Synthesis of Novel Well-Defined Substituted Polystyrenes Functionalized with Two and Four Benzyl Bromide Moieties in Each Monomer Unit and Their Application to Densely Branched Polymer Synthesis

Sang Woog Ryu, Hitoshi Asada, and Akira Hirao*

Polymeric and Organic Materials Department, Graduate School of Science and Technology, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: Three kinds of new substituted polystyrene derivatives functionalized with two or four benzyl bromide moieties in every monomer unit were successfully synthesized via living anionic polymerizations, functionalization reactions with the 1,1-diphenylalkyl anion prepared from 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene and *sec*-BuLi, and transformation reactions with LiBr−$(CH_3)_3SiCl$. These polymers were precisely controlled in chain length and quantitatively functionalized with benzyl bromide moieties. The synthesis of well-defined densely branched polystyrenes and graft copolymers carrying two or more branches in all repeating units were attempted using the coupling reactions of such benzyl bromide-functionalized polystyrenes with living anionic polymers of styrene, isoprene, and *tert*-butyl methacrylate in THF at −40 °C. The coupling reaction was found to proceed quantitatively under appropriate conditions to afford densely branched polymers carrying two branches in each repeating unit. In contrast, the coupling reaction of the polystyrene functionalized with four benzyl bromide moieties with living anionic polymers of styrene was incomplete and only two polystyrene chains could be introduced in each repeating unit. The structures of the resulting branched polystyrenes were investigated by intrinsic viscosity measurement. These polymers may adopt starlike rather than rodlike structures in toluene as evidenced by their g' values.

Introduction

Because branched polymers exhibit interesting and unique properties in bulk and solution originating from their inherent branched structures, these polymers have been widely studied from synthetic and theoretical points of view.[1−10] Among them, the poly(macromonomer)s accessible by living polymerization of well-defined macromonomers belong to the most interesting class of branched polymers from an architectural point of view because they are considered as one of the ultimate densely branched polymers that have a single branch in each repeating unit of backbone polymer and precisely controlled backbone and branched segments in chain length.[11−14]

It has been believed for a long time that such densely branched polymers cannot be synthesized by means of the "grafting-onto" method because of serious steric limitation arising from crowding of branched chains. However, Deffieux and Schappacher and others have recently reported the first successful synthesis of densely graft copolymers structurally similar to the above-mentioned poly(macromonomer)s by the methodology based on the grafting-onto method.[15,16] Their methodology involves the living cationic polymerization of 2-chloroethyl vinyl ether and the subsequent coupling reaction of the resulting poly(2-chloroethyl vinyl ether) with polystyryllithium. Quite surprising was that the coupling reaction virtually quantitatively proceeded to introduce the polystyrene segment into all repeating units of the poly(2-chloroethyl vinyl ether). More recently, Hirao and co-workers and Hadjichristidis and co-workers have also successfully synthesized similar densely branched polystyrenes and graft copolymers by quantitatively coupling poly(halomethylstyrene)s with living anionic polymers of styrene, isoprene, 2-vinylpyridine, and *tert*-butyl methacrylate (^{t}BMA).[17−20]

The above-mentioned results strongly indicate that no steric limitation as predicted is practically present in these coupling systems under appropriate conditions. Then, a question has been raised on how many branched chains can be introduced into the repeating unit of a backbone polymer by analogous coupling reactions. Roovers and co-workers previously reported that the coupling reaction of poly(1,3-butadienyl)lithium with the hydrosilylated poly(1,3-butadiene) substituted with $SiCl_2$ groups went essentially to completion to allow the introduction of two branches into all of the available $SiCl_2$ groups, although the number of reaction sites that were hydrosilylated was not quantitative.[21] Very recently, we successfully demonstrated that DPE-end-capped polystyryllithium quantitatively undergoes a coupling reaction with a new functionalized polystyrene with two benzyl bromide moieties in each monomer unit to introduce two polystyrene segments into each repeating unit of the backbone polymer.[22]

In this contribution, we first report on the synthesis of new well-defined functionalized polystyrenes functionalized with not only two but also four benzyl bromide moieties in each monomer unit via living anionic polymerization, functionalization, and functional group transformation reactions. Second, we reported on the more detailed synthesis of densely branched polystyrenes and graft copolymers carrying two or more branches in each repeating unit by the coupling reaction of these benzyl bromide-functionalized polystyrene derivatives with living anionic polymers.

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Experimental Part

Materials. All reagents used in this study were purchased from Aldrich Japan, unless otherwise stated, and purified in the usual manner. Both styrene and DPE were finally distilled over dibutylmagnesium (3 mol %) on the vacuum line. Isoprene was distilled at 0 °C on the vacuum line after addition of BuLi (3 mol %). *tert*-Butyl methacrylate (^{t}BMA) was distilled over trioctylaluminum (2 mol %) on the vacuum line. 4-Chlorostyrene and *tert*-butyldimethylchlorosilane were obtained from Hokko Chemical Industry Co., Ltd., Japan, and Shinnetsu Chemical Co. Ltd., respectively. Diphenylmethylpotassium was prepared in THF at 25 °C for 24 h by the reaction of potassium naphthalenide with a 1.1-fold excess of diphenylmethane. LiBr was dried at 150 °C for 48 h under high vacuum. Li_2CuCl_4 was prepared simply by mixing LiBr (1.84 g, 21.2 mmol) and $CuCl_2$ (1.43 g, 10.6 mmol) in THF (80 mL) under an atmosphere of nitrogen. 3-*Tert*-butyldimethylsilyloxymethylstyrene[23,24] and 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene[25] were synthesized according to the procedures reported previously.

Measurements. Both ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DPX (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$. Size-exclusion chromatography (SEC) was obtained at 40 °C using THF as a carrier solvent with a TOSOH HLC 8020 instrument. Three polystyrene gel columns ($TSK_{gel}G4000H_{XL}$ + $G3000H_{XL}$ + $G2000H_{XL}$ or $G5000H_{XL}$ + $G4000H_{XL}$ + $G3000H_{XL}$) were used. Measurable molecular weight ranges in these columns are from 10^3 to 4×10^6 g/mol. Calibration curves were made to determine M_n and M_w/M_n values with standard polystyrene and polyisoprene samples and poly(^{t}BMA) samples with known M_n values prepared in our laboratory. Fractionation by SEC was performed at 40 °C with THF as an eluent using a TOSOH HLC 8020 fully automatic instrument equipped with a TSK-$4000H_{HR}$ column (measurable molecular weight range: from 10^3 to 4×10^6 g/mol). Static light-scattering (SLS) measurements were performed with an Ootsuka Electronics Photal SLS-600R instrument (He−Ne laser, 633 nm) in THF or benzene. The refractive index increments (d*n*/d*c*) of the polymers have been measured by an Ootsuka Electronics Photal DRM-1020. Intrinsic viscosity was measured by a Ubbelohde-type capillary viscometer in toluene at 35 °C. FT-IR spectra were run with a JIR-AQS20M, JEOL.

