Precise Synthesis of Dendrimer-like Star-Branched Poly(methyl methacrylate)s up to Seventh Generation by an Iterative Divergent Approach Involving Coupling and Transformation Reactions

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Received April 12, 2005; Revised Manuscript Received August 10, 2005

ABSTRACT: The synthesis of dendrimer-like star-branched poly(methyl methacrylate)s (PMMAs) were carried out by an iterative divergent approach which involved a coupling reaction of α -functionalized living PMMA with two *tert*-butyldimethylsilyloxymethylphenyl (SMP) groups with benzyl bromide (BnBr) chain-end-functionalized PMMA and a transformation reaction of the introduced SMP groups into BnBr functionalities. The dendrimer-like star-branched PMMAs up to the seventh generation have been successfully synthesized by repeating these two reactions seven times. The resulting polymers all were well-defined in branched architecture, precisely controlled in chain length and degree of end-functionality, and extremely narrow in molecular weight distribution ($M_w/M_n < 1.03$). The seventh-generation PMMA herein synthesized was 1.97×10^6 in M_w value and consisted of 508 PMMA segments. Furthermore, the 512 SMP termini were presented along its periphery. Viscosity measurement indicates that the dendrimer-like star-branched polymer in each generation possesses smaller hydrodynamic volume than the corresponding linear polymer with the same molecular weight. The g' value became smaller as the generation proceeded.

Introduction

For recent several years, the syntheses of various branched polymers with complex architectures have been greatly developed along with rapid progress of living polymerization.¹⁻¹⁹ These branched polymers have attracted much attention from theoretical and practical viewpoints because of their unique and interesting properties in solution, melt, and solid states as well as their usefulness and potential as specialty functional polymers. Furthermore, it is expected with use of their copolymers that new nanoscale supramolecules and specially shaped nanoobjects with threedimensional ordered structures have been fabricated by inducing microdomain arrangement and self-organization at the molecular level. $^{20-30}$ Recently, dendrimerlike star-branched polymers and copolymers have appeared as a new face among such branched polymers. Their branched architectures are similar to well-known dendrimers but consisted of dendritically branched polymer segments emanating from a central core. Therefore, dendrimer-like star-branched polymers possess radially branched architectures and topologically layered structures based on both dendrimers and starbranched as well as hyperbranched polymers.

Hedrick and co-workers reported the first successful synthesis of a series of dendrimer-like star-branched polymers by a divergent growth approach using repetitive living ring-opening polymerization of ϵ -caprolactone, followed by functionalization and deprotection of an AB₂ branching juncture formed at the chain ends between generations.³¹ Amphiphilic dendrimer-like starbranched copolymers were also synthesized in a similar manner by combination of living ring-opening polymerization of ϵ -caprolactone and atom transfer controlled

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radical polymerization of either 2-hydroxyethyl methacrylate or ω -methacrylate ethylene oxide macromonomer.³² Furthermore, various dendritic-linear block copolymers and constitutional isomers of dendrimer-like star-branched polymers have recently been synthesized by the controlled ring-opening polymerization of lactones from orthogonally protected multifunctional initiators.³³⁻³⁸ Similarly, Gnanou and co-workers reported the synthesis of amphiphilic and water-soluble dendrimer-like star-branched copolymers by the combining of living anionic polymerization of ethylene oxide and atom transfer controlled radical polymerization of styrene or *tert*-butyl acrylate, followed by hydrolysis.³⁹⁻⁴¹ Although their well-defined architectures and controlled chain lengths have been demonstrated by several analyses, there still remains the question regarding the uniformity of all polymer segments starting from the multifunctional initiators.

Knauss and co-workers have proposed the methodology based on the convergent living anionic polymerization for the synthesis of the hyperbranched polymers structurally analogous to the above-mentioned dendrimer-like star-branched polymers.⁴² The methodology involved the successive linking reaction and living anionic polymerization where polystyryllithium, 4-(chlorodimethylsilyl)styrene, styrene, and 4-(chlorodimethylsilyl)styrene were sequentially added in this order. The resulting copolymers have a less perfect structure but offer the advantage of a convenient one-pot synthesis.

Hadjichristidis and Chalari have recently synthesized the second-generation dendrimer-like star-branched polymers by an alternative methodology.⁴³ In this methodology, new living anionic off-center graft copolymers were first prepared by the addition reaction of ω -styryl macromonomers to living anionic polymers, followed by the polymerization of isoprene and the subsequent in-situ coupling reaction with either CH₃- $SiCl_3$ or $SiCl_4$. Obviously, the resulting dendrimer-like star-branched copolymers thus synthesized have a high molecular and compositional homogeneity, since the intermediated living anionic off-center graft copolymers were well controlled in chain length and the subsequent coupling reaction proceeded quantitatively. The method has been extended to the synthesis of the third- and fourth-generation dendrimer-like star-branched polymers. Unfortunately, the linking efficiency was not necessarily high enough at the synthetic stage of the fourth-generation polymer.

More recently, we have reported the successful synthesis of dendrimer-like star-branched poly(methyl methacrylate)s (PMMAs) by a novel methodology based on the iterative divergent approach.44 It involves a coupling reaction of α -functionalized living anionic PMMA with two *tert*-butyldimethylsilyloxymethylphenyl (SMP) groups with benzyl bromide (BnBr) chain-endfunctionalized PMMA and a transformation reaction of the introduced SMP groups into BnBr functionalities. These two reactions proceeded virtually quantitatively and therefore could be repeated three times to afford the first-, second-, and third-generation dendrimer-like star-branched PMMAs. A new amphiphilic dendrimerlike star-branched copolymer consisting of PMMA and poly(2-hydroxyethyl methacrylate) segments could be also synthesized by a similar method. The resulting polymers were undoubtedly well-defined in architecture and precisely controlled in chain length, since an "arm first method" based on living anionic polymerization and the iterative reaction sequence with quantitative nature were employed.

Herein, we report on the further synthesis of dendrimer-like star-branched PMMAs with higher generations by using the above-mentioned methodology in order to examine the possibility and limitation on how many times the iterative process can be repeated. The objective of the present study is to establish the proposed methodology as a more general and versatile synthetic procedure for dendrimer-like star-branched polymers.

