Synthesis of Well-Defined Polystyrene-*b*-Aromatic Polyether Using an Orthogonal Initiator for Atom Transfer Radical Polymerization and Chain-Growth Condensation Polymerization

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ABSTRACT: Well-defined diblock copolymers of polystyrene and aromatic polyether were synthesized by the combination of atom transfer radical polymerization (ATRP) and chain-growth condensation polymerization (CGCP) from an orthogonal initiator. A polystyrene macroinitiator was first synthesized by the ATRP of styrene in the presence of 4-fluorobenzenesulfonyl chloride (FBS−Cl) as an orthogonal initiator, then the terminal chlorine of the polystyrene was dehalogenated with $Et_3SiH/Pd(OAc)_2$. The CGCP of potassium 5-cyano-4-fluoro-2-propylphenolate (**1**) was then carried out with the polystyrene macroinitiator in sulfolane at 150 °C. However, not only polystyrene-*b*-aromatic polyether but also macrocycles of **1** were obtained, due to transetherification of the *p*-sulfonylphenyl ether linkage of the macroinitiator with **1**. In contrast, the CGCP of **1** from another polystyrene macroinitiator bearing a keto group, which was prepared similarly by the ATRP of styrene with 4-(1-bromoethyl)-4′-fluorobenzophenone (FBP−Br) as an orthogonal initiator, followed by reduction of the terminal C−Br bond with Bu_3SnH, afforded only well-defined polystyrene-*b*-aromatic polyether. This diblock copolymer self-assembled in THF to form spherical aggregates.

Introduction

Rod−coil block copolymers containing a condensation polymer or oligomer as a rod segment have recently received much attention as intriguing polymer architectures, because they self-assemble into unique nanoarchitectures that cannot be produced by self-assembly of coil−coil block copolymers.[1] In these block copolymers, the condensation oligomer or polymer segments have been obtained by stepwise synthesis[2] or conventional polycondensation.[3] The former method gives segments with precisely defined structure, but can be tedious, while the latter method affords segments with a broad molecular weight distribution.

Condensation polymerization that proceeds in a chain-growth polymerization manner (chain-growth condensation polymerization) from an initiator has recently been developed,[4] and allows easier synthesis of block copolymers of condensation polymers and coil polymers. Furthermore, the condensation polymer segments possess a narrow molecular weight distribution, and so the rod−coil block copolymers including these segments as a rod component also have a narrow molecular weight distribution when the coil segment is synthesized by living polymerization. The reported synthetic approaches to well-defined rod−coil block copolymers by means of chain-growth condensation polymerization can be classified into three categories: (1) coupling reaction between condensation polymer and coil polymer,[5] (2) living polymerization for coil polymer from a macroinitiator synthesized via chain-growth condensation polymerization,[6] and (3) chain-growth condensation polymerization from a macroinitiator synthesized via living polymerization.[7] The disadvantage of the first approach is difficulty of separation of the obtained block copolymer from unreacted starting homopolymers. In the second and third approaches, the macroinitiators have to be prepared by transformation of the polymer end group in several steps.

A more convenient approach is to use an orthogonal initiator,[8] which has two different initiating sites for two kinds of polymerization, with one of the initiating sites being inert with respect to polymerization from the other initiating site. A block copolymer would be obtained simply by chain-growth condensation polymerization and living polymerization from this initiator. To our knowledge, this approach has never been applied to the synthesis of rod−coil block copolymers, although coil−coil block copolymers such as polylactone-*b*-polystyrene and polylactone-*b*-polyMMA have been synthesized via this approach.[8] Here, we report the synthesis of well-defined block copolymers of polystyrene and aromatic polyether by the use of an orthogonal initiator for atom transfer radical polymerization (ATRP) and chain-growth condensation polymerization (CGCP) (Scheme 1). The orthogonal initiators employed herein are 4-fluorobenzenesulfonyl chloride (FBS−Cl) and 4-(1-bromoethyl)-4′-fluorobenzophenone (FBP−Br). The benzenesulfonyl chloride moiety[9] in FBS−Cl and the 1-bromoethylbenzene moiety[10] in FBP−Br initiates ATRP of styrene in the presence of a copper catalyst. The fluorobenzene moiety having an electron-withdrawing group at the para position initiates CGCP of monomer **1**, leading to the aromatic polyether.[11]

Experimental Section

Measurements. ^1H, ^{13}C, and ^{19}F NMR spectra were obtained on JEOL ECA-600 and 500 instruments using tetramethylsilane (0.00 ppm in ^1H and ^{13}C NMR) as an internal standard and C_6F_6 (0.00 ppm in ^{19}F NMR) as an external standard, respectively. IR spectra were recorded on a JASCO FT/IR-410. Column chromatography was performed on silica gel (Kieselgel 60, 230−400 mesh, Merck) or basic alumina (alumina, activated, abt. 300 mesh, Wako). Analytical thin-layer chromatography (TLC) was performed on silica gel (Silica gel 60 F_{254}, aluminum sheets, Merck) or aluminum oxide (Aluminum oxide 60 F_{254}, neutral, aluminum sheets, Merck). The M_n and M_w/M_n values of polymers were measured with a

