Synthesis of Well-Defined Star−Linear Block Polystyrenes by Coupling Reaction of Chain-Functionalized Polystyrenes with a Definite Number of Benzyl Bromide Moieties with Polystyryllithiums

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ABSTRACT: The synthesis of specially designed chain-functionalized polystyrenes with a definite number of benzyl bromide moieties by an iterative divergent methodology is described. Such functionalized polystyrenes involve α,ω-chain-end-functionalized polystyrenes with benzyl bromide moieties, in-chain-functionalized polystyrenes with benzyl bromide moieties, and in-chain-functionalized polystyrenes with benzyl bromide moieties that are placed at two sites in a chain. The number of benzyl bromide moieties varied from 2 to 16 at each place. Three series of well-defined star−linear block polystyrenes of the types star-*block*-linear-*block*-star, linear-*block*-star-*block*-linear, and linear-*block*-star-*block*-linear-*block*-star-*block*-linear have been successfully synthesized by coupling these benzyl bromide-chain-functionalized polystyrenes with polystyryllithiums end-capped with 1,1-diphenylethylene.

Introduction

The synthesis of nonlinear star−linear block polymers, where multiarmed star branched segments are connected by a linear polymer segment, has been of special interest because of their unique branched and topological architectures.[1] Well-defined star−linear block polymers involving H-shaped, π-shaped, super-H-shaped, star-*block*-linear, and star-*block*-linear-*block*-star (so-called dumbbell or pom-pom) polymers have been synthesized mainly by means of living anionic polymerization. For example, H-, π-, and super-H-shaped and the related advanced polymers have been successfully synthesized by the reaction of difunctional living anionic polymers with multifunctionalized chlorosilanes, followed by linking reactions with living anionic polymers, similar to the methodology employed in the synthesis of miktoarm stars.[2−17] Furthermore, star-*block*-linear and star-*block*-linear-*block*-star polymers have also been synthesized by linking block copolymers containing short segments containing silyl chlorides with living anionic polymers.[18−20] The synthesis of dumbbell-like polymers by the addition reaction of living anionic polymers with fullerene has been reported.[21] A new convenient synthetic procedure for pom-pom polymers based on the convergent anionic polymerization methodology using 4-chlorodimethylsilylstyrene has recently been reported, although the resulting polymers are not well-defined in architecture.[22] In addition, various dendritic−linear block polymers categorized as such nonlinear block polymers have been synthesized in recent years by many research groups.[23−31] Nevertheless, there are many difficulties and limitations for the synthesis of star−linear block polymers with well-defined and various architectures, and the development of new synthetic methodologies is a very important challenge even at the present time.

We have recently developed a novel promising methodology based on an iterative divergent approach for the synthesis of chain-end-functionalized polymers with a definite number of benzyl bromide moieties.[32,33] The methodology involves only two sets of the reactions for the entire iterative reaction sequence: a coupling reaction of the terminal benzyl bromide moiety with the functionalized 1,1-diphenylalkyl anion to introduce two 3-*tert*-butyldimethylsilyloxymethylphenyl groups at the chain end and a transformation reaction into two benzyl bromide moieties. By repeating the reaction sequence four more times, chain-end-functionalized polystyrenes with 2, 4, 8, 16, and 32 benzyl bromide moieties have been synthesized without difficulty.

The work reported herein extends the above-mentioned iterative methodology to the synthesis of α,ω-chain-end-functionalized polystyrenes with benzyl bromide moieties, in-chain-functionalized polystyrenes with benzyl bromide moieties, and in-chain-functionalized polystyrenes with benzyl bromide moieties that are placed at two sites in a chain. They have been designated by $(BnBr)_nPS(BnBr)_n$, $PS(BnBr)_nPS$, and $PS(BnBr)_nPS(BnBr)_nPS$, where the subscript "*n*" corresponds to the number of benzyl bromide moieties. We also describe the successful synthesis of a series of well-defined star-*block*-linear-*block*-star, linear-*block*-star-*block*-linear, and linear-*block*-star-*block*-linear-*block*-star-*block*-linear polystyrenes by coupling these benzyl bromide-functionalized polystyrenes with polystyryllithiums end-capped with 1,1-diphenylethylene (DPE).

Experimental Section

Materials. Unless stated otherwise, all reagents (>98% purities) were purchased from Aldrich Japan and used as received. Styrene and DPE were washed with 10% NaOH and dried over $CaCl_2$. They were distilled twice from CaH_2 under reduced pressure. Styrene was finally distilled from dibutylmagnesium (ca. 3 mol %) on a vacuum line into ampules equipped with break-seals prewashed with 1,1-diphenylhexyllithium in heptane. DPE was distilled from its 1,1-diphenylhexyllithium solution on a vacuum line into ampules with break-seals prewashed with potassium naphthalenide in THF. Tetrahydrofuran (THF) (99%, Mitsubishi Chemical Co., Ltd.) was refluxed over Na wire overnight, distilled from $LiAlH_4$ under nitrogen, and finally distilled from its sodium naphtha-

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lenide solution on a vacuum line. Chloroform, acetonitrile, and trimethylsilyl chloride (98%, Tokyo Kasei Kogyo Co., Ltd.) were distilled from CaH_2 under nitrogen. Dibutylmagnesium, *tert*-butyldimethylsilyl chloride (99%, Shinetsu Chemical Co., Ltd.), and *sec*-BuLi (1.3 M in cyclohexane) were used as received. LiBr (99%, Koso Chemical Co., Ltd.) was dried under a high vacuum (10^{-6} Torr) at 100 °C for 12 h. 1-(4-Bromobutyl)-4-(*tert*-butyldimethylsilyloxymethyl)benzene (**1**) and 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**2**) were synthesized according to our previously reported procedures.[34]

Measurements. All ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX (300 MHz for ^1H and 75 MHz for ^{13}C) in $CDCl_3$. Chemical shifts were reported in ppm relative to chloroform (δ 7.24 for ^1H, δ 77.1 for ^{13}C NMR spectra). Size exclusion chromatography (SEC) was obtained with Tosoh instrument with HLC 8020 UV (254 nm) or 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 of bead size 5 μm and pore size of 200, 75, and 20 Å or 650 (bead size 9 μm), 200, and 75 Å were used. A calibration curve was made to determine M_n and M_w/M_n values with polystyrene standards. These sets of the column covered the molecular weight range from 1×10^3 to 4×10^5. Vapor pressure osmometry (VPO) measurements for determining absolute M_n value were made with a Corona 117 instrument in benzene solution at 40 °C with a highly sensitive thermoelectric couple (TM-32K: sensitivity = 35 000 μV ± 10%/1 M) and very exact temperature control. Therefore, M_n values up to 100 kg/mol could be determined within an analytical error of ±5%. The apparatus constant was obtained by measuring standard polystyrene samples (M_n: 5.73, 9.61, 17.0, and 36.9 kg/mol) and calibrating their values against M_n values. Static light scattering (SLS) equipped with a He–Ne laser (λ = 632.8 nm) was perfomed with Ohotuka Electronics DSL-600R instrument in THF or benzene at 25 °C. The refractive index increment (d*n*/d*c*) in THF or benzene at 25 °C was determined for each star–linear block polymer with an Ohotsuka Electronics DRM-1020 refractometer operating at 632.8 nm. A Berry plot was used to determine M_w values. Intrinsic viscosities of star-branched polymers were measured by Ubbelohde viscometers in toluene at 35 °C.

