Macromolecules **2009**, *42*, 682−693

Precise Synthesis and Characterization of Fourth-Generation Dendrimer-like Star-Branched Poly(methyl methacrylate)s and Block Copolymers by Iterative Methodology Based on Living Anionic Polymerization

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Received October 2, 2008; Revised Manuscript Received November 25, 2008

ABSTRACT: A series of the fourth-generation (4G) dendrimer-like star-branched poly(methyl methacrylate)s, (PMMA)s, with high branch densities have been synthesized by the iterative "arm-first" divergent methodology. It involves a two-reaction sequence in each iterative process: (1) a linking reaction of α-functionalized living anionic PMMA with either two or four *tert*-butyldimethylsilyloxymethylphenyl (SMP) groups with benzyl bromide (BnBr)-chain-end-functionalized PMMA and (2) a transformation reaction of the SMP groups into BnBr functions. Accordingly, the branch segments are introduced by the (1) linking reaction based on termination reaction using premade living anionic polymers. The two-reaction sequence has been repeated four times to build up the 4G dendrimer-like star-branched polymers composed of four branch junctures in three generations and two branch junctures in one generation. Likewise, three block copolymers with the same dense 4G branched architectures have been synthesized by the linking reaction of the 3G brominated PMMA with either of living anionic polymers of *tert*-butyl methacrylate, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate, and 2-vinylpyridine. Unfortunately, however, the synthesis of a highly dense 4G polymer composed of four branch junctures in all generations was not successful possibly due to steric hindrance. The resulting dendrimer-like star-branched (PMMA)s have been analyzed by RALLS, SAXS, and viscosity measurements to obtain their hydrodynamic radii, radii of gyration, intrinsic viscosities, and g' values. The relationship between either of such values and the branched structures, generation, or molecular weight will be discussed. The observation of the largest and most dense 4G polymer by AFM was attempted in order to directly visualize the dendrimer-like star-branched polymer.

Introduction

Along with rapid progress in living/controlled polymerization, a number of complex and/or hybrid branched polymers have been synthesized because of the synthetic challenges associated with preparing them and because they offer unique physical properties quite different from linear polymers. Among them, dendrimer-like star-branched polymers have recently appeared as a new class of hyperbranched polymers.[1−4] Although these polymers resemble well-known dendrimers in branched architecture, they are composed of polymer chains between branch junctions and, accordingly, much higher in molecular weight and much larger in molecular size than dendrimers as shown in Figure 1.

Dendrimer-like star-branched polymers are recognized as nano-ordered globular macromolecules from their architectures and some analytical results and have many characteristic structural features such as hierarchic hyperbranched structures, generation-based radial architectures, different branch densities between core (inside) and shell (outside), and many junction points and end-groups. It is also possible to synthesize a variety of block copolymers with the same branched architectures by introducing different polymer segments at each generation. Such block copolymers may possibly be phase-separated at the molecular level, followed by self-organizing, to generate unique and characteristic nanosize ordered suprastructures and supramolecular assemblies because of their hierarchic hyper-

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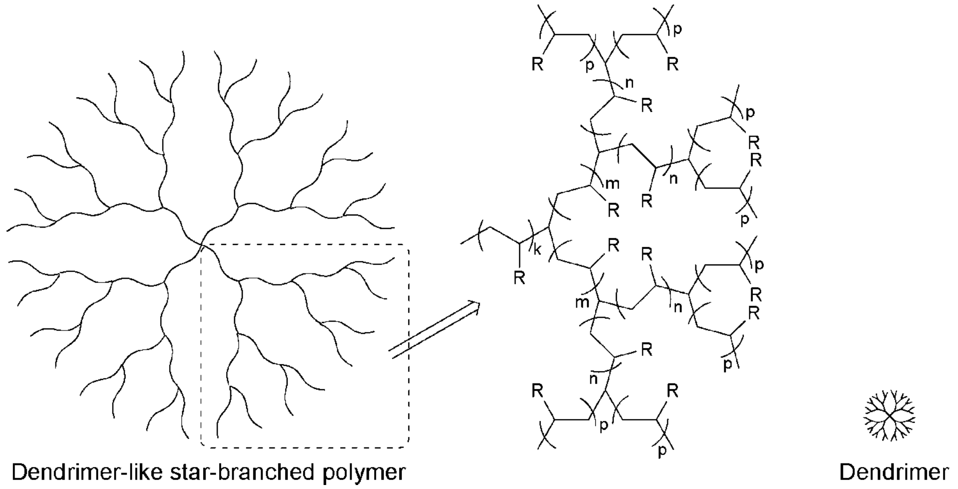
10.1021/ma802209n CCC: $40.75



Dendrimer-like star-branched polymer

Dendrimer

Figure 1. Dendrimer-like star-branched polymer and dendrimer.

branched architectures as well as heterophase structures. Moreover, the formation of alternative or several separated layer structures is highly probable. Interesting morphologies and nanostructured materials have been indeed reported by several research groups.[5−15] Thus, dendrimer-like star-branched polymers and block copolymers are promising specialty functional materials with many possible applications to drug, vaccine, and gene encapsulated delivery devices, surface modifiers, functional nanosize spheres and micelles, surfactant, molecular recognition systems, microelectronic materials, etc.

Dendrimer-like star-branched polymers have been so far synthesized by either iterative "core-first" divergent or "arm-first" convergent methodology using living polymers as building blocks. In the "core-first" methodology, an initiation procedure is usually employed to introduce branch segments.[5−11,16−18] Typically, an appropriate monomer is first polymerized with a multifunctional initiator in a living/controlled manner, and then each of the propagating chain ends is modified to convert to two or more initiation sites. The two reaction sequence, i.e., living/controlled polymerization and chain-end modification, are repeated to construct high-generation polymers. Although defined structures of the resulting polymers are suggested in most cases, there always remains a question on the uniformity of all polymer chains propagated from the multi-initiation sites at each generation. Moreover, it is difficult to accurately determine how many initiation sites work. In the "arm-first" methodology, the parts of dendrimer-like star-branched polymer, so-called dendron in the dendrimer chemistry, are first prepared by using premade living polymers.[14,15,19−21] Then, the dendrons thus prepared are linked with a multifunctional core compound to build up the objective polymers. Thus, a termination procedure is used for the introduction of branch segments in this methodology. Therefore, well-defined structures of the resulting polymers are readily checked by comparing the total molecular weights of the final polymers with those of dendrons and premade living polymers. In practice, the well-defined second- and third- generation (2G and 3G) polymers have been successfully synthesized by Hadjichristidis et al., Hutchings et al., and Monteriro et al.[14,15,19−21] Unfortunately, however, the synthesis of higher generation dendrimer-like star-branched polymers seems difficult because the linking reaction among high molecular weight dendrons is required at the final stage.

A variety of dendrimer-like star-branched polymers have been so far synthesized by the two methodologies, but most of the synthetic examples are limited to the 3G stages and 10^5 g/mol orders in molecular weight because of experimental difficulties. The synthesis of the 7G dendrimer-like star-branched polystyrene by the "core-first" methodology based on initiation procedure has been recently reported by Matmour and Gnanou.[22] Once again, there is no description on the uniformity of the branch segments.

For a recent few years, we have been developing a novel iterative "arm-first" divergent methodology in order to synthesize high-generation and high-molecular-weight dendrimer-like star-branched polymers with well-defined and characterized structures.[23−28] The termination procedure using premade living anionic polymers is used to introduce branch segments like the case of "arm-first" convergent methodology mentioned above. Basically, only two sets of reaction conditions are needed for the entire iterative synthetic sequence: (1) a linking reaction between the living anionic polymer α-functionalized with two 3-*tert*-butyldimethylsilyloxymethylphenyl (SMP) groups and either a core compound having four benzyl bromide (BnBr) functions or BnBr-chain end-functionalized polymer and (2) a transformation reaction of the SMP groups into BnBr functions. The two reactions are corresponding to the introduction of branch segments and chain-end modification leading to the next introduction, respectively. By repeating these reactions, a series of well-defined dendrimer-like star-branched poly(methyl methacrylate)s, (PMMA)s, up to the 7G have been successfully synthesized. The resulting polymers all have four segments emanating from the core and two branch junctures in all the layers from 2G to 7G. Since heterogeneous initiation and propagation from multi-initiation sites and linking reactions among high-molecular-weight dendrons are avoided in the proposed methodology, it may be possible to synthesize high-generation and high-molecular-weight polymers with well-defined structures. In fact, the well-defined structures of the resulting polymers from 1G to 7G were guaranteed by comparing both molecular weights of the starting premade living (PMMA)s and the final polymers obtained at all generation stages. The 7G polymer was a huge macromolecule possessing a M_w value of 2.0×10^6 g/mol ($M_w/M_n = 1.02$) and consisting of 508 PMMA segments with 512 BnBr termini.[24] Furthermore, a series of highly branched (PMMA)s have been synthesized by the same methodology using living PMMA α-functionalized with four SMP groups as a new building block. The final 3G polymer possesses four segments branched at the cores as well as at all junctions and a high loading capacity of 256 BnBr termini that are equal to the number of BnBr termini of the 6G polymer mentioned above.[26]

In this paper, we describe the extension of the present methodology to the synthesis of dendrimer-like star-branched (PMMA)s and block copolymers possessing four segments branched at every junction. The objective of this study is to examine the synthetic possibility and limitation of 4G and/or higher generation dendrimer-like star-branched polymers with higher branched architectures. The steric hindering effect possibly encountered during the synthesis of such dense polymers will be described. Furthermore, the characterization of the resulting polymers by RALLS, SAXS, viscosity, and AFM measurements, which provide information on the size and shape, will be discussed.