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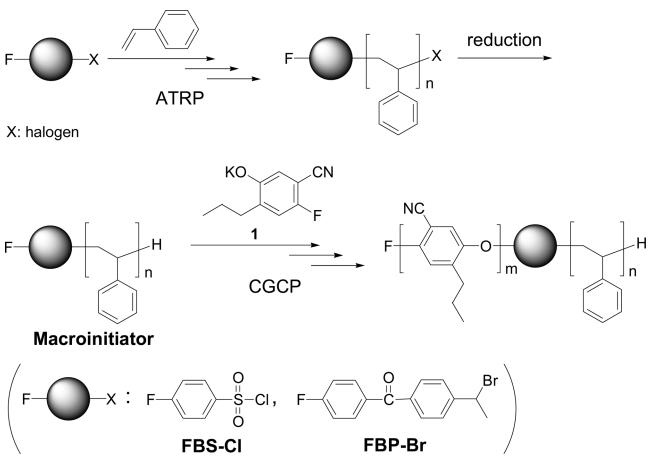
Scheme 1



TOSOH HLC-8020 gel permeation chromatography (GPC) unit [eluent, tetrahydrofuran (THF); calibration, polystyrene standards] using two TSK-gel columns (2 × Multipore H_{XL}-M). Isolation of macrocycles of **1** was carried out with a Japan Analytical Industry LC-908 Recycling Preparative HPLC (eluent: chloroform) using two TSK-gel columns (2 × G 2000H_{HR}). MALDI−TOF mass spectra were recorded on a Shimadzu/Krotos Kompact MALDI IV tDE in the linear mode using a laser (λ = 337 nm). Sample solutions of polymer (1 mg), with dithranol (30 mg) as a matrix, were prepared in chloroform (5.5 mL). Scanning electron microscopy (SEM) was carried out with Hitachi S-4000. Samples were prepared by dropping of copolymer solution (1 mg/mL) in THF (polystyrene selective solvent) on glass plate and dried at 25 °C for 3 days. Transmission electron microscopy (TEM) was carried out with a JEOL JEM-2000EX/FX II. Samples were prepared by dropping of copolymer solution (1 mg/mL) in THF (polystyrene selective solvent) on a Cu grid and dried at 25 °C for 3 days. Gas chromatograph mass spectrometer (GCMS) was carried out with a Shimadzu GCMS-QP5050A.

Materials. Potassium 5-cyano-4-fluoro-2-propylphenolate (**1**)[11] and 2-chloro-1-(4-fluorobenzenesulfonyl)-2-phenylethane (**4**)[9] were prepared according to the previously established procedures. FBS−Cl and CuCl were purified according to the literature.[9] Styrene was washed with 1 M aqueous NaOH solution to remove the inhibitor and then with water, dried over anhydrous $MgSO_4$, and distilled over CaH_2 under reduced pressure before use. Fluorobenzene, triethylsilane, sulfolane, 4-fluoroanisole, and (1-chloroethyl)benzene were distilled under reduced pressure. AIBN and 4,4′-dinonyl-2,2′-bipyridyl (bpy9) were recrystallized from methanol and ethanol, respectively. CuBr, palladium(II) acetate, tributyltin hydride, 4-ethylbenzoyl chloride, *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), 4,4′-diflorobiphenyl, and anhydrous toluene were used as received.

ATRP of Styrene with FBS−Cl. Styrene (5.2 g, 50 mmol), FBS−Cl (49 mg, 0.25 mmol), bpy9 (42 mg, 0.10 mmol), and CuCl (7.4 mg, 7.5 × 10^{-2} mmol) were placed in a Teflon tube. The tube was sealed and degassed by means of six freeze−pump−thaw cycles, filled with argon and heated at 110 °C for 25 h. After the tube had been cooled, the reaction mixture was filtered through a short column of basic alumina (eluent, $CHCl_3$). After removal of $CHCl_3$ in vacuo, the residue was dissolved in a small amount of toluene, and the solution was poured into CH_3OH with vigorous stirring. This purification by precipitation was conducted three times. The precipitated polymer was collected and dried in vacuo to give 2.8 g of MIFBS−Cl (M_n = 8100, M_w/M_n = 1.38). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−6.24 (m, 5n H), 2.59−1.11 (m, 3n H). ^{19}F NMR (565 MHz, $CDCl_3$): δ 57.8.

Reduction of MIFBS−Cl. Palladium(II) acetate (4.3 mg, 0.02 mmol) was placed in a round-bottomed flask equipped with a three-way stopcock and dried at 250 °C under reduced pressure for 30 min. The flask was cooled to room temperature under an argon atmosphere. Into the flask was added a solution of MIFBS−Cl (0.705 g, 0.1 mmol) and triethylsilane (0.35 g, 3.0 mmol) in anhydrous toluene (7 mL). The reaction mixture was stirred at ambient temperature for 24 h, then filtered through a short column of basic alumina (eluent, $CHCl_3$). The $CHCl_3$ was removed in vacuo. The residue was taken up in a small amount of $CHCl_3$, and the solution was poured into CH_3OH with vigorous stirring. The precipitated polymer was collected and dried in vacuo to give 0.68 g of MIFBS−H (97%) (M_n = 8200, M_w/M_n = 1.36): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29−6.16 (m, 5n H), 2.36−1.02 (m, 3n H). ^{19}F NMR (565 MHz, $CDCl_3$): δ 57.6.

