606 *Macromolecules* **2009**, *42*, 606−611

Synthesis of Well-Defined Miktoarm Star Copolymers of Aromatic Polyether and Polystyrene by Chain-Growth Condensation Polymerization and Atom Transfer Radical Polymerization

Yuka Yamazaki, Naomi Ajioka, Akihiro Yokoyama, and Tsutomu Yokozawa*

Department of Material and Life Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Received October 14, 2008; Revised Manuscript Received December 4, 2008

ABSTRACT: Well-defined AB_2 and A_2B type miktoarm star copolymers consisting of aromatic polyether arms as the A segment and polystyrene arms as the B segment were synthesized from trifunctional initiators. Atom transfer radical polymerization (ATRP) of styrene was carried out in the presence of 3,5-bis(1-bromoethyl)-4′-fluorobenzophenone as a trifunctional initiator, and then the terminal C−Br bond of the polymer was reduced with Bu_3SnH. The obtained polystyrene macroinitiators were used for aromatic polyether segment construction via chain-growth condensation polymerization (CGCP). The GPC trace showed a clear shift toward the higher-molecular-weight region with retention of low polydispersity, and no peak was detected in the lower-molecular-weight region. Accordingly, the target AB_2 type miktoarm star copolymers were synthesized without step-growth polycondensation. The synthesis of A_2B type miktoarm star copolymers was carried out similarly using 1-bromomethyl-3,5-bis(4-fluorobenzoyl)benzene as a trifunctional initiator. The A_2B type miktoarm star copolymers, which contained two arms of aromatic polyether units with high crystallinity, exhibited higher solubility than AB type diblock copolymer or AB_2 type miktoarm star copolymers. As in the case of the AB type diblock copolymer, the AB_2 and A_2B type miktoarm star copolymers self-assembled to form spheres of 150−600 nm diameter when a THF solution of the copolymers was allowed to dry on a glass plate. Similar spherical aggregates were obtained from a THF-methanol solution of the A_2B type miktoarm star copolymer, whereas the AB_2 type afforded fiber-like structures under the same conditions.

Introduction

Miktoarm star copolymers (the Greek word mikto, *μικτο*, means “mixed”) are nonlinear block copolymers composed of different arms. Compared with linear block copolymers, miktoarm star copolymers exhibit dramatic differences in morphology and properties. Recently, a number of miktoarm star copolymers have been synthesized by various methods, and their properties have been studied. Monteiro and co-workers synthesized three-arm miktoarm star copolymers using a combination of atom transfer radical polymerization (ATRP) and click chemistry.[1] Hadjichristidis and co-workers prepared miktoarm star copolymers consisting of two kinds of polymers with almost the same volume fraction, and found that these polymers showed various morphologies from lamellar to bicontinuous cubic and cylindrical structures, depending on the number of arms.[2−4] Lecommandoux, Taton, and co-workers used a straightforward synthetic approach based on ATRP or the combination of ATRP and another living polymerization to prepare water-soluble miktoarm star copolymers containing a single polystyrene (PSt) block and two ionogenic hydrophilic blocks, such as poly(acrylic acid) or poly(L-glutamic acid) (PGA). Preliminary study with dynamic light scattering demonstrated that these A_2B type miktoarm star copolymers formed pH-responsive spherical micelles in aqueous media.[5] Recently, the same authors reported the self-assembling properties in bulk of linear PSt-*b*-PGA and miktoarm star PSt-*b*-$(PGA)_2$ block copolymers that were thoroughly characterized by FTIR, WAXS, SAXS, and AFM.[6] However, there have been only a few reports on the study of miktoarm star copolymers containing condensation polymers or oligomers. Lee and co-workers investigated linear and branching rod-coil molecules in which each of the coil segments possessed identical volume fraction, and found that these polymers showed different self-assembling properties from those of conventional coil-coil molecules.[7,8] In their studies, the rod segments were prepared by stepwise synthesis, which made it difficult to obtain higher-molecular-weight rod segments. If rod-coil miktoarm star copolymers whose rod segments have high molecular weight with low polydispersity can be synthesized, they may show unique morphology and properties.

We have recently developed chain-growth condensation polymerization (CGCP), in which condensation polymerization proceeds in a chain-growth polymerization manner from an initiator,[9] and this polymerization method has allowed easier access to block copolymers containing condensation polymers and coil polymers.[10,11] In the course of our study focused on the controlled synthesis of poly(1-cyano-4-propyl-2,5-phenylene oxide)s by CGCP, we have found that aromatic polyether with low polydispersity showed higher crystallinity than did the polymer with a broader molecular weight distribution.[12,13] In addition, we synthesized well-defined diblock copolymers, such as aromatic polyether-*b*-PSt[14] and aromatic polyether-*b*-polyacrylonitrile,[15] by the combination of CGCP and ATRP. The aromatic polyether-*b*-polyacrylonitrile self-assembled to afford bundle-like and spherical aggregates from DMF solution, depending on the length of the polyacrylonitrile units.[15] However, the aromatic polyether-*b*-PSt self-assembled in THF to form spherical aggregates independently of the lengths of the segments.[14]

Herein, we report the synthesis and self-assembly of well-defined AB_2 and A_2B miktoarm star copolymers composed of poly(1-cyano-4-propyl-2,5-phenylene oxide) as the A segment and PSt as the B segment (Scheme 1). We designed these copolymers in order to compare the self-assembling property of the miktoarm star copolymers with that of diblock copolymers composed of the same polymer segments.[14] The AB_2 type miktoarm star copolymer was synthesized starting from ATRP of St with a trifunctional initiator containing two benzylic halide

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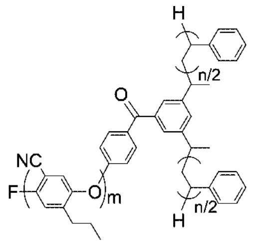
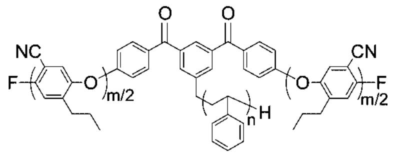
* Corresponding author. E-mail: yokozt01@kanagawa-u.ac.jp. Telephone: +81-45-481-5661. Fax: +81-45-413-9770.

