Macromolecular Research, Vol. 14, No. 3, pp 272-286 (2006)

Precise Synthesis of Dendron-Like Hyperbranched Polymers and Block Copolymers by an Iterative Approach Involving Living Anionic Polymerization, Coupling Reaction, and Transformation Reaction

Akira Hirao*, Yuji Tsunoda, Akira Matsuo, Kenji Sugiyama, and Takumi Watanabe

Polymeric and Organic Materials Department, Graduate School of Science and Engineering, Tokyo Institute of Technology, H-127, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

Received October 11, 2005; Revised October 26, 2005

Abstract: Dendritic hyperbranched poly(methyl methacrylate)s (PMMA)s, whose branched architectures resemble the "dendron" part(s) of dendrimer, were synthesized by an iterative methodology consisting of two reactions in each iteration process: (a) a coupling reaction of α-functionalized, living, anionic PMMA having two *tert*-butyldimethylsilyloxymethylphenyl (SMP) groups with benzyl bromide (BnBr)-chain-end-functionalized PMMA, and (b) a transformation reaction of the introduced SMP groups into BnBr functionalities. These two reactions, (a) and (b), were repeated three times to afford a series of dendron-like, hyperbranched (PMMA)s up to third generation. Three dendron-like, hyperbranched (PMMA)s different in branched architecture were also synthesized by the same iterative methodology using a low molecular weight, functionalized 1,1-diphenylalkyl anion prepared from *sec*-BuLi and 1,1-bis(3-*tert*-butyldime-thylsilyloxymethylphenyl)ethylene in the reaction step (b) in each iterative process. Furthermore, structurally similar, dendron-like, hyperbranched block copolymers could be successfully synthesized by the iterative methodology using α-functionalized, living, anionic poly(2-(perfluorobutyl) ethyl methacrylate) (PRfMA) in addition to α-functionalized, living PMMA. Accordingly, the resulting block copolymers were comprised of both PMMA and PRfMA segments with different sequential orders. After the block copolymers were cast into films and annealed, their surface structures were characterized by angle-dependent XPS and contact angle measurements. All three samples showed significant segregation and enrichment of PRfMA segments at the surfaces.

Keywords: dendron-like hyperbranched polymer, living anionic polymerization, successive synthesis, fluoropolymer, surface structure.

Introduction

Dendrimer-like star-branched polymers have recently appeared as a new kind of hyperbranched polymers. They resemble well-known dendrimers in branched architectures, but comprise dendritically branched polymer segments emanating from a central core. Such polymers are of particular interest as specific functional polymers with a variety of potential applications, because of the unique topological hyper-branched architecture, the high functionality resulting from many chain ends and branching points, the different branching density between core and outside shell, and the possible formation of several layered structures with different characters.

In 1998, Hedrick and his coworkers reported the first successful synthesis of a series of dendrimer-like star-branched polymers.[1] These polymers were synthesized by a divergent growth approach using repetitive living ring-opening polymerization of ε-caprolactone, functionalization, and deprotection of an AB_2 branching juncture formed at the chain ends between generations. Amphiphilic block copolymers with the same branched architectures were also synthesized by the combining of living ring-opening polymerization of ε-caprolactone and atom transfer controlled radical polymerization of either 2-hydroxyethyl methacrylate or ω-methacrylate ethylene oxide macromonomer.[2] Furthermore, the synthesis of various dendritic-linear block copolymers and constitutional isomers of dendrimer-like star-branched polymers have been recently reported by the same research group.[3-8] Soon after, Gnanou and his coworkers reported the synthesis of similar amphiphilic and water-soluble dendrimer-like star-branched block copolymers by combination of living anionic polymerization of ethylene oxide with atom transfer controlled radical polymerization of styrene or *tert*-

*Corresponding Author. E-mail: ahirao@polymer.titech.ac.jp

butyl acrylate, followed by hydrolysis.[9-14] Although these polymers were considered to possess well-defined architectures and precisely controlled chain lengths, the uniformity of all polymer segments starting from the multifunctional initiators remains a question.

Hadjichristidis and Chalari have recently synthesized a series of second-generation dendrimer-like star-branched block copolymers by the coupling reaction of either CH_3SiCl_3 or $SiCl_4$ with living anionic off-center graft copolymers newly prepared by the addition reaction of ω-styryl macromonomers to living anionic polymers, followed by the polymerization of isoprene.[15] The methodology has been further extended to the synthesis of third-, followed by fourth-generation dendrimer-like star-branched polymers. Although the resulting copolymers possessed a high molecular and compositional homogeneity, the linking efficiency was not necessarily high enough at the synthetic stage of the fourth-generation polymer. Knauss and his coworkers have reported the convenient procedure for the synthesis of hyperbranched polymers structurally analogous to the above-mentioned dendrimer-like star-branched polymers by the convergent living anionic polymerization involving successive linking reaction and living anionic polymerization.[16] The resulting polymers have a less perfect structure, but offer the advantage of a convenient one-pot synthesis.

More recently, we have reported the synthesis of dendrimer-like star-branched poly(methyl methacrylate)s (PMMA)s by a new development of the methodology based on an iterative divergent approach.[17,18] It involves a coupling reaction of α-functionalized living anionic PMMA with two *tert*-butyldimethylsilyloxymethylphenyl (SMP) groups with chain-end-functionalized PMMA with benzyl bromide (BnBr) functionalities and a transformation reaction of the introduced SMP groups into BnBr functionalities. Because the two reactions proceeded quantitatively, they could be repeated three times to afford the dendrimer-like star-branched (PMMA)s up to third-generation. With use of the same methodology, the synthesis of a structurally similar dendrimer-like star-branched block copolymer consisting of PMMA and poly(2-hydroxyethyl methacrylate) segments was also successfully achieved. Since the synthesis is based on an "*arm-first method*" using α-functionalized living PMMA and quantitative two reactions, the resulting polymers were well-defined in architecture and precisely controlled in chain length.

Herein, we report on the synthesis of new dendritic hyperbranched (PMMA)s and block copolymers consisting of PMMA and poly(2-(perfluorobutyl)ethyl methacrylate) (PRfMA) segments by the above-mentioned iterative methodology. Furthermore, the resulting block copolymers thus synthesized are characterized by angle-dependent X-ray photoelectron spectroscopy (XPS) and contact angle measurements in order to examine the surface segregation and enrichment of PRfMA segment.

Experimental

Materials. All chemicals (> 98% purities) were purchased from Aldrich, Japan, and used as received unless otherwise stated. (2-Perfluorobutyl)ethyl methacrylate (RfMA) was distilled over CaH_2 twice under reduced pressures and finally distilled over trioctylaluminium (3 mol%) on a vacuum line into ampoules equipped with break-seals that were pre-washed with potassium naphthalenide in THF. Acetone was distilled over K_2CO_3. Methyl methacrylate (MMA), THF, heptane, chloroform, acetonitrile, $(CH_3)_3SiCl$, LiCl, and LiBr were purified according to the reported procedures described elsewhere.[17] 1,1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl) ethylene (**1**) was synthesized according to our procedure previously reported.[19]

Film Preparation. The polymer films for contact angle and XPS measurements were prepared by spin coating (40,000 rpm, 20 sec) onto cover glasses from 3.0-5.0 wt% polymer THF solutions. The films were dried at 25 °C for 24 h and annealed at 100 °C for additional 2 h under vacuum (10^{-3} torr) to allow the polymer chains to reach their equilibrium configurations.

Measurements. Both ^1H and ^{13}C NMR spectra were measured on a Bruker DPX300 (300 MHz for ^1H and 75 MHz for ^{13}C) in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $CDCl_3$ (7.26 for ^1H NMR and 77.1 for ^{13}C 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 μm (pore sizes of 200, 75, and 20 Å) or bead size 9 m (pore sizes of 650, 200, and 75 Å) were used. These sets of the column covered the molecular weight ranges $10^3 \sim 4 \times 10^5$ and $10^4 \sim 4 \times 10^6$ g/mol, respectively. To determine M_n and M_w/M_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-methylpentyllitium in presence of a 5-fold excess of LiCl in THF at -78 °C. Intrinsic viscosities were measured with an Ubbelhode viscometer in THF at 25 °C. Right angle laser light scatterings (RALLS) were measured on an Asahi Techneion Viscotek Model 302 TDA with triple detector software. Three polystyrene gel columns, a TSKgel G2000H_{HR} and two TSKgel GMH_{HR}-H, were used. THF was used as a carrier solvent at a flow rate of 1.0 mL/min. Contact angles of the polymer films were measured with a Kyowa Interface Science CA-A using water and dodecane droplets. Angle-dependent X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer 5500MT with a monochromatic Al Kα X-ray source.

Synthesis of Chain-End-Functionalized PMMA with Two BnBr Moieties (A-Br_2). The polymerization and the coupling reaction were carried out under high vacuum conditions (10^{-6} torr) in sealed glass reactors equipped with break

seals. All reactors were pre-washed with 1,1-diphenylhexyl lithium in heptane after being sealed off from a vacuum line. The transformation and re-transformation reactions were carefully performed under a nitrogen atmosphere.

MMA was polymerized in THF at -78 °C for 1 h with the functionalized anionic initiator prepared from **1** and *sec*-BuLi. The two SMP groups at the PMMA chain-end were treated with $(CH_3)_3SiCl$-LiBr to transform into BnBr functionalities. The procedures are as follows: The functionalized anionic initiator was prepared by mixing *sec*-BuLi (0.200 mmol) in heptane (3.84 mL) with **1** (0.310 mmol) in THF (3.78 mL) at -78 °C and the mixture was allowed to stand for additional 20 min. After addition of LiCl (0.988 mmol) in THF (3.88 mL) to the reaction mixture, MMA (20.7 mmol) in THF (15. 6 mL) was mixed at once with stirring at -78 °C. The polymerization was continued in THF at -78 °C for 1 h. After quenching with degassed methanol, the solvent was removed under reduced pressure. The residue was dissolved in benzene and the solution was filtrated through a celite column to remove LiCl and $LiOCH_3$. The polymer was purified by reprecipitation from THF to methanol and freezed-drying from its absolute benzene solution to afford the polymer (2.13 g, 97 %).