Experimental Section

Materials. All chemicals (>98% purities) were purchased from Aldrich, Japan, and used as received unless otherwise stated. MMA, *tert*-butyl methacrylate, 2-vinylpyridine, LiCl, LiBr, $(CH_3)_3SiCl$, and acetonitrile were purified by the reported procedures described elsewhere.[23,24] (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl methacrylate,[29] 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**), 1,1-bis(3-(2,2-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)-4-methylhexyl)phenyl)ethylene (**2**), and 1,1,4,4-tetrakis(3-bromomethylphenyl)butane (**3**) were synthesized and purified according to our procedures previously reported.[23,24]

Measurements. Both ^1H and ^{13}C NMR spectra were measured on a Bruker DPX300 (300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR) in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $CDCl_3$ (δ 7.26 for ^1H NMR and δ 77.1 for ^{13}C NMR). Size exclusion chromatography (SEC) and right angle laser light scattering (RALLS) were measured on an Ashahi Techneion Viscotek Model 302 TDA with triple detector software. Three detectors, right angle laser light scattering, RI detector, and viscometer, were used. The d*n*/d*c* values were automatically measured by this instrument. They were also separately measured with an Ohotsuka Electronics DMR-1020 refractometer operating at 633 nm. THF was used as an eluent at a flow rate of 1.0 mL/min at 30 °C. Three polystyrene gel columns (pore size (bead size): 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm)) were used. Six PMMA standard samples were used to make conventional calibration curves, and three polystyrene standard samples were used for RALLS. Molecular weights compared with linear PMMA standard ($M_{n,SEC}$) and molecular weight distributions (M_w/M_n) were calculated from the conventional first-order calibration plots. Absolute molecular weights ($M_{w,RALLS}$) were calculated using the triple detector software. Intrinsic viscosities were measured with an Ubbelohde viscometer in THF at 25 °C.

Small-angle X-ray scattering (SAXS) measurements were conducted at the 4C1 beamline of the Pohang Light Source (PLS) facility with 2.5 GeV power at the Pohang University of Science and Technology.[30,31] The wavelength of the monochromatized X-ray beam was 1.45 Å, and the sample-to-detector distances (SDD) of 3.0, 2.0, and 1.0 m were used. SAXS patterns were measured at 25 °C using a two-dimensional (2D) charge-coupled device (CCD) detector (Mar USA, Inc.). Polymer solutions with a concentration of 1.0 wt % were prepared in THF, and solution cells with two thin mica windows and 0.7 mm cell gap were used. Each of 2D SAXS data was circular averaged from the beam center and then normalized to the incident X-ray beam intensity, which was monitored by an ionization chamber placed in front of the sample and corrected further for the scattering run of the used solvent.

Atomic force microscopy (AFM) analysis was conducted at the University of Bordeaux-1 and ENSCPB-CNRS according to the procedures previously reported.[32−34] Polymer solutions with a concentration of 0.01 wt % in CH_2Cl_2 were spin-cast on highly oriented pyrolyic graphite (HOPG) substrates in air ambient conditions. The spin-cast samples were analyzed after complete evaporation of the solvent at room temperature. All AFM images were recorded in air with a Dimension microscope (Digital Instruments, Santa Barbara, CA), operated in tapping mode. The probes were commercially available silicon tips with a spring constant of 40 N/m, a resonance frequency lying in the 270−320 kHz range, and a radius of curvature of less than 10 nm. Both the topography and the phase signal images were recorded with the highest resolution available, i.e., 512 × 512 data points.

Synthesis of Dendrimer-like Star-Branched (PMMA)s. All of the polymerizations and linking reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors equipped with break-seals. The reactors were always prewashed with 1,1-diphenylhexyllithium in heptane and used after being sealed off from a vacuum line. Since the synthetic procedure of the dendrimer-like star-branched (PMMA)s is almost the same as that reported elsewhere in our previous papers,[23,24,26−28] the synthesis of the 4G dendrimer-like star-branched PMMA abbreviated as $(A\text{-}A_2\text{-}A_8\text{-}(A\text{-}Si_4)_{32})_4$, where A and $A\text{-}Si_4$ indicate PMMA and PMMA having four SMP termini, is described in detail.

The functional anionic initiator was prepared by mixing *sec*-BuLi (0.195 mmol) in heptane (4.67 mL) with **1** (0.312 mmol) in THF (6.43 mL) at −78 °C and allowing to stand at −78 °C for 20 min. After addition of LiCl (1.19 mmol) in THF (8.53 mL), MMA (21.1 mmol) in THF (15.4 mL) was added at once with stirring, and the polymerization was continued at −78 °C for 30 min. The resulting α-functionalized living PMMA with two SMP groups was in situ added to **3** (0.0269 mmol) dissolved in THF (2.86 mL) at −78 °C, and the reaction mixture was allowed to react at −40 °C for 24 h. The reaction was quenched with methanol, and the polymer was precipitated in methanol. The 1G 4-arm star-branched polymer, $(A\text{-}Si_2)_4$, was isolated in 95% yield by fractional precipitation using benzene and methanol. The resulting polymer (1.10 g, SMP group = 0.190 mmol) was then treated with a mixture of $(CH_3)_3SiCl$ (19.5 mmol) and LiBr (19.6 mmol) in acetonitrile (80 mL) at 40 °C for 24 h and quenched with methanol (5 mL). After removal of solvent, the residue was dissolved in a small amount of THF and poured into methanol to precipitate the polymer. It was purified by reprecipitation from THF into methanol twice and freeze-drying from its absolute benzene solution to afford the brominated polymer abbreviated as $(A\text{-}Br_2)_4$ in 98% yield.[35] The $A\text{-}Br_2$ indicates a chain-end-functionalized PMMA with two BnBr groups.

Living PMMA α-functionalized with four SMP groups was prepared by the polymerization of MMA (19.4 mmol) with the functionalized anionic initiator from 2 (0.271 mmol) and *sec*-BuLi (0.170 mmol) in the presence of LiCl (0.732 mmol) in THF (22.0 mL) at −78 °C for 30 min and then reacted with the brominated polymer $(A\text{-}Br_2)_4$ (0.362 g, BnBr moiety = 0.0630 mmol) dissolved in THF (5.21 mL). The reaction mixture was allowed to react at −40 °C for 24 h. The same work-up, followed by isolation, gave the 2G PMMA (1.03 g), $(A\text{-}(A\text{-}Si_4)_2)_4$, in 90% yield. The 2G PMMA, $(A\text{-}(A\text{-}Si_4)_2)_4$ (0.600 g, SMP group = 0.132 mmol), was treated with a mixture of $(CH_3)_3SiCl$ (14.1 mmol) and LiBr (14.0 mmol) in acetonitrile (60 mL) at 40 °C for 24 h and then quenched with methanol (5 mL). After removal of solvent, the residue was dissolved in a small amount of THF and poured into methanol to precipitate the polymer. It was purified by reprecipitation from THF into methanol twice and freeze-drying from its absolute benzene solution to afford the 2G brominated PMMA, $(A\text{-}(A\text{-}Br_4)_2)_4$, in 93% yield.

The same reaction sequence was repeated two more times to afford the 3G, followed by 4G (PMMA)s, $(A\text{-}A_2\text{-}A(Si_4)_8)_4$, and $(A\text{-}A_2\text{-}A_8\text{-}(A\text{-}Si_4)_{32})_4$. In each of both cases, a 2.0-fold excess of living PMMA was used toward each BnBr reaction site, and the reaction time was extended from 24 to 48 h. Yields of polymers isolated were 92 and 93%, respectively. All of the polymers were carefully characterized by ^1H and ^{13}C NMR, FT-IR, SEC, and RALLS, respectively. Their molecular weights and molecular weight distributions are listed in Tables 1 and 2. ^1H NMR chemical shifts of the resulting polymers all are very similar to each other except for the peak areas and the chemical shifts of the terminal groups. The following ^1H NMR chemical shifts are those of the 3G brominated polymer, $(A\text{-}A_2\text{-}(A\text{-}Br_4)_8)_4$, and the 4G polymer, $(A\text{-}A_2\text{-}A_8\text{-}(A\text{-}Si_4)_{32})_4$, as typical examples: $(A\text{-}A_2\text{-}(A\text{-}Br_4)_8)_4$: δ 7.2−6.6 (m, aromatic), 4.45 (s, 256H, $-CH_2-Br$), 3.7−3.4 (m, $-O-CH_3$), 2.1−1.6 (m, $-CH_2-C(CH_3)-$), 1.1−0.5 (m, $-CH_2-C(CH_3)-$), $(A\text{-}A_2\text{-}A_8\text{-}(A\text{-}Si_4)_{32})_4$: 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, $-CH_2-$

Table 1. Synthesis of Dendrimer-like Star-Branched (PMMA)s Composed of Four Branches at All Junctions

	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		
type[a]	calcd	SEC	^{1}H NMR	calcd	RALLS	M_w/M_n[b]
(A-Si_4)$_4$	52.8	46.5	52.2	53.9	51.6	1.02
(A-(A-Si_4)$_4$)$_4$	260	156	263	268	272	1.03
(A-A_4-(A-Si_4)$_{16}$)$_4$	1300	522	1340	1340	1390	1.03
(A-A_4-A_{16}-(A-Si_4)$_{64}$)$_4$	4610	675	3680	4980	3960	1.08

[a] M_n of arm polymer = 13.1−16.4 kg/mol (M_w/M_n = 1.02−1.03). [b] Measured by SEC.

