MOS and CHO involves the following steps: radicals produced by the decomposition of AIBN initiate radical polymerization of MOS; the propagating radical undergoes electron transfer to $Ph_2I^+PF_6^-$ to form the corresponding polymer cation, accompanied by the formation of phenyl radical which can initiate radical polymerization of MOS; the polymeric cation initiates cationic polymerization of MOS; once the propagating cation reacts with CHO, the resulting oxonium ion does not react with MOS because of the lower acidity of the oxonium ion, leading to the formation of block copolymers of MOS and CHO. In the radical/cation transformation polymerization, a significant amount of homopolymer of CHO was formed through chain transfer in the cationic polymerization. We also synthesized other block copolymers composed of radically and cationically polymerized sequences using the radical/cation transformation polymerization.[7,8]

In this paper, we report the synthesis of block copolymers of 4-(*tert*-butyldimethylsiloxy)styrene (BDMSOS) and CHO using the radical/cation transformation polymerization (Scheme 1). BDMSOS units were transformed to 4-hydroxystyrene (HOS) units with tetrabutylammonium fluoride, thus yielding an amphiphilic block copolymer. We also studied briefly the association behavior of the amphiphilic block copolymers of HOS and CHO in methanol.

Experimental Section

Materials. Cyclohexene oxide (CHO) (Nacalai Tesque) and 1,2-dichloroethane (Nacalai Tesque) were dried with CaH_2 and distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) (Wako) was recrystallized from methanol. *N*,*N*-Dimethylformamide (DMF) (Nacalai Tesque) was dried with CaH_2 overnight. Other reagents were used without further purification.

4-(*tert*-Butyldimethylsiloxy)styrene (BDMSOS) was prepared by alkali hydrolysis of 4-acetoxystyrene (Aldrich) followed by reaction with *tert*-butyldimethylsilyl chloride (Aldrich) according to the procedure of Hirao et al.[9]

Radical/Cation Transformation Polymerization of 4-Substituted Styrene and CHO. A typical procedure of radical/cation transformation polymerization of BDMSOS and CHO is described below.

A solution of AIBN in 1,2-dichloroethane (24 mM, 0.5 mL), a solution of diphenyliodonium hexafluorophospate ($Ph_2I^+PF_6^-$) (TCI) in 1,2-dichloroethane (48 mM, 0.5 mL), BDMSOS (480 mg, 2.0 mmol), and CHO (485 mg, 4.9 mmol) were charged in a glass ampule. This ampule was connected to a high-vacuum line and degassed by three freeze−thaw cycles with an oil rotary pump and by three freeze−thaw cycles with an oil diffusion pump. After this ampule was sealed under high vacuum, it was immersed in an oil bath thermostated at 80 °C in the dark for 4 h. When the reaction mixture was poured into excess methanol (50 mL) containing a small amount of ammonia, polymer was obtained as precipitate. The polymer was purified by reprecipitation with THF−methanol three times and dried in vacuo; yield 73.4%. IR (KBr) ν_{max}: 3017 (aromatic CH), 2956 (CH), 2926 (CH), 2858 (CH), 1607 (aromatic ring), 1509 (aromatic ring), 1450 (CH_2), 1251 (CH_3), 1172 (CC), 1163 (CC), 1082 (CO). ^1H NMR (CD_3Cl): δ 0.0−0.2 (CH_3Si), 0.8−1.0 (CH_3C), 1.1−2.0 (CH_2 and CH), 3.2−3.5 (CH_2−O and CH−O), 6.0−6.5 (phenyl).

Deprotection of Polymers Containing BDMSOS Units. A typical procedure of deprotection of BDMSOS units in the polymers obtained is described below.

Poly(BDMSOS) (100 mg, 0.43 mmol of monomer units) was added to a solution of tetrabutylammonium fluoride (Bu_4NF) in tetrahydrofuran (THF) (Aldrich) (1.0 M, 2.4 mL). The reaction mixture was stirred at room temperature overnight. Then the reaction mixture was poured into a saturated aqueous ammonium chloride (100 mL) to precipitate the deprotected polymer. The polymer obtained was purified by washing with water and hexane and dried in vacuo. The quantitative deprotection was confirmed by ^1H NMR; yield 93.7%. IR (KBr) ν_{max}: 3360 (OH), 3005 (aromatic CH), 2961 (CH), 2905 (CH), 1598 (aromatic ring), 1503 (aromatic ring), 1435 (aromatic ring), 1361 (aromatic ring), 1225 (CC), 1163 (CC). ^1H NMR (acetone-d_6): δ 1.2−2.1 (CH_2 and CH), 6.2−6.8 (phenyl), 7.7−8.0 (OH).