Under a nitrogen atmosphere, the α-functionalized PMMA (2.09 g, 0.383 mmol for SMP group) was dissolved in a mixed solvent of acetonitrile (15 mL) and chloroform (60 mL), followed by addition of LiBr (1.85 g, 21.3 mmol) and $(CH_3)_3SiCl$ (2.15 mL, 16.9 mmol) to the solution. The reaction mixture was allowed to stir at 40 °C for 24 h under nitrogen and then quenched with methanol (5 mL). After removal of the solvent, the residue was extracted with chloroform and the organic layer was washed with water, and concentrated. The residue dissolved in benzene was filtrated through a celite column to remove LiBr. The resulting polymer was reprecipitated from THF into hexane, and freeze-dried from its absolute benzene solution. Since a small amount of benzyl chloride functionality was present in the polymer, the polymer (2.07 g) and LiBr (3.39 g, 39.0 mmol) were dissolved in acetone (60 mL) and refluxed for an additional 1 h to re-transform the chloride into bromide. After cooling to room temperature, the solvent was removed under reduced pressure. The residual polymer dissolved in benzene was purified by filtration through a celite column, reprecipitation from THF to hexane, and freeze-drying from its absolute benzene solution to afford **A**-Br_2 (2.04 g, 98%). After this treatment, the resonance at 4.53 ppm corresponding to the benzyl chloride methylene protons completely disappeared. Chain-end-functionalized PMMA with two SMP groups, ^{1}H NMR ($CDCl_3$): δ 7.2-6.9 (m, Ar), 4.66 (s, 4H, -CH_2-O-), 3.7-3.4 (m, -O-CH_3), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-), 0.90 (s, 18H, C(CH_3)$_3$), 0.04 (s, 12H, Si(CH_3)$_2$). **A**-Br_2, ^{1}H NMR ($CDCl_3$): δ 7.2-6.9 (m, Ar), 4.45 (s, 4H, -CH_2-Br), 3.7-3.4 (m, -O-CH_3), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.1-0:6 (m, -CH_2-C(CH_3)-).

Synthesis of a First-Generation Dendron-Like Hyperbranched PMMA (A-A_2) and the Brominated Polymer (A-(ABr_2)$_2$). A first-generation dendron-like hyperbranched PMMA (**A**-A_2) was synthesized by the coupling of **A**-Br_2 with the α-functionalized living PMMA. The brominated polymer (**A**-(ABr_2)$_2$) was obtained by the transformation reaction of **A**-A_2 with $(CH_3)_3SiCl$-LiBr, followed by re-transformation with LiBr. The procedures are as follows: MMA (21.0 mmol) in THF (15.0 mL) was polymerized with the functionalized anionic initiator prepared from **1** (0.314 mmol) and *sec*-BuLi (0.215 mmol) in the presence of LiCl (0.771 mmol) in THF (23.4 mL) at -78 °C for 1 h. A THF solution of **A**-Br_2 (0.656 g, 0.121 mmol for BnBr moiety) was added to the living PMMA solution at -78 °C and allowed to react at -40 °C for 24 h. After quenching with degassed methanol, the solvent was removed under reduced pressure. The resulting mixture dissolved in a small amount of THF was poured into methanol to precipitate the polymers. The polymers were dried for 10 h under vacuum and then dissolved in benzene (30 mL). Methanol (180 mL) was added slowly to the benzene solution at room temperature, followed by cooling the mixture to 0 °C and allowed to stand for 30 min at 0 °C. The coupled polymer was selectively precipitated under the conditions. The starting PMMA used in excess in the reaction was readily recovered from the supernatant solution. The coupled polymer thus fractionated was reprecipitated from THF to methanol and freeze-dried from its absolute benzene solution to afford the first-generation polymer, **A**-A_2 (1.52 g, 79%).

Under an atmosphere of nitrogen, the **A**-A_2 (1.48 g, 0.186 mmol for SMP group) was dissolved in a mixed solvent of acetonitrile (15 mL) and chloroform (60 mL), followed by addition of LiBr (0.810 g, 9.32 mmol) and $(CH_3)_3SiCl$ (1.39 g, 10.9 mmol) to the solution. The reaction mixture was allowed to stir at 40 °C for 24 h and then quenched with methanol (5 mL). After removal of the solvents, the reaction mixture was extracted with chloroform and the organic layer was washed with water, and concentrated. The polymer was purified by reprecipitation from THF to methanol twice and freeze-drying from its absolute benzene solution. Since the presence of a small amount of benzyl chloride was observed by ^{1}H NMR analysis, the resulting polymer (1.44 g) and LiBr (1.29 g, 14.8 mmol) were dissolved in acetone (60 mL) and refluxed for 1 h to re-transform the chloride into bromide. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting polymer was purified by reprecipitation from THF to methanol and freeze-drying from its benzene solution to afford **A**-(**A**-Br_2)$_2$ (1.39 g, 94%). **A**-A_2, ^{1}H NMR ($CDCl_3$): δ 7.2-6.6 (m, Ar), 4.65 (s, 8H, -CH_2-O-), 3.7-3.4 (m, -O-CH_3), 2.1-1.5 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-), 0.90 (s, 36H, C(CH_3)$_3$), 0.04 (s, 24H, Si(CH_3)$_2$). **A**-(**A**-Br_2)$_2$, ^{1}H NMR ($CDCl_3$): δ 7.2-6.9 (m, Ar), 4.45 (s, 8H, -CH_2-Br), 3.7-3.4 (m, -O-CH_3), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.2-0.6 (m, -CH_2-C(CH_3)-).

Synthesis of a Second-Generation Dendron-Like Hyperbranched PMMA (A-A_2-A_4) and the Brominated Polymer (A-A_2-(A-Br_2)$_4$). The title second-generation polymer (A-A_2-A_4) was synthesized by the coupling reaction of A-(A-Br_2)$_2$ with α-functionalized living PMMA. The brominated polymer (A-A_2-(A-Br_2)$_4$) was obtained by the transformation reaction of A-A_2-A_4 with $(CH_3)_3SiCl$-LiBr, followed by the re-transformation with LiBr. The procedures are as follows: MMA (21.4 mmol) in THF (15.0 mL) was polymerized with the functionalized initiator prepared from *sec*-BuLi (0.205 mmol) and **1** (0.309 mmol) in the presence of LiCl (0.786 mmol) in THF (8.30 mL) at -78 °C for 1 h. A THF solution of A-(A-Br_2)$_2$ (0.559 g, 0.0708 mmol for BnBr moiety) was added to the resulting living PMMA solution at -78 °C and allowed to react at -40 °C for 24 h. The same treatment as the case of the first-generation polymer gave the second-generation polymer, A-A_2-A_4 (1.12 g, 86%). The brominated polymer (A-A_2-(A-Br_2)$_4$) was similarly synthesized by the same procedure used for the synthesis of the A-(A-Br_2)$_2$ mentioned above. The second-generation polymer, A-A_2-A_4, ^{1}H NMR ($CDCl_3$): δ 7.2-6.6 (m, Ar), 4.66 (s, 16H, -CH_2-O-), 3.8-3.4 (m, -O-CH_3), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.3-0.6 (m, -CH_2-C(CH_3)-), 0.90 (s, 72H, C(CH_3)$_3$), 0.04 (s, 48H, Si(CH_3)$_2$). The brominated polymer, A-A_2-(A-Br_2)$_4$, ^{1}H NMR ($CDCl_3$): δ 7.2-6.9 (m, Ar), 4.45 (s, 8H, -CH_2-Br), 3.7-3.4 (m, -O-CH_3), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-).

Synthesis of a Third-Generation Dendron-Like Hyperbranched PMMA (A-A_2-A_4-A_8). The title third-generation polymer was synthesized by the coupling reaction of A-A_2-(A-Br_2)$_4$ with α-functionalized living PMMA. The brominated polymer (A-A_2-A_4-(A-Br_2)$_8$) was obtained by the transformation and re-transformation of A-A_2-A_4-A_8. The procedures are as follows: MMA (mmol) was polymerized with the functionalized anionic initiator prepared from **1** (0.269 mmol) and *sec*-BuLi (0.176 mmol) in the presence of LiCl (0.725 mmol) in THF (9.01 mL) at -78 °C for 1 h. A THF solution of A-A_2-(A-Br_2)$_4$ (0.650 g, 0.0705 mmol for BnBr moiety) was added to the living polymer solution at -78 °C with stirring and the reaction was continued at -40 °C for 24 h. The same treatment as the case of the second-generation polymer gave the third-generation polymer, A-A_2-A_4-A_8 (1.30 g, 91%). The third-generation polymer, A-A_2-A_4-A_8, ^{1}H NMR ($CDCl_3$): δ 7.2-6.7 (m, Ar), 4.66 (s, 16H, -CH_2-O-), 3.7-3.4 (m, -O-CH_3), 2.2-1.6 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-), 0.90 (s, 72H, C(CH_3)$_3$), 0.04 (s, 48H, Si(CH_3)$_2$).

Synthesis of a Second-Generation Dendron-Like Hyperbranched MMA with a Different Branched Architecture, A-A_2-A_8. The brominated polymer, A-(A-Br_2)$_2$, was synthesized as mentioned in the preceding section. The number of BnBr functionality of the A-(A-Br_2)$_2$ doubled by the reacting with the functionalized anion prepared from **1** and *sec*-BuLi, followed by treatment with $(CH_3)_3SiCl$-LiBr and subsequently with LiBr. The resulting A-(A-Br_4)$_2$ was coupled with α-functionalized living PMMA to afford the title polymer, A-A_2-A_8. The procedures are as follows: The functionalized anion prepared from *sec*-BuLi (0.105 mmol) in heptane (3.01 mL) and **1** (0.143 mmol) in THF (3.45 mL) at -78 °C for 20 min was added to a THF solution (7.37 mL) of A-(A-Br_2)$_2$ (0.487 g, 0.0616 mmol for BnBr moiety) and the reaction mixture was allowed to react at -78 °C for additional 20 min. After quenching with degassed methanol, the solvents were removed under reduced pressure. The residue dissolved in THF (5 mL) was poured into methanol to precipitate the polymer. It was purified by reprecipitation from THF to methanol and freeze-drying from its absolute benzene solution to afford a polymer having eight SMP termini (0.490 g, 95%). ^{1}H NMR ($CDCl_3$): δ 7.2-6.6 (m, Ar), 4.66 (s, 16H, -CH_2-O-), 3.7-3.3 (m, -O-CH_3), 2.2-1.6 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-), 0.90 (s, 72H, C(CH_3)$_3$), 0.04 (s, 48H, Si(CH_3)$_2$).

Under a nitrogen atmosphere, resulting polymer (0.470 g, 0,112 mmol for BnBr moiety) was dissolved in a mixed solvent of acetonitrile (10 mL) and chloroform (40 mL), followed by addition of LiBr (0.465 g, 5.35 mmol) and $(CH_3)_3SiCl$ (0.677 mL, 5.31 mmol) to the solution. The reaction mixture was allowed to stir at 40 °C for 24 h and then quenched with methanol (5 mL). The same work-up as that used for A-(A-Br_2)$_2$ gave the brominated polymer, A-(A-Br_4)$_2$ (0.440 g, 94%). ^{1}H NMR ($CDCl_3$): δ 7.2-6.9 (m, Ar), 4.45 (s, 16H, -CH_2-Br), 3.7-3.4 (m, -O-CH_3), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.2-0.6 (m, -CH_2-C(CH_3)-).