Experimental Section

Materials. All chemicals (>98% purities) were purchased from Aldrich, Japan, and used as received unless otherwise stated. Methyl methacrylate (MMA) was washed with 5% NaOH and water and dried over MgSO₄. It was distilled over CaH₂ twice under reduced pressures and finally distilled from its trioctylaluminum solution (3 mol %) under the high-vacuum conditions (10⁻⁶ Torr). THF, chloroform, acetonitrile, (CH₃)₃-SiCl, LiCl, and LiBr were purified according to the reported procedures described elsewhere.⁴⁵ 1,1-Bis(3-*tert*-butyldimeth-ylsilyloxymethylphenyl)ethylene (1) was synthesized according to our procedure previously reported.⁴⁶

Measurements. Both ¹H and ¹³C NMR spectra were measured on a Bruker DPX300 (300 MHz for ¹H and 75 MHz for ¹³C) in CDCl₃. Chemical shifts were recorded in ppm downfield relative to CDCl_3 (δ 7.26 for ¹H NMR and δ 77.1 for ¹³C NMR). Size-exclusion chromatograms (SEC) were measured with a TOSOH HLC-8020 at 40 °C with UV (254 nm) or refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min. Three polystyrene gel columns whose bead size 5 μ m (pore sizes of 200, 75, and 20 Å) or bead size 9 μ m (pore sizes of 650, 200, and 75 Å) were used. These sets of the column covered the molecular weight ranges $10^{3}-4$ imes 10^5 and 10^4-4 imes 10^6 g/mol, respectively. To determine $M_{
m n}$ and $M_{\rm w}/M_{\rm n}$ values of the resulting polymers, a calibration curve was made with six PMMA standard samples prepared by the living anionic polymerization of MMA initiated with 1,1-diphenyl-3-methylpentyllithium in the presence of a 5-fold excess of LiCl in THF at -78 °C. Fractionation by SEC was performed with a flow rate of 5.0 mL/min at 40 °C using a TOSOH HLC 8020 type fully automatic instrument equipped with a $TSK_{gel}G5000\dot{H}_{HR}$ column (measurable molecular weight range: $10^{3}-4 \times 10^{6}$). All runs for fractionation were made with THF as an eluent. The measurements for static light scattering (SLS) were performed with an Ohtsuka Electronics Photal SLS-600R instrument equipped with a He-Ne laser (632.8 nm) in THF at 25 °C. Berry plots were used to determine $M_{\rm w}$ values of the dendrimer-like star-branched PMMAs herein synthesized. The refractive index increment (dn/dc) in THF at 25 °C was determined with an Ohtsuka Electronics DPM-1020 refractometer operating at 632.8 nm. Intrinsic viscosities were measured with an Ubbelohde viscometer in THF at 25 $^{\circ}\mathrm{C}.$ Vapor pressure osmometry (VPO) measurement was made with a Corona 117 instrument in benzene at 40 °C with a highly sensitive thermoelectric couple and with equipment of very exact temperature control.

Synthesis of 1,1,4,4-Tetra(3-bromomethylphenyl)butane (2). The reaction of 1 with potassium naphthalenide was carried out under high-vacuum conditions (10⁻⁶ Torr) in sealed glass reactors equipped with break-seals. All reactors were prewashed with potassium naphthalenide in THF after being sealed off from a vacuum line. A THF solution (26.9 mL) of 1 (4.10 g, 8.75 mmol) was added to potassium naphthalenide (11.0 mmol) in THF (25.2 mL) at -78 °C with stirring, and the reaction was allowed to stand at $-78\ ^\circ\mathrm{C}$ for 1 h and then quenched with degassed methanol. After removal of the solvents, the residue was washed successively with ether and methanol, followed by freeze-drying from its absolute benzene solution to afford a light yellow solid (3.89 g). Under nitrogen, the resulting solid was dissolved in dry acetonitrile (70 mL), followed by addition of LiBr (3.20 g, 36.8 mmol) and (CH₃)₃-SiCl (5.70 mL, 44.8 mmol) to the solution. The reaction mixture was allowed to stir at 40 °C for 24 h under nitrogen. The reaction was terminated with water (5 mL). After removal of the solvents, the resulting mixture was then extracted with chloroform and the organic layer was washed with water, dried over MgSO₄, and concentrated. Flash column chromatography on silica gel (hexane/dichloromethane, 1/2, v/v) and freezedrying from its absolute benzene solution afforded 2.73 g of 2 (3.72 mmol, 85%) as a white solid; mp 131-133 °C.

¹H NMR: δ 7.28–7.07 (m, 16H, aromatic), 4.45 (s, 8H, $-CH_2$ –Br), 3.91 (s, 2H, Ph–CH–Ph), 2.01 (s, 4H, $-CH_2$ – CH_2 –). ¹³C NMR: δ 145.0, 138.1, 129.1, 128.5, 128.0, 127.2 (aromatic), 55.1 (Ph–CH–Ph), 34.0 ($-CH_2$ – CH_2 –), 33.8 ($-CH_2$ –Br).

Synthesis of First-Generation Dendrimer-like Star-Branched PMMA, G-1. All the polymerizations and coupling reactions were carried out under high-vacuum conditions in sealed glass reactors equipped with break-seals. All reactors were prewashed with lithium naphthalenide in THF after being sealed off from a vacuum line. On the other hand, the transformation and retransformation reactions were carefully performed under nitrogen.