Table 2. Synthesis of 4G Dendrimer-like Star-Branched (PMMA)s Composed of Two and/or Four Branches at Each Junction

	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		
type[a]	calcd	SEC	^{1}H NMR	calcd	RALLS	M_w/M_n[b]
(A-A_4-A_{16}-(A-Si_2)$_{32}$)$_4$	2350	511	2380	2400	2360	1.02
(A-A_4-A_8-(A-Si_2)$_{32}$)$_4$	1860	450	1910	1920	1920	1.03
(A-A_2-A_8-(A-Si_2)$_{32}$)$_4$	1910	420	1960	1950	1960	1.02

[a] M_n of arm polymer = 9.96−13.1 kg/mol (M_w/M_n = 1.01−1.03). [b] Measured by SEC.

$C(CH_3)-$) 1.1−0.5 (m, $-CH_2-C(CH_3)-$), 0.90 (s, 2304H, $-Si-C(CH_3)_3$), 0.03 (s, 1536H, $Si(CH_3)_2$).

Synthesis of Dendrimer-like Star-Branched Block Copolymers. Three 4G dendrimer-like star-branched block copolymers abbreviated as (A-A_4-A_8-B_{32})$_4$, (A-A_2-A_8-C_{32})$_4$, and (A-A_4-A_8-D_{32})$_4$ (A: PMMA; B: poly(*tert*-butyl methacrylate); C: poly((2,2-dimethyl-1,3-dioxolane-4-yl)methyl methacrylate); D: poly(2-vinylpyridine)) were synthesized by the linking reaction with either of the same 3G brominated polymer, (A-A_4-(A-Br_4)$_8$)$_4$ or (A-A_2-(A-Br_4)$_8$)$_4$, as those used for the synthesis of the 4G PMMA. In this linking reaction at the fourth iterative stage, the living anionic polymers of either of *tert*-butyl methacrylate, (2,2-dimethyl-1,3-dioxolane-4-yl)methyl methacrylate, or 2-vinylpyridine were used instead of living PMMA.

1. Block Copolymer (A-A_4-A_8-B_{32})$_4$. *tert*-Butyl methacrylate (12.3 mmol, 0.919 M THF solution) was polymerized with diphenylmethylpotassium (0.173 mmol, 0.0340 M THF solution) at −78 °C for 1 h. The 3G brominated PMMA, (A-A_4-(A-Br_4)$_8$)$_4$ (0.178 g, 0.0383 mmol for BnBr moiety, 0.0371 g/mL THF solution), was added to the living polymer solution at −78 °C, and the mixture was allowed to react at −40 °C for 48 h. After quenching with degassed methanol, the solvent was removed under the reduced pressure. The residual polymer mixture dissolved into a small amount of THF was poured into methanol. By this operation, the objective linked polymer (A-A_4-A_8-B_{32})$_4$ was selectively precipitated, while the poly(*tert*-butyl methacrylate) used in excess remained in the solution. After reprecipitation from THF into methanol twice, the resulting polymer was freeze-dried from its absolute benzene solution (0.440 g, 77%). ^{1}H NMR: δ 7.2−6.6 (m, aromatic), 3.7−3.4 (m, $-O-CH_3$), 2.1−1.6 (m, $-CH_2-C(CH_3)-$), 1.6−1.3 (m, $-O-C(CH_3)_3$), 1.1−0.6 (m, $-CH_2-C(CH_3)-$).

2. Block Copolymer (A-A_2-A_8-C_{32})$_4$. The initiator was prepared by adding Et_2Zn (2.33 mmol, 0.977 M THF solution) to diphenylmethylpotassium (0.193 mmol, 0.0311 M THF solution) at −78 °C and allowing the mixture to stand for 20 min at −78 °C. Then, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (7.12 mmol, 0.629 M THF solution) was added to this initiator to polymerize at −78 °C for 1 h. The 3G brominated PMMA, (A-A_2-(A-Br_4)$_8$)$_4$ (0.178 g, 0.0383 mmol for BnBr moiety, 0.0371 g/mL THF solution), was added to the living solution at −78 °C, and the mixture was allowed to react at −40 °C for 48 h. The reaction was quenched with degassed methanol, and the reaction mixture was allowed to stand in the air for 12 h to precipitate zinc compound. After filtration, the solution was concentrated under reduced pressure. The residue was dissolved in a small amount of THF, and the solution was poured into diethyl ether. The objective linked polymer (A-A_2-A_8-C_{32})$_4$ was selectively precipitated, while excess homopolymer of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate remained in diethyl ether. After reprecipitation from THF into methanol twice, the resulting polymer was freeze-dried from its absolute benzene solution (0.420 g, 80%). ^{1}H NMR: δ 7.2−6.6 (m, aromatic), 4.4−4.2 (m, $-CH_2-CH\text{-}CH_2-$), 4.2−3.8 (m, $-CH_2-CH-CH_2-$), 3.7−3.4 (m, $-O-CH_3$), 2.1−1.6 (m, $-CH_2-C(CH_3)-$), 1.5−1.3 (m, $-O-C(CH_3)_2-O-$), 1.1−0.6 (m, $-CH_2-C(CH_3)-$).

3. Block Copolymer (A-A_4-A_8-D_{32})$_4$. 2-Vinylpyridine (8.71 mmol, 1.10 M THF solution) was polymerized with diphenylmethylpotassium (0.0998 mmol, 0.0311 M THF solution) at −78 °C for 1 h. Then, *tert*-butyl methacrylate (0.852 mmol, 0.234 M THF solution) was added to end-cap the living poly(2-vinylpyridine) followed by adding the 3G brominated PMMA, (A-A_4-(A-Br_4)$_8$)$_4$ (0.191 g, 0.0411 mmol for BnBr moiety, 0.0371 g/mL THF solution), at −78 °C. The reaction was allowed to stand at −40 °C for 48 h. After termination with degassed methanol, the solvents were removed under the reduced pressure. The polymer mixture was dissolved in ethanol (30 mL), and then hexane (55 mL) was slowly added to the solution with stirring. After cooling the mixture to 0 °C, it was allowed to stand at 0 °C for an additional 1 h. The objective block copolymer was selectively precipitated, while excess poly(2-vinylpyridine) remained in the mixed solution. The resulting polymer was purified by reprecipitation from THF into hexane twice and freeze-dried from its absolute benzene solution (0.480 g, 77%). ^{1}H NMR: δ 8.4−6.1 (m, aromatic), 3.7−3.4 (m, $-O-CH_3$), 2.8−2.1 (m, $-CH_2-CH-$), 2.1−1.3 (m, $-CH_2-C(CH_3)-$, $-CH_2-CH-$, $-O-C(CH_3)_3$), 1.1−0.6 (m, $-CH_2-C(CH_3)-$).

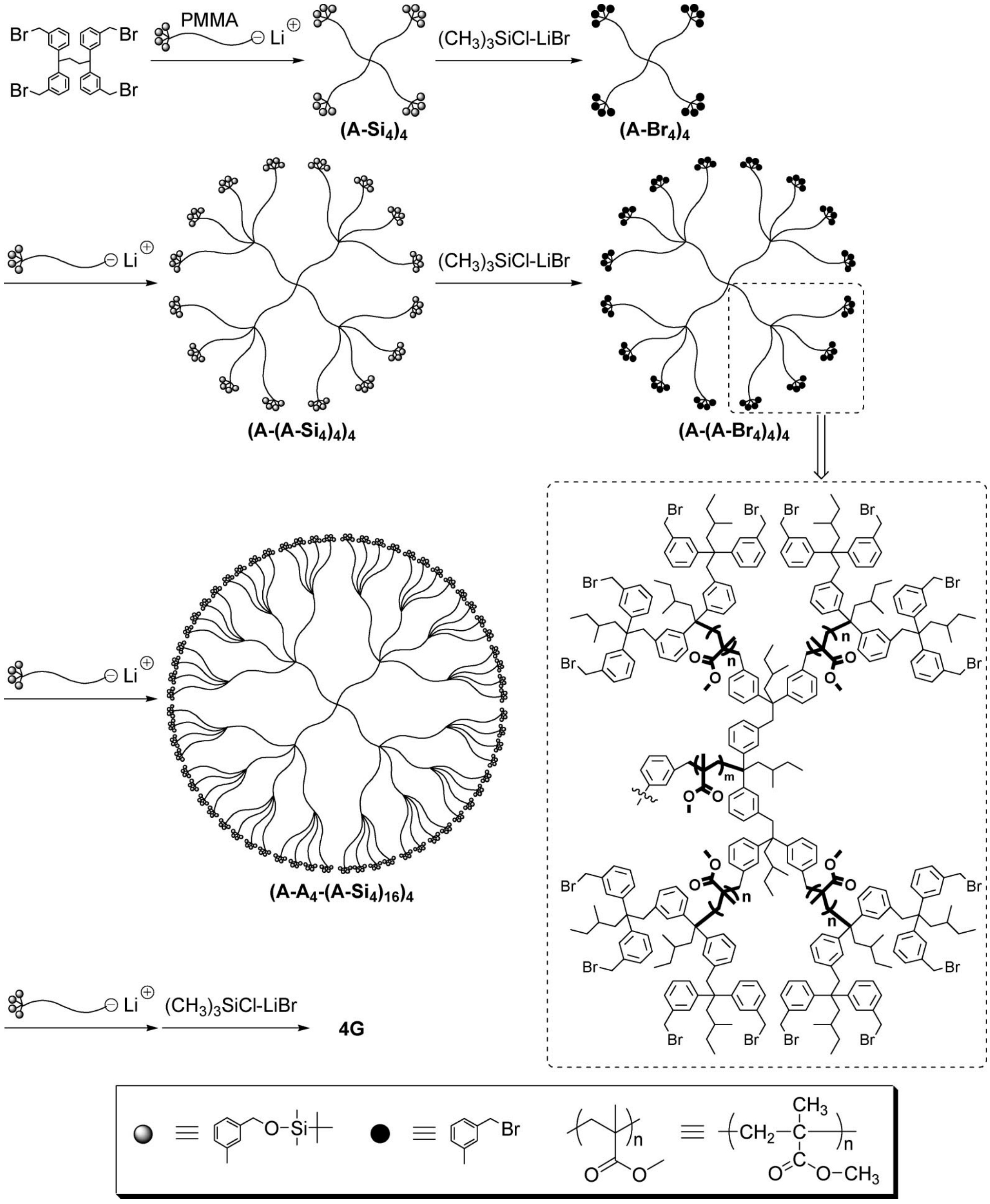
Synthesis of Amphiphilic Dendrimer-like Star-Branched Block Copolymers (A-A_4-A_8-B'_{32})$_4$, (A-A_2-A_8-C'_{32})$_4$, and (A-A_4-A_8-D'_{32})$_4$ (A: PMMA; B′: Poly(methacrylic acid); C′: Poly(2,3-dihydroxypropyl methacrylate); D′: Poly(2-vinylpyridinium hydrochloride)). Three 4G amphiphilic dendrimer-like star-branched block copolymers were obtained by treating the original block copolymers with either of $(CH_3)_3SiCl-LiBr$, 2 N HCl, or 2 N HCl.

