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Precise Synthesis of Dendrimer-Like Star-Branched Polystyrenes and Block Copolymers Composed of Polystyrene and Poly(methyl methacrylate) Segments by an Iterative Methodology Using Living Anionic Polymerization

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ABSTRACT: A series of well-defined dendrimer-like star-branched polystyrenes (PS)s has been synthesized by developing a new iterative methodology based on “arm-first” divergent approach. In the methodology, the following three reaction steps are needed for the entire iterative synthetic sequence: (1) a linking reaction of α-3-(*tert*-butyldimethylsilyloxy)propyl- (TBDMSOP-) functionalized polystyryllithium end-capped with 1,1-diphenylethylene with either a core compound with four benzyl bromide (BnBr) functions or chain-end−BnBr-functionalized PS, (2) a transformation reaction of the terminal TBDMSOP group into 3-bromopropyl group, and (3) an introduction reaction of two BnBr functions *via* the 3-bromopropyl group. The synthetic sequence has been repeated five times to successfully synthesize dendrimer-like star-branched (PS)s up to the fifth-generation (5G). The final 5G polymer was 1.88×10^6 in M_w value ($M_w/M_n = 1.05$) consisting of 124 PS branch segments. By using α-functionalized living PMMA with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups convertible to BnBr functions in the iterative process of the new methodology, two kinds of the 3G dendrimer-like star-branched block copolymers composed of PS, PMMA, PS and PMMA, PS, PMMA introduced at the 1G, 2G, and 3G generations, respectively, have also been successfully synthesized. The resulting polymers all herein synthesized were observed to have precisely controlled molecular weights and compositions and narrow molecular weight distributions ($M_w/M_n \leq 1.05$). Their expected and well-defined structures and low degrees of homogeneity were guaranteed by agreement of both observed and calculated molecular weights of the final polymers obtained at all generation stages.

Introduction

Dendrimer-like star-branched polymers have recently appeared as a new class of hyperbranched polymers.[1−4] Although they are similar in branched architecture to well-known dendrimers, these polymers are composed of high-molecular-weight polymer chains between the junction points and accordingly, much higher in molecular weight and much larger in molecular size than dendrimers. Dendrimer-like star-branched polymers are recognized as nano-ordered three-dimensional globular macromolecules from their hyperbranched architectures and some analytical results, and they have many characteristic structural features such as hierarchic hyperbranched structures, generation-based radial architectures, different branch densities between core and outermost layer, and many junctures and end-groups. Furthermore, in contrast to linear polymers, they are expected to behave as individual entities in solution and in bulk like dendrigraft polymers.[5−7] Some block copolymers with the same branched architectures obtained by introducing different polymer segments at each generation have also been synthesized. Their different polymer segments may be phase-separated at molecular level, followed by self-organizing, to generate nanosize ordered suprastructures and supramolecular assemblies quite different from those produced from linear block copolymers and even asymmetric star-branched polymers because of the above-mentioned structural features. In fact, some interesting morphologies and nanostructured materials have been so far reported, although most studies have been at preliminary stages.[8−18] Thus, dendrimer-like star-branched polymers and block copolymers are promising specialty functional materials with many potential applications especially in the fields of nano science and technology.

Similar to the dendrimer syntheses in organic chemistry, the syntheses of dendrimer-like star-branched polymers have been carried out by the “core-first” divergent and “arm-first” convergent methodologies using living polymers as building blocks. In the “core-first” divergent methodology,[8−14,19−21] typically, an appropriate monomer is first polymerized with a multifunctional initiator in a living/controlled manner and then, each of the propagating chain-ends is modified to convert to two or more initiation sites. The two reaction steps, i.e., living/controlled polymerization and chain-end modification, are repeated to construct the dendrimer-like star-branched polymers. Thus, an initiation procedure is employed to prepare branch segments. Although defined structures of the resulting polymers are suggested in most cases, there always remains a question on the uniformity of all polymer segments propagated from multi-initiation sites especially at high generations. Moreover, it is difficult to determine how many initiation sites do really work. In the “arm-first” convergent methodology,[15,17,18,22−25] the parts of dendrimer-like star-branched polymer, so-called dendron in

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dendrimer chemistry, are first prepared by using premade living polymers. Then, the dendrons are linked with a multifunctional core compound to build up the dendrimer-like star-branched polymers. Thus, a termination procedure using premade living polymers is used for the introduction of branch segments in both the dendrons and dendrimers. Therefore, the well-defined structures of the resulting polymers are readily checked by comparing the molecular weights of the final polymers with those calculated from the molecular weights of the starting premade living polymers. However, the synthesis of higher generation polymers by this methodology seems difficult because the linking reaction among higher-molecular-weight dendrons is required at the final stage.

Several dendrimer-like star-branched polymers and block copolymers have been synthesized so far by the above-mentioned two methodologies, but most of the synthetic examples are limited to the 3G stages and 10^5 orders in molecular weight because of experimental difficulties using high-molecular-weight polymers as building blocks. Very recently, the synthesis of 7G dendrimer-like star-branched polystyrene by the "core-first" divergent methodology has been reported, but there is no description on the uniformity of the branch segments.[26] For such situations, the synthesis of high-generation and high-molecular-weight dendrimer-like star-branched polymers with well-defined and characterized structures is still a big challenging subject even at the present time.

In order to synthesize high-generation and high-molecular-weight polymers, we have been developing, for a recent few years, a new iterative methodology which is based on an *"arm-first" divergent approach* having both the advantages of the above-mentioned methodologies.[16,27−32] In this methodology, the termination procedure using premade living anionic polymers is used to introduce branch segments like the case of "arm-first" convergent methodology mentioned above. Accordingly, the structures of the resulting polymers are checked by comparing the molecular weights of the final polymers with those calculated from the molecular weights of premade living polymers and guaranteed by agreement between the both molecular weights. Basically, only two reaction steps are needed for the entire iterative synthetic sequence: (1) a linking reaction of the living anionic polymer α-functionalized with two 3-*tert*-butyldimethylsilyloxymethylphenyl (SMP) groups with either a core compound with four benzyl bromide (BnBr) functions or chain-end-BnBr-functionalized polymer and (2) a transformation reaction of the SMP groups into BnBr functions. The two reactions are corresponding to the introduction of branches and chain-end modification leading to the next introduction, respectively. By repeating the reaction sequence involving the two reaction steps, dendrimer-like star-branched polymers are stepwise synthesized. Since heterogeneous initiation and propagation from multi-initiation sites and linking reaction among high-molecular-weight dendrons in the above-mentioned two methodologies are completely avoided, it may be possible to synthesize high-generation and high-molecular-weight polymers with well-defined structures. In fact, a series of well-defined dendrimer-like star-branched poly(methyl methacrylate)s (PMMA)s up to 7G have been successfully synthesized. Their expected and well-defined structures were confirmed by agreement of the molecular weights calculated and observed of the final polymers obtained at all generation stages. The 7G polymer was a huge macromolecule possessing a M_w value of 2×10^6 g/mol ($M_w/M_n = 1.02$) and consisting of 508 PMMA with 512 termini.[28]

To the best of our knowledge, this methodology, based on "arm-first" divergent approach, is probably the most reliable procedure at the moment for the synthesis of high-generation and high-molecular-weight dendrimer-like star-branched polymers with well-defined structures. However, the controversial point of this methodology is that the living anionic polymer amenable to the iterative process is limited only to living anionic PMMA. Very unfortunately, living anionic polystyrene (PS) of the most representative living polymer cannot be used in the iterative process of the methodology because of the practical difficulty in experimental performance which will be mentioned later. Therefore, we report herein on an alternative methodology which is applicable to the synthesis of high-generation, high-molecular-weight dendrimer-like star-branched (PS)s with well-defined structures.

Experimental Section

Materials. All chemicals (>98% purities) were purchased from Aldrich, Japan, and used as received unless otherwise stated. $(C_4H_9)_4NF$ (1.0 M solution in THF), CBr_4 (Tokyo Kasei Kogyo Co., Ltd., Japan), PPh_3, $(CH_3)_3SiBr$ (Tokyo Kasei Kogyo Co., Ltd., Japan), 3-*tert*-butyldimethylsiloxy-1-propyllithium (0.8 M solution in cyclohexane, FMC Co., Ltd.), and *sec*-BuLi (1.3 M solution in cyclohexane) were used without purification. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), 1,1-diphenylethylene (DPE), styrene, methyl methacrylate (MMA), *tert*-butylbenzene, THF, chloroform, acetonitrile, $(CH_3)_3SiCl$, LiCl, and LiBr were purified according to the reported procedures described elsewhere.[33,34] 1,1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) and 1,1,4,4-tetrakis (3-bromomethylphenyl)butane (**2**) used as a core compound were synthesized according to our procedures previously reported.[28,35]

Measurements. Size exclusion chromatography (SEC) and right angle laser light scattering (RALLS) were performed on an Ashahi Techneion Viscotek Model 302 TDA with triple detector software. The d*n*/d*c* values were automatically measured by this instrument. They were also separately measured with an Otsuka Electronics DMR-1020 refractometer operating at 633 nm in order to make sure the values. THF was used as an eluent at a flow rate of 1.0 mL/min at 30 °C. Three polystyrene columns (pore size (bead size): 650 Å (9 μm), 200 Å (5 μm), 75 Å (5 μm)) were used. Calibration curve was made with standard PS samples for determining M_n and M_w/M_n values. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a BRUKER DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $CDCl_3$ (δ 7.26 for ^{1}H NMR and δ 77.1 for ^{13}C NMR).

Synthesis of 1G PS with a 3-(*tert*-Butyldimethylsiloxy)propyl (TBDMSOP) Terminus at Each Chain-End (4-Arm Star-Branched PS), 1G-Si. All the polymerizations and linking reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors equipped with break-seals. All reactors were prewashed with red-colored 1,1-diphenylhexyllithium (*ca.* 0.05 M) in heptane after being sealed off from a vacuum line and used.

