

HIGHLIGHT

Precise Synthesis of Well-Defined Dendrimer-Like Star-Branched Polymers by Iterative Methodology Based on Living Anionic Polymerization

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Received 3 July 2006; Accepted 24 July 2006

DOI: 10.1002/pola.21701

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Dendrimer-like star-branched polymers recently developed as a new class of hyperbranched polymers, which resemble well-known dendrimers in branched architecture, but comprise polymer chains between junctions, are reviewed in this highlight article. In particular, we

focus on the precise synthesis of various dendrimer-like star-branched polymers and block copolymers by the recently developed methodology based on iterative divergent approach using living anionic polymers and 1,1-bis(3-*tert*-butyldimethylsilyloxy methylphenyl)ethylene. © 2006 Wiley Periodicals,

Inc. *J Polym Sci Part A: Polym Chem* 44: 6659–6687, 2006

Keywords: dendrimer-like star-branched polymer; iterative methodology; living anionic polymerization; transformation reaction; 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene



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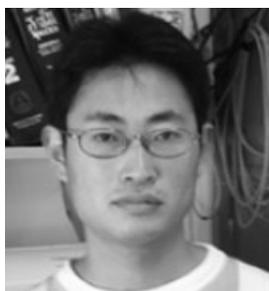
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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 44, 6659–6687 (2006)
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INTRODUCTION

In the past two decades, the syntheses of various branched polymers with complex architectures have been greatly

developed along with rapid progress of living polymerization. These branched polymers have attracted much attention from theoretical, synthetic, and practical viewpoints because of their unique and interesting properties in solu-

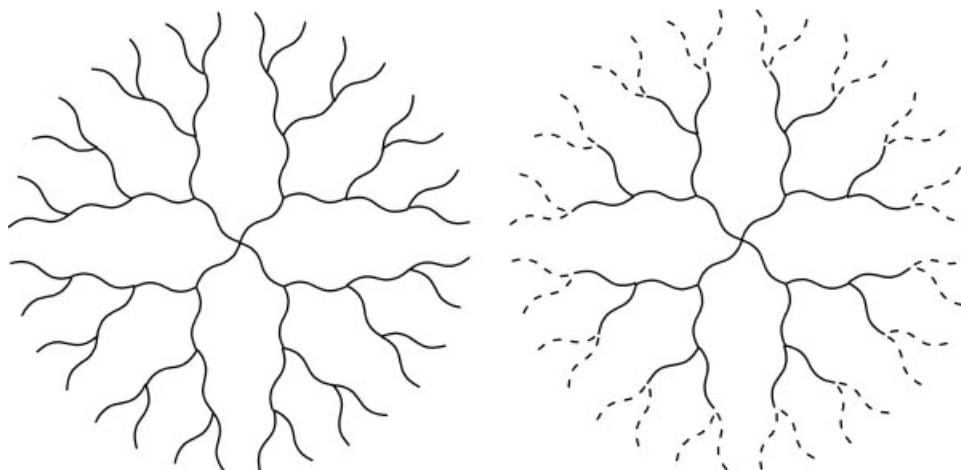


Figure 1. Fourth-generation dendrimer-like star-branched polymer and its block copolymer.

tion, melt, and solid states as well as their usefulness and potential as specialty functional polymers.^{1–24} Among such branched polymers, dendrimer-like star-branched polymers and block copolymers have recently appeared as a new class of hyperbranched polymers. These polymers resemble well-known dendrimer in branched architecture, but comprise dendritically branched polymer chains emanated from a central core or focal point and two or more branches at every junction as repeating units. The synthesis of such branched polymers generally follows a generation-based growth methodology and a very rapid increase in molecular weight is observed by repeating only a few synthetic steps to construct a polymer of one generation. Accordingly, the resulting polymers are much higher in molecular weight and much larger in molecular size than dendrimers. By using the methodology with quantitative nature of reactions to create the reaction sites at the chain-ends and living polymer chains as building blocks in each of all generations, the precise synthesis of dendrimer-like star-branched polymers can be achieved. To make the image clearer, the fourth-generation dendrimer-like star-branched polymer and its block copolymer are shown in Figure 1.

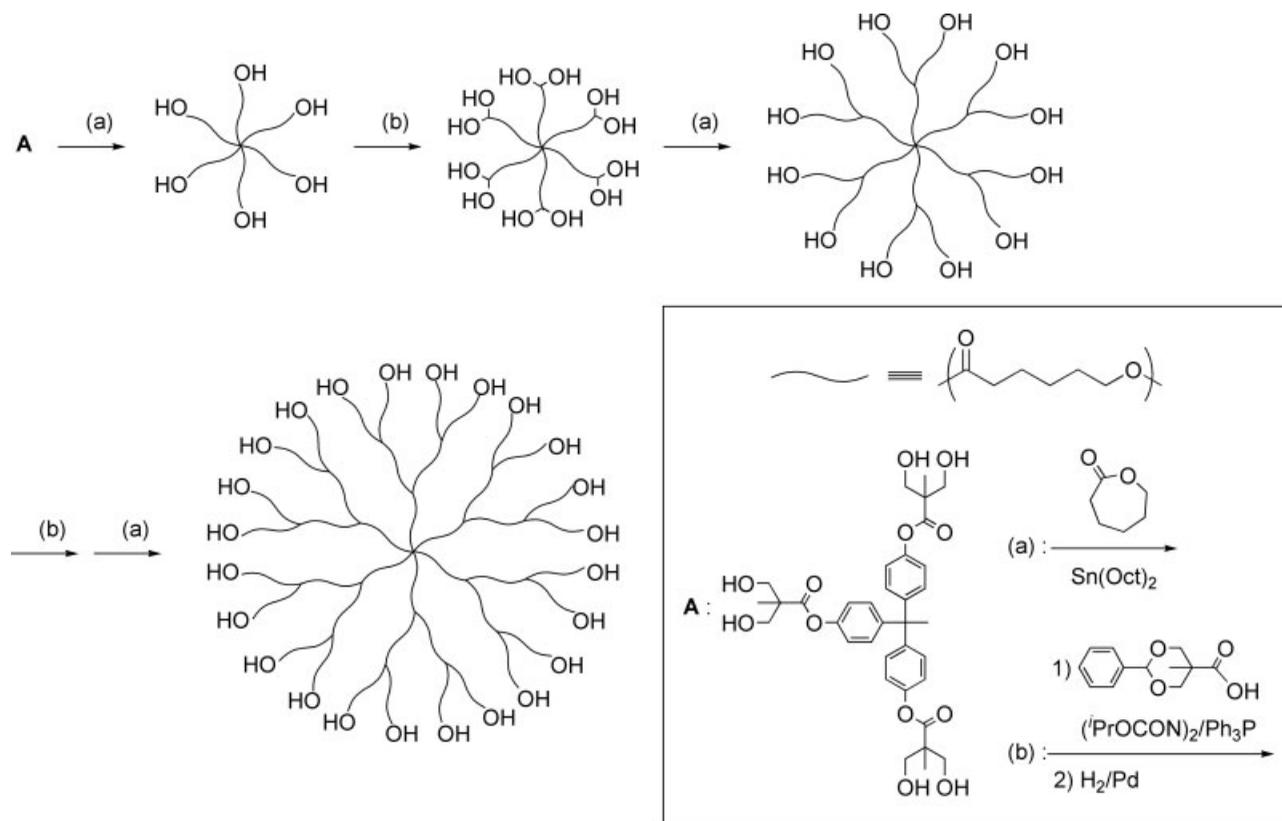
Because of the many connections of their repeating units, dendrimer-like star-branched polymers are highly branched globular macromolecules that are typically several 10 nm in size and carry a multiplicity of many functional groups at chain-ends and branch points. Their core parts are quite different in branch density from the outer layers. Similarly branched block copolymers endowed with asymmetric heterophase structures may have abilities to form several layered structures with different characters and a richer variety of periodic nano-ordered morphological supramolecular structures and molecular assemblies with promising applications in nanotechnology. This review aims the

introduction of the synthetic examples of dendrimer-like star-branched polymers and block copolymers' well-defined architectures reported to date and the synthesis of the same branched polymers by a new iterative methodology recently developed by us.

DENDRIMER-LIKE STAR-BRANCHED POLYMERS AND BLOCK COPOLYMERS REPORTED TO DATE

Iterative Divergent Strategy Based on “Core-First” Initiation Method

The first successful synthesis of an entire array of dendrimer-like star-branched polymers was reported by Hedrick and Trollsås in 1998,²⁵ although the synthesis of such architectures was already contemplated by Gnanou and Six in 1995.²⁶ Scheme 1 shows the synthetic route based on a divergent growth approach combining repetitive living polymerization and chain-end functionalization. In the first iterative process, a hexahydroxyl-functionalized initiator was used for the living ring opening polymerization of ϵ -caprolactone to prepare a six-arm star-branched polymer. All chain-ends of the resulting star were then functionalized with a diol-protected agent, which was deprotected to use as a “macro-initiator” for the living polymerization of ϵ -caprolactone, resulting in the formation of a second-generation polymer. The same iteration generated a third generation polymer composed of 42 poly(ϵ -caprolactone) segments. By changing the functionalities of the initiator and end-functionalized agent in each generation, a series of dendrimer-like star-branched poly(ϵ -caprolactone)s with different branching extents could be synthesized.^{27–29}



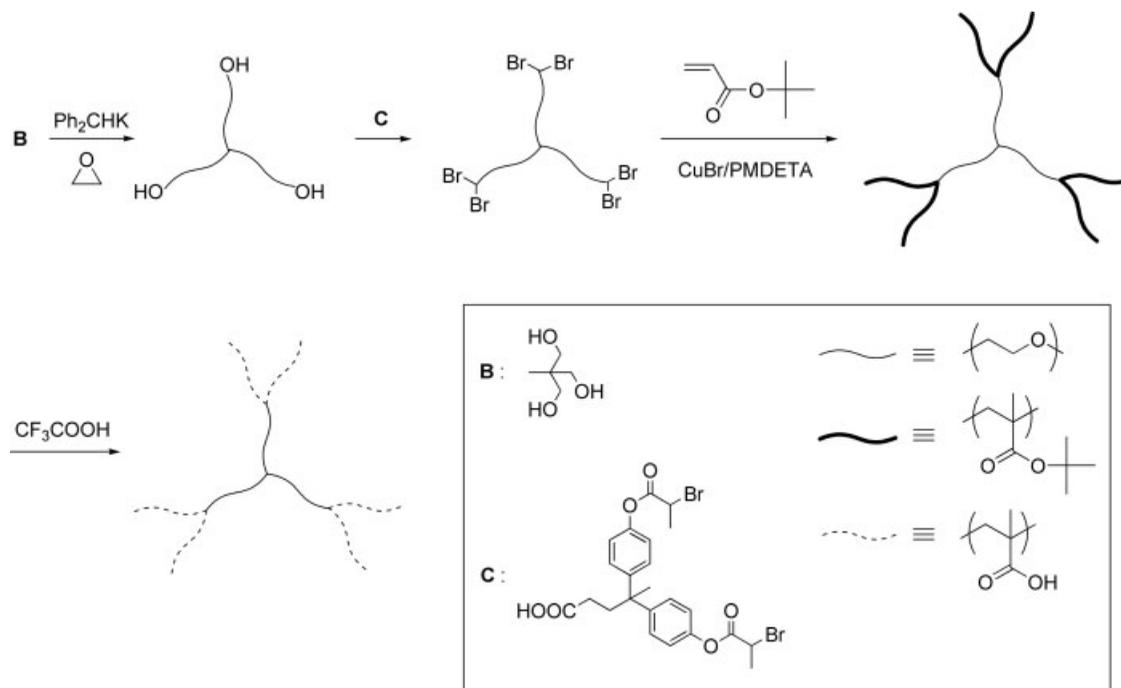
Scheme 1. Synthetic scheme of the first-, second-, and third-generation dendrimer-like star-branched poly(ϵ -caprolactone)s by repeating living polymerization of ϵ -caprolactone and chain-end-modification.

They also synthesized various layered block copolymers with the same branched architectures in a similar way by a combination of ring opening and atom transfer controlled radical polymerizations.^{27,30} As mentioned earlier, the same hexahydroxyl functional compound was used as an initiator for the ring opening living polymerization of ϵ -caprolactone to prepare a six-arm star-branched polymer. Capping the chain ends with an agent containing two activated bromide moieties produced a macro-initiator usable for subsequent atom transfer polymerization. In fact, methyl methacrylate (MMA) could be polymerized with this macro-initiator to give the objective dendrimer-like star-branched block copolymer. Amphiphilic character was introduced into the block copolymer by the atom transfer controlled radical polymerization of either 2-hydroxyethyl methacrylate or ω -methacrylate ethylene oxide macromonomer with the aforementioned macro-initiator.

The same group has also recently demonstrated the possible use of dendrimer-like star-branched polymers as a size-controllable sacrificial template for the preparation of nanoporous organosilicates applicable to ad-

vanced microelectronic materials.^{31,32} These materials could be yielded by mixing the polymers with organosilicates to facilitate nanophase morphologies, followed by removal of the polymers by thermolysis. It was observed that the hyperbranched topology, generation, and end-group functionality play important roles in the size control based on phase separation.

Almost at the same time after the first synthesis of dendrimer-like star-branched polymers reported by Hedrick and coworkers, Gnanou and coworkers also proposed a successive generation-growth methodology convenient for the same branched polymer synthesis, which involves two elementary reaction steps, controlled/living polymerization from multifunctional precursors and chain-end-functionalization to create at least two initiating sites per arm, and repeats the two reaction steps.^{33–36} With this methodology, they were successful in synthesizing various amphiphilic and water-soluble dendrimer-like star-branched block copolymers. Scheme 2 shows the synthetic route for such a block copolymer composed of poly(ethylene oxide) (PEO) and poly(acrylic acid) segments by a combination of the living anionic polymerization of ethylene



Scheme 2. Synthetic scheme of dendrimer-like star-branched block copolymer composed of PEO and poly(acrylic acid) segments by a combination of two living/controlled polymerizations and chain-end-functionalization.

oxide (EO) and the subsequent atom transfer controlled radical polymerization of *tert*-butyl acrylate, followed by hydrolysis. Very recently, the synthesis of a dendrimer-like star-branched PEO up to the eighth generation with a molar mass of 900 kg/mol and as many as 384 external hydroxyl functions has been achieved by repeating the living anionic polymerization of EO and chain-end modification.³⁷

Percec and his coworkers reported the divergent synthesis of dendrimer-like star-branched PMMA by an iterative methodology that involves Cu-catalyzed controlled radical polymerization of MMA and a chain-end modification with a multifunctional agent named TERMINI by them.^{38–40} The TERMINI serves as a chain terminator as well as a masked multifunctional initiator that enables the quantitative re-initiation of the controlled radical polymerization of MMA. As illustrated in Scheme 3, dendritic polymers up to the fourth-generation ($M_{n \text{ max}} = 464 \text{ kg/mol}$) were obtained by repeating the two reactions.

In each of the methodologies proposed, living/controlled polymerizations as well as the quantitative nature of the reactions for chain-end modification are carefully chosen to perform multiple reaction steps without problem. The resulting polymers were considered to possess well-defined architectures and precise controlled chain lengths that were confirmed by several analytical techniques. However, the uniformity of all

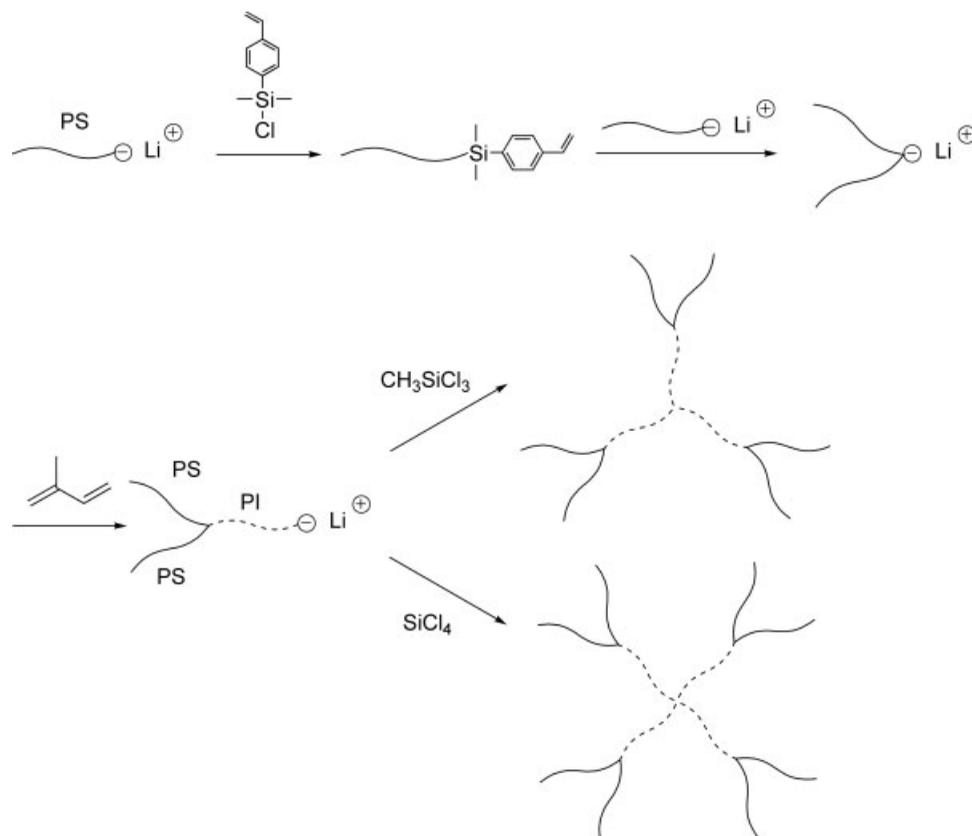
polymer segments starting from the multifunctional initiators still remains a question, especially in the synthesis of higher generation polymers.