4-(3-Brompropyl)styrene. It was synthesized by the Li_2CuCl_4-mediated coupling reaction of (4-vinylphenyl)magnesium chloride with 1,3-dibromopropane according to the modified procedure previously reported.[26] 4-(3-Bromopropyl)styrene was obtained in 70% yield by fractional distillation (77−79 °C /0.05 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10 (m, 2H, $CH_2CH_2CH_2$), 2.70 (t, 2H, CH_2Br), 3.30 (t, 2H, Ar−CH_2), 5.20 (d, 1H, CH_2=), 5.70 (d, 1H, CH_2=), 6.66 (q, 1H, CH=), 7.14 (d, 2H, Ar C2, 6 H), 7.31 (d, 2H, Ar C3, 5 H).

1-Bromo-4-*tert*-butyldimethylsilyloxymethylbenzene. It was synthesized by the silylation of 4-bromobenzyl alcohol with *tert*-butyldimethylchlorosilane and imidazole in DMF. The title compound was obtained in 97% yield by distillation under reduced pressure (97−99 °C/2.0 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 6H, Si−CH_3), 0.94 (s, 9H, Si−C−CH_3), 4.68 (s, 2H, Ar−CH_2), 7.20 (d, 2H, Ar C3, 5 H), 7.46 (d, 2H, Ar C3, 5 H).

4-[3-(4-*tert*-Butyldimethylsilyloxymethylphenyl)propyl]styrene (1). The title compound, **1**, was synthesized in 65% yield as a colorless liquid by the Li_2CuCl_4-mediated coupling reaction of 4-(3-bromopropyl)styrene with the Grignard reagent prepared from Mg and 1-bromo-4-*tert*-butyldimethylsilyloxymethylbenzene. After the usual workup, the crude product was purified by flash column chromatography (hexanes and then a mixed solvent of hexanes and ethyl acetate (9/1, v/v) as an eluent). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 6H, Si−CH_3), 0.93 (s, 9H, Si−C−CH_3), 1.95 (m, 2H, $CH_2CH_2CH_2$), 2.60 (t, 4H, $CH_2CH_2CH_2$), 4.71 (s, 2H, O−CH_2), 5.20 (d, 1H, CH_2=), 5.70 (d, 1H, CH_2=), 6.70 (q, 1H, CH=), 7.12−7.34 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ −5.12 ($SiCH_3$), 18.5 (Si−C), 26.1 ($SiCCH_3$), 33.0, 35.2 ($CH_2CH_2CH_2$), 65.0 (CH_2-OSi), 112.9 (CH_2=), 136.8 (CH=), 126.3, 128.4, 128.7, 135.2, 138.9, 140.9, 142.1 (Ar C).

The monomer, **1**, was freeze-dried three times from its absolute benzene solution and further dried in a vacuum line at 40 °C for 10 h.

Anionic Polymerization of 1. The anionic polymerization of **1** was carried out with *sec*-BuLi in THF at −78 °C for 10−30 min under high vacuum conditions (10^{-6} Torr) using the break-seal technique. The polymer was precipitated in a large amount of methanol, reprecipitated twice from THF solution into methanol, and finally freeze-dried from its absolute benzene solution for 24 h: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 6H, Si−CH_3), 0.60−0.80 (m, 6H, CH_3), 0.97 (s, 9H, Si−C−CH_3), 1.17−2.16 (m, 5H, CH_2−CH− and $CH_2CH_2CH_2$), 2.58 (t, $CH_2CH_2CH_2$), 4.73 (s, 2H, CH_2O), 6.53−7.29 (m, 8H, ArH). IR (thin film on a silicon wafer): 767, 834, 1243 cm^{-1} (Si−CH_3), 1071 cm^{-1} (Si−O−C).

The M_n value was determined by ^{1}H NMR using two resonances at 4.73 ppm (CH_2OSi protons) and at 0.60−0.80 ppm (CH_3 protons of the initiator residue). The M_w values were measured by SLS.

Synthesis of PS−1Br. For the synthesis of **PS−1Br**, the transformation reaction of the *tert*-butyldimethylsilyloxymethylphenyl group of poly(**1**) into a benzyl bromide moiety was carried out by treatment with $(CH_3)_3SiCl$−LiBr in a mixed solvent of acetonitrile and chloroform (3/5, v/v) at 40 °C for 24 h.

Under an atmosphere of nitrogen, a solution of poly(**1**) (0.950 g, 2.59 mmol for the *tert*-butyldimethylsilyloxymethylphenyl group) dissolved in dry chloroform (30 mL) was added to a mixed solvent of chloroform (20 mL) and acetonitrile (30 mL) containing trimethylsilyl chloride (3.15 g, 29 mmol) and LiBr (2.61 g, 30 mmol) at 25 °C for 0.5 h. The reaction mixture was then heated to 40 °C and allowed to stir for an additional 24 h. It was poured into water, extracted with chloroform, and dried over $MgSO_4$. The polymer was recovered by precipitation in hexanes after concentration of the organic solvent by evaporation and reprecipitated twice from the chloroform solution into methanol. It was freeze-dried twice from its absolute benzene solution to afford **PS−1Br** of 0.77 g (95% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.67 (m, CH_3), 1.29−2.30 (m, CH_2−CH− and $CH_2CH_2CH_2$), 2.56 (t, $CH_2CH_2CH_2$), 4.47 (s, CH_2Br), 6.51−7.29 (m, ArH). IR (thin film on silicon wafer): 604, 1220 cm^{-1} (CH_2−Br). Elemental analysis: $(C_{18}H_{19}Br)_n$ calculated; C 68.58, H 6.07, Br 25.35, observed; C 68.54, H 6.26, Br 25.93.

Synthesis of PS−2Br. The title functionalized polymer, **PS−2Br**, was synthesized by the reaction of **PS−1Br** with the 1,1-diphenylalkyl anion prepared from 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**2**) and *sec*-BuLi, followed by treatment with $(CH_3)_3SiCl$ with LiBr. A THF (6.21 mL) solution of **2** (0.750 g, 1.61 mmol) chilled to −78 °C was added into *sec*-BuLi (1.40 mmol) in heptane (3.00 mL) at −78 °C and the reaction mixture was allowed to stand for an additional 1 h at −78 °C. To the resulting functionalized 1,1-diphenylalkyl anion was added dropwise **PS−1Br** (0.33 g, 1.05 mmol for the benzyl bromide moiety) dissolved in THF (13 mL) at −78 °C and the mixture was allowed to stand at −78 °C for 72 h. The polymer was precipitated in methanol, reprecipitated twice from THF to methanol, and freeze-dried from its absolute benzene solution. A polymer yield was 0.76 g (95% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, Si−CH_3), 0.55−0.75 (m, CH_3), 0.97 (s, Si−C−CH_3), 1.05−2.18 (m, CH_2−CH− and $CH_2CH_2CH_2$), 2.56 (t, $CH_2CH_2CH_2$), 3.50 (s, $CH_2C(Ar)_2$), 4.74 (s, 2H, CH_2O), 6.48−7.29 (m, ArH). IR (thin film on silicon wafer): 776, 838, 1253 cm^{-1} (Si−CH_3), 1081 cm^{-1} (Si−O−C).