Living Anionic Polymerization of Styrene. All polymerizations were carried out under high vacuum (10^{-6} Torr) in sealed glass reactors equipped with break-seals. All reactors were prewashed with either 1,1-diphenylhexyllithium in heptane or sodium naphthalenide in THF after being sealed off from a vacuum line. Polystyryllithium was prepared by the polymerization of styrene with either lithium naphthalenide or *sec*-BuLi in THF at −78 °C for 20 min. In the case of using polystyryllithium as an arm segment, polystyryllithium was end-capped with a 1.5-fold excess of DPE in THF at −78 °C for 0.5 h. A small portion was always taken to determine the M_n and M_w/M_n values prior to the next reaction. The concentrations of styrene and initiators were usually in the ranges 0.4–0.8 and 0.02–0.11 M, respectively. Typical examples are described in the next sections.

Synthesis of α,ω-Chain-End-Functionalized Polystyrenes with 1, 1, 4, 8, and 16 Benzyl Bromide Moieties. The chain-end-functionalized polystyrene with two benzyl bromide moieties at both chain ends, $(BnBr)_2PS(BnBr)_2$, was synthesized as follows: All polymerizations and reactions using the functionalized anion were carried out in sealed reactors equipped with break-seals under high-vacuum conditions (10^{-6} Torr). Anionic polymerization was carried out by adding styrene (3.64 g, 35.0 mmol) in THF solution (40.5 mL) prechilled at −78 °C to lithium naphthalenide (0.703 mmol) in THF solution (3.55 mL) with shaking at −78 °C for 20 min. A THF solution (4.20 mL) containing **1** (0.844 mmol) was added to the resulting living polymer at −78 °C for 1 h. The reaction was terminated with degassed methanol (5 mL), and the reaction mixture was poured into a large amount of methanol (400 mL) to precipitate the polymer. The resulting polymer (3.76 g, 98%) was purified by reprecipitation twice from THF into methanol and freeze-drying from its absolute benzene solution for at least 24 h (3.68 g, 96%).

The functionalized polymer (3.60 g, 0.329 mmol for *tert*-butyldimethylsilyloxymethylphenyl group) dissolved in chloroform (35 mL) was added dropwise to a mixture of LiBr (2.86 g, 32.9 mmol) and $(CH_3)_3SiCl$ (4.48 g, 41.2 mmol) in a mixed solvent of acetonitrile (28 mL) and chloroform (75 mL) at 25 °C for 0.5 h. The reaction mixture was then allowed to stir at 40 °C for an additional 5 h. It was poured into water and extracted with chloroform (30 mL) four times. The combined organic layer was dried over $MgSO_4$. The organic layer was concentrated under reduced pressure followed by precipitation into a large amount of methanol (400 mL) gave the benzyl bromide-chain-end-functionalized polymer, $(BnBr)_1PS(BnBr)_1$ (3.42 g, 96%). It was purified by reprecipitating twice and freeze-drying from its absolute benzene solution for 24 h (3.35 g, 94%). The expected structure of $(BnBr)_1PS(BnBr)_1$ was confirmed by ^1H NMR, FT-IR, elemental analysis, SEC, and VPO.

The functionalized 1,1-diphenylalkyl anion prepared from *sec*-BuLi (0.727 mmol) in heptane (2.40 mL) and **2** (0.872 mmol) in THF (8.75 mL) was added to a THF solution (33 mL) of the $(BnBr)_1PS(BnBr)_1$ (3.28 g, 0.303 mmol for benzyl bromide group) at −78 °C. The reaction mixture was allowed to stir for an additional 30 min. Then, the reaction was terminated with degassed methanol (5 mL), and the reaction mixture was poured into a large amount of methanol (350 mL) to precipitate the polymer. The resulting polymer (3.43 g, 97%) was purified by reprecipitation twice from THF into methanol and freeze-drying from its absolute benzene solution for at least 24 h for the transformation reaction (3.33 g, 94%).

A solution of the functionalized polymer (2.93 g, 0.250 mmol for *tert*-butyldimethylsilyloxymethylphenyl group) dissolved in chloroform (30 mL) was added dropwise to a mixture of LiBr (4.34 g, 50 mmol) and $(CH_3)_3SiCl$ (6.79 g, 62.5 mmol) in a mixed solvent of acetonitrile (23 mL) and chloroform (60 mL) at 25 °C for 0.5 h. The same workup as mentioned above gave the expected polymer, $(BnBr)_2PS(BnBr)_2$ (2.76 g, 96%). It was purified by reprecipitating twice and freeze-drying from its absolute benzene solution for 24 h (2.62 g, 95%). ^1H NMR: δ 7.2–6.2 (m, 522H, aromatic), 4.39–4.35 (m, 8H, $-CH_2Br$), 3.4–3.2 (m, 4H, $-(Ph)_2C-CH_2-Ph-$), 2.5–0.8 (m, 325H, CH_2-CH-), 0.8–0.5 (m, 12H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{859}H_{871}Br_4$: C, 89.60; H, 7.62; Br, 2.78. Found: C, 89.20; H, 7.78; Br, 2.84. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$). Chain-end-functionalized polystyrenes with 4, 8, and 16 benzyl bromide moieties at both chain ends were synthesized in a similar manner.

$(BnBr)_4PS(BnBr)_4$. ^1H NMR: δ 7.2–5.8 (m, 554H, aromatic), 4.36–4.29 (m, 16H, $-CH_2Br$), 3.4–3.0 (m, 12H, $-(Ph)_2C-CH_2-Ph-$), 2.5–0.8 (m, 345H, CH_2-CH-), 0.8–0.5 (m, 36H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{939}H_{963}Br_8$: C, 87.51; H, 7.53; Br, 4.96. Found: C, 87.40; H, 7.33; Br, 4.84. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

$(BnBr)_8PS(BnBr)_8$. ^1H NMR: δ 7.2–5.8 (m, 618H, aromatic), 4.37–4.29 (m, 32H, $-CH_2Br$), 3.4–2.7 (m, 28H, $-(Ph)_2C-CH_2-Ph-$), 2.5–0.8 (m, 385H, CH_2-CH-), 0.8–0.2 (m, 84H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{1099}H_{1147}Br_{16}$: C, 84.43; H, 7.39; Br, 8.18. Found: C, 83.77; H, 7.40; Br, 8.00. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

$(BnBr)_{16}PS(BnBr)_{16}$. ^1H NMR: δ 7.2–5.6 (m, 746H, aromatic), 4.5–4.1 (m, 64H, $-CH_2Br$), 3.5–2.6 (m, 60H, $-(Ph)_2C-CH_2-Ph-$), 2.5–0.8 (m, 465H, CH_2-CH-), 0.8–0.2 (m, 180H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{1419}H_{1515}Br_{32}$: C, 80.67; H, 7.23; Br, 12.10. Found: C, 80.01; H, 7.23; Br, 12.30. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

Unfortunately, all of the benzyl bromide-functionalized polystyrenes by MALDI–TOF mass spectrometry were not successful, presumably due to the presence of benzyl bromide moieties and somewhat high molecular weights.

Synthesis of In-Chain-Functionalized Polystyrenes with 1, 2, 4, 8, and 16 Benzyl Bromide Moieties. The functionalized polystyrene with two benzyl bromide moieties at the middle of polymer chain $PS(BnBr)_2PS$ was synthesized as follows: Polystyryllithium ($M_n = 9.0_0$ kg/mol, 1.08 g, 0.120 mmol) in THF (11.0 mL) was added to a chain-end-functionalized polystyrene with the DPE moiety[35] ($M_n = 8.7_5$ kg/mol, 0.963 g, 0.110 mmol for DPE moiety) in THF (10.0 mL) at −78 °C, and the reaction mixture was allowed to stir for an additional 1 h. Then, **1** (0.145 mmol) in THF (2.90 mL) was added to the mixture at −78 °C, and the reaction mixture was allowed to stir for an additional 1 h. After the reaction was terminated with degassed methanol, the reaction mixture was poured into a large amount of methanol (200 mL) to precipitate the polymer. The resulting polymer was isolated in 96% yield by fractional precipitation using a mixture of cyclohexane and hexanes (350 mL/300 mL) at 5 °C. The polymer was reprecipitated from THF to methanol three times and freeze-dried from its absolute benzene solution on a vacuum line for 24 h (1.85 g, 92%).