Iterative Convergent Strategy Based on “Arm-First” Termination Method

Hadjichristidis and Chalari were successful in synthesizing a series of second generation dendrimer-like star-branched block copolymers by the linking reaction of either CH_3SiCl_3 or SiCl_4 with living anionic off-center graft copolymers prepared by the addition reaction of ω -styryl macromonomers to living anionic polymers, followed by the anionic polymerization of isoprene.⁴¹ The synthetic outline is illustrated in Scheme 4. Very recently, the methodology has been further extended to the synthesis of third generation dendrimer-like star-branched block copolymers as shown in Scheme 5.⁴²

Since their synthetic procedure is based on an “arm-first” termination methodology using premade living anionic polymers as arm segments, the resulting copolymers possess undoubtedly a high molecular and compositional homogeneity.

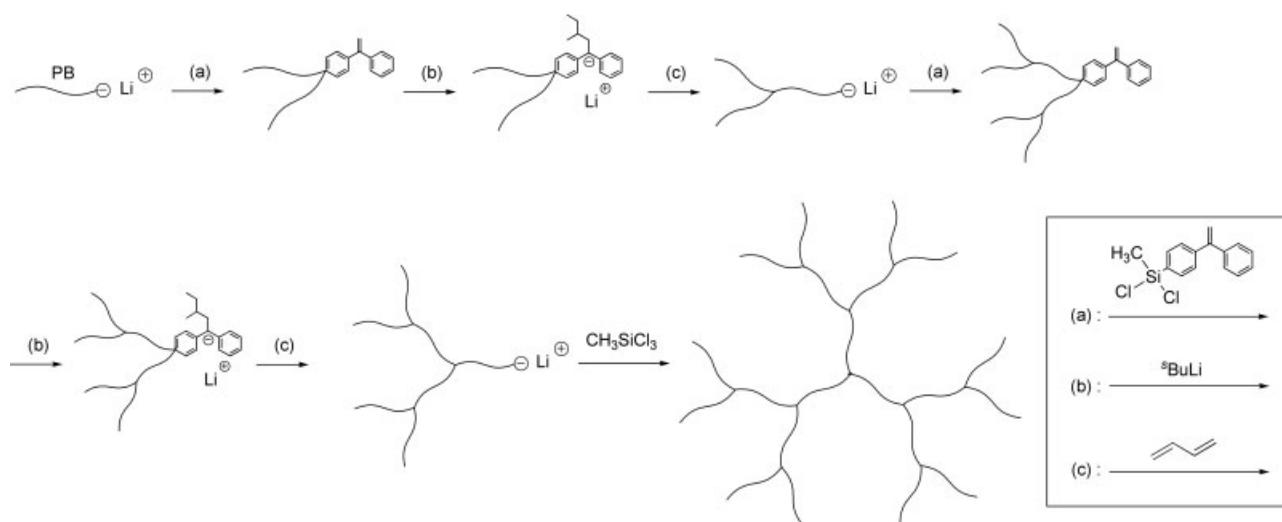
Hutchings and Roberts-Bleming have recently reported the synthesis of dendrimer-like star-branched polystyrenes (PS) by developing a condensation reaction of AB_2 PS macromonomers close to a step growth condensation reaction of AB_2 often used in the synthesis of



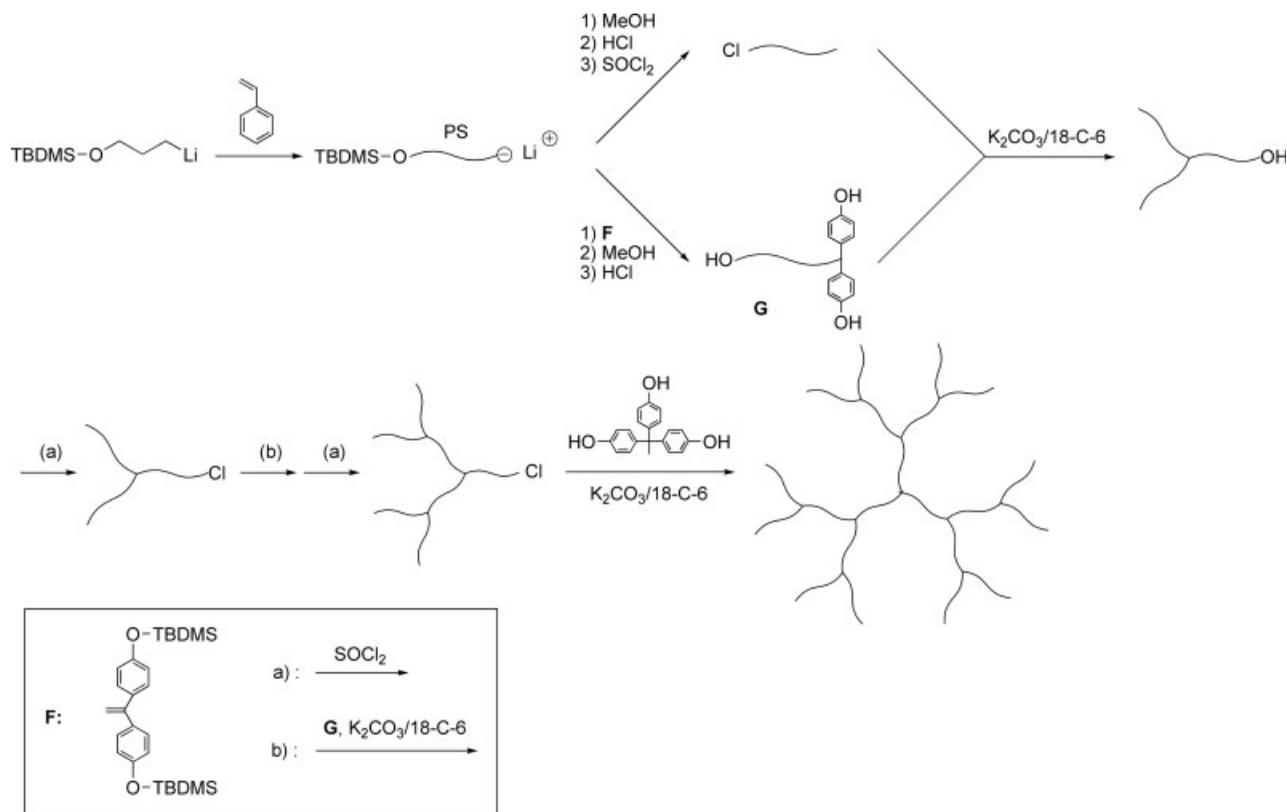
Scheme 4. Synthetic scheme of the second-generation star-branched polymers by the reaction of living anionic off-center branched polymer with either MeSiCl_3 or SiCl_4 .

4-(chlorodimethylsilyl)styrene was not uniform, the molecular weight distributions remain relatively narrow, the M_w/M_n values being less than 1.2 in the polymers obtained

after the second process. The resulting polymers have a less perfect structure, but offer the advantage of a convenient one-pot synthesis.



Scheme 5. Synthetic scheme of the third-generation star-branched polymers by the reaction of living dendron-like polymer with MeSiCl_3 .



Scheme 6. Synthetic scheme of the third-generation star-branched polystyrene by convergent approach using AB₂ PS macromonomer.

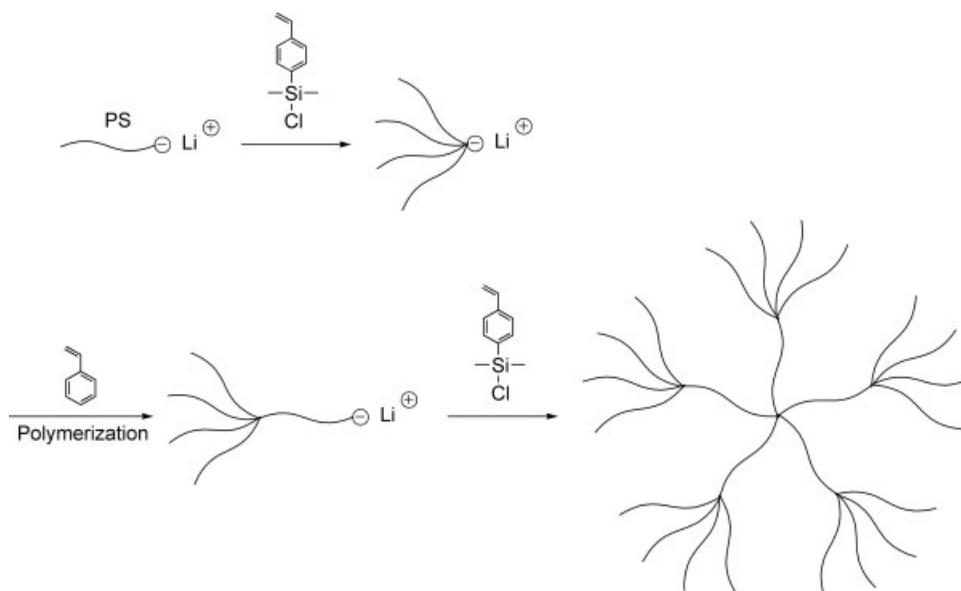
ITERATIVE DIVERGENT METHODOLOGY RECENTLY DEVELOPED BY US

Dendrimer-Like Star-Branched PMMA

In a recent few years, we have been developing a new methodology based on iterative divergent approach for the synthesis of well-defined dendrimer-like star-branched polymers.^{16,45} The methodology involves only two elementary reaction steps, a linking reaction of α -functionalized living poly(methyl methacrylate) (PMMA) with two *tert*-butyldimethylsilyloxymethylphenyl (SMP) groups with either benzyl bromide (BnBr)-multi-functionalized compounds or BnBr-chain-functionalized PMMA and a transformation reaction of the SMP group into BnBr functionality. The SMP group represents a key precursory functional group convertible to a highly reactive BnBr functionality capable of reacting quantitatively with a living anionic polymer of MMA.⁴⁶ The α -functionalized living PMMA with two SMP groups is employed as a functional building block in each iterative process to construct repeating units of each generation. This living functionalized polymer can be obtained by the anionic

polymerization of MMA in THF at -78 °C for 0.5 h with the SMP-functionalized 1,1-diphenylalkyl anion prepared from *sec*-BuLi and 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**). Prior to the polymerization, the addition of a threefold or more excess of LiCl was essential to narrow the molecular weight distribution. In practice, the distribution index, M_w/M_n , was reduced from around 1.2 to less than 1.05 by this addition. Unless otherwise stated, the living PMMA used in the synthesis is adjusted to be around 10 kg/mol in M_n value.

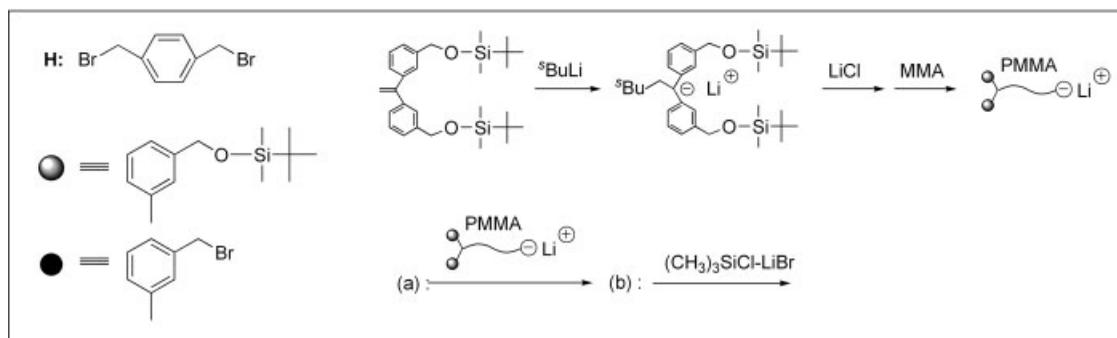
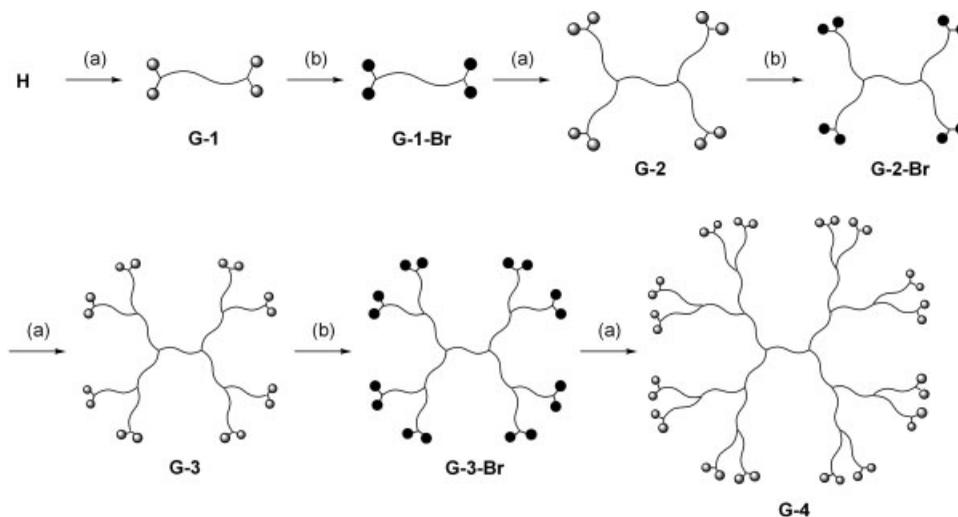
The synthetic procedure elaborated on the basis of the aforementioned iterative methodology is outlined in Scheme 8. In the first iterative process, α -functionalized living PMMA with two SMP groups initially prepared was reacted with α,α' -dibromoxylene of a core agent to link the two PMMA chains, followed by treatment with a 1:1 mixture of (CH₃)₃SiCl and LiBr to transform the four SMP termini into BnBr functions. The linking reaction proceeded with 100% efficiency within a few hours under the conditions in THF at -40 °C, but the reaction mixture was generally allowed to stand for 24 h by way of precaution. Since



Scheme 7. Synthetic scheme of the second-generation star-branched polystyrene by convergent living anionic polymerization.

a 1.5-fold excess of SMP- α -functionalized living PMMA was generally used over each BnBr function to complete the reaction, the linked polymer was isolated

from the deactivated living PMMA used in excess by fractional precipitation. This polymer corresponds to a first generation polymer, referred to as **G-1**. The trans-



Scheme 8. Synthetic scheme of the first-, second-, third-, and fourth-generation dendrimer-like star-branched (PMMA)s, **G-1** to **G-4**, by iterative methodology.