1. Amphiphilic Block Copolymer (A-A_4-A_8-B'_{32})$_4$. The title block copolymer was obtained by treatment of (A-A_4-A_8-B_{32})$_4$ with a 1:1 mixture of $(CH_3)_3SiCl$ and LiBr, followed by hydrolysis as follows: Under an atmosphere of nitrogen, (A-A_4-A_8-B_{32})$_4$ (0.120 g, 0.579 mmol for *tert*-butyl methacrylate unit) and LiBr (0.190 g, 2.19 mmol) were dissolved in a mixed solvent of chloroform (10 mL) and acetonitrile (10 mL). Then, $(CH_3)_3SiCl$ (0.350 mL, 2.79 mmol) was slowly added to the solution at 25 °C, and the mixture was allowed to react at 40 °C for 24 h. After quenching with methanol, the solvents were removed under reduced pressure. The residue was dissolved in a small amount of methanol, and the solution was poured into a mixture of chloroform (60 mL) and acetonitrile (30 mL) to precipitate the polymer. After filtration, the resulting polymer was dried in vacuo for 24 h (0.870 g, 99%).

2. Amphiphilic Block Copolymer (A-A_2-A_8-C'_{32})$_4$. The title polymer was obtained by hydrolysis of the poly((2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate) segments of (A-A_2-A_8-C_{32})$_4$: To (A-A_2-A_8-C_{32})$_4$ (0.100 g, 0.313 mmol for acetal group) dissolved in THF (20 mL) was added 2 N HCl (2 mL), and the mixture was allowed to react at 25 °C for 12 h. After removal of solvents, the residues were dissolved in a small amount of THF, and the solution was poured into methanol to precipitate the objective polymer. After filtration, the resulting polymer was dried in vacuo for 24 h (0.0850 g, 97%).

3. Amphiphilic Block Copolymer (A-A_4-A_8-D'_{32})$_4$. The title polymer was obtained by treatment of (A-A_4-A_8-D_{32})$_4$ with 2 N HCl. To (A-A_4-A_8-D_{32})$_4$ (0.100 mg, 0.570 mmol for 2-vinylpyridine unit) dissolved in THF (20 mL) was added. 2 N HCl (2 mL) and the mixture were allowed to react at 25 °C for 12 h. The polymer precipitated as a white solid was corrected by filtration. The resulting polymer was dried in vacuo at 25 °C for 24 h (0.115 g, 95%).

Scheme 1. Synthesis of 4G Dendrimer-like Star-Branched PMMA Composed of Four Branches at All Junctions



Results and Discussion

Dendrimer-like Star-Branched (PMMA)s Having Highly Branched Architectures with Four Branch Junctures. Most of the dendrimer-like star-branched polymers so far synthesized have two polymer segments branched at the junction (two branch juncture), although the degree of branching at the core varies from 2 to even 12 in number. As an exceptional case, Hedrick and co-workers previously reported the synthesis of a highly branched 2G polymer having six segments branched at the core and four junctures at the second layer ($M_n = 76\,300$, $M_w/M_n = 1.12$) by the "arm-first" divergent methodology.[17d]

As mentioned in Introduction, we have recently succeeded in synthesizing highly dense dendrimer-like star-branched (PMMA)s up to the 3G with four branch junctures in all the layers including the cores.[26] The synthetic methodology for such polymers is similar to that previously reported,[23,24] except for making use of living PMMA α-functionalized with four SMP groups. Since the branch density is considered to become higher along with generation by generation, it is of especially interest to synthesize the 4G or higher generation polymers with four branch junctures. The synthetic procedure is outlined in Scheme 1.

At the first stage in the iteration, a 4-arm star-branched PMMA, $(A\text{-}Si_4)_4$, where A and $A\text{-}Si_4$ indicate PMMA and PMMA with four SMP termini, was synthesized by the linking reaction of a 2.0-fold excess of living PMMA α-functionalized with four SMP groups with **3** at −40 °C for 24 h, followed by treatment with $(CH_3)_3SiCl{-}LiBr$ to transform the SMP groups into BnBr function. Then, the resulting brominated polymer, $(A\text{-}Br_4)_4$, where $A\text{-}Br_4$ indicates PMMA with four BnBr termini, reacted with living PMMA α-functionalized with four SMP groups to quantitatively afford the 2G dendrimer-like star-branched polymer, $(A\text{-}(A\text{-}Si_4)_4)_4$. Likewise, the 3G polymer, $(A\text{-}A_4\text{-}(A\text{-}Si_4)_{16})_4$, could be synthesized by repeating the two reactions one more time. As listed in Table 1, all the polymers synthesized by this procedure were observed to have precisely controlled molecular weights with narrow molecular weight distributions, clearly indicating the expected and well-defined structures of the resulting polymers.

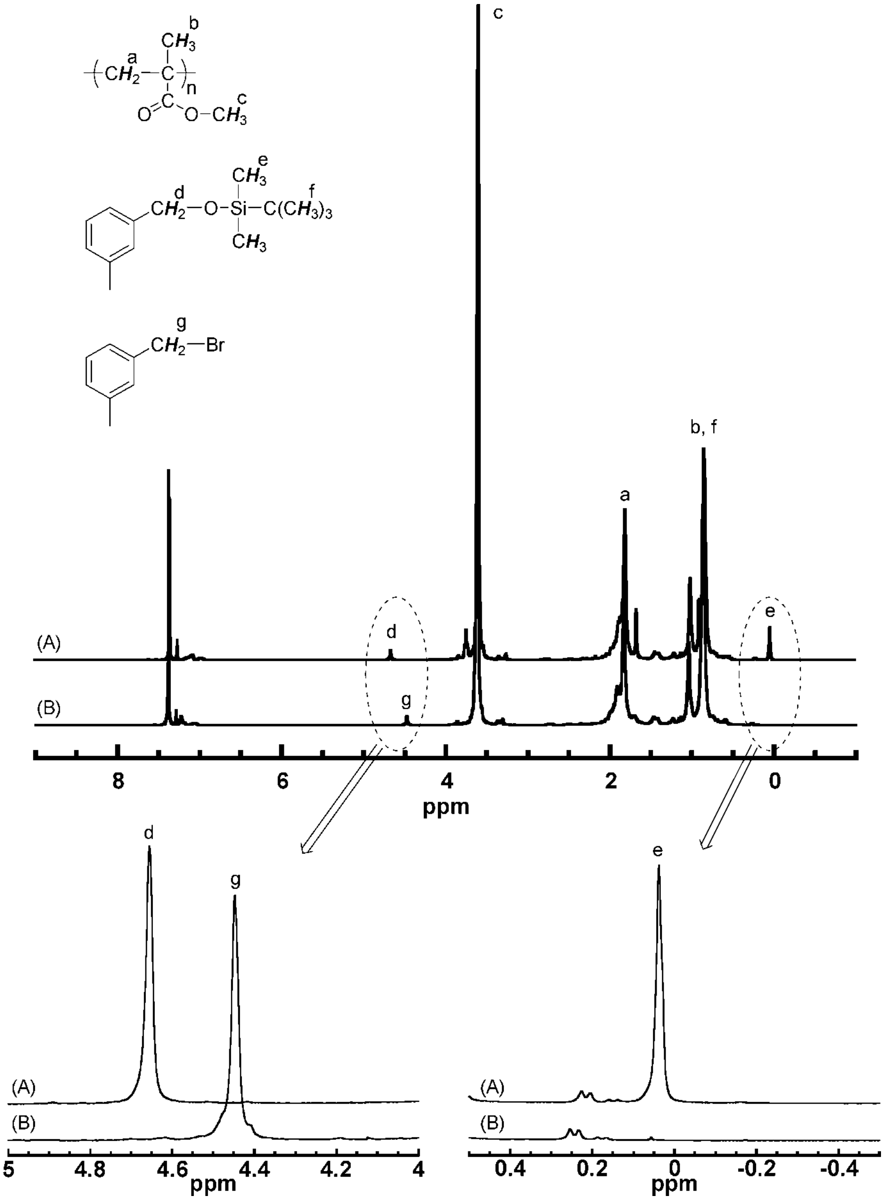


Figure 2. ^{1}H NMR spectra of (A-A_4-(A-Si_4)$_{16}$)$_4$ (A) and (A-A_4-(A-Br_4)$_{16}$)$_4$ (B).

