Synthesis of Branched Polymers by Means of Living Anionic Polymerization. 12. Anionic Synthesis of Well-Defined Star-Branched Polymers by Using Chain-End-Functionalized Polystyrenes with Dendritic Benzyl Bromide Moieties

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ABSTRACT: A series of five well-defined chain-end-functionalized polystyrenes with 2, 4, 8, 16, and 32 benzyl bromide moieties that were dendritically distributed were synthesized by an iterative methodology using only two sets of the reactions in each iterative reaction sequence. By coupling of these benzyl bromide-functionalized polystyrenes with 1,1-diphenylethylene (DPE)-end-capped polystyryllithium or polyisoprenyllithium in THF at −40 °C, 3-, 5-, 9-, 17-, and 33-arm star-branched polystyrenes as well as AA'_8 and AB_8 asymmetric star-branched polymers were quantitatively synthesized. Moreover, a new chain-end-functionalized polystyrene with 16 phenols could successfully be synthesized by a similar coupling reaction between chain-end-functionalized polystyrene with 8 benzyl bromide moieties and the functionalized 1,1-diphenylalkyl anion prepared from *sec*-BuLi and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)-ethylene, followed by deprotection. The well-defined structures and branched architectures of the resulting star-branched and chain-end-multifunctionalized polymers were confirmed by SEC, vapor pressure osmometry (VPO), ^{1}H NMR, SLS, and viscosity measurements.

Introduction

Star-branched polymers are one of the most important classes of branched polymers. Star-branched polymers with well-defined chain structures and branched architectures are especially important model polymers for elucidating the effect of chain branching on polymer properties and morphologies.[1−8] The most successful methods for the synthesis of such well-defined star-branched polymers have been mainly based on coupling reactions of living anionic polymers of styrene and 1,3-diene monomers with multifunctional chlorosilanes.[9] A variety of star-branched polymers with from 3 to 18 arms have been synthesized by this coupling method. Furthermore, the 32-, 64-, and even 128-arm star-branched polymers are now available by using specially designed carbosilane dendrimers in the coupling reaction.[10,11]

In the early years of star-branched polymer synthesis, multifunctional benzyl halide derivatives were often used as the electrophilic coupling agents with living anionic polymers.[12,13] Unfortunately, the coupling reaction with multifunctional benzyl halide derivatives was complicated by serious side reactions such as metal−halogen exchange, benzyl proton abstraction, and single electron transfer reactions. The reaction products were usually mixtures of star-branched polymers with different number of arms. Recently, however, Gauthier and Möller reported that such side reactions can be significantly reduced in the coupling reaction of chloromethylated polystyrene and polystyryllithium by end-capping polystyryllithium with 1,1-diphenylethylene (DPE) in the presence of THF; the coupling efficiency is nearly quantitative.[14] More recently, we demonstrated that the coupling reaction of poly(3-halomethylstyrene)s with DPE-end-capped polystyryllithiums is virtually quantitative in THF at −40 °C.[15−17] Hadjichristidis and coworkers also reported that the coupling efficiency of the reaction of poly(4-chloromethylstyrene) with either DPE-end-capped polystyryllithium or polyisoprenyllithium is near 100% under similar conditions.[18]

On the basis of these successful results, the use of multifunctional benzyl halide derivatives should be reconsidered in the synthesis of star-branched polymers by the coupling reaction with living anionic polymers. We have recently successfully synthesized several well-defined star-branched polymers by the coupling reaction of specially designed chain-functionalized polymers having a definite number of benzyl halide moieties with living anionic polymers of styrene, α-methylstyrene, and isoprene.[19−23] We recently developed an iterative methodology based on a divergent approach, with which well-defined chain-end-functionalized polystyrenes with a definite number of 2−32 dendritic benzyl bromide moieties.[24] Herein we report the successful synthesis of well-defined star-branched polystyrenes by coupling these chain-end-functionalized polystyrenes with dendritic benzyl bromide moieties with living anionic polymers of styrene. The synthesis of asymmetric star-branched polymers whose arms differ in molecular weight and chemical composition and a new chain-end-functionalized polystyrene with 16 phenols will also be reported.

Experimental Section

Materials. The reagents (>98% purities) were purchased from Aldrich Japan and used as received unless otherwise stated. Styrene (99%, Koso Chemical Co., Ltd. Japan) and deuterated styrene (98%, Aldrich Japan) were purified according to the usual procedure and finally distilled from dibutylmagnesium (ca. 3 mol %) on the vacuum line into ampules equipped with break seals that were prewashed with 1,1-diphenylhexyllithium in heptane. Isoprene (99%, Tokyo Kasei

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Kogyo Co., Ltd.) was washed with NaOH (10%) aqueous solution and dried over $MgSO_4$. After removing $MgSO_4$ by filtration, it was distilled from CaH_2 under nitrogen, and finally distilled from *n*-BuLi (ca. 2 mol %) at 0 °C on the vacuum line into ampules with break seals that were prewashed with 1,1-diphenylhexyllithium in heptane. DPE (97%, Aldrich Japan) was distilled from CaH_2 under reduced pressure and then distilled from its 1,1-diphenylhexyllithium solution on the vacuum line into ampules with break seals that was prewashed with potassium naphthalenide in THF. Tetrahydrofuran (THF) (99%, Mitsubishi Chemical Co., Ltd.) was refluxed over Na wire overnight and distilled from $LiAlH_4$ under nitrogen. It was finally distilled from its sodium naphthalenide solution on the vacuum line. Chloroform (99%, Nakarai tesque Co. Ltd. Japan), DMF (99%, Nakarai tesque Co., Ltd.), acetonitrle (99%, Nakarai tesque Co., Ltd.), and trimethylsilyl chloride (98%, Tokyo Kasei Kogyo Co., Ltd.) were distilled from CaH_2 under a nitrogen atomosphere. Dibutylmagnesium (99%, Aldrich Japan), *tert*-butyldimethylsilyl chloride (99%, Shinetsu Chemical Co., Ltd.), $(C_4H_9)_4NF$ (1.0 M, in THF, Aldrich Japan), and *sec*-BuLi (1.3 M, in cyclohexane, Aldrich Japan) were used as received. LiBr (99%, Koso Chemical Co., Ltd.) was dried under the high vacuum (10^{-6} Torr) at 100 °C for 12 h. 1,1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene **(1)** and 1-(4-bromobutyl)-4-*tert*-butyldimethylsilyloxymethylbenzene were synthesized according to the procedures previously reported.[25] 1,1-Bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene was synthesized according to the method previously reported.[26]

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 sizes 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. Fractionation by SEC was performed with a flow rate of 5.0 mL/min at 40 °C using Tosoh HLC 8020 type fully automatic instrument equipped with a TSK-G4000H_{HR} column (bead size = 5 μm, 300 mm in length and 7.8 mm in diameter; separatable molecular range = 1×10^3 to 4×10^5). All runs for fractionation were made with THF as an eluent. The concentration of the polymer solution for fractionation was adjusted to 10−20% w/v, depending on the molecular weight of the sample. 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 with equipment of very exact temperature control. Therefore, M_n values up to 100 kg/mol could be determined within an analytical error of ±5%. 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 (dn/dc) in THF or benzene at 25 °C was determined for each star-branched polymer with an Ohotsuka Electronics DRM-1020 refractometer operating at 632.8 nm. FT-IR spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. Intrinsic viscosities of star-branched polymers were measured by Ubbelhobe viscometers in toluene at 35 °C.