Table 1. Characterization of **G-1** to **G-4**

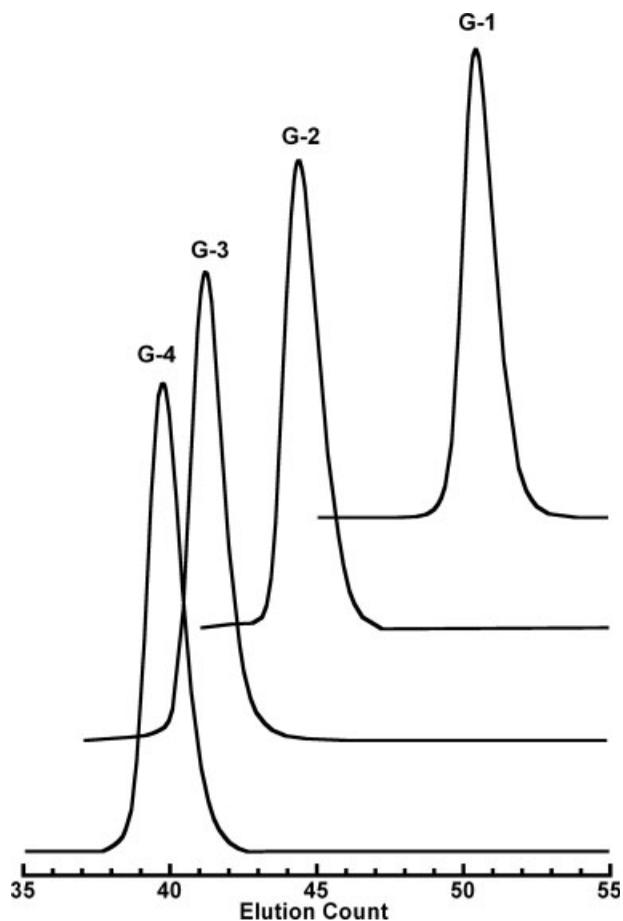
Type	M_n (10^{-3})			M_w (10^{-3})		M_w/M_n
	Calcd	SEC	$^1\text{H NMR}$	Calcd	SLS	
G-1	12.0	12.5	12.6	–	–	1.01
G-1-Br	12.4	12.8	12.3	–	–	1.02
G-2	55.6	48.6	56.1	56.7	57.9	1.02
G-2-Br	55.2	47.8	54.9	–	–	1.02
G-3	143	105	142	147	146	1.03
G-3-Br	143	104	141	–	–	1.02
G-4	321	195	320	331	330	1.03

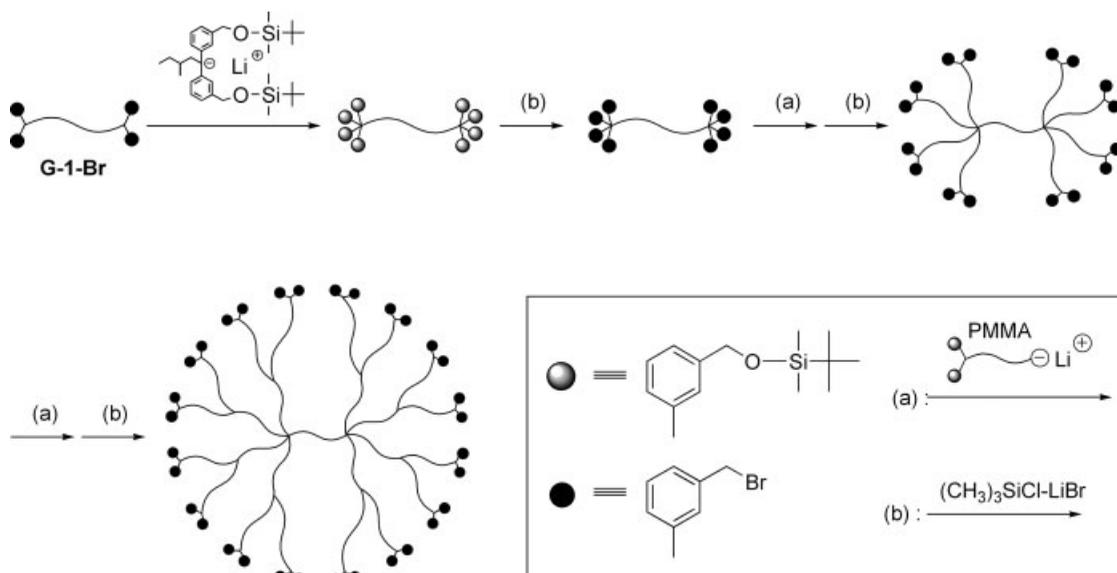
formation of the SMP group into BnBr function with a 50-fold excess of $\text{LiBr}-(\text{CH}_3)_3\text{SiCl}$ at 40°C for a few hours was also quantitative as confirmed by the disappearance of the three resonances at 4.66, 0.90, and 0.04 ppm characteristic to SMP group and by appearance of a new resonance at 4.45 ppm assignable to the BnBr methylene protons at the expected intensity. Thus, the reaction proceeded smoothly and quantitatively.⁴⁷ In the same spectrum, the resonances for PMMA main chain were observed to remain unchanged, indicating that PMMA is completely stable under the transformation conditions. The characterization results (^1H and ^{13}C NMR, elemental analysis, SEC, and VPO) revealed that the resulting brominated PMMA, referred to as **G-1-Br**, as well as the first generation PMMA, **G-1**, possessed the expected structures in chain length and degree of terminal BnBr and SMP functionalities. The results are summarized in Table 1.

In the second iterative process, the two reactions were repeated starting with the **G-1-Br** under the identical conditions. The resulting second-generation polymers, **G-2** and **G-2-Br**, were found to possess the expected structures with narrow molecular weight distributions. Although the M_n values estimated from SEC were somewhat smaller than that predicted from their branched structures, the M_n and M_w values determined by ^1H NMR and SLS agreed quite well with those expected (see Table 1). The ^1H NMR spectrum indicated that all BnBr functionalities had completely reacted to introduce the expected numbers of PMMA segments.

These results clearly indicate that the two reaction steps in each iterative process warrant their selection as suitable synthetic procedures for the introduction of branches as well as branching points. Accordingly, the same reaction sequence involving the two reaction steps were repeated two more times to successively synthesize a third, **G-3**, followed by a fourth generation dendrimer-like star-branched PMMA, **G-4** via **G-3-Br**. The M_n values of **G-3** and **G-4** are determined

with high accuracy by ^1H NMR because of the presence of many SMP groups introduced at their periphery of the outermost layers and found to agree well with those predicted. There was also good agreement of M_w values between absolutely determined by SLS and calculated from feed ratios in each polymer sample. As shown in Figure 2, SEC traces of all generation polymers, **G-1**, **G-2**, **G-3**, and **G-4**, exhibit that each peak is sharp and symmetrically monomodal in distribution and moves to higher molecular weight side as increasing the generation. Moreover, all of the analytical results clearly indicate their high degrees of molecular and branched structural homogeneity. The final product, **G-4** ($M_n = 320$ kg/mol and $M_w/M_n = 1.03$), was composed of 30 PMMA segments and carried 32 SMP termini. Once again, the excellence of the developed iterative methodology is demonstrated by the successful synthesis of four generation polymers with quantitative efficiency. Since the **G-4** has the same SMP termini convertible to BnBr functions used as next reaction sites, the iterative process may possibly be continued.

**Figure 2.** SEC profiles of **G-1** to **G-4**.



Scheme 9. Synthetic scheme of the first-, second-, and third-generation dendrimer-like star-branched (PMMA)s by iterative methodology using “branching” technique.

Application of Iterative Methodology to SMP-Functionalized DPE Derivatives: Synthesis of Dendrimer-Like Star-Branched Polymers with Different Branched Architectures

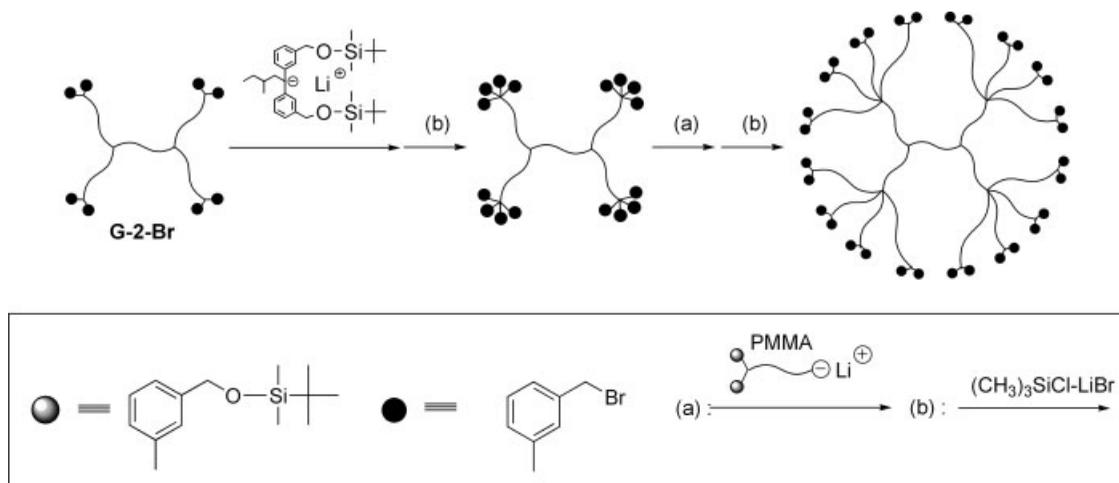
In the preceding section, dendrimer-like star-branched polymers up to the fourth-generation were successfully synthesized by the iterative methodology using α,α' -dibromoxylene as a core agent and α -functionalized living PMMA with two SMP groups convertible to two BnBr reaction sites as a building block in each iterative process. Accordingly, the resulting polymers of all generations have a degree of branching equal to two at every junction. If the reaction site would increase in number, more than two polymer segments could be introduced at the junction, resulting in an increase in degree of branching.

Interestingly, the increasing of the BnBr reaction site can be readily accomplished by using the present iterative methodology, originally developed for the synthesis of dendrimer-like star-branched polymers.^{23,46} As illustrated in Scheme 9, the BnBr reaction sites of **G-1** can indeed double from four to eight in number by reacting them with the SMP-functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi instead of SMP- α -functionalized living PMMA, followed by transformation of the SMP groups into BnBr functions. As confirmed from ¹H and ¹³C NMR spectra and elemental analysis, the polymer had a complete degree of BnBr-end-functionality with a multiplicity equal to four at each chain-end.⁴⁸ The resulting brominated polymer was subjected to the iterative reaction sequence involving the

linking reaction with α -functionalized living PMMA with two SMP groups and the transformation reaction. A second-generation polymer, followed by a third-generation polymer, were successively obtained by repeating twice the reaction sequence. In this synthesis, the final product was composed of 26 PMMA segments and carried 32 BnBr termini. One more polymer of the same third-generation could be synthesized by using this “branching” technique at the third iterative process as shown in Scheme 10.

The two BnBr reaction sites at each chain-end of the **G-1** could be derivatized into four times as many BnBr functions by repeating twice the two reaction steps involving the reaction of the BnBr reaction sites with the SMP-functionalized anion and the transformation reaction. A new third-generation PMMA was successfully synthesized starting from the brominated PMMA with 8 BnBr reaction sites at each chain-end as illustrated in Scheme 11. Thus, this success permits the design and possible synthesis of dendrimer-like star-branched polymers constructed by more densely branch segments.

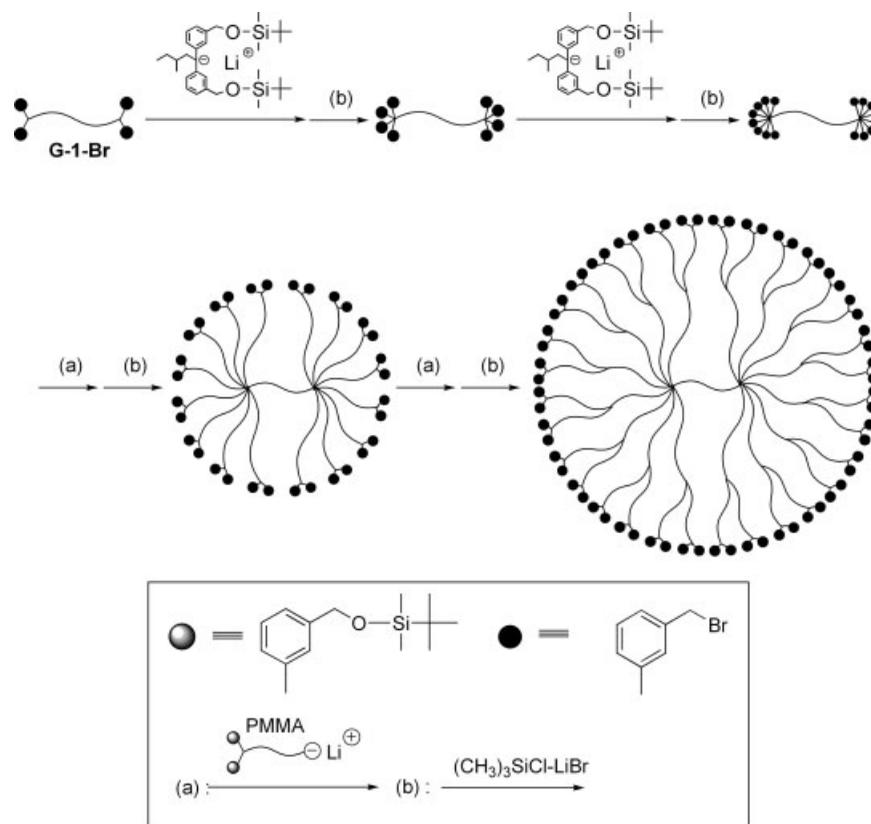
For the same synthetic purpose, we have proposed a more convenient alternative procedure based on the application of the iterative methodology to the synthesis of substituted DPE derivatives as illustrated in Scheme 12.⁴⁹ As can be seen, 1,1-bis(3-bromomethylphenyl)ethylene (**2**) was first prepared in 68% isolated yield by the deprotection of **1** with (C₄H₉)₄NF, followed by the bromination with PBr₃. At the same time,



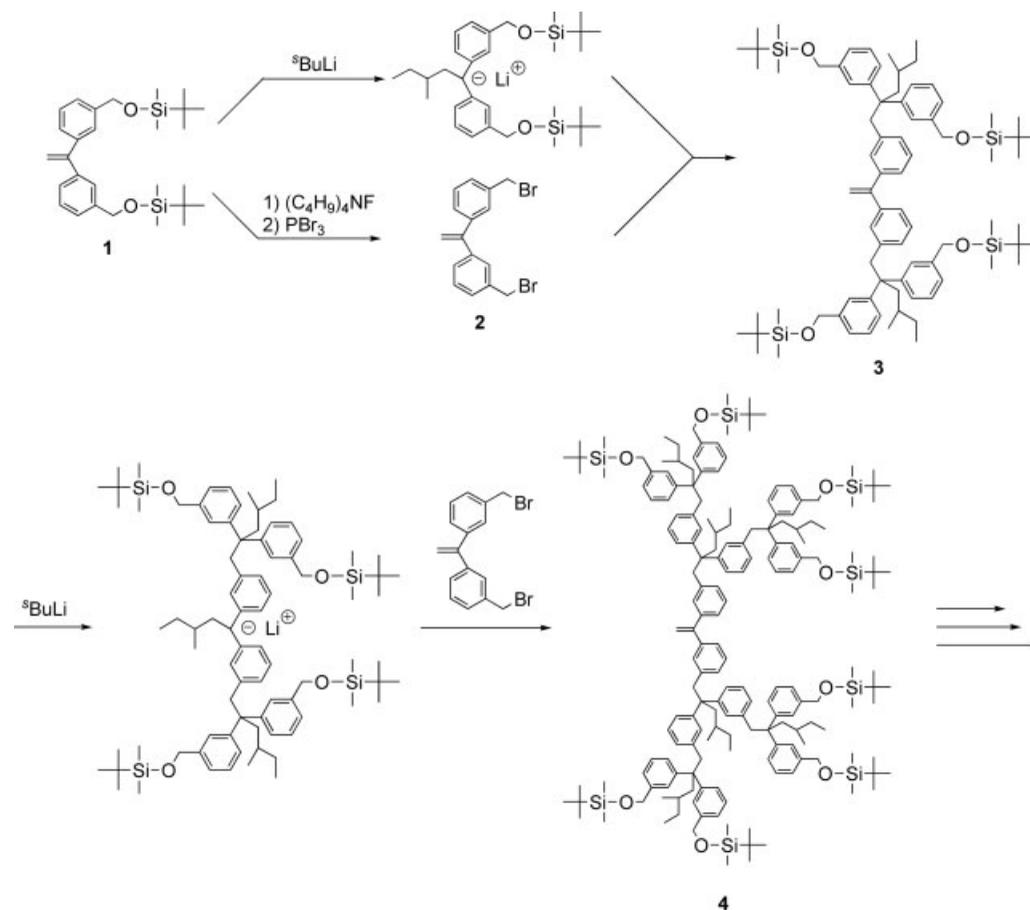
Scheme 10. Synthetic scheme of the third-generation dendrimer-like star-branched PMMA with four arms at every junction of the outermost layer.