A chloroform solution (20 mL) of the polymer (1.80 g, 0.0986 mmol for *tert*-butyldimethylsilyloxymethylphenyl group) was added dropwise to a mixture of LiBr (0.44 g, 5.0 mmol) and $(CH_3)_3SiCl$ (0.54 g, 5.0 mmol) in a mixed solvent of acetonitrile (15 mL) and chloroform (40 mL) at 25 °C for 0.5 h. The reaction mixture was then allowed to stand at 40 °C for an additional 5 h and poured into water. The same workup described above gave the expected polymer, PS(BnBr)$_1$PS. It was purified by reprecipitation three times and freeze-drying from its absolute benzene solution (1.72 g, 96%). ^{1}H NMR: δ 7.2−6.3 (m, 847H, aromatic), 4.46 (s, 2H, $-CH_2Br$), 2.5−0.8 (m, 532H, CH_2-CH-), 0.8−0.5 (m, 12H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{1391}H_{1405}Br$: C, 91.79; H, 7.78; Br, 0.44. Found: C, 91.82; H, 7.80; Br, 0.45. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

The functionalized 1,1-diphenylalkyl anion from *sec*-BuLi (0.112 mmol) in heptane (2.20 mL) and **2** (0.135 mmol) in THF (2.70 mL) was added to a THF solution (17 mL) of the PS(BnBr)$_1$PS (1.70 g, 0.0934 mmol for benzyl bromide moiety) at −78 °C. The reaction mixture was allowed to stir for an additional 30 min. Then, the reaction was terminated with degassed methanol (5 mL), and the reaction mixture was poured into a large amount of methanol (200 mL) to precipitate the polymer. The resulting polymer (1.69 g, 97%) was purified by reprecipitation twice from THF into methanol and freeze-drying from its absolute benzene solution for at least 24 h for the transformation reaction (1.62 g, 93%).

A chloroform solution (15 mL) of the functionalized polymer (1.62 g, 0.0869 mmol for *tert*-butyldimethylsilyloxymethylphenyl group) was added dropwise to a mixture of LiBr (0.76 g, 8.7 mmol) and $(CH_3)_3SiCl$ (1.18 g, 10.9 mmol) in a mixed solvent of acetonitrile (15 mL) and chloroform (35 mL) at 25 °C for 0.5 h. The reaction mixture was then allowed to stir at 40 °C for additional 5 h. It was poured into water and extracted with chloroform (30 mL) four times. The combined organic layer was dried over $MgSO_4$. The organic layer was concentrated under reduced pressure followed by precipitation into a large amount of methanol (200 mL) gave the expected polymer, PS(BnBr)$_2$PS (1.53 g, 95%). It was purified by reprecipitating twice and freeze-drying from its absolute benzene solution for 24 h (1.50 g, 93%). ^{1}H NMR: δ 7.2−6.1 (m, 855H, aromatic), 4.40−4.36 (s, 4H, $-CH_2Br$), 3.4−3.2 (m, 2H, $-(Ph)_2C-CH_2-Ph-$), 2.5−0.8 (m, 537H, CH_2-CH-), 0.8−0.3 (m, 18H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{1411}H_{1428}Br_2$: C, 91.38; H, 7.76; Br, 0.86. Found: C, 91.57; H, 7.70; Br, 0.78. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

Similarly, PS(BnBr)$_4$PS, PS(BnBr)$_8$PS, and PS(BnBr)$_{16}$PS were synthesized. Their analytical data were as follows:

PS(BnBr)$_4$PS. ^{1}H NMR: δ 7.2−5.9 (m, 871H, aromatic), 4.40−4.36 (m, 8H, $-CH_2Br$), 3.5−3.1 (m, 6H, $-(Ph)_2C-CH_2-Ph-$), 2.5−0.8 (m, 547H, CH_2-CH-), 0.8−0.3 (m, 30H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{1451}H_{1474}Br_4$: C, 90.61; H, 7.72; Br, 1.66. Found: C, 91.10; H, 7.80; Br, 1.33. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

PS(BnBr)$_8$PS. ^{1}H NMR: δ 7.2−5.8 (m, 903H, aromatic), 4.37−4.32 (m, 16H, $-CH_2Br$), 3.5−2.7 (m, 14H, $-(Ph)_2C-CH_2-Ph-$), 2.5−0.8 (m, 567H, CH_2-CH-), 0.8−0.2 (m, 24H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{1531}H_{1566}Br_8$: C, 89.24; H, 7.66; Br, 3.10. Found: C, 89.20; H, 7.74; Br, 3.03. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

PS(BnBr)$_{16}$PS. ^{1}H NMR: δ 7.2−5.8 (m, 967H, aromatic), 4.4−4.2 (m, 32H, $-CH_2Br$), 3.5−2.7 (m, 30H, $-(Ph)_2C-CH_2-Ph-$), 2.5−0.8 (m, 607H, CH_2-CH-), 0.8−0.2 (m, 24H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{1691}H_{1750}Br_{16}$: C, 86.97; H, 7.55; Br, 5.48. Found: C, 87.01; H, 7.62; Br, 5.41. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

Synthesis of In-Chain-Functionalized Polystyrenes with 1, 2, 4, and 8 Benzyl Bromide Moieties Placed at Two Sites in a Chain. In-chain-functionalized polystyrene with one benzyl bromide moiety introduced at two sites in a chain, PS(BnBr)PS(BnBr)PS, was synthesized as follows: Polystyryllithium (1.94 g, 0.22 mmol) in THF (20 mL) was added to α,*ω*-chain-end-functionalized polystyrene with DPE moieties (0.918 g, 0.10 mmol) in THF (10 mL) at −78 °C, and the reaction mixture was allowed to stir for an additional 1 h. Then, **1** (0.35 mmol) in THF (5.5 mL) was added at −78 °C, and the reaction mixture was allowed to stand for an additional 1 h. The resulting polymer was isolated by fractional precipitation using a mixture of cyclohexane and hexanes (450 mL/180 mL) at 5 °C (2.59 g, 95%). The polymer was reprecipitated from THF to methanol three times and freeze-dried from its absolute benzene solution on a vacuum line for 24 h (2.49 g, 91%).

