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Precise Synthesis of Dendrimer-Like Star-Branched Poly(methyl methacrylate)s with Different Branched Architectures up to Third-Generation by Iterative Methodology

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Summary: Four kinds of dendrimer-like star-branched poly(methyl methacrylate)s (PMMA)s with different branched architectures have been synthesized up to the third-generation by developing the iterative divergent methodology which involves the following two elementary reactions: (a) a coupling reaction between α-functionalized living anionic PMMA having two or four 3-*tert*-butyldimethylsilyloxymethylphenyl (SMP) groups and benzyl bromide (BnBr)-multi-functionalized core compound(s) or BnBr-chain-end-multi-functionalized PMMA, and (b) a transformation reaction of the introduced SMP group into BnBr function. The number of segments branched at the junction point could be readily controlled by adjusting BnBr reaction sites of the core and the polymer chain-end in number. Characterization results on molecular weight, molecular weight distribution, and end-group functionality revealed that the resulting branched polymers all herein synthesized were well-defined in branched architecture and precisely controlled in chain length. In order to evaluate the solution properties of the third-generation polymers, their viscosities and hydrodynamic radii were measured by viscometer and RALLS, respectively, and discussed.

Keywords: branched architecture; dendrimer-like star-branched polymer; iterative divergent methodology; living anionic polymerization; poly(methyl methacrylate)

Introduction

Dendrimer-like star-branched polymers have recently been synthesized as a new kind of hyperbranched polymers. They resemble well-known dendrimers in branched architectures, but are made up by dendritically branched high molecular weight polymer segments emanating from a central core. Therefore, they are much higher in molecular weight and much bigger in molecular size than dendrimers consisting of small molecules. Because of the nano-size globular-like structure, the unique topological hyperbranched architecture, the presence of many chain-ends and branch points, and possible formation of several layered structures and molecular assemblies, the synthesis of such polymers have received much attention from theoretical and potentially applicable points of view. However, only limited examples have been reported even at the present time due to their synthetic difficulties.[1–16]

We have recently demonstrated the successful synthesis of a series of well-defined dendrimer-like star-branched poly(methyl methacrylate)s (PMMA)s and their block copolymers by developing a novel methodology based on iterative divergent approach which involves only two elementary reaction steps: (a) a coupling reaction between

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α-functionalized living anionic polymer having two SMP groups and BnBr-multi-functionalized core compound(s) or BnBr-chain-end-multi-functionalized polymer and a transformation reaction of the introduced SMP group into BnBr functionality.[17] In this methodology, the SMP group represents a key precursor stable enough toward the living anionic polymer and quantitatively convertible to a highly reactive BnBr functionality. The α-functionalized living anionic polymer with two SMP groups is employed as a functionalized building block in each iterative process to construct repeating units of each generation. Since the two reaction steps quantitatively proceeded, they could be repeated at least seven times to synthesize a series of dendrimer-like star-branched (PMMA)s up to the seventh-generation.[18] Similarly, the synthesis of a structurally similar dendrimer-like star-branched block copolymer consisting of PMMA and poly(2-hydroxyethyl methacrylate) segments was also achieved by employing the living anionic polymer of 2-hydroxyethyl methacrylate at the final iteration.[17] The resulting polymers possessed a high degree of structural and compositional homogeneity as confirmed by molecular characterization results.

In this paper, we describe the synthesis of four kinds of dendrimer-like star-branched (PMMA)s with different branch densities up to the third-generation by extending the above-mentioned methodology. The aim of the present study is to establish the iterative methodology so far developed as a more general and versatile synthetic procedure for dendrimer-like star-branched polymers with structural variation.

Experimental

Materials

All chemicals (>98% purities) were purchased from Aldrich, Japan, and used as received unless otherwise stated. Dichloromethane, acetone, THF, MMA, heptane, acetonitrile, $(CH_3)_3SiCl$, LiBr, and LiCl were purified according to the reported procedures described elsewhere.[18,19] 1, 1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**), 1, 1-bis(3-bromomethylphenyl)ethylene (**2**), 1, 1-bis(3-(2,2-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)-4-methylhexyl)phenyl)ethylene (**3**), and 1,1,4,4-tetra(3-bromomethylphenyl)-butane (**5**) were synthesized according to our procedures previously reported.[18,20,21]

Measurement

Both ^1H and ^{13}C NMR spectra were measured on a Bruker DPX300 (300 MHz for ^1H and 75 MHz for ^{13}C) in $CDCl_3$. Size-exclusion chromatography (SEC) was carried out in THF at 40 °C with a TOSOH HLC-8020 with UV (254 nm) and refractive index detection. A calibration curve was made with six PMMA samples prepared by us. Right angle laser light scatterings (RALLS) were measured in THF at 30 °C on an Asahi Techneion Viscotek Model 302 TDA with triple detector software. Intrinsic viscosities were measured with an Ubbelhode viscometer in THF at 25 °C.