10.1021/ma802317j CCC: $40.75

Scheme 1



AB_2 type miktoarm star copolymer



A_2B type miktoarm star copolymer

moieties as ATRP initiation sites and one 4-fluorobenzophenone moiety as a CGCP initiation site. Then the C−Br end-group of the precursors was reduced with Bu_3SnH to afford a macroinitiator, which was used for CGCP to construct the aromatic polyether segments. The A_2B type miktoarm star copolymers were synthesized in a similar manner. We also studied the self-assembly of these miktoarm star copolymers, and found that they exhibited unique morphology, depending on their structure and the nature of the solvent.

Experimental Section

Measurements. ^{1}H, ^{13}C and ^{19}F NMR spectra were obtained on JEOL ECA-600 and ECA-500 instruments using tetramethylsilane (0.00 ppm in ^{1}H NMR) and the midpoint of $CDCl_3$ (77.0 ppm in ^{13}C NMR) as internal standards 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 (activated, abt. 300 mesh, Wako). Analytical thin-layer chromatography (TLC) was performed on silica gel (Silica gel 60 F_{254}, aluminum sheets, Merck). GC was performed on a Shimadzu GC-14B gas chromatograph equipped with a Shimadzu fused silica capillary column CBP1-W12-100 (12 m length, 0.53 mm i.d.) and a flame ionization detector (FID). The M_n and M_w/M_n values of polymers were measured with a TOSOH HLC-8020 gel permeation chromatography (GPC) unit [eluent: tetrahydrofuran (THF); calibration: polystyrene standards] using two TSK-gel columns (2 × Multipore H_{XL}-M). Scanning electron microscopy (SEM) was carried out with a Hitachi S-4000. Transmission electron microscopy (TEM) was carried out with a JEOL JEM-2000EX/FX II. Atomic force microscopy (AFM) was carried out with a SII SPA 400 operating in the dynamic force microscope (DFM) mode. Polymer solutions (1 mg/mL) were prepared by dissolving a polymer only in THF, or adding methanol to a THF solution of the polymer (THF/methanol = 2/1, v/v). Samples were prepared by dropping the polymer solution onto a glass plate (SEM), a Cu grid (TEM) or a silicon wafer (AFM), and allowing it to dry at 25 °C for 3 days.

Materials. Potassium 5-cyano-4-fluoro-2-propylphenolate (**4**)[12,13] and 4-(1-bromoethyl)-4′-fluorobenzophenone (**1b**)[14] were prepared according to the established procedures. Synthesis of 3,5-bis(1-bromoethyl)-4′-fluorobenzophenone (**1a**), 1-bromomethyl-3,5-bis(4-fluorobenzoyl)benzene (**6**), and 1,3-bis(4-fluorobenzoyl)benzene (**9**) is described in the Supporting Information. Styrene was washed with 1 M aqueous NaOH to remove the inhibitor and then with water, dried over anhydrous $MgSO_4$, and distilled over CaH_2 under reduced pressure before use. Fluorobenzene, sulfolane, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), and 4-fluoroanisole were distilled under reduced pressure. 4,4′-Dinonyl-2,2′-bipyridyl (bpy9) was recrystallized from ethanol. CuBr was purified by stirring in acetic acid. After filtration, it was washed with 2-propanol and then dried in vacuum. $CuBr_2$, tributyltin hydride, and anhydrous toluene were used as received.

Synthesis of AB_2 Type PSt Macroinitiator 3. St (3.02 g, 29.0 mmol), **1a** (60.0 mg, 0.15 mmol), bpy9 (119 mg, 0.29 mmol), CuBr (21.0 mg, 0.15 mmol), and 4-fluoroanisole (366 mg, 2.90 mmol, used as an internal standard) were placed in a glass tube. The tube was degassed by means of three freeze−pump−thaw cycles, filled with argon, sealed, and heated at 110 °C for 35 min. After the tube had been cooled to room temperature, unreacted St in the reaction mixture was removed in vacuo, and a solution of Bu_3SnH (2.12 g, 7.28 mmol) in anhydrous toluene (3.0 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 four times. The precipitated polymer was collected and dried in vacuo to give 307 mg (65%) of **3a** (M_n = 3460, M_w/M_n = 1.07). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78−7.53 (m, 2 H), 7.31−6.29 (m, 5n + 5 H), 2.40−1.26 (m, 3n + 4 H), 1.07−0.82 (m, 6 H). ^{19}F NMR (470 MHz, $CDCl_3$) δ 55.4.

