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Synthesis of Well-Defined Star-Branched Polymers by Coupling Reaction of Star-Branched Polymer Anions Comprised of Three Polymer Segments with Chain-End-Functionalized Polystyrenes with a Definite Number of Benzyl Bromide Moieties

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ABSTRACT: For the synthesis of well-defined regular and asymmetric star-branched polymers, we have developed a new methodology using specially designed star-branched polymer anions comprised of three polymer segments in the coupling reaction with chain-end-functionalized polystyrenes with a definite number of benzyl bromide moieties (PS(BnBr)$_n$). The most advantageous feature of this methodology is that three same or different polymer chains in composition can be simultaneously introduced at the core of star-branched polymer by a one-step reaction via one benzyl bromide functionality of the reaction site. By coupling these polymer anions with PS(BnBr)$_2$, PS(BnBr)$_4$, and PS(BnBr)$_8$, an array of 7-, 13-, and 25-armed regular star-branched polystyrenes as well as 7-armed $A_2B_2C_2D$ and 13-armed $A_4B_4C_4D$ asymmetric star-branched polymers have been successfully synthesized in ca. 100% yields. Their A, B, C, and D segments are poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), and polystyrene, respectively. The resulting star-branched polymers were well-defined in branched architecture and precisely controlled in chain length. All of these results strongly demonstrate the synthetic versatility and potential of the developed methodology for the synthesis of both regular and asymmetric star-branched polymers with structural variation.

Introduction

Star-branched polymers have widely been studied for a long time from theoretical and synthetic viewpoints, since their behaviors and properties in bulk, melt, and solutions are distinct from those of the corresponding linear counterparts.[1−8] For this reason, many star-branched polymers comprised of same arm segments, so-called regular star-branched polymers, have been synthesized so far.[6,9−15] In recent several years, more complex asymmetric star-branched polymers whose arms differ in composition have received considerable attention. Because of their heterophase dissimilar structures in addition to chain-branching architectures, they are expected to phase-separate at molecular level and promote self-assembly to fabricate new and interesting supramolecular nanoscopic objects.[16−20]

In general, asymmetric star-branched polymers are much more difficult in synthesis than the corresponding regular star-branched polymers, since two or more reactions with quantitative character and isolation of intermediate polymers during the syntheses are often required. Although several reliable procedures for the synthesis of asymmetric star-branched polymers have been developed[21−43] and well reviewed by Hadjichristidis and co-workers,[44] the main problem is the lack of general and systematic synthetic methodologies, and therefore new synthetic development is still desired even at the present time.

We have recently developed a new synthetic methodology using polymer anions comprised of two same or different polymer chains in the coupling reaction with benzyl bromide chain-end-functionalized polymers that can permit the synthesis of a variety of regular and asymmetric star-branched polymers.[45,46] As illustrated in Scheme 1, these polymer anions are prepared by the addition reaction of living anionic polymers to DPE chain-end-functionalized polymers. The polymer anions thus prepared readily and quantitatively coupled with chain-end-functionalized polymers with two benzyl bromide moieties, thus forming both regular and asymmetric star-branched polymers of the types A_5 and A_2B_2C (see also Scheme 1). Moreover, we have demonstrated to synthesize A_9, A_{17}, and A_{33} regular as well as quite new A_5B_4, A_9B_8, and $A_{17}B_{16}$ asymmetric star-branched polymers by coupling such polymer anions with chain-end-functionalized polystyrenes with 4, 8, and even 16 benzyl bromide moieties. Thus, two same or different polymer chains could be simultaneously introduced at the cores of star-branched polymers by a one-step reaction via one benzyl bromide functionality.

As a further extension of the above-mentioned methodology, we herein report on a methodology using specially designed star-branched polymer anions comprised of three same or different polymer chains in the coupling reaction with benzyl bromide chain-end-functionalized polystyrenes. The objective of the present study is to examine the versatility and synthetic potential of the methodology using such polymer anions and establish it as a more general procedure, which allows readily access to synthetically difficult asymmetric star-branched polymers.[47]

Experimental Section

Materials. All chemicals (≥98% purities) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Japan), and used as received unless otherwise stated. Bu_2Mg (1.0 M solution in heptane, Aldrich, Japan) and *sec*-BuLi (1.3 M solution in cyclohexane, Aldrich, Japan) were used without purification.

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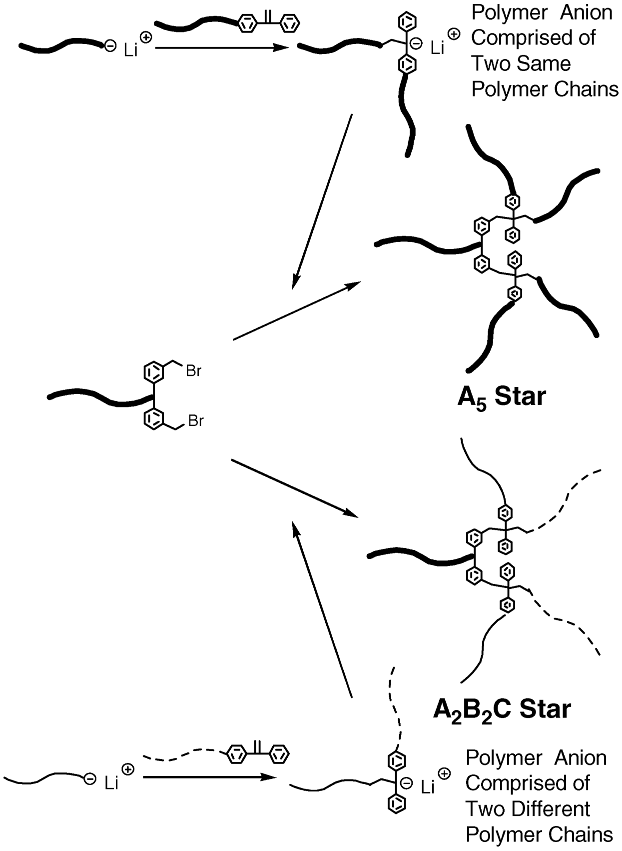
Scheme 1. Synthesis of A_5 and A_2B_2C Star-Branched Polymers



Tetrahydrofuran (THF) (99%, Mitsubishi Chemical Co., Ltd.) was refluxed over Na wire for 12 h and distilled over $LiAlH_4$ under nitrogen. It was finally distilled from its sodium naphthalenide solution on a vacuum line. Styrene, 4-methoxystyrene, 4-methylstyrene, and DPE were washed with 10% NaOH(aq), dried over $MgSO_4$, and distilled over CaH_2. 4-Trimethylsilylstyrene was synthesized according to the procedure previously reported[48] and distilled over CaH_2. All monomers were finally distilled over Bu_2Mg (ca. 5 mol %) on the vacuum line into ampules equipped with break-seals that were prewashed with potassium naphthalenide in THF. DPE was finally distilled from its 1,1-diphenylhexyllithium solution in heptane on the vacuum line. 1,1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**),[49] 1,1-bis(3-chloromethylphenyl)ethylene (**2**),[50] 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene (**3**),[36] and chain-end-functionalized polystyrenes with a definite number of benzyl bromide moieties were synthesized and purified according to our procedures previously reported.[51]

Measurements. Both ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured in $CDCl_3$ using a Bruker DPX spectrometer. Size-exclusion chromatography (SEC) was performed on a Tosoh HLC 8020 instrument with UV (254 nm) and refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Three polystyrene gel columns (pore size (bead size): 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm)) were used. Measurable molecular weight ranges are 10^3−4×10^5. Calibration curve was made with standard polystyrene samples for determining both M_n and M_w/M_n values. Fractionation by SEC was performed with a flow rate of 5.0 mL/min at 40 °C using a Tosoh HLC 8020 type fully automatic instrument equipped with a $TSK_{gel}G5000H_{HR}$ column. All runs for fractionation were made with THF as an eluent. Static light scattering (SLS) measurements were performed with an Ootsuka Electronics DLS-7000 instrument equipped with a He−Ne laser (633 nm) in THF at 25 °C. The refractive index increment (dn/dc) in THF at 25 °C was determined for each star-branched polymer with an Ootsuka Electronics DRM-1020 refractometer operating at 633 nm. Intrinsic viscosities were measured with an Ubbelohde viscometer in toluene at 35 °C.