1,1,4,4-Tetrakis(3-(2,2-bis(3-bromomethylphenyl)-4-methylhexyl)phenyl)butane (6)

Under high vacuum conditions (10^{-6} torr), a THF (23.9 mL) solution of **1** (16.7 mmol) pre-cooled at −78 °C was added to *sec*-BuLi cyclohexane solution (1.0 M, 13.9 mL) at −78 °C and the mixture was allowed to stand for 20 min at −78 °C. Then, **5** (1.44 g, 1.96 mmol) dissolved in THF (33.2 mL) at pre-cooled at −78 °C was slowly added to the above mixture and the resulting solution was allowed to stir at −78 °C for additional 30 min. The reaction was terminated with degassed methanol, followed by removal of the solvents, crude 1,1,4,4-tetrakis(3-(2,2- bis-(3-*tert*- butyldimethylsilyloxymethylphenyl)-4-methylhexyl)phenyl)butane was obtained as a yellowish syrup. The crude product (ca. 6 g) dissolved in THF (50 mL) was mixed with a THF solution of Bu_4NF (1.0 M, 15.0 mL) and the mixture was allowed to stir at 25 °C for 12 h. Evaporation of all the solvents, followed by drying by vacuum pump for overnight, yielded a yellow solid of crude 1, 1,4,4-tetrakis(3-(2,2-bis(3-hydroxymethylphenyl)-4-methylhexyl)phenyl)butane. Under a nitrogen, the crude product (ca. 5.5 g) dissolved in CH_2Cl_2 (100 mL) was slowly added to PBr_3 (213 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was allowed to stir at 25 °C for an additional 1h and quenched with water at 0 °C. After usual work-up, followed by evaporation of solvent, the residue was dissolved in a small amount of THF and precipitated in methanol. The product was readily purified by reprecipitation from THF to methanol twice and freeze-drying from its absolute benzene solution. Thus, pure **6** was isolated as a white solid. ^{1}H NMR: δ 7.17–6.17 (m, 48H, aromatic), 4.35 (s, 16H, $-CH_2-Br$), 3.42–3.31 (m, 8H, $Ph-CH_2-C(Ph)_2$ and m, 2H, $Ph-CH-Ph$), 1.91–1.71 (m, 8H, $-CH_2CH(CH_3)CH_2CH_3$, and m, 4H, $-CH_2-CH_2-$), 1.40 (s, 4H, $-CH_2CH(CH_3)CH_2CH_3$), 0.91–0.76 (m, 8H, $-CH_2CH(CH_3)CH_2CH_3$), 0.68 (t, 12H, $J = 5.69$ Hz, $-CH_2CH(CH_3)CH_2CH_3$), 0.44 (t, $J = 7.41$ Hz, $-CH_2CH(CH_3)CH_2CH_3$).

Synthesis of Dendrimer-Like Star-Branched (PMMA)s by Iterative Methodology

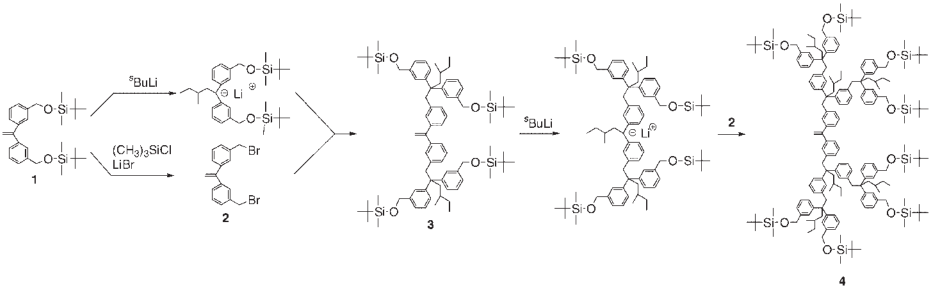
All polymerizations and coupling reactions were carried out under high-vacuum conditions (10^{-6} torr) in sealed glass reactor equipped with break-seals. All reactors were pre-washed with 1,1-diphenylhexyl lithium in heptane after being sealed off from a vacuum line. The transformation and re-transformation reactions were carefully performed under a nitrogen atmosphere. The methodology was carried out by the same procedures as those previously reported.[18,21]