Herein, we have attempted to synthesize a 4G polymer by further continuing the iterative process. The 3G polymer, (A-A_4-(A-Si_4)$_{16}$)$_4$, was brominated with $(CH_3)_3SiCl-LiBr$ under the same conditions. SEC profiles of the polymers before and after the bromination were identical in shape and distribution. The ^{1}H NMR spectra showed that the signals assignable to the silyl methyl protons at 0.03 ppm completely disappeared, and the peaks for benzyl methylene protons of the SMP group at 4.65 ppm were moved to 4.45 ppm, corresponding to methylene protons of the BnBr moiety (Figure 2).

Thus, obviously, the SMP groups were quantitatively transformed into BnBr functions to afford the 3G brominated polymer, (A-A_4-(A-Br_4)$_{16}$)$_4$, with 256 BnBr termini at its periphery. Then, the brominated polymer was reacted with living PMMA having four SMP termini under the conditions at −40 °C for 48 h. A 4-fold excess of living PMMA toward each BnBr reaction site was used in this reaction because high steric hindrance was considered. The SEC profile of the reaction mixture as shown in Figure 3 exhibits only two sharp peaks corresponding to the linked product and deactivated living PMMA used in excess in the reaction.

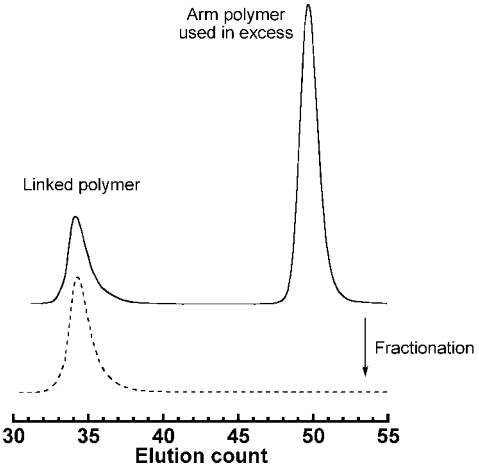
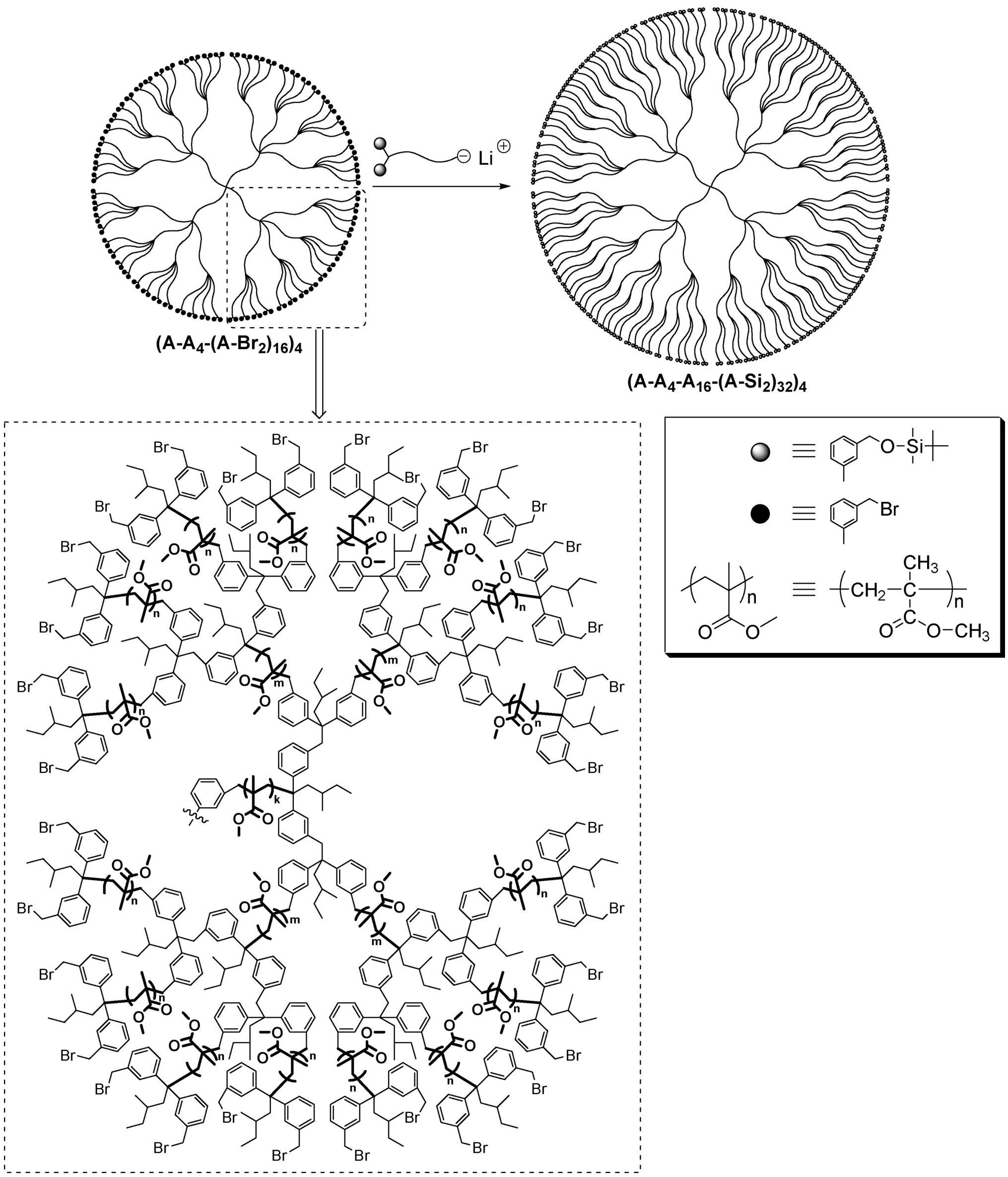


Figure 3. SEC profiles of 4G polymer before and after fractionation.

The linked product eluted at the higher molecular weight region was isolated in 92% yield by fractional precipitation,

Scheme 2. Synthesis of 4G Dendrimer-like Star-Branched PMMA Composed of Two and/or Four Branches at Each Junction, $(A\text{-}A_4\text{-}A_{16}\text{-}(A\text{-}Si_2)_{32})_4$



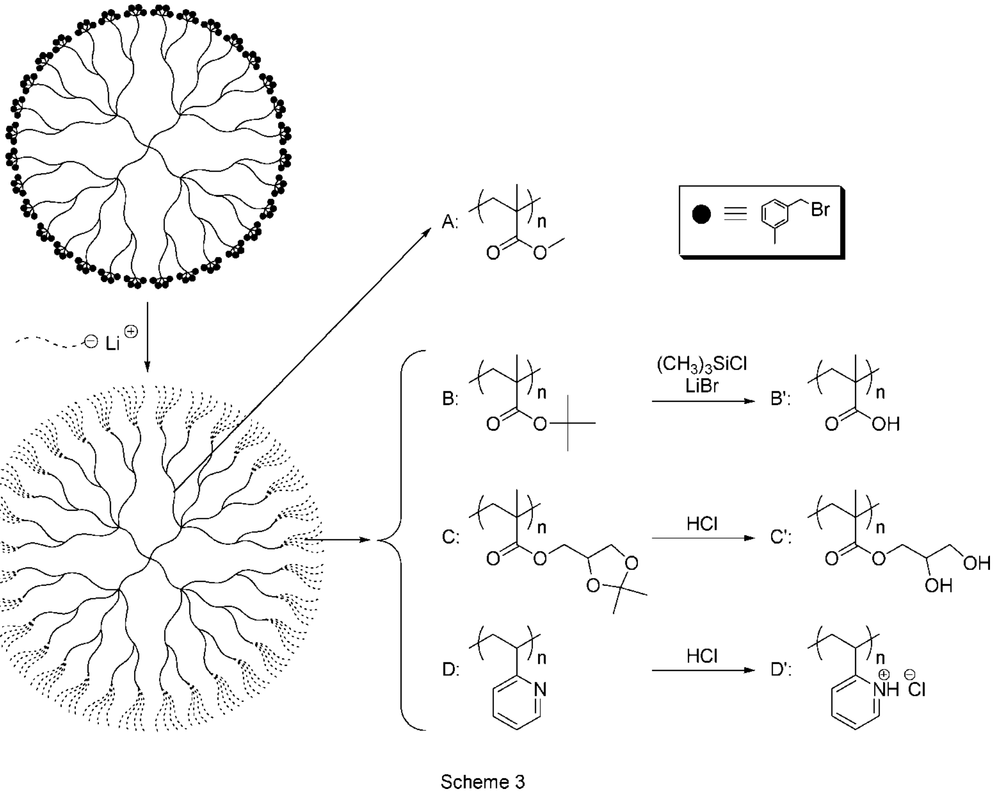
and the isolated polymer exhibited a sharp monomodal SEC distribution as shown in the same Figure 3. The results are also listed in Table 1.

The M_n and M_w values determined by ^{1}H NMR and RALLS were 3.68×10^6 and 3.96×10^6 g/mol, which were smaller than the expected values of 4.61×10^6 and 4.98×10^6 g/mol. On the basis of the two M_w values, the linking efficiency was estimated to be 72%, indicating that 184, but not the theoretical value of 256, branch segments could be introduced into the outermost layer of the 4G polymer. Several attempts were made to introduce more branch segments by taking the longer reaction time or increasing the ratio of living PMMA to BnBr reaction site, but the efficiency of the linking reaction was not improved in each case. Thus, we have realized that four branches are quantitatively introduced into the available BnBr reaction sites in the first (core), second, and third layers, but not in the fourth layer, possibly due to the steric hindrance among living PMMA chains and the branches already introduced into the fourth layer. Therefore, this result provides important information on the steric hindrance in the synthesis of highly branched polymers with four branch junctures. Apart from the incomplete linking reaction at the fourth-iterative stage, it should be however mentioned that the final 4G polymer possessed a very high molecular weight of over 3.5 million g/mol and a large number of 736 (184 × 4) SMP termini convertible to BnBr functionalities. In addition, the polymer had a narrow molecular weight distribution, strongly indicating that the branch segments could be homogeneously introduced. The 4G polymer thus synthesized can be abbreviated as $(A\text{-}A_4\text{-}A_{16}\text{-}(A\text{-}Si_4)_{46})_4$ because the number of branch segments in the outermost layer is 46 (184/4).