The resulting A-(A-Br_4)$_2$ (0.370 g, 0.0873 mmol for BnBr moiety) dissolved in THF (6.20 mL) was reacted with the α-functionalized living anionic PMMA (2.23 g, 0.227 mmol) in THF (29.7 mL) at -40 °C for 24 h. The same work-up as that used for A-A_2-A_4 gave the objective A-A_2-A_8 (0.980 g, 80%). ^{1}H NMR ($CDCl_3$): δ 7.2-6.6 (m, Ar), 4.66 (s, 32H, -CH_2-O-), 3.7-3.4 (m, -O-CH_3), 2.1-1.5 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-), 0.90 (s, 144H, C(CH_3)$_3$), 0.04 (s, 96H, Si(CH_3)$_2$).

Synthesis of a Second-Generation Dendron-Like Hyperbranched MMA with a Different Branched Architecture, A-A_4-A_8. The A-Br_2 was synthesized according to the procedure mentioned in the preceding section, followed by treatment with the functionalized anion prepared from *sec*-BuLi and **1**. The resulting polymer was treated with $(CH_3)_3SiCl$-LiBr and subsequently with LiBr to afford A-Br_4. ^{1}H NMR ($CDCl_3$): δ 7.2-6.8 (m, Ar), 4.45 (s, 8H, -CH_2-Br), 3.7-3.4 (m, -O-CH_3), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-).

The resulting A-Br_4 was coupled with the α-functionalized living PMMA under the same conditions, resulting in the formation of a first-generation dendron-like hyperbranched polymer, A-A_4. ^{1}H NMR ($CDCl_3$): δ 7.2-6.6 (m, Ar), 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)-), 1.1-0.6 (m, -CH_2-C(CH_3)-), 0.90 (s, 72H, C(CH_3)$_3$),

0.04 (s, 48H, $Si(CH_3)_2$).

The **A-A_4-A_8** was synthesized by the bromination of **A-A_4**, followed by the coupling of α-functionalized living PMMA under the identical conditions mentioned above. ^{1}H NMR ($CDCl_3$): **A-(A-Br_2)$_4$**, δ 7.2-6.9 (m, Ar), 4.45 (s, 16H, -CH_2-Br), 3.7-3.4 (m, -O-CH_3), 2.2-1.6 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-). **A-A_4-A_8**, δ 7.2-6.6 (m, Ar), 4.66 (s, 32H, -CH_2-O-), 3.7-3.4 (m, -O-CH_3), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.1-0.6 (m, -CH_2-C(CH_3)-), 0.90 (s, 144H, C(CH_3)$_3$), 0.04 (s, 96H, $Si(CH_3)_2$).

Synthesis of a Second-Generation Block Copolymer Comprised of PMMA (A) and PRfMA (B) Segments, B-A_2-A_4. The synthetic outline of the title polymer will be described in the results and discussion. Starting from **B**-Br_2, **B-A_2**, followed by **B-A_2-A_4** was synthesized by the same iterative methodology. The **B**-Br_2 was synthesized by the living anionic polymerization of RfMA with the functionalized initiator prepared from *sec*-BuLi and **1**, followed by treatment with $(CH_3)_3SiCl$-LiBr and subsequently with LiBr. The procedures are as follows: The functionalized initiator was prepared by the reaction of *sec*-BuLi (0.404 mmol) in heptane (7.08 mL) with **1** (0.574 mmol) in THF (9.25 mL) at -78 °C for 20 min. LiCl (2.28 mmol) in THF (15.6 mL) was added to the reaction mixture, followed by mixing RfMA (5.69 mmol) in THF (23.4 mL) at once with stirring at -78 °C. The polymerization of RfMA was continued in THF at -78 °C for additional 10 min. After quenching with degassed methanol, the polymer was precipitated in methanol. It was purified by reprecipitation from THF to methanol and freeze-drying from its absolute benzene solution to afford a chain-end-functionalized PRfMA with two SMP groups (1.93 g, 91%). ^{1}H NMR ($CDCl_3$): δ 7.2-6.8 (m, Ar), 4.65 (s, 4H, -CH_2-O-), 4.4-4.1 (m, -O-CH_2-), 2.6-2.3 (m, -CH_2-CF_2-), 2.1-1.7 (m, -CH_2-C(CH_3)-), 1.2-0.5 (m, -CH_2-C(CH_3)-), 0.89 (s, 18H, C(CH_3)$_3$), 0.03 (s, 12H, $Si(CH_3)_2$).

Under nitrogen, the resulting polymer (1.85 g, 0.660 mmol for SMP group) was dissolved in a mixed solvent of acetonitrile (15 mL) and chloroform (60 mL), followed by addition of LiBr (3.00 g, 34.5 mmol) and $(CH_3)_3SiCl$ (4.39 mL, 35.0 mmol) to the solution. The reaction mixture was allowed to stir at 40 °C for 24 h and then quenched with methanol (5 mL). After removal of the solvents, the residue was dissolved in THF and the resulting solution was poured into methanol to precipitate the polymer. It was purified by reprecipitation from THF into methanol and freeze-drying from its absolute benzene solution. Then, the resulting polymer (1.79 g) and LiBr (3.02 g, 34.8 mmol) were dissolved in acetone (60 mL) and refluxed for 1 h. The same work-up as above gave **B**-Br_2 (1.54 g, 83%). ^{1}H NMR ($CDCl_3$): δ 7.2-6.8 (m, Ar), 4.43 (s, 4H, -CH_2-Br), 4.4-4.1 (m, -O-CH_2-), 2.6-2.3 (m, -CH_2-CF_2-), 2.1-1.7 (m, -CH_2-C(CH_3)-), 1.2-0.5 (m, -CH_2-C(CH_3)-).

The **B**-Br_2 thus synthesized was coupled with α-functionalized living PMMA to afford a first-generation polymer, **B-A_2**. The resulting **B-A_2** was treated with $(CH_3)_3SiCl$-LiBr and subsequently with LiBr to transform the four SMP termini into BnBr functionalities. The procedures are as follows: MMA (21.2 mmol) was polymerized with the functionalized initiator prepared from *sec*-BuLi (0.204 mmol) and **1** (0.304 mmol) in the presence of LiCl (1.08 mmol) in THF (28.0 mL) at -78 °C for 10 min. A THF (10.2 mL) solution of **B**-Br_2 (0.248 g, 0.0901 mmol for BnBr moiety) was added to the resulting living PMMA solution at -78 °C and allowed to react at -40 °C for 24 h. After quenching with degassed methanol, the solvent was removed under reduced pressure. The residue dissolved in a small amount of THF was poured into methanol to precipitate the polymers. Methanol (100 mL) was added to the benzene solution (30 mL) of the polymers, followed by cooling to 0 °C, to precipitate the coupled polymer, **B-A_2**, selectively. The isolated block polymer was purified by reprecipitation from THF to methanol and freeze-drying from its absolute benzene solution to afford a first-generation polymer, **B-A_2** (1.02 g, 89%). ^{1}H NMR ($CDCl_3$): δ 7.2-6.7 (m, Ar), 4.66 (s, 8H, -CH_2-O-), 4.4-4.1 (m, -O-CH_2-), 3.7-3.4 (m, -O-CH_3), 2.6-2.3 (m, -CH_2-CF_2-), 2.1-1.7 (m, -CH_2-C(CH_3)-), 1.3-0.5 (m, -CH_2-C(CH_3)-), 0.90 (s, 36H, C(CH_3)$_3$), 0.04 (s, 24H, $Si(CH_3)_2$).

Under nitrogen, the resulting **B-A_2** (0.921 g, 0.141 mmol for SMP group) was dissolved in a mixed solvent of acetonitrile (15 mL) and chloroform (60 mL). LiBr (0.613 g, 7.05 mmol) and $(CH_3)_3SiCl$ (0.880 mL, 6.91 mmol) was added to the solution and the reaction mixture was allowed to stir at 40 °C for 24 h. The same work-up mentioned above gave **B-(A-Br_2)$_2$** (0.857 g, 93%). ^{1}H NMR ($CDCl_3$): δ 7.2-6.8 (m, Ar), 4.45 (s, 8H, -CH_2-Br), 4.4-4.1 (m, -O-CH_2-), 3.7-3.4 (m, -O-CH_3), 2.6-2.3 (m, -CH_2-CF_2-), 2.1-1.6 (m, -CH_2-C(CH_3)-), 1.2-0.5 (m, -CH_2-C(CH_3)-).

A second-generation block copolymer, **B-A_2-A_4**, was synthesized by the coupling reaction of **B-(A-Br_2)$_2$** with α-functionalized living PMMA. The procedure is as follows: MMA (21.1 mmol) was polymerized with the functionalized initiator prepared from *sec*-BuLi (0.213 mmol) and **1** (0.278 mmol) in the present of LiCl (0.803 mmol) in THF (26.5 mL) at -78 °C for 10 min. A THF (9.52 mL) solution of **A-(A-Br_2)$_2$** (0.435 g, 0.0669 mmol for BnBr moiety) was added to the resulting living PMMA solution at -78 °C and allowed to react at -40 °C for 24 h. Usual work-up gave the polymer mixtures. After dissolving them in benzene (30 mL), methanol (110 mL) was added to the resulting solution to selectively precipitate the objective coupled polymer. The resulting polymer was purified by reprecipitation from THF to methanol and freeze-drying from its absolute benzene solution to afford a second-generation block copolymer, **B-A_2-A_4** (0.897 g, 78 %). ^{1}H NMR ($CDCl_3$): δ 7.2-6.7 (m, Ar), 4.66 (s, 16H, -CH_2-O-), 4.4-4.1 (m, -O-CH_2-), 3.7-3.4 (m, -O-CH_3), 2.6-2.3 (m, -CH_2-CF_2-), 2.1-1.7 (m, -CH_2-C(CH_3)-), 1.2-0.5 (m, -CH_2-C(CH_3)-), 0.90 (s, 72H, C(CH_3)$_3$), 0.04 (s, 48H, $Si(CH_3)_2$).

Two dendron-like hyperbranched block copolymers, **A-**

B_2-A_4 and **A-A_2-B_4**, were also synthesized in similar ways except for the addition order of α-functionalized living polymer (either PMMA or PRfMA) in the reaction step (a). The synthesis of α-functionalized living polymers and the reaction conditions are exactly the same as those employed. Their ^{1}H NMR spectra measured in $CDCl_3$ are as follows:

A-B_2: δ 7.2-6.7 (m, Ar), 4.66 (s, 8H, -CH_2-O-), 4.4-4.1 (m, -O-CH_2-), 3.7-3.4 (m, -O-CH_3), 2.6-2.3 (m, -CH_2-CF_2-), 2.1-1.7 (m, -CH_2-C(CH_3)-), 1.2-0.5 (m, -CH_2-C(CH_3)-), 0.90 (s, 36H, C(CH_3)$_3$), 0.03 (s, 24H, Si(CH_3)$_2$).