Preparation of Living Anionic Polymers. All polymerizations were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors with break-seals. The reactors were always prewashed with the initiator solutions after being sealed off from the vacuum line. Polystyryllithium (PSLi), poly(4-trimethylsilylstyryl)lithium (PSiSLi), poly(4-methylstyryl)lithium (PMSLi), and poly(4-methoxystyryl)lithium (PMOSLi) were prepared by the *sec*-BuLi-initiated polymerization of the corresponding styrene derivatives in THF at −78 °C for 20 min, 1 h, 1 h, and 1 h, respectively. Monomers and initiators were used in the concentration ranges of ca. 0.8−1.0 M and ca. 0.04−0.4 M, respectively.

Preparation of Polymer Anions. Typical experiments for the preparation of three types of polymer anions, **A**, **B**, and **C**, are as follows:

*Type **A***: The polymer anion, **A**, was prepared by the addition reaction of PSLi to in-chain-functionalized polystyrene with DPE moiety (PS-D-PS). For this synthesis, the PS-D-PS was first prepared. PSLi (M_n (SEC) = 11.4 kg/mol, M_w/M_n (SEC) = 1.03, 2.36 g, 0.205 mmol) in THF (25.0 mL) was end-capped with DPE (0.248 mmol) in THF (4.05 mL) at −78 °C for 30 min. The resulting DPE end-capped PSLi was then added to a solution of **2** (0.0975 mmol) in THF (3.85 mL) at −78 °C. After 30 min, the polymer mixture was quenched with degassed MeOH (5.0 mL) and poured into a large amount of MeOH (200 mL) to precipitate the polymers. The resulting PS-D-PS was isolated by fractional precipitation using a mixture of cyclohexane and hexane (200 mL/70 mL) at 5 °C. The isolated polymer was purified by reprecipitating twice from THF into MeOH and then freeze-drying thrice from its absolute benzene solution for 6 h (2.30 g, 90%, M_n (SEC) = 23.0 kg/mol, M_w/M_n = 1.02, and the degree of DPE functionalization (^1H NMR) = 0.99_5). The objective polymer anion, **A**, was prepared by adding PSLi (M_n(SEC) = 10.8 kg/mol, M_w/M_n (SEC) = 1.03, 0.554 g, 0.0513 mmol) in THF (5.10 mL) to a THF (13.5 mL) solution of the PS-D-PS (1.25 g, 0.0543 mmol) at −78 °C and allowing the mixture to stand for an additional 20 h.

*Type **B***: The polymer anion, **B**, was prepared by the reaction of PSLi with another type of in-chain-functionalized polystyrene with DPE moiety. At first, the in-chain-functionalized polystyrene with DPE moiety was prepared. PSLi (M_n (SEC) = 10.5 kg/mol, M_w/M_n (SEC) = 1.03, 2.21 g, 0.210 mmol) in THF (24.0 mL) was added at −78 °C to a THF solution (25.0 mL) of chain-end-functionalized polystyrene with DPE moiety[52] (M_n (SEC) = 10.9 kg/mol, M_w/M_n (SEC) = 1.03, and the degree of DPE functionalization = 1.0_2, 2.52 g, 0.231 mmol). After 1 h, the reaction mixture was in-situ added at −78 °C to a THF solution (4.03 mL) of **3** (0.248 mmol), prepurified by Bu_2Mg (0.0836 mmol) prior to the addition, and was allowed to stand for an additional 1 h. The reaction mixture was poured into a large amount of MeOH (500 mL) to precipitate the polymers. The resulting in-chain-functionalized polystyrene with DPE moiety was isolated by fractional precipitation using a mixture of cyclohexane and hexane (500 mL/180 mL) at 5 °C. The isolated polymer was purified by reprecipitating twice from THF into MeOH and freeze-drying thrice from its absolute benzene solution for 6 h (4.35 g, 92%, M_n (SEC) = 21.4 kg/mol, M_w/M_n (SEC) = 1.02, and the degree of DPE functionalization (^1H NMR) = 0.98_5). The objective polymer anion, **B**, was prepared by adding PSLi (M_n (SEC) = 10.7 kg/mol, M_w/M_n (SEC) = 1.03, 0.502 g, 0.0469 mmol) in THF (4.87 mL) to a solution of the above-prepared in-chain-functionalized polystyrene with DPE moiety (1.06 g, 0.0493 mmol) in THF (10.0 mL) at −78 °C and allowing the polymer mixture to stand for 6 h.

*Type **C***: The polymer anion, **C**, was prepared by the reaction of *sec*-BuLi with the core-functionalized star-branched polystyrene with DPE moiety, which was obtained by the in-situ reaction of **B** with **3**. At first, the core-functionalized star-branched polystyrene with DPE moiety was prepared by adding the polymer anion, **B** ((M_n)s (SEC) = 10.5 + 10.0 + 11.2 kg/mol, $M_{n,total}$ = 31.7 kg/mol, 3.96 g, 0.125 mmol), in THF

(40.0 mL) to a THF solution (2.52 mL) of **3** (0.150 mmol), prepurified by Bu_2Mg (0.0721 mmol) prior to the addition, and allowing the reaction mixture to stand for 1 h. The reaction mixture was poured into a large amount of MeOH (400 mL) to precipitate the polymers. The resulting core-functionalized star-branched polystyrene with DPE moiety was isolated by fractional precipitation using a mixture of cyclohexane and hexane (400 mL/140 mL) at 5 °C. The isolated polymer was purified by reprecipitating twice from THF into MeOH and freeze-drying thrice from its absolute benzene solution for 6 h (3.48 g, 88%, M_w (SLS) = 32.3 kg/mol, M_w/M_n (SEC) = 1.02, and the degree of DPE functionalization (^{1}H NMR) = 0.98_0). The objective polymer anion, **C**, was prepared by adding *sec*-BuLi (0.0583 mmol) in heptane (1.50 mL) to a solution of the above-prepared core-functionalized star-branched polystyrene with DPE moiety (2.08 g, 0.0655 mmol) in THF (21.0 mL) at −78 °C and allowing the reaction mixture to stand for 2 h.

Reaction of Polymer Anions with PS(BnBr)$_n$. All coupling reactions of the polymer anions with PS(BnBr)$_n$ (n = 2, 4, 8, and 16) were carried out in THF at −78 °C for 24 or 168 h. A 1.5-fold excess of polymer anion toward benzyl bromide functionality was always employed in the reaction. A typical experiment for the reaction of the polymer anion, **C**, with PS(BnBr)$_8$ is as follows:

The polymer anion, **C** ((M_n)s (SEC) = 10.5 + 10.0 + 11.2 kg/mol, $M_{n,total}$ = 31.7 kg/mol, 1.86 g, 0.0583 mmol), in THF (22.5 mL) was in-situ added to a THF solution (3.50 mL) of PS(BnBr)$_8$ (M_n = 13.9 kg/mol, M_w/M_n (SEC) = 1.02, 0.0752 g, 0.00541 mmol, benzyl bromide functionality = 0.00541 × 8 = 0.0433 mmol) at −78 °C. The reaction mixture was allowed to stand at −78 °C for 24 h and then poured into a large amount of MeOH (200 mL) to precipitate the polymers. The highest molecular weight fraction was isolated by fractional precipitation using a mixture of cyclohexane and hexane (200 mL/50 mL) at 5 °C. The isolated polymer was reprecipitated twice from THF into MeOH, freeze-dried thrice from its absolute benzene solution for 6 h (1.26 g, 88%), and then characterized by ^{1}H NMR, SEC, SLS, and viscosity measurements.