The title polymer, G-1, was synthesized by the living anionic polymerization of MMA with the functionalized initiator prepared from sec-BuLi and 1, followed by coupling with 2. The procedure is as follows: The functionalized anionic initiator was prepared by the reacting of sec-BuLi (0.672 mmol) in heptane (3.48 mL) with 1 (0.931 mmol) in THF (5.51 mL) at -78 °C for 0.5 h. After addition of LiCl (2.09 mmol) in THF (8.75 mL) at -78 °C to the reaction mixture, a THF solution (14.5 mL) of MMA (20.4 mmol) was added at once with stirring at -78 °C. The polymerization was continued in THF at -78°C for an additional 0.5 h. Then, 2 (0.105 mmol, 0.420 mmol for BnBr moiety) in THF (4.25 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 24 h. After quenching with degassed methanol, the mixture was poured into hexane to precipitate the polymers. The polymers were dissolved in benzene, and the resulting solution was filtrated through a Celite column to remove LiCl, LiBr, and LiOCH₃. They were characterized by SEC to compare their peak areas. Then, hexane (75 mL) was added slowly to the benzene (40 mL) solution containing polymers at room temperature, followed by cooling to 0 °C to precipitate the coupled polymer (1.27 g, 85%). The starting PMMA used in excess in the reaction was readily recovered from the supernatant solution. The resulting polymer was purified by reprecipitation from THF to hexane and freeze-drying from its absolute benzene solution to afford G-1 (1.13 g, 76%).

¹H NMR: δ 7.2–6.6 (m, aromatic), 4.66 (s, 16H, $-CH_2-O-$), 3.7–3.4 (m, $-O-CH_3$), 2.1–1.6 (m, $-CH_2-C(CH_3)-$), 1.1– 0.5 (m, $-CH_2-C(CH_3)-$), 0.90 (s, 72H, $-C(CH_3)_3$), 0.04 (s, 48H, Si(CH_3)₂).

Synthesis of First-Generation Dendrimer-like Star-Branched PMMA with Eight Benzyl Bromide (BnBr) Moieties, G-1-Br. The title polymer, G-1-Br, was synthesized by treatment of G-1 with (CH₃)₃SiCl-LiBr to transform the terminal tert-butyldimethylsilyloxymethylphenyl (SMP) groups into benzyl bromide (BnBr) functionalities. The procedure is as follows: Under nitrogen, G-1 (0.790 g, 0.457 mmol for SMP group) was dissolved in a mixed solvent of acetonitrile (15 mL) and chloroform (60 mL), followed by addition of LiBr (2.01 g, 23.1 mmol) and (CH₃)₃SiCl (3.65 mL, 28.7 mmol) to the solution. The reaction mixture was allowed to stir at 40 °C for 24 h under nitrogen and then quenched with water (5 mL). After removal of the solvents, the resulting mixture was extracted with chloroform, and the organic layer was washed with water and concentrated. The resulting polymer was purified by reprecipitation twice from THF to methanol and freeze-drying from its absolute benzene solution. It was observed by ¹H NMR analysis that a small resonance at 4.53 ppm assignable to the methylene protons of benzyl chloride was present. Therefore, the resulting polymer (0.74 g) and LiBr (3.54 g, 40.7 mmol) were dissolved in acetone (50 mL) and refluxed for an additional 1 h to retransform the chloride into bromide. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting polymer was purified by the reprecipitation from THF to methanol and freeze-drying from its absolute benzene solution to afford G-1-Br (0.63 g, 80%).

¹H NMR: δ 7.2–6.6 (m, Ar), 4.45 (s, 16H, $-CH_2$ –Br), 3.7– 3.4 (m, O–CH₃), 2.1–1.6 (m, $-CH_2$ –C(CH₃)–), 1.1–0.5 (m, $-CH_2$ –C(CH₃)–).

After this treatment, the resonance at 4.53 ppm corresponding to the benzyl chloride methylene protons completely disappeared.

Synthesis of Second-Generation Dendrimer-like Star-Branched PMMA, G-2. The title polymer, G-2, was synthesized by the coupling reaction of G-1-Br with α -functionalized living anionic PMMA initiated with the functionalized anion prepared from sec-BuLi and 1. The procedure is as follows: Under high-vacuum conditions, MMA (2.14 g, 21.4 mmol) was polymerized with the functionalized anionic initiator prepared from sec-BuLi (0.662 mmol) and 1 (0.951 mmol) in the presence of LiCl (2.10 mmol) in THF (20.5 mL) at -78 °C for 0.5 h. A THF solution (12.7 mL) of G-1-Br (0.630 g, 0.347 mmol for BnBr moiety) was added to the resulting living PMMA solution at -78 °C, and the mixture was allowed to react at -40 °C for 24 h. After quenching with degassed methanol, the mixture was poured into hexane to precipitate the polymers. The resulting polymers were characterized by SEC to directly compare their peak areas. They were redissolved in THF, and the resulting THF solution was poured into methanol. Fortunately, the objective coupled polymer was precipitated selectively, while the deactivated PMMA used in excess was soluble in methanol due to the low molecular weight ($M_{\rm n} = 3.77$ kg/ mol). The coupled polymer was further purified by reprecipitation twice from THF to methanol and freeze-drying from its absolute benzene solution to afford G-2 (1.48 g, 77%).

¹H NMR: δ 7.2–6.6 (m, aromatic), 4.66 (s, $3\overline{2}$ H, –CH₂–O–), 3.7–3.5 (m, –O–CH₃), 2.1–1.6 (m, –CH₂–C(CH₃)–), 1.1–0.6 (m, –CH₂–C(CH₃)–), 0.90 (s, 144H, –C(CH₃)₃), 0.04 (s, 96H, Si(CH₃)₂).

Synthesis of Second-Generation Dendrimer-like Star-Branched PMMA with 16 BnBr Moieties, G-2-Br. The title polymer, G-2-Br, was synthesized by the same procedures as those employed in the synthesis of G-1-Br. At first, G-2 (1.25 g, 0.461 mmol for SMP group) was reacted with a mixture of LiBr (2.06 g, 23.7 mmol) and (CH₃)₃SiCl (3.50 mL, 27.5 mmol) in acetonitrile/chloroform (15 mL/60 mL) at 40 °C for 24 h. The polymer was precipitated in methanol, reprecipitated twice from THF to methanol, and freeze-dried from its absolute benzene solution for 24 h. After the workup similar to that mentioned above, the resulting polymer was then treated with LiBr (3.96 g, 45.6 mmol) in acetone (50 mL) at reflux temperature for 1 h. The objective **G-2-Br** was obtained by precipitation in methanol and purified by reprecipitation twice, followed by freeze-drying (1.00 g, 81%).

