

INVITED REVIEW

Dendrimer-like star-branched polymers: novel structurally well-defined hyperbranched polymers

Akira Hirao and Hee-Soo Yoo

The precise synthesis of dendrimer-like star-branched polymers (DSPs), a novel class of structurally well-defined hyperbranched polymers, is described. The synthesis uses stepwise iterative methodologies based on the ‘arm-first’ divergent approach. The first methodology involves two reaction steps: (1) a linking reaction of an α -multifunctionalized living polymer(s) either with a core(s) substituted plural number of benzyl bromide (BnBr) functions or a chain-end-(BnBr)_n-functionalized polymer(s) attached to the repeating unit and (2) a transformation reaction to the BnBr function that is used as the next reaction site. The two steps are repeated to construct high-molecular-weight ($1.94 \times 10^6 \text{ g mol}^{-1}$, $M_w/M_n=1.02$) and high-generation (seventh generation) DSPs. The second methodology is the same as the first except for the use of a functionalized living AB diblock copolymer instead of the α -multifunctionalized living polymer(s). With this methodology, a higher molecular weight ($1.43 \times 10^7 \text{ g mol}^{-1}$, $M_w/M_n=1.05$) DSP was successfully synthesized, although the number of branch segments was not exactly, rather on average, defined by the living anionic polymerization of the B segment. The resulting DSPs were characterized by right angle laser light scattering (RALLS), small-angle X-ray scattering and viscosity measurements to obtain the hydrodynamic radii, radii of gyration, intrinsic viscosity values and g' values (branching factors). The relationship among such values that reveals the sizes, volumes, shapes, and generation and branched architecture is discussed. To visualize the synthesized DSPs, an atomic force microscopy measurement was attempted.

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INTRODUCTION

Along with the recent rapid advances in living/controlled polymerization systems, a variety of well-defined branched polymers have been synthesized. Among such polymers, a series of branched polymers, as shown in Figure 1, has emerged since 1995 as a novel class of structurally well-defined hyperbranched polymers. Although several names have been proposed for such polymers, they are currently called ‘dendrimer-like star-branched polymers’ (DSPs) based on their branched architectures, which are similar to those of dendrimers. Various hyperbranched polymers, such as dendrigrafts, comb-bursts, arborescents and hyperMacs, that are structurally similar to DSPs have also been synthesized, but these polymers exhibit an irregular architecture with incompletely reacted branched points throughout the structures. In contrast, the DSPs introduced in this review are highly ordered and regularly branched polymers, and therefore, differ from the other above-mentioned hyperbranched polymers in their structural perfection.

To aid in the understanding of the specific hyperbranched architectures of DSPs, the representative fifth generation (5G) polymer and its block copolymer are shown in Figure 1. As one can see, they

are similar to DSPs in that they possess branched architectures to well-established dendrimers, but they are composed of many polymer chains that are linked to each other between the junctions in all generations. Accordingly, they are much higher in molecular weight and much larger in molecular size than dendrimers of the same generation. DSPs are believed to be nano-ordered globular macromolecules, as predicted from molecular models and some analytical results. They have many characteristic features, such as specific topological hyperbranched architectures, hierarchical generation-based (or layered) structures, different branch densities between the core and outermost layers, and many junctions and chain-end groups that are capable of carrying many functional groups.

Dendrimer-like star-branched block copolymers (DSBPs) with different polymer segments introduced at each generation have also been synthesized. They are quite novel block copolymers composed of generation-based layered block structures. Their thermodynamically immiscible polymer segments may be phase-separated at the molecular level, then self-organized, to produce new nano-ordered periodic suprastructures and supramolecular assemblies that are different from those formed by linear block copolymers and even asymmetric

star-branched polymers. Furthermore, the formation of alternative or several separated layer structures is highly probable due to the generation-based structures (see also Figure 1). Thus, both DSPs and DSBPs are promising materials that possess specialty functional polymers with many potential applications, especially in the fields of nanoscience and nanotechnology, such as nanosize reactors with layered reaction sites that can carry enzymes and catalysts, multi-compartment micelles, carriers of drugs and genetic materials, shape-persistent nanoscale electronic and optical devices. Several reviews of DSPs have been published.^{1–7}