Living Anionic Polymerizations of Styrene, Styrene-*d*$_8$, Isoprene, 2-Vinylpyridine, and *tert*-Butyl methacrylate. All polymerizations were carried out under high vacuum conditions (10^{-6} Torr) in sealed glass reactors equipped with break seals. All reactors were prewashed with either 1,1-diphenylhexyllithium solution in heptane or sodium naphthalenide solution in THF after being sealed off from a vacuum line. Styrene and styrene-*d*$_8$ were polymerized with *sec*-BuLi in THF at −78 °C for 20 min. Isoprene was polymerized with *sec*-BuLi in heptane at 40 °C for 2 h. Heptane was then evaporated under vacuum and THF was added to the residual mixture at −78 °C. End-capping was carried out at −78 °C by adding a 1.5-fold excess of DPE to polystyryllithium (15 min) and polyisoprenyllithium (24 h), respectively. 2-Vinylpyridine was polymerized with 1,1-diphenyl-3-methylpentyllithium in THF at −78 °C for 1 h. *tert*-Butyl methacrylate was polymerized with diphenylmethylpotassium in THF at −78 °C for 20 min.

Synthesis of Chain-End-Functionalized Polystyrene with Two Benzyl Bromide Moieties (G-1). The functionalized polystyrene **G-1** was synthesized as follows: The first reaction was carried out in a sealed reactor equipped with break seals under high vacuum conditions (10^{-6} Torr). The 1,1-diphenylalkyllithium derivative prepared from *sec*-BuLi (1.29 mmol) in heptane (4.30 mL) and **1** (1.42 mmol) in THF (14.2 mL) was added to a THF (47 mL) solution containing chain-end-functionalized polystyrene with one benzyl bromide moiety,[25] **G-0** (4.76 g, 1.07 mmol), at −78 °C for 1 h. The reaction mixture was allowed to stand in THF at −78 °C for an additional 1 h. After the reaction was terminated with degassed methanol (5 mL), the reaction mixture was poured into a large amount of methanol (500 mL) to precipitate the polymer. The resulting polymer, **P-1** (5.04 g, 98%), was purified by reprecipitating twice from THF into methanol and freeze-drying from its absolute benzene solution for at least 24 h for the next reaction (4.94 g, 96%).

The transformation reaction was carried out under a nitrogen atmosphere. A solution of **P-1** (4.89 g, 1.00 mmol) dissolved in chloroform (30 mL) was added dropwise to a mixture of LiBr (8.68 g, 100 mmol) and $(CH_3)_3SiCl$ (10.9 g, 100 mmol) in a mixed solvent of acetonitrile (30 mL) and chloroform (90 mL) at 25 °C for 0.5 h. The reaction mixture was then allowed to stand at 40 °C for an additional 5 h, then poured into water, and extracted with chloroform (30 mL) four times. The combined organic layer was dried over $MgSO_4$. Removal of solvent under reduced pressure followed by precipitation into a large amount of methanol (500 mL) gave the expected polymer, **G-1** (4.75 g, 96%). It was purified by reprecipitating twice and freeze-drying from its absolute benzene solution (4.65 g, 94%). ^1H NMR: δ 7.2−6.2 (m, 216H, aromatic), 4.39−4.34 (m, 4H, $-CH_2Br$), 3.4−3.2 (m, 2H, $-(Ph)_2C-CH_2-Ph-$), 2.5−1.2 (m, 130H, CH_2-CH-), 0.8−0.5 (m, 12H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{356}H_{360}Br_2$: C, 89.10; H, 7.56; Br, 3.33. Found: C, 88.50; H, 7.76; Br, 3.57. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$). Similarly, chain-end-functionalized polystyrenes with 4 (**G-2**), 8 (**G-3**), 16 (**G-4**), and 32 (**G-5**) benzyl bromide moieties were synthesized. The detailed synthetic procedure has been reported elsewhere.[24]

G-2: ^1H NMR δ 7.2−5.9 (m, aromatic), 4.40−4.34 (m, 8H, $-CH_2Br$), 3.4−3.0 (m, 6H, $-(Ph)_2C-CH_2-Ph-$), 2.5−1.2 (m, CH_2-CH-), 0.8−0.4 (m, 24H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{400}H_{410}Br_4$: C, 86.71; H, 7.46; Br, 5.83. Found; C, 86.32; H, 7.62; Br, 5.96. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

G-3: ^1H NMR δ 7.2−5.8 (m, aromatic), 4.36−4.32 (m, 16H, $-CH_2Br$), 3.5−2.7 (m, 8H, $-(Ph)_2C-CH_2-Ph-$), 2.5−1.2 (m, CH_2-CH-), 0.8−0.4 (m, 48H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{476}H_{498}Br_8$: C, 83.35; H, 7.32; Br, 9.33. Found: C, 83.11; H, 7.55; Br, 9.72. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

G-4: ^1H NMR δ 7.2−5.7 (m, aromatic), 4.35 (s, 32H, $-CH_2$-Br), 3.5−2.6 (m, 30H, $-(Ph)_2C-CH_2-Ph-$), 2.4−1.2 (m, CH_2-CH-), 0.8−0.2 (m, 96H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{636}H_{682}Br_{16}$: C, 79.52; H, 7.16; Br, 13.32. Found: C, 79.39; H, 7.76; Br, 13.13. FT-IR (KBr, cm^{-1}): 1208 s ($-CH_2Br$).

G-5:^1H NMR δ 7.2−5.5 (m, aromatic), 4.33 (s, 64H, $-CH_2$-Br), 3.5−2.6 (m, 62H, $-(Ph)_2C-CH_2-Ph-$), 2.4−1.2 (m, CH_2-CH-), 0.8−0.3 (m, 192H, $-CH(CH_3)CH_2CH_3$). Anal. Calcd for $C_{956}H_{1049}Br_{32}$: C, 76.05; H, 7.00; Br, 16.95. Found: C, 75.50; H, 7.46; Br, 17.00. IR (KBr, cm^{-1}): 1208 s($-CH_2Br$).