Synthesis of 4-Ethyl-4′-fluorobenzophenone. A solution of 4-ethylbenzoyl chloride (4.00 g, 23.7 mmol), $AlCl_3$ (3.85 g, 28.5 mmol), and fluorobenzene (9.11 g, 94.8 mmol) was refluxed for 3 h. The reaction was quenched with 1 M hydrochloric acid, and the mixture was extracted with ethyl acetate three times. The combined organic layer was washed with a 1 M aqueous solution of NaOH and water, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 2/1), followed by recrystallization from methanol to give 4.59 g of the ketone as a white solid (85%): mp 67.5−68.5 °C. IR (KBr): 2972, 2936, 2880, 1928, 1649, 1597, 1500, 1414, 1156, 932, 855, 813 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (dd, J = 5.6 and 8.8 Hz, 2 H), 7.71 (d, J = 8.3 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.15 (t, J = 8.6 Hz, 2 H), 2.74 (q, J = 7.6 Hz, 2 H) 1.28 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.0, 165.2 (d, $^1J_{CF}$ = 254.4 Hz), 149.5, 135.0, 134.1, 132.5 (d, $^3J_{CF}$ = 9.6 Hz), 130.2, 127.8, 115.3 (d, $^2J_{CF}$ = 21.6 Hz), 28.9, 15.2. ^{19}F NMR (565 MHz, $CDCl_3$): δ 55.5.

Synthesis of FBP−Br. A mixture of 4-ethyl-4′-fluorobenzophenone (0.60 g, 2.6 mmol), NBS (0.41 g, 2.3 mmol), and BPO (19.0 mg, 0.08 mmol) in CCl_4 (12.9 mL) was refluxed for 6 h. The solution was cooled to 0 °C, and the precipitated solid was filtered off. The filtrate was washed with 1 M aqueous Na_2CO_3, saturated aqueous $Na_2S_2O_3$, and brine. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 2/1) to give 0.62 g of FBP−Br as a pale yellow solid (87%): mp 76−77 °C. IR (KBr): 3067, 2987, 2933, 1926, 1650, 1595, 1500, 1413, 1227, 1154, 969, 766, 594 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (dd, J = 5.4 and 8.9 Hz, 2 H), 7.75 (d, J = 8.6 Hz, 2 H), 7.56 (d, J = 8.0 Hz, 2 H), 7.17 (t, J = 8.6 Hz, 2 H), 5.23 (q, J = 7.0 Hz, 1 H), 2.08 (t, J = 6.9 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.5, 165.4 (d, $^1J_{CF}$ = 254.3 Hz), 147.5, 137.3, 133.6, 132.6 (d, $^3J_{CF}$ = 8.4 Hz), 130.3, 126.9, 115.5 (d, $^2J_{CF}$ = 21.6 Hz), 47.9, 26.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ 56.3.

ATRP of Styrene with FBP−Br and Reduction of the Terminal C−Br Bond with Bu_3SnH in One Pot. Styrene (1.04 g, 10.0 mmol), FBP−Br (31 mg, 0.10 mmol), bpy9 (82 mg, 0.20 mmol), CuBr (14 mg, 0.10 mmol), and 4-fluoroanisole (128 mg, 1.00 mmol) as an internal standard were placed in a Teflon tube. The tube was sealed and degassed by means of six freeze−pump−thaw cycles, filled with argon, and heated at 110 °C for 2.5 h. After the tube had been cooled to room temperature, styrene in the reaction mixture was removed in vacuo, and a solution of Bu_3SnH (1.45 g, 5.00 mmol) in anhydrous toluene (2 mL) was added. The mixture was stirred at 85 °C for 3 h, and filtered through a short column of basic alumina (eluent, $CHCl_3$). After removal of $CHCl_3$ in vacuo, the residue was again dissolved in a small amount of $CHCl_3$, and the solution was poured into CH_3OH with vigorous stirring. This purification by precipitation was conducted three times. The precipitated polymer was collected and dried in vacuo to give 0.24 g of MIFBP−H (M_n = 3070, M_w/M_n = 1.09). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36−6.21 (m, 5n H), 2.51−1.13 (m, 3n H). ^{19}F NMR (565 MHz, $CDCl_3$): δ 55.3.

Synthesis of Polystyrene-*b*-aromatic Polyether. MIFBP−H (0.15 g, 2.5 × 10^{-2} mmol), **1** (0.096 g, 0.44 mmol), 4,4′-difluorobiphenyl (0.084 g, 0.44 mmol) as an internal standard, and sulfolane (4.2 mL) were placed in a Teflon tube. The tube was sealed and degassed by means of five freeze−pump−thaw cycles, filled with argon, and heated at 150 °C for 5 h. After the tube had

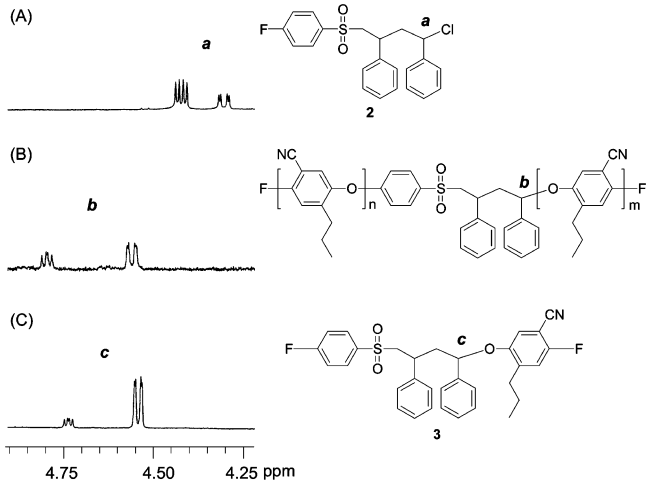
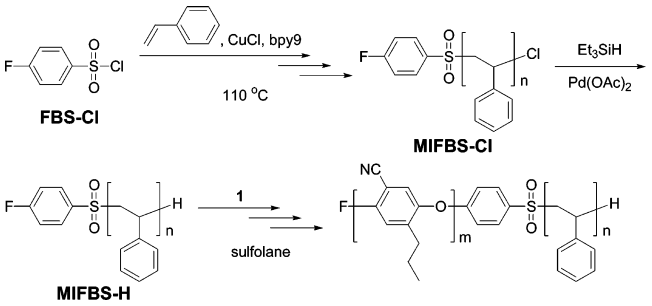


Figure 1. ^{1}H NMR spectra in $CDCl_3$ at 25 °C: (A) model initiator **2**; (B) the product obtained by the CGCP of **1** with model initiator **2**; (C) model product **3**.