Under an atmosphere of nitrogen, the resulting polymer (0.69 g, 1.82 mmol for *tert*-butyldimethylsilyloxmethylphenyl group) dissolved in chloroform (10 mL) was treated with $(CH_3)_3SiCl$ (2.06 g, 19 mmol) and LiBr (2.61 g, 30 mmol) in a mixed solvent of chloroform (7 mL) and acetonitrile (10 mL) at 40 °C for 24 h. The same workup used in the case of **PS−1Br** gave an objective **PS−2Br** of 0.57 g (95% yield):^{1}H NMR (300 MHz, $CDCl_3$): δ 0.48−0.68 (m, CH_3), 0.95−1.95 (m, CH_2−CH− and $CH_2CH_2CH_2$), 2.46 (t, $CH_2CH_2CH_2$), 3.50 (s, CH_2C-

(Ar)$_2$), 4.36 (s, CH$_2$Br), 6.37−7.17 (m, ArH). IR (thin film on silicon wafer): 573, 1210 cm^{-1} (CH$_2$−Br). Elemental analysis: $(C_{38}H_{42}Br_2)_n$ calculated, C 69.30, H 6.43, Br 24.27; observed, C 69.41, H 6.52, Br 24.12.

Synthesis of PS′−2Br. The title functionalized polymer, **PS′−2Br**, was synthesized by the reaction of poly(3-bromomethylstyrene) with the functionalized 1,1-diphenylalkyl anion prepared from **2** and *sec*-BuLi, followed by treatment with (CH$_3$)$_3$SiCl with LiBr according to the procedure used for the synthesis of **PS−2Br**. **PS′−2Br** was obtained in 93% yield. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.45−0.66 (m, CH$_3$), 0.90−1.95 (m, CH$_2$−CH), 4.36 (s, CH$_2$Br), 6.30−7.17 (m, ArH). IR (thin film on silicon wafer): 573, 1210 cm^{-1} (CH$_2$−Br). Elemental analysis: $(C_{29}H_{32}Br_2)_n$ calculated, C 64.46, H 5.97, Br 29.57; observed, C 64.41, H 5.52, Br 29.72.

Synthesis PS−4Br. The title functionalized polymer, **PS−4Br**, was synthesized by the reaction of **PS−2Br** with the functionalized 1,1-diphenylalkyl anion prepared from **2** and *sec*-BuLi, followed by treatment with (CH$_3$)$_3$SiCl with LiBr. A THF (6.83 mL) solution of **2** (0.825 g, 2.41 mmol) chilled to −78 °C was added into *sec*-BuLi (2.10 mmol) in heptane (4.50 mL) at −78 °C and the reaction mixture was allowed to stand for an additional 1 h. To the resulting functionalized 1,1-diphenylalkyl anion was added dropwise **PS−2Br** (0.52 g, 1.58 mmol for the benzyl bromide moiety) dissolved in THF (19 mL) at −78 °C and the mixture was allowed to stand at −78 °C for 72 h. The polymer was precipitated in methanol, reprecipitated twice from THF to methanol, and freeze-dried from its absolute benzene solution. A polymer yield was 1.10 g (90% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.10 (s, Si−CH$_3$), 0.47 (s, CH$_3$), 0.74 (s, CH$_3$), 0.98 (s, Si−C−CH$_3$), 1.20−2.20 (m, CH$_2$−CH− and CH$_2$CH_2CH$_2$), 2.58 (t, CH_2CH$_2$CH_2), 3.15, 3.51 (s, CH$_2$C(Ar)$_2$), 4.73 (s, CH$_2$O−Si), 6.00−7.40 (m, ArH). IR (thin film on silicon wafer): 779, 838, 1253 cm^{-1} (Si−CH$_3$), 1084 cm^{-1} (Si−O−C).

Under an atmosphere of nitrogen, the resulting polymer (0.50 g, 1.29 mmol for the *tert*-butyldimethylsilyloxymethylphenyl group) dissolved in chloroform (11 mL) was treated with (CH$_3$)$_3$SiCl (2.28 g, 21 mmol) and LiBr (2.09 g, 24 mmol) in a mixed solvent of chloroform (8 mL) and acetonitrile (11 mL) at 40 °C for 24 h. The same workup used in the case of **PS−2Br** gave an objective **PS−4Br** of 0.39 g (90% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.48−0.68 (m, CH$_3$), 0.95−1.95 (m, CH$_2$−CH− and CH$_2$CH_2CH$_2$), 2.46 (t, CH_2CH$_2$CH_2), 3.15, 3.51 (s, CH$_2$C(Ar)$_2$), 4.36 (s, CH$_2$Br), 6.37−7.17 (m, ArH). IR (thin film on silicon wafer): 573, 1210 cm^{-1} (CH$_2$−Br). Elemental analysis: $(C_{78}H_{88}Br_4)_n$ calculated, C 69.65, H 6.59, Br 23.76; observed, C 69.66, H 6.67, Br 23.63.

Synthesis of Branched Polymers Carrying Two Branches in Each Repeating Unit. Branched polymers carrying two branches in each repeating unit were synthesized by the coupling reaction of **PS−2Br** with any of the living anionic polymers of styrene, isoprene, or ^{t}BMA. To the living anionic polymer solution was added **PS−2Br** dissolved in THF (ca. 5 wt %) at −78 °C and the mixture was allowed to stand at −40 °C for an appropriate time. The living anionic polymer was usually used in 1.5−2.0-fold molar excesses relative to the benzyl bromide moiety. After the reaction was quenched with degassed methanol, the polymer was precipitated in a large amount of methanol. The resulting polymer was isolated by either fractional precipitation or fractionation with SEC, reprecipitated from THF to methanol twice, and freeze-dried from its absolute benzene solution.

A representative synthetic procedure is as follows: Polystyryllithium was prepared by the polymerization of styrene (2.41 g, 23.2 mmol) in THF (30 mL) with *sec*-BuLi (0.269 mmol) in heptane (3.32 mL) at −78 °C for 15 min. It was divided into two portions (0.179 and 0.090 mmol). One of them (0.090 mmol) was quenched with degassed methanol for the determination of the M_n and M_w/M_n values of the polystyrene. A THF (6.45 mL) solution containing DPE (0.269 mmol) was added to the other polystyryllithium (0.179 mmol) solution at −78 °C for 0.5 h for end-capping. To the DPE-end-capped polystyryllithium (0.179 mmol) was added **PS−2Br** (0.0398 g, 0.121 mmol for the benzyl bromide moiety) dissolved in THF (5.00 mL) at −78 °C. The reaction mixture was allowed to stand at −40 °C for an additional 1h. After the reaction was quenched with degassed methanol, the crude polymer mixture was precipitated in methanol. The objective branched polymer was isolated by fractional precipitation using cyclohexane and hexanes (3/5, v/v) at 5 °C (1.55 g, 93% yield). The isolated polymer was reprecipitated twice from THF to methanol and freeze-dried twice from its benzene solution: ^{1}H NMR δ 0.60−0.70 (m, CH$_3$), 0.90−2.30 (m, CH$_2$−CH), 6.50−7.20 (m, ArH).

Similarly, the coupling reaction of either **PS′−2Br** or **PS−4Br** with DPE-end-capped polystyryllithium was carried out under identical conditions.