1 was converted to the functionalized anion by treatment with *sec*-BuLi and then *in situ* reacted with **2** to give a new substituted DPE derivative with four SMP groups, **3**, in essentially 100% yield. Similarly, it was possible to readily synthesize a DPE derivative with

eight SMP groups, **4**, by repeating the same reaction sequence starting from **3**. Thus, the iterative methodology using the aforementioned reaction sequence can gain easy access to DPE derivatives with four, eight, and possibly more SMP groups.^{50,51}



Scheme 11. Synthetic of the first-, second-, and third-generation dendrimer-like star-branched (PMMA)s by iterative methodology using "branching" technique.



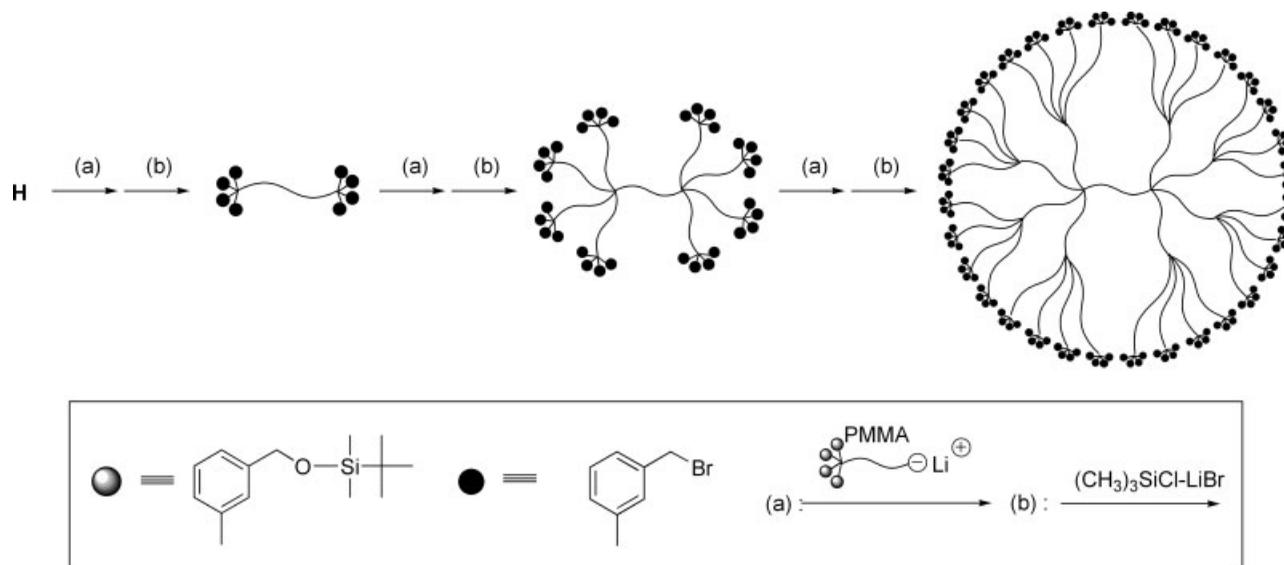
Scheme 12. Successive synthesis of DPE derivatives with two, four, followed by eight SMP groups by iterative methodology using **2** and SMP-functionalized anions.

The **3** thus synthesized was reacted with *sec*-BuLi to convert to the functionalized anion, with which MMA was quantitatively polymerized in the presence of a threefold excess of LiCl under the conditions in THF at $-78\text{ }^\circ\text{C}$ for 1 h. The resulting PMMA exhibited a sharp monomodal SEC distribution eluted at the expected counts, the M_w/M_n values being 1.02 and possessed an expected degree of SMP-end-functionality equal to four. A series of dendrimer-like star-branched polymers with a branching multiplicity to four at each generation up to the third-generation were successfully synthesized by repeating the same iterative process with use of the α -functionalized living PMMA with four SMP groups in each linking reaction stage as illustrated in Scheme 13. Similarly, the synthesis of the same generation PMMA with a branching multiplicity to two or four was achieved by appropriately using α -functionalized living PMMA with either two or four SMP groups as shown in Scheme 14. Although the resulting polymers are exactly the same in branched architecture as the polymers shown in Schemes 9 and

10, the superiority of this “DPE” method is evident to the aforementioned method, which always requires an extra reaction sequence with the functionalized anion, followed by transformation. A new synthetic development designed to rapidly increase the degree of branching may be feasible by combining the two methods.

Application of Iterative Methodology to BnBr-Functionalized Core Compounds: Synthesis of Dendrimer-Like Star-Branched Polymers with Different Branched Architectures

By increasing the BnBr reaction site of the core agent from two to four in number, it is expected to obtain architecturally different dendrimer-like star-branched polymers, in which four polymer chains radially emerge from a central core. For this synthesis, a new core compound with four BnBr moieties, **5**, was synthesized by the dimerization of **1** via radical coupling reaction of the radical anion intermediate generated from **1** and potassium naphthalenide, followed by treat-

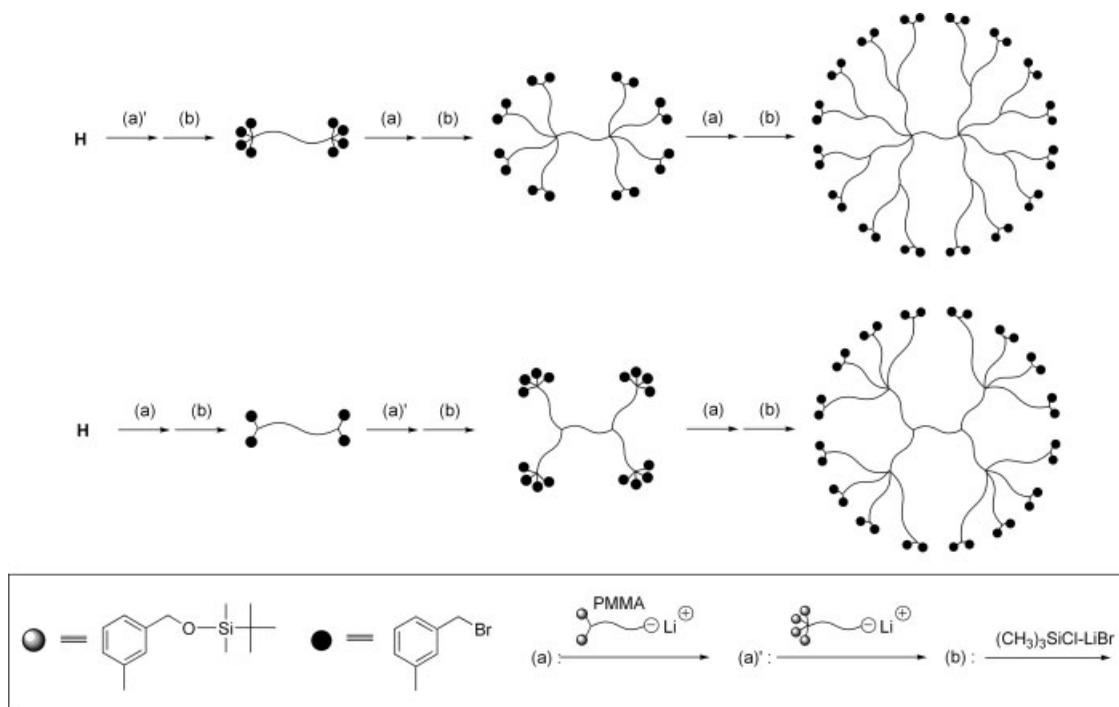


Scheme 13. Synthetic scheme of the first-, second-, and third-generation dendrimer-like star-branched (PMMA)s by iterative methodology using α,α -dibromoxylene as a core compound and α -functionalized living PMMA with four SMP groups as a building block.

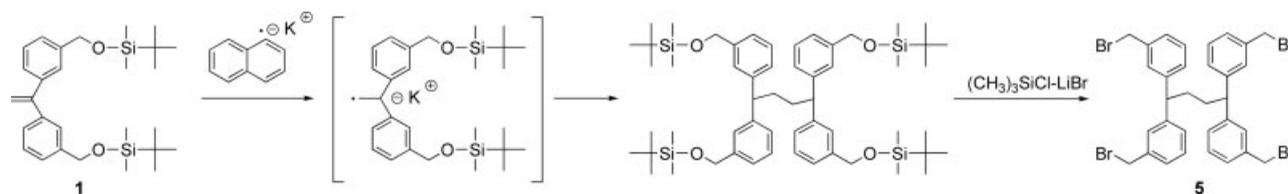
ment with $\text{LiBr}-(\text{CH}_3)_3\text{SiCl}$, as illustrated in Scheme 15.⁵² The two reactions proceeded essentially quantitatively.

New branched polymers consisting of four core arms were readily obtained by developing the iterative

methodology with a combination of **5** and α -functionalized living PMMA with two SMP groups. The polymers of three generations are illustrated in Figure 3. Furthermore, a series of three generations of more densely branched polymers could also be synthesized



Scheme 14. Synthetic scheme of the first-, second-, and third-generation dendrimer-like star-branched (PMMA)s by iterative methodology using α -functionalized living PMMA with two and/or four SMP groups.

Scheme 15. Synthetic scheme of **5**.

by the same methodology using α -functionalized living PMMA with four SMP groups as a building block to construct all repeating units as illustrated in Scheme 16.⁴⁹ The first and second iterative processes were conducted in the same manners as those mentioned already. The linking reaction was carried out in THF at $-40\text{ }^{\circ}\text{C}$ with a 2.0-fold excess of α -functionalized living PMMA with four SMP groups and the reaction mixture was allowed to react for 24 h. In each case, only two sharp SEC peaks for the linked product and the deactivated living PMMA used in excess were observed and the linking efficiency was virtually quantitative on the basis of the two peak areas. The structural characterization referring to the resulting polymers after isolation by fractional precipitation are summarized in Table 2.

Excellent agreement of the M_n and M_w values between the calculated and that determined by ^1H NMR and SLS and the expected numbers of SMP termini demonstrate the successful synthesis of a first-, followed by a second-generation PMMA. Taking the steric hindrance into consideration, a 4.0-fold excess of α -functionalized living PMMA with four SMP groups was employed in the linking reaction at the third iterative process. Agreement of the molecular weights (both M_n and M_w) of the isolated polymer between predicted and determined was also satisfactory

as listed in the same table. The polymers of all three generations shown in Figure 4 exhibited sharp monomodal SEC distributions. The third-generation PMMA thus synthesized ($M_n = 1340\text{ kg/mol}$ and $M_w/M_n = 1.03$) was composed of 84 precisely controlled PMMA segments and carried as many as 256 SMP termini. By appropriately combining α -functionalized living PMMA with two and four SMP groups in the linking reaction at each iteration stage, it was possible to synthesize the third-generation dendrimer-like star-branched polymers with a branching multiplicity to either two or four at each generation as shown in Figure 5.

Again importantly, the core compounds having eight, sixteen, or more BnBr functions can be also successively synthesized by the present iterative methodology. For example, the BnBr moieties of **5** doubled to eight in number by reacting with the functionalized anion from **1** and *sec*-BuLi, followed by treatment with LiBr-(CH_3)₃SiCl to transform the SMP groups into BnBr functions. A new compound with eight BnBr moieties, **6**, was thus obtained. Similarly, a compound even with 16 BnBr moieties, **7**, was synthesized starting from **6** by repeating the same two reactions.⁵³ Their synthetic routes are illustrated in Scheme 17. Moreover, if the functionalized anion prepared from **4** and *sec*-BuLi would be used in the reaction with **5**,

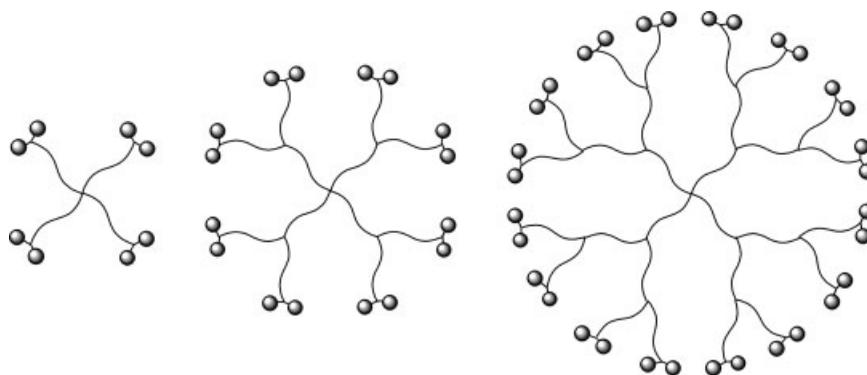
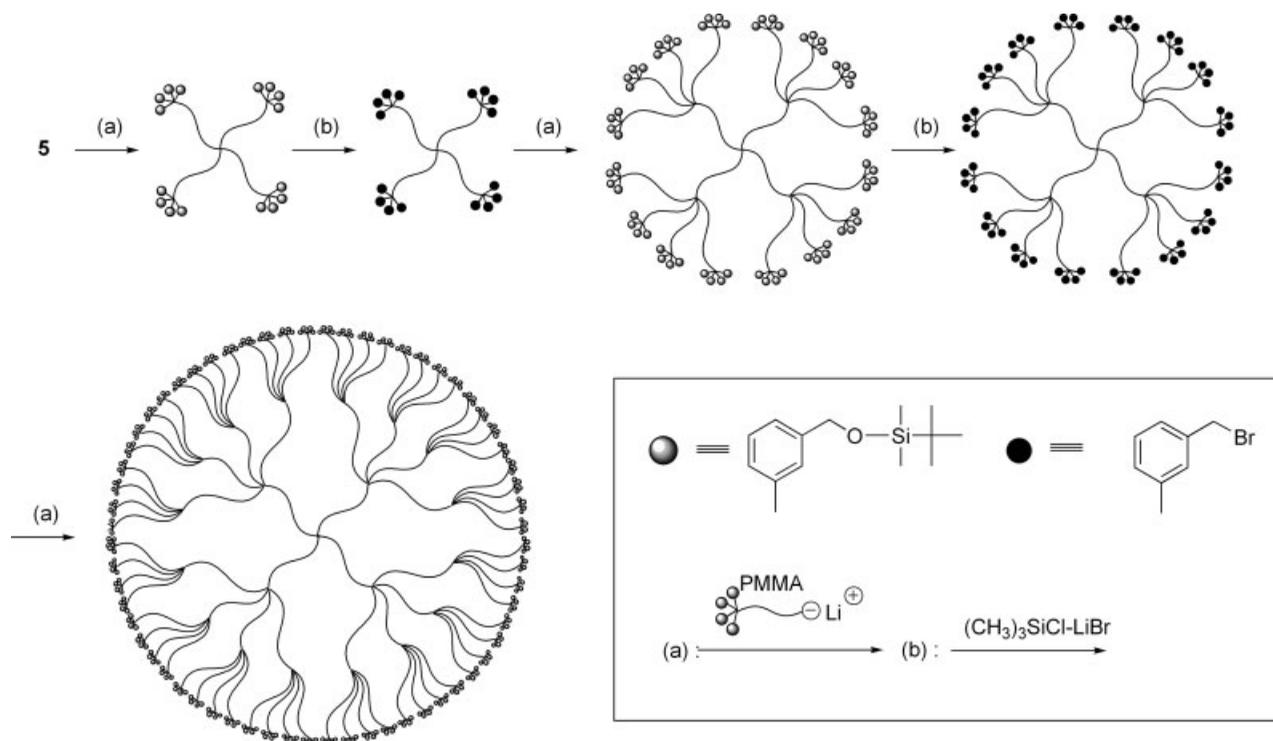


Figure 3. The first-, second-, and third-generation dendrimer-like star-branched (PMMA)s with four core arms.