A-(B-Br_2)$_2$: δ 7.2-6.8 (m, Ar), 4.45 (s, 8H, -CH_2-Br), 4.4-4.0 (m, -O-CH_2-), 3.7-3.4 (m, -O-CH_3), 2.6-2.3 (m, -CH_2-CF_2-), 2.1-1.7 (m, -CH_2-C(CH_3)-), 1.2-0.5 (m, -CH_2-C(CH_3)-).

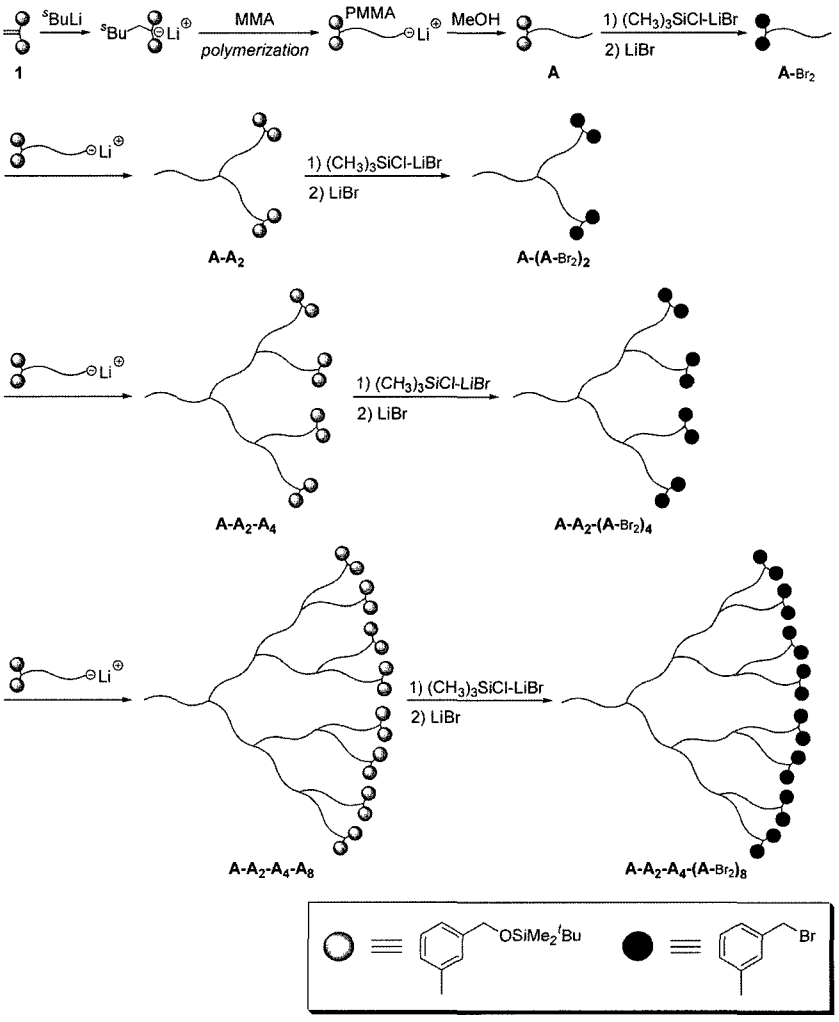
A-B_2-A_4: δ 7.2-6.7 (m, Ar), 4.66 (s, 16H, -CH_2-O-), 4.4-4.1 (m, -O-CH_2-), 3.7-3.4 (m, -O-CH_3), 2.6-2.3 (m, -CH_2-CF_2-), 2.2-1.7 (m, -CH_2-C(CH_3)-), 1.2-0.5 (m, -CH_2-C(CH_3)-), 0.90 (s, 72H, C(CH_3)$_3$), 0.04 (s, 48H, Si(CH_3)$_2$).

A-A_2-B_4: δ 7.2-6.7 (m, Ar), 4.66 (s, 16H, -CH_2-O-), 4.4-4.1 (m, -O-CH_2-), 3.7-3.4 (m, -O-CH_3), 2.6-2.3 (m, -CH_2-CF_2-), 2.1-1.7 (m, -CH_2-C(CH_3)-), 1.2-0.5 (m, -CH_2-C(CH_3)-), 0.90 (s, 72H, C(CH_3)$_3$), 0.04 (s, 48H, Si(CH_3)$_2$).

Results and Discussion

Synthesis of Dendron-Like Hyperbranched (PMMA)s. Branched architectures of the hyperbranched polymers herein targeted resemble those of dendrimers constructed from one side, so-called "*dendrons*". Their branching points are separated by linear PMMA segments with M_n values of 10 kg/mol and therefore the resulting polymers are much higher in molecular weight than dendrons consisting of small chain spacers. The iterative methodology employed for the synthesis of the dendron-like hyperbranched polymers is the same as that for the synthesis of dendrimer-like star-branched polymers previously proposed and developed by us.[17,18] The synthetic outline is illustrated in Scheme I. Throughout this synthesis, an α-functionalized living anionic PMMA with two SMP groups convertible to BnBr functionalities is used as a key building block. This functionalized living polymer is readily obtained by the anionic

Scheme I



polymerization of MMA with the functionalized anion from **1** and *sec*-BuLi in THF at -78 °C for 1 h. A 5-fold excess of LiCl toward *sec*-BuLi is always added to narrow the molecular weight distribution. The α-functionalized PMMA thus prepared is always adjusted to be around 10 kg/mol in M_n value.

In the first iteration reaction sequence, the α-functionalized living anionic PMMA was prepared by the above-mentioned procedure and terminated with degassed methanol, followed by treatment with $(CH_3)_3SiCl$-LiBr to transform the two SMP termini into two BnBr functionalities.

As was observed in the ^1H NMR spectrum of the resulting polymer as shown in Figure 1(A), three characteristic resonances at 4.66, 0.90, and 0.04 ppm (signals, d, e, and f) for benzyl methylene protons of the silyl ether and two different methyl protons of the *tert*-butyldimethylsilyl group were completely disappeared. A new resonance at 4.45 ppm corresponding to the BnBr methylene protons appeared in the same spectrum. However, a small resonance (*ca.* 5%) at 4.53 ppm assignable to methylene protons of the benzyl chloride (BnCl) functionality was also observed. This is undoubtedly resulted from the halogen exchange reaction between BnBr function and LiCl generated from $(CH_3)_3$ SiCl and LiBr. The chloride was readily re-transformed into the bromide by treatment with a 50-fold excess of LiBr in acetone. The resonance at 4.53 ppm completely disappeared by this treatment as shown in Figure 1(B). Likewise, the ^{13}C NMR spectrum also showed quantitative transformation. SEC profile of the resulting polymer showed a sharp monomodal distribution (see Figures 2(A) and 2(B)). Thus, a chain-end-functionalized PMMA with two BnBr moieties (**A**-Br_2) was quantitatively prepared from the α-functionalized living anionic PMMA.

An α-functionalized living PMMA was again prepared and then coupled with the **A**-Br_2 in THF at -40 °C. A 1.5-fold excess of α-functionalized living PMMA was used toward each BnBr moiety. After 24 h, the reaction was terminated with degassed methanol. As shown in Figure 3(A), SEC profile of the reaction mixture exhibits only two distinct sharp monomodal peaks corresponding to the coupled product and the deactivated α-functionalized living PMMA used in excess in the reaction. Neither intermediate polymer nor higher molecular weight shoulder was present at all. The coupling efficiency was virtually quantitative based on the two peak areas. The higher molecular weight fraction was isolated in 79% yield by the fractional precipitation using benzene and methanol. It was purified by reprecipitation twice, followed by freeze-drying and characterized by

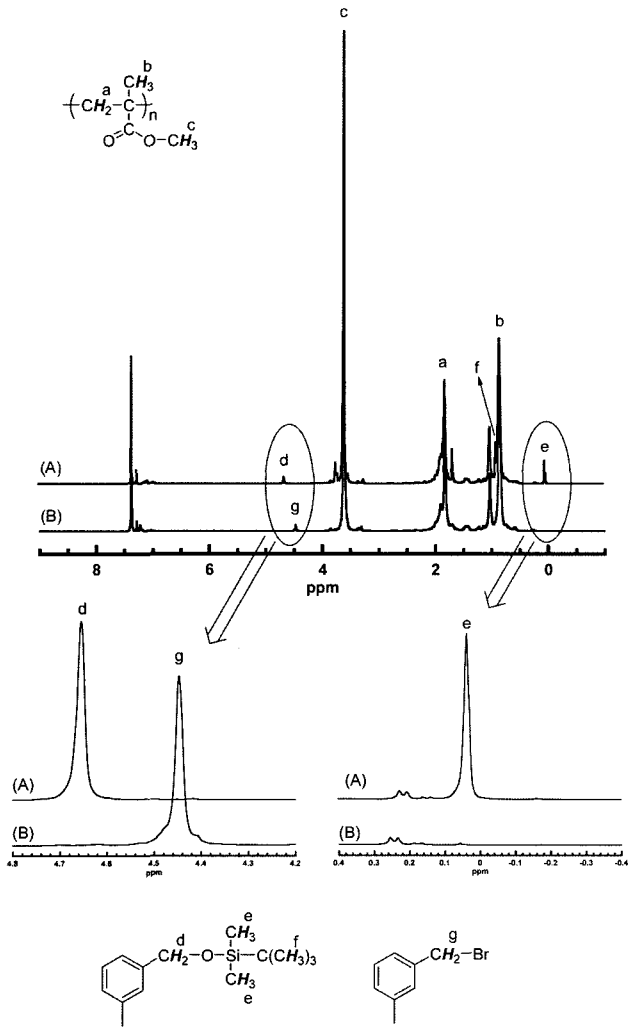


Figure 1. ^1H NMR spectra of chain-end-functionalized PMMA with two SMP groups (A) and the brominated polymer, **A**-Br_2, obtained by transformation and re-transformation reactions (B).