Scheme 2



been cooled, the solution was added dropwise into vigorously stirred 1 M hydrochloric acid to afford a precipitate. The polymer thus obtained was dissolved in a small amount of $CHCl_3$, and the solution was poured into CH_3OH with vigorous stirring. The precipitated polymer was collected and dried in vacuo to give 0.19 g (87%) of block copolymer (M_n = 7620, M_w/M_n = 1.22). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29−6.16 (m, 5n + 2m H), 2.84−2.52 (m, 2m H), 2.46−1.14 (m, 3n + 2m H), 1.03−0.82 (m, 3m H). ^{19}F NMR (565 MHz, $CDCl_3$): δ 50.6.

Results and Discussion

1. Block Copolymerization from FBS−Cl. (1) ATRP of Styrene from FBS−Cl. As shown in Scheme 2, the ATRP of styrene was first carried out from FBS−Cl, because aromatic polyether, poly**1**, has a low solubility in organic solvents. Styrene was polymerized with a CuCl/4,4′-dinoyl-2,2′-bipyridyl (bpy9) catalyst system in the presence of FBS−Cl ($[\text{styrene}]_0/[\text{FBS−Cl}]_0$ = 200/1) in bulk at 110 °C according to the reported procedure for ATRP of styrene with a benzenesulfonyl chloride initiator.[9] The obtained polystyrene macroinitiator (MIFBS−Cl) having the 4-fluorobenzenesulfonyl group as an end group possessed M_n of 8100 and M_w/M_n of 1.38, as evaluated by GPC based on polystyrene standards.

In our initial plan for the synthesis of the block copolymer, the CGCP of **1** would next be carried out from the terminal fluorine of MIFBS−Cl. However, we thought the polymerization of **1** might occur from not only the terminal fluorine, but also the terminal chlorine of MIFBS−Cl. To examine this issue, a model initiator **2**, shown in Figure 1, was prepared as a diastereomeric mixture,[12] and then the polymerization of **1** with **2** was examined. Thus, the CGCP of **1** was carried out with **2** ($[\mathbf{1}]_0/[\mathbf{2}]_0$ = 10/1) in sulfolane at 150 °C to give an aromatic polyether with M_n of 3940 and a relatively low polydispersity

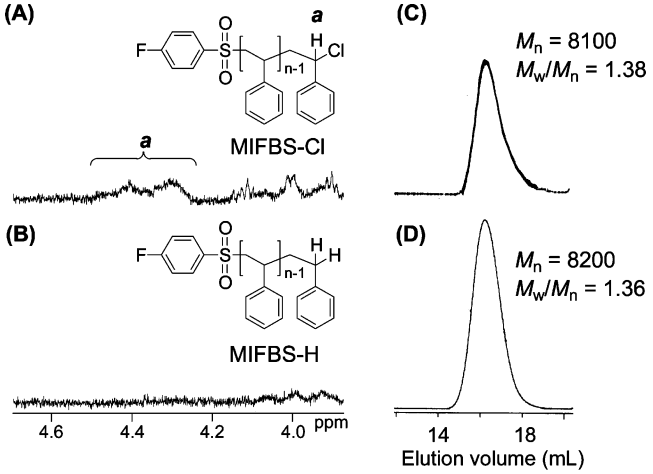


Figure 2. ^{1}H NMR spectra of (A) MIFBS−Cl and (B) the product after reduction of MIFBS−Cl (MIFBS−H) in $CDCl_3$ at 25 °C, and GPC profiles of (C) MIFBS−Cl and (D) MIFBS−H.

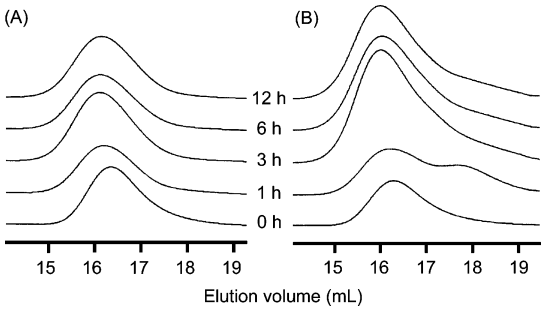
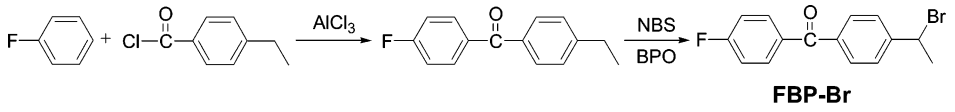


Figure 3. GPC profiles of the products obtained by the block copolymerization of **1** from MIFBS−H in sulfolane ($[\mathbf{1}]_0$ = 0.06 M, $[\text{MIFBS−H}]_0$ = 0.0028 M) at 150 °C detected by (A) RI and (B) UV.