Synthesis of Chain-End-Functionalized Poly(styrene-*d*$_8$) with Eight Benzyl Bromide Moieties (G′-3). **G′-3** was synthesized by a similar procedure as that employed for the synthesis of **G** series. As a starting polymer, chain-end-functionalized poly(styrene-*d*$_8$) with one benzyl bromide moiety (**G′-0**) was synthesized by reaction of poly(styryllithium-*d*$_8$) with a 1.2-fold excess of 1-(4-bromobutyl)-4-*tert*-butyldimethylsilyloxymethylbenzene in THF at −78 °C for 5 min, followed by treatment with a 50-fold excess of LiBr−$(CH_3)_3$SiCl at 40 °C for 5 h. A chain-end-functionalized poly(styrene-d_8) with two benzyl bromide moieties, **G′-1**, was synthesized by reaction of **G′-0** with a 1.2-fold excess of the functionalized 1,1-diphenylalkyl anion prepared from *sec*-BuLi and 1.1-fold excess of **1** in THF, followed by treatment with LiBr−$(CH_3)_3$SiCl. Similarly, **G′-2** and **G′-3** were successively synthesized by repeating the two reactions twice.

G′-1: $M_{n(calcd)} = 4.9_8$ kg/mol, $M_{n(SEC)} = 5.1_4$ kg/mol, $M_{n(VPO)} = 5.2_6$ kg/mol, $M_w/M_n = 1.04$. The degree of end-functionalization = 1.9_8. ^{1}H NMR: δ 7.1−6.3 (m, 12H, aromatic), 4.38−4.32 (m, 4H, −CH_2Br), 3.4−3.2 (m, 2H, −$(Ph)_2$C−CH_2−Ph−), 2.5−0.8 (m, 16H, CH_2−CH−), 0.7−0.5 (m, 12H, −CH(CH_3)-CH_2CH_3). Anal. Calcd for $C_{346}H_{24}D_{325}Br_2$: C, 83.17; H, 4.85; Br, 3.20. Found: C, 84.07; H, 5.58; Br, 3.57. FT-IR (KBr, cm^{-1}): 1208 s (−CH_2Br).

G′-2: $M_{n(calcd)} = 5.6_7$ kg/mol, $M_{n(SEC)} = 4.2_4$ kg/mol, $M_{n(VPO)} = 5.7_1$ kg/mol, $M_w/M_n = 1.04$. The degree of end-functionalization = 3.9_4. ^{1}H NMR: δ 7.2−5.9 (m, 28H, aromatic), 4.35−4.29 (m, 8H, −CH_2Br), 3.4−3.0 (m, 6H, −$(Ph)_2$C−CH_2−Ph−), 2.5−0.8 (m, 26H, CH_2−CH−), 0.8−0.3 (m, 24H, −CH(CH_3)-CH_2CH_3). Anal. Calcd for $C_{385}H_{70}D_{325}Br_4$: C, 81.57; H, 1.24; Br, 5.63. Found: C, 82.60; H, 3.83; Br, 6.02. FT-IR (KBr, cm^{-1}): 1208 s (−CH_2Br).

G′-3: $M_{n(calcd)} = 7.0_4$ kg/mol, $M_{n(SEC)} = 5.9_0$ kg/mol, $M_{n(VPO)} = 6.9_3$ kg/mol, $M_w/M_n = 1.03$. The degree of end-functionalization = 7.9_7. ^{1}H NMR δ 7.2−5.8 (m, 60H, aromatic), 4.36−4.31 (m, 16H, −CH_2Br), 3.4−2.7 (m, 14H, −$(Ph)_2$C−CH_2−Ph−), 2.5−0.8 (m, 46H, CH_2−CH−), 0.8−0.4 (m, 48H, −CH(CH_3)-CH_2CH_3). Anal. Calcd for $C_{465}H_{162}D_{325}Br_8$: C, 79.31; H, 2.32; Br, 9.07. Found: C, 79.50; H, 3.39; Br, 8.74. FT-IR (KBr, cm^{-1}): 1208 s (−CH_2Br).

Synthesis of 3-, 5-, 9-, 17-, and 33-Arm Star-Branched Polystyrenes. The 3-, 5-, 9-, 17-, and 33-arm star-branched polystyrenes were synthesized as in the representative reaction procedure of the 33-arm star-branched polystyrene: Polystyryllithium was prepared by polymerization of styrene (1.40 g, 13.4 mmol) in THF (14.0 mL) with *sec*-BuLi (0.270 mmol) in heptane (2.70 mL) at −78 °C for 20 min, followed by treatment with DPE (0.405 mmol) in THF (4.05 mL) at −78 °C for 15 min for end-capping. **G-5**, (0.0848 g, 0.00563 × 32 = 0.180 mmol per benzyl bromide moiety) dissolved in THF (2.54 mL) was added at once to the DPE-end-capped polystyryllithium at −78 °C. The reaction mixture was then allowed to stand at −40 °C for an additional 1 h. After the reaction was terminated with degassed methanol (5 mL), the reaction mixture was poured into a large amount of methanol (300 mL) to precipitate the polymer. The star-branched polystyrene was isolated nearly quantitatively by fractional precipitation using a mixture of cyclohexane and hexanes (400 mL/300 mL) at 5 °C (0.993 g, 95%). The polymer was reprecipitated twice from THF to methanol and freeze-dried from its absolute benzene solution (0.980 g, 94%). $M_{n(calcd)} = 186$ kg/mol, $M_{n(SEC)} = 70._6$ kg/mol, $M_{w(SLS)} = 196$ kg/mol, $M_w/M_n = 1.02$. ^{1}H NMR δ 7.2−5.7 (m, aromatic), 3.5−2.7 (m, −$(Ph)_2$C−CH_2−Ph−), 2.5−0.8 (m, CH_2−CH−), 0.7−0.5 (m, −CH(CH_3)CH_2CH_3).

Synthesis of Asymmetric Star-Branched Polymers Having Different Arms in Molecular Weight and Chemical Composition. The asymmetric AA′$_8$ and AB$_8$ star-branched polymers were synthesized by coupling either **G-3** ($M_n = 6.8_5$ kg/mol) or **G′-3** ($M_n = 7.0_4$ kg/mol) with living anionic polymers of styrene, isoprene, 2-vinylpyridine, and *tert*-butyl methacrylate as in the synthesis of the regular star-branched polystyrenes. The A′ and B segments were polystyrene ($M_n = 9.8_1$ and 4.6_3 kg/mol), polyisoprene ($M_n = 4.1_9$ kg/mol), poly(2-vinylpyridine) ($M_n = 5.3_6$ kg/mol), and poly(*tert*-butyl methacrylate) ($M_n = 4.8_7$ kg/mol), respectively. The coupling reactions were carried out in THF at −40 °C for 24 h and quenched with degassed methanol.