The 1G polymer, **1G-Si**, was synthesized by the linking reaction of **2** with the α-functionalized living anionic polystyrene that was prepared by the polymerization of styrene with 3-*tert*-butyldimethylsiloxy-1-propyllithium (TBDMSOPLi), followed by end-capping with DPE. The procedure is as follows: Styrene (40.3 mmol) in *tert*-butylbenzene solution (18.3 mL) was polymerized with TBDMSOPLi (0.482 mmol) in heptane solution (4.30 mL) in the presence of TMEDA (1.78 mmol) in heptane solution (3.40 mL) at 0 °C for 0.5 h and at 25 °C for additional 2 h. After the reaction mixture was cooled to −78 °C, THF (29.1 mL) was added, and subsequently, DPE (0.525 mmol) in THF solution (1.40 mL) was added for end-capping. Then, **2** (0.101 mmol, 0.404 mmol for BnBr moiety) in THF solution (1.70 mL) was added *in situ* to the resulting living PS solution at −78 °C. The reaction mixture was allowed to react at −78 °C for 0.5 h, terminated with degassed methanol, and poured into a large amount of methanol to precipitate the polymers. The objective linked polymer was isolated in 83% yield by fractional precipitation using cyclohexane and hexane at 5 °C. The α-functionalized PS used in excess in the reaction was recovered from the supernatant solution. The isolated 1G polymer (a 4-arm star-branched PS), **1G-Si**, was purified by reprecipitation from its THF solution to methanol and freeze-drying from its absolute benzene solution. ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 3.46 (s, $-CH_2-O-Si$), 2.4−1.1 (m, $-CH_2-CH-$), 0.86 (s, $-C(CH_3)_3$), 0.01 (s, $Si(CH_3)_2$).

Synthesis of 1G PS with a 3-Bromopropyl Terminus at Each Chain-End (Total of Four 3-Bromopropyl Termini), 1G-Br. The brominated 1G polymer, **1G-Br**, was prepared by treatment of **1G-Si** with $(C_4H_9)_4NF$, followed by reaction with CBr_4 and PPh_3. Under nitrogen, **1G-Si** (0.880 g, 0.0893 mmol for TBDMSOP group) dissolved in THF (20 mL) was mixed with $(C_4H_9)_4NF$ (4.47 mmol) in THF solution (4.47 mL) at 0 °C. The reaction mixture was allowed to stir at 25 °C for 24 h. After quenching with a small amount of water, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. It was purified by reprecipitation twice from THF to methanol and freeze-drying from its absolute benzene solution (0.84 g, 96%). ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 3.47 (s, $-CH_2-OH$), 2.4−1.1 (m, $-CH_2-CH-$).

Under nitrogen, the resulting polymer (0.84 g) dissolved in THF (20 mL) was mixed with CBr_4 (1.41 g, 4.25 mmol) and PPh_3 (1.12 g, 4.27 mmol) at 0 °C. The reaction mixture was allowed to stir at 25 °C for 12 h. After quenching with a small amount of water, the reaction mixture was poured into methanol to precipitate the polymer. It was purified by reprecipitation twice from THF to methanol and freeze-drying from its absolute benzene solution. The 1G PS with 3-brompropyl terminus at each chain-end, **1G-Br**, was obtained in 97% yield (0.81 g). ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 3.24 (s, $-CH_2-Br$), 2.4−1.1 (m, $-CH_2-CH-$).

Synthesis of 1G PS with Two BnBr Termini at Each Chain-End, 1G-Br$_2$. The title polymer, **1G-Br$_2$**, was prepared by the reaction of **1G-Br** with the functionalized DPE-derived anion obtained from *sec*-BuLi and **1**, followed by treatment with $(CH_3)_3SiBr$. The procedure is as follows: Under high-vacuum conditions, the functionalized anion was prepared by reacting of *sec*-BuLi (0.277 mmol) in heptane solution (4.20 mL) with **1** (0.406 mmol) dissolved in THF (7.30 mL) at −78 °C for 0.5 h. Then, the above-synthesized **1G-Br** (0.810 g, 0.0822 mmol for TBDMSOP group) dissolved in THF (13.5 mL) was added to the DPE-derived anion with stirring at −78 °C and the reaction was continued for an additional 1 h. The reaction mixture was poured into a large amount of methanol to precipitate the polymer. It was purified by reprecipitation twice from THF to methanol and freeze-drying from its absolute benzene solution (0.670 g, 83% yield). ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 4.67 (s, $Ph-CH_2$-O-Si), 2.4−1.1 (m, $-CH_2-CH-$), 0.90 (s, $-C(CH_3)_3$), 0.7−0.4 (m, $-CH(CH_3)-CH_2-CH_3$), 0.03 (s, $Si(CH_3)_2$).

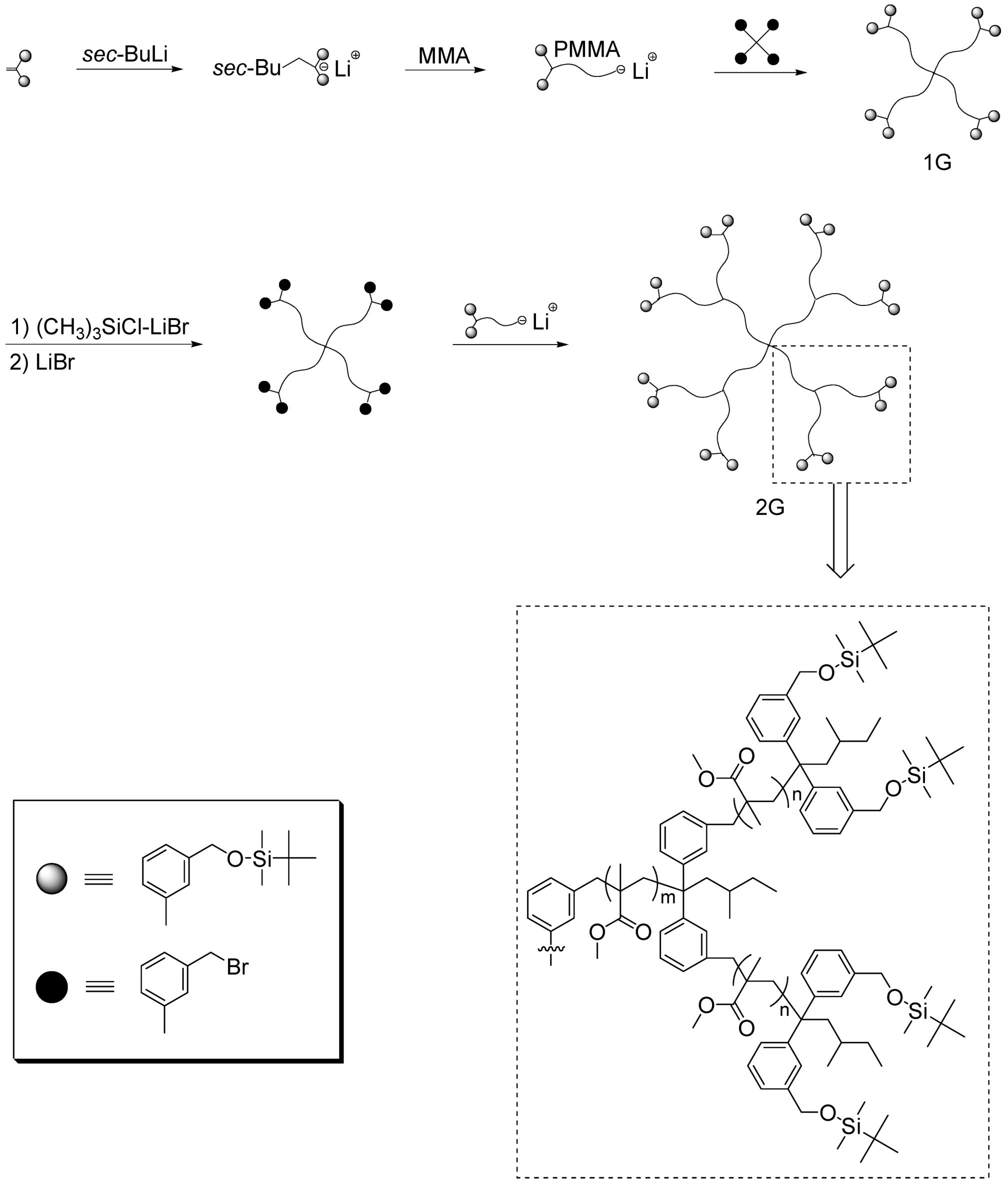
Under nitrogen, the resulting polymer (0.670 g, 0.136 mmol for SMP group) dissolved in a mixed solvent of acetonitrile (15 mL) and chloroform (60 mL) was added to $(CH_3)_3SiBr$ (1.04 mL, 6.80 mmol) at 0 °C and the reaction mixture was allowed to react at 40 °C for 24 h. After quenching with a small amount of water, the reaction mixture was poured into methanol to precipitate the polymer. The resulting polymer was purified by reprecipitation twice from THF to methanol and freeze-drying from its absolute benzene solution. The expected 1G PS with two BnBr termini (total eight BnBr termini), **1G-Br$_2$**, was obtained in 86% yield (0.580 g). ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 4.43 (s, $Ph-CH_2-Br$), 2.4−1.1 (m, $-CH_2-CH-$), 0.7−0.4 (m, $-CH(CH_3)-CH_2-CH_3$).