Scheme 16. Synthetic scheme of the first-, second-, and third-generation dendrimer-like star-branched (PMMA)s by iterative methodology using **5** as a core agent and α -functionalized living PMMA with four SMP groups as a building block.

followed by transformation of the SMP groups into BnBr functions, a compound with 32 BnBr moieties could be obtained. Both **6** and **7** could also be prepared essentially quantitatively by reacting the SMP-functionalized DPE derivatives, **3** and **4**, with potassium naphthalenide, followed by treatment with LiBr- $(\text{CH}_3)_3\text{SiCl}$ as illustrated in Scheme 18.⁵³

Another series of dendrimer-like star-branched polymers up to the third-generation were synthesized by repeating the iterative process using **6** as a core agent and α -functionalized living PMMA with two SMP groups as building blocks. In these polymers, eight PMMA chains emerge radially from a central core and two polymer chains are branched at every junction at the next two layers toward the outer side

as illustrated in Scheme 19. Monomodal, sharp, and symmetrical SEC peaks were obtained for all three generations and good agreement of molecular weights

Table 2. Characterization of **G-1** to **G-3** Synthesized by Using **3** and **5**

Type	M_n (10^{-3})		$^1\text{H NMR}$	M_w (10^{-3})		M_w/M_n
	Calcd	SEC		Calcd	SLS	
G-1	52.8	46.5	52.2	53.9	51.6	1.02
G-2	260	156	263	268	272	1.03
G-3	1300	522	1340	1340	1390	1.03

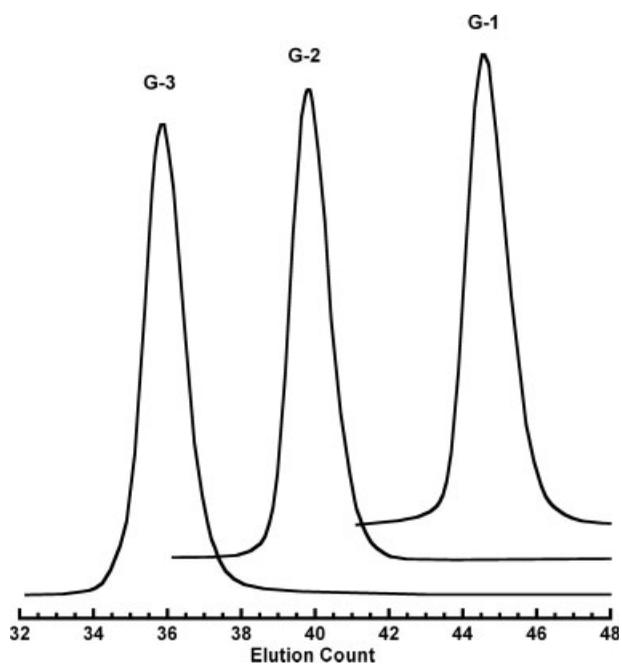


Figure 4. SEC profiles of **G-1** to **G-3**.

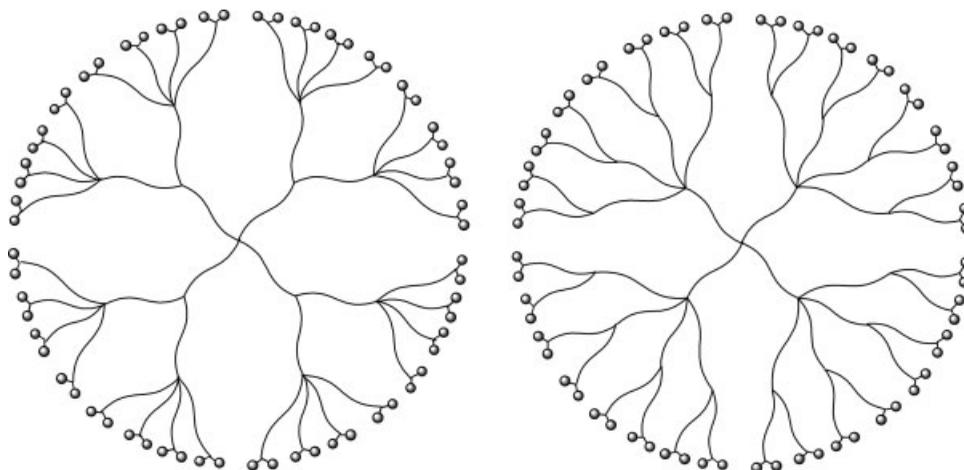
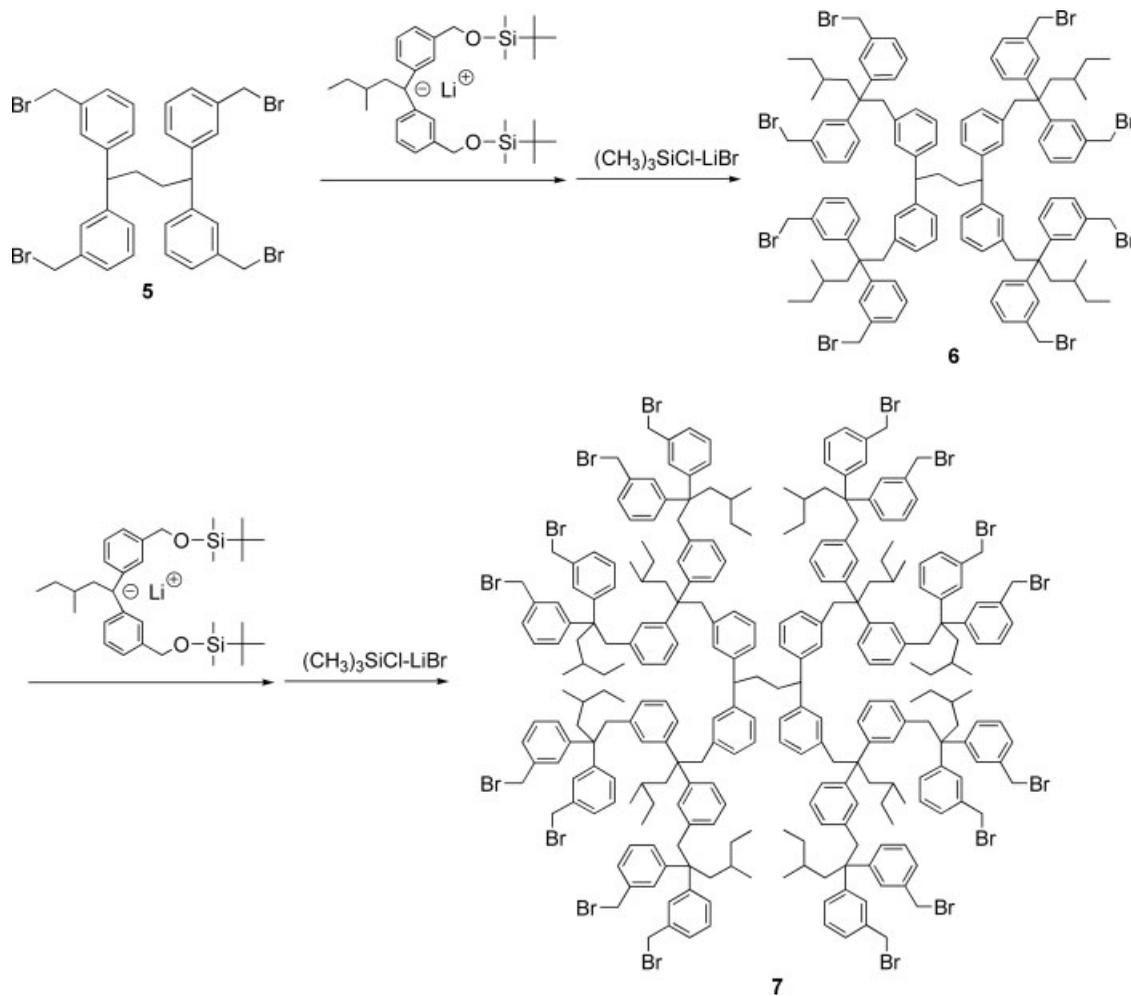


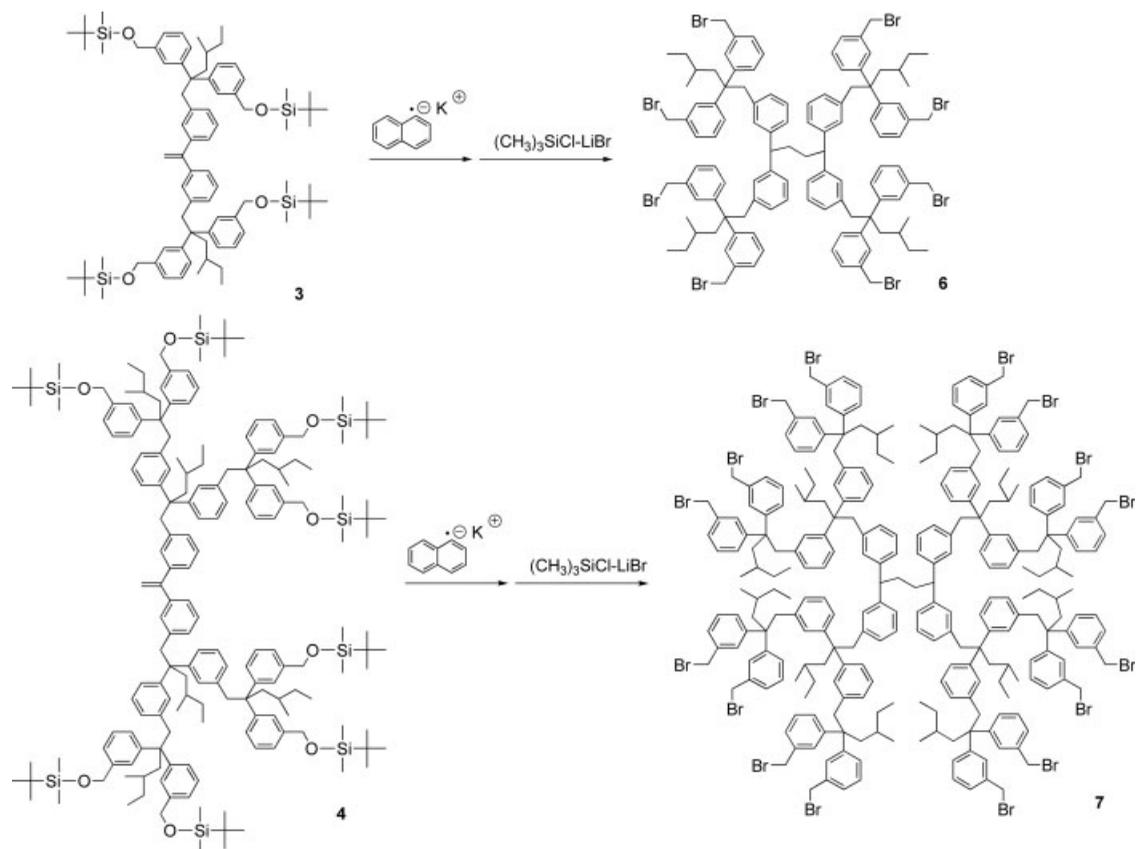
Figure 5. SEC profiles of third-generation star-branched (PMMA)s with two and/or four branches at every junction.

and degrees of end-functionalization between expected and determined was observed in all cases (Fig. 6 and Table 3). The final third-generation polymer

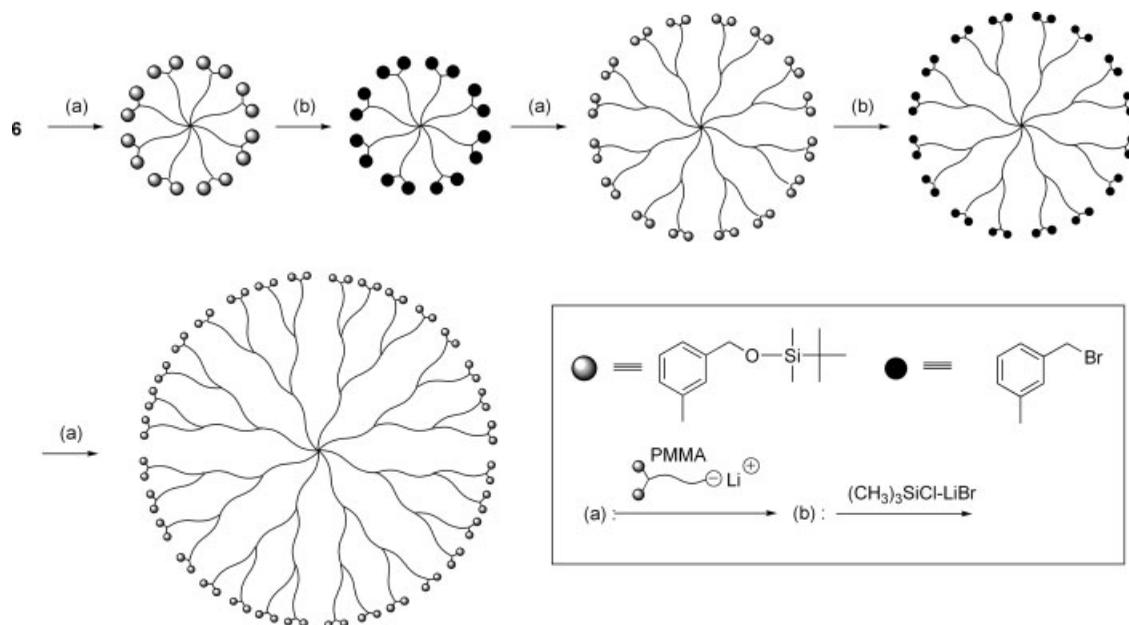
($M_n = 620$ kg/mol and $M_w/M_n = 1.03$) was made up of 56 PMMA segments and possessed 64 SMP termini.⁵⁴



Scheme 17. Successive synthesis of 6 followed by 7 by iterative methodology.



Scheme 18. Synthetic scheme of 6 or 7 by radical coupling reaction of either 3 or 4, followed by transformation.



Scheme 19. Synthetic scheme of the first-, second-, and third-generation dendrimer-like star-branched (PMMA)s by iterative methodology using 6 as a core agent and α -functional living PMMA with two SMP groups as a building block.

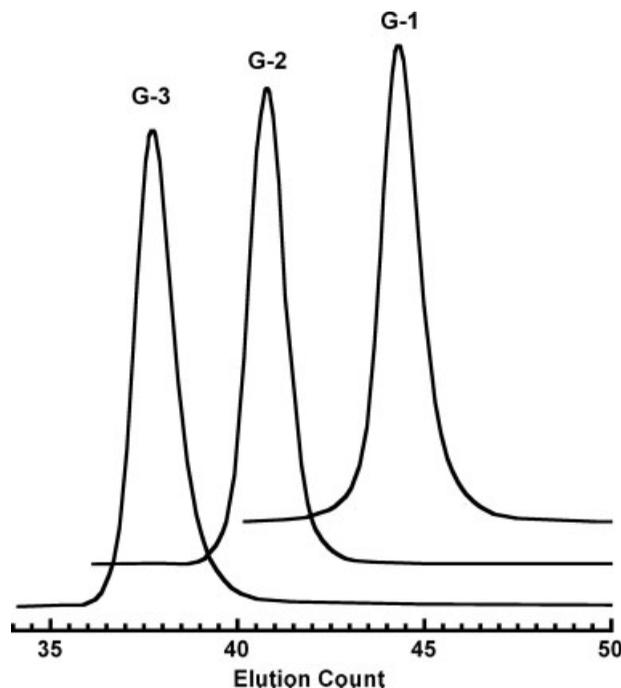


Figure 6. SEC profiles of G-1 to G-3.

We have demonstrated the possible extension of the iterative methodology to the successive synthesis of BnBr-functionalized compounds as well as SMP-functionalized DPE derivatives described in the preceding section. Thus, the iterative methodology shows synthetic capabilities for both core agents and initiator parts, which can be used in the iterative methodology for the synthesis of a large diversity of dendrimer-like star-branched polymers with different branched architectures.

Dendrimer-Like Star-Branched PMMA up to Seventh-Generation

To explore the effectiveness of the presently developed iterative methodology, we have, herein, examined how many times the iterative process can be repeated.⁵² The core agent, **5**, and α -functionalized living PMMA with two SMP groups are employed to synthesize dendrimer-like star-branched polymers of as high as possible generations. Accordingly, the first four polymer chains emerge radially from a core and two branches are always grown at the junction in each generation in all the resulting polymers. Throughout the synthesis, the M_n value of SMP- α -functionalized living PMMA is limited to around 4 kg/mol. The reason is that the objective branched polymers insoluble in methanol can be readily isolated from the deactivated excess PMMA segments that are completely soluble in methanol.