¹H NMR: δ 7.2–6.6 (m, Ar), 4.45 (s, 32H, –CH₂–Br), 3.7– 3.4 (m, O–CH₃), 2.1–1.6 (m, –CH₂–C(CH₃)–), 1.1–0.6 (m, –CH₂–C(CH₃)–).

Synthesis of G-3. The title G-3 was synthesized by the coupling reaction of G-2-Br with the α -functionalized living anionic PMMA under the similar conditions to those employed in the synthesis of G-2.

¹H NMR: δ 7.2–6.6 (m, aromatic), 4.66 (s, 64H, –CH₂–O–), 3.7–3.4 (m, –O–CH₃), 2.1–1.6 (m, –CH₂–C(CH₃)–), 1.1–0.5 (m, –CH₂–C(CH₃)–), 0.90 (s, 288H, –C(CH₃)₃), 0.04 (s, 192H, Si(CH₃)₂).

Synthesis of G-3-Br. The title **G-3-Br** was synthesized by the transformation reaction with $(CH_3)_3SiCl-LiBr$, followed by the retransformation with LiBr under the identical conditions with those employed in the synthesis of **G-2-Br**.

¹H NMR: δ 7.2–6.6 (m, Ar), 4.45 (s, 64H, –CH₂–Br), 3.7– 3.4 (m, O–CH₃), 2.1–1.6 (m, –CH₂–C(CH₃)–), 1.1–0.5 (m, –CH₂–C(CH₃)–).

Furthermore, G-4, G-4-Br, G-5, G-5-Br, G-6, G-6-Br, and G-7 were synthesized according to the coupling and transformation reactions similar to those employed as mentioned above. A 3.0-fold excess of the α -functionalized living PMMA was used in the coupling reaction for the synthesis of G-4 and G-5, respectively. A 3.5-fold excess and a 5.0-fold excess of the α -functionalized living PMMA were used for the synthesis of G-6 and G-7. A 250-fold excess of (CH₃)₃SiCl-LiBr was employed for the synthesis of G-6-Br. In the retransformation reaction of G-4-Br, G-5-Br, or G-6-Br with a 50-fold excess of LiBr in acetone at refluxing for 1 h, undesirable dimeric products were formed in 5–10% yields. Therefore, they were removed by fractionation with SEC. The characterization results of the resulting dendrimer-like star-branched PMMAs are as follows:

G-4: ¹H NMR: δ 7.2–6.6 (m, aromatic), 4.66 (s, 128H, $-CH_2$ –O–), 3.8–3.4 (m, $-O-CH_3$), 2.1–1.6 (m, $-CH_2$ –C(CH₃)–), 1.1–0.5 (m, $-CH_2$ –C(CH₃)–), 0.90 (s, 576H, $-C(CH_3)_3$), 0.04 (s, 384H, Si(CH₃)₂).

G-4-Br: ¹H NMR: δ 7.2–6.6 (m, Ar), 4.45 (s, 128H, $-CH_2$ – Br), 3.7–3.4 (m, O– CH_3), 2.1–1.6 (m, $-CH_2$ – $C(CH_3)$ –), 1.1– 0.5 (m, $-CH_2$ – $C(CH_3)$ –).

G-5: ¹H NMR: δ 7.2–6.6 (m, aromatic), 4.66 (s, 256H, $-CH_2-O-$), 3.8–3.4 (m, $-O-CH_3$), 2.1–1.6 (m, $-CH_2-C(CH_3)-$), 1.1–0.5 (m, $-CH_2-C(CH_3)-$), 0.90 (s, 1152H, $-C(CH_3)_3$), 0.04 (s, 768H, Si(CH_3)₂).

G-5-Br: ¹H NMR: δ 7.2–6.6 (m, Ar), 4.45 (s, 256H, $-CH_2$ –Br), 3.8–3.4 (m, $O-CH_3$), 2.1–1.6 (m, $-CH_2$ –C(CH₃)–), 1.1–0.5 (m, $-CH_2$ –C(CH₃)–).

G-6: ¹H NMR: δ 7.2–6.6 (m, aromatic), 4.65 (s, 512H, $-CH_2-O-$), 3.7–3.4 (m, $-O-CH_3$), 2.1–1.6 (m, $-CH_2-C(CH_3)-$), 1.1–0.5 (m, $-CH_2-C(CH_3)-$), 0.90 (s, 2304H, $-C(CH_3)_3$), 0.04 (s, 1536H, Si(CH_3)₂).

G-6-Br: ¹H NMR: δ 7.2–6.6 (m, Ar), 4.45 (s, 512H, $-CH_2$ –Br), 3.7–3.4 (m, O– CH_3), 2.1–1.6 (m, $-CH_2$ –C(CH_3)–), 1.1–0.5 (m, $-CH_2$ –C(CH_3)–).

G-7: ¹H NMR: δ 7.2–6.6 (m, aromatic), 4.66 (s, 1024H, $-CH_2-O-$), 3.7–3.4 (m, $-O-CH_3$), 2.1–1.6 (m, $-CH_2-C(CH_3)-$), 1.1–0.5 (m, $-CH_2-C(CH_3)-$), 0.90 (s, 4608H, $-C(CH_3)_3$), 0.04 (s, 3072H, Si(CH_3)₂).

After the coupling reaction, the polymers were first precipitated in hexane for comparing their SEC peak areas. Then, the coupled products were readily isolated in near quantitative yields by the selective precipitation from THF to methanol, since the deactivated PMMAs used in excess were soluble in methanol due to their low molecular weights ($M_n = 3.5-4.1$



kg/mol). The resulting coupled polymers were purified by reprecipitation twice from THF to methanol and freeze-dried from their absolute benzene solutions. The pure polymers were obtained in 80-90% yields. After the transformation reaction with $(CH_3)_3SiCl-LiBr$, the polymers were also isolated nearly quantitatively by precipitation in methanol. Undesirable dimeric products were formed in 5-10% yields in the subsequent retransformation reaction of LiBr with **G-4-Br**, **G-5-Br**, or **G-6-Br**. Therefore, they were isolated in 70-80% yields by fractionation with SEC.