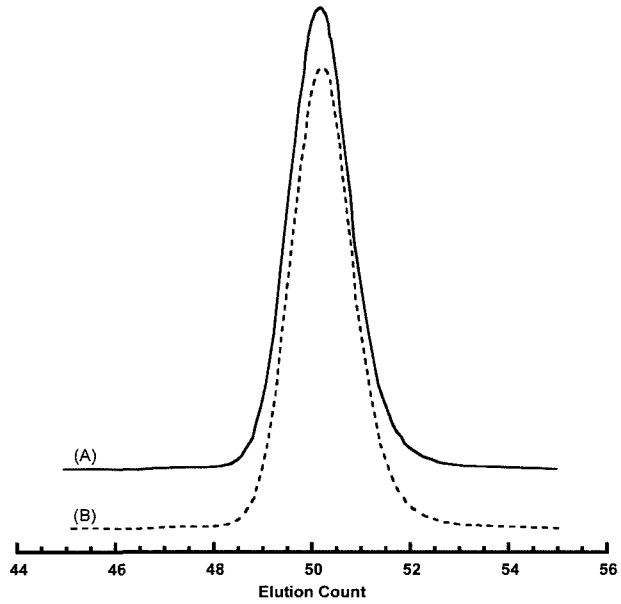


Figure 2. SEC profiles of chain-end-functionalized PMMA with two SMP groups (A) and the brominated polymer, **A**-Br_2, obtained by transformation and re-transformation reactions (B).

Table I. Synthesis of Dendron-Like Hyperbranched PMMAs up to the Third Generation

Type	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		M_w/M_n	Functionality[a]		
	Calcd	SEC	^{1}H NMR	Calcd	RALLS		Calcd	SMP	BnBr
A	10.9	11.9	10.9	-	-	1.02	2	2.00	-
A-Br_2	10.8	11.5	10.8	-	-	1.02	2	-	2.00
A-A_2	31.8	34.1	32.7	32.4	33.9	1.02	4	4.16	-
A-(A-Br_2)$_2$	31.6	32.9	32.5	-	-	1.02	4	-	4.15
A-A_2-A_4	74.2	63.0	74.2	75.7	77.3	1.01	8	8.00	-
A-A_2-(A-Br_2)$_4$	73.8	65.4	73.8	-	-	1.02	8	-	7.90
A-A_2-A_4-A_8	186	132	187	190	191	1.02	16	16.2	-

[a]Estimated by ^{1}H NMR.

^{1}H NMR, SEC, and RALLS, respectively. The results are summarized in Table I.

The isolated polymer exhibited a sharp monomodal SEC distribution, the M_w/M_n value being 1.02 (see Figure 3(B)). Since the M_n value estimated by SEC was not reliable due to its branched structure, it was determined by ^{1}H NMR using two resonances at 3.6 ppm for methoxy protons of the PMMA side chain and 0.04 ppm for silylmethyl protons of the *tert*-butyldimethylsilyl group, respectively. Furthermore, the absolute M_w value was directly determined by RALLS. These values were in good agreement with those predicted. Thus obviously, the α-functionalized living PMMA with two SMP groups quantitatively coupled with the **A**-Br_2 to afford a first-generation polymer referred to as **A**-A_2. It should be mentioned that the **A**-A_2 is a 3-arm star-branched PMMA rather than dendron-like hyperbranched polymer, two PMMA segments of which possess two SMP termini at each chain-end.

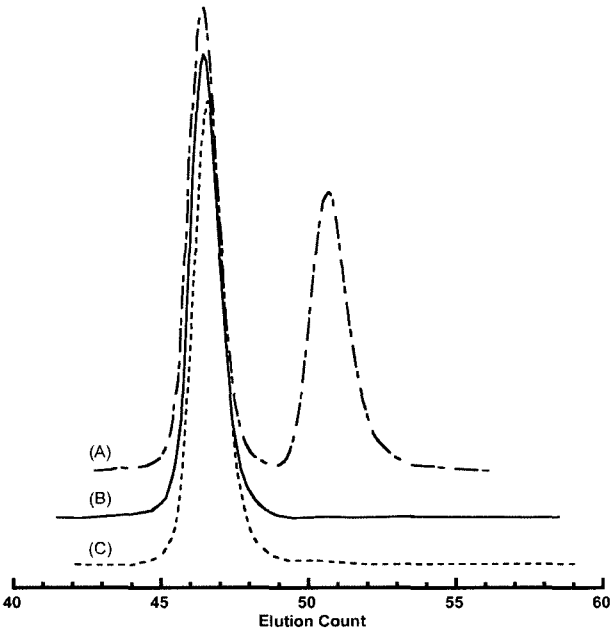


Figure 3. SEC profiles of the reaction mixture (A), a first-generation **A**-A_2 isolated by fractional precipitation (B), and the brominated polymer, **A**-(**A**-Br_2)$_2$, obtained by transformation and re-transformation reactions (C).

The SMP termini of **A**-A_2 were again transformed into BnBr functionalities by treating with $(CH_3)_3SiCl$-LiBr and subsequently with LiBr under the same conditions. The ^{1}H NMR spectrum of the resulting polymer clearly showed that the transformation was quantitative. The SEC profile exhibited a sharp monomodal distribution and was almost identical to that of **A**-A_2 in shape and elution count (see Figure 3(C)). The M_n value determined by ^{1}H NMR agreed with the predicted value. The polymer thus obtained was referred to as **A**-(**A**-Br_2)$_2$. The characterization results are also listed in Table I.

With use of the **A**-(**A**-Br_2)$_2$ as a starting polymer, the second, followed by the third iterative reaction sequence involving the coupling and transformation reactions, were performed under the same conditions. All the reactions proceeded effectively and quantitatively. Since small amounts of the BnCl moiety were also generated after the transformation reactions at the second and third iterations, the resulting polymers were treated with LiBr in acetone after the transformation reaction with $(CH_3)_3SiCl$-LiBr. Thus, second- and third-generation polymers and their brominated polymers, **A**-A_2-A_4 and **A**-A_2-A_4-A_8, **A**-A_2-(**A**-Br_2)$_4$ and **A**-A_2-A_4-(**A**-Br_2)$_8$, were obtained. The results are also summarized in Table I.

As may be seen, these polymers all are precisely controlled in chain length and degrees of SMP and BnBr functionalities as confirmed by ^{1}H NMR, ^{13}C NMR, SEC, and RALLS. Their SEC profiles exhibited sharp monomodal distributions without any shoulders and tailings. These analytical results strongly indicate that both **A**-A_2-A_4 and **A**-A_2-A_4-A_8 possess the expected dendron-like hyperbranched architectures consisting of seven and fifteen PMMA segments and **A**-A_2-(**A**-Br_2)$_4$ and **A**-A_2-A_4-(**A**-Br_2)$_8$ also possess similar branched architectures having eight and sixteen BnBr moieties at their chain-ends. Going from **A**, **A**-A_2, **A**-

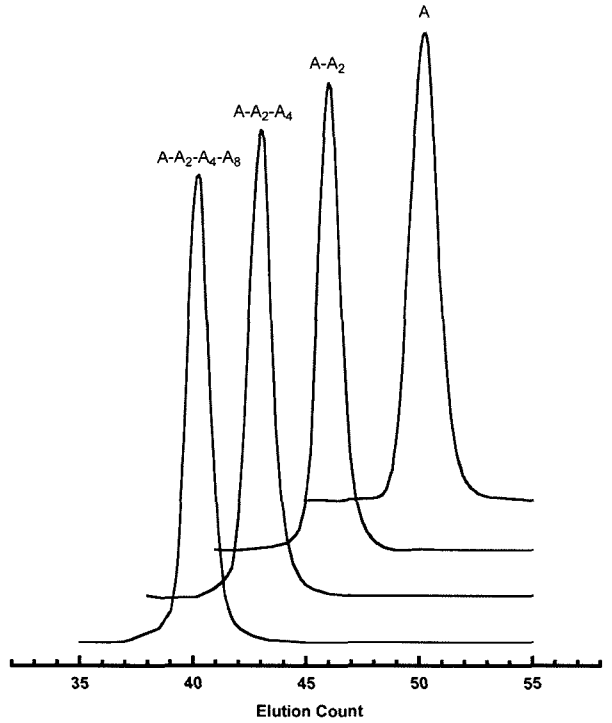
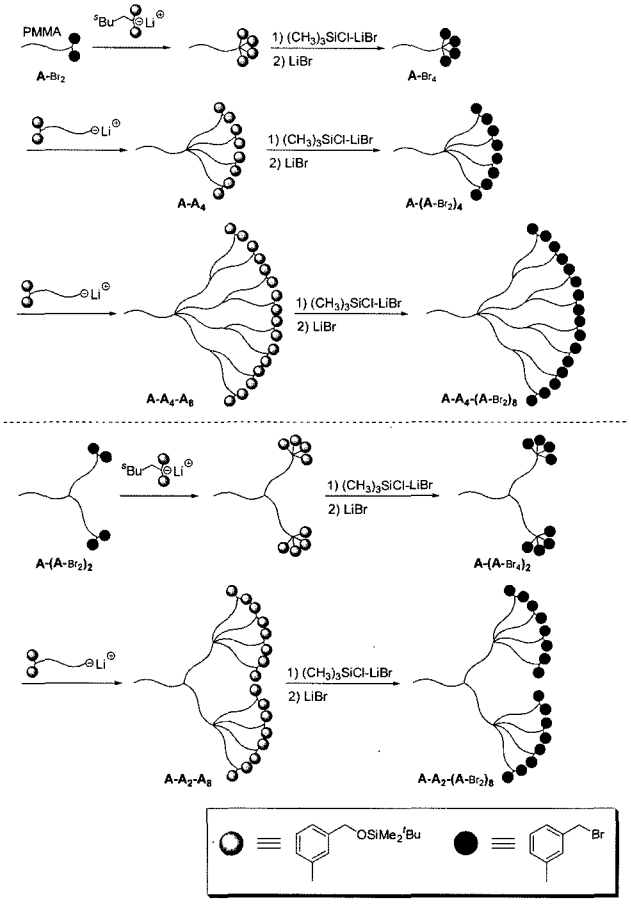


Figure 4. SEC profiles of the dendron-like hyperbranched (PMMA)s.

Scheme II



$\mathbf{A_2\text{-}A_4}$, to $\mathbf{A\text{-}A_2\text{-}A_4\text{-}A_8}$, the SEC peak moves to a higher molecular weight side as shown in Figure 4. Thus, the synthesis of the objective dendron-like hyperbranched (PMMA)s up to third-generation was achieved without problem. Since the $\mathbf{A\text{-}A_2\text{-}A_4\text{-}(A\text{-}Br_2)_8}$ possesses the same BnBr moieties, the same iterative process can be further continued to afford higher generation polymers.