Table 1. Anionic Polymerization of 1 with *sec*-BuLi in THF for 10−30 min[a]

1 (mM)	*sec*-BuLi (mM)	M_n (kg/mol) calcd	SEC	^{1}H NMR	M_w (kg/mol) SLS	M_w/M_n SEC
198	10.4	7.08	6.00	6.98		1.03
295	5.46	19.8	15.5	19.4	20.5	1.02
296	3.16	34.9	26.1	32.9	33.2	1.06

[a] Yields of polymers were quantitative in all cases.

Results and Discussion

Synthesis of Functionalized Polystyrenes with Two and Four Benzyl Bromide Moieties in Each Monomer Unit. We have recently reported the synthesis of functionalized polystyrenes with two benzyl bromide moieties in each monomer unit, **PS−2Br**.[22] Because the synthetic procedure has been reported only briefly, we describe the more detailed procedure of **PS−2Br** from a synthetic point of view in the present study. In addition, the synthesis of a structurally analogous benzyl bromide-functionalized polystyrene, **PS′−2Br**, is presented in this section. We also describe the synthesis of a new functionalized polystyrene with four benzyl bromide moieties in each monomer unit, **PS−4Br**.

(1) Synthesis of PS−2Br. The synthetic procedure of **PS−2Br** is illustrated in Scheme 1. As can be seen, two reaction sequences are required for the synthesis. In the first reaction sequence, polystyrene functionalized with one benzyl bromide moiety in each monomer unit, **PS−1Br**, is prepared by the living anionic polymerization of **1**, followed by a transformation reaction. The second reaction sequence involves the reacting of **PS−1Br** with the functionalized 1,1-diphenylalkyl anion prepared from **2** and *sec*-BuLi, followed by a transformation reaction, thus forming the requisite **PS−2Br**.

The anionic polymerization of **1** was carried out with *sec*-BuLi in THF at −78 °C. On addition of **1** to *sec*-BuLi, an immediate color change from colorless to orange red was observed. The color characteristic to the polystyryl anion generated from **1** appeared to remain unchanged during the course of the polymerization. The yield of polymers was quantitative. The results are summarized in Table 1.

The ^{1}H NMR analysis as shown in Figure 1A indicates the expected structure of poly(**1**). The SEC profiles of poly(**1**) samples showed sharp symmetrical monomodal distributions, their M_w/M_n values being less than 1.06 (see Figure 2A). The observed molecular weights by ^{1}H NMR and SLS agreed well with the calculated values in all cases. These results as well as red coloration in the system clearly indicate the living character of the anionic polymerization of **1** under such conditions.[27]

The transformation of poly(**1**) into **PS−1Br** was carried out by treating it with a 10-fold excess of (CH$_3$)$_3$SiCl−LiBr. ^{1}H NMR analysis of the resulting polymer as shown in Figure 1B indicates that the three charac-

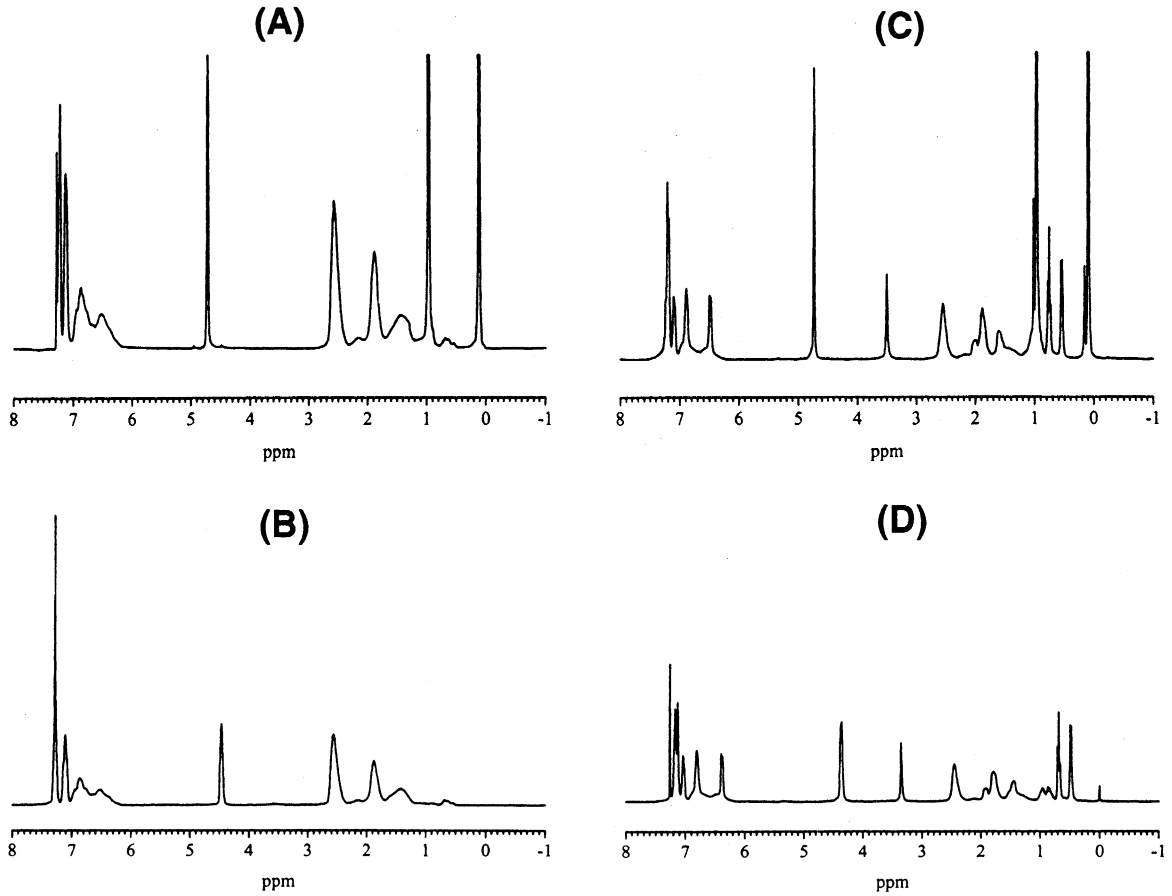
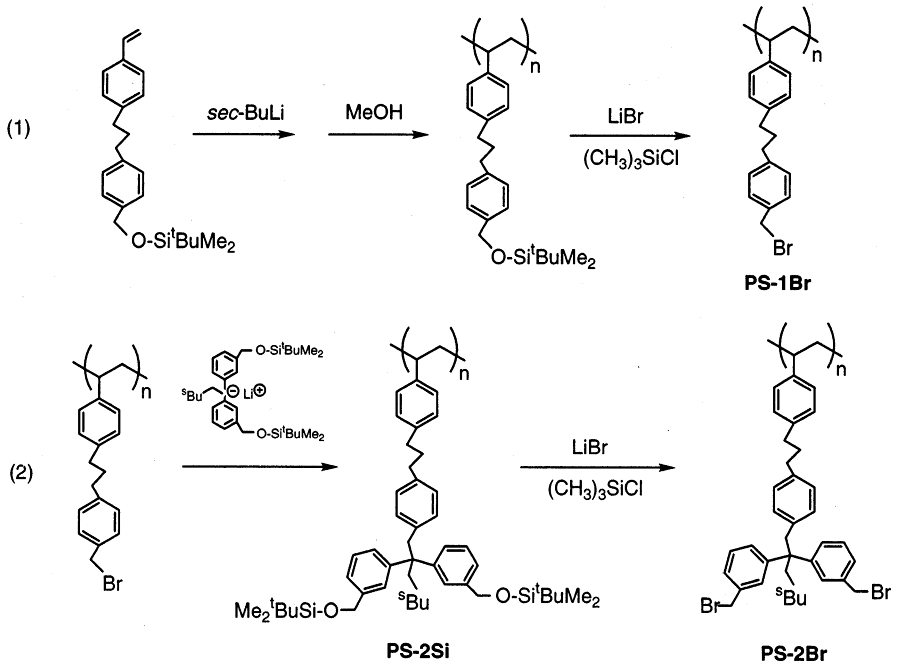


Figure 1. ^{1}H NMR spectra of poly(**1**) (A), **PS−1Br** (B), **PS−2Si** (C), and **PS−2Br** (D).