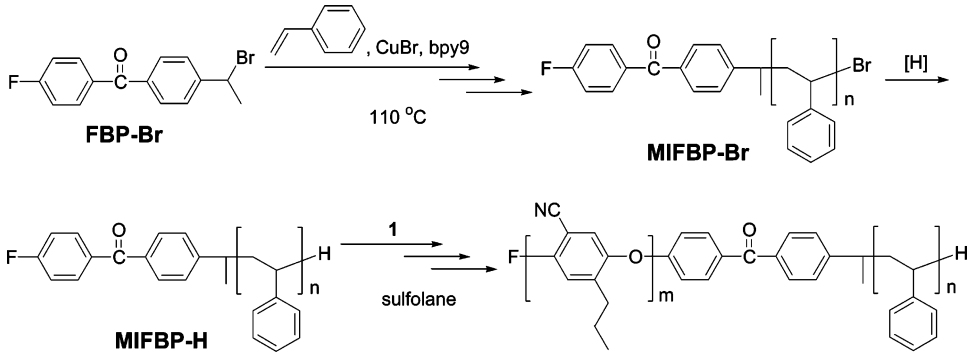
(M_w/M_n = 1.22). In the ^{1}H NMR spectrum of the aromatic polyether thus obtained, the signals ***a*** of the chlorobenzylic proton of **2** at δ 4.42 and 4.31 ppm were completely absent (Figure 1A), and a new set of signals ***b*** at δ 4.80 and 4.57 ppm appeared (Figure 1B). A model compound **3**, in which **1** can react only with the terminal chlorine of **2**, was also prepared,[12] and its ^{1}H NMR spectrum was compared with that of the product of the polymerization of **1** with **2**. The signals ***c*** at δ 4.74 and 4.55 ppm of the model compound **3** agreed well with the signals ***b*** of the polymer (Figure 1C). Accordingly, the CGCP of **1** is likely to take place from not only the terminal fluorine, but also the chlorine of MIFBS−Cl, i.e., selective polymerization of **1** from the terminal fluorine of MIFBS−Cl cannot be expected.

However, this implies that the terminal chlorine from the initial ATRP process can be used for the CGCP as well; the rod−coil block copolymer of aromatic polyether and polystyrene can be easily synthesized without a need to involve orthogonal initiator FBS−Cl. Accordingly, we checked that the CGCP of **1** carried out with (1-chloroethyl)benzene as a model initiator in sulfolane at 150 °C gave an aromatic polyether with a relatively broad polydispersity (M_w/M_n = 1.42). Furthermore, production of styrene was confirmed by GCMS. These results indicate that the secondary benzylic chloride not only initiates slowly the CGCP of **1** but also undergoes elimination of hydrogen chloride with phenoxide monomer **1**. If the CGCP of **1** is carried out from the terminal chlorine of polystyrene macroinitiator, some amount of polystyrene macroinitiator will remain because of the elimination of hydrogen chloride at the polystyrene end. Therefore, we judged that this method is not appropriate.

Scheme 3



Scheme 4



To prevent the polymerization of **1** from the terminal chlorine of MIFBS−Cl, the reduction of the C−Cl bond of MIFBS−Cl was conducted with triethylsilane (Et_3SiH) in the presence of a Pd catalyst at room temperature. This reduction system is known to reduce the C−Cl bond selectively even when carbonyl and sulfonyl groups are present in a substrate.[13] In the ^{1}H NMR spectrum of the product, the signal at 4.30−4.50 ppm due to the benzylic proton on carbon adjacent to chlorine of MIFBS−Cl completely disappeared (Figure 2A, B), and the GPC elution curves were almost identical before and after the reduction (Figure 2C, D). Therefore, the dehalogenation of the chlorine of MIFBS−Cl occurred quantitatively without cleavage of the backbone or coupling between the polymers. The polymer obtained after the reduction was designated as MIFBS−H.

(2) CGCP of 1 from Macroinitiator MIFBS−H. Monomer **1** was polymerized with MIFBS−H ($[\mathbf{1}]_0/[\text{MIFBS−H}]_0 = 20/1$) in sulfolane at 150 °C for 12 h. Figure 3 shows the GPC profiles of MIFBS−H and the polymerization products obtained at 1, 3, 6, and 12 h. In the GPC profiles detected by RI, the elution curves shifted toward the higher-molecular-weight region with time, implying the formation of the block copolymer (Figure 3A). In the GPC profiles detected by UV, however, a peak whose molecular weight is lower than that of MIFBS−H was observed at 1 h, although the main peaks shifted toward the higher-molecular-weight region. To identify the low-molecular-weight compound detected by UV, it was separated by preparative HPLC and analyzed by means of matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectrometry. The spectrum[12] contains only one series of peak, the values of which correspond to macrocycles of **1**. For example, the 10-mer macrocycle of this distribution is expected to produce a signal at m/z 159.06 × 10 (repeat unit) = 1590.6, and in fact a signal is observed at 1588.6. The linear polymer of **1** [159.06n (repeat unit) + 19.0 (F) + 1.0 (H)] is absent (m/z 1610.7 was not detected).

One might think that the formation of the macrocycles of **1** can be accounted for by the self-condensation of **1**, followed by cyclization. However, **1** does not undergo self-condensation under these conditions.[11] We think that transetherification between **1** and the polymer would occur at the ether linkage between the monomer unit and MIFBS−H segment to generate the homopolymer of **1** before cyclization (Scheme S2), because the ether linkage between the monomer units did not undergo transetherification under the conditions used to polymerize **1** from an initiator.[11] In polycondensation leading to poly(ether sulfone)s that have a strongly electron-withdrawing sulfonyl group at the para position of the ether linkage, transetherification with the monomer phenoxide or a fluoride ion is known to occur easily at high reaction temperature.[14] Consequently, the sulfonyl group in initiator MIFBS−H caused the side reaction in the synthesis of the block copolymer of polystyrene and poly**1**.