Synthesis of 2G Dendrimer-Like Star-Branched PS with TBDMSOP Terminus at Each Chain-End (Total Eight TBDMSOP Termini), 2G-Si. The title 2G polymer, **2G-Si**, was synthesized by the linking reaction of **1G-Br$_2$** with α-TBDMSOP-functionalized PSLi end-capped with DPE. Under high-vacuum conditions, styrene (15.2 mmol) in *tert*-butylbenzene solution (6.90 mL) was polymerized with TBDMSOPLi (0.170 mmol) in heptane solution (4.70 mL) in the presence of TMEDA (0.536 mmol) at 0 °C for 0.5 h and at 25 °C for additional 2 h. The resulting living PS solution was cooled to −78 °C, followed by addition of THF (8.80 mL), and subsequently, DPE (0.215 mmol) in THF solution (5.80 mL) was added to end-cap the chain-end anion. Then, **1G-Br$_2$** (0.580 g, 0.118 mmol for BnBr function) dissolved in THF (9.70 mL) was added to the resulting end-capped living PS solution and the reaction mixture was allowed to react at −78 °C for 0.5 h. The reaction mixture was poured into a large amount of methanol to precipitate the polymers. The linked polymer eluted at the higher molecular weight side was isolated by fractional precipitation using a mixture of cyclohexane and hexane at 5 °C, purified by reprecipitation from THF to methanol, and freeze-drying from its absolute benzene solution. The objective 2G dendrimer-like star-branched PS with TBDMSOP terminus at each chain-end (total eight TBDMSOP termini), **2G-Si**, was obtained in 77% yield. ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 3.46 (s, $-CH_2-O-Si$), 2.4−1.1 (m, $-CH_2-CH-$), 0.86 (s, $-C(CH_3)_3$), 0.01 (s, $-Si(CH_3)_2$).

Synthesis of 3G, 4G, and 5G Dendrimer-Like Star-Branched (PS)s with a TBDMSOP Terminus at Each Chain-End (Total of 16, 32, and 64 TBDMSOP Termini), 3G-Si, 4G-Si, and 5G-Si. The title 3G, 4G, and 5G polymers were synthesized by repeating the same reaction sequence involving the three reaction steps under the conditions similar to those mentioned above. The three reactions are as follows: (1) the bromination of TBDMSOP terminus to 3-bromopropyl group in each chain-end, (2) the introduction of two BnBr functions *via* 3-bromopropyl group in each chain-end, and (3) the linking reaction between the terminal benzyl brominated PS and α-TBDMSOP-functionalized PSLi end-capped with DPE. The ^{1}H NMR spectra of all polymers are as follows: ^{1}H NMR, **2G-Br**: δ 7.2−6.2 (m, aromatic), 3.24 (s, $-CH_2-Br$), 2.4−1.1 (m, $-CH_2-CH-$), **2G-Si$_2$**: δ 7.2−6.2 (m, aromatic), 4.68 (s, $Ph-CH_2-O-Si$), 2.4−1.1 (m, $-CH_2-CH-$), 0.91 (s, $-C(CH_3)_3$), 0.7−0.4 (m, $-CH(CH_3)-CH_2-CH_3$), 0.03 (s, $Si(CH_3)_2$), **2G-Br$_2$**: δ 7.2−6.2 (m, aromatic), 4.43 (s, $Ph-CH_2-Br$), 2.4−1.1 (m, $-CH_2-CH-$), 0.7−0.4 (m, $-CH(CH_3)-CH_2-CH_3$), **3G-Si**: δ 7.2−6.2 (m, aromatic), 3.46 (s, $-CH_2-O-Si$), 2.4−1.1 (m, $-CH_2-CH-$), 0.85 (s, $-C(CH_3)_3$), 0.01 (s, $Si(CH_3)_2$), **(3G-Br)**: δ 7.2−6.2 (m, aromatic), 3.24 (s, $-CH_2-Br$), 2.4−1.1 (m, $-CH_2-CH-$), **3G-Si$_2$**: δ 7.2−6.2 (m, aromatic), 4.67 (s, $Ph-CH_2-O-Si$), 2.4−1.1 (m, $-CH_2-CH-$), 0.90 (s, $-C(CH_3)_3$), 0.7−0.4 (m, $-CH(CH_3)-CH_2-CH_3$), 0.03 (s, $Si(CH_3)_2$), **3G-Br$_2$**: δ 7.2−6.2 (m, aromatic), 4.43 (s, $Ph-CH_2-Br$), 2.4−1.1 (m, $-CH_2-CH-$), 0.7−0.4 (m, $-CH(CH_3)-CH_2-CH_3$), **4G-Si**: δ 7.2−6.2 (m, aromatic), 3.49 (s, $-CH_2-O-Si$), 2.4−1.1 (m, $-CH_2-CH-$), 0.86 (s, $-C(CH_3)_3$), 0.01 (s, $Si(CH_3)_2$), **4G-Br**: δ 7.2−6.2 (m, aromatic), 3.23 (s, $-CH_2-Br$), 2.4−1.1 (m, $-CH_2-CH-$), **4G-Si$_2$**: δ 7.2−6.2 (m, aromatic), 4.67 (s, $Ph-CH_2-O-Si$), 2.4−1.1 (m, $-CH_2-CH-$), 0.90 (s, $-C(CH_3)_3$), 0.7−0.4 (m, $-CH(CH_3)-CH_2-CH_3$), 0.03 (s, $Si(CH_3)_2$), **4G-Br$_2$**: δ 7.2−6.2 (m, aromatic), 4.43 (s, $Ph-CH_2-Br$), 2.4−1.1 (m, $-CH_2-CH-$), 0.7−0.4 (m, $-CH(CH_3)-CH_2-CH_3$), **5G-Si**: δ 7.2−6.2 (m, aromatic), 3.45 (s, $-CH_2-O-Si$), 2.4−1.1 (m, $-CH_2-CH-$), 0.86 (s, $-C(CH_3)_3$), 0.01 (s, $Si(CH_3)_2$).

Synthesis of 3G Dendrimer-Like Star-Branched Block Copolymer Composed of PS, PMMA, and PS Segments Introduced at 1G, 2G, and 3G. The 1G PS with two BnBr termini at each chain-end, **1G-Br$_2$**, was prepared according to the procedures as mentioned above. Under high-vacuum conditions, MMA (19.4 mmol) in THF solution (13.4 mL) was polymerized with the functionalized DPE-derived anion prepared from *sec*-BuLi (0.243 mmol) in heptane solution (3.40 mL) and **1** (0.335 mmol) in THF solution (5.40 mL) at −78 °C for 20 min. Prior to the polymerization, LiCl (0.781 mmol) in THF solution

Scheme 1. Synthetic Outline of 1G and 2G Dendrimer-Like Star-Branched (PMMA)s

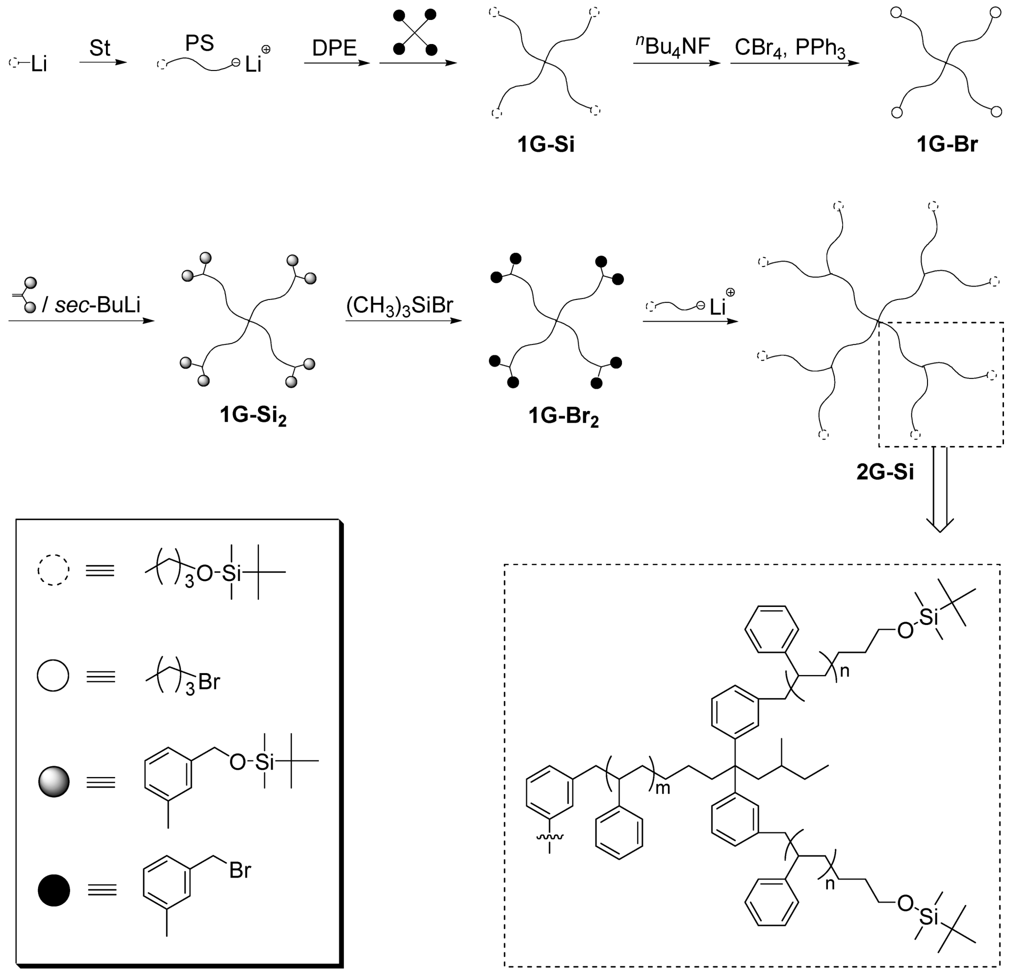


(6.30 mmol) was added at −78 °C to narrow the molecular weight distribution. The polymerization was continued for 0.5 h. Then, the **1G-Br$_2$** (0.610 g, 0.124 mmol for BnBr function) dissolved in THF (10.2 mL) was added to the resulting living PMMA solution at −78 °C and the reaction mixture was allowed to stand in THF at −40 °C for additional 24 h. After the reaction was quenched with degassed methanol, the objective 2G dendrimer-like block copolymer composed of PS (1G) and PMMA segments (2G) was isolated in 79% yield by fractional precipitation using a mixture of THF, benzene, and methanol, purified by reprecipitation twice from THF to methanol, and obtained by freeze-drying from its absolute benzene solution. ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 4.66 (s, Ph−CH_2−O−Si), 3.7−3.5 (m, −O−CH_3), 2.4−1.2 (m, −CH_2−CH− and −CH_2−C(CH$_3$)−), 1.1−0.5 (m, −CH$_2$−C(CH_3)−), 0.91 (s, −C(CH_3)$_3$), 0.05 (s, Si(CH_3)$_2$).