Synthesis of 7-Armed $A_2B_2C_2D$ and 13-Armed $A_4B_4C_4D$ Asymmetric Star-Branched Polymers. The title asymmetric star-branched polymers were synthesized by the coupling reaction of PS(BnBr)$_2$ or PS(BnBr)$_4$ with core-functionalized three-armed ABC asymmetric star-branched polymers with 1,1-diphenylalkyl anion that were prepared by the same approach used for the preparation of polymer anion, **B**. A typical procedure for the synthesis of a seven-armed asymmetric $A_2B_2C_2D$ star-branched polymer is as follows:

Preparation of Chain-End-Functionalized Poly(4-trimethylsilylstyrene) with DPE Moiety. PSiSLi (M_n (^{1}H NMR) = 10.2 kg/mol, M_w/M_n (SEC) = 1.03, 3.57 g, 0.350 mmol) in THF (35.0 mL) was end-capped with DPE (0.389 mmol) in THF (5.22 mL) at −78 °C for 30 min, followed by treating with **3** (0.396 mmol) in THF (4.25 mL), which was prepurified with Bu_2Mg (0.0889 mmol) prior to the addition. The reaction mixture was allowed to stand at −78 °C for an additional 1 h. The reaction mixture was poured into a large amount of MeOH (350 mL) to precipitate the polymer. The resulting chain-end-functionalized poly(4-trimethylsilylstyrene) (PSiS) with DPE moiety was purified by reprecipitating twice from THF into MeOH and then freeze-drying thrice from its absolute benzene solution for 6 h (3.56 g, 98%, M_n (^{1}H NMR) = 10.6 kg/mol, M_w/M_n (SEC) = 1.03, and the degree of DPE functionalization (^{1}H NMR) = 1.0_9).

Preparation of In-Chain-Functionalized Block Copolymer with DPE Moiety between Poly(4-trimethylsilylstyrene) and Poly(4-methoxystyrene) Blocks. PMOSLi (M_n (^{1}H NMR) = 10.2 kg/mol, M_w/M_n (SEC) = 1.04, 2.55 g, 0.250 mmol) in THF (25.2 mL) was added at −78 °C to a THF solution (30.7 mL) of the chain-end-functionalized PSiS with DPE moiety prepared as above (2.91 g, 0.275 mmol). After 1 h, the reaction mixture was in-situ added to **3** (0.301 mmol) in THF (5.11 mL), which was prepurified by Bu_2Mg (0.0827 mmol) prior to the addition, and allowed to stand at −78 °C for an additional 1 h. It was then poured into a large amount of MeOH (500 mL) to precipitate the polymers. The resulting in-chain-functionalized block copolymer with DPE moiety was isolated by SEC fractionation. The isolated polymer was purified by reprecipitating twice from THF into MeOH and freeze-drying thrice from its absolute benzene solution for 6 h (4.69 g, 85%, M_n (^{1}H NMR) = 20.8 kg/mol, M_w/M_n (SEC) = 1.02, and the degree of DPE functionalization (^{1}H NMR) = 0.99_5).

Preparation of Core-Functionalized Three-Armed ABC Asymmetric Star-Branched Polymers with 1,1-Diphenylalkyl Anion. PMSLi (M_n (^{1}H NMR) = 9.83 kg/mol, M_w/M_n (SEC) = 1.02, 0.483 g, 0.0491 mmol) in THF (4.99 mL) was added to a THF (12.2 mL) solution of the above-prepared in-chain-functionalized block copolymer with DPE moiety (1.12 g, 0.0540 mmol) at −78 °C, and the resulting polymer mixture was allowed to stand for 6 h at −78 °C to prepare the title star-branched polymer anion.

Synthesis of Seven-Armed Asymmetric $A_2B_2C_2D$ Star-Branched Polymer. The polymer anion (0.0491 mmol) prepared as above in THF (17.2 mL) was in-situ added at −78 °C to PS(BnBr)$_2$ (M_n = 10.4 kg/mol, M_w/M_n (SEC) = 1.03, 0.153 g, 0.0142 mmol, benzyl bromide functionality = 0.0142 × 2 = 0.0284 mmol) in THF (3.50 mL). The reaction mixture was allowed to stand at −78 °C for 24 h and then poured into a large amount of MeOH (150 mL) to precipitate the polymers. The highest molecular weight fraction was isolated by SEC fractionation. The isolated polymer was reprecipitated twice from THF into MeOH, freeze-dried twice from its absolute benzene solution for 6 h (0.826 g, 81%), and characterized by ^{1}H and ^{13}C NMR, SEC, and SLS measurements.

Similarly, a 13-armed $A_4B_4C_4D$ asymmetric star-branched polymer was synthesized (1.11 g, 87% after SEC fractionation) under the same conditions as above.

Results and Discussion

Synthesis of Chain-End-Functionalized Polystyrenes with a Definite Number of Benzyl Bromide Moieties. The title benzyl bromide-functionalized polymers were synthesized by the recently developed our methodology based on an iterative divergent approach. In the methodology, only two sets of the reactions are needed for the entire iterative reaction sequence which involves a coupling reaction of the terminal benzyl bromide functionality with the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi and a transformation reaction of the introduced *tert*-butyldimethylsilyloxymethylphenyl groups into the benzyl bromide functionalities by treatment with a 1:1 mixture of LiBr and $(CH_3)_3SiCl$, as illustrated in Scheme 2. By repeating the same reaction sequence three times starting from chain-end-functionalized polystyrene with two benzyl bromide moieties (PS(BnBr)$_2$),[53] a series of chain-end-functionalized polystyrenes with 4, 8, and 16 benzyl bromide moieties (PS(BnBr)$_4$, PS(BnBr)$_8$, and PS(BnBr)$_{16}$) were synthesized. The characterization results are summarized in Table 1.

As can be seen, these polymers all are precisely controlled in chain length and degree of terminal benzyl bromide functionality. The molecular weight of the functionalized polystyrenes thus synthesized increases as the iteration is repeated, while the polystyrene main chain always remains unchanged in molecular weight.

Reaction of Polymer Anion (A) with PS(BnBr)$_2$. The synthesis of seven-armed regular star-branched polystyrene was attempted by coupling a new polymer anion comprised of three polystyrene chains with PS(BnBr)$_2$, as shown in Scheme 3. The polymer anion used in this synthesis was prepared by the following two reaction steps (see also Scheme 3): The first reaction step involved the preparation of in-chain-functionalized polystyrene with DPE moiety (PS-D-PS) by reacting 1,1-bis(3-chloromethylphenyl)ethylene (**2**) with a 2.2-fold

Scheme 2. Synthesis of Chain-End-Functionalized Polystyrenes with Benzyl Bromide Moieties Based on an Iterative Divergent Approach

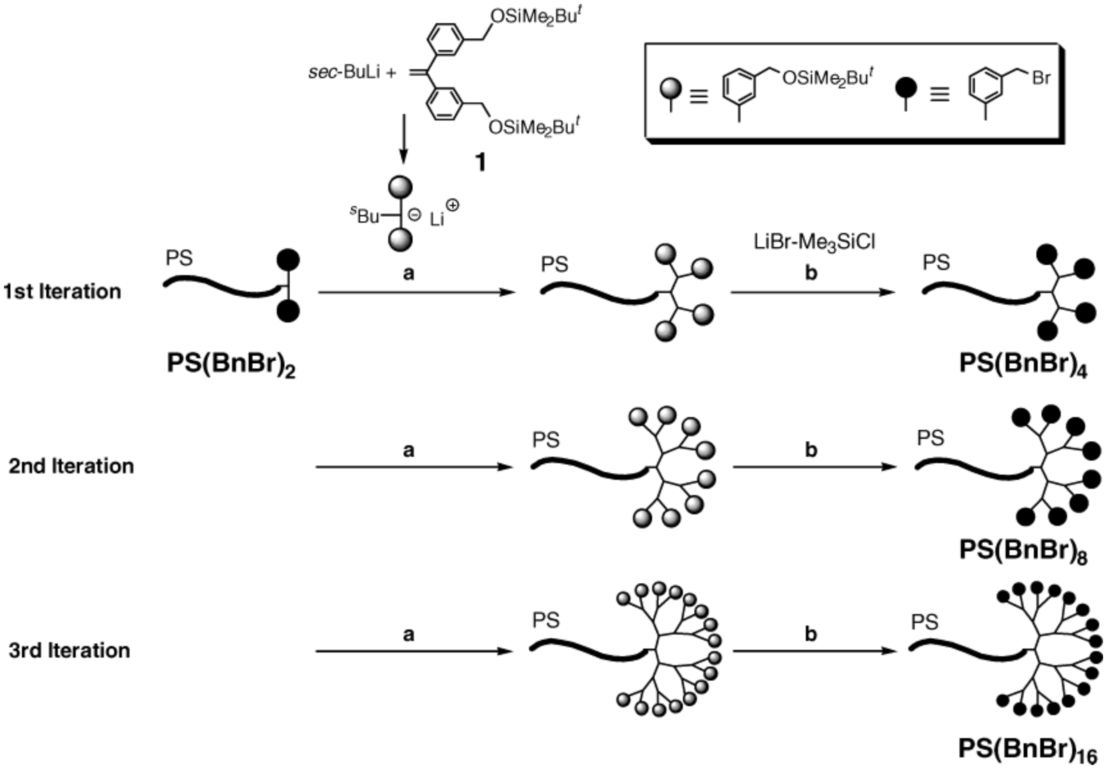


Table 1. Synthesis of PS(BnBr)$_n$^{a}

M_n (kg/mol)^b				M_w/M_n	functionality^c	
calcd	SEC	^{1}H NMR	VPO	SEC	calcd	^{1}H NMR
9.33	9.33	9.50	9.85	1.03	2	2.0_8
10.0	9.90	10.0	10.5	1.03	4	3.9_4
11.4	10.3	11.9	12.4	1.02	8	8.0_0
14.1	11.1	14.7	15.0	1.02	16	15.8