Synthesis of AB_2 Type Miktoarm Star Copolymer 5. A solution of **3a** (20.2 mg, 5.84 × 10^{-3} mmol) and **4** (22.8 mg, 0.105 mmol) in sulfolane (1.0 mL) was placed in a glass tube. The tube was degassed by means of five freeze−pump−thaw cycles, filled with argon, sealed, and heated at 150 °C for 6 h. After the tube had been cooled, the reaction mixture 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 CH_2Cl_2, and the solution was poured into CH_3OH with vigorous stirring. The precipitated polymer was collected and dried in vacuo to give 19 mg (52%) of **5b** (M_n = 9430, M_w/M_n = 1.18). IR (KBr) 2961, 2926, 2230, 1602, 1488, 1485, 1390, 1192, 912, 698 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74−7.58 (m, 2 H), 7.38−6.28 (m, 5n + 2m + 5 H), 2.84−2.56 (m, 2m + 2 H), 2.43−1.22 (m, 3n + 2m + 8 H), 1.12−0.81 (m, 3m H). ^{19}F NMR (470 MHz, $CDCl_3$) δ 50.7.

Synthesis of A_2B Type PSt Macroinitiator 7. ATRP of St with **6** was carried out in the same manner as in the case of the synthesis of **3**, by heating of a mixture of St (4.02 g, 38.6 mmol), **6** (80.0 mg, 0.193 mmol), bpy9 (158 mg, 0.386 mmol), CuBr (27.7 mg, 0.193 mmol), and 4-fluoroanisole (487 mg, 3.86 mmol, used as an internal standard) at 110 °C for 50 min, followed by reduction with Bu_3SnH (2.89 g, 9.94 mmol) in anhydrous toluene (3.9 mL) at 85 °C for 3 h. Purification by precipitation in the same manner afforded 342 mg (62%) of **7a** (M_n = 3000, M_w/M_n = 1.07). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85−7.75 (m, 5 H), 7.62−7.53 (m, 2 H), 7.31−6.30 (m, 5n + 4 H), 2.49−1.18 (m, 3n + 3 H). ^{19}F NMR (470 MHz, $CDCl_3$) δ 56.8.

Synthesis of A_2B Type Miktoarm Star Copolymer 8. CGCP of **4** with **7a** was carried out in the same way as for the synthesis of **5**, by heating a solution of **7a** (37.5 mg, 12.5 × 10^{-3} mmol) and **4** (54.3 mg, 0.25 mmol) in sulfolane (1.0 mL) at 150 °C for 6 h. Purification of the crude product gave 45.9 mg (59%) of **8a** (M_n = 8530, M_w/M_n = 1.08). IR (KBr) 2927, 2232, 1601, 1487, 1392, 1191, 911, 757, 699 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92−7.78 (m, 5 H), 7.64−7.55 (m, 2 H), 7.33−6.31 (m, 5n + 2m + 4 H), 2.77−2.58 (m, 2m H), 2.02−1.27 (m, 3n + 2m + 3 H), 1.04−0.88 (m, 3m H). ^{19}F NMR (470 MHz, $CDCl_3$) δ 50.7.

Results and Discussion

1. Synthesis of AB_2 Type Miktoarm Star Copolymers 5.

*(1) ATRP of Styrene from AB_2 Type Initiator **1a**.* Synthesis of well-defined miktoarm star copolymers consisting of one aromatic polyether arm and two PSt arms was carried out by ATRP of St with **1a** as a trifunctional initiator, followed by reduction of the terminal C−Br bond of **2** with Bu_3SnH, and then CGCP of **4** with the PSt macroinitiator **3** to construct the

Scheme 2

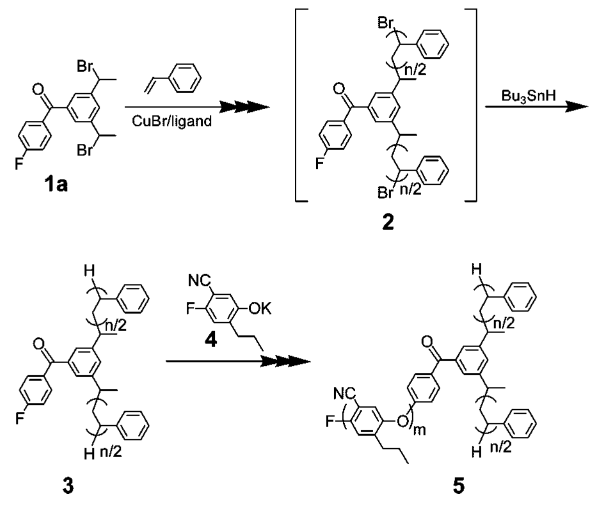


Table 1. Synthesis of AB$_2$ Type PSt 2 by ATRP[a]

entry	$[St]_0/[\mathbf{1a}]_0/[CuBr]_0/[ligand]_0$	ligand	time (min)	M_n (M_w/M_n)[b]	GPC profile
1	200/1/2/2	PMDETA	45	38900 (1.69)	leading
2	200/1/2/4	bpy9	90	10590 (1.09)	leading
3	200/1/1/2	bpy9	35	2980 (1.07)	monomodal

[a] ATRP of styrene was carried out with **1a**, CuBr and ligand at 110 °C. [b] Determined by GPC based on polystyrene standards (eluent: THF).