Results and Discussion

Dendrimer-Like Star-Branched (PMMA)s with Four Segments Branched at Each Junction Point

As mentioned in introduction, we previously demonstrated the successful synthesis of various dendrimer-like star-branched polymers by developing the iterative methodology. Since α-functionalized living PMMA with two SMP groups convertible to two BnBr reaction sites was used as a building block, the resulting polymers always possessed a degree of branching equal to two in each of all generations except for the core parts. If the BnBr reaction sites could be increased in number, more than two polymer segments may possibly be introduced at the junction point, resulting in an increase in branch density.

Very recently, we have successfully applied the iterative methodology developed for the polymer syntheses to the synthesis of multi-functionalized DPE derivatives with more than two SMP groups as illustrated in Scheme 1. At first, 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) was brominated with $(CH_3)_3SiCl$-LiBr to afford 1,1-bis(3-bromomethylphenyl)ethylene (**2**). At the same time, **1** was reacted with *sec*-BuLi to convert to the corresponding functionalized anion, which was then coupled with **2**, to essentially quantitatively yield a new substituted DPE



Scheme 1.
Synthetic scheme of **3** and **4**.

with four SMP groups, **3**. Similarly, a DPE derivative with eight SMP groups, **4**, was successively synthesized from **3** by repeating the same reaction sequence. Thus, the iterative methodology starting from **1** can gain easy access to multi-functionalized DPE derivatives with four, eight, and possibly more SMP groups.

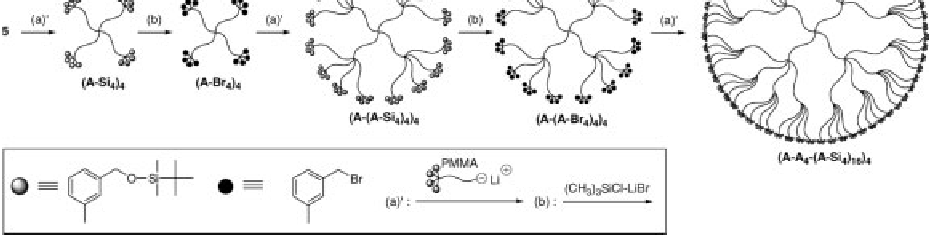
Like α-functionalized living PMMA with two SMP groups, α-functionalized living PMMA with four SMP groups was readily obtained by treatment of **3** with *sec*-BuLi, followed by living anionic polymerization of MMA. As illustrated in Scheme 2, a new series of densely dendrimer-like star-branched (PMMA)s with four segments branched at all junction points have been synthesized up to the third-generation by the iterative methodology using the α-functionalized living PMMA with four SMP groups thus prepared.[22] In order to compare the previous results, the living PMMA herein used was always adjusted to be around 10 000 in M_n value. In the first iterative process, a 2.0-fold excess of α-functionalized living PMMA with four SMP groups was reacted with a core compound having four BnBr moieties, **5**, in order to complete the reaction. The reaction mixture shows two sharp SEC peaks corresponding to the coupling product and deactivated living PMMA used in excess in the reaction, respectively. The coupling efficiency was virtually quantitative based on the two peak areas. The objective coupling product was isolated in 90% yield by fractional precipitation using benzene and methanol. The characterization results are summarized in Table 1.

Table 1.
Synthesis of dendrimer-like star-branched PMMAs with four segments branched at each junction point.