Thus far, DSPs have been synthesized by either stepwise iterative ‘core-first’ divergent or ‘arm-first’ convergent methodologies using living polymers as building blocks that are linked between the junctions. In the ‘core-first’ divergent methodology,^{8–16} the synthesis initiates growth at a multifunctionalized initiator and continues outward by iterating the same or a similar synthetic sequence. An initiation reaction is used to introduce the polymer segments. Typically, as shown in Scheme 1, an appropriate monomer is first polymerized with a multifunctional initiator in a living manner, and then each of the growing chain-ends is modified to convert them to two or more initiation sites. The reaction sequence, that is, the living polymerization and the chain-end modification reaction, is repeated to buildup high-generation DSPs. A variety of DSPs and DSBPs has been synthesized by developing this methodology with living/controlled polymerization and/or living anionic polymerization of vinyl and cyclic monomers. Most of the synthesized polymers are limited to the 4G stage and to the order of 10^5 g mol^{-1} in molecular weight, except for two examples, which were 7G and 8G polymers having M_n values of up to $1.9 \times 10^7 \text{ g mol}^{-1}$ (Matmour and Guanou¹⁴).

Given a suitable choice of living polymerization and chain-end modification, the isolation step in each iterative process becomes unnecessary; therefore, this methodology is suited for large-scale synthesis. Furthermore, the steric hindrance appears to decrease by increasing the number of generations because the synthesis proceeds in an outward direction. On the other hand, a serious drawback always remains with the uniformity of all polymer chains propagated from multi-initiation sites at each generation (heterogeneous propagation). Furthermore, because the number of initiation sites increases exponentially with each generation, it is not possible to accurately determine how many reaction sites initiate the polymerization (insufficient initiation). Thus, insufficient initiation and heterogeneous propagation reactions are likely to occur, especially in higher generation polymer synthesis, which could lead to structural imperfections or defects. More important, the structures of the resulting polymers are not certain to be well defined, even by acceptable agreement

between the calculated and observed molecular weights in the final polymer obtained with this methodology.

As a complementary alternative, a stepwise iterative methodology based on an ‘arm-first’ convergent approach has been proposed, as illustrated in Scheme 2.^{17–20} In this methodology, a dendron having a single reaction site, a part of a DSP, is first prepared by using pre-made living polymers with known molecular weights. Then, the dendrons are linked with a multifunctional core compound to build up the corresponding DSP. The important point of this methodology is that a termination reaction is used to introduce a polymer chain linked between the junctions.

Therefore, the well-defined structures of the resulting polymers can readily be checked by comparing the total molecular weights of the final polymers with those of the dendrons and pre-made living polymers, and strong agreement between the two values indicates that the structures are of high quality. Such agreement also indicates structural perfection. In practice, 2G and 3G DSPs with well-defined structures have been successfully synthesized by this methodology. Because the linking reaction among sterically bulky and high-molecular-weight dendrons is inevitable in the final reaction step and because the molecular weight of the dendron is necessarily a multiple of the reaction step, it becomes increasingly difficult to proceed to higher generations. Accordingly, the methodology is generally limited to the synthesis of 2G and/or 3G polymers. Thus, several difficulties arise in the synthesis of DSPs with the two methodologies mentioned above. Therefore, the development of a methodology capable of synthesizing high-generation and high-molecular-weight DSPs with well-defined structures is still desired even at the present time.

STEPWISE ITERATIVE METHODOLOGY BASED ON AN ‘ARM-FIRST’ DIVERGENT APPROACH

Methodology using α -functionalized living anionic polymers as building blocks

Dendrimer-like star-branched poly(methyl methacrylate)s. To synthesize high-generation and high-molecular-weight DSPs, we recently developed a new stepwise iterative methodology based on an ‘arm-first’ divergent approach, which has the advantages of both of the two methodologies mentioned above.^{21,22} In this methodology, a termination reaction using pre-made living anionic polymers of known molecular weights is employed to introduce polymer chains in a similar way to the ‘arm-first’ convergent approach. Accordingly, the structure of the resulting polymer can readily be examined by directly comparing the molecular weight of the final polymer with the molecular weight calculated from the pre-made living polymer. Agreement between both values confirms that the structure is well defined. Furthermore, the steric hindrance may be reduced as the iteration proceeds because the synthesis initiates growth from the core and continues outward in the divergent manner.