Journal of Polymer Science: Part A: Polymer Chemistry
DOI 10.1002/pola

The synthesis of the same branched polymers up to the third-generation by the iterative methodology was already described in the preceding section, although their PMMA arms were *ca.* 10 kg/mol in M_n value. As expected, all the reaction stages using living (PMMA)s with M_n values of *ca.* 4 kg/mol proceeded efficiently under the same conditions to quantitatively afford the first- (**G-1**), second- (**G-2**), followed by the third-generation polymer (**G-3**) as shown in Scheme 20. The results are listed in Table 4.

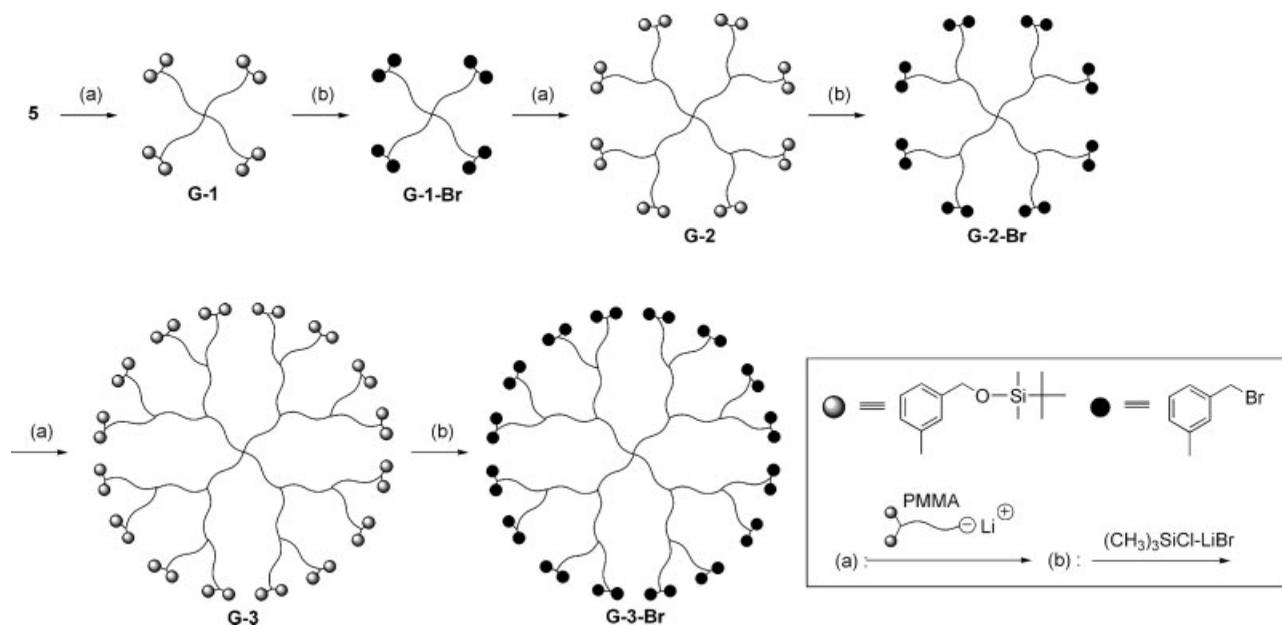
As can be seen, these polymers are precisely controlled in chain length and degrees of SMP-end-functionality. The resulting **G-2** and **G-3** possessed the expected dendrimer-like star-branched architectures composed of 12 and 28 PMMA segments and **G-2-Br** and **G-3-Br** also had similar branched architectures carrying 16 and 32 BnBr moieties at their outer layers.

Scheme 21 illustrates the synthetic procedure of fourth- and fifth-generation polymers, **G-4** and **G-5**, by repeating the same iterative process. Since the terminal BnBr reaction sites rapidly increases from 16 to 32, followed by 64 in number, a 3.0-fold excess of SMP- α -functionalized living PMMA was used in each of the linking reactions with **G-3-Br** or **G-4-Br**. Moreover, the reaction time was extended from 24 to 48 h for the same reason. Under such conditions, the linking reactions proceeded satisfactorily to give both **G-4** and **G-5** quantitatively. Similar to **G-1**, **G-2**, and **G-3**, these polymers were easily isolated simply by precipitating the polymers in methanol. Combined molecular characterization results shown in Table 4 revealed the expected structures of **G-4** and **G-5** composed of 60 and 124 PMMA segments, respectively.

Similarly, the synthesis of a sixth-generation PMMA, **G-6**, followed by a seventh-generation PMMA, **G-7**, has been achieved by repeating the same iterative process two more times as illustrated in Scheme 22. As SMP- α -functionalized living PMMA must react with large numbers of 128 and 256 BnBr reaction sites for the synthesis of **G-6** and **G-7**, a 3.5-fold excess of the living PMMA is used in the reaction with **G-5-Br** and use of a 5.0-fold excess of the living PMMA and a

Table 3. Characterization of G-1 to G-3 Synthesized by Using **3** and **5**

Type	M_n (10^{-3})			M_w (10^{-3})		M_w/M_n
	Calcd	SEC	$^1\text{H NMR}$	Calcd	SLS	
G-1	98.3	65.3	98.3	99.3	98.9	1.01
G-2	263	130	262	268	272	1.01
G-3	620	263	612	638	623	1.03



Scheme 20. Synthetic scheme of the first-, second-, and third-generation dendrimer-like star-branched (PMMA)s by iterative methodology using **5** as a core agent and α -functional living PMMA with two SMP groups as a building block.

longer reaction time of 72 h are taken in the reaction with **G-6-Br**. Under such conditions, both the linking reactions went essentially to completion thus to provide the objective **G-6** and **G-7**, respectively. However, the transformation reaction from **G-6** into **G-6-Br** was insufficient with a usual amount of a 50-fold excess of $\text{LiBr}-(\text{CH}_3)_3\text{SiCl}$, but complete with a 250-fold excess of $\text{LiBr}-(\text{CH}_3)_3\text{SiCl}$. In addition, an undesirable dimer was by-produced in *ca.* 10% by this treatment.⁵⁵ All of these polymers possessed the expected molecular weights, degrees of BnBr or SMP functionalities, and narrow monomodal SEC distributions as confirmed by ^1H and ^{13}C NMR, SEC, and SLS analyses. These data clearly revealed a high degree of structural and architectural perfection in each of all generation polymers. It should be noted that the resulting polymers, **G-6** and **G-7**, are composed of 252 and 508 PMMA segments and carry 256 and 512 SMP groups convertible to BnBr reaction sites at their peripheries of the most outer layers. The **G-7** reached to nearly two million in controllable molecular weight.⁵² Figures 7 and 8 show ^1H NMR spectra and SEC profiles of all the generation polymers.

Interestingly, the three resonances at 4.66, 0.90, and 0.04 ppm characteristic to benzyl methylene and methyl protons of the SMP group remain almost unchanged in each of all polymers. SEC peak of each polymer is sharp and monomodal in distribution and moves to a higher molecular weight region as the iteration proceeds.

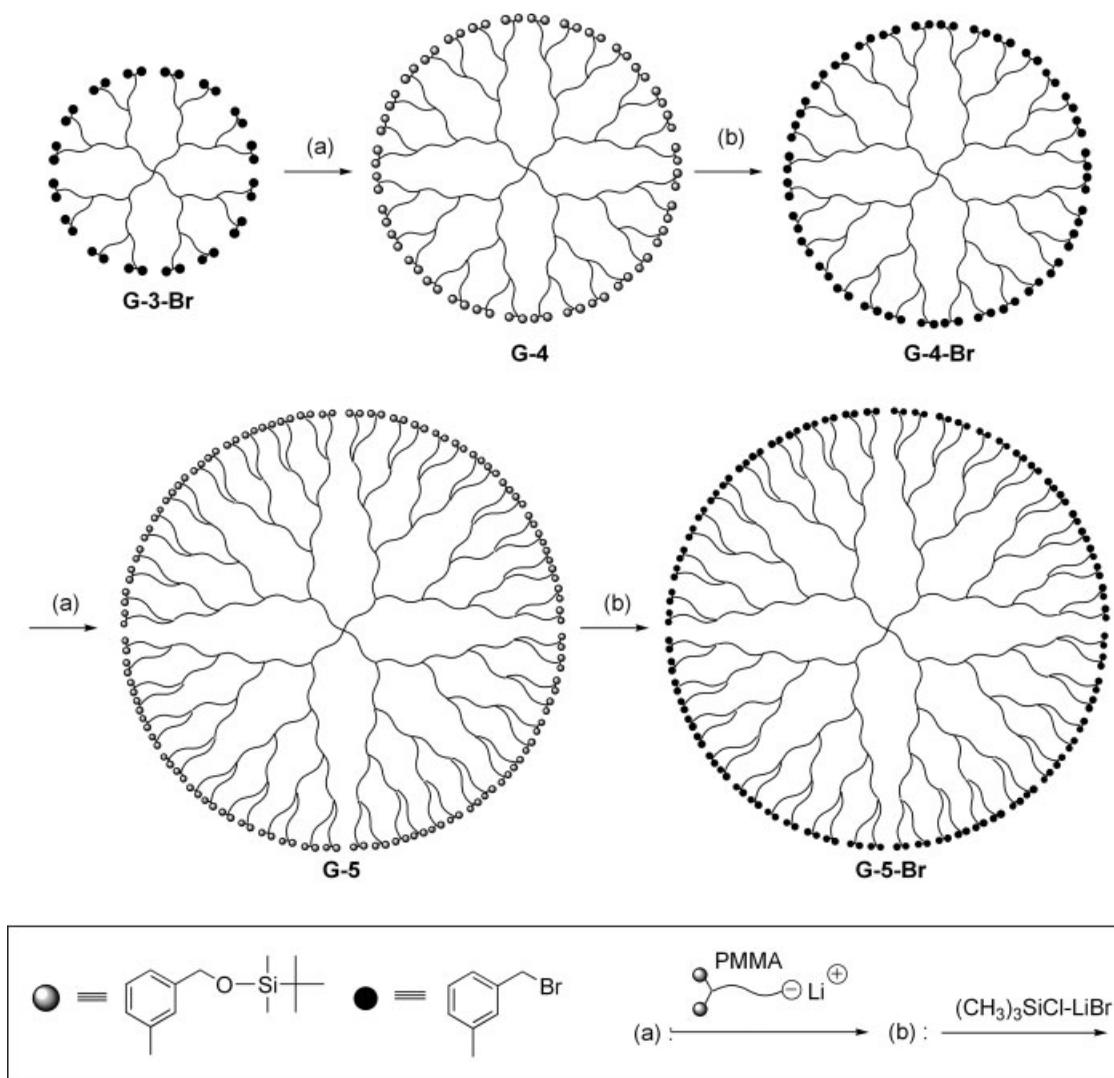
Once again, the successful synthesis of dendrimer-like star-branched polymers up to seventh-generation demonstrates that the present methodology stands enough as a synthetic procedure for higher generation branched polymers. Undoubtedly, this success owes strongly the quantitative nature of the iterative reaction process involving the linking and transformation reactions.

Dendrimer-Like Star-Branched Block Copolymers

One of the most advantageous features of the present iterative methodology provides an easy access to the same branched architectural block copolymers with different repeating units in chemical structure. They may

Table 4. Characterization of **G-1** to **G-7**

Type	M_n (10^{-3})			M_w (10^{-3})		M_w/M_n
	Calcd	SEC	^1H NMR	Calcd	SLS	
G-1	14.6	13.8	14.2	14.9	14.8	1.02
G-2	43.0	36.9	42.9	43.9	44.2	1.02
G-3	97.3	66.1	98.4	99.2	105	1.02
G-4	219	115	219	223	230	1.02
G-5	452	178	449	462	472	1.03
G-6	980	282	974	1000	1060	1.02
G-7	1960	414	1940	1980	1970	1.02

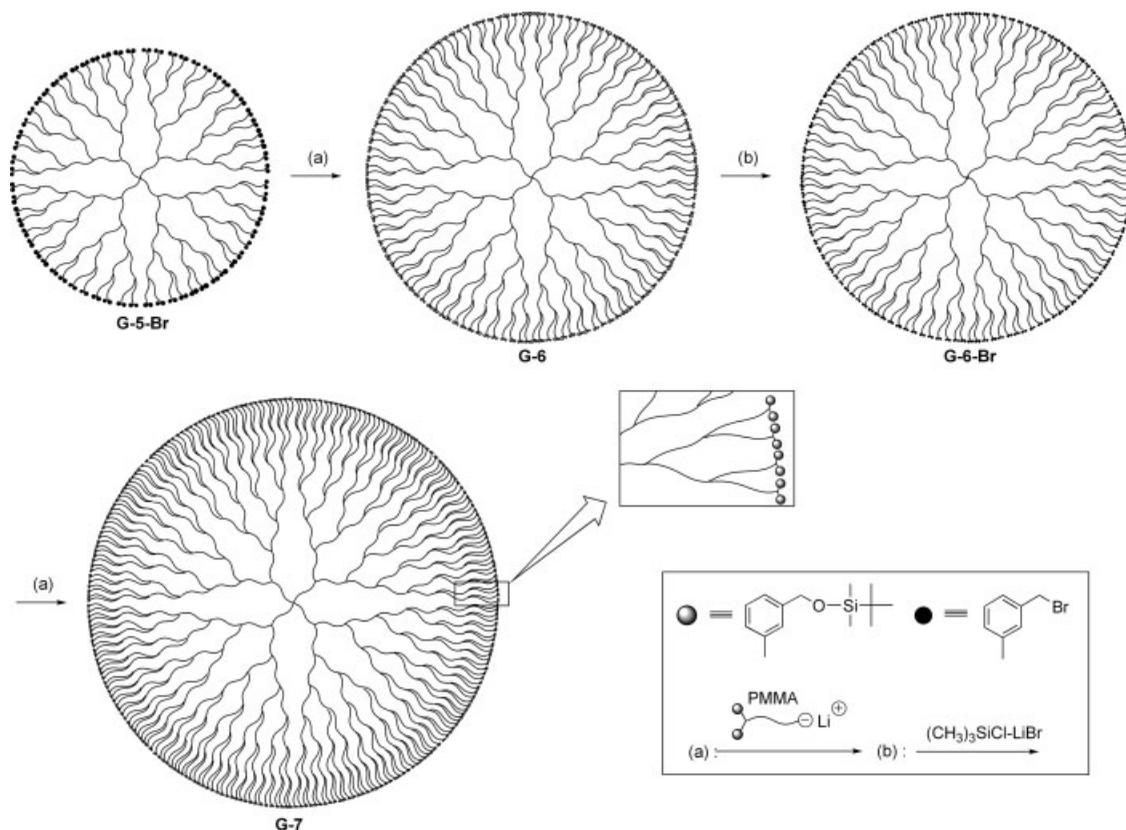


Scheme 21. Synthetic scheme of the fourth- and fifth-generation dendrimer-like star-branched (PMMA)s by iterative methodology.

be synthesized by reacting a different SMP- α -functionalized living anionic polymer in each linking reaction stage. Since many examples of the living anionic polymerization of methacrylate monomers substituted with functional groups have been reported so far,^{56,57} a large diversity of functional polymer segments can be introduced into the branched polymers.