Type	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		M_w/M_n
	Calcd	SEC	^{1}H NMR	Calcd	RALLS	
A_4	52.8	46.5	52.2	53.9	51.6	1.02
$(A\text{-}A_4)_4$	236	122	234	241	247	1.02
$(A\text{-}A_4\text{-}A_{16})_4$	938	350	959	947	939	1.03

The M_n value determined by ^{1}H NMR end-group analysis using three resonances at 0.04, 3.59, and 7.25–6.40 ppm (silylmethyl protons of the SMP groups, methoxy protons of the main chain, and phenyl proton of the central core) agreed well that calculated. As expected from the branched architecture, the M_n value estimated by SEC was somewhat smaller than that calculated. The M_w value absolutely determined by RALLS was in good agreement with the calculated value. A narrow molecular weight distribution was attained, the M_w/M_n value being 1.02. It should be mentioned that the first-generation polymer was a four-arm star-branched polymer but not a dendrimer-like star-branched polymer.

The four SMP groups introduced at each chain-end (total sixteen in number) were transformed into BnBr functions by treatment with a 50-fold excess of a $(CH_3)_3SiCl$ and LiBr mixture in acetonitrile at 40 °C for 24 h. The ^{1}H NMR spectrum of the polymer obtained after the reaction revealed the



Scheme 2.
Synthetic scheme of $(\mathbf{A\text{-}A_4\text{-}A_{16}})_4$.

absence of both benzylmethylene and *tert*-butyldimethylsilyl protons observed at 4.66, 0.90, and 0.04 ppm and the presence of methylene protons of the BnBr function at 4.45 ppm. In addition, a small signal ($<5\%$) was observed at 4.53 ppm assigned to methylene protons of the benzyl chloride moiety. It was readily re-transformed into BnBr function by treatment with a 50-fold excess of LiBr in acetone. The SEC peak of polymer obtained after the transformation reaction remains unchanged in both shape and distribution. Accordingly, the bromination of the first-generation PMMA proceeded quantitatively.

With use of the brominated polymer thus obtained, the same reaction sequence involving the coupling and transformation reactions was repeated. In this iterative process, a 4-fold excess of living PMMA was used and the reaction time was extended form 24 h to 48 h, taking the steric hindering effect into the consideration. Under such conditions, the coupling reaction was complete. The isolated polymer by fractional precipitation ($\sim$85 %) was characterized by SEC, ^{1}H NMR, and RALLS measurements (see Table 1). Agreement of the molecular weights (M_n and M_w) between calculated and observed is quite satisfactory and a narrow molecular weight distribution is attained. The number of the terminal SMP group observed by ^{1}H NMR was very close to the theoretical value of 64. These analytical results clearly indicate the successful synthesis of the expected polymer possessing second-generation dendrimer-like star-branched architecture. The transformation reaction was similarly carried out by treatment of the polymer with $(CH_3)_3SiCl$ and LiBr under the same conditions.

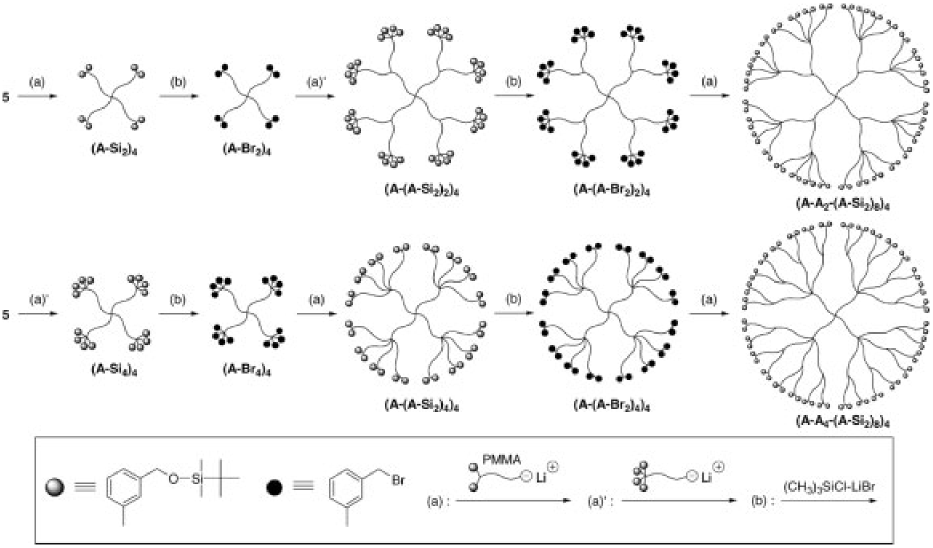
In order to synthesize the third-generation polymer, the same reaction sequence was again repeated with use of the brominated second-generation polymer as a starting material. The polymer was yielded essentially quantitatively and isolated in 80 % yield by fractional precipitation. Both M_n and M_w values measured by ^{1}H NMR and RALLS show good match with those calculated (see also Table 1). The molecular weight distribution was found to be narrow. Moreover, comparison of the degrees of SMP-end functionality expected and observed gave excellent agreement.