Measurements. FT/IR spectra were recorded on a JASCO FT/IR-410 spectrometer. ^1H NMR 270 MHz spectra were measured on a JEOL JNM-EX270 spectrometer in $CDCl_3$ or acetone-d_6 at 30 °C. GPC measurements were carried out at 40 °C on a TOSOH CCP & 8010 system equipped with TOSOH TSKgel G2000H$_{XL}$ and G3000H$_{XL}$ columns (bead size: 5 μm) connected in series, using THF as eluent at a flow rate of 0.8 mL/min. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. Molecular weights were calibrated with polystyrene standards (TSK standard polystyrene). ESR spectra were obtained on a JEOL JES RE2X spectrometer at X-band utilizing 100 kHz field modulation and 1 mW microwave power with a 5 mm sample tube. ESR measurements for benzene

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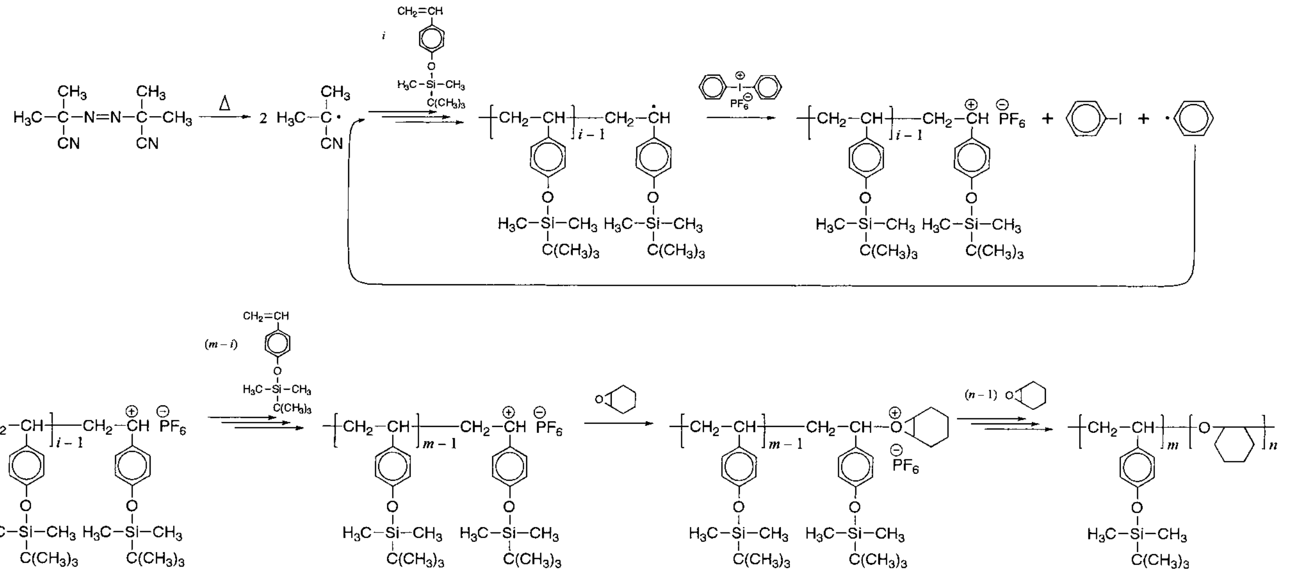
Scheme 1. Radical/Cation Transformation Polymerization of BDMSOS and CHO