As illustrated in Scheme 23, a fourth-generation dendrimer-like star-branched block copolymer composed of 16 PMMA and 14 poly(2-hydroxyethyl methacrylate) (PHEMA) segments, **G-4-OH**, was successfully synthesized by reacting the third-generation brominated PMMA (four core arms and two branches at every junction) with a living anionic polymer of the silyl-protected HEMA, followed by deprotection to regenerate the original hydroxyl group.⁴⁵ The

hydroxyl-protection of HEMA was achieved by treatment of HEMA with *tert*-butyldimethylsilyl chloride and the deprotection was conducted with $(C_4H_9)_4NF$ under neutral conditions.^{58,59} As expected, the resulting **G-4-OH** showed the solubilities different from both the original block copolymer before deprotection and the fourth-generation PMMA with the same branched architecture. It was soluble in THF, pyridine, DMF, and DMSO, but insoluble in benzene, carbon tetrachloride, chloroform, dichloromethane, diethyl ether, acetone, ethyl acetate, and water. It swelled in both methanol and ethanol. The solution behavior of **G-4-OH** was followed by 1H NMR analysis with various solvent polarities using $CDCl_3$ and CD_3OD selectively soluble for PMMA and PHEMA, respectively. The results indicate that the **G-4-OH** associates to form



Scheme 22. Synthetic scheme of the sixth- and seventh-generation dendrimer-like star-branched (PMMA)s by iterative methodology.

micelles at both higher (98/2, v/v) and lower (5/95, v/v) ratios of $\text{CDCl}_3/\text{CD}_3\text{OD}$ and the micelles thus formed are different in structure and reversely respond to change in the polarity of the solvent. Such behaviors are similar to those reported by Hedrick et al.,²⁸ and Gnanou and co-workers.³³

Similarly, a variety of dendrimer-like star-branched block copolymers have been synthesized by the reaction of the third-generation brominated PMMA with either living anionic polymers of the following functionalized methacrylate monomers as shown in Figure 9. Since the first four PMMA segments radially emerged from a central core in the brominated PMMA used in the linking reaction, all of the resulting block copolymers were composed of 28 PMMA and 32 functionalized polymer segments as illustrated in Scheme 24. *N,N*-Dimethylamino- and epoxy-functionalized polymer chains were introduced as repeating units at the fourth-generation by reacting living anionic polymers of 2-(*N,N*-dimethylamino)ethyl⁶⁰ and glycidyl methacrylates,⁶¹ respectively. The quantitative introduction of diol- and glucose (tetraol)-functionalized segments could be achieved via the following two reaction steps: (1) the linking reaction of living anionic polymers of methacrylates substituted

with 2,2-dimethyldioxolane⁶² and 1,2:5,6-diisopropylidene- α -D-glucopyranose moieties;⁶³ (2) deprotection of their acetal protected functionalities under weak acidic conditions. Carboxyl-functionalized segment was also introduced quantitatively by reacting with living poly(*tert*-butyl methacrylate), followed by hydrolysis of the *tert*-butyl ester moiety. Interestingly, *N,N*-dimethylamino- and carboxyl-functionalized segments could be converted to water-soluble cationic and anionic segments by treatment with CH_3I and NaOH . Thus, introduction of these functionalized segments endows with interesting and useful characters such as hydrophilicity, water-solubility, acid, base, ion, chirality, and high reactivity.

The only deficiency of the introduced functionalities is incompatibility with the transformation reaction with $\text{LiBr-(CH}_3)_3\text{SiCl}$. Accordingly, the aforementioned living anionic polymers can be used only in the linking reaction of the final process to introduce their functional segments at periphery of the outermost layers. On the other hand, these living polymers cannot be employed in the iterative process involving the transformation reaction.

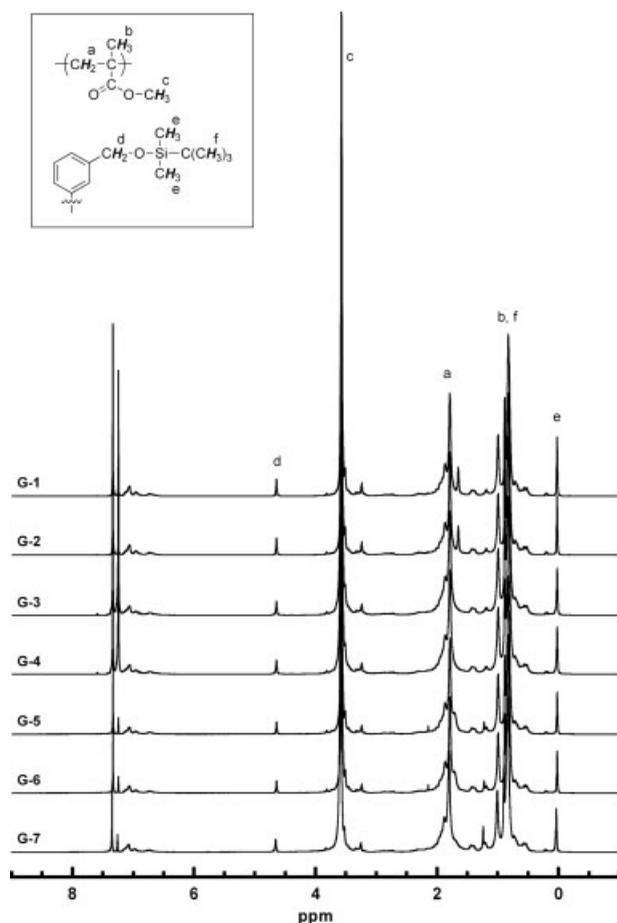


Figure 7. ^1H NMR spectra of G-1 to G-7.

To introduce a functionalized segment at any desired generation, the complete stability of the functional group toward the transformation reaction is required. It is also essential that the methacrylate monomer with the functional group undergoes living anionic polymerization. Fortunately, some of the functional groups such as long chain alkyl, perfluoroalkyl,⁶⁴ and oligo(ethylene glycol) methyl ether^{65,66} were found to satisfy such requirements. Since these functionalities remain completely unchanged under the transformation reaction conditions, the following third-generation block copolymers can be synthesized as shown in Figure 10. Either of the functionalized segments could be indeed introduced into the second layer between the core and outermost layer, indicating that their functionalities were stable enough during the transformation reaction of the second iterative process. It is of course possible to introduce these functionalized segments into the outermost layers as shown in the same figure. They are expected to show hydrophobic, hydrophobic and lipophobic, and water-soluble and LCST characters.

Throughout the synthetic studies of star-branched polymers previously reported by our group, it was observed that the same BnBr functionalities introduced at polymer chain ends or in chains are capable of reacting smoothly and quantitatively with various living anionic polymers. These polymers involve highly reactive living anionic polymers of styrene, 1,3-butadiene, isoprene, and 2-vinylpyridine and a less reactive

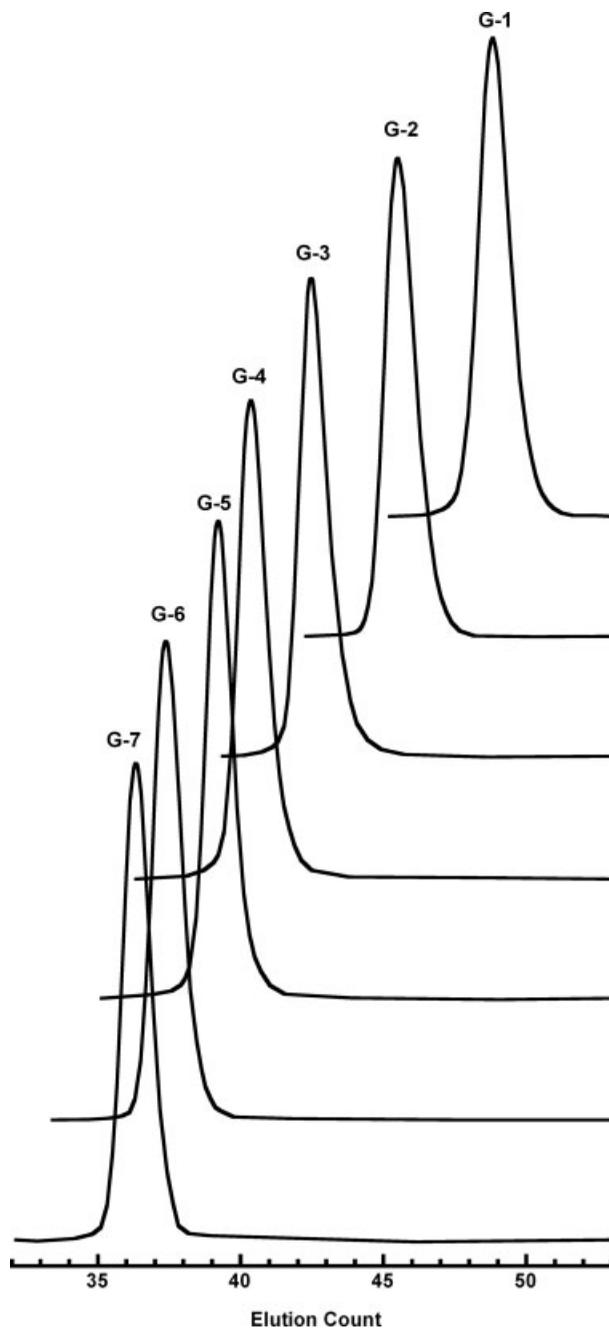
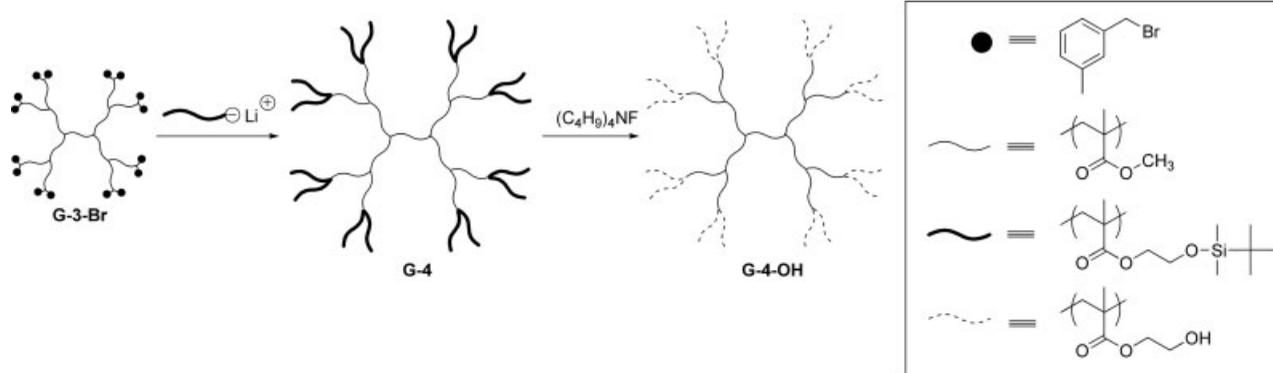


Figure 8. SEC profiles of G-1 to G-7.



Scheme 23. Synthetic scheme of the fourth-generation dendrimer-like star-branched block copolymer composed of PMMA and PHEMA segments.

living poly(ethylene oxide).^{13,16} When either of the living anionic polymers of styrene, 1,3-butadiene, or isoprene is used in the linking reaction, the end-capping with DPE prior to the reaction becomes essential to avoid the side reactions such as metal-bromine exchange, and a Wurtz-type coupling reaction and ester attack. On the basis of these facts, it may be possible to introduce such polymer segments into the outermost layers of dendrimer-like star-branched polymers. Furthermore, as living polystyrenes with a wide variety of functional groups are now available,⁶⁷⁻⁶⁹ they can be also used in the synthesis of new branched

block copolymers with functional groups as shown in Scheme 25.

The functional 1,1-diphenylalkyl anions prepared from the corresponding DPE derivatives and RLi can be regarded as functionalized agents capable of reacting with the BnBr termini to introduce their functions. We have already demonstrated the effectiveness of this type of functionalization in the quantitative reaction of the BnBr termini with the anion from **1** and *sec*-BuLi to double the SMP group convertible to BnBr function. Therefore, this reaction in conjunction with brominated branched polymers provides an efficient procedure for the introduction of various peripheral functional groups into the outermost layers as illustrated in Scheme 26. The possible functional groups are almost the same as those usable in the living anionic polymerization of functional styrene derivatives mentioned earlier.^{69,70} Finally, needless to say, a wide variety of nucleophiles can undergo reaction with highly reactive BnBr functions to introduce appropriate functional groups.

Morphological behaviors and possible formation of molecular assemblies of dendrimer-like branched block copolymers will be of the next research subject in the very near future.

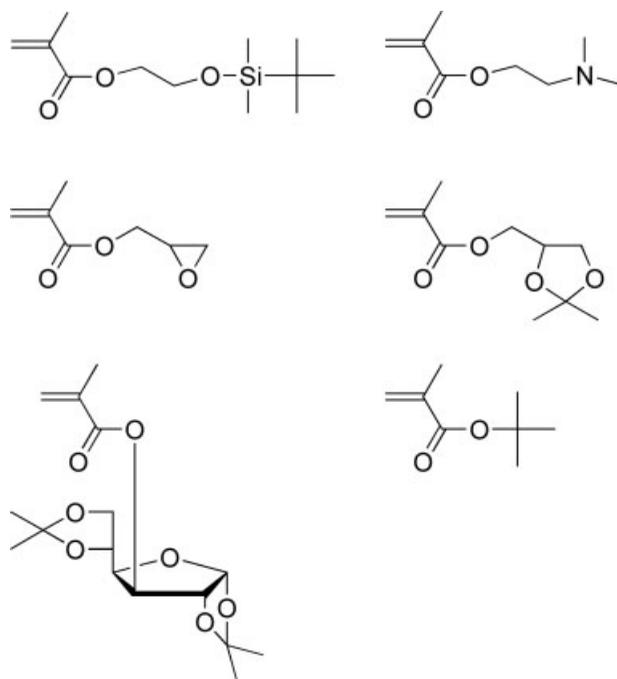
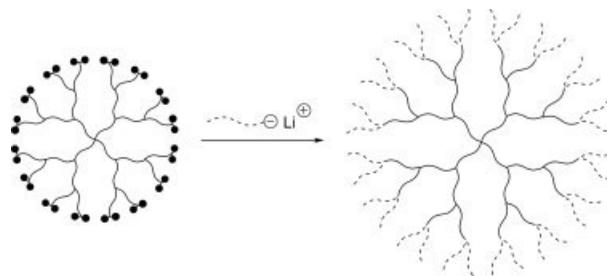


Figure 9. Methacrylate monomers with functional groups.



Scheme 24. Synthetic scheme of the fourth-generation dendrimer-like star-branched block copolymer composed of PMMA and functionalized polymer segments.

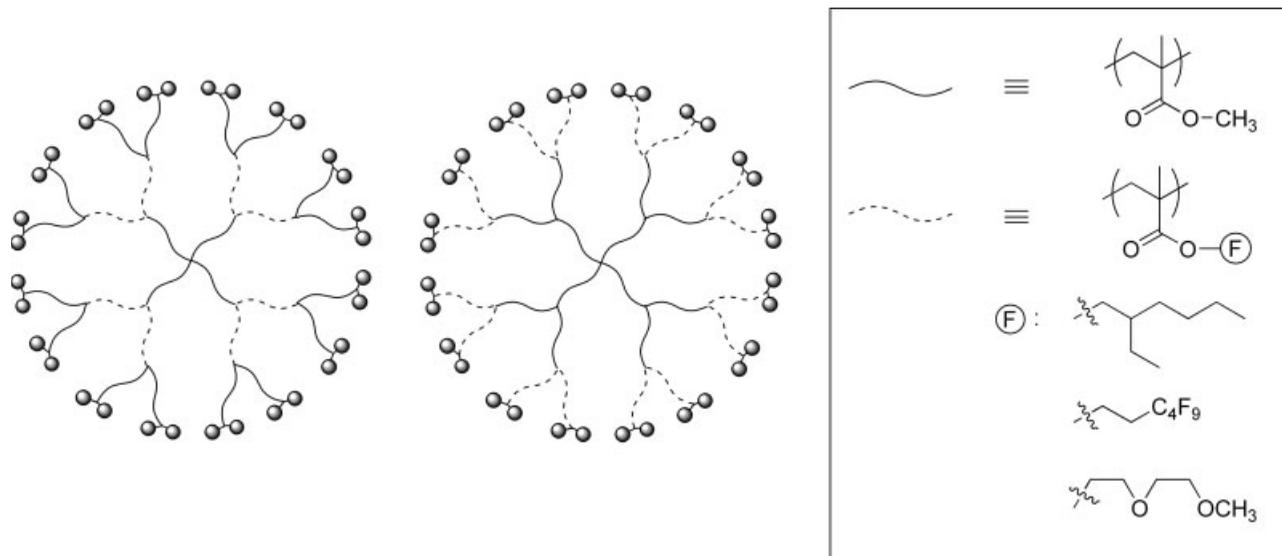


Figure 10. The third-generation dendrimer-like star-branched block copolymers having functionalized segment at either the second- or the third generation.