The resulting AA′$_8$ and AB$_8$ star-branched polymers were isolated by fractionation with SEC. These isolated star-branched polymers were purified by two reprecipitations from THF into methanol or heptane and freeze-drying from their benzene solutions.

Synthesis of Chain-End-Functionalized Polystyrene with 16 Phenols. The functionalized polystyrene was synthesized by coupling **G-3** with a functionalized 1,1-diphenylalkyl anion in a sealed reactor equipped with break seals under high vacuum conditions. In a typical experiment, a THF (6.72 mL) solution of **G-3** ($M_n = 6.8_5$ kg/mol, 0.0981 × 8 = 0.785 mmol for benzyl bromide moiety) was added to a functionalized 1,1-diphenylalkyl anion prepared from 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (1.13 mmol) and *sec*-BuLi (0.942 mmol) in THF (20.7 mL) at −78 °C for 1 h. The reaction mixture was allowed to stand at −78 °C for 24 h. After the reaction was terminated with degassed methanol (5 mL), the reaction mixture was poured into a large amount of methanol (200 mL) to precipitate the polymer (0.985 g, 99%). The polymer was purified by two reprecipitations from THF into methanol and freeze-drying from its benzene solution for at 24 h (0.980 g, 99%).

The polymer (0.980 g, 0.0961 × 16 = 1.54 mmol for the silyl-protected phenol functionality) dissolved in THF (9.80 mL) was treated with $(C_4H_9)_4$NF (6.20 mL, 6.20 mmol, 1.0 M in THF) at 25 °C for 2 h. After the solvent was removed under reduced pressure, the residual polymer was dissolved in a small amount of THF and poured into methanol. The polymer was preciptated, reprecipitated two more times from THF to methanol, and freeze-dried from its absolute benzene solution. The yield of polymer was 99% (0.796 g). $M_{n(calcd)} = 8.3_6$ kg/mol, $M_{n(SEC)} = 6.2_1$ g/mol, $M_w/M_n = 1.04$. ^{1}H NMR: δ 7.2−5.8 (m, aromatic), 3.5−2.7 (m, −$(Ph)_2$C−CH_2−Ph−), 2.5−0.8 (m, CH_2−CH−), 0.7−0.2 (m, −CH(CH_3)CH_2CH_3).

Results and Discussion

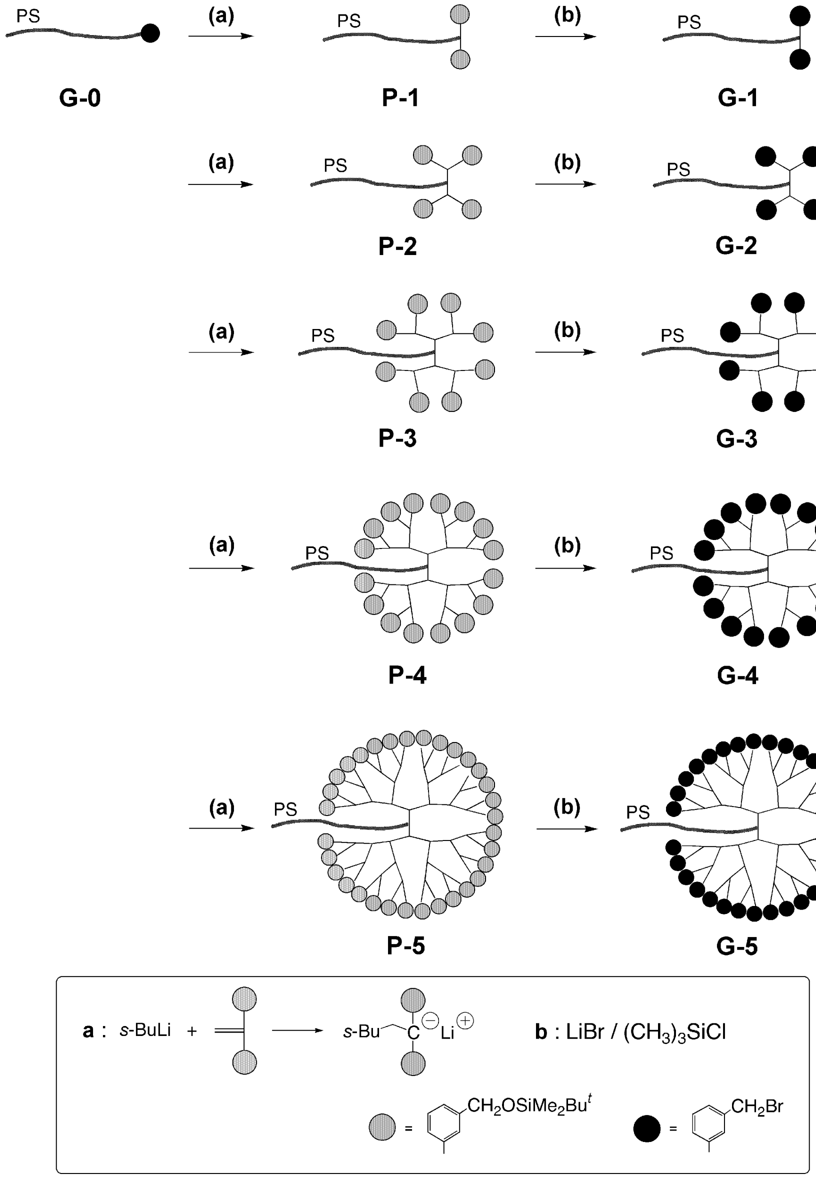
Synthesis of Chain-End-Functionalized Polystyrenes with Dendritic Benzyl Bromide Moieties. A new iterative methodology for the synthesis of the chain-end-functionalized polystyrenes was recently reported elsewhere[24] and is outlined in Scheme 1. Basically, only two sets of reactions are needed for the entire iterative synthetic sequence: a coupling reaction of the terminal benzyl bromide moieties with the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi and a transformation reaction of the introduced *tert*-butyldimethylsilyloxymethylphenyl groups into benzyl bromide moieties by treatment with a 1:1 mixture of LiBr and $(CH_3)_3$SiCl.

The first iteration starts with chain-end-functionalized polystyrene with one benzyl bromide moiety (**G-0**).[25] **G-0** was reacted with the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi. The transformation reaction of the two introduced *tert*-butyldimethylsilyloxymethylphenyl groups into benzyl bromide moieties was followed by treatment with LiBr−$(CH_3)_3$SiCl in a mixed solvent of acetonitrile and chloroform. Both reactions proceeded cleanly and quantitatively, thus forming chain-end-functionalized polystyrene with two benzyl bromide moieties (**G-1**).