Synthesis of Dendron-Like Hyperbranched (PMMA)s with Different Branched Architectures. The number of polymer segments always doubles at the branching junction in the dendron-like hyperbranched (PMMA)s synthesized in the preceding section, since each polymer segment possesses two terminal BnBr reaction sites capable of coupling with α-functionalized living PMMA. As reported previously, the BnBr reaction site is possible to double in number by the similar iterative methodology using the functionalized 1,1-diphenylalkyl anion in the coupling reaction.[20-22] As illustrated in Scheme II, the BnBr function of A-Br_2 could indeed increase from two to four in number by the reacting of A-Br_2 with the functionalized anion prepared from 1 and *sec*-BuLi in THF at -78 °C for 20 min, followed by transformation into BnBr functionalities. The ^{1}H NMR analysis showed that all BnBr functionalities had completely reacted and four SMP groups were introduced. The four SMP groups were then transformed into four BnBr moieties by treating with $(CH_3)_3SiCl$-LiBr and subsequently with LiBr. Quantitative transformation was confirmed by ^{1}H and ^{13}C NMR analyses. Thus, a new chain-end-functionalized PMMA with four BnBr moieties, A-Br_4, was successfully synthesized. The results are summarized in Table II.

The synthesis of first-generation polymer was achieved by coupling the **A**-Br_4 with α-functionalized living PMMA under the same conditions. SEC profile of the reaction mixture shown in Figure 5(A) exhibits only two single sharp peaks corresponding to the coupled product and the deactivated α-functionalized living PMMA used in excess in the reaction. The coupling efficiency was found to be quantitative based on the two peak areas. The higher molecular weight coupled product was isolated in 80% yield by fractional precipitation and characterized by ^{1}H NMR, SEC, and RALLS, respectively. The results are also summarized in Table II.

As shown in Figure 5(B), the isolated polymer exhibits a sharp monomodal distribution. The same ^{1}H NMR spectrum shows that all BnBr functionalities had completely reacted and four PMMA segments with eight SMP termini are introduced. The M_n and M_w values determined by ^{1}H NMR and RALLS agreed well with those predicted. Thus, a first-generation polymer, $\mathbf{A\text{-}A_4}$, was successfully obtained. The resulting polymer was treated with $(CH_3)_3SiCl$-LiBr and then with LiBr to transform the SMP groups into BnBr function-

Table II. Synthesis of Dendron-Like Hyperbranched PMMAs with Different Branched Architectures

Type	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		M_w/M_n	Functionality[a]		
	Calcd	SEC	^{1}H NMR	Calcd	RALLS		Calcd	SMP	BnBr
A-Br_2	10.8	11.5	10.8	-	-	1.02	2	-	2.00
A-A_2	31.8	34.1	32.7	32.4	33.9	1.02	4	4.16	-
A-(A-Br_2)$_2$	31.6	32.9	32.5	-	-	1.02	4	-	4.15
A-A_2-A_4	74.2	63.0	74.2	75.7	77.3	1.01	8	8.00	-
A-Br_4	11.5	12.4	11.5	-	-	1.03	4	-	3.98
A-A_4	50.0	41.3	49.6	51.0	51.6	1.02	8	7.90	-
A-(A-Br_2)$_4$	49.6	40.0	49.2	-	-	1.02	8	-	8.12
A-A_4-A_8	135	97.5	136	138	143	1.02	16	16.2	-
A-(A-Br_4)$_2$	33.2	31.3	33.2	-	-	1.02	8	-	8.00
A-A_2-A_8	115	90.2	114	117	120	1.02	16	15.8	-

[a]Estimated by ^{1}H NMR.

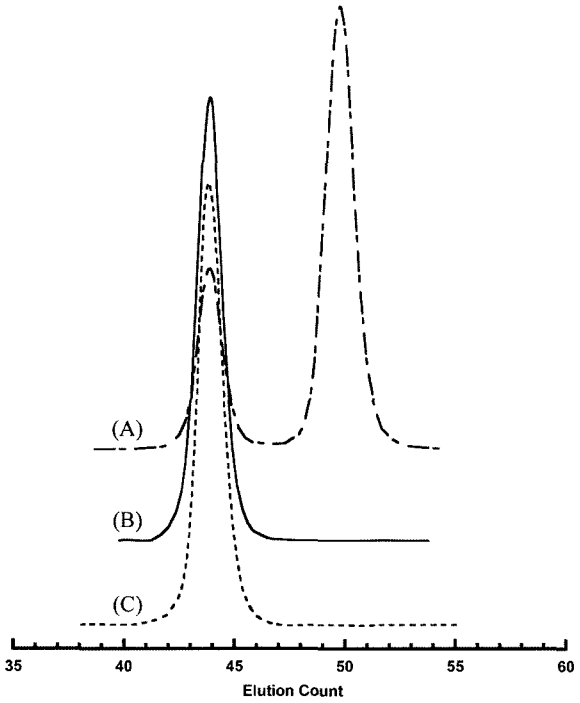


Figure 5. SEC profiles of the reaction mixture (A), a first-generation **A-A_4** isolated by fractional precipitation (B), and the brominated polymer, **A-(A-Br_2)$_4$**, obtained by transformation and re-transformation reactions (C).

alities to afford the brominated polymer, **A-(A-Br_2)$_4$**. A second-generation polymer was synthesized by the coupling of the **A-(A-Br_2)$_4$** with α-functionalized living PMMA. As expected, the reaction was quantitative to afford the objective second-generation dendron-like hyperbranched PMMA, **A-A_4-A_8**. The M_n and M_w values were determined to be 136 and 143 kg/mol by ^{1}H NMR and RALLS, respectively. These values correspond well to the target values as listed in Table II. Four PMMA segments, followed by eight PMMA segments with sixteen SMP termini, were introduced by the first and second iteration processes as illustrated in Scheme II.

It is also possible to double the BnBr functionality of the first-generation brominated polymer, **A-(A-Br_2)$_2$**, by treatment with the functionalized anion prepared from **1** and *sec*-BuLi, followed by transformation into BnBr functionalities. The subsequent coupling reaction of the resulting polymer, **A-(A-Br_4)$_2$**, with α-functionalized living PMMA gave the requisite second-generation dendron-like hyperbranched PMMA, **A-A_2-A_8**, consisting of eleven PMMA segments and sixteen SMP termini. The expected structure of the resulting **A-A_2-A_8** was confirmed by ^{1}H NMR, SEC, and RALLS, respectively, as listed in Table II. Thus, three different well-defined second-generation dendron-like hyperbranched (PMMA)s in branched architecture, **A-A_2-A_4**, **A-A_2-A_8**, and **A-A_4-A_8**, were successfully synthesized by the same iterative methodology. The branched architecture can readily be controlled by the reacting of the brominated polymer at each iteration stage with the functionalized anion prepared from **1** and *sec*-BuLi. Needless to say, all of the polymers synthesized possess terminal BnBr functionalities and hence the iteration process can be further repeated to synthesize higher generation dendron-like hyperbranched polymers.

Synthesis of Dendron-Like Hyperbranched Block Copolymers Consisting of PMMA and Poly(2-(perfluorobutyl)ethyl methacrylate) (PRfMA) Segments. One of the advantageous features of the iterative methodology developed here is that a variety of dendron-like hyperbranched block copolymers may be synthesized by changing the living anionic polymer to be reacted in the coupling reaction. Since many living anionic polymers of substituted methacrylate monomers with functional groups have been synthesized at the present time,[23-35] various functional segments can be intentionally incorporated into dendron-like hyperbranched polymers.

In this section, we have synthesized a series of dendron-like hyperbranched block copolymers consisting of PMMA and PRfMA segments in order to design and synthesize effective surface-functionalized materials. At first, the anionic polymerizability of RfMA and the stability of the resulting PRfMA toward the conditions of coupling and transformation reactions were examined to make sure a possible use of α-functionalized living PRfMA. Similar to the results previously reported by us,[30] RfMA underwent living anionic polymerization with the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi in THF at -78 °C in the presence of LiCl. However, the polymers having M_n values of higher than 10 kg/mol were always precipitated during the polymerization at -78 °C. Therefore, molecular weight distribution of the resulting polymer was broadened. For this reason, the polymers of M_n values of 3~5 kg/mol were used in our synthesis.

The resulting α-functionalized PRfMA with two SMP groups was treated with $(CH_3)_3SiCl$-LiBr and then with LiBr under the same conditions employed above. As can be seen in Figures 6(A) and 6(B), ^{1}H NMR analysis shows that the two SMP termini are completely transformed into BnBr functionalities and other signals remain unchanged, indicating that the transformation reaction proceeds cleanly and quantitatively. SEC peaks of the polymers before and after such treatments were sharp and monomodal and eluted at similar counts. Thus, a well-defined chain-end-functionalized PRfMA with two BnBr functionalities, **B**-Br_2, was obtained without problem. Then, the coupling reaction of the **B**-Br_2 with α-functionalized living PMMA was carried out in THF at -40 °C for 24 h. SEC profile of the reaction mixture showed only two single peaks for the coupled product and the deactivated α-functionalized PMMA used in excess and neither shoulder nor intermediate polymer was formed. The higher molecular weight product was isolated in 89% yield by fractional precipitation and characterized by ^{1}H NMR, SEC, and RALLS, respectively. The results are summarized in

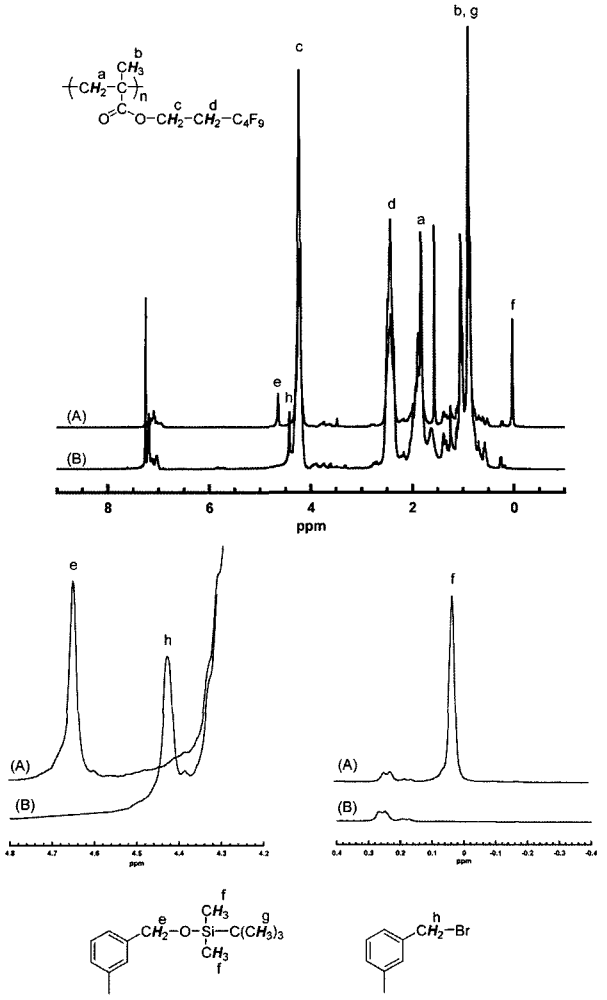


Figure 6. ^{1}H NMR spectra of chain-end-functionalized PRfMA with two SMP groups (A) and the brominated polymer, **B**-Br_2, obtained by transformation and re-transformation reactions (B).