The resulting polymer (2.45 g, 0.0896 mmol for *tert*-butyldimethylsilyloxymethylphenyl group) dissolved in chloroform (25 mL) was mixed with LiBr (0.78 g, 9.0 mmol) and $(CH_3)_3SiCl$ (1.22 g, 11.2 mmol) in acetonitrile (20 mL) and chloroform (50 mL), and the reaction mixture was allowed to stir at 40 °C for 5 h. The same workup mentioned above gave an in-chain-functionalized polystyrene with one benzyl bromide moiety introduced at two sites in chain, PS(BnBr)$_1$PS(BnBr)$_1$PS (2.38 g, 96%). ^{1}H NMR: δ 7.2−6.2 (m, 1264H, aromatic), 4.4−4.2 (m, 4H, $-CH_2Br$), 2.5−0.8 (m, 781H, CH_2-CH-), 0.8−0.5 (m, 12H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{2079}H_{2091}Br_2$: C, 91.68; H, 7.74; Br, 0.59. Found: C, 91.92; H, 7.55; Br, 0.49. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$). In-chain-functionalized polystyrene with two benzyl bromide moiety introduced at two sites in chain, PS(BnBr)$_2$PS(BnBr)$_2$PS, was synthesized by using the PS(BnBr)$_1$PS(BnBr)$_1$PS in a similar mannar employed for the synthesis of PS(BnBr)$_2$PS. ^{1}H NMR: δ 7.2−6.2 (m, 1274H, aromatic), 4.4−4.2 (m, 8H, $-CH_2Br$), 3.4−3.2 (m, 4H, $-(Ph)_2C-CH_2-Ph-$), 2.5−0.8 (m, 791H, CH_2-CH-), 0.8−0.3 (m, 24H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{2119}H_{2137}Br_4$: C, 91.14; H, 7.71; Br, 1.14. Found: C, 91.30; H, 7.70; Br, 0.97. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

Similarly, PS(BnBr)$_4$PS(BnBr)$_4$PS and PS(BnBr)$_8$PS(BnBr)$_8$PS were synthesized. Analytical results of these polymers were as follows:

PS(BnBr)$_4$PS(BnBr)$_4$PS. ^{1}H NMR: δ 7.2−6.0 (m, 1274H, aromatic), 4.4−4.2 (m, 16H, $-CH_2Br$), 3.4−2.8 (m, 12H, $-(Ph)_2C-CH_2-Ph-$), 2.5−0.8 (m, 811H, CH_2-CH-), 0.8−0.3 (m, 50H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{2199}H_{2229}Br_8$: C, 90.15; H, 7.67; Br, 2.18. Found: C, 90.06; H, 7.80; Br, 2.25. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

PS(BnBr)$_8$PS(BnBr)$_8$PS. ^{1}H NMR: δ 7.2−6.0 (m, 1338H, aromatic), 4.5−4.2 (m, 32H, $-CH_2Br$), 3.5−2.7 (m, 28H, $-(Ph)_2C-CH_2-Ph-$), 2.5−0.8 (m, 851H, CH_2-CH-), 0.8−0.3 (m, 98H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{2359}H_{2413}Br_{16}$: C, 88.42; H, 7.59; Br, 3.99. Found: C, 88.57; H, 7.69; Br, 3.80. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

Functionality of Benzyl Bromide Moiety. Functionality of the benzyl bromide moiety introduced in the chain was determined by comparing the signal area at 4.4−4.2 ppm assigned to the bromomethylene protons with those at 0.8−0.2 ppm of the methyl protons of initiator fragments or at 7.2−5.7 ppm of the aromatic protons of polystyrenes estimated from their molecular weights determined by SEC and VPO. Since the methyl and aromatic protons from the fragments of the functionalized 1,1-diphenylalkyl anion prepared from **2** and *sec*-BuLi are also involved in these signals, these signal areas are taken into consideration for the determination. Therefore, the analytical error was usually in the range between 5 and 10%. To determine the functionality more accurately, methoxybenzene was added as an internal standard.

Molecular Weight Determination. Molecular weights of all of the chain-functionalized polystyrenes with benzyl bromide moieties synthesized here were determined by SEC, VPO, and ^{1}H NMR measurements. The molecular weights deter-

Table 1. Synthesis of α,ω-Chain-End-Functionalized Polystyrenes with 1, 2, 4, 8, and 16 Benzyl Bromide Moieties

polymer	M_n (kg/mol) calcd	SEC[a]	VPO	^{1}H NMR	M_w/M_n[a]	benzyl bromide functionality calcd	^{1}H NMR
$(BnBr)_1PS(BnBr)_1$	$10._8$	$10._8$	$10._7$	$10._9$	1.05	2	2.0_0
$(BnBr)_2PS(BnBr)_2$	$11._5$	9.5_2	$11._4$	$11._6$	1.05	4	3.9_6
$(BnBr)_4PS(BnBr)_4$	$12._8$	$10._2$	$12._6$	$12._8$	1.06	8	8.0_0
$(BnBr)_8PS(BnBr)_8$	$15._6$	$11._9$	$15._3$	$13._6$	1.06	16	$15._8$
$(BnBr)_{16}PS(BnBr)_{16}$	$21._1$	$13._5$	$20._5$	$20._4$	1.06	32	$32._1$

[a] Estimated from SEC relative to polystyrene.

mined by ^{1}H NMR are as follows: Molecular weights of the starting polystyrenes partly sampling prior to the reactions were measured by comparing the ^{1}H NMR signal areas at 7.2−5.7 ppm of the aromatic protons with those at 0.8−0.2 ppm of the methyl protons of initiator fragments in addition to SEC and VPO measurements. In the case of difunctional living polystyrenes, their molecular weights were determined by SEC and VPO. Molecular weights of the terminal end groups including benzyl bromide moieties were calculated on the basis of the functionalization degrees of benzyl bromide moieties measured by ^{1}H NMR as mentioned above. Molecular weights of the chain-functionalized polystyrenes with benzyl bromide moieties were obtained by adding molecular weights of the terminal groups to those of the starting polystyrenes.

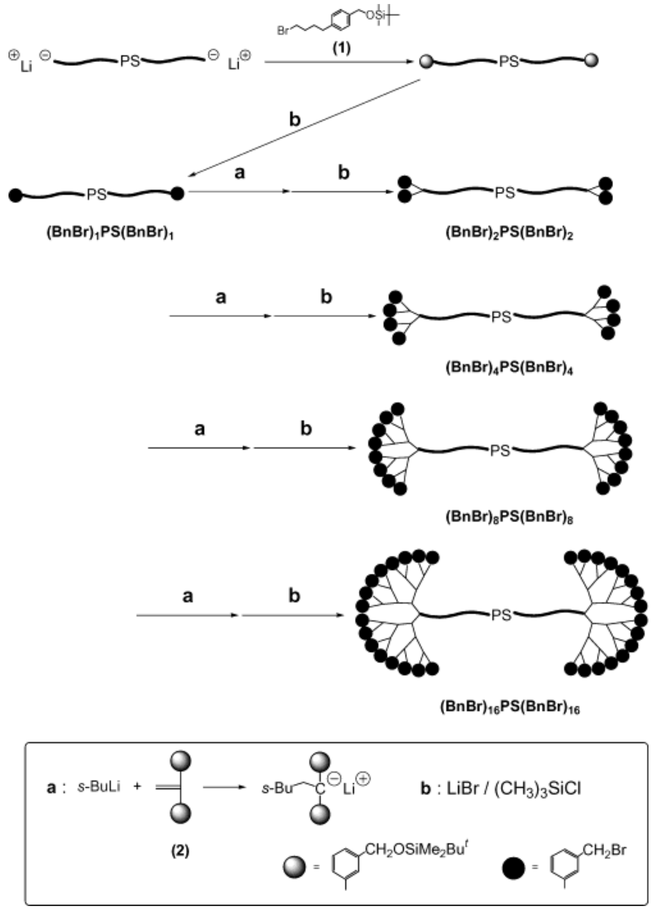
Synthesis of Star-*block*-Linear-*block*-Star, Linear-*block*-Star-*block*-Linear, and Linear-*block*-Star-*block*-Linear-*block*-Star-*block*-Linear Polystyrenes. A series of star-*block*-linear-*block*-star, linear-*block*-star-*block*-linear, and linear-*block*-star-*block*-linear-*block*-star-*block*-linear polystyrenes were synthesized by the coupling of corresponding chain-functionalized polystyrenes with benzyl bromide moieties with a 1.2-fold excess of polystyryllithium end-capped with DPE in THF at −78 °C for 1 h. The representative synthetic procedure of a star-*block*-linear-*block*-star polystyrene each of whose star segment possessed 16 arms is as follows:

Polystyryllithium was prepared by the polymerization of styrene (1.25 g, 12.0 mmol) in THF (12.0 mL) with *sec*-BuLi (0.639 mmol) in heptane (6.41 mL) at −78 °C for 20 min, followed by addition of DPE (0.766 mmol) in THF (7.75 mL) solution at −78 °C for 0.5 h for end-capping. A THF solution (6.30 mL) of the $(BnBr)_{16}PS(BnBr)_{16}$ (0.316 g, $0.0166 \times 32 = 0.532$ mmol for benzyl bromide moieties) was added at once to the DPE-end-capped polystyryllithium at −78 °C. The reaction mixture was allowed to stir at −78 °C for an additional 1 h. After terminating the reaction with degassed methanol (5 mL), the reaction mixture was poured into a large amount of methanol (300 mL) to precipitate the polymer. The objective star−linear block polystyrene was isolated by fractionational precipitation using a mixture of cyclohexane and hexanes (150 mL/150 mL) at 5 °C (1.35 g, 94%). The polymer was reprecipitated twice from THF to methanol and freeze-dried from its absolute benzene solution for 24 h (1.31 g, 91%). $M_{n(calcd)} = 86.0$ kg/mol, $M_{n(SEC)} = 37.0$ kg/mol, $M_{w(SLS)} = 89.5$ kg/mol, and $M_w/M_n = 1.03$. ^{1}H NMR: δ 7.2−5.7 (m, aromatic), 3.5−2.7 (m, $-(Ph)_2C-CH_2-Ph-$), 2.5−0.8 (m, CH_2-CH-), 0.7−0.5 (m, $-CH(CH_3)CH_2CH_3$).

Results and Discussion

Synthesis of α,ω-Chain-End-Functionalized Polystyrenes with 2, 4, 8, and 16 Benzyl Bromide Moieties. A series of α,ω-chain-end-functionalized polystyrenes with benzyl bromide moieties have been synthesized by the iterative divergent methodology starting from difunctional living anionic polystyrene. The synthetic outline is illustrated in Scheme 1. At first, a difunctional polystyryllithium (LiPSLi) was prepared by the living anionic polymerization of styrene with lithium naphthalenide and then reacted in situ with 1-(4-bromobutyl)-4-(*tert*-butyldimethylsilyloxymethyl)benzene (**1**), followed by treatment with $(CH_3)_3SiCl-LiBr$. Thus, an α,ω-chain-end-functionalized polystyrene with one benzyl bromide moiety, $(BnBr)_1PS(BnBr)_1$, was synthesized. The results are summarized in Table 1.

Scheme 1. Synthesis of $(BnBr)_nPS(BnBr)_n$



The coupling reaction of the $(BnBr)_1PS(BnBr)_1$ with the functionalized 1,1-diphenylalkyl anion from **2** and *sec*-BuLi and the subsequent transformation reaction with $(CH_3)_3SiCl-LiBr$ were carried out as a first iteration. The resulting polymer showed a sharp monomodal SEC distribution. It was almost identical in shape and distribution to the polymer before the transformation reaction. The M_n values determined by SEC and VPO agreed well with those predicted. The degree of chain-end-functionalization was virtually quantitative ($f = 3.9_6$). In the ^{1}H NMR spectrum of the polymer obtained after the transformation, no signals at 0.05, 0.90, and 4.59 ppm corresponding to $Si-CH_3$, $C(CH_3)_3$, and $Si-O-CH_2$ protons of the *tert*-butyldimethylsilyloxymethylphenyl group completely disappeared. On the other hand, the resonance at 4.35 ppm assigned to methylene protons of the benzyl bromide moieties was alternatively observed. The bromine content observed by elemental analysis (2.84%) agreed fairly with that calculated (2.78%). FT-IR clearly showed an absorption band at 1208 cm^{-1} characteristic of a CH_2Br group.

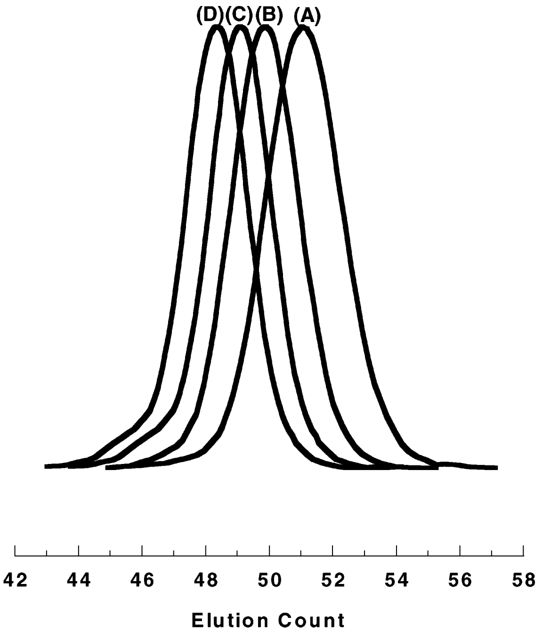


Figure 1. SEC profiles of $(BnBr)_2PS(BnBr)_2$ (A), $(BnBr)_4PS(BnBr)_4$ (B), $(BnBr)_8PS(BnBr)_8$ (C), and $(BnBr)_{16}PS(BnBr)_{16}$ (D).

Thus, all analytical data indicate that a well-defined $(BnBr)_2PS(BnBr)_2$ has been obtained in 96% yield. The same chain-end-functionalized polystyrene, $(BnBr)_2PS(BnBr)_2$, could also be obtained by the reaction of difunctional LiPSLi with **2**, followed by treatment with $(CH_3)_3SiCl-LiBr$. With the use of the $(BnBr)_2PS(BnBr)_2$ as a starting polymer, the same two reactions were repeated three more times to afford $(BnBr)_4PS(BnBr)_4$, $(BnBr)_8PS(BnBr)_8$, and $(BnBr)_{16}PS(BnBr)_{16}$. As shown in Figure 1, these polymers exhibit sharp monomodal SEC distributions, M_w/M_n values being less than 1.06. Their M_n values estimated by SEC were always somewhat smaller than those predicted, presumably due to the dendritic sphere structures of benzyl bromide moieties introduced at the both chain ends. On the other hand, the M_n values determined by VPO and ^1H NMR spectra agreed well with those predicted in all cases.

The degrees of chain-end-functionalization by ^1H NMR spectra agreed with the values expected within analytical limits. Furthermore, their bromine contents observed by elemental analysis also support quantitative introduction in all polymer samples. All of the results clearly indicate that each iteration proceeds satisfactorily to afford the objective α,ω-chain-end-functionalized polystyrenes with a definite number of benzyl bromide moieties. In this polymer series, the molecular weight of the polystyrene main chain of each polymer sample always remains unchanged, while the dendritic end group increases in both molecular weight and size as the iteration proceeds.