The synthetic outline is illustrated in Scheme 3. The methodology involves two reaction steps in each of the iterative synthetic sequences: (1) a linking reaction of an α -chain-end, two 3-*tert*-butyldimethylsilyloxymethylphenyl-functionalized living anionic poly(methyl methacrylate) (α -(SiOMP)₂-PMMA) with either a multifunctional core substituted with benzyl bromide (BnBr) moieties (only for the first iteration) or a chain-end-(BnBr)₂-functionalized PMMA connected to the core or the repeating unit and (2) a transformation reaction of the introduced SiOMP group to the BnBr function, which is able to be used as the next reaction site. By repeating the two reaction steps in each iterative process, a series of DSPs are built up generation-by-generation. Thus, both the insufficient initiation and heterogeneous propagation reactions with multiple initiation sites in the

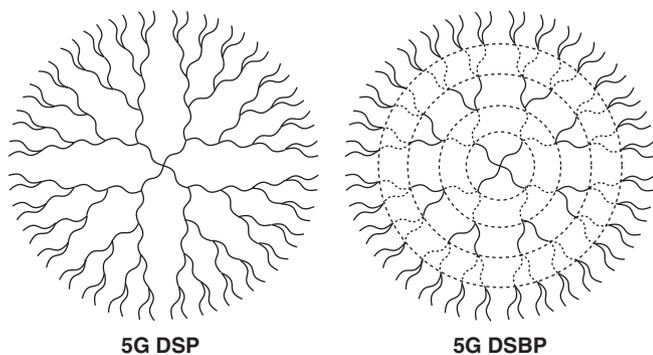
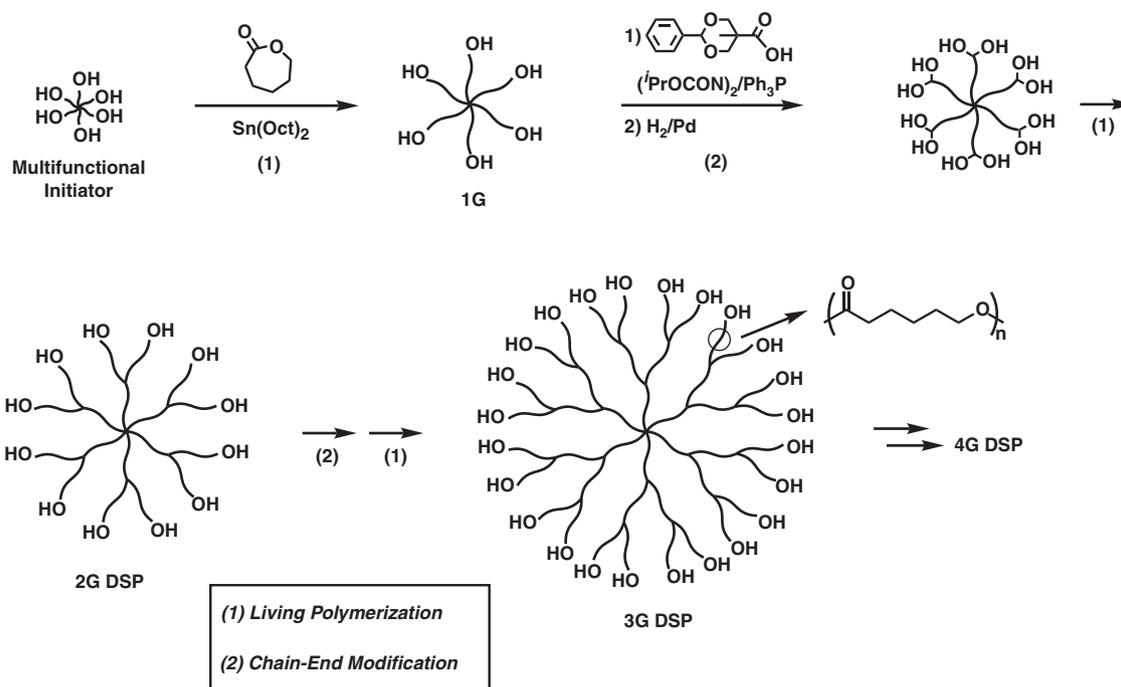
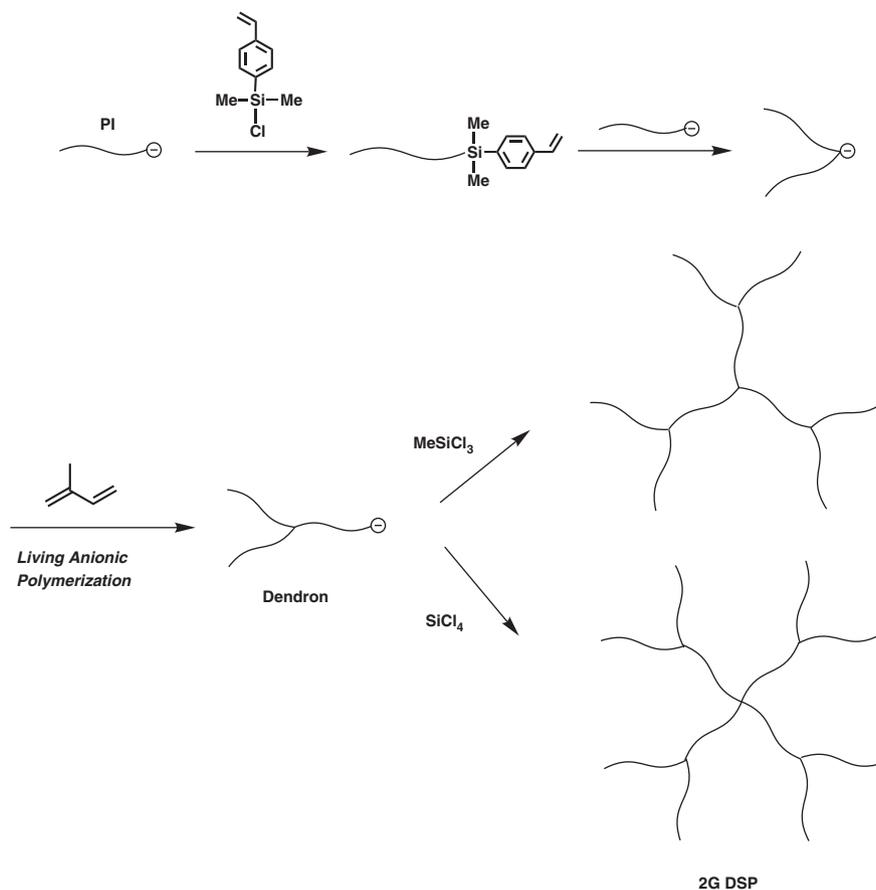