The second- and third-generation polymers synthesized are comprised of 20 and 84 PMMA segments bearing 64 and 256 BnBr functions at their termini. They can be represented by $(\mathbf{A}\text{-}\mathbf{A}_4)_4$ and $(\mathbf{A}\text{-}\mathbf{A}_4\text{-}\mathbf{A}_{16})_4$, respectively. Thus, the iterative methodology using α-functionalized living PMMA with four SMP groups works satisfactorily to synthesize densely dendrimer-like star-branched (PMMA)s with four segments branched at all junctions.

Dendrimer-Like Star-Branched (PMMA)s with Two and/or Four Segments Branched at Each Junction Point

By appropriately changing either α-functionalized living PMMA with two SMP or four SMP groups in the coupling reaction step, it is possible to synthesize two more three-generation dendrimer-like star-branched polymers. As illustrated in Scheme 3, for example, α-functionalized living PMMA with two SMP groups was coupled with **5** in the first iterative process. The resulting four-arm star-branched polymer was treated with $(CH_3)_3SiCl$-LiBr to give the brominated polymer, which was then coupled with α-functionalized living PMMA with four SMP groups to afford the second-generation polymer. This in turn could be brominated with $(CH_3)_3SiCl$-LiBr under the same condition, followed by coupling with α-functionalized living PMMA with two SMP groups, resulting in the formation of the third-generation polymer. It possessed four segments branched at the core and two followed by four segments branched at the junctions toward the outermost layer. Therefore, the structure of this polymer can be represented as $(\mathbf{A}\text{-}\mathbf{A}_2\text{-}\mathbf{A}_8)_4$.

Similarly, the other third-generation polymer represented by $(\mathbf{A}\text{-}\mathbf{A}_4\text{-}\mathbf{A}_8)_4$ could be synthesized by coupling α-functionalized living PMMA with four SMP groups with **5** in the first iteration and then by reacting α-functionalized living PMMA with two SMP group in the second iteration, followed by reacting α-functionalized living PMMA



Scheme 3.
Synthetic scheme of **(A-A$_2$-A$_8$)$_4$** and **(A-A$_4$-A$_8$)$_4$**.

with two SMP groups in the third iterative process (also see Scheme 3).

The expected and well-defined structures of the two series polymers were confirmed by the characterization results summarized in Table 2. Their SEC profiles are shown in Figure 1. All of the polymers exhibit to have symmetrically sharp monomodal distributions.

Dendrimer-Like Star-Branched Polymers with Eight Segments Branched at the Core

By increasing the BnBr reaction sites of the core compound from four to more in number, it is expected to obtain architecturally different dendrimer-like star-branched polymers, in which more than four polymer chains radially emerge from a central core. The core compound having four BnBr moieties, **5**, used for the above-mentioned polymer syntheses was prepared by the dimmerization of **1** *via* radical coupling reaction of the radical anion intermediates generated from **1** and potassium naphthalenide, followed by treatment with $(CH_3)_3SiCl$-LiBr. Again interestingly, the core compound having more than four BnBr moieties can be synthesized by utilizing the present iterative

Table 2.
Synthesis of dendrimer-like star-branched PMMAs with two and/or four branches at each junction and eight segments branched at the core.

Type	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		M_w/M_n
	Calcd	SEC	^{1}H NMR	Calcd	RALLS	
A$_4$	46.4	42.1	46.0	47.3	45.6	1.02
(A-A$_2$)$_4$	145	120	146	146	147	1.01
(A-A$_2$-A$_8$)$_4$	502	239	504	512	514	1.02
A$_4$	52.8	46.5	52.2	53.9	51.6	1.02
(A-A$_4$)$_4$	216	127	217	220	219	1.02
(A-A$_4$-A$_8$)$_4$	551	254	554	567	568	1.03
A$_8$	98.3	65.3	98.3	99.3	98.9	1.01
(A-A$_2$)$_8$	263	130	262	268	268	1.01
(A-A$_2$-A$_4$)$_8$	620	263	612	638	623	1.03