Synthesis of In-Chain-Functionalized Polystyrenes with 2, 4, 8, and 16 Benzyl Bromide Moieties. For the synthesis of in-chain-functionalized polystyrenes with a definite number of benzyl bromide moieties as illustrated in Scheme 2, an in-chain-functionalized polystyrene with one benzyl bromide moiety is needed as a starting material. At first, a polymer anion was prepared by reacting chain-end-functionalized polystyrene with DPE moiety with a 1.1-fold excess of polystyryllithium (PSLi) and then reacted in situ with a 1.2-fold excess of **1** toward PSLi to introduce 3-*tert*-butyldimethylsilyloxymethylphenyl group in the chain via the anion generated at the linking point. The reaction mixture exhibits two SEC peaks corresponding to the linked polymer and excess polystyrene as shown in Figure 2A. The linked polymer was isolated in 96% yield by fractional precipitation. As shown in Figure 2B, the isolated polymer exhibits a sharp monomodal SEC distribution. The introduced 3-*tert*-butyldimethylsilyloxymethylphenyl group in the chain was transformed into benzyl bromide moiety by treatment with $(CH_3)_3SiCl-LiBr$. The resulting polymer also showed a sharp monomodal SEC distribution (see Figure 2C). The M_n values determined by SEC and VPO agreed with that

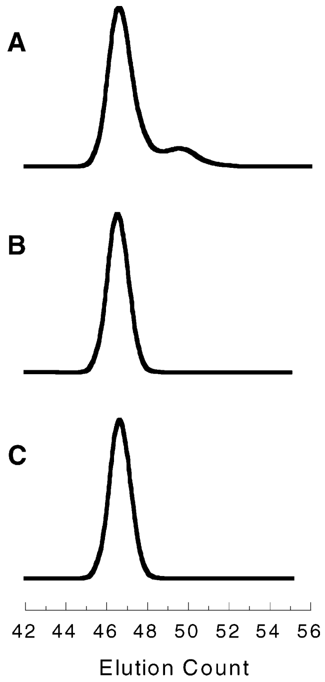


Figure 2. SEC profiles of the reaction mixture (A), the in-chain-functionalized polystyrene with one *tert*-butyldimethylsilyloxymethylphenyl group isolated by fractional precipitation (B), and the in-chain-functionalized polystyrene with one benzyl bromide moiety (C).

Scheme 2. Synthesis of PS(BnBr)$_n$PS

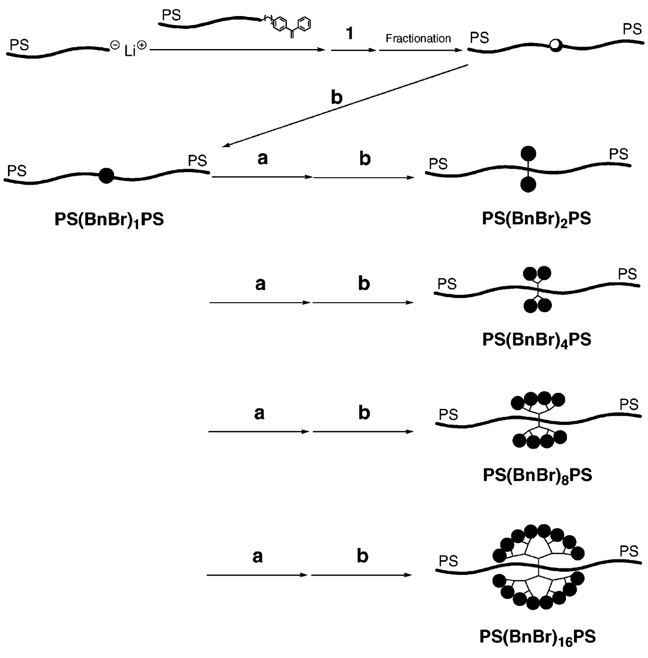
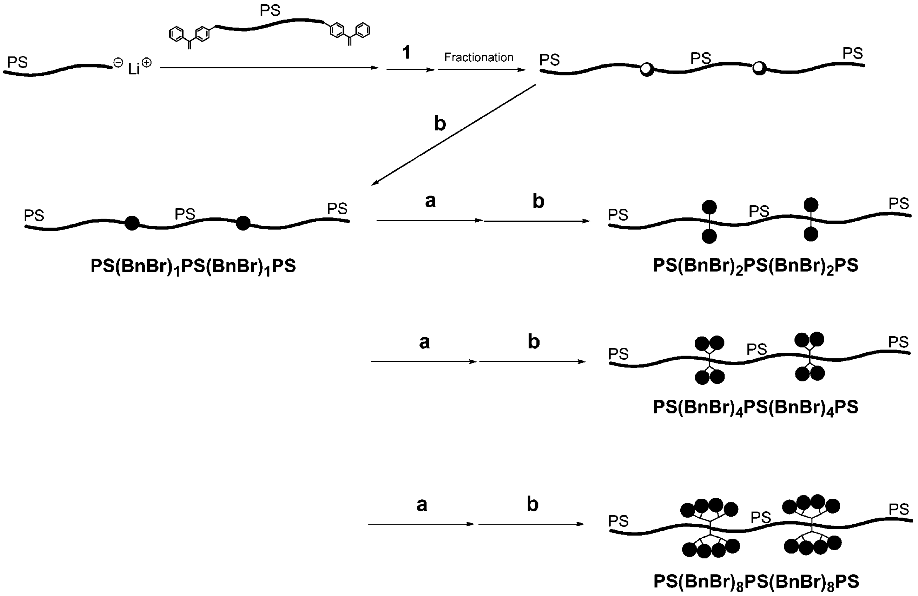


Table 2. Synthesis of In-Chain-Functionalized Polystyrenes with 1, 2, 4, 8, and 16 Benzyl Bromide Moieties

polymer	M_n (kg/mol) calcd	SEC[a]	VPO	^{1}H NMR	M_w/M_n[a]	benzyl bromide functionality calcd	^{1}H NMR
PS(BnBr)$_1$PS	$18._2$	$18._1$	$17._9$		1.04	1	1.0_0
PS(BnBr)$_2$PS	$18._5$	$18._8$	$18._3$	$17._1$	1.04	2	1.9_7
PS(BnBr)$_4$PS	$19._2$	$19._2$	$19._0$	$20._8$	1.03	4	3.9_7
PS(BnBr)$_8$PS	$20._6$	$19._1$	$20._8$	$19._0$	1.03	8	7.7_6
PS(BnBr)$_{16}$PS	$23._3$	$19._9$	$23._5$	$23._1$	1.04	16	$15._9$

[a] Estimated from SEC relative to polystyrene.

Scheme 3. Synthesis of PS(BnBr)$_n$PS(BnBr)$_n$PS



calculated. The degree of benzyl bromide functionality determined by ^{1}H NMR spectrum was quantitative ($f = 1.0_0$). The results are summarized in Table 2. In this polymer, the benzyl bromide moiety was placed at the middle of the polymer chain because PSLi was almost identical in molecular weight to the DPE-chain-end-functionalized polystyrene. It is of course possible to place the benzyl bromide moiety at essentially any position in a polymer chain only by changing the molecular weights of the both polymers.

With use of the PS(BnBr)$_1$PS thus synthesized, the coupling and transformation reactions in the iterative reaction sequence were carried out under the identical conditions as mentioned above. All analytical data of the resulting polymer indicate that the expected in-chain-functionalized polystyrene with two benzyl bromide moieties, PS(BnBr)$_2$PS, was obtained from PS(BnBr)$_1$PS. Similarly, PS(BnBr)$_4$PS, PS(BnBr)$_8$PS, followed by PS(BnBr)$_{16}$PS were synthesized successively by repeating three more times the iterative reaction sequence. Their results are also summarized in Table 2. Thus, the iterative methodology could also be applied to the synthesis of a series of in-chain-functionalized polystyrenes with a definite number of benzyl bromide moieties.