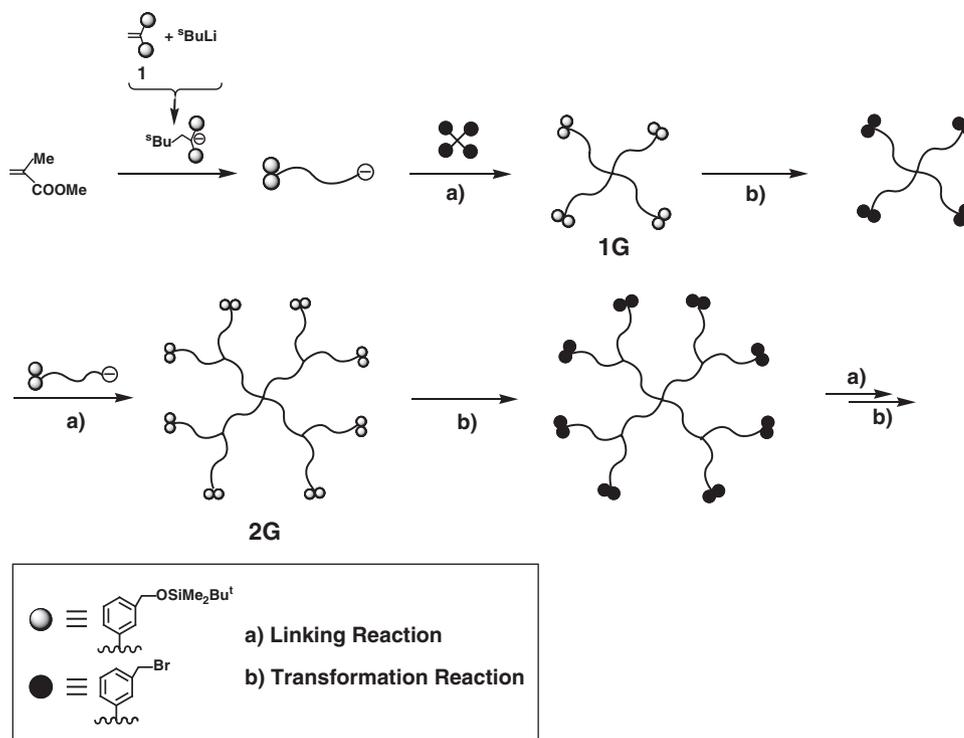
Figure 1 Fifth generation (5G) dendrimer-like star-branched polymer (DSP) and dendrimer-like star-branched block copolymer (DSBP).



Scheme 1 Synthesis of DSPs by stepwise iterative methodology based on the 'core-first' divergent approach. 1G, first generation; 2G, second generation; 3G, third generation; 4G, fourth generation; DSP, dendrimer-like star-branched polymer.



Scheme 2 Synthesis of dendrimer-like star-branched polymers (DSPs) by stepwise iterative methodology based on the 'arm-first' convergent approach. 2G, second generation. PI, polyisoprene.



Scheme 3 Synthesis of a series of dendrimer-like star-branched poly(methyl methacrylate)s to second generation (2G) by a stepwise iterative methodology based on ‘arm-first’ divergent approach.

‘core-first’ divergent approach and the linking reaction among the high-molecular-weight dendrons in the ‘arm-first’ convergent approach are completely avoided.

As shown in Scheme 3, an α -(SiOMP)₂-functionalized living PMMA is first prepared by the living anionic polymerization of methyl methacrylate (MMA) with a specially designed functional initiator from *sec*-BuLi and 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (1) in tetrahydrofuran (THF) at -78°C . A threefold excess of LiCl was added before the polymerization to narrow the molecular weight distribution. The living PMMA was adjusted to have an M_n value of $\sim 4000\text{ g mol}^{-1}$ throughout the synthesis. The α -functionalized living PMMA prepared in this way was then linked with a core compound substituted with four BnBr functions in THF at -40°C for 24 h, resulting in a four-arm star-branched PMMA with 100% yield. Although the obtained polymer corresponds to a 1G polymer in this synthesis, it is a four-arm star-branched polymer (but not a DSP). Following treatment with a 1:1 mixture of $(\text{CH}_3)_3\text{SiCl}$ and LiBr, the two SiOMP groups at each chain-end (a total of eight SiOMP groups) were transformed into two BnBr functions. In the second iteration, the resulting brominated 1G polymer was linked with another α -(SiOMP)₂-functionalized living PMMA prepared in a similar manner. The reaction was observed to proceed quantitatively to yield a 2G polymer, which was the first polymer possessing a dendrimer-like star-branched architecture in this synthesis. Because the linking and transformation reactions quantitatively proceeded in each iterative process, the same reaction sequence was repeated four more times to form 3G, 4G, 5G and 6G DSPs, followed by 7G DSPs (see Scheme 4). All of the reactions were followed by ^1H nuclear magnetic resonance spectroscopy, size exclusion chromatography and static light scattering (SLS), and confirmed to be virtually quantitative. In each linking reaction step, α -(SiOMP)₂-functionalized living PMMA was always used in excess to complete the reaction; therefore, fractionation was needed to isolate the target polymers.