The M_n value of PMMA segment in each generation was measured by SEC as well as ¹H NMR using two resonances at 3.6 and 0.04 ppm corresponding to methoxy protons of the side chain and silylmethyl protons of the tert-butyldimethylsilyloxy group, respectively. The chain-end-functionalization degrees (BnBr and SMP groups) of the dendrimer-like starbranched polymers were measured by ¹H NMR using two resonances at either 4.66 or 4.45 and 3.6 ppm, corresponding to methylene protons of either \equiv Si-OCH₂C₆H₄or BrCH₂C₆H₄- and methoxy protons of the side chain, respectively. The $M_{\rm n}$ values of dendrimer-like star-branched polymers were obtained by ¹H NMR using the chain-end-functionalization degrees and $M_{\rm n}$ values of PMMA arm segments. The absolute molecular weight values were also determined by VPO and SLS.

Results and Discussion

1,1,4,4-Tetra(3-bromomethylphenyl)butane (2) as a New Core Compound Functionalized with Four BnBr Moieties. As mentioned in the introduction, we previously synthesized a series of the first, second-, and third-generation dendrimer-like starbranched PMMAs (G'-1, G'-2, and G'-3), whose central parts were made up of the linear PMMA segments branched at the both chain ends as illustrated in Scheme $1.^{44}$

As can be seen, p- α , α '-dibromoxylene is used as a core compound for the synthesis of **G**'-**0** by the first coupling reaction with α -functionalized living PMMA with two SMP groups convertible to BnBr functionalities. Herein, we have synthesized a structurally different series of dendrimer-like star-branched polymers, in which four arm segments are radially emanating from a central core. A new core compound functionalized with four BnBr moieties, $\mathbf{2}$, was used in this synthesis. The synthesis of $\mathbf{2}$ was achieved by the following two reaction steps as illustrated in Scheme 2.

=

OSiMe^tBu ●

The first step involves the coupling reaction of the radical anion intermediate generated from 1 and potassium naphthalenide, followed by quenching the resulting dianionic species with degassed methanol. In the second reaction step, the four SMP groups were transformed into BnBr functionalities by treatment with $(CH_3)_3SiCl-LiBr$. The two reactions proceeded virtually quantitatively. The objective 2 was isolated in 85% yield by column chromatography and freeze-dried from its absolute benzene solution for 24 h under high-vacuum conditions. The 2 thus synthesized is designed in such a way that one BnBr moiety is substituted with each benzene ring for reducing the steric hindering effect.

First-, Second-, and Third-Generation Dendrimer-like Star-Branched PMMAs. Scheme 3 shows the synthetic outline of the first-, second-, and thirdgeneration dendrimer-like star-branched PMMAs. The target polymers resemble dendrimers in branched architecture, but their branching points are separated by linear PMMA segments with M_n values of 3.5–4.1 kg/ mol instead of small chain spacers. Therefore, the resulting polymers are much higher in molecular weight than usual dendrimers. The methodology based on the iterative divergent approach herein employed is exactly the same as that previously proposed by us except for the core compound.⁴⁴ For the synthesis of the firstgeneration polymer, the α -functionalized living anionic PMMA with two SMP groups convertible to BnBr









Table 1. Synthesis of First-, Second-, and Third-Generation Dendrimer-like Star-Branched PMMAs

	$M_{ m n} imes 10^{-3}$			$M_{ m w} imes 10^{-3}$			$functionality^a$		
type	calcd	SEC	¹ H NMR	calcd	SLS	$M_{ m w}/M_{ m n}$	calcd	SMP	BnBr
G-1	14.6	13.8	14.2	14.9	14.8^{b}	1.02	8	7.80	
G-1-Br	14.1	13.7	13.8			1.02	8		7.82
G-2	43.0	36.9	42.9	43.9	44.2	1.02	16	16.0	
G-2-Br	42.2	35.0	42.1			1.02	16		15.8
G-3	97.3	66.1	98.4	99.2	105	1.02	32	32.6	
G-3-Br	95.7	63.5	96.8			1.03	32		32.4

^{*a*} Estimated by ¹H NMR. ^{*b*} M_n (by VPO) × (M_w/M_n).

functionalities was prepared by the living anionic polymerization of MMA with the functionalized 1,1diphenylalkylanion prepared from 1 and sec-BuLi in THF at -78 °C for 0.5 h. Prior to the polymerization, a 3-fold excess of LiCl toward sec-BuLi was added to narrow the molecular weight distribution.⁴⁵ The living PMMA thus prepared was then coupled with 2 in THF at -78 °C for 0.5 h, and the reaction mixture was allowed to stand at -40 °C for 24 h. A 1.5-fold excess of living polymer for the BnBr functionality was used. The reaction was terminated with degassed methanol, and the polymer was precipitated in hexane. As shown in Figure 1A, the SEC profile of the reaction mixture exhibits only two distinct sharp monomodal peaks corresponding to the coupled product and deactivated living PMMA used in excess in the reaction. Neither intermediate polymer nor higher molecular weight

shoulder was present. The coupling efficiency was virtually quantitative on the basis of the two peak areas. The higher molecular weight fraction was isolated in 85% yield by the fractional precipitation using a mixture of benzene and hexane. It was purified by reprecipitation, followed by freeze-drying and characterized by ¹H NMR, SEC, and VPO. The results are summarized in Table 1.

The isolated polymer exhibited a sharp monomodal SEC distribution, a M_w/M_n value being 1.02 (see Figure 1B). Since the M_n value estimated by SEC was not reliable due to the branched structure, the absolute M_n value was determined to be 14.5 kg/mol by VPO and in good agreement with that calculated. The ¹H NMR spectrum as shown in Figure 2A clearly exhibits three characteristic resonances at 4.66, 0.90, and 0.04 ppm assignable to the silyl benzyl methylene protons and



Figure 1. SEC profiles of the reaction mixture (A), G-1 obtained after fractional precipitation (B), and G-1-Br obtained after transformation reaction (C).

methyl protons of the *tert*-butyldimethylsilyloxy groups in the expected intensities. It was found that the SMP groups introduced in the polymer corresponded to 7.8 groups per polymer close to the theoretical value of eight. Furthermore, the M_n value measured by the same ¹H NMR spectrum agreed with that calculated. Thus, obviously, the α -functionalized living PMMA with two SMP groups effectively coupled with each of the four BnBr functionalities of **2** to afford the first-generation polymer, **G-1**. It should be mentioned that **G-1** is not a dendrimer-like star-branched polymer, but a four-arm star-branched polymer.