Under nitrogen, the SMP termini of the 2G block copolymer (1.22 g, 0.135 mmol for SMP group) were reacted with LiBr (0.590 g, 6.79 mmol) and (CH$_3$)$_3$SiCl (0.870 mL, 6.78 mmol) dissolved in a mixed solvent of acetonitrile (15 mL) and chloroform (60 mL). The reaction mixture was allowed to react at 40 °C for 24 h and quenched with a small amount of water. After the polymer was precipitated in methanol, it was purified by reprecipitation twice from THF to methanol and freeze-drying from its absolute benzene solution. Since a very small amount (< 5%) of benzyl chloride function (BnCl) (4.53 ppm) was by-produced, the polymer and LiBr (10.2 mmol) were dissolved in acetone (50 mL) and the reaction mixture was refluxed for 1 h to retransform the BnCl into BnBr function.[36] The polymer was precipitated in methanol, purified by reprecipitation twice from THF to methanol, and freeze-drying from its absolute benzene solution. The benzyl brominated polymer was obtained in 76% yield. ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 4.66 (s, Ph−CH_2−Br), 3.7−3.5 (m, −O−CH_3), 2.4−1.2 (m, −CH_2−CH− and −CH_2−C(CH$_3$)−), 1.1−0.5 (m, −CH$_2$−C(CH_3)−).

The 3G dendrimer-like star-branched block copolymer was synthesized by the linking reaction of α-TBDMSOP-functionalized PSLi end-capped with DPE with the 2G block copolymer with two BnBr termini at each chain-end as follows: Styrene (7.83 mmol) in *tert*-butylbenzene solution (3.80 mL) was polymerized with TBDMSOPLi (0.0810 mmol) in heptane solution (2.50 mL) in the presence of TMEDA (0.356 mmol) in heptane solution (1.50 mL) at 0 °C for 0.5 h and at 25 °C for additional 2 h. The living PS solution thus prepared was cooled to −78 °C, followed by addition of THF (8.60 mL), and subsequently, DPE (0.124 mmol) in THF solution (3.10 mL) was added to end-cap

Scheme 2. Synthetic Outline of 1G and 2G Dendrimer-Like Star-Branched (PS)s



the chain-end anion for 1 h. Then, the 2G benzyl brominated block copolymer (0.500 g, 0.0556 mmol for BnBr function) dissolved in THF (8.30 mL) was added to the DPE-end-capped living PS solution and the reaction mixture was allowed to react at −78 °C for 0.5 h. The reaction mixture was poured into a large amount of methanol to precipitate the polymers. The objective 3G block polymer was isolated by fractional precipitation using a mixture of cyclohexane and hexane at 5 °C, purified by reprecipitation from THF to methanol, and freeze-drying from its absolute benzene solution. The polymer was obtained in 81% yield. ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 3.7−3.5 (m, $-CH_2-O-Si$ and $-O-CH_3$), 2.4−1.2 (m, $-CH_2-CH-$ and $-CH_2-C(CH_3)-$), 1.1−0.5 (m, $-C(CH_3)_3$ and $-CH_2-C(CH_3)-$), 0.02 (s, $Si(CH_3)_2$).

Synthesis of 3G Dendrimer-Like Star-Branched Block Copolymer Composed of PMMA, PS, and PMMA Segments Introduced at 1G, 2G, and 3G. The 1G PMMA with two BnBr functions at each chain-end was prepared by procedures similar to those previously reported. Both the 2G and 3G dendrimer-like star-branched block copolymers were synthesized according to the procedures similar to those mentioned above.[27,28,32] For these syntheses, α-TBDMSOP-functionalized PSLi end-capped with DPE and α-functionalized living PMMA with two SMP groups were reacted at the 2G and 3G stages, respectively. The intermediate and objective polymers all were obtained in accordance with those designed structures. ^{1}H NMR: 2G block copolymer with TBDMSOP group at each chain-end, δ 7.2−6.2 (m, aromatic), 3.7−3.5 (m, $-CH_2-O-Si$ and $-O-CH_3$), 2.4−1.2 (m, $-CH_2-CH-$ and $-CH_2-C(CH_3)-$), 1.1−0.5 (m, $-C(CH_3)_3$) and $-CH_2-C(CH_3)-$), 0.01 (s, $Si(CH_3)_2$); 2G block copolymer with 3-bromopropyl group at each chain-end, δ 7.2−6.2 (m, aromatic), 3.7−3.5 (m, $-O-CH_3$), 3.23 (s, $-CH_2-Br$), 2.4−1.2 (m, $-CH_2-CH-$ and $-CH_2-C(CH_3)-$), 1.1−0.5 (m, $-CH_2-C(CH_3)-$); 2G block copolymer with two SMP groups at each chain-end, δ 7.2−6.2 (m, aromatic), 4.66 (s, $Ph-CH_2-O-Si$), 3.7−3.5 (m, $-O-CH_3$), 2.4−1.2 (m, $-CH_2-CH-$ and $-CH_2-C(CH_3)-$), 1.1−0.4 (m, $-CH(CH_3)-CH_2-CH_3$ and $-CH_2-C(CH_3)-$), 0.89 (s, $-C(CH_3)_3$), 0.02 (s, $Si(CH_3)_2$); 2G block copolymer with two BnBr groups at each chain-end, δ 7.2−6.2 (m, aromatic), 4.42 (s, $Ph-CH_2-Br$), 3.7−3.5 (m, $-O-CH_3$), 2.4−1.2 (m, $-CH_2-CH-$ and $-CH_2-C(CH_3)-$), 1.1−0.4 (m, $-CH(CH_3)-CH_2-CH_3$ and $-CH_2-C(CH_3)-$).

The final 3G dendrimer-like star-branched block copolymer was obtained in 75% yield. ^{1}H NMR: δ 7.2−6.2 (m, aromatic), 4.66 (s, $Ph-CH_2-O-Si$), 3.7−3.5 (m, $-O-CH_3$), 2.4−1.2 (m, $-CH_2-CH-$ and $-CH_2-C(CH_3)-$), 1.1−0.5 (m, $-CH_2-C(CH_3)-$), 0.90 (s, $-C(CH_3)_3$), 0.05 (s, $Si(CH_3)_2$).

Results and Discussion

Synthesis of 1G and 2G Dendrimer-Like Star-Branched (PS)s. Scheme 1 shows the synthetic outline of the 1G and 2G dendrimer-like star-branched (PMMA)s by our previous iterative methodology mentioned in introduction part.[27,28,32] As was seen in the first iterative process, living PMMA α-functionalized with two SMP groups reacted with the core compound having four BnBr functions, **2**, to synthesize a chain-end-SMP-functionalized 4-arm star-branched PMMA as the 1G polymer. The terminal SMP groups were then transformed into BnBr functions used as the next reaction sites by treatment with $(CH_3)_3SiCl$-LiBr. In the second iteration, the brominated 1G polymer reacted with living PMMA α-functionalized with two SMP groups to synthesize the 2G dendrimer-like star-branched PMMA.

As can be seen in this scheme, the α-SMP-functionalized living PMMA plays a key role as a reactive prepolymer for the preparation of arm segments composed of each generation. The simultaneous introduction of two SMP groups convertible to two BnBr functions is also essential for continuing the next reaction step. This key living polymer is obtained by the anionic polymerization of MMA with the DPE-derived anion prepared by the 1:1 addition reaction of *sec*-BuLi with **1**. In general, a 1.5-fold or more excess of **1** toward *sec*-BuLi is employed to completely yield the anion. Importantly in the subsequent polymerization, an excess unreacted **1** has no influence on the anionic polymerization of MMA at all because **1** is too low in reactivity to react with the propagating chain-end enolate anion and intact during and even after the polymerization.

In contrast to the polymerization of MMA, the presence of an excess **1** is very problematic in the anionic polymerization of styrene, since **1** readily reacts with the propagating chain-end styrylanion to incorporate in the PS chain. Accordingly, the SMP groups are introduced not only at the objective α-terminal chain-end, but also randomly into the PS chain. However, when more than the stoichiometric amount of *sec*-BuLi is used in the reaction with **1**, nonfunctionalized living PS is produced by the polymerization of styrene with the residual *sec*-BuLi. After the transformation reaction of SMP groups into BnBr functions, either more than two or less than two PS chains is introduced at the next linking reaction step to result in the formation of ill-defined dendrimer-like star-branched (PS)s. In order to synthesize well-defined dendrimer-like star-branched (PS)s in the same manner as the case of the dendrimer-like star-branched (PMMA)s, it is essential to use the pure DPE-derived anion with precise stoichiometric control between **1** and *sec*-BuLi to prepare PS α-functionalized with two SMP groups. However, precise stoichiometric control is very difficult to be achieved in practical experimental performance, since there are unavoidable experimental errors in any of measurements (concentration and amount) of both highly reactive *sec*-BuLi and **1**, and more seriously, stoichiometric control is required for a number of times to synthesize high-generation dendrimer-like star-branched (PS)s. Thus, the previously reported methodology successful for the synthesis of well-defined dendrimer-like star-branched (PMMA)s is not directly applicable as such to the synthesis of well-defined dendrimer-like star-branched (PS)s.

In order to successfully synthesize well-defined dendrimer-like star-branched (PS)s, we have herein proposed an alternative strategy using a different functionalized anionic initiator, 3-*tert*-butyldimethylsilyloxy-1-propyllithium (TBDMSOPLi), instead of the DPE-derived anion used before. A synthetic outline for the 1G and 2G dendrimer-like star-branched (PS)s is illustrated in Scheme 2.