Since **G-1** had the same end groups as the starting polymer, **G-0**, the same two reactions could be repeated in the second iteration. Chain-end-functionalized polystyrene with four benzyl bromide moieties (**G-2**) was synthesized from **G-1**. Similarly, the third, fourth, and fifth iterations were performed successively. The polymer obtained at each stage in the iteration was used as a starting material in the next iteration. A series of five benzyl bromide-end-functionalized polystyrenes, **G1**−**G5**, were thus synthesized. The yields were virtually quantitative in all cases. At each step in the iteration, the number of benzyl bromide moieties doubles. The benzyl bromide moieties thus introduced were dendritically distributed at the chain ends.

As shown in Figure 1, parts A−E, all of the resulting polymers exhibit single SEC peaks with narrow molec-

Scheme 1. Synthesis of G-1−G-5



ular weight distributions. The peak moves to higher molecular weights going from **G-1** to **G-5**. The M_n values observed by SEC relative to polystyrene were always somewhat smaller than those calculated, presumably due to the dendritic structures of benzyl bromide moieties introduced at the chain ends.

The characterization results of **G-1**−**G-5** are summarized in Table 1. The resulting polymers, **G-1**−**G-5**, have been precisely controlled in molecular weights, molecular weight distributions, and chain-end functionalities. We were thus successful in synthesizing the expected chain-end-functionalized polystyrenes with 2, 4, 8, 16, and 32 benzyl bromide moieties. The synthetic success also indicates that the iterative reaction sequence can be repeated at least five times without problem.

Synthesis of 3-, 5-, 9-, 17-, and 33-Arm Star-Branched Polystyrenes with Well-Defined Architectures. As mentioned in introduction, we previously reported that various star-branched polymers could be synthesized by the coupling reaction of benzyl halide-functionalized polystyrenes with living anionic polymers of styrene, α-methylstyrene, and isoprene.[19−22] The benzyl bromide-functionalized polystyrenes, **G-1**−**G-5**, synthesized herein are therefore attractive building blocks for the synthesis of star-branched polymers.

Table 1. Synthesis of Chain-End-Functionalized Polystyrenes with 2, 4, 8, 16, and 32 Benzyl Bromide Moieties[a]

	M_n (kg/mol)					benzyl bromide functionality	
polymer	calcd	SEC[c]	VPO	^{1}H NMR	M_w/M_n[c]	calcd	^{1}H NMR
G-1	4.7_9	4.2_3	4.8_0	4.7_5	1.04	2	2.0_0
G-2	5.4_7	4.9_6	5.4_2	5.6_4	1.04	4	3.9_2
G-3	6.8_5	5.6_0	6.7_8	6.9_5	1.03	8	8.0_8
G-4	9.5_9	7.0_5	9.6_4	9.9_4	1.04	16	$15._9$
G-5	$15._0$	8.5_4	$14._8$	$15._6$	1.03	32	$32._0$
G′-3[b]	7.0_4	5.9_0	6.9_3	NM[d]	1.03	8	7.9_7

[a] Yields of polymer were 100% in all cases. [b] Chain-end-functionalized poly(styrene-d_8) with eight benzyl bromide moieties. [c] Estimated from SEC relative to polystyrene. [d] Not measured.

We attempted to synthesize regular star-branched polystyrenes by coupling **G-1**−**G-5** with DPE-end-capped polystyryllithiums. Polystyryllithiums were used in a 1.5-fold molar excess relative to the benzyl bromide

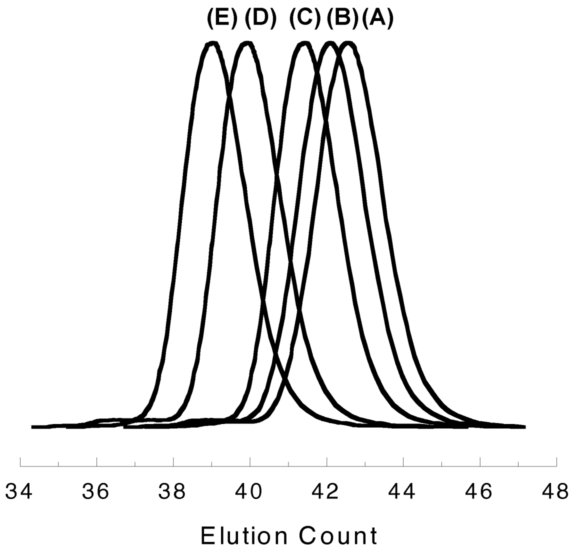


Figure 1. SEC profiles of G-1 (A), G-2 (B), G-3 (C), G-4 (D), and G-5 (E).

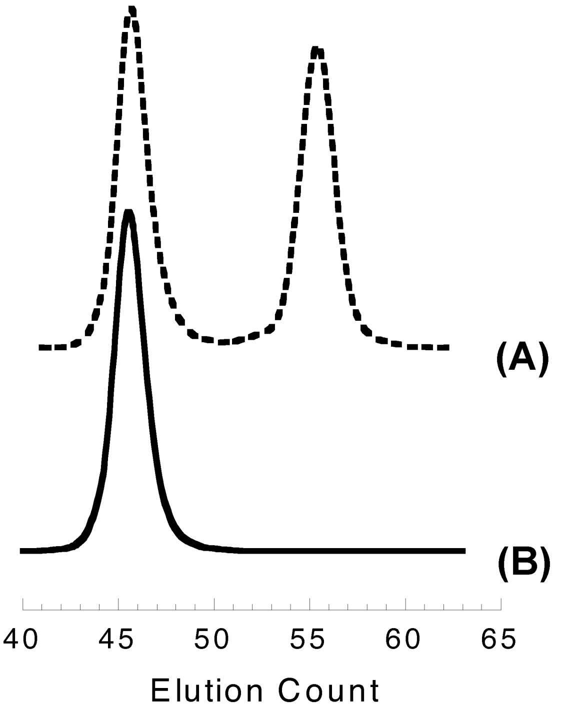


Figure 2. SEC profiles of crude reaction mixture (A) and the 33-arm star-branched polystyrene isolated by fractional precipitation (B).

moieties and set up a M_n value of around 5 kg/mol, similar to those of the polystyrene parts of **G** series polymers. The resulting polymers are therefore substantially regular type star-branched polystyrenes.