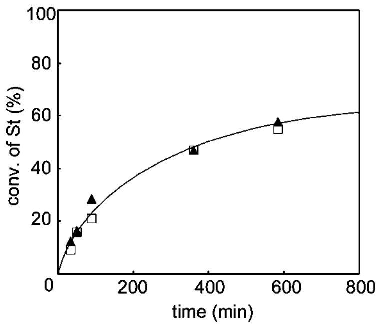


Figure 1. Time-conversion curves for the ATRP of St with **1a** (filled triangles, $[St]_0/[\mathbf{1a}]_0/[CuBr]_0/[bpy9]_0 = 200/1/1/2$) and with **1b** (squares, $[St]_0/[\mathbf{1b}]_0/[CuBr]_0/[bpy9]_0 = 200/2/1/2$) at 110 °C.

Scheme 3

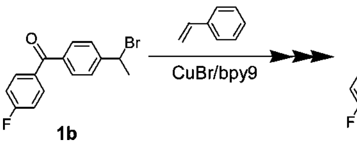


Table 2. Polymerization of 4 with 3[a]

entry	macroinitiator **3**[b]	$[\mathbf{4}]_0/[\mathbf{3}]_0$	temp (°C)	time (h)	convn of **4**[c] (%)	**5**	M_n (M_w/M_n)[d]
1	**3a**	14	150	5	100	**5a**	7490 (1.17)
2	**3a**	18	150	6	100	**5b**	9430 (1.18)
3	**3a**	24	150	7.5	100		8070 (1.29)
4	**3a**	36	150	10	100		8120 (1.41)
5	**3b**	18	150	5	100		12300 (1.20)
6	**3b**	18	125	13	100	**5c**	9900 (1.12)
7	**3c**	18	125	15	100	**5d**	14980 (1.12)

[a] Polymerization was carried out in sulfolane ($[\mathbf{4}]_0 = 0.105$ M). [b] **3a**: $M_n = 3460$, $M_w/M_n = 1.07$. **3b**: $M_n = 6330$, $M_w/M_n = 1.09$. **3c**: $M_n = 11240$, $M_w/M_n = 1.08$. [c] Determined by GC. [d] Determined by GPC based on polystyrene standards (eluent: THF).

aromatic polyether segment (Scheme 2). In order to synthesize well-defined PSt **2** by ATRP of St with **1a**, we optimized the ligand and the ratio of the catalyst to St in the ATRP at 110 °C (Table 1). When the polymerization of St was carried out with the CuBr/PMDETA catalyst system[16,17] in the presence of **1a** ($[St]_0/[\mathbf{1a}]_0/[CuBr]_0/[PMDETA]_0 = 200/1/2/2$), the GPC profile of the obtained PSt showed a leading peak in the higher-molecular-weight region (entry 1, Figure S1a). Considering the high reactivity of the propagating terminal C−Br bond, this leading peak is probably due to a product formed by the coupling of PSts in the reaction mixture. To reduce the reactivity, bpy9 was used as a ligand instead of PMDETA,[18] but a small leading peak remained (entry 2, Figure S1b). We next changed the ratio of the catalyst to St, and found that polymerization with a decreased amount of the catalyst gave PSt **2a** with a relatively narrow molecular weight distribution (entry 3, Figure S1c). In the ^{1}H NMR spectrum of the PSt obtained by the polymerization under the same conditions, the signal of the initiating site of **1a** was not observed, and the integration ratio of signals indicates that the ratio of the initiator unit to the propagation terminal unit was 1:2 (Figure S2). Furthermore, the absence of the signal of **1a** in the ^{19}F NMR spectrum of the product obtained by the polymerization under the same conditions for 6 min (conversion of St = 3%) revealed that the initiator **1a** was consumed completely at the early stage of the polymerization. After the polymerization for 35 min, unreacted St was removed from the reaction mixture under reduced pressure, and the terminal C−Br bond of **2a** was reduced with Bu_3SnH in toluene at 85 °C. The GPC profile of the polymer **3a** obtained after the reduction showed a monomodal peak with a low polydispersity ($M_n = 3460$, $M_w/M_n = 1.07$). Other **3**s with $M_n = 6330$ (**3b**) and 11240 (**3c**) were also synthesized in the same manner.

As mentioned above, the ^{1}H and ^{19}F NMR spectra demonstrated that the ATRP of St with **1a** proceeded via bidirectional propagation from **1a**. However, it was uncertain whether or not the initiation reaction occurred concurrently at the two ATRP-initiation sites of **1a**. To confirm concurrent initiation, the polymerization of St with an initiator **1b** having one ATRP-initiation site was conducted under the same conditions using twice the amount of **1b** compared with the polymerization with **1a** (Scheme 3). If the initiation reactions at the two initiation sites of **1a** occur concurrently in this polymerization, the rates of the two polymerizations should be the same, because the initial concentrations of the ATRP initiation site of **1a** and **1b** in the reaction mixture are the same. Figure 1 depicts the time-conversion curves for the polymerizations, and demonstrates that the polymerization rates were almost identical. Therefore, it turns out that the concurrent initiation did indeed occur in the ATRP of St with **1a**.