This new methodology is also based on "arm-first" divergent approach having the advantages mentioned above, but one more reaction step is added as an extra end-functionalization reaction to avoid the 1:1 addition reaction that requires precise stoichiometric control between **1** and *sec*-BuLi. At first, styrene was polymerized with TBDMSOPLi as an initiator in *tert*-butylbenzene at 0 °C for 0.5 h and 25 °C for additional 2 h. In this polymerization, the addition of a 3-fold or more excess TMEDA prior to the polymerization was needed to narrow the molecular weight distribution. The resulting α-terminal TBDMSOP-functionalized living PS, after addition of an equal volume of THF at −78 °C, was end-capped with DPE and subsequently reacted *in situ* with **2** at −78 °C. As shown in Figure 1a, the SEC profile of the reaction mixture exhibits two sharp peaks corresponding to the linked product and the deactivated α-TBDMSOP-functionalized

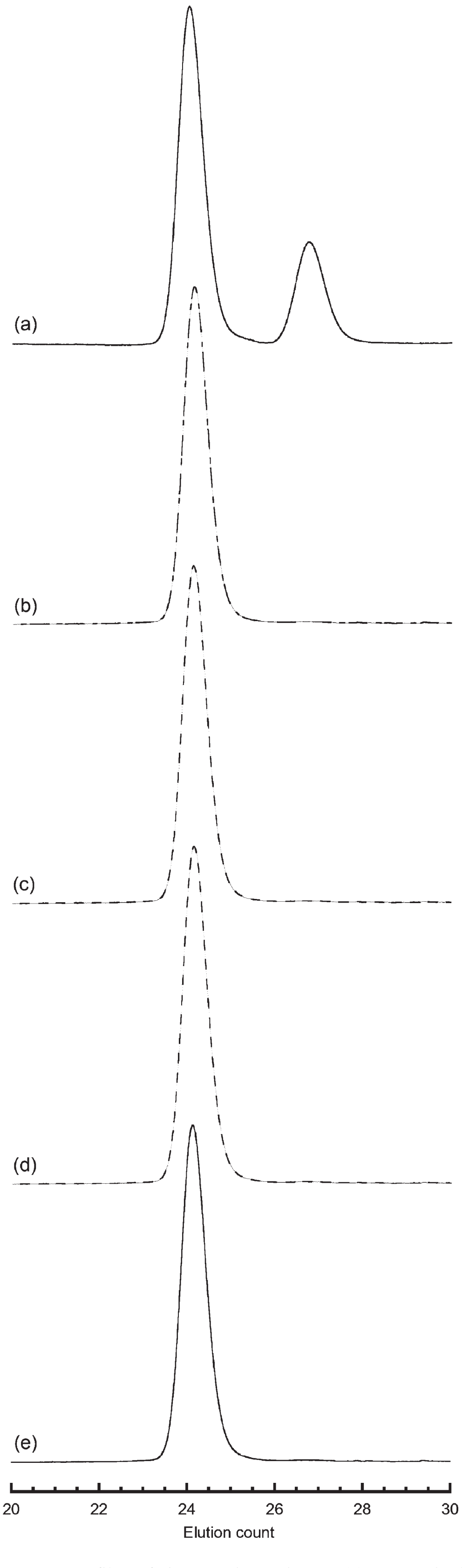


Figure 1. SEC profiles of the reaction mixture (a), **1G-Si** isolated by fractional precipitation (b), **1G-Br** (c), **1G-Si$_2$** (d), and **1G-Br$_2$** (e).

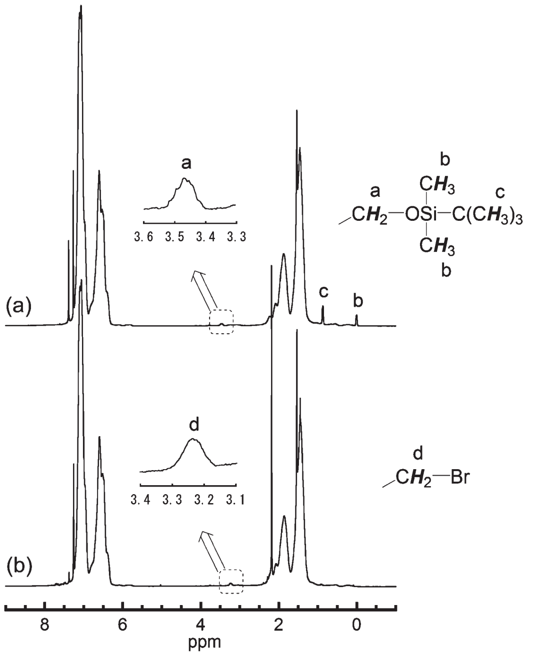


Figure 2. ^{1}H NMR spectra of **1G-Si** (a) and **1G-Br** (b).

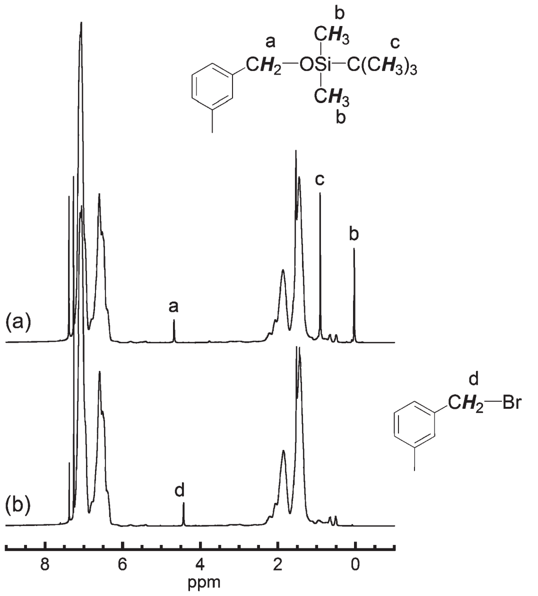


Figure 3. ^{1}H NMR spectra of **1G-Si$_2$** (a) and **1G-Br$_2$** (b).

living PS used in excess in the reaction. The reaction efficiency was found to be almost quantitative by comparing the two peak areas. The objective polymer was isolated in 83% yield by fractional precipitation. The isolated polymer possessed a narrow monomodal SEC distribution, the M_w/M_n value being 1.03 (see Figure 1b). The M_n value (34.7 kg/mol) estimated by SEC was somewhat lower than that calculated (39.7 kg/mol) as expected from its star-branched architecture. On the other hand, both M_n and M_w values determined by ^{1}H NMR and SEC−RALLS are in good agreement with those calculated as listed in Table 1. The ^{1}H NMR spectrum clearly shows three characteristic resonances at 3.46, 0.86, and 0.01 ppm assignable to the Si−O−CH$_2$ protons and Si−CH$_3$ and C−CH$_3$ protons of the *tert*-butyldimethylsilyl group with reasonable intensities (see Figure 2a). Thus, the expected 4-arm star-branched PS with TBDMSOP terminus at each chain-end (total four TBDMSOP termini) was successfully synthesized. Although the resulting polymer is not a dendrimer-like star-branched PS in architecture, it corresponds to the 1G polymer in this synthesis and is referred to as **1G-Si**.

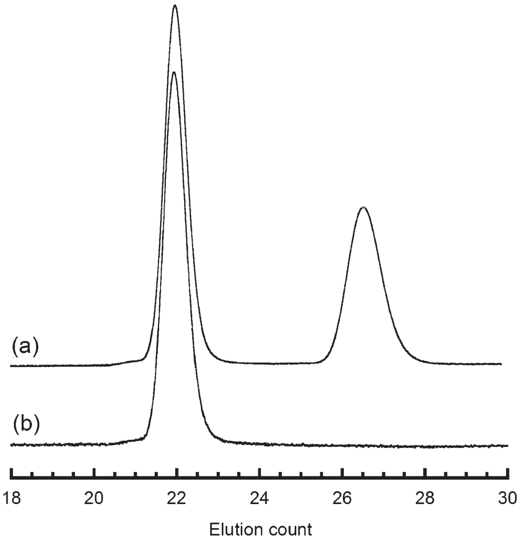


Figure 4. SEC profiles of the reaction mixture (a) and **2G-Si** isolated by fractional precipitation (b).

The TBDMSOP termini were deprotected with $(C_4H_9)_4NF$ in THF and subsequently brominated by treatment with CBr$_4$ and PPh$_3$ in THF. The resulting polymer was purified by reprecipitation twice and freeze-drying and characterized by SEC and ^{1}H NMR, respectively. The SEC profiles of the two polymers after the reactions were observed to be almost identical with those before the reactions in shape and molecular weight. The complete conversion to the bromide was confirmed by the ^{1}H NMR analysis showing that the above-mentioned three resonances at 3.46, 0.86, and 0.01 ppm had completely disappeared and instead a new resonance at 3.24 ppm corresponding to BrCH$_2$ protons of the 3-bromopropyl termini is observed (see Figure 2b).