[a] Yields of PS(BnBr)$_n$ were 100% in all cases. [b] M_n values of polystyrene main chains determined by SEC were always 8.93 kg/mol. [c] Functionality of benzyl bromide moieties.

excess of PSLi. To avoid the attack of PSLi on the C=C bond of **2**, PSLi was end-capped with DPE prior to the reaction. The reaction proceeded cleanly and quantitatively in THF at −78 °C for 0.5 h. The PS-D-PS was isolated in 90% yield by fractional precipitation. In the second reaction, PSLi was again reacted with a 1.1-fold excess of the isolated PS-D-PS in THF at −78 °C for 20 h for preparing the polymer anion. In this reaction, PS-D-PS was used in excess to consume PSLi completely.

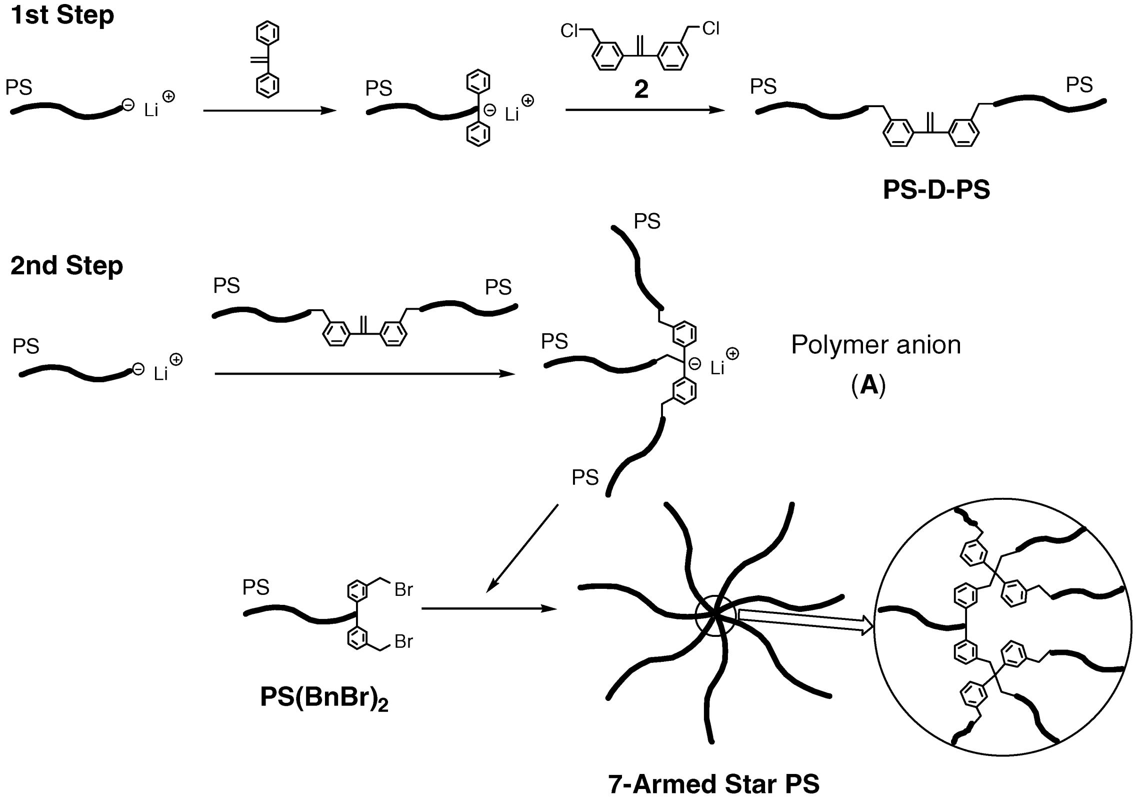
The resulting polymer anion (M_n = 33.8 kg/mol) comprised of three polystyrene chains ((M_n)s = 10.8 + 11.5 + 11.5 kg/mol) can be regarded as a core-functionalized three-armed star-branched polystyrene with a 1,1-diphenylalkyl anion. As illustrated in Scheme 4, the steric hindrance around the anion directly connected to the three polymer chains appears greater than that of the anion connected to two polymer chains. The polymer anion thus prepared, referred to as a type **A**, was not isolated and used in-situ in the next coupling reaction with PS(BnBr)$_2$.

The coupling reaction of the polymer anion with PS(BnBr)$_2$ was carried out in THF at −78 °C for 24 h. A 1.4-fold excess of the polymer anion toward benzyl bromide functionality was employed in the reaction. The SEC profile of the reaction mixture is shown in Figure 1. The highest molecular weight major peak presumably for the objective star-branched polymer is observed in addition to three low molecular weight peaks. On the basis of their molecular weights, three peaks are corresponding to the deactivated PSLi, PS-D-PS, and deactivated polymer anion used in excesses in the reactions, as shown in Figure 1A. The deactivated PSLi may have resulted from the reaction of PSLi with small amounts of impurities in PS-D-PS. Moreover, an intermediate four-armed star-branched polymer may be present between the major peak and the peak of the deactivated polymer anion. A yield of the star-branched polymer was estimated to be 56% from these peak areas and feed ratios.

The star-branched polymer isolated by fractional precipitation exhibited a sharp monomodal SEC distribution, as shown in Figure 1B. The results are summarized in Table 2. As expected from its branched structure, the M_n value measured by SEC was somewhat smaller than the calculated value assuming that the reaction proceeded quantitatively. On the other hand, the absolute M_w value of 82.5 kg/mol measured by SLS was very close to the expected value of 81.3 kg/mol. Thus, obviously, the star-branched polymer anion could react with PS(BnBr)$_2$ to afford the requisite seven-armed star-branched polystyrene, although the yield was not quantitative. It is likely that the steric bulkiness around the anion might prevent the coupling reaction from proceeding completely.

Reaction of Polymer Anions (B) with PS(BnBr)$_n$ (n = 2, 4, and 8). As mentioned above, the low coupling yield was likely, at least partially, attributed to steric hindrance around the anion of **A**. Therefore, we have designed another polymer anion referred to as a type **B** in such a way as to reduce the steric hindrance around anion, as illustrated in Scheme 5. At first, PSLi was reacted with a 1.1-fold excess of DPE chain-end-functionalized polystyrene, followed by treatment with 1-(4-

Scheme 3. Synthesis of 7-Armed Regular Star-Branched Polystyrene by Coupling a Polymer Anion, A, Comprised of Three Polystyrene Chains with PS(BnBr)$_2$



Scheme 4. Polymer Anions Comprised of Two and Three Polymer Chains

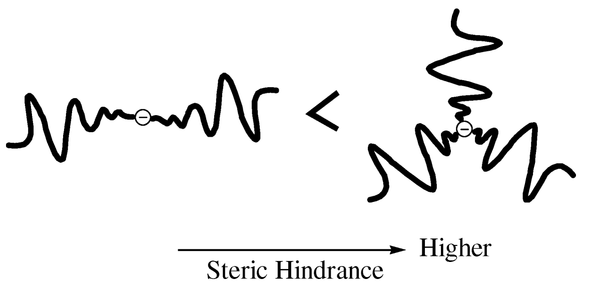


Table 2. Reaction of Polymer Anion, A, with PS(BnBr)$_2$[a]

M_n (kg/mol)		star polymer M_n (kg/mol)		star polymer M_w (kg/mol)		M_w/M_n
polymer anion, **A**	PS(BnBr)$_n$	calcd	SEC	calcd[b]	SLS[c]	SEC
33.8 (10.8 + 11.5 + 11.5)	10.8	78.2	61.8	81.3	82.5	1.04

[a] Yield of seven-armed star-branched polystyrene was 56%. [b] Calculated from M_n (calcd) and M_w/M_n (SEC). [c] In THF at 25 °C. dn/dc = 0.188 mL/g.