The coupling reactions were unexpectedly rapid in THF at −40 °C. For example, even the reaction of **G-5** with DPE-end-capped polystyryllithium proceeded with 93% efficiency in only 10 min and was complete within 1 h. Figure 2A shows a representative SEC profile of the crude reaction mixture. After the reaction, a new sharp single peak presumably for the expected star-branched polymer appears at the higher molecular weight side. Only two peaks for the star-branched polymer and the unreacted polystyrene used in excess in the reaction were observed in this SEC profile. Neither intermediate material nor tailing of the higher molecular weight peak was observed, indicating that the coupling reaction proceeded without side reactions.

The higher molecular weight polymer was isolated nearly quantitatively by fractional precipitation using a mixture of cyclohexane and hexanes (4/3, v/v) at 5 °C. Four other star-branched polystyrenes were similarly synthesized and isolated. The results are summarized in Table 2.

All of the isolated polymers have monomodal SEC distributions without any shoulders and tailings, indicating that they are pure and free of prepolymers and arm segments. The molecular weight distributions are very narrow, M_w/M_n values being less than 1.05. A typical SEC profile is shown in Figure 2B. As expected from their branched architectures, the M_n values observed by SEC relative to polystyrene are much smaller than those calculated. The absolute M_w values of all polymer samples were therefore determined by SLS and compared to the predicted M_w values calculated using the M_w/M_n values determined by SEC. The agreement between the two values is excellent in all cases, although there are small deviations attributed to uncertainties in their observed molecular weights by SLS (star-branched polymer) and SEC (arm segment). These results demonstrate that the expected 3-, 5-, 9-, 17-, and even 33-arm star-branched polystyrenes with well-defined structures were synthesized successfully.

One of the best methods to confirm branched architecture of regular star-branched polymer is to determine g' values, defined as $[\eta]_{star}/[\eta]_{linear}$ where $[\eta]_{star}$ and $[\eta]_{linear}$ are intrinsic viscosities of star-branched polymer and the linear polymer with the same molecular weights under the same conditions. The intrinsic viscosities of the star-branched polystyrenes synthesized in this study were measured in toluene at 35 °C. The values of $[\eta]_{linear}$ were calculated from the established equation, $[\eta] = 1.29 \times 10^{-4} M_w^{0.71}$.[27] Since g' have been correlated with the arm number both theoretically and experimentally,[1,2,8,28,29] we also calculated g' values by the following equation, eq 1, proposed by Douglas, Roovers, and Freed.[29]

$$g' = \{[(3f - 2)/f^2]^{0.58}[0.724 - 0.015(f - 1)]\}/0.724 \quad (1)$$

These results are summarized in Table 3. As expected, the viscosity of the star-branched polystyrenes was always smaller than that of the linear counterparts. The g' values determined experimentally are fairly consistent with these calculated from the equation except for the case of the 33-arm star-branched polystyrene. The expected branched architectures of the 3-, 5-, 9-, and 17-arm star-branched polystyrenes are thus evident.

In contrast, the experimental g' value of the 33-arm star-branched polystyrene was definitely higher than the calculated value of 0.08. Similar trends have been reported for star-branched polymers with many arms, including 32, 64, and 128 arms.[10,11] We therefore calculated the g' value of our 33-arm star-branched polystyrene using the following equation, eq 2, based on the experimental results proposed by Roovers.[30]

$$\log g' = 0.36 - 0.80 \log f \ (f\text{: arm number}) \quad (2)$$

The g' value thus calculated was 0.14, close to the experimental value of 0.13. Thus, the expected branched architecture of the 33-arm star-branched polystyrene can also be demonstrated. It should be mentioned that these equations were generally applied for star-branched

Table 2. Synthesis of 3-, 5-, 9-, 17-, and 33-Arm Star-Branched Polystyrenes

	segment (M_n; kg/mol)	M_n (kg/mol)		M_w (kg/mol)				no. of arms	
type	A/A′	calcd	SEC[a]	calcd[b]	$\mathrm{SLS}_{\mathrm{THF}}$[c]	d*n*/d*c*	M_w/M_n[a]	calcd	obsd
AA'_{2}	$5.6_2/5.8_9$	17.4	14.5	17.9	17.8	0.189	1.03	3	2.9_8
AA'_{4}	$4.6_3/5.1_7$	25.8	18.7	26.8	26.6	0.187	1.04	5	4.9_7
AA'_{8}	$4.6_3/4.5_7$	42.8	23.8	44.0	44.7	0.187	1.03	9	9.0_9
AA'_{16}	$4.6_3/4.7_4$	84.2	34.9	88.1	87.6 (88.0[d])	0.189 (0.101[d])	1.05	17	$16._9$ ($17._0$[d])
AA'_{32}	$4.6_3/5.4_2$	186	70.6	190	196 (191[d])	0.185 (0.100[d])	1.02	33	$33._7$ ($33._2$[d])

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

Table 3. Intrinsic Viscosity and *g*′ Values for 3-, 5-, 9-, 17-, and 33-Arm Star-Branched Polystyrenes

		$[\eta]_{\mathrm{star}}$[b]	$[\eta]_{\mathrm{linear}}$[c]	$g' = [\eta]_{\mathrm{star}}/[\eta]_{\mathrm{linear}}$		
					calcd	
no. of arms	M_w (kg/mol)[a]	dL/g	dL/g	exptl	eq 1[d]	eq 2[e]
3	17.8	0.111	0.134	0.83	0.83	
5	26.6	0.114	0.179	0.64	0.63	
9	44.7	0.119	0.212	0.46	0.42	0.40
17	87.6	0.109	0.417	0.26	0.24	0.24
33	196	0.0937	0.738	0.13	0.083	0.14

[a] Determined by SLS. [b] In toluene at 35 °C. [c] Calculated from $[\eta]_{\mathrm{linear}} = 1.29 \times 10^{-4} M^{0.71}$ (see ref 27). [d] $g' = [(3f - 2)/f^2]^{0.58} [0.724 - 0.015(f - 1)]/0.724$. [e] $\log g' = 0.36 - 0.80 \log f$ $(f > 6)$.

polymers having arm molecular weights larger than the ones used in this study.

As mentioned before, the coupling reaction even with **G-5** was very rapid. The star-branched polystyrene with 33 arms was readily and quantitatively obtained within 1 h. It thus seems that there is no steric limitation in any of the coupling reactions in THF at −40 °C. It may be possible to further increase the number of benzyl bromides introduced at the polymer chain-ends simply by repeating the two reactions in the iteration. Accordingly, star-branched polystyrenes with more arms may potentially be synthesized.

Synthesis of Asymmetric Star-Branched Polymers with Arms Different in Molecular Weight and Chemical Composition. If polystyryllithium with a different molecular weight and another living anionic polymer are used in the coupling reaction, asymmetric star-branched polymers whose arms differ in molecular weight and chemical composition can be synthesized.