The G-1 thus synthesized was treated with a 50-fold excess of (CH₃)₃SiCl-LiBr in a mixture of acetonitrile and chloroform (1/4, v/v) at 40 °C for 24 h to transform the SMP groups into BnBr functionalities. The polymer was isolated by precipitation, purified by reprecipitation twice, and characterized by ¹H NMR and SEC. The ¹H NMR spectrum shown in Figure 2B indicates quantitative transformation by the disappearance of the three characteristic resonances at 4.66, 0.90, and 0.04 ppm as mentioned above. Likewise, the ¹³C NMR spectrum showed no signals of the tert-butyldimethylsilyloxy group. Instead, a new resonance at 4.45 ppm corresponding to the benzyl bromide methylene protons appeared. In addition, a small resonance (ca. 5%) at 4.53 ppm assignable to methylene protons of the benzyl chloride functionality was observed. This may be formed by a halogen exchange reaction of the BnBr function with LiCl generated from (CH₃)₃SiCl and LiBr.⁴⁷ The chloride was readily retransformed into the bromide by treatment with a 50-fold excess of LiBr in acetone. As can be seen in Figure 2C, the resonance at 4.53 ppm completely disappeared by this treatment. The SEC profile of the polymer obtained after the reaction showed a sharp monomodal distribution that was almost identical with G-1 in shape and elution count (see Figure 1C). The calculated M_n value agreed well with the value



Figure 2. ¹H NMR spectra of chain-end-functionalized starbranched PMMAs obtained before transformation reaction (A), after treatment with (CH₃)₃SiCl-LiBr (B), and after retransformation reaction with LiBr (C).

determined by ¹H NMR. The polymer thus obtained was referred to as **G-1-Br**. The results are also listed in Table 1.

With use of **G-1-Br** as a starting polymer, the secondgeneration, followed by the third-generation PMMA, was synthesized by repeating the same iterative reaction sequence involving the coupling and transformation reactions under the similar conditions, as illustrated in Scheme 3. All the reactions proceeded effectively as expected. Since small amounts of the benzyl chloride were generated after the transformation reactions at the second and third iterations, the resulting polymers were treated with LiBr in acetone. The results of the secondand third-generation polymers, G-2, G-2-Br, G-3, and **G-3-Br**, are also summarized in Table 1. As may be seen, these polymers all are precisely controlled in chain length and degrees of SMP and BnBr functionalities. Their SEC profiles exhibited sharp monomodal distributions without any shoulders and tailings. These analytical results strongly indicate that both G-2 and G-3 possess the expected dendrimer-like star-branched architectures consisting of 12 and 28 PMMA segments and G-2-Br and G-3-Br also possess similar branched

Scheme 4. Synthesis of Fourth- and Fifth-Generation Dendrimer-like Star-Branched PMMAs



Table 2. Synthesis of Fourth- and Fifth-Generation Dendrimer-like Star-Branched PMMAs

	$M_{ m n} imes 10^{-3}$			$M_{ m w} imes 10^{-3}$			functionality ^a		
type	calcd	SEC	¹ H NMR	calcd	SLS	$M_{ m w}/M_{ m n}$	calcd	SMP	BnBr
G-4 G-4-Br	219 216 459	115 105	219 216 440	223	230	$1.02 \\ 1.02 \\ 1.02$	64 64	64.0	64.0
G-5 G-5-Br	452 445	178 189	$449 \\ 442$	462	472	1.03	$\frac{128}{128}$	127	126

^a Estimated by ¹H NMR.

architectures having 16 and 32 BnBr moieties at their chain ends. Thus, the objective dendrimer-like starbranched PMMAs were successfully synthesized up to the third generation.

Fourth- and Fifth-Generation Dendrimer-like Star-Branched PMMAs. To effectively synthesize the fourth- and fifth-generation polymers, G-4 and G-5, the α -functionalized living PMMA used in the coupling reaction with G-3-Br (and G-4-Br) was increased in amount to a 3.0-fold excess because of rapid increase of



Figure 3. SEC profiles of the reaction mixture (A) and fourthgeneration dendrimer-like star-branched PMMA after fractional precipitation (B).

the terminal BnBr moiety from 16 to 32 (and 64) in number. The reaction time was extended to 48 h for the same reason. The synthetic scheme is illustrated in Scheme 4. The coupling reaction of the α -functionalized living PMMA with G-3-Br was carried out under such conditions. As shown in Figure 3A, the SEC profile of the reaction mixture exhibits only two distinct sharp monomodal peaks corresponding to the coupled product and deactivated living PMMA used in excess in the reaction. On the basis of the two peak areas, the reaction efficiency was virtually quantitative. Similar to the cases of G-2 and G-3, the coupled product was readily isolated only by precipitating the polymers into methanol, since the deactivated PMMA used in excess was soluble in methanol due to the low $M_{\rm n}$ value of 3.98 kg/ mol. The polymer was purified by reprecipitation and characterized by ¹H NMR, SEC, and SLS. The results are summarized in Table 2. As shown in Figure 3B, the SEC peak of the isolated polymer is monomodal and extremely narrow $(M_w/M_n = 1.02)$. The ¹H NMR analysis clearly indicates that all of the BnBr functions had reacted and new resonances are observed at 0.90 and 0.04 ppm, which are characteristic of the *tert*-butyldimethylsilyl methyl protons (see Figure 4A). In addition, a resonance at 4.66 ppm for the silvl benzyl methylene protons was observed. The same spectrum indicates that the SMP functionality of the polymer corresponds to 64 groups per polymer of the expected value. The M_n and $M_{\rm w}$ values determined by ¹H NMR and SLS agreed with those predicted. Thus, the synthesis of **G-4** was achieved without problem.