Scheme 1. Synthesis of PS−2Br



teristic resonances at 4.73, 0.97, and 0.10 ppm corresponding to the benzyl protons and methyl protons of the *tert*-butyldimethylsilyloxymethyl group had completely disappeared and a new resonance is observed at 4.47 ppm, which is assigned to the bromomethylene protons. The degree of benzyl bromide functionalization was determined to be quantitative by comparing the integral ratio of the bromomethylene protons with either methyl protons of the *sec*-butyl group or aromatic protons of the side chain. The bromine percent of 25.93% observed by elemental analysis satisfactorily agreed with that calculated (25.35%).

The SEC analysis revealed that all **PS−1Br** samples possessed symmetrical monomodal peaks with narrow molecular weight distributions (M_w/M_n < 1.03). Neither shoulder nor tailing was observed at all (see Figure 2B).

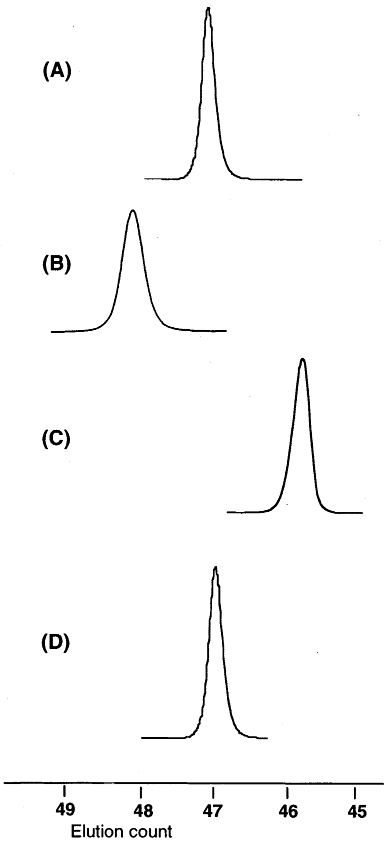


Figure 2. SEC Profiles of poly(**1**) (A) (M_n = 26.1 kg/mol), **PS−1Br** (B) (M_n = 20.3 kg/mol), **PS−2Si** (C) (M_n = 38.1 kg/mol), and **PS−2Br** (D) (M_n = 26.8 kg/mol).

Table 2. Synthesis of PS−1Br

M_n (kg/mol)			M_w (kg/mol)	M_w/M_n
calcd	SEC	^{1}H NMR	SLS	SEC
6.01	4.23	6.01		1.02
16.7	10.6	16.7	17.0	1.02
28.3	20.3	27.2	27.7	1.02

Again, in all cases, the observed molecular weights by ^{1}H NMR and SLS agreed quite well with calculated values. These results are summarized in Table 2.

The reaction of **PS−1Br** with the functionalized 1,1-diphenylalkyl anion prepared from **2** and *sec*-BuLi was carried out in THF at −78 °C for 72 h. The ^{1}H NMR shows that new resonances at 0.97 and 0.10 ppm for two methyl protons of the *tert*-butyldimethylsilyl group appear at reasonable ratios and the resonance at 4.47 ppm for the bromomethylene protons completely shifts to 4.74 ppm assigned to the silyloxymethylene protons (see Figure 1C). As shown in Figure 2C, the resulting polymer, **PS−2Si**, possesses a sharp monomodal SEC distribution. Thus, two 3-*tert*-butyldimethylsilyloxymethylphenyl groups were introduced into every monomer unit via one benzyl bromide moiety.

The subsequent transformation reaction with $(CH_3)_3SiCl-LiBr$ was carried out under the same conditions used in the case of **PS−1Br**. The ^{1}H NMR clearly indicates the complete transformation into **PS−2Br** (see Figure 1D). Agreement between the bromine contents of 24.12% observed by elemental analysis and 24.27% of the predicted value was quite satisfactory.

The SEC analysis reveals that the resulting polymer possesses sharp symmetrical monomodal distribution (see in Figure 2D). The observed molecular weights by both ^{1}H NMR (M_n) and SLS (M_w) agreed quite well with those predicted. The results are summarized in Table 3. Thus, the second reaction sequence also proceeds cleanly and quantitatively to afford functionalized polystyrenes with two benzyl bromide moieties in each monomer unit. In the present study, three **PS−2Br** samples with different molecular weights ($M_w(DP_w)$ = 12.0 kg/mol (18.2), 35.5 kg/mol (53.8), and 59.6 kg/mol (90.5)) were prepared for the synthesis of densely branched polymers.

Table 3. Synthesis of PS−2Br, PS′−2Br, and PS−4Br

	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n
polymer	calcd	SEC	^{1}H NMR	SLS	DP_w	SEC
PS−2Br	12.0	7.36	11.9	12.0	18.2	1.01
PS−2Br	33.8	17.3	34.8	35.5	53.8	1.02
PS−2Br	56.4	26.8	56.6	59.6	90.5	1.02
PS′−2Br	45.5	23.6	47.5	48.4	89.3	1.02
PS−4Br	63.9	20.0	66.0	65.9	50.0	1.02

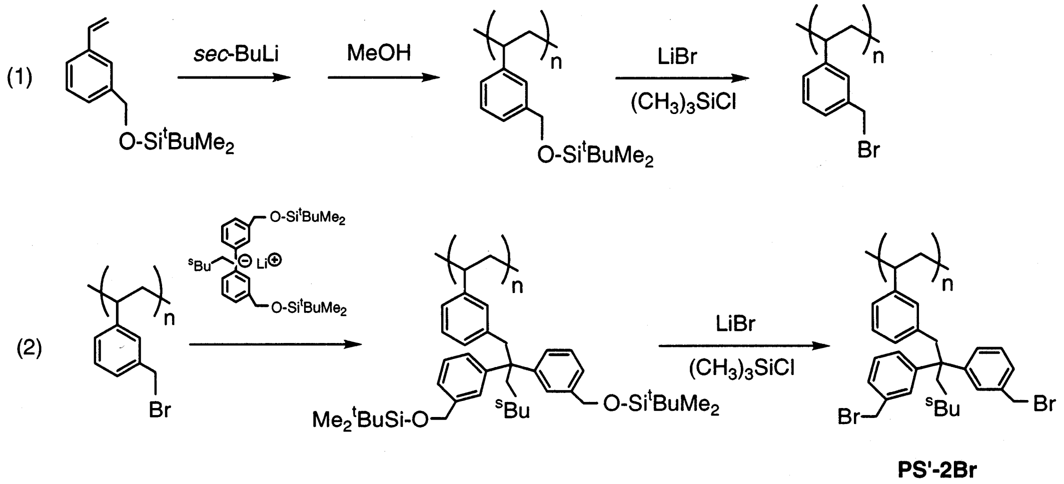
A structurally analogous benzyl bromide-functionalized polystyrene derivative, **PS′−2Br**, was synthesized in a fashion similar to the poly(3-bromomethylstyrene), precisely controlled in chain length as a starting polymer. The synthetic outline is illustrated in Scheme 2. The results are also summarized in Table 3. In **PS′−2Br**, the benzyl bromide moieties are located in the neighborhood of the main chain, whereas the $CH_2CH_2CH_2-C_6H_4$ group separates them from the main chain in **PS−2Br**.