As mentioned above, we could introduce 184 PMMA branch segments into the outermost layer of the 4G PMMA. The number of 184 corresponds to the introduction of almost three branches on the average into all the junctions in the outermost layer. We therefore consider that it may be possible to readily introduce two branches at all the junctions. In order to ascertain this possibility, a new 3G polymer with 128 BnBr termini at its periphery, $(A\text{-}A_4\text{-}(A\text{-}Br_2)_{16})_4$, was prepared and reacted with living PMMA α-functionalized with two SMP groups in THF at −40 °C for 48 h, as shown in Scheme 2.

The SEC profile of the reaction mixture showed only two peaks corresponding to the linked product and the deactivated living PMMA α-functionalized with four SMP groups used in excess. It was estimated that the efficiency of the linking reaction

Scheme 3. Synthesis of 4G Dendrimer-like Star-Branched Block Copolymers



is quantitative on the basis of the two peak areas. The objective polymer, after the isolation by fractional precipitation, exhibited a sharp monomodal distribution and was characterized by SEC, ^{1}H NMR, and RALLS, as listed in Table 2.

Both the M_n and M_w values determined by ^{1}H NMR and RALLS agreed well with those predicted, and a narrow molecular weight distribution was attained, the M_w/M_n ratio being 1.02. The introduction of 256 SMP termini was confirmed by ^{1}H NMR analysis. Accordingly, all of the results clearly indicate the successful synthesis of the 4G dendrimer-like star-branched PMMA of the expected structure of $(A\text{-}A_4\text{-}A_{16}\text{-}(A\text{-}Si_2)_{32})_4$. No steric hindering effect was observed at all in the linking reaction of this stage. Thus, 128 PMMA segments were completely introduced at the fourth layer to construct two branch junctures as shown in Scheme 2.

Now, a question arises regarding the synthetic possibility of other two 4G polymers, abbreviated as $(A\text{-}A_2\text{-}A_8\text{-}A_{32})_4$ and $(A\text{-}A_4\text{-}A_8\text{-}A_{32})_4$. They have two branch junctures in the second and third layers, respectively. In order to synthesize both the polymers, two 3G brominated polymers, $(A\text{-}A_2\text{-}(A\text{-}Br_4)_8)_4$ and $(A\text{-}A_4\text{-}(A\text{-}Br_4)_8)_4$, were prepared and reacted with living PMMA α-functionalized with two SMP groups under the same conditions. The two linking reactions were found to proceed quantitatively as estimated from the SEC profiles of the reaction mixtures. The objective polymers were isolated by fractional precipitation and analyzed by SEC, ^{1}H NMR, and RALLS.

The analytical results listed in Table 2 clearly indicate that the two 4G polymers are well-defined and expected in structure. Thus, the steric hindrance caused during the synthesis of highly dense branched 4G polymer, $(A\text{-}A_4\text{-}A_{16}\text{-}(A\text{-}Si_4)_{64})_4$, is completely eliminated by introducing two branch juncture at least in one layer between generations. Again, this finding is very important and indicative from a viewpoint of the steric hindering effect for molecularly designing and precisely synthesizing highly branched polymers with four branch junctures. We first thought that the surface area and space would be broadened more and more along with generation by generation and four branch junctures could be introduced at higher generations. However, the surface may be more crowded and sterically hindered in practice than one might imagine. Finally, the resulting 4G polymers possessed 256 SMP termini, but it was possible to double the SMP terminus from 256 to 512 in number by using living PMMA with four SMP groups in the linking reaction at the fourth iterative stage.

Synthesis of Dense 4G Dendrimer-like Star-Branched Block Copolymers. Similar to living PMMA, another living anionic polymer should react with the brominated polymer to afford a next generation dendrimer-like star-branched block copolymer with an additional functionality. Furthermore, the different segments introduced would cause microphase separation, followed by self-organization, to form quite new nano-ordered suprastructures and molecular assemblies because of their characteristic branch architectures. In order to synthesize such block copolymers, three different living anionic polymers of *tert*-butyl methacrylate, (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl methacrylate, and 2-vinylpyridine were prepared and reacted with the 3G brominated polymer $((A\text{-}A_4\text{-}(A\text{-}Br_4)_8)_4$ or $(A\text{-}A_2\text{-}(A\text{-}Br_4)_8)_4$ under the same conditions, as shown in Scheme 3.

In the case of living poly(2-vinylpyridine), the propagating chain-end anion was end-capped with a small amount of *tert*-butyl methacrylate prior to the linking reaction to avoid the undesirable ester attack reported previously.[36] In each case, SEC profile of the reaction mixture exhibited only two sharp peaks corresponding to the linked product and the living anionic polymer used in excess in the reaction. Neither intermediate polymer nor low-molecular-weight tailing was observed in either of SEC profiles. The linked polymers were isolated in 70−80% yields by selective precipitation and characterized by ^{1}H NMR, SEC, and RALLS. The results are summarized in Table 3.

The isolated polymers were observed to have narrow monomodal SEC distributions (M_w/ M_n < 1.04). The agreement of

Table 3. Synthesis of 4G Dendrimer-like Star-Branched Block Copolymers

	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		
type[a]	calcd	SEC	^{1}H NMR	calcd	RALLS	M_w/M_n[b]
(A-A_4-A_8-B_{32})$_4$	1900	504	1900	1980	1980	1.04
(A-A_2-A_8-C_{32})$_4$	1440	371	1440	1480	1510	1.03
(A-A_4-A_8-D_{32})$_4$	1930	404	1950	2010	2010	1.04

[a] A = PMMA, B = poly(*tert*-butyl methacrylate), C = poly((2,2-dimethyl-1,3-dioxolane-4-yl)methyl methacrylate), D = poly(2-vinylpyridine). [b] Measured by SEC.

the molecular weights or block ratios between observed and calculated is quite satisfactory in each of all cases. Thus, the linking reaction worked well to afford the expected block copolymers as shown in Scheme 3. Thus, the present methodology also allows the synthesis of well-defined block copolymers with 4G dense dendrimer-like star-branched architectures.

In order to provide further functionalities, the resulting block copolymers were treated with $(CH_3)_3SiCl/LiBr$, 2 N HCl, and 2 N HCl, respectively. Under such treatment, the PMMA blocks were stable and remained unchanged. On the other hand, both the poly(*tert*-butyl methacrylate) and poly((2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate) blocks were readily hydrolyzed to give poly(methacrylic acid) and poly((2,3-dihydroxy)-propyl methacrylate) segments, respectively. The poly(2-vinylpyridine) block was converted to poly(2-vinylpyridinium hydrochloride). All these reactions were carefully monitored by ^{1}H NMR, FT-IR, and elemental analysis and found quantitative in all cases, as illustrated in Scheme 3. Table 4 shows the solubility data of the resulting polymers as well as the original block copolymers. The data of 4G dendrimer-like star-branched PMMA are also listed as a reference.

The three original block copolymers were very similar to the 4G PMMA in solubility. Very interestingly, however, the block copolymer can be dissolved in hexane or methanol by introducing either poly(*tert*-butyl methacrylate) or poly(2-vinylpyridine) block into the outermost fourth layer. Their solubilities were dramatically changed by the further treatments which provide high polarity and water solubility. In fact, the resulting block copolymers showed almost opposite solubilities of their original polymers, as is seen in Table 4. Unfortunately, the resulting block copolymers were not soluble in water, although 128 water-soluble segments were present at the outermost fourth layers and might cover the cores, second, and third layers consisting of PMMA segments.

The incorporation of the above-mentioned segments with functionalities such as basicity, acidity, water solubility, and ionic character would be expected to allow access to a wide range of physical and chemical characteristics. Furthermore, various unique and interesting morphologies as well as supramolecular assemblies in bulk and selective solvents are also expected in the block copolymers, and their detailed studies are in progress.

Hydrodynamic Radii and Radii of Gyration of 3G and 4G Dendrimer-like Star-Branched Polymers. In order to obtain information on molecular sizes of the dendrimer-like star-branched polymers herein synthesized, the analyses by RALLS and SAXS were performed in THF to measure their hydrodynamic radii, R_h, and radii of gyration, R_g. The samples measured were four 3G polymers —(A-A_2-A_4)$_4$, (A-A_2-A_8)$_4$, (A-A_4-A_8)$_4$, and (A-A_4-A_{16})$_4$—and five 4G polymers—(A-A_2-A_4-A_8)$_4$, (A-A_2-A_8-A_{32})$_4$, (A-A_4-A_8-A_{32})$_4$, (A-A_4-A_{16}-A_{32})$_4$, and (A-A_4-A_{16}-A_{46})$_4$. The results are summarized in Table 5.