2. Block Copolymerization from FBP−Br. (1) ATRP of Styrene from FBP−Br. To suppress the transetherification at the ether linkage between the monomer unit and the initiator unit, a less strongly electron-withdrawing group should be introduced at the para position with respect to the fluorine in the macroinitiator. In the reported CGCP of **1** with 4-fluoro-4′-trifluoromethylbenzophenone as an initiator, transetherification did not take place, and poly**1** with a low polydispersity was obtained.[11] Accordingly, a new orthogonal initiator, FBP−Br, bearing a keto group at the para position of the fluorine was prepared. Thus, 4-ethylbenzoyl chloride was reacted with fluorobenzene in the presence of $AlCl_3$ to give a ketone, which was then brominated at the benzylic position with *N*-bromosuccinimide (NBS) in the presence of benzoyl peroxide (BPO) to yield FBP−Br (Scheme 3).

The ATRP of styrene with FBP−Br as an initiator ($[\text{styrene}]_0/[\text{FBP−Br}]_0 = 100/1$) was conducted with the same CuBr/bpy9 catalyst system in bulk at 110 °C for 2.5 h (Scheme 4). The resulting polymer (MIFBP−Br) had M_n of 2900 and M_w/M_n of 1.08, and was characterized by ^{1}H and ^{19}F NMR spectroscopy. The ^{1}H NMR spectrum of the polymer showed the signal of the −CHBr end group of polystyrene at 4.59−4.34 ppm and the signals of the initiator unit at 7.86−7.74, 7.68−7.51, and 1.02−0.80 ppm, as well as the typical signals of polystyrene.[12] In the ^{19}F NMR spectrum, the signal of the aromatic fluorine was observed at 55.3 ppm.

In a manner similar to that described above, reduction of the terminal C−Br bond of MIFBP−Br with Et_3SiH was attempted in the presence of $Pd(OAc)_2$. Surprisingly, however, the GPC elution curve of the product showed a bimodal peak, and the molecular weight of the peak in the higher-molecular-weight region was almost double that of the main peak (Figure 4A). Therefore, bimolecular radical coupling between the polymers appears to take place during the dehalogenation of the terminal bromine with this reducing system, which was effective for the reduction of terminal chlorine, as noted above.

Trialkyltin hydrides are known to be common dehalogenation agents, and Matyjaszewski et al. reported that the terminal C−Br bond of polystyrene obtained by ATRP was reduced with this

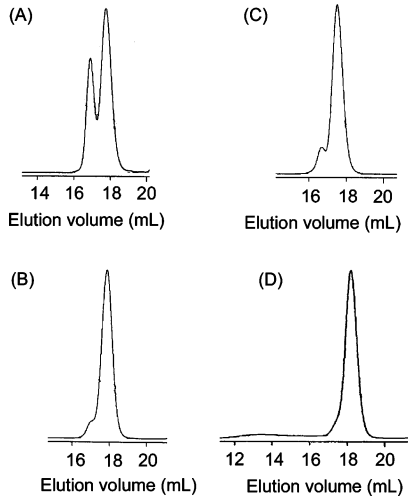


Figure 4. GPC profiles of reduced MIFBP−Br: (A) $[MIFBP-Br]_0/[Pd(OAc)_2]_0/[Et_3SiH]_0 = 1.0/0.11/10$; (B) $[MIFBP-Br]_0/[CuBr/2bpy9]_0/[Bu_3SnH]_0 = 1.0/1.0/3.1$; (C) $[MIFBP-Br]_0/[AIBN]_0/[Bu_3SnH]_0 = 1.0/0.52/3.2$; (D) one-pot reaction, $[Bu_3SnH]_0/[FBP-Br]_0 = 3.0$.

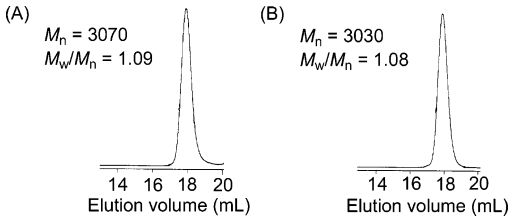


Figure 5. GPC profiles of (A) MIFBP−Br and (B) MIFBP−H obtained by the reduction of MIFBP−Br of different M_n with Bu_3SnH: $[Bu_3SnH]_0/[FBP-Br]_0 = 50$.

reagent and a Cu catalyst.[15] According to this report, we treated MIFBP−Br with Bu_3SnH in the presence of CuBr/bpy9 in toluene at 110 °C, but the GPC profile of the product showed a small shoulder in the higher-molecular-weight region (Figure 4B). Even when AIBN was used instead of CuBr/bpy9, the shoulder was still observed (Figure 4C). We next tried a one-pot reaction. Thus, the ATRP of styrene was carried out at 110 °C (about 16% conversion), then after cooling, a solution of Bu_3SnH in toluene was added, and the reaction mixture was heated at 85 °C. The GPC profile of the product did not show the shoulder, but a broad peak was observed in the much higher molecular weight region (Figure 4D). This peak is probably due to polystyrene formed by the polymerization of the residual styrene in the reaction mixture initiated by tributyltin radical.

Accordingly, styrene remaining in the reaction mixture was removed in vacuo after the ATRP, and then a solution of Bu_3SnH ($[Bu_3SnH]_0/[FBP-Br]_0 = 50$) in toluene was added, followed by heating at 85 °C.[16] The GPC profile after reduction showed a monomodal peak with a low polydispersity (M_n = 3030, $M_w/M_n = 1.08$) (Figure 5B). In the ^1H NMR spectrum of the product, the signal of the −CHBr end group at 4.50 ppm had disappeared completely. The signal of the methine proton of the biphenyl carbinol moiety, which could be formed by the reduction of the keto group of the FBP−Br unit, was not observed, either. In addition, the ^{19}F NMR spectrum showed only one signal at 55.3 ppm. Therefore, this reduction method turned out to be effective for the synthesis of a nonbrominated macroinitiator, MIFBP−H. Other MIFBP−Hs of different molecular weight (M_n = 6080 and 12700) were also prepared without side reactions by this method.