(2) CGCP of 4 from Macroinitiator 3. We first used the macroinitiator **3a** ($M_n = 3460$, $M_w/M_n = 1.07$) for the synthesis of AB$_2$ type miktoarm star copolymer. The monomer **4** was polymerized with $[\mathbf{4}]_0/[\mathbf{3a}]_0 = 14$, 18, 24 and 36 in sulfolane at 150 °C, and the results are summarized in Table 2. When the polymerization was carried out with $[\mathbf{4}]_0/[\mathbf{3a}]_0 = 14$ and 18, the monomer **4** was consumed in 5 and 6 h, respectively, and polymers with low polydispersity were obtained (entries 1 and 2). The GPC trace of the product showed a clear shift toward the higher-molecular-weight region while retaining low polydispersity (Figure 2). In the ^{1}H NMR spectrum of the product, the signals of the aromatic polyether were observed, as well as those of PSt. Furthermore, the ^{19}F NMR spectrum of the product showed only one signal assignable to the end group of the aromatic polyether, and the signal of the initiation site of **3a** was not observed (Figure S3). These results indicated that the desired AB$_2$ type miktoarm star copolymer **5** had been formed via CGCP of **4** from the initiation site of **3a** without self-polycondensation of **4**. On the other hand, the GPC profiles of the polymers obtained by the polymerization with $[\mathbf{4}]_0/[\mathbf{3a}]_0 = 24$ and 36 showed tailing toward the lower-molecular-weight region, resulting in broad molecular weight distributions (entries

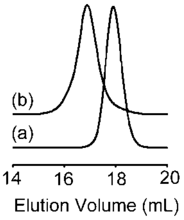


Figure 2. GPC profiles of (a) polystyrene macroinitiator **3a** (M_n = 3460, M_w/M_n = 1.07), and (b) miktoarm star copolymer **5b** (M_n = 9430, M_w/M_n = 1.18) synthesized by the polymerization of **4** with **3a** ($[\mathbf{4}]_0/[\mathbf{3a}]_0$ = 18) in sulfolane at 150 °C for 6 h.

Scheme 4

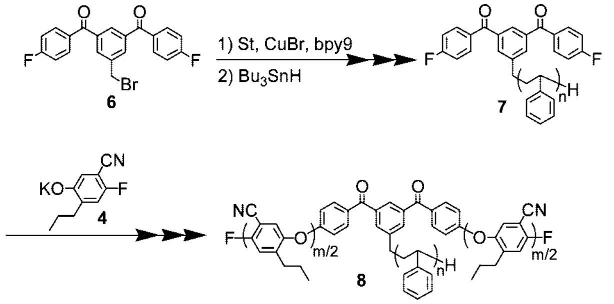


Table 3. Synthesis of A_2B Type PSt Macroinitiator 7 by ATRP[a]

entry	$[St]_0/[\mathbf{6}]_0/[CuBr]_0/[bpy9]_0$	time (min)	convn of St (%)	**7**	M_n (M_w/M_n)[b]	GPC profile
1	200/1/1/2	50	11.8	**7a**	3000 (1.07)	monomodal
2	200/1/1/2	120	26.8	**7b**	7000 (1.08)	monomodal
3	200/1/1/2	405	54.5		12630 (1.14)	shoulder
4[c]	300/1/1/2	300	33.3	**7c**	9590 (1.10)	monomodal

[a] ATRP of styrene was carried out with CuBr and bpy9 at 110 °C. [b] Determined by GPC based on polystyrene standards (eluent: THF). [c] Reduction of the C−Br bond with Bu_3SnH was carried out in the presence of $CuBr_2$ (0.15 equiv to CuBr) as an additive.

Table 4. Polymerization of 4 with 7[a]

entry	macroinitiator **7**[b]	$[\mathbf{4}]_0/[\mathbf{7}]_0$	temp (°C)	time (h)	convn of **4**[c](%)	**8**	M_n (M_w/M_n)[d]
1[e]	**7a**	20	150	6	100	**8a**	8530 (1.08)
2[e]	**7a**	30	150	6	100	**8b**	11060 (1.13)
3[e]	**7a**	40	150	10	100		5570 (1.87)
4[f]	**7b**	20	125	9	100	**8c**	10470 (1.07)
5[f]	**7c**	20	125	5	100	**8d**	12710 (1.08)

[a] Polymerization was carried out in sulfolane. [b] **7a**: M_n = 3000, M_w/M_n = 1.07. **7b**: M_n = 7000, M_w/M_n = 1.08. **7c**: M_n = 9590, M_w/M_n = 1.10. [c] Determined by GC. [d] Determined by GPC based on polystyrene standards (eluent: THF). [e] $[\mathbf{4}]_0$ = 0.167 M. [f] $[\mathbf{4}]_0$ = 0.105 M.

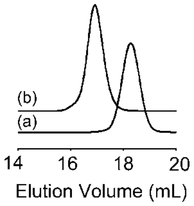


Figure 3. GPC profiles of (a) polystyrene macroinitiator **7a** (M_n = 3000, M_w/M_n = 1.07), and (b) A_2B type miktoarm star copolymer **8a** (M_n = 8530, M_w/M_n = 1.08) synthesized by the polymerization of **4** with **7a** ($[\mathbf{4}]_0/[\mathbf{7a}]_0$ = 20) in sulfolane at 150 °C for 6 h.