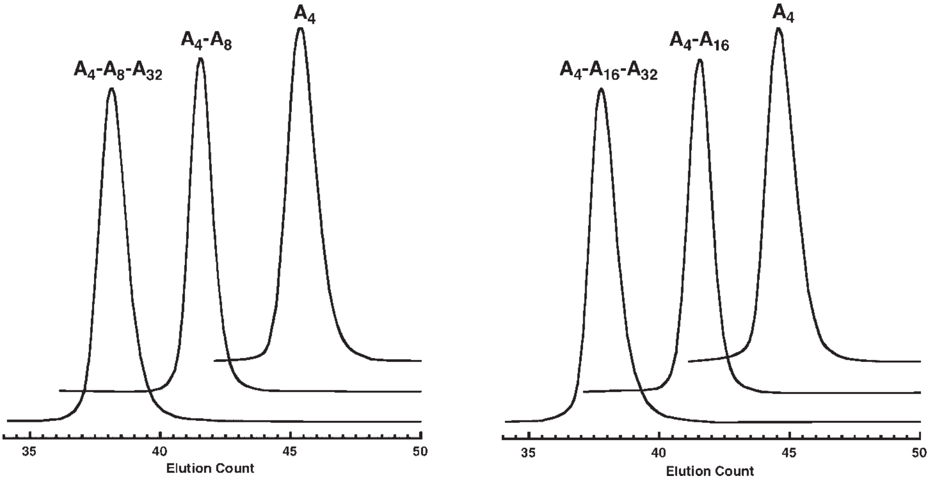


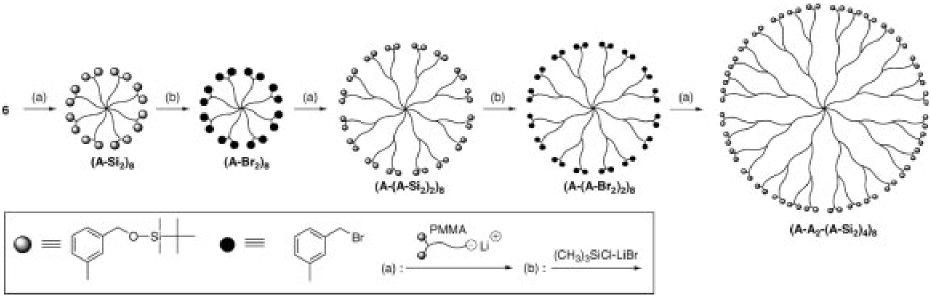
Figure 1.
SEC profiles of dendrimer-like star-branched PMMAs with two and/or four segments branched at each junction point.

methodology. In fact, the four BnBr moieties of **5** doubled to eight in number by reacting with the functionalized anion generated from **1** and *sec*-BuLi, followed by treatment with $(CH_3)_3SiCl$-LiBr to transform the SMP groups into BnBr functions as illustrated in Scheme 4.[23] Thus, a core compound having eight BnBr moieties, **6**, was synthesized from **5** as a starting material. The compound having 16 or more BnBr moieties may possibly be synthesized by repeating the same reaction sequence.

A series of dendrimer-like star-branched (PMMA)s have been synthesized up to the third-generation by repeating the iterative process using **5** as a core compound and α-functionalized living PMMA with two SMP groups as a building block. In the resulting third-generation polymers, eight PMMA segments emerge radially from the central core and two polymer segments are branched at every junction at the next two layers as illustrated in Scheme 5. All of the iterative processes satisfactorily proceed without any difficulty to afford the expected and well-defined polymers (see Table 2). The third-generation polymer represented as **$(A$-A_2-$A_4)_8$** was made up of 56 PMMA segments and possessed 64 SMP termini convertible to BnBr functions.

Solution Properties of Third-Generation Dendrimer-Like Star-Branched Polymers

In order to evaluate the solution properties of four third-generation dendrimer-like star-branched (PMMA)s herein synthesized,



Scheme 4.
Synthetic scheme of **$(A$-A_2-$A_4)_8$**.

Table 3.
Intrinsic viscosities and hydrodynamic radii of dendrimer-like star-branched PMMAs.