The brominated 4-arm star-branched PS thus synthesized was reacted with the DPE-derived anion prepared from a 1.5-fold excess of **1** and *sec*-BuLi in THF at −78 °C to introduce two SMP groups at each chain-end (total eight SMP groups). The SEC profile of the polymer obtained after the reaction showed a sharp monomodal distribution almost identical with the brominated polymer as well as the starting **1G-Si** (see Figure 1c). As can be seen in the ^{1}H NMR spectrum shown in Figure 3a, the resonance at 3.24 ppm observed in Figure 2b had completely disappeared, while the resonances at 4.67, 0.90, and 0.03 ppm assigned to the silyloxy benzyl methylene protons, and C−CH$_3$ and Si−CH$_3$ protons of the *tert*-butyldimethylsilyl groups newly appear with the expected intensities. Thus, the two SMP groups could be quantitatively introduced at the polymer chain-ends *via* 3-bromopropyl termini by the reaction with the DPE-derived anion. The polymer, referred to as **1G-Si$_2$**, was then treated with $(CH_3)_3SiBr$ in a mixture of acetonitrile and chloroform (1/4, *v*/*v*) at 40 °C for 24 h to transform the SMP groups into BnBr functions. The ^{1}H NMR analysis shown in Figure 3b clearly indicates the quantitative transformation into BnBr function by the complete disappearance of the above-mentioned three characteristic resonances at 4.67, 0.90, and 0.03 ppm and a new resonance observed at 4.43 ppm which is characteristic of the benzyl bromide methylene protons. The polymer showed a sharp monomodal

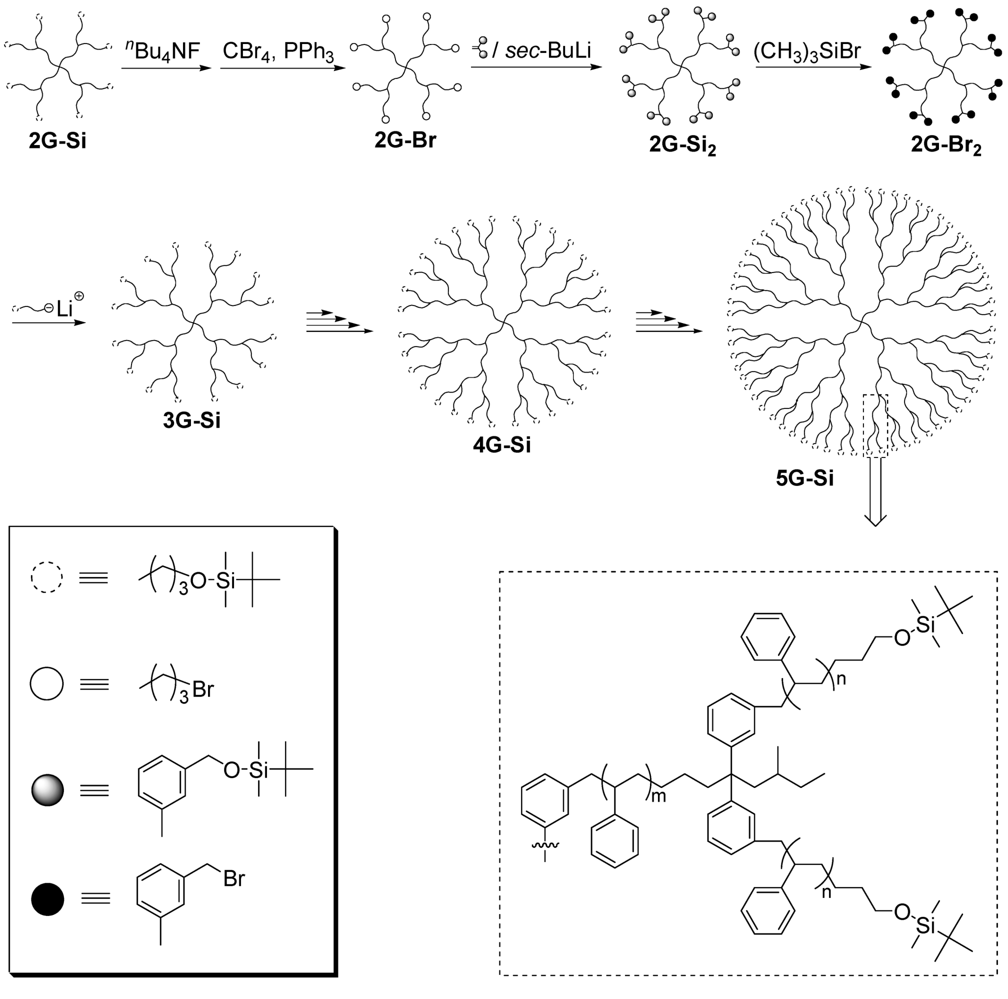
Table 1. Synthesis of Dendrimer-Like Star-Branched (PS)s, 1G to 2G

	$M_n \times 10^{-3}$ (g/mol)				$M_w \times 10^{-3}$ (g/mol)		
polymer generation	calcd	SEC	^{1}H NMR	RALLS	calcd	RALLS	M_w/M_n
1G	39.7	34.7	39.5	39.3	40.5	39.4	1.02
2G	113	102	123	127	116	128	1.03

Table 2. Synthesis of Dendrimer-Like Star-Branched (PS)s, 3G to 5G

	$M_n \times 10^{-3}$ (g/mol)				$M_w \times 10^{-3}$ (g/mol)		
polymer generation	calcd	SEC	^{1}H NMR	RALLS	calcd	RALLS	M_w/M_n
3G	305	209	300	305	320	311	1.05
4G	688	314	667	669	722	704	1.05
5G	1730	542	1800	1800	1820	1880	1.05

Scheme 3. Synthetic Outline of 3G, 4G, and 5G Dendrimer-Like Star-Branched (PS)s



SEC distribution very similar in shape and molecular weight to those of the starting **1G-Si$_2$** (see parts d and e of Figure 1). Thus, the end-functionalization from one 3-bromopropyl group to two BnBr functions at each PS chain-end was successfully performed and the polymer thus obtained is referred to as **1G-Br$_2$**.

A new α-TBDMSOP-functionalized living PS end-capped with DPE was prepared in a similar manner, followed by addition of an equal amount of THF at −78 °C, and subsequently reacted *in situ* with the above-prepared **1G-Br$_2$**. The SEC profile of the reaction mixture exhibits two distinct peaks for the linked polymer and the deactivated α-functionalized living PS used in excess in the reaction (see Figure 4a). The reaction efficiency was observed to be almost quantitative by comparing the two peak areas. The objective polymer was isolated in 77% yield by fractional precipitation (see Figure 4b) and characterized by ^{1}H NMR, SEC, and SEC−RALLS, respectively. The results are also listed in Table 1. As can be seen, the resulting polymer possesses well-controlled molecular weights in agreement with those calculated and a narrow molecular weight distribution. These characterization results clearly indicate that the linking reaction of **1G-Br$_2$** with α-TBDMSOP functionalized living PS end-capped with DPE quantitatively undergoes as desired to afford the 2G polymer with well-defined and expected structures. The resulting polymer is the 2G dendrimer-like star-branched PS and referred to as **2G-Si**.

The new methodology herein proposed works satisfactorily to successfully synthesize the 1G and 2G dendrimer-like star-branched (PS)s by adding one more extra end-functionalization reaction to introduce two BnBr termini at each chain-end. As the methodology is based on “arm-first” divergent approach as can be seen in Scheme 2, the resulting 1G and 2G polymers are guaranteed in structure by good agreement of the molecular weights between observed and calculated in each of both the polymers. Since it has been demonstrated that the three reaction steps, i.e., the linking and two end-functionalization reactions, proceeded cleanly and quantitatively as mentioned above, the same reaction sequence involving the three reaction steps will be repeated to successively synthesize higher generation polymers.

Successive Synthesis of the Third-, Fourth-, and Fifth-Generation (3G, 4G, and 5G) Dendrimer-Like Star-Branched (PS)s. The synthetic outline for the 3G and 4G, followed by 5G dendrimer-like star-branched (PS)s is illustrated in Scheme 3. By using the 2G polymer, **2G-Si**, as a starting material, the two end-functionalization and linking reactions were again carried out in the iterative process. The TBDMSOP termini of **2G-Si** were brominated by treatment with $(C_4H_9)_4NF$, followed by reacting with CBr_4 and PPh_3 under the same conditions. The reactions were followed by ^1H NMR, SEC, and SEC−RALLS, respectively, and found to proceed quantitatively to afford the brominated 2G polymer, **2G-Br**. Then, two BnBr functions at each chain-end were introduced by the reaction of the **2G-Br** with the DPE-derived anion prepared from **1** and *sec*-BuLi and subsequent bromination with $(CH_3)_3SiBr$. Finally, the linking reaction of the 2G polymer with two BnBr termini at each chain-end, **2G-Br₂**, with α-TBDMSOP-functionalized PSLi end-capped with DPE was carried out under the same conditions as the case of **2G-Si**. The SEC profile of the polymer, after the isolation by fractional precipitation, exhibits a sharp monomodal distribution. The resulting polymer possesses the observed molecular weights consistent with the predictable values and a narrow molecular weight distribution as listed in Table 2.

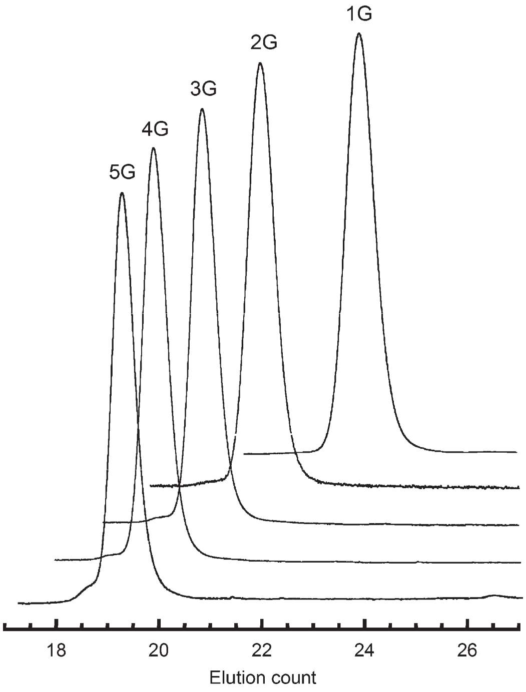


Figure 5

Thus, the 3G dendrimer-like star-branched PS with well-defined structures, **3G-Si**, was successfully synthesized. Needless to say, the three reaction steps in the iterative process proceeded cleanly and quantitatively, similar to those in the iterative processes mentioned in the preceding section.

By using the **3G-Si** as a starting material, the same reaction sequence was sequentially repeated two more times in order to synthesize the 4G and 5G dendrimer-like star-branched (PS)s. The reactions and the intermediate polymers were monitored by SEC and SEC−RALLS in molecular weight distribution and molecular weight and by ^1H NMR in terminal group structure. As listed in Table 2, all the polymers were observed to have precisely controlled molecular weights and narrow molecular weight distributions. Thus, the successive synthesis of a series of dendrimer-like star-branched (PS)s going from 1G to 5G has been quite successful by developing the new methodology illustrated in Schemes 2 and 3. As often mentioned, the well-defined structures of all the polymers synthesized by this methodology could be completely guaranteed by good agreement of their molecular weights between calculated and observed. The SEC profiles of all the polymers from **1G-Si** to **5G-Si** are shown in Figure 5 to compare their shapes and molecular weights. As you can see, sharp and monomodal distributions are observed in all of the samples and the molecular weight increases as increasing the generation as expected. The final 5G polymer, **5G-Si**, has also the terminal TBDMSOP group at each chain-end (total of 64 TBDMSOP termini); the same reaction sequence can be repeated to further synthesize higher generation polymers. The excellence of the new methodology herein proposed is thus obvious.