Table III. The ^{1}H NMR spectrum showed that the two BnBr functionalities had completely reacted and two PMMA seg-

Table III. Synthesis of Dendron-Like Hyperbrandched Block Copolymers Consisting of PMMA and PRfMA Segments

Type	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		M_w/M_n	Functionality[a]		
	Calcd	SEC	^{1}H NMR	Calcd	RALLS		Calcd	SMP	BnBr
B	5.20	4.97	5.61	-	-	1.06	2	2.00	-
B-Br_2	5.10	4.94	5.51	-	-	1.05	2	-	2.14
B-A_2	25.6	24.8	25.5	26.1	26.5	1.02	4	3.87	-
B-(A-Br_2)$_2$	25.4	26.8	25.3	-	-	1.02	4	-	4.01
B-A_2-A_4	67.9	58.1	68.5	69.2	68.5	1.02	8	8.08	-
A-B_2	18.2	15.7	18.2	18.7	18.6	1.03	4	4.00	-
A-(B-Br_2)$_2$	18.0	13.3	18.0	-	-	1.04	4	-	3.88
A-B_2-A_4	58.8	48.4	57.9	60.0	62.2	1.02	8	7.82	-
A-A_2-B_4	50.2	35.5	50.3	51.2	40.4	1.02	8	8.08	-

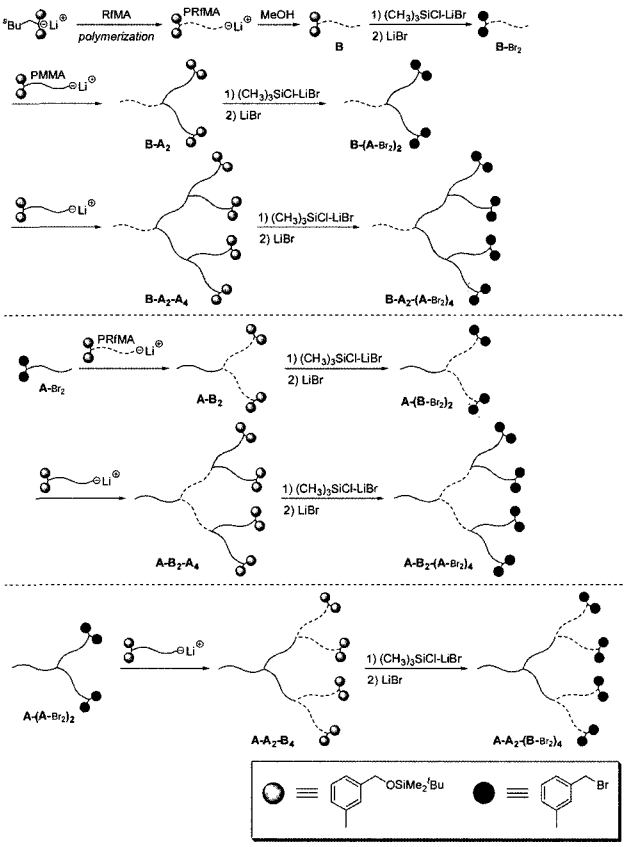
[a]Estimated by ^{1}H NMR.

ments were introduced. The M_n and M_w values determined by ^{1}H NMR and RALLS were in good agreement with the target values. Accordingly, the coupling reaction proceeded cleanly to afford a first-generation polymer referred to as **B-A$_2$**. This polymer can be regarded as a 3-arm asymmetric star-branched polymer consisting of one PRfMA and two PMMA segments. Thus obviously, α-functionalized living anionic PRfMA is usable to incorporate the PRfMA segment into dendron-like hyperbranched polymers.

As illustrated in Scheme III, a second-generation dendron-like hyperbranched block copolymer, **B-A$_2$-A$_4$**, was synthesized by transforming the four SMP termini of **B-A$_2$** into four BnBr functionalities, followed by coupling the brominated polymer, **B-(ABr$_2$)$_2$**, with α-functionalized living PMMA. The resulting polymer was observed to have the expected structure as listed in Table III. Similarly, both dendron-like hyperbranched block copolymers, **A-B$_2$-A$_4$** and **A-A$_2$-B$_4$**, were synthesized by appropriately changing the reaction order of α-functionalized living PMMA and PRfMA. The expected structure and M_n value of the resulting **A-B$_2$-A$_4$** were confirmed by comparing the integral ratio of two signals at 3.6 and 0.04 ppm for methoxy proton of the PMMA side chain and silylmethyl proton of the *tert*-butyldimethylsilyl group in the ^{1}H NMR spectrum. Additional evidence for the structure of **A-B$_2$-A$_4$** was provided by good agreement between the M_w values determined by RALLS and predicted. In the case of **A-A$_2$-B$_4$** polymer, the calculated M_n value was in good agreement with that determined by the ^{1}H NMR spectrum using the above-mentioned two signals at 3.6 and 0.4 ppm. However, the same spectrum measured in either $CDCl_3$ or d_8-THF showed that the content of PRfMA was somewhat lower than the expected value based on PMMA segment. It was also observed that the M_w value determined by RALLS in THF was relatively smaller than the target value. Accordingly, we consider that the unexpected lower PRfMA content and the smaller M_w value may be resulted from the aggregation of PRfMA segments in such solvents and therefore the measurements should be performed in perfluorocarbon media. Thus, the synthesis of three dendron-like hyperbranched block copolymers was achieved by the same iterative methodology with the appropriate choice of either of α-functionalized living anionic polymers of MMA and RfMA. As is seen in Scheme III, the three block copolymers have the same branched architecture obtained by the second-generation stage, but the difference in these polymers is the placement of the PRfMA segment.

Surface Characterization of Dendron-Like Hyperbranched Block Copolymers. The surface (and/or polymer-air interfacial) properties of multi-component polymer systems such as polymer blends, random, graft, and block copolymers and even chain-end-functionalized polymers can be quite different from those of the bulk by introducing particular functional groups into their polymer chains.[30,31,36-46]

Scheme III



It is now well established that a functional group that has a lower surface energy than its original polymer chain preferentially segregates to enrich at the surface. Such a segregation effect is especially accentuated when a series of perfluoroalkyl (Rf) groups are employed as functional groups. In fact, the significant surface segregation behavior can be observed in almost all multi-component polymer systems containing Rf group(s) and/or Rf-functionalized polymer segments by various surface analytical methods, resulting in drastic change of their surface properties to hydrophobic as well as lipophobic characters.

In contrast to many studies using Rf-functionalized block copolymers, little has been studied on the surface characterization of branched block copolymers containing Rf-functionalized polymer segments because of their synthetic difficulty and limitation. The dendron-like hyperbranched block copolymers consisting of PMMA and PRfMA segments synthesized here are very attractive materials in order to elucidate how the branched architecture can influence the surface structure. For this reason, the three dendron-like hyperbranched block copolymers, **B-A$_2$-A$_4$**, **A-B$_2$-A$_4$**, and **A-A$_2$-B$_4$**, were cast into films followed by annealing and their surface characters and structures were examined by contact angle and angle-dependent XPS measurements.

Surface structures and degrees of enrichment of the speci-

Table IV. Atomic % of Film Surface of Dendron-Like Hyperbranched Block Copolymers by Angle-Dependent XPS

Type	XPS Atomic-% (%) (F/C)				
	10° TOA[a]	20° TOA	45° TOA	80° TOA[a]	Bulk[b]
B-A_2-A_4	15.4/61.9	12.9/63.6	9.08/65.5	8.65/65.6	2.87/70.7
A-B_2-A_4	17.7/61.2	16.9/61.5	11.5/64.3	10.5/64.3	4.42/70.0
A-A_2-B_4	36.4/51.1	32.0/53.4	23.4/58.5	21.3/59.4	13.5/65.2
PMMA	-	-	-	-	71.4/0
PRfMA	-	-	-	-	42.9/47.6

[a]10 and 80° TOA (Take-off angle) correspond to approximately 20 and 100 Å depths, respectively.
[b]Calculated value from chemical composition of the polymer.

fied atom and/or functional group can be quantitatively discussed by atomic composition as a function of depth measured by angle-dependent XPS. Table IV shows the results of the F/C atomic % ratios at 10, 20, 45, and 80° take-off angles (TOA)s obtained for the annealed cast films of **B-A_2-A_4**, **A-B_2-A_4**, and **A-A_2-B_4**. The (TOA)s of 10 and 80° approximately correspond to 20 and 100 Å depths from outmost top surface, respectively. In addition, the results of homopolymers of MMA and RfMA with similar molecular weights are also listed as references in this table.

In all cases, the values of F atomic % at 10° TOA were much higher than they were in bulk. Furthermore, the values at 10° TOA were always higher than those at 80° TOA. These results clearly indicate that the PRfMA segments are preferentially segregated and enriched at the film surfaces of all polymer samples. Among the three samples, **A-A_2-B_4** was much higher than those of **B-A_2-A_4** and **A-B_2-A_4** in F atomic % at 10° TOA and close to the value of RfMA homopolymer. Accordingly, it means that the film surface is completely covered with PRfMA segment.

Since contact angle measurement is also convenient and useful for obtaining information on the surface character, contact angles of the three films were measured by using water and dodecane droplets, respectively. The results are summarized in Table V. The contact angles of **B-A_2-A_4**, **A-B_2-A_4**, and **A-A_2-B_4** with water droplet were much higher than 78.0° of PMMA, strongly indicating that PRfMA segments are segregated more or less at the surfaces to form hydrophobic surfaces. The contact angle value increases from **B-A_2-A_4**, **A-B_2-A_4**, to **A-A_2-B_4** and of particular interest is that **A-A_2-B_4** is comparable to PRfMA in value. A similar tendency was observed in the contact angle measurement using dodecane droplet. The contact angle of PMMA could not be measured by getting wet with dodecane, while **B-A_2-A_4**, **A-B_2-A_4**, and **A-A_2-B_4** showed measurable values and the value increased in this order. Again, the contact angle of **A-A_2-B_4** is comparable to that of PRfMA, indicating the formation of lipophobic surfaces covered with PRfMA segments.

Table V. Contact Angle Values of Dendron-Like Hyperbranched Block Copolymers

Type	Contact Angle (°)	
	Water	Dodecane
B-A_2-A_4	93.7	32.3
A-B_2-A_4	97.0	34.4
A-A_2-B_4	106	53.5
PMMA	78.0	n.d.[a]
PRfMA	105	56.2

[a]Not determined.