Synthesis of In-Chain-Functionalized Polystyrenes with Benzyl Bromide Moieties Placed at Two Sites in a Chain. We have extended the iterative methodology to the synthesis of in-chain-functionalized polystyrenes with benzyl bromide moieties that are introduced at two sites in a chain, as illustrated in Scheme 3. For this synthesis, in-chain-functionalized polystyrene with two anions in a chain was prepared by reacting α,ω-chain-end-functionalized polystyrene with DPE moieties with a 2.2-fold excess of PSLi and then reacted in situ with **1** to introduce two *tert*-butyldimethylsilyloxymethylphenyl groups via the generated two anions. The reaction mixture showed only two SEC peaks corresponding to the linked polymer and deactivated polystyrene used in excess in the reaction. The objective polymer eluted at a higher molecular weight side was isolated in 95% yield by fractional precipitation. Then, the two 3-*tert*-butyldimethylsilyloxymethyl groups introduced into the chain were completely transformed to two benzyl bromide moieties by treatment with $(CH_3)_3SiCl-LiBr$.

The resulting polymer exhibited a sharp monomodal SEC distribution. The observed M_n values by SEC and VPO agreed well with that predicted. The functionalization degree determined by ^{1}H NMR spectrum was quantitative ($f = 2.0_0$). Thus, an in-chain-functionalized polystyrene with two benzyl bromide moieties placed at two sites in a chain, PS(BnBr)$_1$PS(BnBr)$_1$PS, was synthesized successfully. The results are summarized in Table 3.

With Use of the PS(BnBr)$_1$PS(BnBr)$_1$PS as a starting material, PS(BnBr)$_2$PS(BnBr)$_2$PS, PS(BnBr)$_4$PS(BnBr)$_4$PS, followed by PS(BnBr)$_8$PS(BnBr)$_8$PS were synthesized successively by repeating three times the iterative reaction sequence under the similar conditions. All analytical characterizations by ^{1}H NMR, elemental analysis, FT-IR, SEC, and VPO clearly indicate that the resulting polymers possess the expected and well-defined structures (see Table 3). In these polymers, the benzyl bromide moieties are always introduced at the one-third and two-thirds of the chains, since the molecular weights of polymers used in the prepolymer synthesis are set up to be around 10 kg/mol.

Table 3. Synthesis of In-Chain-Functionalized Polystyrenes with Bromide Moieties Placed at Two Sites in a Chain

	M_n (kg/mol)					benzyl bromide functionality	
polymer	calcd	SEC[a]	VPO	^{1}H NMR	M_w/M_n[a]	calcd	^{1}H NMR
$PS(BnBr)_1PS(BnBr)_1PS$	$27._2$	$27._0$	$27._5$		1.04	2	2.0_0
$PS(BnBr)_2PS(BnBr)_2PS$	$27._9$	$28._3$	$28._1$	$25._7$	1.04	4	4.0_1
$PS(BnBr)_4PS(BnBr)_4PS$	$29._3$	$28._4$	$29._7$	$27._1$	1.04	8	8.0_5
$PS(BnBr)_8PS(BnBr)_8PS$	$32._0$	$28._8$	$32._4$	$30._5$	1.04	16	$16._0$

[a] Estimated from SEC relative to polystyrene.

Table 4. Synthesis of Star−Linear Block Polystyrenes

	segment (M_n; kg/mol)	M_n (kg/mol)		M_w (kg/mol)			
type	A/A′	calcd	SEC[a]	calcd[b]	SLS[c]	d*n*/d*c*	M_w/M_n[a]
$(A')_2A(A')_2$	$10._7/2.0_9$	17.4	15.2	18.1	18.3	0.189	1.04
$(A')_4A(A')_4$	$10._7/1.8_4$	24.8	16.2	26.1	26.0	0.185	1.05
$(A')_8A(A')_8$	$10._7/2.1_0$	45.8	24.8	47.2	47.1	0.187	1.03
$(A')_{16}A(A')_{16}$	$10._7/2.1_9$	86.0	37.0	89.3	89.5	0.189	1.03
$A(A')_4A$	$4.3_7/1.0_6$	14.0	10.7	14.4	14.5	0.185	1.03
$A(A')_8A$	$8.7_5/2.2_8$	37.7	26.4	38.8	38.6	0.187	1.03
$A(A')_{16}A$	$8.7_5/1.9_1$	52.6	27.9	54.0	53.8	0.189	1.03
$A(A')_2A(A')_2A$	$8.8_2/2.0_7$	36.8	31.5	38.3	38.3	0.187	1.04
$A(A')_4A(A')_4A$	$8.8_2/2.1_8$	46.1	34.8	47.8	48.0	0.190	1.04
$A(A')_8A(A')_8A$	$8.8_2/2.5_0$	70.7	41.5	72.3	72.5	0.187	1.02

[a] Estimated from SEC relative to polystyrene. [b] Calculated from $M_{n(calcd)}$ and M_w/M_n values. [c] Measured in THF.

Table 5. Intrinsic Viscosity and *g*′ Values for Star−Linear Block Polystyrenes

				$g' = [\eta]_{star}/[\eta]_{linear}$	
type	M_w (kg/mol)[a]	$[\eta]_{branch}$,[b] dg/L	$[\eta]_{linear}$,[c] dg/L	exptl	star polymer[d]
$(A')_2A(A')_2$	18.3	0.115	0.137	0.84	0.71 (4 arm)
$(A')_4A(A')_4$	26.0	0.104	0.176	0.59	0.46 (8 arm)
$(A')_8A(A')_8$	47.1	0.108	0.268	0.40	0.25 (16 arm)
$A(A')_4A$	14.5	0.0885	0.117	0.74	0.56 (6 arm)
$A(A')_8A$	38.6	0.126	0.234	0.54	0.39 (10 arm)
$A(A')_{16}A$	53.8	0.119	0.295	0.41	0.22 (18 arm)
$A(A')_2A(A')_2A$	38.7	0.180	0.232	0.78	0.56 (6 arm)
$A(A')_4A(A')_4A$	48.0	0.179	0.272	0.66	0.39 (10 arm)
$A(A')_8A(A')_8A$	72.5	0.171	0.364	0.47	0.22 (18arm)

[a] Determined by SLS. [b] In toluene at 35 °C. [c] Calculated from $[\eta]_{linear} = 1.29 \times 10^{-4}M^{0.71}$ (see ref 43). [d] $g' = [(3f - 2)/f^2]^{0.58}[0.724 - 0.015(f - 1)]/0.724$ (see ref 44).

In summary, the iterative divergent methodology could be extended to the syntheses of well-defined chain-functionalized polystyrenes with a definite number of benzyl bromide moieties of the types $(BnBr)_nPS(BnBr)_n$, $PS(BnBr)_nPS$, and $PS(BnBr)_nPS(BnBr)_nPS$. They are well-defined in architecture and well controlled in chain length and can be used as new reactive chain-functionalized polymers with many potential applications.

Synthesis of Well-Defined Star-*block*-Linear-*block*-Star, Linear-*block*-Star-*block*-Linear, and Linear-*block*-Star-*block*-Linear-*block*-Star-*block*-Linear Polystyrenes. As reported previously, the benzyl bromide moieties of chain-functionalized polymers cleanly and quantitatively coupled with PSLi end-capped with DPE (designated as PSD′Li) in THF at below −40 °C to afford a variety of star-branched polymers[33,36−39] and comblike polymers.[39−42] Therefore, we expect that various star−linear block polymers can be synthesized by the coupling reaction of PSD′Li with a series of $(BnBr)_nPS(BnBr)_n$, $PS(BnBr)_nPS$, and $PS(BnBr)_nPS(BnBr)_nPS$ synthesized in this study.