3 and 4). The lower-molecular-weight polymer in the tail is probably a homopolymer of **4** generated by self-polycondensation due to poor solubility of the block copolymer with increasing amounts of the **4** unit, as in the case of the synthesis of diblock copolymer containing a large amount of the **4** unit.[14]

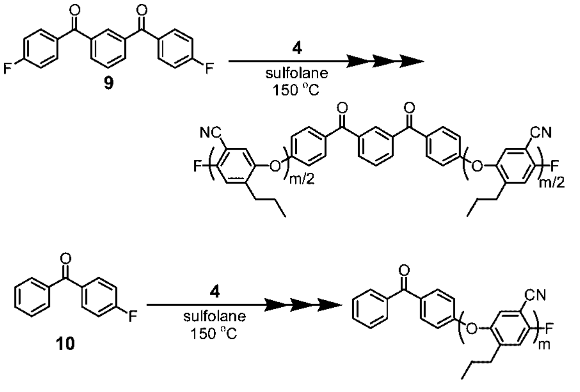
The synthesis of the AB_2 type miktoarm copolymer was further carried out with macroinitiators of higher molecular weight, **3b** (M_n = 6330, M_w/M_n = 1.09) and **3c** (M_n = 11240, M_w/M_n = 1.08), at the $[\mathbf{4}]_0/[\mathbf{3}]_0$ ratio of 18. The polymerization with **3b** at 150 °C resulted in the formation of the miktoarm star copolymer as well as the homopolymer of **4** (entry 5, Figure S4). However, the polymerization at lower temperature, 125 °C, proceeded without self-polycondensation, and afforded well-defined miktoarm star copolymer **5c** with a narrow molecular weight distribution (entry 6). The polymerization of **4** with higher-molecular-weight macroinitiator **3c** at 125 °C also proceeded in a chain-growth polymerization manner to give the miktoarm star copolymer **5d** (entry 7).

2. Synthesis of A_2B Type Miktoarm Star Copolymers 8. *(1) ATRP of Styrene from A_2B Type Initiator 6.* The A_2B type miktoarm star copolymer **8** was synthesized from the initiator **6** in the same way as described for the synthesis of **5** (Scheme 4). The ATRP of St was first carried out with the CuBr/bpy9 catalyst system in the presence of **6** ($[St]_0/[\mathbf{6}]_0/[CuBr]_0/[bpy9]_0$ = 200/1/1/2) in bulk at 110 °C for 50 min, and then the reduction of the terminal C−Br bond with Bu_3SnH afforded the A_2B type macroinitiator **7a**. The GPC profile of **7a** obtained after the reduction showed a monomodal peak with a low polydispersity (Table 3, entry 1). Polymerization for a longer time (120 min) followed by reduction gave higher-molecular-weight macroinitiator **7b** without side reactions (entry 2). On the other hand, when the polymerization time was further elongated to 405 min, the GPC profile of the product showed tailing toward the lower-molecular-weight region, as well as a shoulder in the higher-molecular-weight region which was thought to be due to products generated by the coupling reaction of the formed polymers (entry 3, Figure S5a). Matyjaszewski and co-workers reported that the coupling reaction of radicals was suppressed by initial addition of Cu(II) species to the reaction mixture.[19] In order to control the ATRP of St with **6** more precisely and to decrease the tailing and the shoulder of the GPC elution curve of the product, the ATRP was conducted with a higher ratio of $[St]_0/[\mathbf{6}]_0$ (increased from 200 to 300) for a shorter reaction time (300 min), and a small amount of $CuBr_2$ (0.15 equiv to CuBr) was added before the reduction of the terminal C−Br bond with Bu_3SnH. As expected, this polymerization proceeded in more controlled manner, affording **7c** with almost complete suppression of the coupling reaction (entry 4, Figure S5b).

(2) CGCP of 4 from Macroinitiator 7. The PSt macroinitiators **7a-c** were used for the synthesis of the A_2B type miktoarm star copolymer **8** via CGCP of **4** with $[\mathbf{4}]_0/[\mathbf{7a}]_0$ = 20, 30, and 40 in sulfolane (Table 4). In the polymerization with $[\mathbf{4}]_0/[\mathbf{7a}]_0$ = 20 and 30 at 150 °C, **4** was consumed in 6 h to yield polymers with low polydispersity (entries 1 and 2). In these cases, the GPC elution curve shifted toward the higher-molecular-weight region while retaining low polydispersity (Figure 3), indicating the formation of well-defined A_2B type miktoarm star copolymers **8a**,**b** without self-polycondensation of **4**. However, the polymerization of **4** with a higher feed ratio ($[\mathbf{4}]_0/[\mathbf{7a}]_0$ = 40) yielded polymer with a broad molecular weight distribution; the GPC elution curve of the polymer showed tailing toward the lower-molecular-weight region (entry 3). When the polymerization of **4** with higher-molecular-weigh macroinitiators **7b**,**c** was carried out at 125 °C with the $[\mathbf{4}]_0/[\mathbf{7}]_0$ ratio of 20, A_2B type miktoarm star copolymers **8c**,**d** with narrow molecular weight distributions were obtained (entries 4 and 5).

To demonstrate the concurrent initiation at the two initiation sites of **7** and the bidirectional propagation of the polymerization of **4**, the polymerizations of **4** with 1,3-bis(4-fluorobenzoyl)benzene (**9**) as a difunctional initiator and with 4-fluorobenzophenone (**10**) as a monofunctional initiator were conducted under the same conditions as used in the polymerization of **4**

Scheme 5



with **7** (Scheme 5), as in the case of the polymerization of St with **1a** and **1b** described above. As shown in Figure 4, the rates of the two polymerizations were almost identical, whereas the polymers obtained by the polymerization of **4** with **9** showed M_n values twice as large as those obtained by the polymerization with **10** at any conversion of the monomer. These results indicated that **7** worked as a difunctional initiator for CGCP of **4** and the initiation reaction occurred concurrently at the two initiation sites of **7**.