We attempted to synthesize AA'_8 and AB_8 asymmetric star-branched polymers by coupling **G-3** with DPE-end-capped polystyryllithium with a M_w value of 10.3 kg/mol and DPE-end-capped polyisoprenyllithium. Both reactions were carried out in THF at −40 °C for 24 h. SEC profiles of the reaction mixtures were very similar to Figure 2A mentioned before. The resulting polymers were isolated by SEC fractionation. The results are summarized in Table 4.

Both isolated polymers exhibited sharp monomodal SEC distributions. The observed M_n values by SEC are not reliable because they are highly branched and consist of two different chains. The absolute M_w values determined by SLS agreed well with those calculated in both polymer samples. In the AB_8 star-branched polymer, the agreement between the composition ratios of [polystyrene]/[polyisoprene] observed by ^{1}H NMR and calculated was excellent. From the composition thus observed and the M_n value of polystyrene part of the A segment, the M_n value of this star-branched could be determined to be 40.5 kg/mol, which is close to the calculated value of 39.7 kg/mol. These results clearly indicate that the synthesis of the asymmetric star-branched polymers was successful. Moreover, we synthesized two additional AB_8 asymmetric star-branched polymers by coupling **G-3** with less reactive living polymers of 2-vinylpyridine and *tert*-butyl methacrylate in THF at −40 °C for 24 h, since such living polymers have recently been reported to react quantitatively with the benzyl bromide-functionalized polystyrenes.[16,31−33] All the results listed in Table 4 clearly demonstrate that living polymers of 2-vinylpyridine and *tert*-butyl methacrylate can be used in the coupling reaction with G series polymers for the synthesis of AB_8 star-branched polymers. Accordingly, the coupling reaction has also proven to be effective for synthesizing asymmetric AA'_8 and AB_8 star-branched polymers with well-defined architectures. Thus, both regular and asymmetric star-branched polymers can readily be synthesized from the same functionalized polystyrene, **G-3**, simply by changing the living polymer used in the coupling reaction. This is an additional advantage of the methodology using a functionalized building block.

One more interesting AB_8 star-branched polymer could be successfully synthesized by the coupling reaction of chain-end-functionalized poly(styrene-d_8) with eight benzyl bromide moieties, **G′-3**, with DPE-end-capped polystyryllithium under the same conditions. The **G′-3** was again synthesized by the same procedure used in the synthesis of **G-3**. The observed M_n value by VPO, molecular weight distribution, and degree of benzyl bromide functionalization were 6.93 kg/mol, 1.03, and 7.9_7, respectively as listed in Table 1. **G′-3** was coupled with a 1.5-fold excess of DPE-end-capped polystyryllithium in THF at −40 °C for 1 h. The results are listed in Table 4. The SEC profile showed a sharp monomodal distribution. The molecular weights calculated and determined by SLS are nearly the same. The resulting AB_8 star-branched polystyrene is interesting because one of the segments is perdeuterated polystyrene, which provides a strong contrast in neutron reflectivity analysis.

The synthesis of asymmetric star-branched polymer is generally much more difficult than that of regular star-branched polymers, since different arm segments cannot be simultaneously introduced in a single reaction.[6,8,34] Using the G series functionalized polystyrenes, one can readily synthesize a series of asymmetric star-branched polymers in which one segment differs either in molecular weight and/or composition from the other segments.

Synthesis of Chain-End-Functionalized Polystyrenes with 16 Phenols. The successful syntheses of **G1−G5** and the star-branched polymers are undoubtedly due to the quantitative nature of the coupling reaction. Therefore, it may be possible to introduce another functionality at the chain ends by coupling with another functionalized 1,1-diphenylalkyl anion. As illustrated in Scheme 2, **G-3** was coupled with the functionalized 1,1-diphenylalkyl anion from *sec*-BuLi and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene

Table 4. Synthesis of AA′$_8$ and AB$_8$ Asymmetric Star-Branched Polymers

	segment (M_n; kg/mol)		M_n (kg/mol)			M_w (kg/mol)				number of arms	
type	A	A′ or B	calcd	SEC^f	^{1}H NMR	calcd^k	SLS$_{THF}$^{l}	dn/dc	M_w/M_n^{a}	calcd	obsd
AA′$_8$	PS^a (4.6_3)	PS^a (9.8_1)	84.7	57.7	NM^g	88.6	88.2	0.189	1.05	9	8.9_6
AB$_8$	PS^a (4.6_3)	PI^c (4.1_9)	39.7	32.5	40.5^h	40.5	41.2	0.119	1.02	9	9.1_4
AB$_8$	PS^a (4.5_6)	P(2VP)^d (5.3_6)	48.4	24.7	49.0^i	49.6	49.9	0.179	1.03	9	9.0_5
AB$_8$	PS^a (4.5_6)	P(^{t}BMA)^e (4.8_7)	44.4	26.2	45.9^j	45.8	46.4	0.0968	1.03	9	9.1_2
AB$_8$	PS-d_8^{b} (4.8_2)	PS^a (4.6_3)	43.4	26.9	NM^g	44.4	46.4	0.176	1.02	9	9.4_2

[a] Polystyrene segment. [b] Poly(styrene-d_8) segment. [c] Polyisoprene segment. [d] Poly(2-vinylpyridine) segment. [e] Poly(*tert*-butyl methacrylate) segment. [f] Estimated from SEC relative to polystyrene. [g] Not measured. [h] [styrene]/[isoprene] = 42/476 (mol/mol, ^{1}H NMR), 42/464 (mol/mol, calcd). [i] [styrene]/[2-vinylpyridine] = 41/396 (mol/mol, ^{1}H NMR), 41/390 (mol/mol, calcd). [j] [styrene]/[*tert*-butyl methacrylate] = 41/275 (mol/mol, ^{1}H NMR), 41/265 (mol/mol, calcd). [k] Determined from $M_{n(calcd)}$ and M_w/M_n values. [l] Measured in THF.