Type	$M_w \times 10^{-3}$ a)	$[\eta]$ (mL/g)		g′ d)	R_h (nm) a)
		$[\eta]_{branched}$ b)	$[\eta]_{linear}$ c)		
$(A\text{-}A_2\text{-}A)_4$	514	33.2	103	0.32	14.7
$(A\text{-}A_4\text{-}A_8)_4$	568	32.2	111	0.29	14.9
$(A\text{-}A_2\text{-}A_4)_8$	623	32.4	118	0.27	15.1
$(A\text{-}A_4\text{-}A_{16})_4$	938	35.1	157	0.22	17.2

a) Measured by RALLS.
b) Measured in THF at 25 °C.
c) Calculated from $[\eta]_{linear} = 1.11 \times 10^{-2} M_w$. (ref. 19).
d) $g' = [\eta]_{branched}/[\eta]_{linear}$.

their intrinsic viscosities and hydrodynamic radii, (R_h)s, were measured by viscometer and RALLS, respectively. The data are given in Table 3 along with their g′ values. The g′ value is defined as $[\eta]_{branch}/[\eta]_{linear}$, where $[\eta]_{branch}$ and $[\eta]_{linear}$ are intrinsic viscosities of the branched polymer and the corresponding linear polymer with the same molecular weight measured under the same conditions.

Very surprisingly, intrinsic viscosity values of the first three samples represented as **$(A\text{-}A_2\text{-}A_8)_4$**, **$(A\text{-}A_4\text{-}A_8)_4$**, and **$(A\text{-}A_2\text{-}A_4)_8$** showed almost the same values. Furthermore, their hydrodynamic radii are very similar to each other, the R_h values being around 15 nm. These polymers are classified into category of the third-generation in synthesis, but different in molecular weight, in number of all PMMA segments included (44, 52, and 56) and particularly in branched architecture. On the other hand, they possess exactly 32 PMMA segments in the outermost layer. This indicates that the intrinsic viscosity and hydrodynamic radius of dendrimer-like star-branched polymer strongly depend on the number of segments in the outermost layer rather than the molecular weight, the number of all polymer chains, and the branched architecture. On the other hand, the $[\eta]_{branch}$ and R_h values of the most densely sample referred to as **$(A\text{-}A_4\text{-}A_{16})_4$** are observed to be somewhat larger than those of other three samples, but not larger than those expected from its molecular weight.

There were the first three samples only ranging from 0.27 to 0.32 in g′ value, while it was 0.22 for the most densely sample. Accordingly, g′ value seems to be also sensitive to the number of segments in the outermost layer rather than the generation and branched architecture. Interestingly, their g′ values are larger than those of 32- and 64-arm star-branched polymers ($g'_{32\text{-arm star}} = 0.14$ and $g'_{64\text{-arm star}} = 0.083$, respectively), indicating that dendrimer-like star-branched polymers are less compact in THF than the corresponding star- branched polymers.[24] The theoretical approach on this subject will of interest in the near future.

Conclusions

We have successfully synthesized four kinds of dendrimer-like star-branched (PMMA)s with different branched architectures up to the third-generation by developing the iterative methodology involving only two elementary reaction steps. The resulting polymers all were well-defined in branched architecture and precisely controlled in chain length. The segments branched at the core as well as at the junction of every layer (or generation) could double in number with use of new core and DPE derivatives which were also synthesized by the same iterative methodology used in the polymer syntheses. On the basis of the successful polymer syntheses herein demonstrated, the iterative methodology offers the potential of providing a general, versatile synthetic procedure with which one can design and synthesize a structural variety of dendrimer-like star-branched polymers.

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[22] The synthesis of the same series of dendrimer-like star-branched (PMMA)s with different molecular weights have been recently reported.[21]

[23] The eight SMP groups of the compound were not completely brominated with $(CH_3)_3SiCl$-LiBr under the same conditions. Although the reason was not understood at the present time, a few unknown compounds were by-produced in some cases. Therefore, an alternative procedure utilized the deprotection of SMP groups with $(C_4H_9)_4NF$, followed by bromination with PBr_3. These two reactions were observed to proceed cleanly under mild conditions to give pure 6 essentially quantitatively. Detailed descriptions are given in experimental section.

[24] J. Roovers, in *Star and Hyperbranched Polymers;* M. K. Mishra, S. Kobayashi, Eds.; New York, **1999**; pp 285–341.