As can be seen, the R_h value measured by RALLS is similar to the R_g value obtained by SAXS in each of all the samples and increases with increasing the M_w value. The ratios of R_g/R_h were in the range 0.83−1.03, except for the (A-A_2-A_4)$_4$ polymer showing 1.16. These values were somewhat higher than those (0.67−0.71) of 2G and 3G dendrimer-like star-branched polymers reported by Hedrick et al.[17d] Although the 3G and 4G polymers are considered to possess the most shell weighted density distribution estimated from their architectures, all data except for that of the (A-A_2-A_4)$_4$ polymer are in good agreement with those of many armed star-branched polymers with high segment densities near the cores.[37,38] As shown in Figure 4, log R_h increases nearly linearly with log M_w by plotting log R_h as a function of log M_w.

Accordingly, the dendrimer-like star-branched polymer has a larger molecular size (namely larger R_h and R_g) as the M_w increases. Although the M_w value changes via branch density and/or generation in the 3G and 4G polymers, the molecular size estimated from R_h and R_g values is strongly correlated only to the M_w value, but not directly reflected by the branch density and generation.

Viscosity Behavior of 3G and 4G Dendrimer-like Star-Branched (PMMA)s and Their Branching Factors, g' Values. In order to study solution behavior of the 3G and 4G polymers, their intrinsic viscosity values, $[\eta]_{\text{dendrimer-like}}$, were measured in THF at 25 °C. Since their molecular weights can be made to widely vary by changes in branch density and generation, it is possible to compare the viscosity with each other even in the same generation. Table 6 summarizes the $[\eta]_{\text{dendrimer-like}}$ values of four 3G polymers—(A-A_2-A_4)$_4$, (A-A_2-A_8)$_4$, (A-A_4-A_8)$_4$, and (A-A_4-A_{16})$_4$—and five 4G polymers—(A-A_2-A_4-A_8)$_4$, (A-A_2-A_8-A_{32})$_4$, (A-A_4-A_8-A_{32})$_4$, (A-A_4-A_{16}-A_{32})$_4$, and (A-A_4-A_{16}-A_{46})$_4$.

Very surprisingly and interestingly, the $[\eta]_{\text{dendrimer-like}}$ values of the four 3G polymers were close to each other and in between 32.2 and 35.2 mL/g, although their molecular weights varied considerably from 2.95×10^5 to 9.39×10^5 g/mol. For instance, the (A-A_4-A_{16})$_4$ polymer was almost equal in $[\eta]$ value to the (A-A_2-A_4)$_4$ polymer, while the former is 3 times higher in M_w value than the latter. Furthermore, it was found that the $[\eta]_{\text{dendrimer-like}}$ value is not correlative with the molecular size estimated from R_h and R_g mentioned above. Similarly, insensitivity of viscosity to molecular weight as well as molecular size was observed among the 4G polymers. The $[\eta]$ value of the (A-A_4-A_{16}-A_{46})$_4$ polymer was the same as that of the (A-A_2-A_4-A_8)$_4$ polymer having one-sixth of the M_w value to that of the former sample. Gauthier and co-workers reported that the intrinsic viscosity of arborecent polymer, so-called dendrigraft polymer, is almost independent of molecular weight, as would be expected for rigid spheres of constant hydrodynamic density.[39] Our dendrimer-like star-branched polymer samples in the given generation appear to behave similarly.

As shown in Table 6, the intrinsic viscosity shows a discernible increase from 3G to 4G polymers, and the 4G polymers as a whole are always higher than the 3G polymers in $[\eta]$ value. Thus, obviously, the dependence of molecular weight on viscosity appears to be present among the generations. Such a contradiction may be attributed to various structure differences of the dendrimer-like star-branched (PMMA)s herein used. For example, the molecular weight, branch density, and branch density distribution (or branched architecture) were different within the same generation polymers. Even in the same series polymers, the branched architecture was changed with increasing the generation. In order to compare all of the values with solution behaviors, the molecular weight should be changed only by changing molecular weight of the branch segment, while the branched architecture and generation remain unchanged or structural variables should be minimized. Detailed studies are in progress.

The branching factors, g' values, can be calculated from the $[\eta]_{\text{dendrimer-like}}/[\eta]_{\text{linear}}$. The $[\eta]_{\text{linear}}$ value is the intrinsic viscosity of the linear PMMA with the same molecular weight under the

Table 4. Solubilities of Dendrimer-like Star-Branched Block Copolymers[a]

	$(A\text{-}A_2\text{-}A_4\text{-}A_8)_4$	$(A\text{-}A_4\text{-}A_8\text{-}B_{32})_4$	$(A\text{-}A_2\text{-}A_8\text{-}C_{32})_4$	$(A\text{-}A_4\text{-}A_8\text{-}D_{32})_4$	$(A\text{-}A_4\text{-}A_8\text{-}B'_{32})_4$	$(A\text{-}A_2\text{-}A_8\text{-}C'_{32})_4$	$(A\text{-}A_4\text{-}A_8\text{-}D'_{32})_4$
hexane	S	S	I	I	I	I	I
benzene	S	S	S	S	I	I	I
acetone	S	S	S	S	I	I	I
THF	S	S	S	S	I	S	I
chloroform	S	S	S	S	I	I	I
methanol	I	I	I	Sw	S	S	S
water	I	I	I	I	I	I	Sw

[a] S: soluble; I: insoluble; Sw: swelling.

Table 5. Hydrodynamic Radii and Radii of Gyration

generation	type	$M_w \times 10^{-3\,a}$	R_h (nm)[a]	R_g (nm)[b]	R_g/R_h
3	$(A\text{-}A_2\text{-}A_4)_4$	295	10.2	11.9	1.16
	$(A\text{-}A_2\text{-}A_8)_4$	514	14.7	12.8	0.871
	$(A\text{-}A_4\text{-}A_8)_4$	568	14.9	12.5	0.839
	$(A\text{-}A_4\text{-}A_{16})_4$	939	17.2	17.3	1.01
4	$(A\text{-}A_2\text{-}A_4\text{-}A_8)_4$	661	13.9	13.6	0.978
	$(A\text{-}A_2\text{-}A_8\text{-}A_{32})_4$	1960	18.1	18.8	1.04
	$(A\text{-}A_4\text{-}A_8\text{-}A_{32})_4$	1920	20.1	19.3	0.960
	$(A\text{-}A_4\text{-}A_{16}\text{-}A_{32})_4$	2360	24.6	20.4	0.829
	$(A\text{-}A_4\text{-}A_{16}\text{-}A_{av.46})_4$	3960	30.2		

[a] Measured by RALLS in THF at 30 °C. [b] Measured by SAXS in THF at 25 °C.

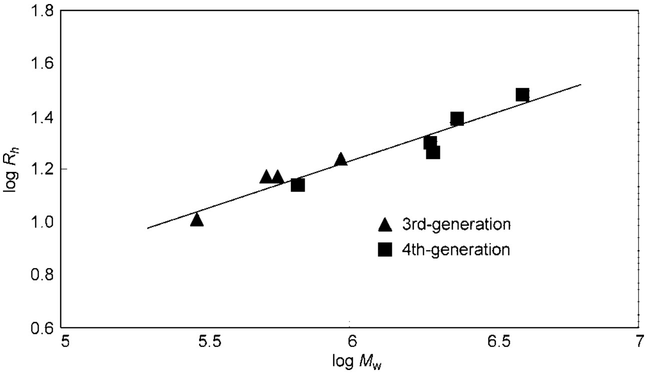


Figure 4. Relationship between log M_w and log R_h.

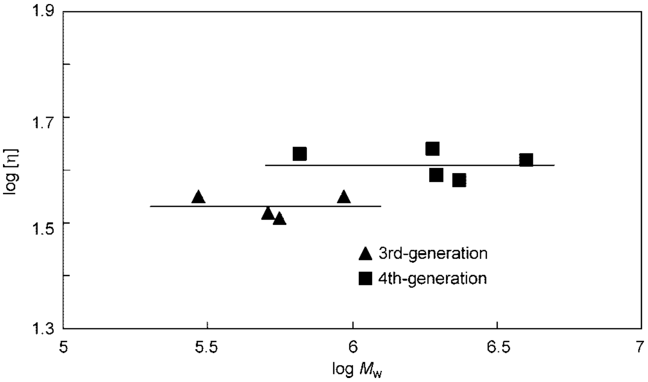


Figure 5. Relationship between log M_w and log [η].

same conditions and obtained from the following equation previously reported.[40]

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

On the basis of the viscosity values, the branching factors, g' values, were calculated for all the 3G and 4G polymer samples and listed in the same Table 6. As expected from the hyperbranched architecture, the $[\eta]_{\text{dendrimer-like}}$ values were always smaller than those of the corresponding linear polymers, and therefore the g' values were less than unity for all polymer samples, indicating that the dendrimer-like star-branched polymers are always smaller in hydrodynamic volume than the linear polymers.

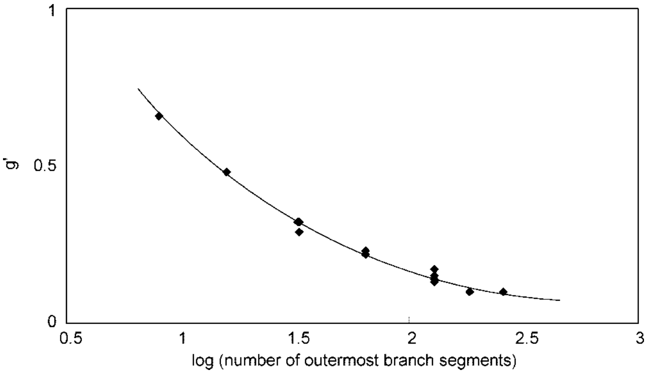


Figure 6. Relationship between log (number of outermost branch segments) and g'.