Hutchings and Roberts-Bleming previously reported the successful synthesis of a similar 3G dendrimer-like star-branched PS consisting of 21 PS segments (M_n = 284 900 g/mol, M_w/M_n = 1.05) by the “arm-first” convergent methodology.[24] However, the objective, the 3G polymer, was formed only in less than 50% yield because the inefficient

Table 3. Synthesis of Dendrimer-Like Star-Branched Block Copolymers, P(S-*b*-MMA₂-*b*-S₄)₄ and P(MMA-*b*-S₂-*b*-MMA₄)₄

	$M_n \times 10^{-3}$ (g/mol)				$M_w \times 10^{-3}$ (g/mol)		M_w/M_n	composition (wt %)	
polymer generation	calcd	SEC	^1H NMR	RALLS	calcd	RALLS		calcd	^1H NMR
				PS/PMMA/PS					
1G	39.7	34.7	39.5	39.3	40.5	39.4	1.02	100/0/0	100/0/0
2G	130	87.7	122	144	134	145	1.03	29/71/0	31/69/0
3G	284	176	284	276	295	278	1.04	13/33/54	13/29/58
				PMMA/PS/PMMA					
1G	40.8	35.2	40.0	43.5	41.6	43.6	1.02	100/0/0	100/0/0
2G	112	84.7	121	117	115	123	1.03	36/64/0	33/67/0
3G	281	168	295	288	289	291	1.03	15/25/60	13/28/59

linking reaction among high molecular weight precursor polymers as a final step was required in this methodology as mentioned in the Introduction. This means that, although the pure product can be obtained in 7% yield by fractionation, the further synthesis of higher generation polymers seems to be very difficult.

Synthesis of Two Dendrimer-Like Star-Branched Block Copolymers Composed of PS, PMMA, PS and PMMA, PS, PMMA Segments Introduced at 1G, 2G, and 3G. It may be possible to synthesize the 3G dendrimer-like block copolymer composed of PS (1G), PS (2G), and PMMA (3G) by the linking reaction of living PMMA with the **2G-Br$_2$** prepared by the present methodology. Likewise, the 3G block copolymer composed of PMMA (1G), PMMA (2G), and PS (3G) can be synthesized by the linking reaction of living PS with the 2G dendrimer-like star-branched PMMA having two BnBr termini at each chain-end obtained by the previous methodology. However, the title 3G block copolymers cannot be synthesized only by using either of both the present and previous methodologies as such. As mentioned above, the big difference between the two methodologies is that one more reaction as an extra end-functionalization step in each iterative process is added in the present methodology. If living PMMA α-functionalized with two SMP groups is usable in the iterative process of the present methodology, it may be possible to synthesize the above-mentioned title dendrimer-like star-branched block copolymers composed of PS and PMMA segments.

In order to examine the possible synthesis of the dendrimer-like star-branched block copolymers by the present methodology, we have used living PMMA with two SMP groups in the iterative process to synthesize the 3G dendrimer-like star-branched block copolymers possessing PS, PMMA, and PS segments introduced at 1G, 2G, and 3G, respectively. The synthetic outline is illustrated in Scheme 4.

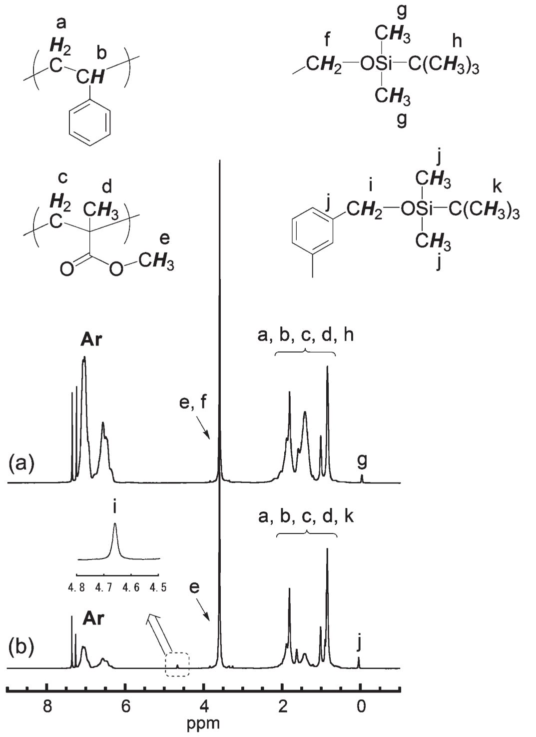
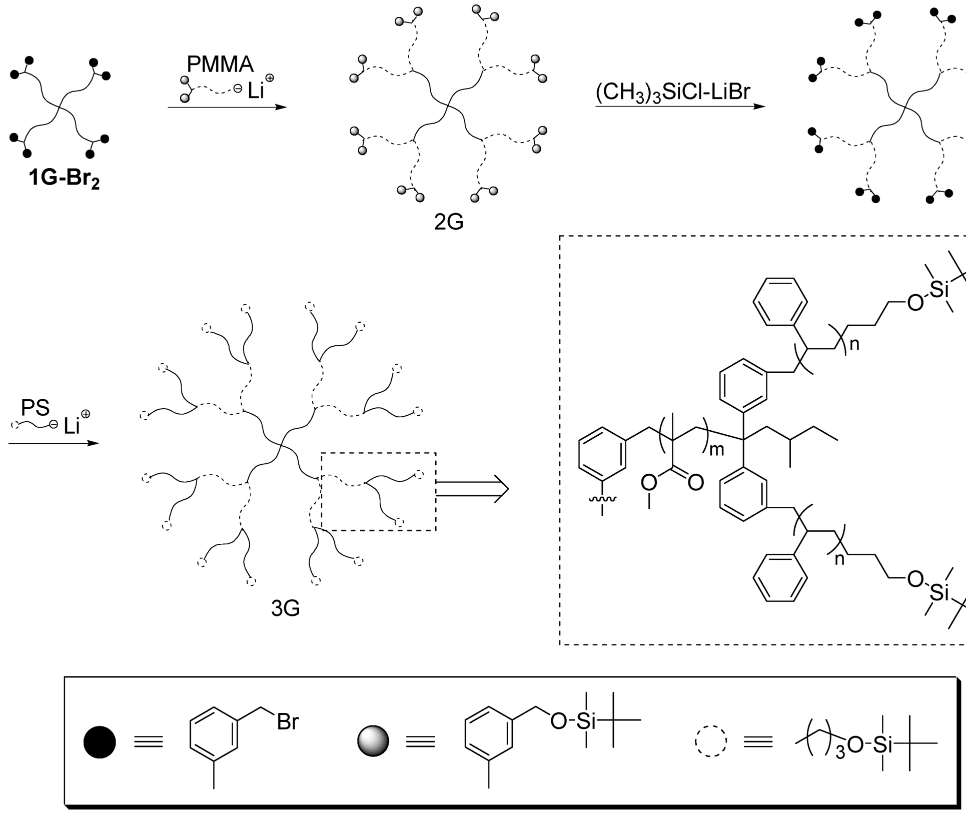
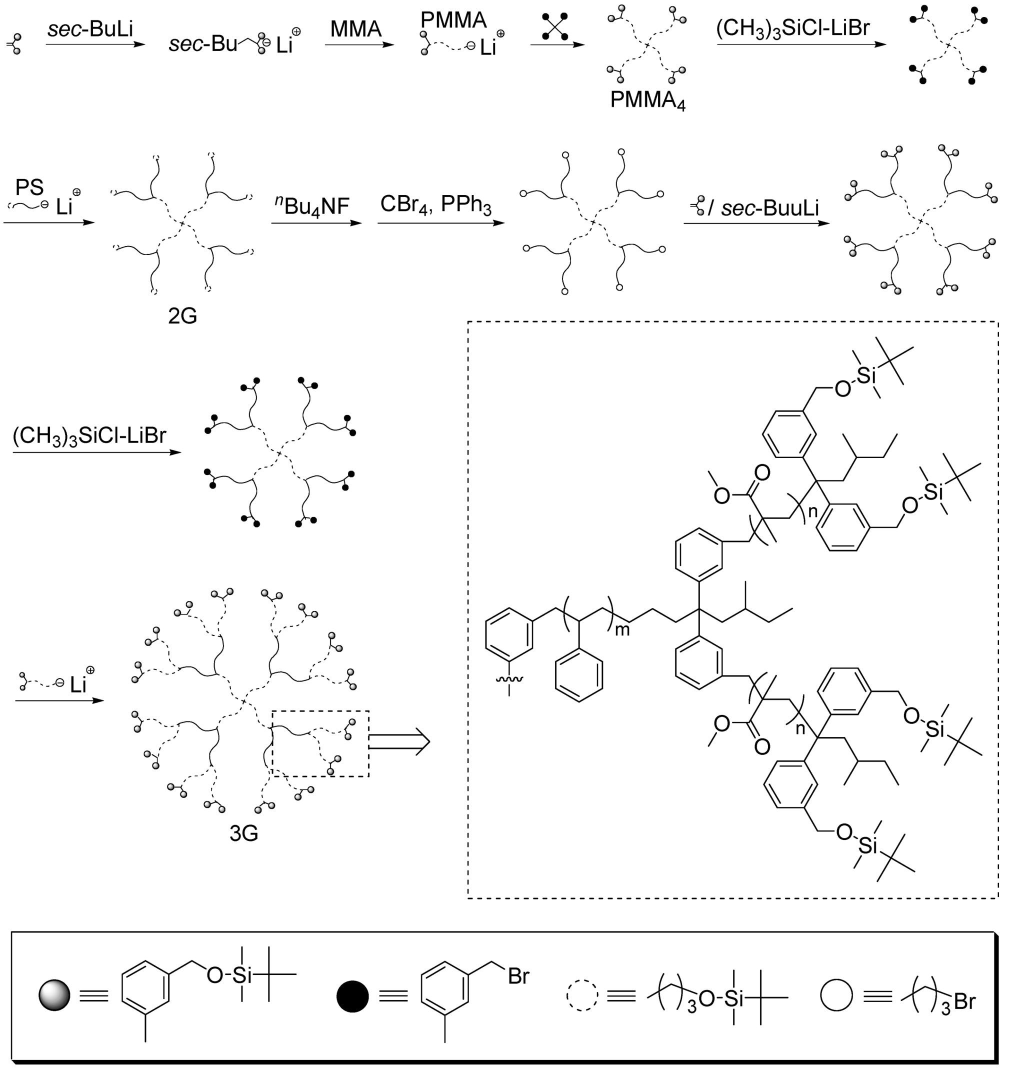


Figure 6. ^{1}H NMR spectra of 2G block copolymer composed of four PS (1G) and eight PMMA (2G) segments (a) and 3G block copolymer composed of four PS (1G), eight PMMA (2G) and 16 PS (3G) segments (b).