Complete transformation reaction of **G-4** was achieved with $LiBr-(CH_3)_3SiCl$, followed by treatment with LiBrunder the identical conditions as mentioned above. After the treatment with LiBr, however, a small amount (ca.



Figure 4. ¹H NMR spectra of fourth-generation dendrimerlike star-branched PMMA before (A) and obtained after transformation reaction (B).

5%) of undesirable dimeric product was formed. Therefore, an extra process was required for removal of this dimeric byproduct by fractionation with SEC in this case. As was seen in Table 2, the isolated polymer, **G-4-Br**, possessed the M_n value and degree of BnBr functionality very near to the expected values (see Figure 4B).

For the synthesis of the fifth-generation polymers, G-5 and G-5-Br, the same iterative reaction sequence was repeated with G-4-Br as a starting polymer. The efficiency of the coupling reaction carried out under the identical conditions was essentially quantitative. The subsequent transformation reaction was performed with LiBr-(CH₃)₃SiCl, followed by treatment with LiBr. On the basis of the ¹H NMR spectra of the resulting polymers and the characterization results listed in Table 2, they proved to be the objective **G-5** and **G-5-Br**, respectively. Thus, the fourth- and fifth-generation polymers consisting of 60 and 124 PMMA segments were successfully synthesized.

Sixth- and Seventh-Generation Dendrimer-like Star-Branched PMMAs. As illustrated in Scheme 5, the α -functionalized living PMMA must be coupled with 128 and 256 BnBr reaction sites for the synthesis of sixth- and seventh-generation polymers, **G-6** and **G-7**. Therefore, further excess amounts of the living polymer were used in the coupling reaction. For example, a 3.5fold excess of the α -functionalized living PMMA was employed in the coupling reaction at the sixth iteration process. For the synthesis of **G-7**, a 5.0-fold excess of the α -functionalized living PMMA was reacted with the BnBr-functionalized sixth-generation polymer for a longer reaction time of 72 h.

Under such conditions, the coupling reaction of the α-functionalized living PMMA with **G-5-Br** went essentially to completion to afford the objective **G-6**. The subsequent transformation reaction was, however, insufficient with a 50-fold excess of (CH₃)₃SiCl-LiBr. Complete transformation was achieved by using a 250fold excess of (CH₃)₃SiCl-LiBr. Again, the benzyl chloride functionality was generated in ca. 5% under such conditions, and the resulting polymer was therefore treated with a 50-fold excess of LiBr to retransform into the BnBr moiety. Since the dimeric product was also formed in ca. 10% by this treatment, it was removed by fractionation with SEC. To synthesize the seventhgeneration polymer, G-7, the G-6-Br thus synthesized was coupled with a 5.0-fold excess of the α -functionalized living PMMA for a longer reaction time to 72 h as mentioned above. The synthetic results of G-6, G-6-Br, and G-7 are summarized in Table 3.

As may be seen, all the polymers are precisely controlled in chain length and degrees of SMP group or BnBr functionality and possess narrow monomodal SEC distributions. Thus, we are successful in synthesizing the sixth- and seventh-generation polymers, **G-6** and

Scheme 5. Synthesis of Sixth- and Seventh-Generation Dendrimer-like Star-Branched PMMAs



Table 3. Synthesis of Sixth- and Seventh-Generation Dendrimer-like Star-Branched PMMAs

		$M_{ m n} imes 10^{-3}$			$M_{ m w} imes 10^{-3}$		$functionality^a$		
type	calcd	SEC	$^{1}\mathrm{H}~\mathrm{NMR}$	calcd	SLS	$M_{ m w}/M_{ m n}$	calcd	SMP	BnBr
G-6	980	282	974	1000	1060	1.02	256	254	
G-6-Br	966	250	960			1.02	256		253
G-7	1960	414	1940	1980	1970	1.02	512	507	

^{*a*} Estimated by ¹H NMR.



Figure 5. ¹H NMR spectra of dendrimer-like star-branched PMMAs G-1 to G-7.

G-7, consisting of 252 and 508 PMMA segments. ¹H NMR spectra and SEC profiles of all the generation dendrimer-like star-branched PMMAs herein synthesized are shown in Figures 5 and 6. As can be seen, the three characteristic resonances at 4.66, 0.90, and 0.04 ppm remain almost unchanged in each of all generation PMMAs. The SEC peak of each generation PMMA is monomodal and narrow and moves to a higher molecular weight region as the iteration proceeds.

On the basis of the successful synthesis of the dendrimer-like star-branched polymers up to the seventh generation, the synthetic approach herein employed is extremely effective. Obviously, the iteration process involving the coupling and transformation reactions always works very satisfactorily. The seventh-generation PMMA, **G-7**, was 1.97×10^6 in M_w value and consisted of 508 PMMA segments. Since the 512 SMP groups convertible to BnBr reaction sites are present along the periphery of **G-7**, it may be possible to synthesize the further generation polymers by repeating the same iteration process.



Figure 6. SEC profiles of dendrimer-like star-branched PMMAs G-1 to G-7.

One problem is that the benzyl chloride function is usually generated in ca. 5% or less by the transformation reaction with (CH₃)₃SiCl-LiBr under the conditions herein employed. The generation of the benzyl chloride becomes serious, since the coupling reaction of the benzyl chloride function with the α -functionalized living PMMA is very sluggish as previously reported by us. Therefore, an additional reaction step is required to retransform the chloride into bromide. Although the retransformation proceeded readily and quantitatively by treatment with LiBr, the additional trouble on the formation of dimeric product (5-10%) was caused by this treatment with use of G-4-Br, G-5-Br, or G-6-Br. Therefore, the reaction conditions of the transformation with (CH₃)₃SiCl-LiBr as well as the retransformation with LiBr should be optimized to effectively synthesize this type dendrimer-like star-branched polymers with higher generation. Since the problem is attributed to the presence of LiCl generated from (CH₃)₃SiCl and LiBr, it may possibly be overcome to directly use (CH₃)₃-SiBr instead of the mixture of (CH₃)₃SiCl and LiBr.