solutions of BDMSOS containing a small amount of di-*tert*-butyl peroxide (*t*BPO) were carried out under photoirradiation using a 500 W ultrahigh-pressure mercury lamp (Ushio USH-500D). In turbidimetric titration measurements, each sample (10 mg) was dissolved in benzene/2-butanone (3:1 v/v). As ethanol was added to the polymer solution in a 1 cm path length quartz cuvette with stirring, turbidity (reported as 100 − %*T*) was measured with a Shimadzu UV-2100 spectrometer at 400 nm at 25 °C. Intervals for mixing were fixed to 5 min for stabilization because we confirmed that turbidity became virtualy constant in this time interval. Thin-layer chromatography (TLC) experiments were performed with silica gel 60 F_{254} TLC plates (Merck) at room temperature using ethanol as eluent. Quasi-elastic light scattering (QELS) measurements were carried out at 25 ± 0.1 °C using an Otsuka Electronics Photal DLS-7000 light scattering spectrometer equipped with an Ar ion laser (60 mW at 488 nm) and detector optics. An ALV-5000E digital multiple-τ correlator (Langen-GmbH) was employed for data collection. Sample solutions were filtered with a 0.2 μm pore size membrane filter prior to measurement. The details of QELS measurements were described previously.[10]

Results and Discussion

Radical/Cation Transformation Polymerization of BDMSOS and CHO. Clear ESR signals were observed for radical polymerization systems of BDMSOS initiated by *t*BPO in benzene (Figure 1a). These signals are reasonably assigned to propagating radicals of BDMSOS based on the simulation (Figure 1b) using hyperfine splitting constants indicated in Figure 1c. When ESR was measured in the presence of $Ph_2I^+PF_6^-$, an electron acceptor, only very weak ESR signals were observed (see Supporting Information), indicating that the propagating radicals of BDMSOS are oxidized to the corresponding cations by $Ph_2I^+PF_6^-$.

As with 4-methoxystyrene and CHO,[5−7] block copolymers of BDMSOS and CHO can be formed using the radical/cation transformation polymerization (Scheme 1). Table 1 lists conditions and results of the radical/cation transformation polymerization of BDMSOS and CHO (runs 1−4). The highest polymer yield was 73.4%. FT/IR and NMR spectra (see Supporting Information) indicated that the polymer was composed of both the 4-substituted styrene and CHO units. These observations suggest the formation of block copolymers, but it is still possible that the polymer consisted of the homopolymers. As mentioned in later subsection, however, fractionation of the deprotected polymer indicated that poly(BDMSOS-*b*-CHO) was preferentially formed.[11]

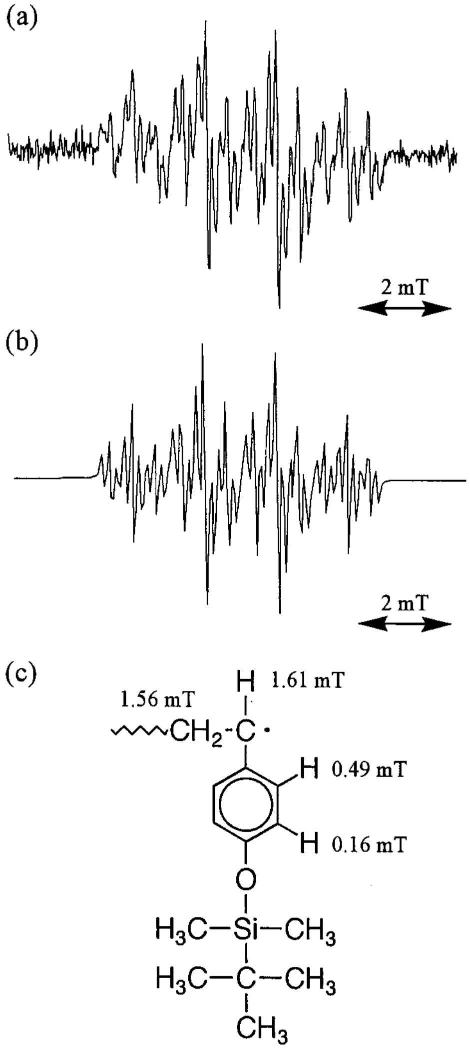


Figure 1. ESR spectra for propagating radicals of BDMSOS: observed (a) and simulated (b) spectra and hyperfine splitting constants used for the simulation (c).