3. Solubility and Self-Assembly of Miktoarm Star Copolymer. The solubility of the AB_2 and A_2B type miktoarm star copolymers, **5d** and **8d**, respectively, was studied compared with that of the AB type diblock copolymer (poly**4**-*b*-PSt)[14] and poly**4** (Table S1). The diblock and miktoarm star copolymers showed higher solubility than poly**4** in various organic solvents. Surprisingly, the A_2B type miktoarm star copolymer **8d** which contains two arms of poly**4** with high crystallinity[13] was soluble in ether and ethyl acetate, in which the AB type diblock copolymer and the AB_2 type miktoarm star copolymer **5d** were insoluble. Solubility is thought to reflect the way in which the PSt segments are connected to the poly**4** unit. That is, in the AB type diblock copolymer and AB_2 type miktoarm star copolymer **5d**, the PSt units are attached at the terminal of the poly**4** unit. However, the PSt unit of the A_2B type miktoarm star copolymer **8d** are connected at the center of the poly**4** unit, which would inhibit the crystallization of the poly**4** unit and result in the higher solubility of the A_2B type miktoarm star copolymer.

We next studied the self-assembly of the miktoarm star copolymers. A solution of the AB_2 type miktoarm star copolymer **5e** (M_n = 7440, M_w/M_n = 1.17, $\mathbf{4}_{12.3}$-*b*-(St$_{15.0}$)$_2$)[20] in THF (1.0 mg/mL), which is a good solvent for the PSt unit and a poor solvent for the poly**4** unit, was dropped onto a glass plate and a Cu grid, and allowed to dry at room temperature. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images revealed the formation of large spherical aggregates of 150−600 nm diameter, which are much larger than the extended length of the miktoarm star copolymers (Figure 5a,b). The filled spherical aggregates shown in the TEM image suggest that these spheres were not vesicles or hollow micelles. Figure S7 shows a typical AFM image of the miktoarm star copolymer **5e**. Statistical analysis of the AFM image revealed that the average diameter and height of spherical aggregates were 550 and 400 nm, respectively, which are consistent with the data obtained from the SEM and TEM images. The self-assembling structure of the A_2B type miktoarm star copolymer **8e** (M_n = 7210, M_w/M_n = 1.07, ($\mathbf{4}_{7.4}$)$_2$-*b*-St$_{33.0}$)[20] obtained from THF solution consisted of spherical aggregates similar to those of the AB_2 type (Figure 5c). Therefore, when THF was used as a solvent, both the AB_2 and A_2B type miktoarm star copolymers self-assembled to give spherical aggregates independently of their polymer structure, as in the case of the AB type diblock copolymers reported previously.[14] On the other hand, the self-assembled structures of these copolymers obtained from a solution in a mixture of THF and methanol (2/1, v/v) changed depending on the polymer structure. Although the A_2B type miktoarm star copolymer **8f** (M_n = 7900, M_w/M_n = 1.08, ($\mathbf{4}_{7.7}$)$_2$-*b*-St$_{37.0}$)[20] in THF-methanol afforded spherical aggregates (Figure 6c) similar to those obtained from THF solution, the AB type diblock copolymer (M_n = 6700, M_w/M_n = 1.16, $\mathbf{4}_{14.3}$-*b*-St$_{28.8}$)[20] and the AB_2 type miktoarm star copolymer **5f** (M_n = 8360, M_w/M_n = 1.14, $\mathbf{4}_{14.7}$-*b*-(St$_{17.5}$)$_2$)[20]

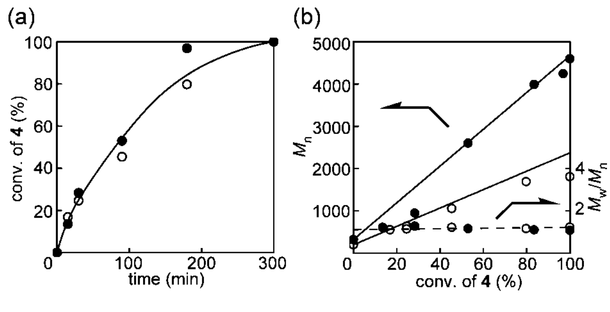


Figure 4. Polymerization of **4** with **9** (filled circles, $[\mathbf{4}]_0/[\mathbf{9}]_0$ = 20) and **10** (open circles, $[\mathbf{4}]_0/[\mathbf{10}]_0$ = 10) in sulfolane at 150 °C ($[\mathbf{4}]_0$ = 0.25 M). (a) Time-conversion curves. (b) The M_n and M_w/M_n values of poly**4** as a function of monomer conversion. The lines represent the calculated M_n values, assuming that all polymer chains contain unit **9** or **10** as an initiation unit.

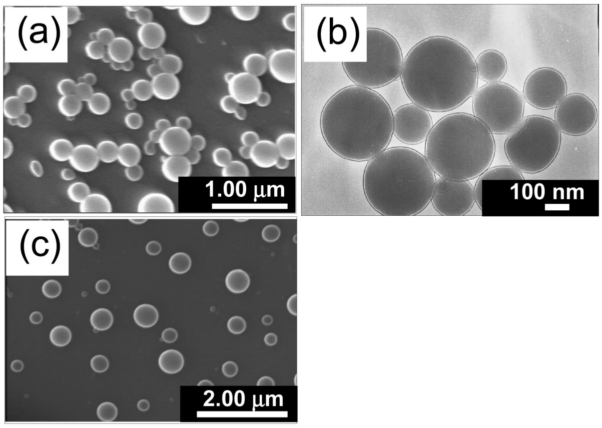


Figure 5. (a) SEM and (b) TEM images of self-assembled **5e** (M_n = 7440, M_w/M_n = 1.17, $\mathbf{4}_{12.3}$-*b*-(St$_{15.0}$)$_2$), and (c) SEM image of self-assembled **8e** (M_n = 7210, M_w/M_n = 1.07, ($\mathbf{4}_{7.4}$)$_2$-*b*-St$_{33.0}$).