Intrinsic Viscosities and g' Values of Dendrimerlike Star-Branched Polymers. To examine the solution behaviors of G-1 to G-7, their intrinsic viscosities were measured, and g' values defined as $[\eta]_{\text{branched}}$ $[\eta]_{\text{linear}}$ were determined. Both $[\eta]_{\text{branched}}$ and $[\eta]_{\text{linear}}$ are intrinsic viscosities of the dendrimer-like star-branched polymer and the corresponding linear polymer with the same molecular weight under the same conditions. They

Table 4. Intrinsic Viscosities of Dendrimer-like Star-Branched PMMA

		$[\eta]$ (m				
type	$M_{ m w} imes 10^{-3a}$	$[\eta]_{\text{dendritic}}^b$	$[\eta]_{ ext{linear}}^c$	g' dendritic d	$g'_{ m star}$	
G-1	14.8^{e}	6.76	8.78	0.77	0.71^{f}	(4 arms)
G-2	44.2	12.5	18.8	0.66	0.46^{f}	(8 arms)
G-3	105	16.3	34.3	0.48	0.25^{f}	(16 arms)
G-4	230	18.9	59.1	0.32	0.14^g	(32 arms)
G-5	472	22.5	97.4	0.23	0.083^{g}	(64 arms)
G-6	1060	24.0	171	0.14	0.048^{g}	(128 arms)
G-7	1970	26.3	263	0.10	0.027^{g}	(256 arms)

^{*a*} Measured by SLS. ^{*b*} Measured in THF at 25 °C. ^{*c*} Calculated from $[\eta]_{\text{linear}} = 1.11 \times 10^{-2} \times M_{\text{w}}$. ^{*d*} Calculated from $g'_{\text{dendritic}} = [\eta]_{\text{dendritic}}/[\eta]_{\text{linear}}$. ^{*e*} M_{n} (by VPO)/($M_{\text{w}}/M_{\text{n}}$). ^{*f*} Calculated from $g'_{\text{star}} = [(3f - 2)/f^2]^{0.58} \times [0.724 - 0.015 \times (f - 1)]/0.724$; f = number of arms ($3 \le f \le 18$) (ref 48). ^{*g*} Calculated from $\log g'_{\text{star}} = 0.36 - 0.80 \times \log f$; f = number of arms ($6 \le f$) (ref 9).

were measured in THF at 25 °C and calculated from eq 1 previously reported.⁴⁵

$$[\eta]_{\text{linear}} = 1.11 \times 10^{-2} M_{\text{w}}^{0.695} \tag{1}$$

The results are summarized in Table 4. As a reference, g' values of star-branched polymers are listed in this table.^{9,48} In each generation, the arm number of star listed in this table is equal to that branched in outer layer of the dendrimer-like star-branched polymer. Since **G-1** is a 4-arm star-branched polymer, the g' value must be the same as that listed. A slight difference between both values (0.77 vs 0.71) may be attributed to the relatively large two SMP groups at each chain end. As estimated from the branched architectures, the $[\eta]_{\text{branched}}$ value was always smaller than that of the corresponding linear polymer, and accordingly, the g value was less than one in each case. Going from G-2 to G-7, the g' value gradually decreased, indicating that the dendrimer-like star-branched polymer became more compact in hydrodynamic volume in solution than the linear polymer with increasing the number of branched segment. The viscosity value of G-7 was only one-tenth as that of the linear polymer with the same molecular weight.

The g' values (0.66 and 0.48) of **G-2** and **G-3** were similar to those (0.59 and 0.46) of the previously synthesized second- and third-generation dendrimerlike star-branched polymers, as shown in Scheme 1.⁴⁴ Accordingly, the g' value seems not so sensitive irrespective of the dendrimer-like branched structure, although higher generation polymers of the both types should be compared. It was found that the g' value of the dendrimer-like star-branched polymer is somewhat larger than that of the star-branched polymer when the arm number branched in outer layer is equal to that of star-branched polymer. The theoretical approach between the g' value (hydrodynamic volume) and branched structure will be of interest in the near future.

Conclusions

The methodology based on the iterative divergent approach provided an effective synthetic route to the dendrimer-like star-branched PMMAs. It involves basically only two reactions, i.e., the coupling and transformation reactions. By repeating the two reactions, the dendrimer-like star-branched polymers up to the seventh generation could be successfully synthesized. The resulting polymers all were well-defined in branched architecture and precisely controlled in chain length and degree of end-functionality. The **G-7** obtained at the final reaction stage in this study was 1.97×10^6 in $M_{\rm w}$ value and consisted of 508 PMMA segments.

Unfortunately, a small amount (ca. 5%) of the less reactive benzyl chloride is usually generated in the transformation reaction, and therefore, an extra reaction step to retransform into the BnBr functionality by treatment with LiBr is required at each iteration stage. Furthermore, dimeric products were formed in 5-10%by this treatment with **G-4-Br**, **G-5-Br**, and **G-6-Br**. Although they are readily and completely removed by fractionation with SEC, the isolation step is also needed in such cases. Therefore, the transformation and retransformation reactions should be optimized.

The synthetic approach herein employed may also provide an excellent synthetic procedure for the copolymers with the same dendrimer-like star-branched architectures. Since many stable living anionic polymers of methacrylate monomers substituted with various functional groups are now available,^{18,49} it may be possible to intentionally incorporate such living polymers into the dendrimer-like star-branched polymers. The resulting polymers are quite novel copolymers possessing dendrimer-like star-branched architectures as well as a variety of functions topologically located in both inner and/or outer layers. Such copolymer characters and functions will provide inherent ability and potential to fabricate unique nanoscale supramolecules and nanoobjects by microdomain arrangement and selforganization at molecular level. We are now under investigation for the synthesis of functionalized dendrimer-like star-branched copolymers by the same proposed methodology.

Acknowledgment. The authors gratefully acknowledge partial support for this work from a Grant-in-Aid for Scientific Research (No. 16655044) from the Ministry of Education, Science, Sports, and Culture of Japan. We also thank both Sumitomo Chemical Co. Ltd. and Denki Kagaku Co. Ltd. for financial support of the work.

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MA050762K