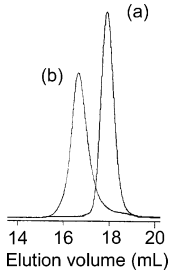


Figure 6. GPC profiles of (a) MIFBP−H **I** (M_n = 3030, M_w/M_n = 1.08) and (b) polystyrene-*b*-poly**1** (M_n = 7620, M_w/M_n = 1.22) synthesized by the polymerization of **1** with MIFBP−H **I** in sulfolane at 150 °C ($[\mathbf{1}]_0 = 0.107$ M, $[\mathbf{1}]_0/[MIFBP-H]_0 = 18$).

(2) CGCP of 1 from Macroinitiator MIFBP−H. MIFBP−H **I** (M_n = 3030, M_w/M_n = 1.08) was first employed as a macroinitiator. Monomer **1** was polymerized with $[\mathbf{1}]_0/[MIFBP-H\ \mathbf{I}]_0$ = 10, 18, 24, and 36 in sulfolane at 150 °C (Scheme 4, Table 1). In the polymerization with $[\mathbf{1}]_0/[MIFBP-H\ \mathbf{I}]_0 = 10$ and 18, **1** was consumed in 5 h to yield polymers with low polydispersity (Table 1, entries 1 and 2). The GPC trace of the product obtained in entry 2 showed a clear shift toward the higher-molecular-weight region while retaining low polydispersity, and the peak in the low-molecular-weight region, which was observed in the polymerization of **1** with MIFBS−H, was not detected (Figure 6). In the ^{19}F NMR spectrum of the product obtained in entry 2, the signal of the initiation site of MIFBP−H disappeared, and only one signal assignable to the end group of poly**1** was observed at 50.5 ppm (Figure 7A). Furthermore, the ^1H NMR spectrum of the product showed the signal ***a*** of the benzophenone unit shifted toward lower magnetic field compared with the signal ***a′*** of MIFBP−H, and the signals ***b***−***d*** of the propyl group of the poly**1** unit (Figure 7B). Those results indicate that **1** underwent CGCP from the fluorine of MIFBP−H to give a block copolymer of polystyrene and poly**1**. On the other hand, the polymerization with $[\mathbf{1}]_0/[MIFBP-H\ \mathbf{I}]_0 = 24$ and 36 gave polymers with relatively broad molecular weight distributions (entries 3 and 4). In particular, the GPC profile of entry 4 showed a tailing toward the lower-molecular-weight region than that of MIFBP−H **I**. When the GPC traces of MIFBP−H **I** and the products obtained by polymerization for 1 and 7 h under the conditions of entry 4 were compared, however, the GPC traces showed a clear shift toward the higher molecular weight region with time, and the profile of the polymer obtained at 1 h had a narrow distribution (M_n = 4700,

Table 1. Polymerization of 1 with MIFBP−H[a]

entry	MIFBP−H[b]	$[\mathbf{1}]_0/[MIFBP-H]_0$	temp (°C)	time (h)	conv. of **1**[c] (%)	M_n(calcd)	M_n (M_w/M_n)[d]
1	**I**	10	150	5	100	4620	5800 (1.13)
2	**I**	18	150	5	100	5900	7620 (1.22)
3	**I**	24	150	7	100	6850	6810 (1.31)
4	**I**	36	150	7	100	8760	5780 (1.46)
5	**II**	18	150	6	100	8960	10 300 (1.25)
6	**III**	18	125	14	100	15 560	14 400 (1.18)

[a] Polymerization was carried out in sulfolane ($[\mathbf{1}]_0 = 0.105$ M). [b] MIFBP−H, **I**: M_n = 3030, M_w/M_n = 1.08. **II**: M_n = 6080, M_w/M_n = 1.07. **III**: M_n = 12 700, M_w/M_n = 1.10. [c] Determined by GC. [d] Determined by GPC based on polystyrene standards (eluent: THF).

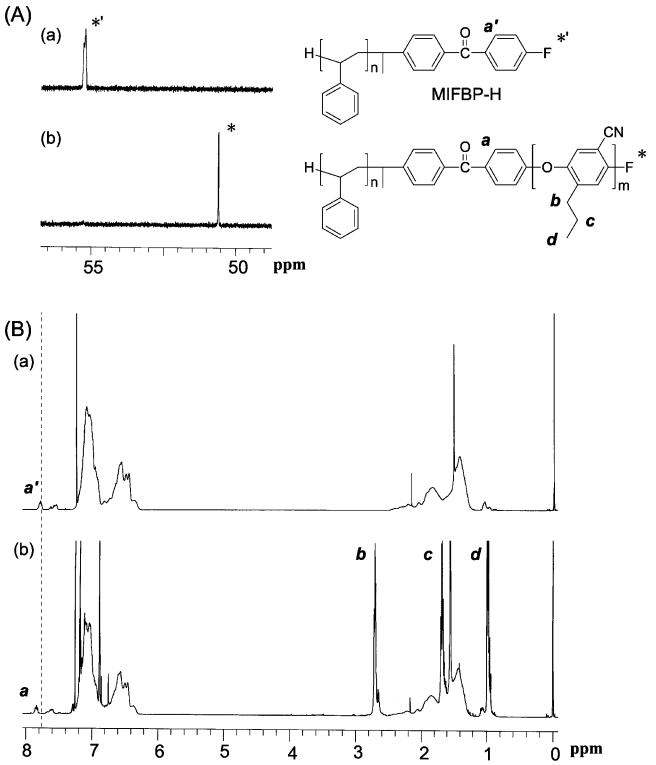


Figure 7. (A) ^{19}F NMR spectra of (a) MIFBP−H **I** and (b) block copolymer in $CDCl_3$ at 25 °C. (B) ^{1}H NMR spectra of (a) MIFBP−H **I** and (b) block copolymer in $CDCl_3$ at 25 °C.