Table 6. Intrinsic Viscosities of Dendrimer-like Star-Branched (PMMA)s

			[η] (mL/g)		
generation	type	$M_w \times 10^{-3\,a}$	$[\eta]_{\text{dendritic}}$[b]	$[\eta]_{\text{linear}}$[c]	g'
3	$(A\text{-}A_2\text{-}A_4)_4$	295	35.2	70.3	0.50
	$(A\text{-}A_2\text{-}A_8)_4$	514	33.2	103	0.32
	$(A\text{-}A_4\text{-}A_8)_4$	568	32.3	111	0.29
	$(A\text{-}A_4\text{-}A_{16})_4$	939	35.1	157	0.22
4	$(A\text{-}A_2\text{-}A_4\text{-}A_8)_4$	661	42.2	123	0.34
	$(A\text{-}A_2\text{-}A_8\text{-}A_{32})_4$	1960	39.1	262	0.15
	$(A\text{-}A_4\text{-}A_8\text{-}A_{32})_4$	1920	43.3	258	0.17
	$(A\text{-}A_4\text{-}A_{16}\text{-}A_{32})_4$	2360	38.1	298	0.13
	$(A\text{-}A_4\text{-}A_{16}\text{-}A_{av.46})_4$	3960	42.1	427	0.099

[a] Measured by RALLS in THF at 30 °C. [b] Measured in THF at 25 °C. [c] Calculated from $[\eta]_{\text{linear}} = 1.11 \times 10^{-2} \times M_w^{0.695}$.

As can be seen, the g' value depends on the molecular weight via branch density even in the same generation and decreases with increasing molecular weight. Furthermore, the g' value appears to evidently and strongly correlate with the number of branch segment of outermost layer even in the different generation. For example, two 3G and one 4G polymers with 32 outmost branch segments, $(A\text{-}A_2\text{-}A_8)_4$, $(A\text{-}A_4\text{-}A_8)_4$, and $(A\text{-}A_2\text{-}A_4\text{-}A_8)_4$, were very close to each other in g' value and within the range between 0.29 and 0.34. With increasing the outermost branch segments to 64 in number, the g' value of the 3G polymer, $(A\text{-}A_4\text{-}A_{16})_4$, was reduced to 0.22 and quite consistent with that ($g' = 0.23$) of the 5G polymer, $(A\text{-}A_2\text{-}A_4\text{-}A_8\text{-}A_{16})_4$, with the same outermost branch numbers reported previously. Moreover, the g' values of the $(A\text{-}A_2\text{-}A_8\text{-}A_{32})_4$, $(A\text{-}A_4\text{-}A_8\text{-}A_{32})_4$, and $(A\text{-}A_4\text{-}A_{16}\text{-}A_{32})_4$ polymers with 128 outermost branches were further reduced and within the range between 0.13 and 0.17. Thus, the g' value significantly decreased with increasing the number of branch segments present in the outermost layer but was comparable to each other among the samples with the same branch numbers even in different generation. This trend is similar to that of star-branched polymer.The relationship between g' value and arm number is theoretically established in star-branched polymers, and for 32-, 64-, and 128-arm stars,

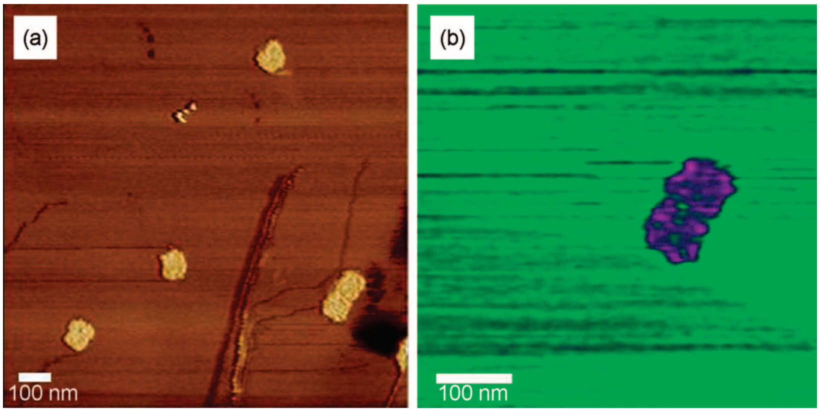


Figure 7. AFM height image (a) and phase image (b) of 4G dendrimer-like star-branched polymer, (A-A_4-A_{16}-(A-Si_4)$_{46}$)$_4$.

their g' values can be calculated to be 0.14, 0.083, and 0.048, respectively.[24] These values are smaller than those of dendrimer-like star-branched polymers with the same numbers of outermost segments. This seems reasonable because one can imagine the branched architectures between star-branched and dendrimer-like star-branched polymers.

AFM Observation of 4G PMMA, (A-A_4-A_{16}-A_{46})$_4$. Recently, the direct visualization of high-molecular-weight architectural polymers such as combs, dendrigrafts, comb-star, and comb-cyclic polymers by AFM imaging has been reported with great success by Matyjaszewski et al. and Deffieux et al.[32−34,41−47] Dendrimers have also been visualized as spherical dome-shaped molecules by AFM and STM.[48,49] Herein, we have attempted to visualize a 4G dendrimer-like star-branched PMMA, the largest in size and highly branched in architecture, (A-A_4-A_{16}-A_{46})$_4$, in this study by AFM tapping mode on highly oriented graphite (HOPG) similar to the previous studies.[32−34]

As shown in Figure 7, the several isolated polymer molecules appear on AFM image as completely flattened objects with an average square size closer to 100 nm and height remained very small to be about 1.6 nm. As the diameter of this sample is estimated to be 60 nm or smaller from the R_h value (30.2 nm) in THF, the average size is larger, while the height seems to be much smaller. Thus, the resulting AFM images may not show the real shape of the polymer sample as would be expected to be globular from the architecture. The polymer molecule may possibly spread out as a monolayer on HOPG and stick flat on the graphite surface due to the still low polymer compactness and strong, favorable interactions between the polymer and the support. Very recently, similar flattened square-shaped objects have been also visualized by AFM analysis using the newly synthesized 3G dendritic hyperbranched polystyrene with a higher M_n value of 1.43 × 10^7, structurally analogous to the above-mentioned sample.[50] Accordingly, these dendrimer-like star-branched polymer samples are considered to be still too soft for the AFM analysis. We are now synthesizing tougher dendrimer-like star-branched polymers with cross-linking or rigid polymer segments.

As described in the Introduction and imagined from the branched architectures, dendrimer-like star-branched polymers are believed to be nanosize globular macromolecules. Very recently, however, the synchrotron SAXS studies of the 3G (A-A_2-A_4)$_4$ and 4G (A-A_2-A_8-A_{32})$_4$ polymers by Ree and coworkers indicate that these polymers reveal ellipsoidal shapes rather than spheres and such ellipsoids are composed of a core part and a shell part where the core part has relatively higher density than the shell part.[51] Detailed SAXS analytical results will appear soon.

Conclusions

We have successfully synthesized a new series of 4G dendrimer-like star-branched (PMMA)s with highly branched architectures composed of four branch junctures in the three generations and two branch junctures in one generation by developing a novel iterative “arm-first” divergent methodology using premade living anionic polymers. The resulting polymers were well-defined in branched architecture and precisely controlled in chain length. By contrast, the 4G polymer consisting of four branch junctures in all generations could not be synthesized under the same conditions. In this synthesis, the final linking reaction proceeded with an efficiency of 72% to introduce 184 (target: 256) branch segments, resulting in the formation of a densely branched sample with a high molecular weight of over 3.5 million g/mol.

The 4G block copolymers with the same highly branched architectures (three four-branch junctures and one two-branch juncture) were successfully synthesized by the linking reaction of the 3G brominated polymers with living anionic polymers of *tert*-butyl methacrylate, (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl methacrylate, and 2-vinylpyridine, respectively. The resulting block copolymers were further treated with $(CH_3)_3SiCl$/LiBr, 2 N HCl, and 2 N HCl to convert the functional segments to more polar and water-soluble poly(methacrylic acid), poly(2,3-dihydroxypropyl methacrylate), and poly(2-vinylpyridinium hydrochloride), respectively. Thus, it was possible to add functionalities to the dendrimer-like star-branched PMMA.

Hydrodynamic radii, R_h, and radii of gyration, R_g, of 3G and 4G polymers were measured in THF by RALLS and SAXS analyses. It was found that the molecular size estimated from R_h and R_g values increases with increasing the molecular weight. Very interestingly, the intrinsic viscosities were observed to be very similar to each other and almost independent of R_h, R_g, molecular weight, and branch architecture in the same generation but showed a discernible increase from the 3G to 4G. The visualization of the largest and most densely 4G polymer, (A-A_4-A_{16}-A_{46})$_4$, was attempted by AFM. Unfortunately, we have not succeeded in observing the expected molecular shape, but a flattened square-shaped object, possibly because the polymer may spread out as a monolayer on HOPG and stick flat on the graphite surface.

Acknowledgment. The synthetic work was supported by a grant (B 18350060) from a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan. A.H. also acknowledges both Japan−France and Japan−Korea Bilateral Joint Projects from Japan Society for the Promotion of Science for supporting the collaboration researches on the present subject. T.W. is thankful for support from the Japan Society for the Promotion of Science Research Fellowships for Young Scientists. M.R. appreciates the financial support from the Korea Science & Engineering Foundation (Korea−Japan Cooperation Project, National Research Laboratory for Polymer Synthesis and Physics, and Center for Integrated Molecular Systems) and the Ministry of Education (BK21 Program). Synchrotron SAXS measurements at PLS were supported by Ministry of Science & Technology and the POSCO Company. M.S., S.C., and A.D. thank the French Centre de la Recherche Scientifique (CNRS) for supporting this work and the French−Japanese Collaboration project.

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MA802209N