(4-bromobutyl)phenyl)-1-phenylethylene (**3**) to introduce DPE moiety at the linking point. After isolation of the resulting DPE in-chain-functionalized polystyrene by fractional precipitation, PSLi was again reacted with the isolated polymer to prepare the polymer anion, **B**. As can be seen, the 1,1-diphenylalkyl anion of **B** is connected to the three polystyrene chains at the two points and spatially free at one side, while that of **A** shown in Scheme 3 is connected to three polystyrene chains at the three points. Therefore, **B** appears to be less sterically hindered than **A**.

To synthesize a seven-armed star-branched polymer, the polymer anion, **B**, was in-situ reacted with PS(BnBr)$_2$ in THF at −78 °C for 24 h. The SEC profile of the reaction mixture is shown in Figure 2A. The major highest molecular weight peak presumably for the star-branched polymer is observed in addition to three small low molecular weight peaks. As mentioned in the preceding section, the additional small low molecular peaks may be corresponding to precursory polymers used in excesses in each of the reaction steps and the terminated PSLi with impurities in the intermediated polymer. This coupling reaction appeared virtually complete estimating from these peak areas and feed ratios. The highest molecular weight fraction was isolated in 85% yield by fractional precipitation and characterized by ^{1}H NMR, SEC, SLS, and viscosity measurements. The results are summarized in Table 3.

As shown in Figure 2B, the isolated polymer exhibited a narrow monomodal distribution (M_w/M_n = 1.04). Again, the M_n value estimated by SEC was somewhat smaller than that calculated as expected from its branched structure. On the other hand, the absolute M_w value measured by SLS agreed well with the expected value. Furthermore, the seven-armed branched architecture could be supported by good agreement between g' values defined as $[\eta]_{star}/[\eta]_{linear}$ experimentally determined and calculated from the established equations. These results clearly indicate that the polymer anion, **B**, is quantitatively coupled with PS(BnBr)$_2$ to afford an expected seven-armed star-branched polystyrene. Thus, changing the microstructure around the anion is very effective in the coupling reaction with PS(BnBr)$_2$. This success prompts us to further examine the synthetic potential of the polymer anion, **B**, for star-branched polymers with more arm segments.

The reaction of the polymer anion, **B**, with PS(BnBr)$_4$ was carried out under identical conditions. The SEC

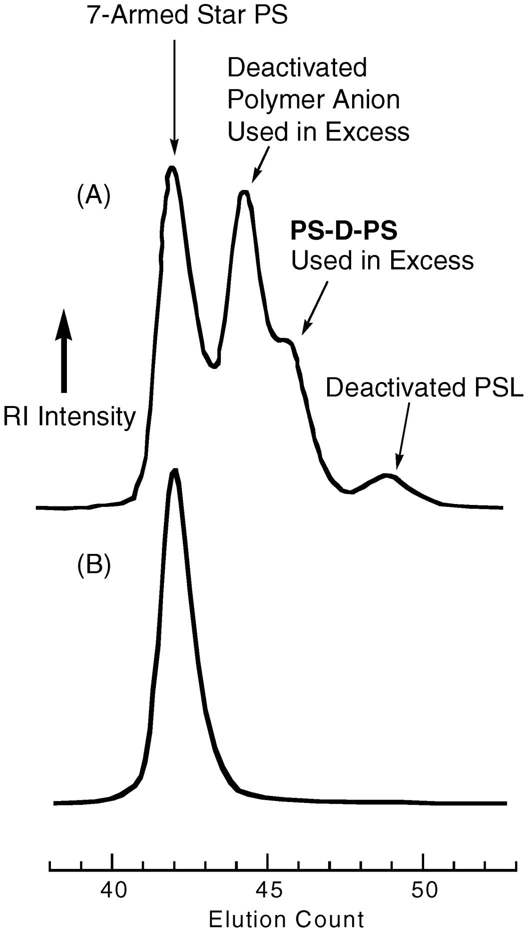


Figure 1. SEC profile of the polymers obtained by the reaction of **A** with PS(BnBr)$_2$: (A) before fractionation; (B) after fractionation.

profile of the reaction mixture was similar to that shown in Figure 2A, indicating that the reaction completely proceeded. The results are also listed in Table 3. The star-branched polymer isolated in 82% yield showed a sharp monomodal SEC distribution ($M_w/M_n = 1.03$). The absolute M_w value measured by SLS was in good agreement with that calculated. The g' value experimentally determined was nearly consistent with the value calculated as 13-armed star-branched polymer. Thus, the objective 13-armed star-branched polystyrene could be successfully synthesized.

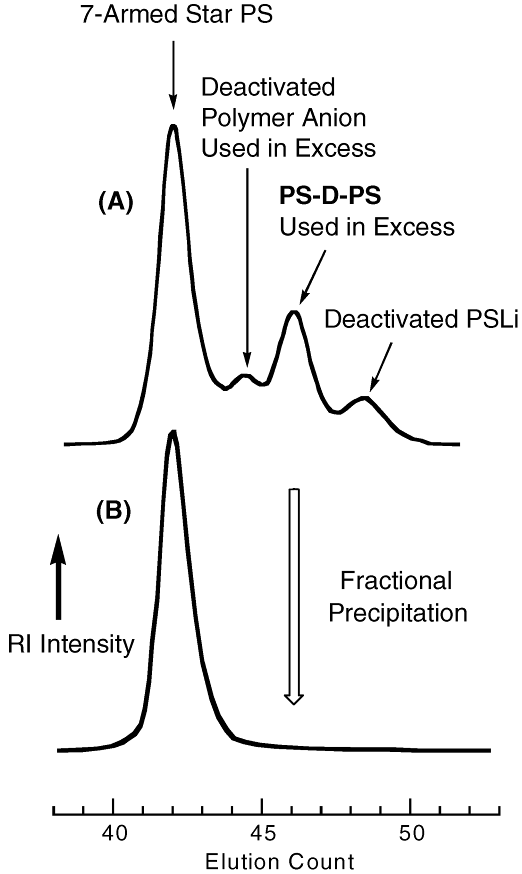


Figure 2. SEC profile of the polymers obtained by the reaction of **B** with PS(BnBr)$_2$: (A) before fractionation; (B) after fractionation.

Similarly, the synthesis of 25-armed star-branched polystyrene was attempted by the coupling reaction of the same polymer anion with PS(BnBr)$_8$. The SEC profile of the reaction mixture showed a sharp monomodal high molecular weight peak for the coupled star-branched polymer and small low molecular weight peaks corresponding to the precursory polymers. The highest molecular weight polymer was isolated and characterized by ^{1}H NMR, SEC, SLS, and viscosity measurements (also see Table 3). Although the polymer exhibited a very narrow molecular weight distribution ($M_w/M_n = 1.02$), the absolute M_w value of 231 kg/mol measured by SLS was somewhat smaller than the expected value of 273 kg/mol. The efficiency of this coupling reaction was calculated to 84% based on these M_w values. Accordingly, it was considered that 6.7 benzyl bromide moieties reacted with the **B** to form star-