Intrinsic Viscosities and g' Values of Dendrimer-Like Star-Branched Polymers

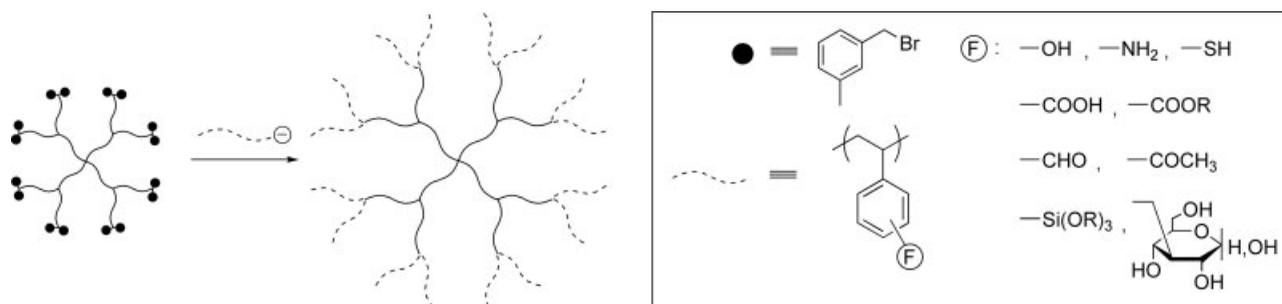
To investigate the branched nature of the dendrimer-like star-branched architecture, the intrinsic viscosities of the first series polymers, **G-1** to **G-7**, were measured and g' values defined as $[\eta]_{\text{branched}}/[\eta]_{\text{linear}}$ were determined.⁵² Both $[\eta]_{\text{branched}}$ and $[\eta]_{\text{linear}}$ are intrinsic viscosities of dendrimer-like star-branched polymer and the corresponding linear polymer with the same molecular weight under the same conditions. The $[\eta]_{\text{branched}}$ values were measured in THF at 25 °C, while the $[\eta]_{\text{linear}}$ values were calculated from the eq 1 previously reported.⁴⁶

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

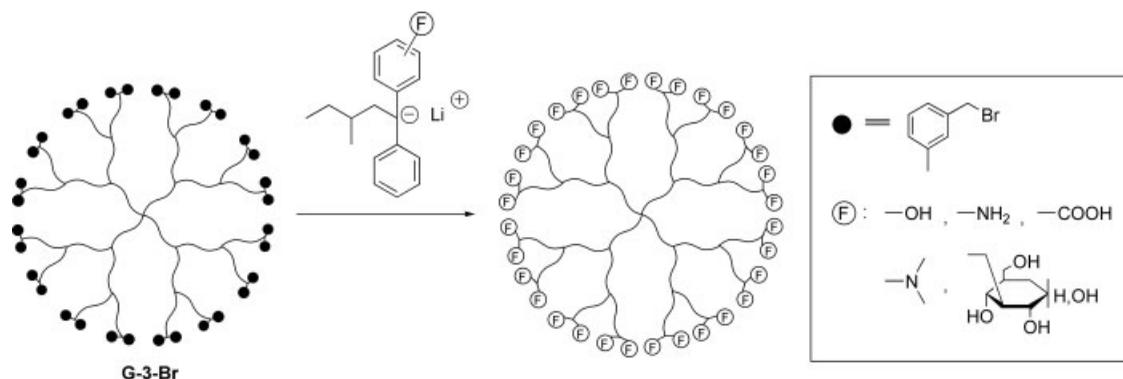
The results are summarized in Table 5. As a reference, g' values of star-branched polymers are listed in this

table.⁷¹ In each generation, the arm number of star is equal to that of branched arm in outermost layer of the dendrimer-like star-branched polymer. In the branched polymers of **G-1** to **G-7**, four PMMA chains emerge radially from a central core in the first generation and two PMMA segments are branched at every junction as repeating units in all generations except for the first-generation. Their branched architectures are therefore represented as A_4 , $(A-A_2)_4$, $(A-A_2-A_4)_4$, $(A-A_2-A_4-A_8)_4$, $(A-A_2-A_4-A_8-A_{16})_4$, $(A-A_2-A_4-A_8-A_{16}-A_{32})_4$, and $(A-A_2-A_4-A_8-A_{16}-A_{32}-A_{64})_4$, respectively, as visualized in Figure 11.

Since **G-1**, represented as A_4 , is a 4-arm star-branched polymer, the g' value must be the same as that of the star listed. A slight difference between both values (0.77 vs. 0.71) may be attributed to the relatively large two SMP groups at each chain-end of **G-1**. As expected from the branched architectures, the $[\eta]_{\text{branched}}$ value was always smaller than that of the



Scheme 25. Synthetic scheme of the third-generation dendrimer-like star-branched block copolymer composed of PMMA and functionalized polystyrene segments.



Scheme 26. Introduction of functional groups at the periphery part (or termini) of the third-generation dendrimer-like star-branched polymer by the reaction of the third-generation brominated PMMA with functionalized 1,1-diphenylalkyl anion.

corresponding linear polymer and hence the g' value was less than one in each case. Going from **G-2** to **G-7**, the $[\eta]_{\text{branched}}$ value increased gradually and nearly saturated at higher generations, although the molecular weight quite rapidly increased. The $[\eta]_{\text{branched}}$ value of **G-7** was only one-tenth as that of the linear polymer with the same molecular weight. This trend is somewhat different from that observed in the case of classical dendrimers. On the other hand, the g' value decreased as the number of generation increased, indicating that the dendrimer-like star-branched polymer became more compact in hydrodynamic volume in solution than the linear polymer. Interestingly, the dendrimer-like star-branched polymer is always larger in g' value than that of the star-branched polymer as listed. This is not however surprisingly as imaged from their branched architectures.

The viscosities and g' values of another two series of dendrimer-like star-branched polymers represented

as **A₄**, (**A-A₄**)₄, and (**A-A₄-A₁₆**)₄ and as (**A-A₂**)₂, (**A-A₂-A₄**)₂, and (**A-A₂-A₄-A₈**)₂ are summarized in Table 6.^{45,49} The second series polymers of all generations have a degree of branching multiplicity equal to four at every junction. In this series, the g' value rapidly decreased going from **A₄**, (**A-A₄**)₄, and (**A-A₄-A₁₆**)₄. In contrast, the extent in decrease of g' value in the third series of less densely branched polymers was similar to that observed in the first series polymers. Accordingly, the g' value appears sensitive to the number of branching at every junction, but not the core arm number. Among the branched polymers of the first and third series, the arm numbers in the outermost layers are 4, 8, and 16 for both of them. Their g' values showed similar values of 0.77, 0.66, 0.48, and 0.80, 0.59, 0.46, respectively. The g' values of 0.77, 0.37, and 0.18 observed in the second series polymers were close to those of 0.77, 0.48, and 0.23 in the first series polymers having 4, 16, and 64 arms in the outermost

Table 5. Intrinsic Viscosity and g' Values of **G-1** to **G-7**

Type	M_w (10^{-3}) ^a	$[\eta]$ (mL/g)		g'		
		$[\eta]_{\text{branched}}$ ^b	$[\eta]_{\text{linear}}$ ^c	Dendritic ^d	Star	
A₄	14.8	6.76	8.78	0.77	0.71 ^e	(4 arms)
(A-A₂) ₄	44.2	12.5	18.8	0.66	0.46 ^e	(8 arms)
(A-A₂-A₄) ₄	105	16.3	34.3	0.48	0.25 ^e	(16 arms)
(A-A₂-A₄-A₈) ₄	230	18.9	59.1	0.32	0.14 ^f	(32 arms)
(A-A₂-A₄-A₈-A₁₆) ₄	472	22.5	97.4	0.23	0.083 ^f	(64 arms)
(A-A₂-A₄-A₈-A₁₆-A₃₂) ₄	1060	24.0	171	0.14	0.048 ^f	(128 arms)
(A-A₂-A₄-A₈-A₁₆-A₃₂-A₆₄) ₄	1970	26.3	263	0.10	0.027 ^f	(256 arms)

^a Measured by SLS.

^b Measured in THF at 25 °C.

^c Calculated from $[\eta]_{\text{linear}} = 1.11 \times 10^{-2} M_w^{0.695}$ (ref. 46).

^d Calculated from $g'_{\text{dendritic}} = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$.

^e Calculated from $g'_{\text{star}} = [(3f-2)/f]^{0.58} \times [0.724 - 0.015 \times (f-1)]/0.724$; f = number of arms ($3 < f < 18$). (ref. 71).

^f Calculated from $\log g'_{\text{star}} = 0.36 - 0.80 \times \log f$; f = number of arms ($6 < f$). (ref. 7).

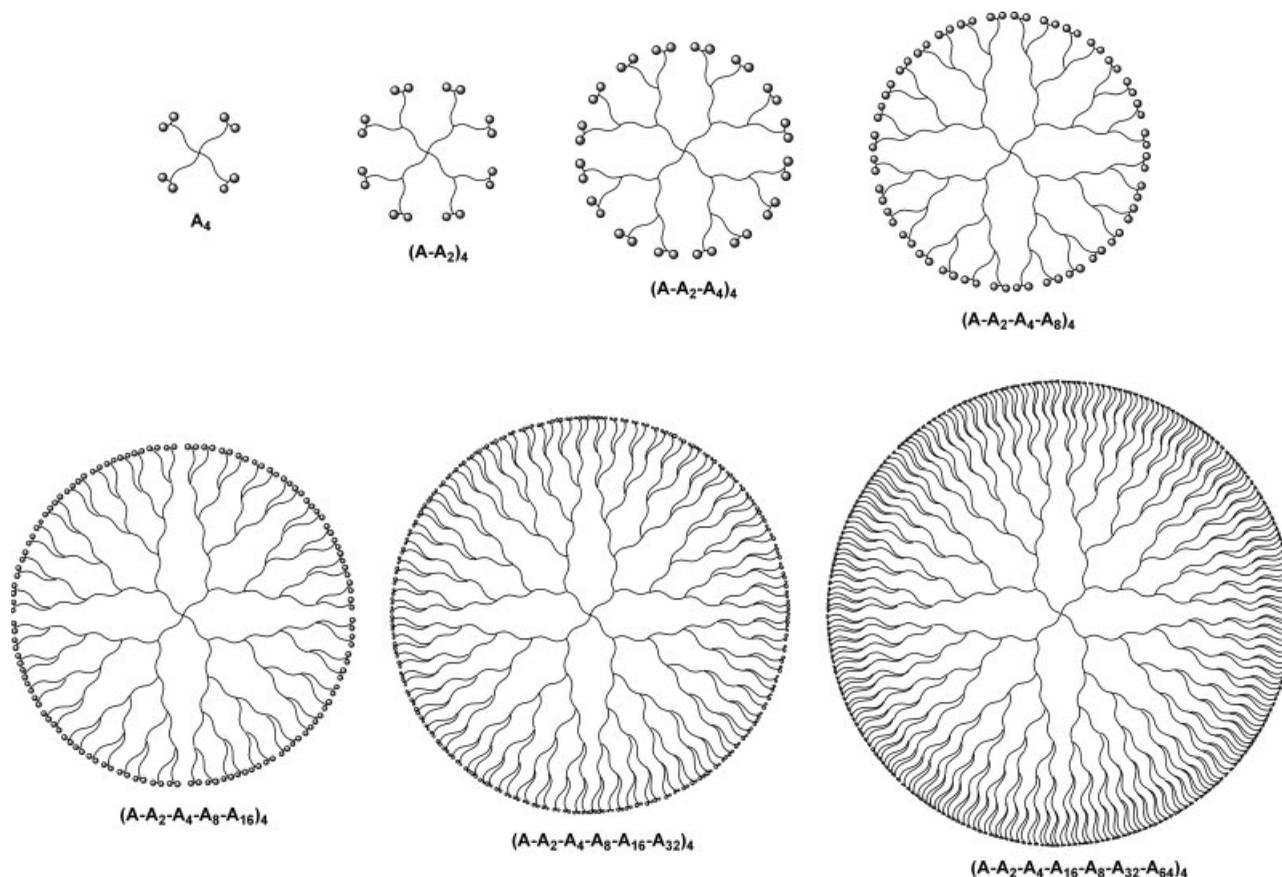


Figure 11. Dendrimer-like star-branched architectures of G-1 to G-7.

layers. Thus interestingly, the g' value is closely related with the arm number in the outermost layer, irrespective of the branched architecture.

For comparison, we have measured the intrinsic viscosities to determine the g' values for the third-generation polymers with different branched architectures.

Table 6. Intrinsic Viscosity and g' Values of A_4 , $(A-A_4)_4$, $(A-A_4-A_{16})_4$ and $(A-A_2)_2$, $(A-A_2-A_4)_2$, and $(A-A_2-A_4-A_8)_2$

Type	M_w (10^{-3}) ^a	[η] (mL/g)		g' dendritic ^d
		[η] _{branched} ^b	[η] _{linear} ^c	
A_4	51.6	16.1	20.9	0.77
$(A-A_4)_4$	272	24.4	66.4	0.37
$(A-A_4-A_{16})_4$	1390	37.3	206	0.18
$(A-A_2)_2$	57.9	18.1	22.7	0.80
$(A-A_2-A_4)_2$	164	25.3	43.1	0.59
$(A-A_2-A_4-A_8)_2$	330	34.7	76.0	0.46

^a Measured by SLS.

^b Measured in THF at 25 °C.

^c Calculated from [η]_{linear} = $1.11 \times 10^{-2} M_w^{0.695}$ (ref. 46).

^d Calculated from $g'_{\text{dendritic}} = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$.

They are represented as $(A-A_2-A_8)_4$, $(A-A_4-A_8)_4$, and $(A-A_2-A_4)_8$, respectively. The results are also listed in Table 7.⁵⁴ Again, all their g' values were in the region of around 0.30 and similar to 0.32 of the first series G-4 with 32 outer arms. On the basis of these agreements, g' value *versus* number of outer arm relationship is plotted in Figure 12. As you can see, most of the plots well fit on the relationship. Interestingly, the

Table 7. Intrinsic Viscosity and g' Values of $(A-A_2-A_8)_4$, $(A-A_4-A_8)_4$, and $(A-A_2-A_4)_8$

Type	M_w (10^{-3}) ^a	[η] (mL/g)		
		[η] _{branched} ^b	[η] _{linear} ^c	g' dendritic ^d
$(A-A_2-A_8)_4$	514	33.2	103	0.32
$(A-A_4-A_8)_4$	568	32.2	111	0.29
$(A-A_2-A_4)_8$	623	32.4	118	0.27

^a Measured by SLS.

^b Measured in THF at 25 °C.

^c Calculated from [η]_{linear} = $1.11 \times 10^{-2} M_w^{0.695}$ (ref. 46).

^d Calculated from $g'_{\text{dendritic}} = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$.

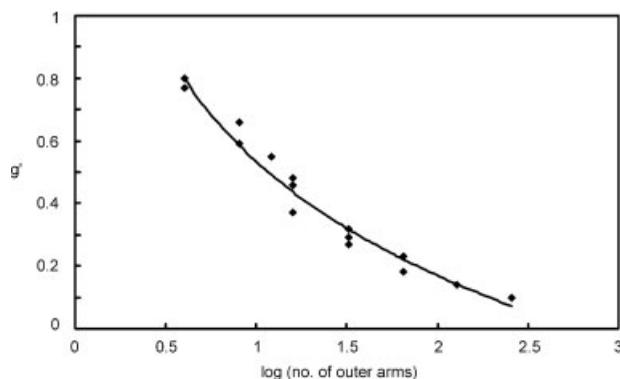


Figure 12. g' value versus arm number of outer arm for dendrimer-like star-branched polymer.

third-generation dendrimer-like star-branched PS with 12 outer arms ($M_n = 285$ kg/mol, $M_w/M_n = 1.05$), (**A-A₂-A₄**)₃, synthesized by Hutchings and Roberts-Bleming had a g' value of 0.55 that was in accord with the value of 0.57 estimated from the relationship shown in Figure 12.⁴³

Very surprisingly, the $[\eta]_{\text{branched}}$ values were very similar to each other among the third-generation polymers listed in Table 7. This indicates that the $[\eta]$ value strongly depends upon the molecular size (or diameter) of branched polymer, but not the molecular weight and branched architecture. The theoretical approach between hydrodynamic volume and branched architecture will be of interest in the near future.

CONCLUSIONS

This review presents the precise synthesis of various dendrimer-like star-branched polymers and copolymers by our developed methodology based on iterative divergent approach involving only two elementary reaction steps in entire iterative reaction sequence. The most important point to be emphasized in this review is a new development of the synthetic procedure based on an iterative concept. The procedure always starts only from a specially designed 1,1-diphenylethylene derivative with two SMP groups, **1**, and works quite efficiently to repeatedly double the number of BnBr functions used as reaction sites to successively construct the framework of the dendrimer-like star-branched polymers. More advantageously and interestingly, it is also possible to apply the same iterative concept to the successive synthesis of BnBr-functionalized compounds and SMP-functionalized DPE derivatives. They are also used as new core agents and initiator parts in the iterative methodology to further synthesize another type of dendrimer-like star-branched

polymers with different branched architectures. Thus, the presently developed methodology based on iterative concept seems far richer than might be expected and will offer the potential of providing a total synthetic system possible for the design and synthesis of a large diversity of dendrimer-like star-branched polymers and their related hyperbranched polymers.

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