For the synthesis of star-*block*-linear-*block*-star polystyrenes, the coupling reaction of PSD′Li with either of the $(BnBr)_nPS(BnBr)_n$ (n = 2, 4, 8, and 16) was carried out in THF at −78 °C. A 1.5-fold excess of PSD′Li to benzyl bromide moiety was used to force the reaction to completion. The M_n value of PSD′Li was designed to be around 2 kg/mol. The reaction proceeded rapidly and finished within 1 h under such conditions. The SEC profile of each reaction mixture always showed only two sharp single peaks corresponding to the coupled product and deactivated polystyrene used in excess in the reaction. Neither intermediate polymer nor higher molecular weight shoulder was observed, indicating that the coupling reaction proceeded cleanly. A typical SEC profile of the reaction mixture obtained by the coupling reaction of PSD′Li with the $(BnBr)_{16}PS(BnBr)_{16}$ is shown in Figure 3B. The coupled polymer eluted at a higher molecular weight side was isolated in 94% yield by fractional precipitation. The isolated polymer exhibits a sharp monomodal SEC distribution, as shown in Figure 3C. Similarly, three other polymers were synthesized and isolated in more than 90% yields. The ^{1}H NMR signals around 4.4 ppm assigned to methylene protons of the benzyl bromide moieties disappeared after the coupling reactions, showing that all of the benzyl bromide moieties had reacted completely. The results are summarized in Table 4.

As expected from their branched architectures, the estimated M_n values by SEC were always smaller than those calculated, assuming that all reaction sites coupled completely. Therefore, the absolute M_w values were determined by SLS and compared with those calculated. The absolute M_w values in each polymer sample agreed quite well with those calculated within the analytical limits. A series of well-defined star-*block*-linear-*block*-star polystyrenes represented as $(A')_2A(A')_2$, $(A')_4A(A')_4$,

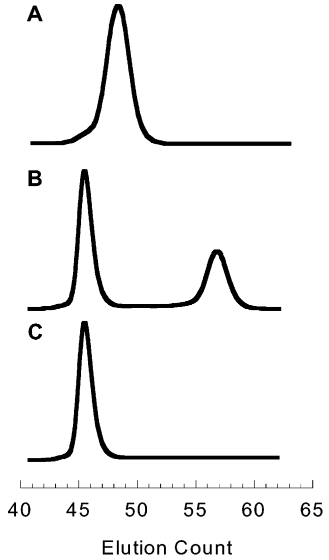


Figure 3. SEC profiles of $(BnBr)_{16}PS(BnBr)_{16}$ (A), the reaction mixture (B), and the star-*block*-linear-*block*-star polystyrene ($(A')_{16}A(A')_{16}$) isolated by fractional precipitation (C).

$(A')_8A(A')_8$, and $(A')_{16}A(A')_{16}$ could be synthesized successfully.

Similarly, a series of linear-*block*-star-*block*-linear and linear-*block*-star-*block*-linear-*block*-star-*block*-linear polystyrenes have been synthesized by the coupling reactions of PSD′Li with the corresponding in-chain-functionalized polystyrenes with benzyl bromide moieties. All the coupling reactions proceeded efficiently, and the objective star−linear block copolymers were isolated in more than 90% yields by fractional precipitation. Their characterization results are also summarized in Table 4. All data clearly indicate that the resulting polymers are well-defined linear-*block*-star-*block*-linear and linear-*block*-star-*block*-linear-*block*-star-*block*-linear polystyrenes with expected structures. These block copolymers have been designated as $A(A')_nA$ and $A(A')_nA(A')_nA$, where a subscript "n" is corresponding to the arm number of star block. It is noteworthy that the coupling reaction of PSD′Li with either of the benzyl bromide-chain-functionalized polystyrenes was complete within 1 h in THF at −78 °C. Thus, no steric limitation is encountered in the coupling reaction by each of any combinations under the conditions employed here.

Intrinsic Viscosities and g' Values of Star−Linear Block Polymers. It is generally recognized that branched polymers have more compact structures and smaller hydrodynamic volumes than those of the linear counterparts in dilute solution. One of the most employed methods to evaluate the branched structure of polymer is to determine the g' value, defined as $[\eta]_{\text{branched}}/[\eta]_{\text{linear}}$, where $[\eta]_{\text{branched}}$ and $[\eta]_{\text{linear}}$ are intrinsic viscosities of branched polymer and the linear polymer with the same molecular weight under the same conditions. The $[\eta]_{\text{branched}}$ values of the star−linear block polymers synthesized in this study were measured in toluene at 35 °C, while the values of $[\eta]_{\text{linear}}$ were calculated from the equation $[\eta] = 1.29 \times 10^{-4} M_w^{0.71}$.[43] The results are summarized in Table 5. The g' values of star-branched polystyrenes with similar branched structures and arm numbers are also listed as references.

In all star−linear block polystyrenes listed except for the $A(A')_4A$, molecular weights of the linear block segment and the star arm segment are around 10 and 2 kg/mol, respectively. Therefore, their $[\eta]_{\text{branched}}$ and g' values can be roughly compared in architecture. As expected, the $[\eta]_{\text{branched}}$ value of star−linear block polymer was always smaller than that of the corresponding linear polymer. Surprisingly, the $[\eta]_{\text{branched}}$ values of star-*block*-linear-*block*-star and linear-*block*-star-*block*-linear polymers were very similar each other, although their molecular weights and architectures were different. On the other hand, the $[\eta]_{\text{branched}}$ values of linear-*block*-star-*block*-linear-*block*-star-*block*-linear polymers were relatively large compared with those of two other star−linear block polymers. Interestingly, the $[\eta]_{\text{branched}}$ value remained almost unchanged with increasing the arm number of star block in each series of the star−linear block polystyrenes.

The g' value of the star−linear block polymer was usually larger than that of the star-branched polymer with the same number of arms. This can be readily imagined, since the star−linear block polymers seem to have less compact structures than the corresponding star-branched polymers. The g' value decreased with increasing the total arm number of star−linear block polymer, and the trend was very similar among the three series of the star−linear block polystyrenes. Thus, the g' value obviously varies as a function of the total arm number but seems not to be affected by the placement of star and linear blocks, in other words, the architecture, among the star−linear block polymers synthesized here. Unfortunately, the present discussion is quite limited, since the polymer samples possess relatively low molecular weights in both main and side chains in this study. More samples varying the number of arms and architectures as well as having higher molecular weights are needed for the detailed discussion.

Conclusions

The iterative divergent methodology developed for the synthesis of chain-end-functionalized polystyrenes with benzyl bromide moieties has been successfully extended to the syntheses of novel well-defined benzyl bromide-chain-functionalized polystyrenes with different architectures represented as $(Br)_nPS(Br)_n$, $PS(Br)_nPS$, and $PS(Br)_nPS(Br)_nPS$. By using these benzyl bromide-chain-functionalized polystyrenes in the coupling reaction with PSD′Li, various star-*block*-linear-*block*-star, linear-*block*-star-*block*-linear, and linear-*block*-star-*block*-linear-*block*-star-*block*-linear polystyrenes whose star blocks have a definite number of arm segments have been synthesized.

In the iterative divergent methodology, the number of the benzyl bromide moieties can further increase by repeating the iterative reaction sequence, and thereby star blocks with more arms may be synthesized. As previously reported, the benzyl bromide moieties are capable of reacting with a variety of living anionic polymers of not only styrene but also isoprene, 2-vinylpyridine, *tert*-butyl methacrylate, methyl methacrylate, and ethylene oxide. Accordingly, the developed methodology followed by the coupling may allow to synthesizing star−linear block copolymers comprising of two different polymer segments.

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