M_w/M_n = 1.18) without the tailing.[12] The observed low-molecular-weight polymer formed in the last stage of polymerization is probably a homopolymer of **1** generated by self-polycondensation, which might have occurred as the block copolymer became insoluble with increasing amounts of the **1** unit in the copolymer, preventing the reaction of **1** with the propagating end of the block copolymer.

The polymerization of **1** was further carried out with MIFBP−H **II** and **III** (**II**, M_n = 6080, M_w/M_n = 1.07; **III**, M_n = 12 700, M_w/M_n = 1.10) with the[**1**]$_0$/[macroinitiator]$_0$ ratio of 18. When MIFBP−H **II** was used, **1** was consumed in 6 h to yield a block copolymer with a narrow molecular weight distribution (entry 5). The polymerization with MIFBP−H **III**, at 150 °C under similar conditions, however, gave not only the block copolymer but also the homopolymer of **1**. To prevent the self-polycondensation, the polymerization was carried out at 125 °C, affording only the block copolymer with a narrow molecular weight distribution (entry 6). When MIFBP−H with higher molecular weight is used as a macroinitiator, self-polycondensation of **1** tends to occur at 150 °C, probably because the space around the initiator moiety of MIFBP−H becomes more sterically congested.

3. Self-Assembly of Block Copolymer. The obtained block copolymers are expected to be arranged to form supramolecular structures by virtue of strong intermolecular interactions of the rigid aromatic polyether units in the block copolymer. Because THF is a good solvent for the polystyrene units, whereas the polyether units are insoluble in it, dilute solution (1.0 mg/mL) of the block copolymers with different length of the polystyrene units in THF were dropped on a glass plate and dried at room temperature. Scanning electron microscopy (SEM) images revealed that relatively large spherical aggregates were formed and that the diameter increased from 300 nm to 1 μm with increasing the length of the polystyrene units (Figure 8a−c). The size of the spherical aggregates is much larger than

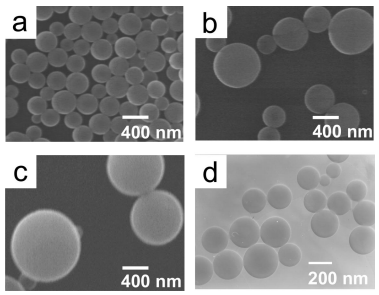


Figure 8. SEM images (a-c) of the block copolymer of polystyrene and aromatic polyether: (a) M_n = 7620, M_w/M_n = 1.22, (b) M_n = 10 300, M_w/M_n = 1.25, (c) M_n = 14 400, M_w/M_n = 1.18. TEM image (d) of the block copolymer (M_n = 7620, M_w/M_n = 1.22).

the length of block copolymer. Furthermore, transmission electron microscopy (TEM) image showed similar spherical aggregates, not hollow structures Jenekhe reported (Figure 8d).[3a,b] Consequently, the obtained aggregates may be onionlike micelle.[17]

Conclusions

We have demonstrated that well-defined polystyrene-*b*-aromatic polyether can be synthesized by using orthogonal initiators FBS−Cl and FBP−Br for ATRP and CGCP. First, the synthesis of the block polymer was attempted by the use of FBS−Cl. The ATRP of styrene with FBS−Cl was carried out, followed by reduction of the terminal C−Cl bond with Et_3SiH in the presence of $Pd(OAc)_2$ to give the macroinitiator MIFBS−H. The CGCP of **1** with MIFBS−H, however, yielded not only the block copolymer, but also macrocycles of **1** because of transetherification of the polymer with **1** at the ether linkage between the MIFBS−H, containing the sulfonyl group, and the monomer unit. Second, macroinitiator containing a keto group, MIFBP−H, was synthesized by ATRP of styrene with FBP−Br, followed by reduction of the terminal C−Br bond with Bu_3-SnH. The CGCP of **1** proceeded well from MIFBP−H to yield polystyrene-*b*-aromatic polyether with low polydispersity. Even when MIFBP−H with higher molecular weight (M_n < 13000) was used, a well-defined block copolymer was obtained. On the other hand, when the feed ratio[**1**]$_0$/[MIFBP−H]$_0$ was greater than 18, not only the block copolymer, but also the homopolymer of **1** was obtained. The obtained block copolymers self-assembled in THF to form the spherical aggregates whose size was dependent on the polystyrene length of the block copolymers. Studies on the detail structures of the aggregates will be reported in the near future.

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Supporting Information Available: Text giving synthetic procedures (including a reaction scheme) for the model compounds **2** and **3**, a figure showing the MALDI−TOF mass spectrum of the macrocycle of **1**, a scheme for the proposed mechanism of formation of macrocyle of **1**, figures showing the ^{1}H NMR spectrum of MIFBP−Br and the GPC analysis of the time course of the polymerization of **1** from MIFBP−H, and a table summarizing the solubility of the block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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