Scheme 2. Synthesis of Chain-End-Functionalized Polystyrene with 16 Phenols

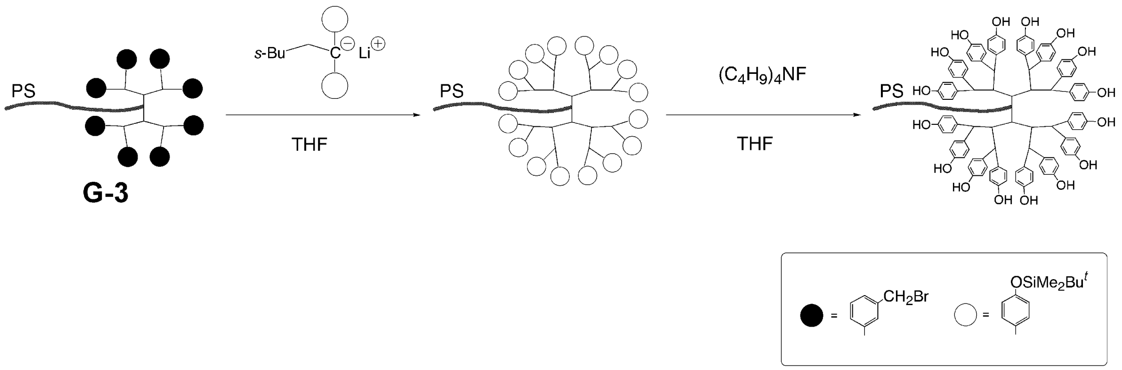


Table 5. Synthesis of Chain-End-Functionalized Polystyrene with 16 Phenol Groups

M_n (kg/mol)					functionality^d	
calcd	SEC^a	VPO	^{1}H NMR	M_w/M_n^{a}	calcd	^{1}H NMR
$10._1$	7.9_9^{b}	$10._6$	$10._3$	1.03^b	16	$15._8$
$23._3$	$20._2$^{c}	$23._0$	$23._5$	1.03^c	16	$16._0$

[a] Estimated from SEC relative to polystyrene. [b] The M_n and M_w/M_n values of the deprotected polystyrene observed by SEC were 6.2_1 kg/mol and 1.04, respectively. [c] The M_n and M_w/M_n values of the deprotected polystyrene observed by SEC were $18._7$ kg/mol and 1.03, respectively. [d] *tert*-Butyldimethylsilyloxyphenyl group.

in THF at −78 °C for 1 h to synthesize a new chain-end-functionalized polystyrene with 16 phenols. The results are summarized in Table 5.

The SEC profile of the resulting polymer showed a sharp monomodal distribution. The FT-IR absorption band for the C−Br bond at 1208 cm^{-1} present in **G-3** completely disappeared after the reaction, and new absorption bands at 836 and 1254 cm^{-1} for the Si−C bond and at 1090 cm^{-1} for the Si−O−C bond clearly appeared in the polymer after the reaction. ^{1}H NMR analysis indicated that all of the benzyl bromide moieties had completely reacted with the anion and two resonances were observed at 0.91 and 0.07 ppm. On the basis of the ratio of two integrals of the resonances at 0.91 ppm (Si−CH$_3$ protons) and at 0.70 ppm (CH$_3$ protons of the initiator residue), the degree of functionalization with 4-*tert*-butyldimethylsilyloxyphenyl was 15.8. As usual, the SEC M_n value was somewhat smaller than that predicted; the M_n values determined by VPO and ^{1}H NMR agreed quite well with that predicted.

The terminal *tert*-butyldimethylsilyloxyphenyl groups were readily and quantitatively deprotected by treatment with $(C_4H_9)_4NF$ in THF to regenerate phenol functionalities. Quantitative deprotection was confirmed by FT-IR and ^{1}H NMR analyses, both of which showed complete disappearance of the *tert*-butyldimethylsilyl groups. In addition, a new absorption band at 3540 cm^{-1}, characteristic of the OH group, was observed in the FT-IR spectrum. The SEC profile of the deprotected polymer showed a sharp monomodal distribution similar to that of the polymer before deprotection. Thus, the coupling reaction proceeded as desired to afford a new chain-end-functionalized polystyrene with 16 phenols that were introduced via 8 benzyl bromide moieties of **G-3**. Additionally, chain-end-functionalized polystyrene having a M_n value of 20 kg/mol with eight benzyl bromide moieties was coupled with the functionalized 1,1-diphenylalkyl anion from *sec*-BuLi and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene in THF at −78 °C for 1 h. The results are summarized in Table 5. The successful synthesis of chain-end-functionalized polystyrene with higher molecular weight having 16 phenols was confirmed by the characterizations of SEC, VPO FT-IR, and ^{1}H NMR. The synthesis of phenol-functionalized polystyrenes with different number of phenol groups and with higher molecular weight segments is now under investigation. Since various substituted DPE derivatives with functional groups tolerant to highly reactive carbanionic species such as organolithium compounds and living anionic polymers of styrene and 1,3-diene monomers have been synthesized,[35−45] this approach may open a new route for the synthesis of chain-end-multifunctionalized polymers with many useful functional groups.

Conclusions

Chain-end-functionalized polystyrenes with 2, 4, 8, 16, and 32 benzyl bromide moieties dendritically distributed at the chain ends were synthesized by an iterative methodology that involves only two sets of the reactions: a coupling reaction and a transformation reaction. Using these benzyl bromide-functionalized polystyrenes as building blocks, all hydrocarbon 3-, 5-, 9-, 17-, and even 33-arm star-branched polystyrenes were quantitatively synthesized by the coupling reaction with DPE-end-capped polystyryllithiums. Asymmetric AA′$_8$

and AB_8 star-branched polymers were also synthesized by a similar coupling reaction of **G-3** with different living anionic polymers. Their well-defined architectures were confirmed by SEC, SLS, ^{1}H NMR, and viscosity measurements. Moreover, a new chain-end-functionalized polystyrene with 16 phenols was successfully synthesized by coupling of **G-3** with the functionalized 1,1-diphenylalkyl anion prepared from 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene and *sec*-BuLi, followed by deprotection. On the basis of the successful polymer syntheses, the methodology combining the iterative synthesis for benzyl bromide-functionalized polymers with the coupling reaction with polymeric and functionalized 1,1-diphenylalkyl anions may possibly become a general and versatile procedure for the synthesis of various well-defined star-branched polymers and chain-end-multifunctionalized polymers. The advantages of the methodology developed in this study are that the coupling reaction, even with **G-5,** proceed very rapidly and quantitatively without any side reactions, and a series of both regular and asymmetric star-branched polymers can be systematically synthesized from the same starting building block. The practical limitation of the iterative synthesis for benzyl bromide-functionalized polystyrenes and synthetic possibility of star-branched polymers with more than 33 arms as well as high molecular weight segments are now under investigation.

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(23) In the coupling reaction of benzyl chloride-functionalized polystyrenes with polystyryllithiums previously reported,[14] the reaction mixtures always showed small extra peaks between the star-branched polymers and the precursor polymers in the SEC profiles. This is likely due to undesirable products formed by possible side reactions such as lithium chloride exchange and/or single electron transfer reactions, followed by coupling between polymer chains. We have recently found that the same coupling reaction proceeds cleanly and quantitatively by end-capping polystyryllithium with DPE.[15−17] No extra peaks were observed at any of the reaction products. Thus, the end-capping very effectively suppresses such side reactions.

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