Scheme 5. Preparation of Polymer Anion, B

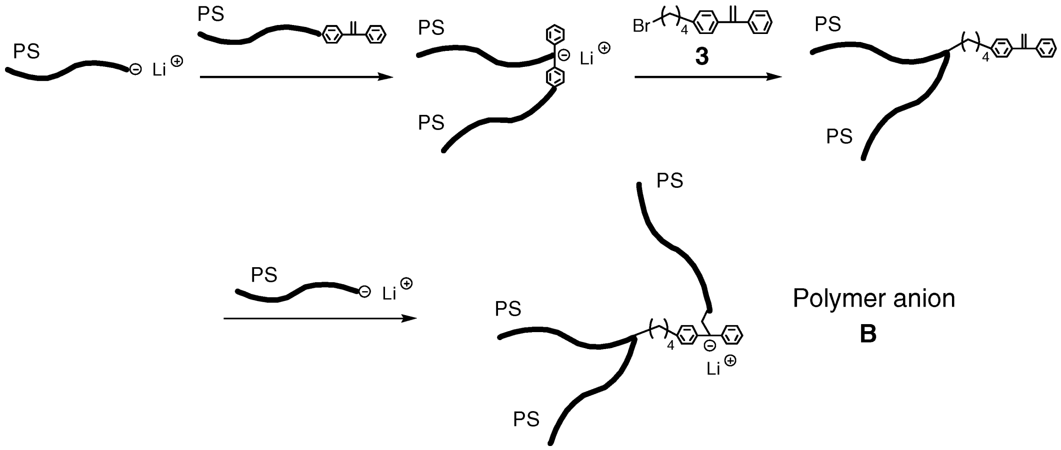
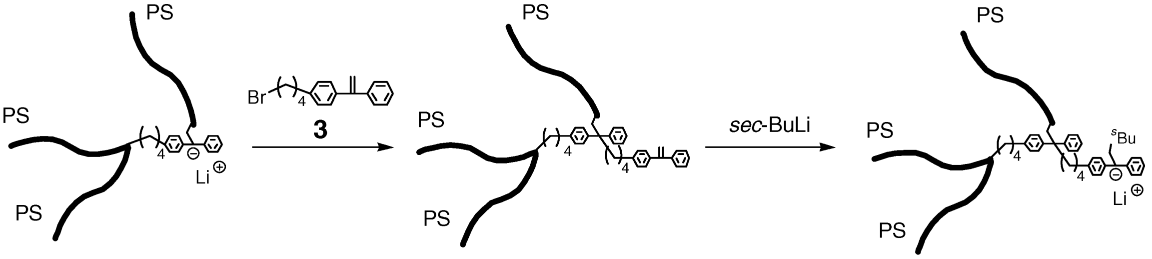


Table 3. Synthesis of Regular Star-Branched Polystyrenes by Coupling Reaction of B with PS(BnBr)$_n$ (n = 2, 4, and 8)[a]

	M_n (kg/mol)		M_w (kg/mol)			M_w/M_n	$g' = [\eta]_{star}/[\eta]_{linear}$[b]		
type	calcd	SEC	calcd[c]	SLS[d]	dn/dc[d]	SEC	expml	calcd from eq 1[e]	calcd from eq 2[f]
7-arm[g]	78.2	62.3	81.3	83.0	0.190	1.04	0.51	0.51	0.48
13-arm[h]	134	73.8	138	145	0.191	1.03	0.33	0.31	0.29
21-arm[i]	268	111	273	231	0.189	1.02	0.20		0.20
17-arm[j]	179	93.2	183	186	0.190	1.02	0.25	0.24	0.24

[a] DPE in-chain-functionalized polystyrenes (M_n = 21.4 kg/mol) were always employed for the reactions. [b] Intrinsic viscosities of star-branched polystyrenes ($[\eta]_{star}$) were measured in toluene at 35 °C. Intrinsic viscosities of linear polystyrenes with the same molecular weights were calculated from the equation $[\eta] = 1.26 \times 10^{-4} M_w(\mathrm{SLS})^{0.71}$ (ref 54). [c] Calculated from M_n (calcd) and M_w/M_n (SEC). [d] Measured in THF at 25 °C. [e] Calculated from the eq 1; $g' = [(3f - 2)/f^{\,2}]^{0.58} \times [0.724 - 0.015 \times (f - 1)]/0.724$: f = arm number ($3 \le f \le 18$) (ref 55). [f] Calculated from the eq 2; $\log g' = 0.36 - 0.80 \times \log f$: f = arm number ($6 \le f$) (ref 56). [g] PSLi (M_n = 12.5 kg/mol) and PS(BnBr)$_2$ (M_n = 10.8 kg/mol) were used. [h] PSLi (M_n = 9.64 kg/mol) and PS(BnBr)$_4$ (M_n = 10.0 kg/mol) were used. [i] PSLi (M_n = 10.7 kg/mol) and PS(BnBr)$_8$ (M_n = 11.4 kg/mol) were used. [j] Synthesized by the coupling reaction of PS(BnBr)$_8$ (M_n = 11.4 kg/mol) with polymer anion comprised of two polystyrene chains prepared from PSLi (M_n = 10.5 kg/mol) and DPE chain-end-functionalized polystyrene (M_n = 10.4 kg/mol, ref 52).

Scheme 6. Preparation of Polymer Anion, C



Polymer anion
B

Polymer anion
C

branched polystyrenes having polystyrene arm segments of 21 in average number. This is confirmed from the viscosity measurement that the g' value calculated as a 21-armed star-branched polymer is quite consistent with that obtained experimentally. Thus, the coupling reaction proceeded efficiently but not quantitatively under the conditions employed, possibly due to the steric hindrance of **B** toward the already introduced polymer segments of intermediated polymers. On the other hand, it was observed that the coupling reaction of the polymer anion (M_n = 20.9 kg/mol) comprised of two polystyrene chains ((M_n)s = 10.5 + 10.4 kg/mol) with PS(BnBr)$_8$ was quantitative to afford a 17-armed star-branched polystyrene. This clearly indicates that the polymer anion, **B**, comprised of three polymer chains is sterically bulkier than the polymer anion comprised of two polymer chains.

Reaction of Polymer Anion (C) with PS(BnBr)$_n$ (n = 8 and 16). The results obtained in the preceding section strongly demonstrate that even a small difference in microstructure around the anion can significantly affect the coupling efficiency of the reaction with PS(BnBr)$_n$. Therefore, we have again designed the microstructure around the anion so as to further reduce the steric hindrance. A less sterically hindered new polymer anion referred to as type **C** was prepared as illustrated in Scheme 6.

The polymer anion, **B**, was first prepared according to the Scheme 5, followed by treatment with **3** to introduce DPE moiety at the core. The resulting core-functionalized star-branched polymer with DPE moiety was treated with 0.9 equiv of *sec*-BuLi in THF at −78 °C for 1 h to prepare the polymer anion, **C**. It was in-situ used in the coupling reaction with PS(BnBr)$_n$. As can be seen in Scheme 5, the 1,1-diphenylalkyl anion of **C** is separated by four methylene chains from the moiety directly connected to the three polystyrene segments and therefore appears sterically less hindered than the corresponding 1,1-diphenylalkyl anion of **B**.

The coupling reaction of the newly prepared **C** with PS(BnBr)$_8$ was carried out under identical conditions. The SEC profile of the reaction mixture is shown in Figure 3A.

There are only two molecular weight peaks eluted at higher and lower molecular weight sides. The major higher molecular weight peak may possibly be corresponding to the star-branched polymer, while the lower molecular weight one is presumably attributed to its precursor polymers, including the deactivated polymer anion and DPE core-functionalized star-branched polymer used in excesses in the reactions. The reaction was estimated to be complete from both peak areas. The high molecular weight fraction was isolated in 88% yield by fractional precipitation and characterized by ^{1}H NMR, SEC, SLS, and viscosity measurements. The results are summarized in Table 4.

The isolated polymer showed a sharp monomodal SEC distribution (see also Figure 3B). The M_w value of 275 kg/mol measured by SLS agreed quite well with the expected value of 272 kg/mol. The agreement of the g' value between experimentally determined and calculated is satisfactory. These results clearly indicate that the new polymer anion, **C**, reacts quantitatively with PS(BnBr)$_8$ to afford a well-defined 25-armed star-branched polystyrene. The superiority of **C** to **B** in the coupling reaction is thus evident, again indicating the significance of the steric hindrance around the anion.