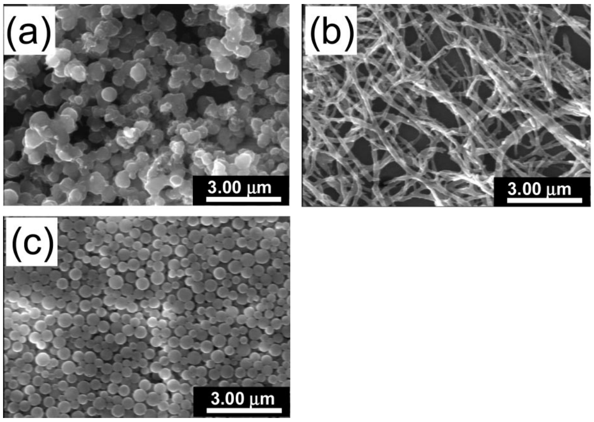


Figure 6. SEM images of self-assembled (a) AB type diblock copolymer (M_n = 6700, M_w/M_n = 1.16, $\mathbf{4}_{14.3}$-*b*-St$_{28.8}$), (b) **5f** (M_n = 8360, M_w/M_n = 1.14, $\mathbf{4}_{14.7}$-*b*-(St$_{17.5}$)$_2$), and (c) **8f** (M_n = 7900, M_w/M_n = 1.08, ($\mathbf{4}_{7.7}$)$_2$-*b*-St$_{37.0}$) in a THF-MeOH (2/1, v/v).

self-assembled to give disordered aggregates (Figure 6a) and fiber-like structure (Figure 6b), respectively. The solvent- and polymer structure-dependent changes of morphology would be induced by the lower solubility of the PSt and poly**4** segments in THF-methanol compared with THF solution. Because the AB_2 type miktoarm star copolymer contains two PSt arms, the fiber-like structure of the polymer would result from the combination of enhanced aggregability of the branched PSt unit and high crystallinity of the poly**4** segment in THF-methanol. On the other hand, the enhancement of the aggregability of the A_2B type miktoarm star copolymer is thought to be insufficient to induce a change of self-assembled structure, probably due to intrinsically high solubility of this polymer in organic solvents, as demonstrated above.

Conclusions

We have demonstrated that well-defined AB_2 and A_2B type miktoarm star copolymers consisting of aromatic polyether as the A segment and PSt as the B segment can be synthesized via a combination of ATRP and CGCP using trifunctional initiators **1a** and **6**. We first tried the synthesis of the AB_2 type miktoarm star copolymer by the use of **1a**. The AB_2 type PSt macroinitiator **3** was synthesized by ATRP of St in the presence of **1a** with CuBr and bpy9, followed by reduction of the terminal C−Br bond of **2** with Bu_3SnH. The model polymerization indicated that the ATRP of St with **1a** was initiated concurrently at the two ATRP-initiation sites of **1a**. The obtained PSt macroinitiator **3** was used for the CGCP to construct the aromatic polyether segment. The polymerization of **4** with **3** in sulfolane afforded the desired miktoarm star copolymers **5** ($M_n \leq 14980$, $M_w/M_n \leq 1.18$) without step-growth polycondensation. Next, the synthesis of the A_2B type miktoarm star copolymers **8** was conducted. The macroinitiator **7** containing two CGCP initiation sites was synthesized by ATRP of St with **6**, followed by reduction of the terminal C−Br bond. The CGCP of **4** proceeded well from **7** to yield the A_2B type miktoarm star copolymer **8** with low polydispersity ($M_n \leq 12710$, $M_w/M_n \leq 1.13$). The concurrent initiation and the bidirectional progress of this polymerization were also confirmed by the model polymerization. The miktoarm star copolymers self-assembled to form spheres of 150−600 nm diameter when their solution in THF was allowed to dry on a glass plate. On the other hand, a fiber-like structure was obtained from the AB_2 type miktoarm star copolymer in THF-methanol, in spite of the formation of spherical aggregates of the A_2B type miktoarm star copolymer under the same conditions. Further experiments are in progress to evaluate the unique self-assembling properties of the miktoarm star copolymers.

Acknowledgment. We gratefully acknowledge grants from a Scientific Frontier Research Project from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We also thank K. Hagiwara, M. Yakou, H. Hosogai, and Prof. K. Tajima for kind help in measurement of SEM, TEM, and AFM.

Supporting Information Available: Text and schemes giving synthetic procedures for the trifunctional initiators (**1a** and **6**) and the model initiator **9**, figures showing the ^1H and ^{19}F NMR spectra of PSt–Br **2**, PSt macroinitiators (**3** and **7**) and miktoarm star copolymers (**5** and **8**) and the GPC profiles of the products obtained by ATRP and CGCP, a table summarizing the solubility of the copolymers, and an AFM image of the miktoarm star copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA802317J