(2) Synthesis of PS−4Br. For the synthesis of a new functionalized polystyrene with four benzyl bromide moieties in each monomer unit, **PS−4Br**, the second reaction sequence employed for the synthesis of **PS−2Br** was cycled by using **PS−2Br** as a starting polymer. The synthetic outline of **PS−4Br** is illustrated in Scheme 3. At first, the **PS−2Br** reacted with the functionalized 1,1-diphenylalkyl anion prepared from **2** and *sec*-BuLi in THF at −78 °C for 72 h. The ^{1}H NMR of the resulting polymer, **PS−4Si**, indicates that all benzyl bromide moieties had completely reacted and instead new resonances at 0.10 and 0.98 ppm, characteristic of the *tert*-butyldimethylsilyl group, appear at the expected integral ratios. Thus, four *tert*-butyldimethylsilyloxymethylphenyl groups could be introduced in every monomer unit via the two benzyl bromide moieties. After the reaction, a sharp monomodal SEC distribution that was similar in shape was observed, while the peak moved to the higher molecular weight side. The transformation reaction with $LiBr-(CH_3)_3SiCl$ was carried out under the same conditions as mentioned before. Quantitative transformation into a benzyl bromide moiety was confirmed by several analytical methods including IR, ^{1}H NMR, and elemental analysis (see Experimental Section). The SEC profile of the resulting polymer exhibited a sharp monomodal distribution. Agreement of the molecular weights between those calculated and observed by ^{1}H NMR or SLS was excellent within experimental limits. The results are also summarized in Table 3.

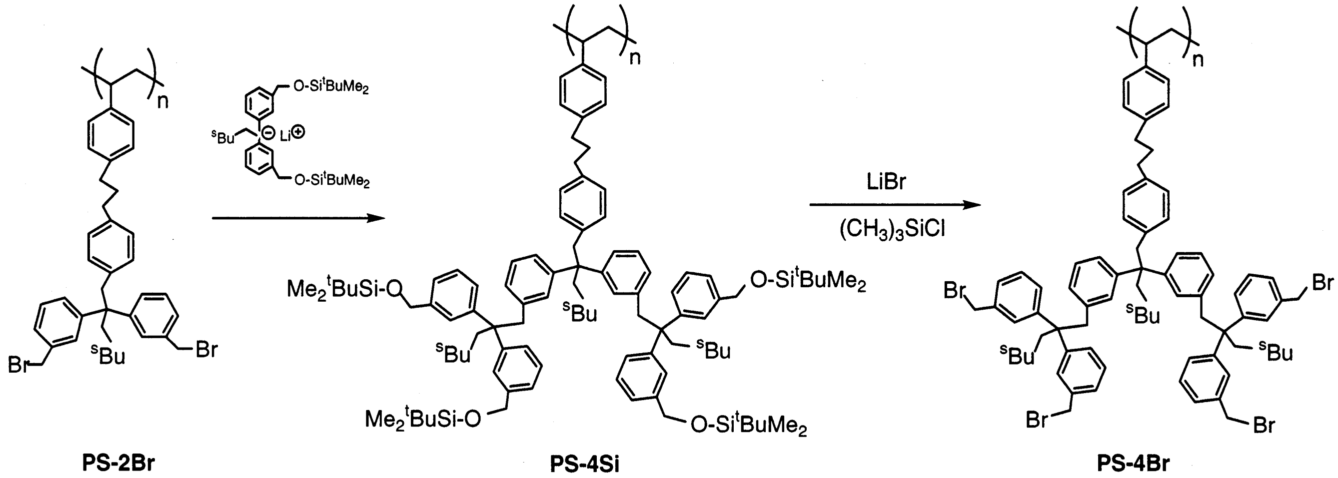
The expected **PS−4Br** was quantitatively obtained from **PS−2Br** by repeating the two reactions used in the synthesis of **PS−2Br** from **PS−1Br**. Therefore, it may be possible to synthesize functionalized polystyrenes with eight or more benzyl bromide moieties from **PS−4Br**.

Synthesis of Branched Polystyrenes Carrying Two Branches in Each Repeating Unit. The cou-

Scheme 2. Synthesis of PS′−2Br



Scheme 3. Synthesis of PS−4Br



pling reaction of either **PS−2Br** or **PS′−2Br** with polystyryllithium end-capped with DPE (PSDLi) was attempted to synthesize densely branched polystyrenes carrying two branches in each repeating unit. The reactions were carried out in THF at −40 °C for 24 h.

Figure 3A shows a representative SEC profile of the crude reaction product obtained by the coupling reaction of **PS−2Br** ($M_w = 12.0$ kg/mol, $DP_w = 18.2$) with PSDLi ($M_w = 9.40$ kg/mol). There are two distinct sharp single peaks eluted at the high and low molecular weight sides corresponding to the branched polymer and the unreacted polystyrene used in excess. The objective branched polymer was isolated in ≈90% by fractional precipitation (see Figure 3B). The results are summarized in Table 4.

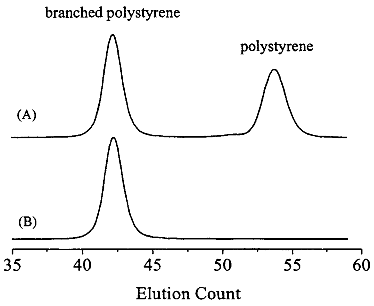


Figure 3. SEC profiles of the crude reaction mixture (A) and the polymer isolated after fractional precipitation (B).

As expected, the M_w value of 128 kg/mol estimated by SEC relative to polystyrene was much smaller than that predicted, assuming that two branched chains were introduced into all repeating units. On the other hand, the M_w value of 365 kg/mol determined by SLS agreed with that predicted ($M_w = 351$ kg/mol). Under the same conditions, two **PS−2Br** samples ($M_w = 35.5$ and 59.6 kg/mol, $DP_w = 53.8$ and 90.5) also quantitatively coupled with (PSDLi)s ($M_w = \approx 10$ kg/mol). Thus, the expected 36-, 108-, and 181-arm densely branched polystyrenes carrying two chains in each repeating unit were successfully synthesized.