Scheme 4. Synthetic Outline of 1G, 2G, and 3G Dendrimer-Like Star-Branched Block Copolymers Composed of PS, PMMA, and PS Segments Introduced at 1G, 2G, and 3G



Scheme 5. Synthetic Outline of 1G, 2G, and 3G Dendrimer-Like Star-Branched Block Copolymers Composed of PMMA, PS, and PMMA Segments Introduced at 1G, 2G, and 3G



The 4-arm star-branched PS with two BnBr termini at each chain-end, **1G-Br$_2$**, was synthesized by the same procedure mentioned in the preceding section. Living PMMA α-functionalized with two SMP groups was prepared by the anionic polymerization of MMA with the DPE-derived anion from **1** and *sec*-BuLi in the presence of LiCl and reacted with the **1G-Br$_2$** in THF at −40 °C for 24 h. Under such conditions, the reaction was found to proceed quantitatively. The analytical results characterized by ^{1}H NMR, SEC, and SEC−RALLS clearly indicated that the resulting polymer was the objective 2G dendrimer-like star-branched block copolymer composed of four PS arms (1G) and eight PMMA arms (2G) as listed in Table 3. The resulting polymer was then brominated with a mixed reagent of $(CH_3)_3SiCl$ and LiBr[37] and reacted with a 1.5-fold excess of α-TBDMSOP-functionalized PSLi end-capped with DPE in THF at −78 °C. Under such conditions, the linking reaction underwent quantitatively to afford the 3G block copolymer possessing four PS (1G), eight PMMA (2G), and sixteen PS segments (3G). Fortunately and importantly, PMMA chains were stable and intact toward the excess α-TBDMSOP-functionalized PSLi end-capped with DPE and PS chains could be linked cleanly at the end of PMMA segment without problem. The results are summarized in Table 3. Figure 6 shows the ^{1}H NMR spectra of both of the 2G and 3G block copolymers thus synthesized.

Next, we have tried to synthesize another type 3G dendrimer-like star-branched block copolymer with four PMMA, eight PS, and 16 PMMA segments introduced at 1G, 2G, and 3G, respectively. As illustrated in Scheme 5, the starting 4-arm star-branched PMMA having two BnBr termini at each chain-end was synthesized by the methodology previously reported. Then, the resulting polymer reacted with a 1.5-fold excess of α-TBDMSOP-functionalized PSLi end-capped with DPE in THF at −78 °C for 24 h. The linking reaction was found to proceed cleanly and quantitatively to afford the 2G block copolymer. The terminal TBDMSOP groups of the 2G block copolymer were brominated by treatment with $(C_4H_9)_4NF$, followed by reacting with CBr_4 and PPh_3. The introduction of two BnBr functions *via* the terminal 3-bromopropyl group was carried out by the reaction with the DPE-derived anion, followed by treatment with a mixture of $(CH_3)_3SiCl$ and LiBr. Very importantly, PMMA chains were observed by ^{1}H NMR spectra to be completely stable and intact during these reaction steps. Finally, the benzyl brominated 2G block copolymer reacted with a 1.5-fold excess of living PMMA α-functionalized with two SMP groups. The well-defined and expected structures of two dendrimer-like star-branched block copolymers with

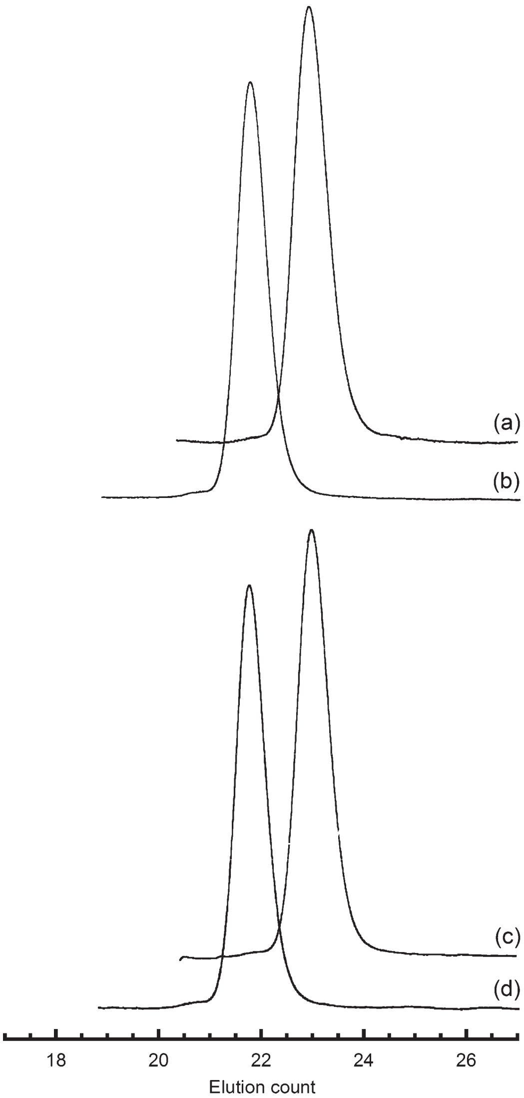


Figure 7. SEC profiles of 2G block copolymer composed of four PS (1G) and eight PMMA (2G) segments (a), 3G block copolymer composed of four PS (1G), eight PMMA (2G), and 16 PS (3G) segments (b), 2G block copolymer composed of four PMMA (1G) and eight PS (2G) segments (c), and 3G block copolymer composed of four PMMA (1G), eight PS (2G), and 16 PMMA (3G) segments (d).

different block sequences were confirmed by the analytical results that all the polymers possessed the predictable molecular weights and compositions and narrow molecular weight distributions as listed in Table 3. The SEC profiles of all of the 2G and 3G block copolymers are shown in Figure 7.

Thus, the present methodology provides a general and versatile synthetic procedure with which either of PS or PMMA segments can be introduced at any generation in a dendrimer-like star-branched block copolymer composed of PS and PMMA segments. The successful synthesis of the two 3G block copolymers clearly demonstrates that both α-functionalized living PS and PMMA with different reactivities are usable without any problem in the iterative process of the present methodology based on "arm-first" divergent approach. The successful synthesis also strongly indicates the possible use of a variety of living anionic polymers ranging from styrene to MMA, which involve living anionic polymers of 1,3-butadiene, isoprene, 2-vinylpyridine, alkyl acrylates, and *N,N*-diethyl acrylamides.[38]

Conclusions

The synthesis of high-generation and high-molecular-weight dendrimer-like star-branched (PS)s with well-defined structures by a new iterative methodology based on "arm-first" divergent approach is described. In this methodology, three reaction steps, i.e., a linking reaction and two end-functionalization reactions are involved in each iterative synthetic sequence and repeated to successfully synthesize a series of dendrimer-like star-branched (PS)s up to the 5G. Furthermore, two kinds of new dendrimer-like star-branched block copolymers composed of PS, PMMA, PS and PMMA, PS, PMMA introduced at 1G, 2G, and 3G have also been synthesized by employing living PMMA α-functionalized two SMP groups convertible to BnBr functions in the iterative reaction sequence of the new methodology. The successful synthesis of two such block copolymers demonstrates that either the PS or the PMMA segment can be introduced at essentially any generation in a dendrimer-like star-branched block copolymers. The resulting polymers all synthesized by the new methodology possessed observed molecular weights and compositions in good agreement with those calculated and extremely narrow molecular weight distributions, strongly indicating very high degrees of compositional homogeneity of the resulting polymers.

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(36) The transformation reaction from SMP group into BnBr function usually proceeded satisfactorily. However, a small resonance (ca. $\leq 5\%$) at 4.53 ppm assignable to methylene protons of the benzyl chloride (BnCl) functionality was often observed. This is undoubtedly due to the formation of BnCl moiety resulting from the halogen exchange reaction between BnBr and LiCl generated from $(CH_3)_3SiCl$ and LiBr. In such a case, the BnCl function was readily and quantitatively retransformed into BnBr by treatment with a 50-fold excess of LiBr in acetone.

(37) Unfortunately, PMMA chains are not completely stable under the conditions of the bromination with $(CH_3)_3SiBr$. Accordingly, a less reactive 1:1 mixture of $(CH_3)_3SiCl$ and LiBr is always used in the bromination reaction of SMP-chain-functionalized PMMA.

(38) We have recently observed that the living anionic polymer of *N,N*-diethylacrylamide reacted quantitatively with **2** to afford a well-defined 4-arm star-branched poly(*N,N*-diethylacrylamide). Since the bromination of α-SMP functionalized poly(*N,N*-diethylacrylamide) was found to be successfully carried out in another experiment, the living anionic polymer of *N,N*-diethylacrylamide may possibly be used in the iterative process of the present methodology.