Table 1. Conditions and Results of Polymerization of BDMSOS and/or CHO Using AIBN in the Presence or Absence of $Ph_2I^+PF_6^-$ [a]

run	BDMSOS (M)	CHO (M)	AIBN (mM)	$Ph_2I^+PF_6^-$ (mM)	yield[b] (%)	$M_w \times 10^{-4}$ [c]	M_w/M_n[c]	unit ratio in polymer[d] BDMSOS:CHO
1	1.0	2.3	6.0	12	73.4	5.1	2.0	1:0.5
2	1.8	2.4	6.0	12	40.2	10.3	1.5	1:0.70
3	1.3	3.1	6.0	12	28.8	4.1	2.2	1:0.70
4	0.7	3.7	6.0	12	14.6	4.8	1.4	1:0.83
5	1.0	0	6.0	0	27.2	4.6	2.0	1:0
6	1.0	0	6.0	12	61.4	3.7	1.8	1:0
7	1.0	0	0	12	0			
8	0	2.5	6.0	12	2.1			

[a] Polymerization was carried out in $(CH_2Cl)_2$ at 80 °C for 4 h under high vacuum. [b] Based on the total monomers. [c] Determined by GPC relative to polystyrene. [d] Determined by ^{1}H NMR.

Table 2. Conditions and Results of Cationic Copolymerization of BDMSOS and CHO[a]

run	BDMSOS (M)	CHO (M)	yield[b] (%)	$M_w \times 10^{-4}$ [c]	M_w/M_n[c]	unit ratio in polymer[d] BDMSOS: CHO
1	2.4	0.5	6.0	20.1	1.8	1:28
2	1.8	2.4	26.8	4.7	1.9	0:1
3	0.7	3.8	40.3	5.9	2.5	0:1

[a] Polymerizations were carried out with 1.7 mM $Et_3O^+PF_6^-$ in $(CH_2Cl)_2$ at 0 °C for 2 h. [b] Based on CHO. [c] Determined by GPC relative to polystyrene. [d] Determined by ^{1}H NMR.

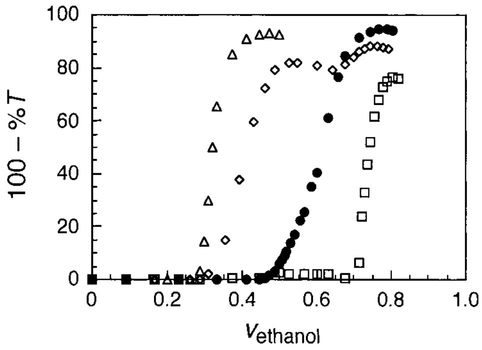


Figure 2. Turbidimetric titration of solutions of poly(CHO) (△), poly(BDMSOS) (□), poly(BDMSOS-*b*-CHO) (●), and a blend of the homopolymers (◇) in benzene/2-butanone (3:1 v/v) with ethanol.

In addition, the copolymer composition seems to depend on comonomer feed ratio.

To confirm the formation of block copolymers, we examined polymerizations under several conditions (runs 5−8 in Table 1). Polymerization of BDMSOS was initiated by AIBN in the absence and presence of $Ph_2I^+PF_6^-$ (runs 5 and 6). BDMSOS was not polymerized in the presence of $Ph_2I^+PF_6^-$ (run 7). Only a small amount of polymer was obtained by polymerization of CHO by AIBN even in the presence of $Ph_2I^+PF_6^-$ (run 8). Furthermore, cationic copolymerization of BDMSOS and CHO initiated by triethyloxonium hexafluorophosphate ($Et_3O^+PF_6^-$) produced polymers composed mainly of CHO (Table 2), indicating that $Et_3O^+PF_6^-$ reacts with CHO much faster than with BDMSOS and oxionium ions derived from CHO do not react with BDMSOS. On the basis of these results, we confirmed that block copolymers of BDMSOS and CHO were obtained by the radical/cation transformation mechanism.