The coupling reaction of the same polymer anion, **C**, with PS(BnBr)$_{16}$ was attempted in order to synthesize 49-armed star-branched polystyrene. In this reaction, a longer reaction time to 168 h was taken because of many reaction sites and more steric hindrance. The SEC profile of the reaction mixture was similar to that shown in Figure 3A. The results are also listed in Table 4. The

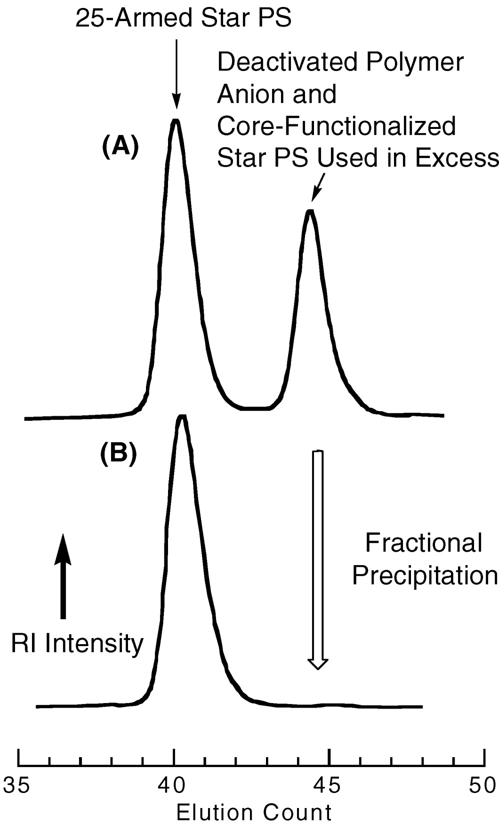


Figure 3. SEC profile of the polymers obtained by the reaction of **C** with PS(BnBr)$_8$: (A) before fractionation; (B) after fractionation.

isolated polymer showed a sharp monomodal SEC distribution ($M_w/M_n = 1.03$). However, the absolute M_w value of 489 kg/mol measured by SLS was smaller than the expected value of 536 kg/mol. Accordingly, the reaction efficiency corresponded to 91%, indicating that the polymer anion, **C**, reacted with 14.5 benzyl bromide functionalities in PS(BnBr)$_{16}$ to afford star-branched polymers with arm segments of 45 in average number. Agreement of g' values between experimentally determined and calculated also indicates the formation of 45-armed star-branched polystyrene. Thus, obviously, the coupling reaction proceeded efficiently but not quantitatively. The incomplete coupling reaction is undoubtedly due to the steric limitation arisen from the polymer anion and the already introduced arm segments of the intermediate polymer. In this case, however, rather surprising was that many segments up to 45 arms could be introduced. It may be expected to synthesize the requisite 49-armed star-branched polymers by further designing the microstructure around the anion.

The reaction efficiency of polymer anion comprised of three polymer chains with PS(BnBr)$_n$ was thus improved significantly by changing the microstructure around the anion. At the present time, we have demonstrated to synthesize a well-defined 25-armed star-branched polystyrene by the methodology using the polymer anion, **C**. There must be a maximum number of the benzyl bromide functionality between 8 and 16 in number, which is required to achieve complete coupling reaction under the conditions employed here. The number may be close to 14 or 15 estimating from the reaction result of **C** with PS(BnBr)$_{16}$.

To examine the effect of molecular weight of polymer anion on the coupling reaction, we have newly prepared a higher molecular weight polymer anion, **C**, with a M_w value of 55 kg/mol ($M_w/M_n = 1.03$) and reacted it with PS(BnBr)$_4$ in THF at −78 °C for 24 h. Unfortunately, the reaction proceeded inefficiently to afford a mixture of various intermediate polymers. The effect of molecular weight of polymer anion on the coupling reaction is thus critical. We are now investigating to optimize the reaction conditions in more detail such as temperature, solvent, concentration, etc., to be able to utilize higher molecular weight polymer anions.

Synthesis of Asymmetric Star-Branched Polymers by Coupling ABC Star-Branched Polymer Anion with PS(BnBr)$_n$. The most advantageous feature of the present methodology using polymer anion is that three polymer chains can be simultaneously introduced by a one-step coupling reaction via one benzyl bromide reaction site. On the basis of the successful results described in the preceding section, we have focus on the synthesis of asymmetric star-branched polymers by the same approach with use of a new polymer anion comprised of three different polymer chains in composition in the coupling reaction with either PS(BnBr)$_2$ or PS(BnBr)$_4$. If the reactions proceed as desired, 7-armed $A_2B_2C_2D$ and 13-armed $A_4B_4C_4D$ asymmetric star-branched polymers will be synthesized as illustrated in Scheme 7.

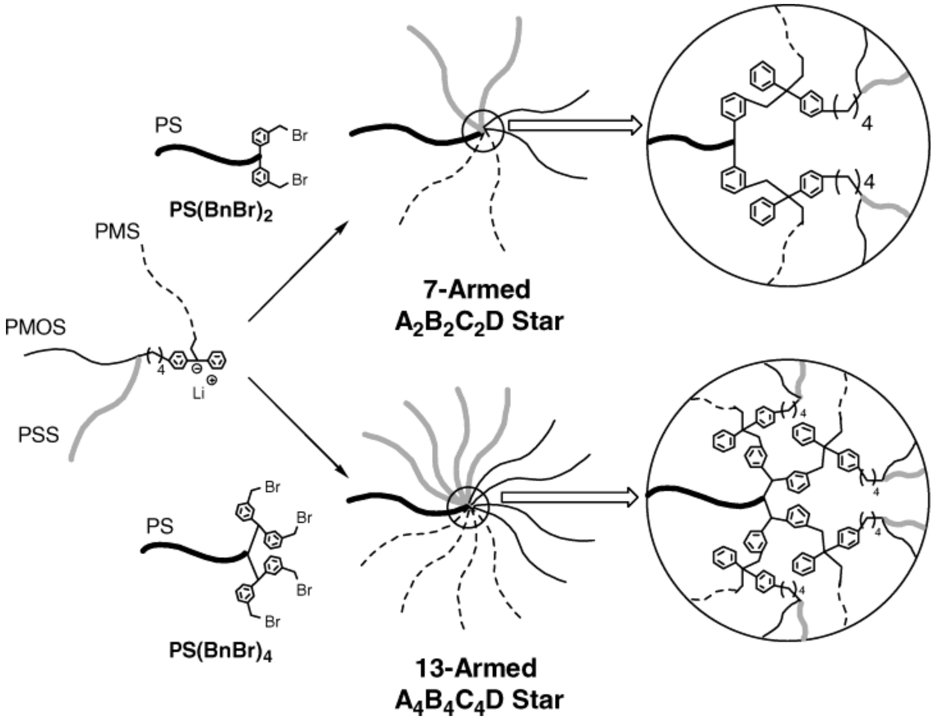
A new polymer anion was prepared by the aforementioned procedure employed for the preparation of polymer anion, **B**. The synthetic outline of the polymer anion comprised of poly(4-trimethylsilylstyrene) (PSiS), poly(4-methoxystyrene) (PMOS), and poly(4-methylstyrene) (PMS) segments is illustrated in Scheme 8. The molecular weight of each segment was adjusted to be around 10 kg/mol. PMOSLi reacted with DPE chain-end-functionalized PSiS, prepared from DPE end-capped PSiSLi and **3**, followed by treatment with **3** to afford in-chain-functionalized block copolymer with DPE moiety between PMOS and PSiS blocks. The resulting functionalized block polymer, after isolation by SEC fractionation, was reacted with PMSLi to prepare the objective polymer anion. The polymer anion thus prepared is a core-functionalized three-armed ABC asymmetric star-branched polymer with 1,1-diphenylalkyl anion. The microstructure around the anion is exactly the same as that of **B**, but the anion is surrounded by three different polymer chains in composition.