Surprisingly, the coupling reaction of **PS−2Br** ($M_w = 12.0$ kg/mol, $DP_w = 18.2$) with PSDLi ($M_w = \approx 10$ kg/mol) was unexpectedly rapid in THF at −40 °C, reaching 70% and 92% efficiencies only after 3 and 10 min, respectively. The reaction went essentially to completion after 1 h. The rate of this coupling reaction was almost comparable to that of poly(3-bromomethylstyrene) with PSDLi.[28]

In contrast, the coupling reaction of **PS′−2Br** ($M_w = 48.4$ kg/mol, $DP_w = 89.3$) with PSDLi ($M_w = 8.72$ kg/mol) was not complete under the same condition. Although a high coupling efficiency of 85% was attained for a longer reaction time of 168 h, it was not still quantitative. The difference between **PS−2Br** and **PS′−2Br** in the coupling reaction strongly indicates the importance of the $CH_2CH_2CH_2C_6H_4$ group used as a

Table 4. Synthesis of Densely Branched Polystyrenes by Coupling Reaction of PS-2Br, PS′-2Br, or PS-4Br with Polystyryllithium End-Capped with DPE in THF at −40 °C for 24 h

polymer			PSDLi[a]	branched polystyrene				
				M_w (kg/mol)			M_w/M_n	
M_w (kg/mol)	DP_w	no. of reaction sites	M_w (kg/mol)	calcd	SEC	SLS	SEC	coupling efficiency
	PS−2Br							
12.0	18.2	36.4	9.40	351	128	365	1.03	104
12.0	18.2	36.4	22.9	843	293	859	1.02	102
12.0	18.2	36.4	55.1	2015	628	2000	1.03	99
12.0	18.2	36.4	93.0	3394	915	3490	1.01	103
35.5	53.8	107	11.0	1212	255	1240	1.05	100
35.5	53.8	107	21.0	2283	431	2260	1.04	99
59.6	90.5	181	9.40	1744	291	1710	1.03	98
59.6	90.5	181[b]	22.6	4134	582	3540	1.03	85
59.6	90.5	181[b]	45.0	8188	1019	5610	1.01	68
	PS′−2Br							
48.4	89.3	179[b]	8.72	1623	204	1380	1.05	85
48.4	89.3	179[b]	18.8	3366	376	2390	1.04	71
	PS−4Br							
65.9	50.0	100[b]	10.1	2167	249	1170	1.03	53
65.9	50.0	100[b]	27.5	5561	513	3090	1.03	55

[a] DPE-end-capped polystyryllithium, $M_w/M_n = 1.02-1.04$. [b] 168 h.

spacer between benzyl bromide moieties and the main chain.

To study the effect of molecular weights of branched and backbone chains on the coupling reaction, we first carried out the coupling reaction of **PS−2Br** ($M_w = 12.0$ kg/mol, $DP_w = 18.2$) with three (PSDLi)s having M_w values of 22.9, 55.1, and 93.0 kg/mol. The results are also summarized in Table 4. The coupling reactions were virtually quantitative in all cases. Any of the branched polymers possessed very narrow molecular weight distributions ($M_w/M_n = 1.01-1.03$) and predictable molecular weights. Without respect to the molecular weight of the branched chain varying from 9.40 to 93.0 kg/mol, the coupling efficiency was always quantitative. It thus seems likely that the coupling reaction with **PS−2Br** ($M_w = 12.0$ kg/mol, $DP_w = 18.2$) is not sensitive to steric hindrance as predicted.

Next, the effect of molecular weight of the backbone polymer on the coupling reaction was studied. Similar to the reaction with **PS−2Br**, a higher molecular weight **PS−2Br** ($M_w = 35.5$ kg/mol, $DP_w = 53.8$) also quantitatively coupled with PSDLi ($M_w = 21.0$ kg/mol). In contrast, the coupling reaction of the highest molecular weight **PS−2Br** ($M_w = 59.6$ kg/mol, $DP_w = 90.5$) with PSDLi ($M_w = 22.6$ kg/mol) was insufficient for 24 h. The efficiency of 85% was achieved after a longer time of 168 h. Thus, the coupling reaction was significantly influenced by the molecular weight of the backbone chain. With use of a higher molecular weight PSDLi ($M_w = 45.0$ kg/mol) in the reaction with the same **PS−2Br**, the efficiency dropped further to 68% under the same conditions after 168 h.

It should be mentioned that there were small variations among M_w values predicted and observed by SLS possibly because of the uncertainties in all of the observed molecular weight values. Because the experimental limitation in the accuracy of the respective molecular weight measurements may possibly be about ±5%, these variations are considered to be within the analytical limits. In this study, the molecular weights of the branched polymers were usually measured two times in THF or additionally in benzene by SLS to determine their molecular weights as accurately as possible. Fortunately, these values were always very close to each other in the same samples.

As mentioned before, the coupling reaction of **PS−2Br** with PSDLi quantitatively proceeded in THF at −78 °C, whereas the reaction was not complete with use of the **PS−2Br** having a relatively high molecular weight ($M_w = 59.6$ kg/mol, $DP_w = 90.5$) under the same conditions. A similar trend was observed in the related coupling reactions previously reported by Deffieux and co-workers[15,16] and Hadjichristidis and co-workers.[20] We are considering the reason for this by a conformation change of the backbone chain. In the case of a short backbone chain like **PS−2Br** ($M_w = 12.0$ kg/mol, $DP_w = 18.2$), the backbone chain can permit a free rotation as the branched chain is introduced, providing less sterically crowding spaces to make the coupling reaction more facile. On the other hand, the long backbone chain might restrict the free rotation after a certain number of branched chains are introduced, resulting in rodlike stiff chain conformation due to the steric crowding among adjacent branches. Further introduction of branched chains becomes more difficult simply by increasing steric crowding of the already introduced branches as the coupling reaction proceeds. Tsukahara et al.[29] and Schmidt and co-workers[30,31] reported that the structure of the poly(macromonomer) was changed from a spherical or starlike to a comblike or cylindrical molecular brush with increasing molecular weight of the backbone chain. Accordingly, the backbone chain was also changed from a flexible to a stiff chain conformation. Because the poly(macromonomer) is not a suitable model, but similar in structure to the densely branched polymers synthesized herein, a similar conformation change of the backbone may occur in our case.

Synthetic Attempts of Branched Polystyrenes Carrying Four Branches in Each Repeating Unit. To synthesize more densely branched polystyrenes carrying four branches, we attempted two coupling reactions of **PS−4Br** ($M_w = 65.9$ kg/mol, $M_w/M_n = 1.02$, $DP_w = 50.0$) with two (PSDLi)s having M_w values of 10.1 and 27.5 kg/mol. The results are also summarized in Table 4.

Unfortunately, the coupling reactions proceeded with disappointingly low efficiencies of 53% and 55% even for a longer reaction time of 168 h. Only two polystyrene chains could be introduced into each repeating unit. The resulting branched polymers exhibited sharp sym-

Table 5. Synthesis of Densely Graft Copolymers by Coupling Reaction of PS−2Br with a Living Anionic Polymer of Isoprene or ^{t}BMA

PS−2Br			living polymer		graft copolymer				
M_w (kg/mol)	DP_w	no. of reaction sites	type	M_w (kg/mol)	M_w (kg/mol)			M_w/M_n	grafting efficiency
					calcd	SEC	SLS	SEC	
59.6	90.5	181	PIDLi[a]	13.3	2450	444	2400	1.02	98
59.6	90.5	181	P(^{t}*BMA*)K[b]	8.12	1513	216	1540	1.02	102

[a] DPE-end-capped polyisoprenyllithium, $M_w/M_n = 1.02$. [b] Living anionic polymer of ^{t}BMA initiated with diphenylmethylpottassium, $M_w/M_n = 1.02$.