Characterization of Block Copolymers of BDMSOS and CHO (Poly(BDMSOS-*b*-CHO)). Figure 2 compares plots of turbidimetric titration for poly(CHO), poly(BDMSOS), a mixture of the two homopolymers, and the polymer obtained by the radical/cation transformation polymerization (run 1 in Table 1), using benzene/2-butanone (3:1 v/v) and ethanol as solvent/precipitant. In the case of poly(CHO), turbidity due to precipitation commences and increases at a volume fraction of ethanol ($v_{ethanol}$) of 0.30 and levels off at $v_{ethanol} > 0.45$. In the case of poly(BDMSOS), turbidity increases significantly with $v_{ethanol}$ in the $v_{ethanol}$ region 0.70−0.80. Turbidity for the mixture of poly(CHO) and poly(BDMSOS) shows a two-step increase in the $v_{ethanol}$ regions 0.30−0.53 and 0.65−0.75 corresponding to precipitation of poly(CHO) and poly(BDMSOS), respectively. On the other hand, in the case of the polymer obtained (run 1 in Table 1), turbidity is nearly constant at $v_{ethanol} \leq 0.45$ and increases rather gradually in the $v_{ethanol}$ region 0.50−0.75. The turbidity increase in this $v_{ethanol}$ region is not due to homopolymers of CHO and BDMSOS, suggesting that the polymer is composed mainly of poly(BDMSOS-*b*-CHO). As described below, this is confirmed by fractionation of the deprotected polymer.

Figure 3. TLC profiles for poly(HOS) (a), poly(CHO) (b), a mixture of the homopolymers (c), and poly(HOS-*b*-CHO) (d) using ethanol as eluent.

Deprotection of Poly(BDMSOS-*b*-CHO) and Characterization of Poly(HOS-*b*-CHO). *tert*-Butyldimethylsiloxy moieties in poly(BDMSOS-*b*-CHO) were quantitatively hydrolyzed in THF using Bu_4NF without any cleavage of poly(CHO) block sequences. The deprotected polymer (run 1 in Table 1) was fractionated into methanol-insoluble fraction (fraction 1), methanol-soluble and hexane-insoluble fraction (fraction 2), and methanol-soluble and hexane-soluble fraction (fraction 3). FT/IR and NMR spectra indicated that fractions 1 and 2 were poly(CHO) and poly(HOS), respectively, and fraction 3 was composed of both CHO and HOS units. Fraction 3 was analyzed by TLC to see whether this fraction contained either of the homopolymers. Figure 3 shows an example of TLC profiles for individual homopolymers, their mixture, and fraction 3, using ethanol as eluent. R_f values for poly(HOS) and poly(CHO) are ca. 0.93 and 0.01, respectively. In the case of the mixture, spots for poly(CHO) and poly(HOS) are clearly seen at respective R_f values. On the other hand, for fraction 3, there are no spots at $R_f \approx 0.93$ and 0.01, but there is a broad band in the R_f region 0.13−0.67. These observations indicate that fraction 3 is poly(HOS-

Table 3. Characteristics of Poly(HOS) and Poly(HOS-*b*-CHO) for QELS Measurements

polymer	unit ratio in copolymer HOS:CHO[a]	$M_w \times 10^{-4}$ [b]	M_w/M_n [b]
1	1:0	3.3	2.7
2	1:0.08	10.3	1.5
3	1:0.50	5.1	2.0

[a] Determined by ^{1}H NMR. [b] Determined by GPC for the polymers (poly(BDMSOS) or poly(BDMSOS-*b*-CHO)) before deprotection.

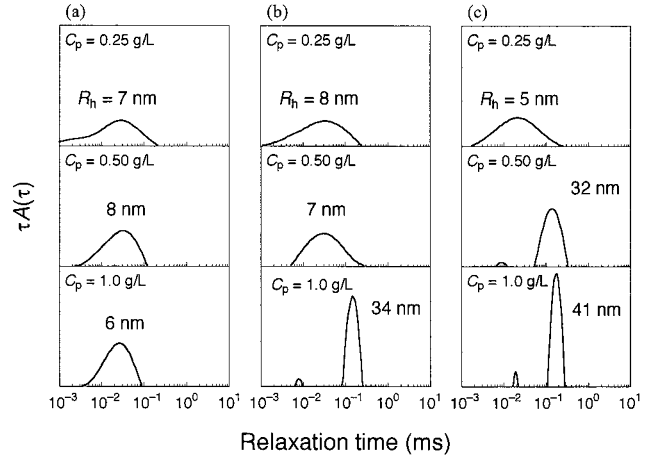


Figure 4. Relaxation time distributions obtained from QELS for poly(HOS) (polymer 1 in Table 3) (a) and poly(HOS-*b*-CHO)s with molar ratios of HOS:CHO = 1:0.08 (b) and 1:0.5 (c) (polymers 2 and 3 in Table 3, respectively) in methanol at varying C_p.

b-CHO) and contains no homopolymers. In addition, weight fractions of fractions 1 (poly(CHO)), 2 (poly(HOS)), and 3 (poly(HOS-*b*-CHO)) were 0.042, 0.021, and 0.937, respectively, indicating that poly(BDMSOS-*b*-CHO) was obtained preferentially by the radical/cation transformation polymerization under proper conditions.