Thus, preferential segregation and significant enrichment of PRfMA segment at the film surface were clearly observed by angle-dependent XPS as well as contact angle measurement with water and dodecane droplets. Both the two measurements showed that degree of PRfMA segment enrichment increased from **B-A_2-A_4**, **A-B_2-A_4**, to **A-A_2-B_4** and the surface structure of **A-A_2-B_4** looks similarly to that of PRfMA. In other word, the surface of **A-A_2-B_4** seems to be completely covered with its PRfMA segments. Among the three samples, obviously, **A-A_2-B_4** is much superior to **B-A_2-A_4** and **A-B_2-A_4** in terms of surface enrichment. At the present time, however, it is rather difficult to discuss the effect of branched architecture on surface enrichment since their fluorine contents are different from each other.

Conclusions

We have demonstrated the successful synthesis of dendron-like hyperbranched (PMMA)s and block copolymers comprised of PMMA and PRfMA segments by the iterative methodology. The methodology involves the following only two reactions in each iterative process: (a) a coupling reaction of α-functionalized living anionic PMMA with two SMP groups with BnBr-chain-end-functionalized PMMA, (b) a transformation reaction of the introduced SMP groups into BnBr functionalities. By repeating the iterative process four times, a series of dendron-like hyperbranched (PMMA)s up to third generation, **A-A_2**, **A-A_2-A_4**, and **A-A_2-A_4-A_8**, were quantitatively obtained. Three dendron-like hyperbranched

(PMMA)s different in branched architecture, **A-A_2-A_4**, **A-A_2-A_8**, and **A-A_4-A_8**, have also been synthesized by the reacting of the brominated polymer with the functionalized 1,1-diphenylalkyl anion in the reaction step (b) in the same iterative methodology. Furthermore, the synthesis of three structural similar dendron-like hyperbranched block copolymers different in sequence, **B-A_2-A_4**, **A-B_2-A_4**, and **A-A_2-B_4**, has been achieved by the coupling of either α-functionalized living PMMA (**A** segment) or PRfMA (**B** segment) in the reaction step (a) in the iterative methodology. Thus advantageously, it is possible to synthesize various dendron-like hyperbranched polymers by changing the agents to be reacted in the reaction steps, (a) and (b). All of the analytical results indicate that the resulting dendron-like hyperbranched (PMMA)s and block copolymers have a high molecular and structural homogeneity. Since the resulting polymers all have BnBr functionalities or SMP termini readily and quantitatively convertible to BnBr functionalities, the same iteration process can be further repeated to afford higher generation dendron-like hyperbranched polymers and block copolymers.

The block copolymers were cast into films, followed by annealing, and characterized by angle-dependent XPS and contact angle measurements in order to examine their surface structures. In all films, preferential surface segregation and significant enrichment of PRfMA segment were clearly observed. It was found that the degree of enrichment increases from **B-A_2-A_4**, **A-B_2-A_4**, to **A-A_2-B_4**. In particular, the surface structure of the film prepared from **A-A_2-B_4** is very similar to that prepared from PRfMA, strongly indicating that the film surface of **A-A_2-B_4** is completely covered with PRfMA segments. At this moment, however, it is rather difficult to discuss the effect of branched architecture on surface enrichment, since their fluorine contents are different from each other. In forthcoming research, the synthesis of higher-generation dendron-like hyperbranched block copolymers is now undertaken to clarify how branched architecture affects surface enrichment and to design and synthesize effective surface functionalized materials based on the dendron-like hyperbranched architecture.

Acknowledgements. 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.

References

(1) M. Trollsås, and J. L. Hedrick, *J. Am. Chem. Soc.*, **120**, 4644 (1998).
(2) J. L. Hedrick, M. Trollsås, C. J. Hawker, B. Atthoff, H. Claesson, A. Heise, R. D. Miller, D. Mecerreyes, R. Jérôme, and Ph. Dubois, *Macromolecules*, **31**, 8691 (1998).
(3) M. Trollsås, H. Claesson, B. Atthoff, and J. L. Hedrick, *Angew. Chem. Int. Ed.*, **37**, 3132 (1998).
(4) M. Trollsås, M. A. Kelly, H. Claesson, R. Siemens, and J. L. Hedrick, *Macromolecules*, **32**, 4917 (1999).
(5) M. Trollsås, B. Atthoff, A. Würsch, J. L. Hedrick, J. A. Pople, and A. P. Gast, *Macromolecules*, **33**, 6423 (2000).
(6) A. Würsch, M. Möller, T. Glauser, L. S. Lim, S. B. Voytek, J. L. Hedrick, C. W. Frank, and J. G. Hilborn, *Macromolecules*, **34**, 6601 (2001).
(7) C. M. Stancik, J. A. Pople, M. Trollsås, P. Lindner, J. L. Hedrick, and A. P. Gast, *Macromolecules*, **36**, 5765 (2003).
(8) M. Trollsås, B. Atthoff, H. Claesson, and J. L. Hedrick, *J. Polym. Sci.; Part A: Polym. Chem.*, **42**, 1174 (2004).
(9) S. Angot, D. Taton, and Y. Gnanou, *Macromolecules*, **33**, 5418 (2000).
(10) Y. Gnanou and D. Taton, *Macromol. Symp.*, **174**, 333 (2001).
(11) V. Héroguez, D. Taton, and Y. Gnanou, *Polymer News*, **26**, 150 (2001).
(12) S. Hou, E. L. Chaikof, D. Taton, and Y. Gnanou, *Macromolecules*, **36**, 3874 (2003).
(13) S. Hou, D. Taton, M. Saule, J. Logan, E. L. Chaikof, and Y. Gnanou, *Polymer*, **44**, 5067 (2003).
(14) B. Lepoittevin, R. Matmour, R. Matmour, R. Francis, D. Taton, and Y. Gnanou, *Macromolecules*, **38**, 2130 (2005).
(15) I. Chalari and N. Hadjichristidis, *J. Polym. Sci.; Part A: Polym. Chem.*, **40**, 1519 (2002).
(16) D. M. Knauss and T. Huang, *Macromolecules*, **36**, 6036 (2003).
(17) A. Matsuo, T. Watanabe, and A. Hirao, *Macromolecules*, **37**, 6283 (2004).
(18) A. Hirao, M. Hayashi, S. Loykulnant, K. Sugiyama, S. W. Ryu, N. Haraguchi, A. Matsuo, and T. Higashihara, *Prog. Polym. Sci.*, **30**, 111 (2005).
(19) A. Hirao and M. Hayashi, *Macromolecules*, **32**, 6450 (1999).
(20) A. Hirao and N. Haraguchi, *Macromolecules*, **35**, 7224 (2002).
(21) N. Haraguchi and A. Hirao, *Macromolecules*, **36**, 9364 (2003).
(22) A. Hirao and A. Matsuo, *Macromolecules*, **36**, 9742 (2003).
(23) L. Leemans, R. Fayt, and Ph. Teyssié, *J. Polym. Sci.; Part A: Polym. Chem.*, **28**, 2187 (1990).
(24) H, Ozaki, A, Hirao, and S. Nakahama, *Macromolecules*, **25**, 1391 (1992).
(25) H. Mori, O. Wakisaka, A. Hirao, and S. Nakahama, *Macromol. Chem. Phys*, **195**, 3213 (1994).
(26) T. Ishizone, T. Tominaga, K. Kitamura, A. Hirao, and S. Nakahama, *Macromolecules*, **28**, 4829 (1995).
(27) H. Zhang and E. Ruckenstein, *J. Polym. Sci.; Part A: Polym. Chem.*, **35**, 2901 (1997).
(28) T. Ishizone, G. Uehara, A. Hirao, S. Nakahama, and K. Tsuda, *Macromol. Chem. Phys.*, **199**, 1827 (1998).
(29) M. Yamada, T. Itoh, R. Nakagawa, A. Hirao, S. Nakahama, and J. Watanabe, *Macromolecules*, **32**, 282 (1999).
(30) T. Ishizone, K. Sugiyama, Y. Sakano, H. Mori, A. Hirao, and S. Nakahama, *Polym. J.*, **31**, 983 (1999).
(31) Y. Tanaka, H. Hasegawa, T. Hashimoto, A. Ribbe, K. Sugiyama, A. Hirao, and S. Nakahama, *Polym. J.*, **31**, 989

(1999).
(32) H. Zhang and E. Ruckenstein, *Macromolecules*, **34**, 3587 (2001).
(33) T. Ishizone, S. Han, S. Okumura, and S. Nakahama, *Macromolecules*, **36**, 42 (2003).
(34) S. Han, M. Hagiwara, and T. Ishizone, *Macromolecules*, **36**, 8312 (2003).
(35) K. Sugiyama, H. Azuma, T. Watanabe, T. Ishizone, and A. Hirao, *Polymer*, **44**, 4157 (2003).
(36) S. Affrossman, P. Bertrand, M. Hartahorne, T. Kiff, D. Leonard, R. A. Pethtick, and R. W. Richards, *Macromolecules*, **29**, 5432 (1996).
(37) J. Genzer, E. Sivaniah, E. J. Kramer, J. Wang, H. Körner, M. Xiang, K. Char, C. K. Ober, B. M. DeKoven, R. A. Bubeck, M. K. Chaudhury, S. Sambasivan, and D. A. Fischer, *Macromolecules*, **33**, 1882 (2000).
(38) J. Genzer, E. Sivaniah, E. J. Kramer, J. Wang, H. Körner, K. Char, C. K. Ober, B. M. DeKoven, R. A. Bubeck, D. A. Fischer, and S. Sambasivan, *Langmuir*, **16**, 1993 (2000).
(39) T. M. Chapman and K. G. Marra, *Macromolecules*, **28**, 2081 (1995).
(40) T. Hayakawa, J. Wang, M. Xiang, X. Li, M. Ueda, C. K. Ober, J. Genzer, E. Sivaniah, E. J. Kramer, and D. A. Fischer, *Macromolecules*, **33**, 8012 (2000).
(41) H. Zhang, J. Pan, and T. H. Hogen-Esch, *Macromolecules*, **32**, 2815 (1998).
(42) H. Sawada, Y. Yoshino, Y. Ikematsu, and T. Kawase, *Eur. Polym. J.*, **36**, 231 (2000).
(43) K. Sugiyama, T. Nemoto, G. Koide, and A. Hirao, *Macromol. Symp.*, **181**, 135 (2002).
(44) A. Hirao, G. Koide, and K. Sugiyama, *Macromolecules*, **35**, 7642 (2002).
(45) A. Hirao, S. Sakai, and K. Sugiyama, *Polym. Adv. Technol.*, **15**, 15 (2004).
(46) K. Sugiyama, S. Sakai, A. El-Shehawy, and A. Hirao, *Macromol. Symp.*, **217**, 1 (2004).