Table 6. Intrinsic Viscosities and g′ Values of Densely Branched Polystyrenes in Toluene at 35 °C

	DP_w (no. of reaction sites)		$[\eta]_{branch}$	$[\eta]_{linear}$[a]	$g' = [\eta]_{star}/[\eta]_{linear}$	
M_w (kg/mol)	backbone	branch	dL/g	dL/g	experimental	calculated[b]
365	18.2 (36.4)	90.0	0.16	1.12	0.15	0.13
859	18.2 (36.4)	219	0.30	2.06	0.14	0.13
2000	18.2 (36.4)	529	0.52	3.75	0.14	0.13
3490	18.2 (36.4)	892	0.52	5.57	0.09	0.13

[a] $[\eta] = 1.26 \times 10^{-4} M_w^{0.71}$. [b] $\log g' = 0.36 - 0.80 \log f$.

metrical monomodal SEC distributions, the M_w/M_n values being <1.03. This indicates that two polystyrene chains are homogeneously distributed throughout the backbone chain and neither three nor four polystyrene chains can be introduced. Thus, the synthesis of more densely branched polystyrenes by the use of **PS−4Br** encountered the problem of incomplete coupling. We are now investigating the coupling reaction with **PS−4Br** by changing reaction variables such as temperature, solvent, and molecular weights of backbone and branched chains and by introducing spacers between benzyl bromide moieties and the main chain.

Synthesis of Graft Copolymers Carrying Two Branches in Each Repeating Unit. To generalize the present methodology, other living anionic polymers, DPE-end-capped polyisoprenyllithium (PIDLi) (M_w = 13.3 kg/mol) and a living anionic polymer of ^{t}BMA (M_w = 8.12 kg/mol) initiated with diphenylmethylpotassium, were used in the coupling reactions with **PS−2Br** (M_w = 59.6 kg/mol, DP_w = 90.5). The reaction of **PS−2Br** with PIDLi was carried out at −40 °C for 24 h. The living polymer of ^{t}BMA was reacted with **PS−2Br** in THF at −40 °C for 336 h (2 weeks) based on the successful synthesis of polystyrene-*graft*-poly(^{t}BMA) carrying a single branch previously reported.[18] The results are listed in Table 5.

SEC profiles of the crude reaction mixtures obtained by the two coupling reactions were similar to those shown in Figure 3A. The objective polymers isolated by SEC fractionation exhibited sharp monomodal SEC distributions (M_w/M_n = 1.02 and 1.02, respectively). Their M_w values determined by SLS agreed with those predicted. Furthermore, the M_n values determined by ^{1}H NMR were also very close to those calculated, indicating almost quantitative efficiencies in these coupling reactions. Agreement between the compositions determined by ^{1}H NMR and those calculated was excellent in each case. Accordingly, the expected densely graft copolymers, polystyrene-*graft*-polyisoprene and polystyrene-*graft*-poly(^{t}BMA), carrying two branches in each repeating unit, were successfully obtained in similar ways. It is rather surprising that a less reactive living anionic polymer of ^{t}BMA efficiently reacts with **PS−2Br** to introduce two poly(^{t}BMA) chains in each repeating unit.

Intrinsic Viscosity of Branched Polystyrene Carrying Double Chains in the Repeating Unit. Branched architecture can be in part demonstrated by comparing the solution viscosity of the branched polymer with that of the linear polymer with the same molecular weight. The branched polystyrenes carrying two branches in each repeating unit should adopt starlike rather than rodlike structures in solution, estimating from their structures where the polymerization degrees of backbone chain are much lower than those of the branched chain. The effect of branching on the molecular dimensions of a star-branched polymer may be expressed as the parameter *g*′ value defined as $[\eta]_{branch}/[\eta]_{linear}$, where $[\eta]_{branch}$ and $[\eta]_{linear}$ are intrinsic viscosities of the branched polymer and linear polymer with the same molecular weight under the same conditions. The relationship between the *g*′ value and arm number of star-branched polymer has been well-established based on theoretical models and experimental results.[32−37]

The $[\eta]_{branch}$ values of four densely branched polystyrenes were measured in toluene at 35 °C. They possess the same polymerization degree of backbone chain (DP_w = 18.2, number of branches = 36.4) and different degrees of polymerization of the polystyrene branch in the range of 90−892. The intrinsic viscosities of linear polystyrenes with same molecular weights were calculated from eq 1.[38] With these values, the *g*′ values for

$$[\eta] = 1.26 \times 10^{-4} M_w^{0.71} \tag{1}$$

the three samples were obtained. Since Roovers proposed eq 2 based on the experimental results,[39] the *g*′ values for the three samples were also calculated as a 36.4-arm star-branched polymer. These data are given

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

in Table 6. As expected, the intrinsic viscosities of the branched polymers were much lower than those of the corresponding linear polymers. The overall experimental *g*′ values were in the range of 0.09−0.15. They were very close to the calculated value of 0.13, assuming that the branched polymers might behave as a 36.4-arm star-branched polymer in solution.

Conclusions

We have successfully synthesized three functionalized polystyrenes with two or four benzyl bromide moieties in every monomer unit, **PS−2Br**, **PS′−2Br**, and **PS−4Br**, via living anionic polymerization, a functionalization reaction with the 1,1-diphenylalkyl anion prepared from **2** and *sec*-BuLi, and a transformation reaction with LiBr−$(CH_3)_3SiCl$. The resulting polymers were precisely controlled in chain length and quantitatively functionalized with benzyl bromide moieties. Densely branched polystyrenes and graft copolymers were synthesized by the coupling reaction of either **PS−2Br** or **PS′−2Br** with living anionic polymers of styrene, isoprene, and *tert*-butyl methacrylate. It has been found that the coupling reaction of **PS−2Br** with living anionic polymers quantitatively proceeds under certain conditions. The resulting polymers possess well-defined structures and architectures in which both backbone and branched chains are precisely controlled in chain length and two branches are introduced into each repeating unit of the backbone chain.

In contrast, the coupling reactions by the combination of a high molecular weight **PS−2Br** ($M_w = 59.6$ kg/mol, $DP_w = 90.5$) and high molecular weight (PSDLi)s ($M_w = 22.6-45.0$ kg/mol) were not complete with 68−85% efficiencies even for a longer reaction time of 168 h. Furthermore, only two polystyrene chains were introduced in each repeating unit under the same conditions in the coupling reaction of **PS−4Br** with PSDLi.

The structures of the resulting densely branched polystyrenes were investigated by intrinsic viscosity measurement. These polymers may adopt starlike rather than rodlike structures in toluene as evidenced by their g' values.

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(28) The coupling reaction of poly(3-bromomethylstyrene) ($M_w = 6.75$ kg/mol, $DP_w = 33.0$) with PSDLi ($M_w = \approx 9$ kg/mol) proceeded with 81% and 95% efficiencies for 3 and 10 min, respectively, and was complete after 1 h under identical conditions in THF at −40 °C.
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