Solubilities of poly(CHO) and poly(HOS) are very different: poly(CHO) is soluble in nonpolar solvents, such as hexane, toluene, benzene, chloroform, diethyl ether, and THF; poly(HOS) is soluble in polar solvents, such as THF, dimethyl sulfoxide, DMF, ethyl acetate, acetonitrile, acetone, ethanol, and methanol, but insoluble in water. The association behavior of poly(HOS-*b*-CHO) in methanol, a selective solvent for poly(HOS), was briefly investigated using QELS. Poly(HOS) and two samples of poly(HOS-*b*-CHO), whose molar ratios of HOS:CHO are 1:0.08 and 1:0.5, were used for the measurement. The characteristics of these polymers are listed in Table 3. Figure 4 compares relaxation time distributions of the poly(HOS) and two block copolymer samples obtained from QELS in methanol at varying polymer concentrations (C_p). At $C_p = 0.25$ g/L, all of the polymers have a unimodal distribution centered at a hydrodynamic radius (R_h) of ca. 5−8 nm, suggesting that the polymer chains exist as single molecules (i.e., unimers) or aggregates formed from a small number of polymer chains. In the case of poly(HOS), the relaxation time distributions are virtually the same, independent of C_p (0.25−1.0 g/L), suggesting that no association of poly(HOS) occurs in methanol in this C_p region. In the case of poly(HOS-*b*-CHO) with an HOS:CHO molar ratio of 1:0.08, although the relaxation time distribution obtained at $C_p = 0.50$ g/L is virtually the same as that obtained at $C_p = 0.25$ g/L, the polymer has a bimodal distribution at $C_p = 1.0$ g/L, indicating that larger aggregates are formed from a number of polymer chains. The apparent value of R_h for the slow mode peak was estimated to be ca. 34 nm. Furthermore, in the case of poly(HOS-*b*-CHO) with molar ratio of HOS:CHO = 1:0.5, the relaxation time distribution indicates that larger aggregates with $R_h \approx 32$ nm are formed at $C_p = 0.50$ g/L. As C_p increases, the width of the slow mode peak becomes narrower and R_h increases.

Conclusion

Amphiphilic block copolymers of HOS and CHO were synthesized by deprotection of poly(BDMSOS-*b*-CHO) synthesized by block copolymerization of BDMSOS and CHO followed by hydrolysis of *tert*-butyldimethylsiloxy protection groups. A radical/cation transformation technique was employed for the block copolymerization using AIBN and $Ph_2I^+PF_6^-$ as initiator and electron acceptor, respectively. Poly(HOS-*b*-CHO) as prepared was fractionated from homopolymers to obtain pure block copolymer in a weight fraction of 0.937. This high block copolymer fraction indicates that poly(BDMSOS-*b*-CHO) was preferentially formed. Poly(HOS-*b*-CHO) was insoluble in water. In methanol, a selective solvent for poly(HOS), poly(HOS-*b*-CHO) had a unimodal distribution in QELS data centered at $R_h \approx 5-8$ nm at $C_p = 0.25$ g/L. This observation suggests that polymer chains exist as single molecules or aggregates of a small number of polymer chains in methanol. At a higher C_p, poly(HOS-*b*-CHO) had a bimodal distribution, indicative of the formation of larger aggregates.

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Supporting Information Available: ESR spectrum taken in the presence of $Ph_2I^+PF_6^-$ and FT/IR and ^{1}H NMR spectra of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) All the polymers obtained by radical/cation transformation polymerization contained only a small amount of homopolymer of BDMSOS. This may be because electron transfer reaction from the propagating radical to the acceptor proceeds much faster than bimolecular termination of propagating radicals, and then the resulting polymeric cations immediately react with CHO to form CHO sequences.

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