Table 4. Synthesis of Regular Star-Branched Polystyrenes by Coupling Reaction of C with PS(BnBr)$_n$ ($n = 8$ and 16)[a]

	M_n (kg/mol)		M_w (kg/mol)			M_w/M_n	$g' = [\eta]_{star}/[\eta]_{linear}$[b]	
type	calcd	SEC	calcd[c]	SLS[d]	dn/dc[d]	SEC	expml	calcd[e]
25-arm[f]	267	108	272	275	0.188	1.02	0.16	0.17
45-arm[g]	520	135	536	489	0.189	1.03	0.10	0.11

[a] Core-functionalized star-branched polystyrenes with DPE moiety ($M_n = 31.7$ kg/mol) were employed for both reactions. [b] $[\eta]_{star}$ was measured in toluene at 35 °C. $[\eta]_{linear}$ was calculated from the equation $[\eta] = 1.26 \times 10^{-4} M_w(\mathrm{SLS})^{0.71}$ (ref 54). [c] Calculated from M_n (calcd) and M_w/M_n (SEC). [d] Measured in THF at 25 °C. [e] Calculated from the equation $\log g' = 0.36 - 0.80 \times \log f$: f = arm number ($6 \leq f$) (ref 56). [f] PS(BnBr)$_8$ ($M_n = 13.9$ kg/mol) was used. [g] PS(BnBr)$_{16}$ ($M_n = 14.1$ kg/mol) was used.

Scheme 7. Synthesis of 7-Armed $A_2B_2C_2D$ and 13-Armed $A_4B_4C_4D$ Asymmetric Star-Branched Polymers



Scheme 8. Preparation of Polymer Anion Comprised of PSiS, PMOS, and PMS Segments

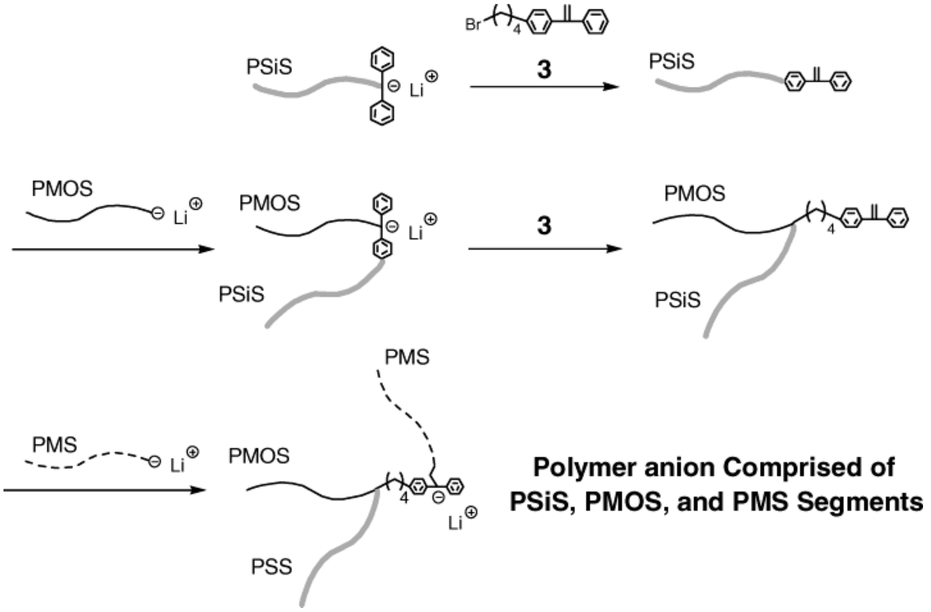


Table 5. Synthesis of 7-Armed $A_2B_2C_2D$ and 13-Armed $A_4B_4C_4D$ Asymmetric Star-Branched Polymers[a]

	M_n (kg/mol)			M_w (kg/mol)			M_w/M_n	composition (A/B/C/D wt %)	
type	calcd	SEC	^{1}H NMR	calcd[b]	SLS[c]	d*n*/d*c*[c]	SEC	calcd	^{1}H NMR
$A_2B_2C_2D$	71.5	51.0	72.0	73.6	77.9	0.171	1.03	27/30/28/15	26/28/31/15
$A_4B_4C_4D$	131	64.5	129	134	133	0.170	1.02	30/33/29/8	28/31/32/9

[a] A, B, C, and D are poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), and polystyrene, respectively. Yields of asymmetric star-branched polymers after fractionation were more than 80% in both cases. [b] Calculated from M_n (calcd) and M_w/M_n (SEC). [c] Measured in THF at 25 °C.

The resulting polymer anion was in-situ reacted with **PS(BnBr)₂** in THF at −78 °C for 24 h. The SEC profile of the reaction mixture was very similar to that shown in Figure 2A. The highest molecular weight fraction was carefully isolated by SEC fractionation and characterized by ^{1}H NMR, SEC, and SLS, respectively. The results are summarized in Table 5.

The isolated polymer exhibits a sharp monomodal SEC distribution. The ^{1}H NMR spectrum shown in Figure 4 clearly exhibits the presence of four PSiS(A), PMOS(B), PMS(C), and PS(D) components by their characteristic resonances at 6.0−7.4 ppm (aromatic protons of PSiS, PMOS, PMS, and PS), at 3.7 ppm (methoxy protons of PMOS), at 2.2 ppm (methyl protons

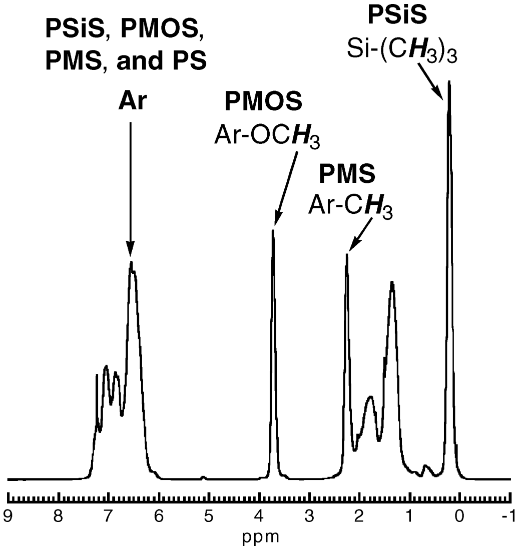


Figure 4. ^{1}H NMR spectrum of seven-armed asymmetric $A_2B_2C_2D$ star-branched polymer.

of PMS), and at 0.21 ppm (silylmethyl protons of PSiS), respectively. The observed composition (PSiS/PMOS/PMS/PS by weight) of 27/30/28/15 by these resonances was very close to the value of 26/28/31/15 calculated from feed ratios. The M_n value could be determined by using the M_n value of PS(BnBr)$_2$ and the observed composition ratio and agreed with that calculated. Moreover, the absolute M_w value measured by SLS was also in good agreement with the calculated value. All of the analytical results indicate the successful formation of a seven-armed $A_2B_2C_2D$ asymmetric star-branched polymer with expected and controlled structures.

We have next carried out the synthesis of a 13-armed $A_4B_4C_4D$ asymmetric star-branched polymer by the coupling reaction of the same polymer anion with PS(BnBr)$_4$. In the resulting star-branched polymer, the calculated M_n and M_w values as well as the composition are in good agreement with those measured by ^{1}H NMR and SLS (see Table 5). Thus, we have demonstrated to synthesize the expected 13-armed $A_4B_4C_4D$ asymmetric star-branched polymer without difficulty by this methodology. These two stars are quite new types of asymmetric star-branched polymers comprised of four different polymer segments.

The possible use of star-branched polymer anion comprised of three polymer chains in the coupling reaction provides a versatile methodology for the synthesis of a variety of star-branched polymers. Simultaneous introduction of three different chains at one reaction site by a one-pot reaction is especially attractive for the synthesis of complex asymmetric star-branched polymers.

Conclusions

To synthesize both regular and asymmetric star-branched polymers, we have developed a new methodology using specially designed polymer anions (or in other words, core-functionalized three-armed star-branched polymer with 1,1-diphenylalkyl anion) comprised of three same or different polymer chains in the coupling reaction with PS(BnBr)$_n$. With this methodology, well-defined 7-, 13-, and 25-armed regular star-branched polystyrenes could be successfully synthesized by carefully designing in such a way as to reduce steric hindrance of the microstructure around the 1,1-diphenylalkyl anion. Furthermore, the same synthetic approach allows the synthesis of quite new 7-armed $A_2B_2C_2D$ and 13-armed $A_4B_4C_4D$ asymmetric star-branched polymers by simply varying from the polymer anion, **B**, to ABC star-branched polymer anion. All of the analytical data of such star-branched polymers indicate a high degree of molecular and compositional homogeneity, demonstrating the versatility and high synthetic potential of the present methodology developed. We are now under investigation on the possible use of star-branched polymer anions comprised of four or more polymer chains in the coupling reaction with PS(BnBr)$_n$.

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