Size exclusion chromatography profiles of the isolated polymers all exhibited narrow monomodal distributions, with M_w/M_n values < 1.03 (Figure 2). The results are summarized in Table 1. Good agreement between the calculated molecular weights and those determined by ^1H nuclear magnetic resonance spectroscopy and SLS was observed for all polymers, which is strong evidence that the 2–7G polymers are the target dendrimer-like star-branched PMMAs with the requisite structures. These analytical results also clearly exhibited well-defined structures of this DSP series. The final 7G polymer is a huge macromolecule having a well-controlled M_n value of $1.94 \times 10^6\text{ g mol}^{-1}$ and a narrow molecular weight distribution with an M_w/M_n value of 1.02. The polymer consists of 508 PMMA segments with 512 highly reactive BnBr termini capable of continuing the next iteration. These polymers possess four branches at the cores and two branches at the junctions in each generation. There were no steric effects even for the largest 7G polymer, although the reaction conditions were not the same throughout the synthesis, but were optimized as the iteration proceeded. For instance, a fivefold excess of α -(SiOMP)₂-functionalized living PMMA and a longer reaction time (72 h) were used for the synthesis of the 7G polymer.

A different series of dendrimer-like star-branched PMMAs up to the 5G stage was also successfully synthesized with the same methodology using a higher molecular weight α -(SiOMP)₂-functionalized living PMMA ($M_n \approx 10\,000\text{ g mol}^{-1}$) at each iteration. In this series, the molecular weight of the polymer reached $1.43 \times 10^6\text{ g mol}^{-1}$ even in the 5G polymer (see also Table 1). Thus, the developed methodology works well for the synthesis of high-generation and high-molecular-weight dendrimer-like star-branched PMMAs with well-defined structures.

The versatility of the methodology is attested by the number of structural variations in the resulting polymers. For instance, a series of more branched dendrimer-like star-branched PMMAs was

successfully synthesized by the same methodology using a living PMMA α -functionalized with four SiOMP groups, as illustrated in Scheme 5.²³ The resulting polymers possess four polymer segments branched at the cores as well as at all junctions and a loading capacity of 256 BnBr termini, as listed in Table 2, which is exactly equal to the number of BnBr termini of the 6G polymer (see Table 1). Furthermore, with the appropriate choice of α -functionalized living PMMA having either two or four SiOMP groups in each iterative process, the structural variations lead to significant changes in the branched architectures of the 3G and 4G dendrimer-like star-branched PMMAs, as shown in Figure 3.²⁴

A new 1,1-diphenylethylene (DPE) derivative substituted with four SiOMP moieties was needed to prepare the above α -(SiOMP)₄-functionalized living PMMA. This was readily synthesized in 100% yield by a reaction of 1,1-(3-bromomethylphenyl)ethylene (**2**) with the functionalized DPE anion derived from **1** and *sec*-BuLi, as shown in Scheme 6.²³ The DPE derivative, **2**, was prepared by the same transformation reaction with (CH₃)₃SiCl/LiBr used in the polymer synthesis, which is also shown in Scheme 6. A similar synthetic route is applicable to core compounds substituted with several BnBr functions. A core compound substituted with four BnBr functions was prepared by a radical coupling reaction of **1** with potassium naphthalenide, followed by the same transformation reaction, as shown in Scheme 7.²⁵ The core compound synthesized in this way was further reacted with the functional DPE-derived anion from **1** and *sec*-BuLi to introduce eight SiOMP groups. The same treatment with Me₃SiCl/LiBr gave a new core compound with eight BnBr functions. With the use of this core, a 3G DSP possessing eight branches at the core and two branches at the junctions in the 2G and 3G layers could be synthesized (see also Figure 3). Thus, the DPE derivative, **1**, is the key compound responsible for the synthesis of a variety of DSPs and their intermediate polymers, as shown in Figures 1–3. Furthermore, it should be emphasized that not only DSPs but also the core compounds and functional initiators making the branch points can be synthesized by using only **1** followed by the linking and transformation reactions.

Similar to living PMMA, another living anionic polymer should react with a brominated DSP to afford a next generation DSBP with

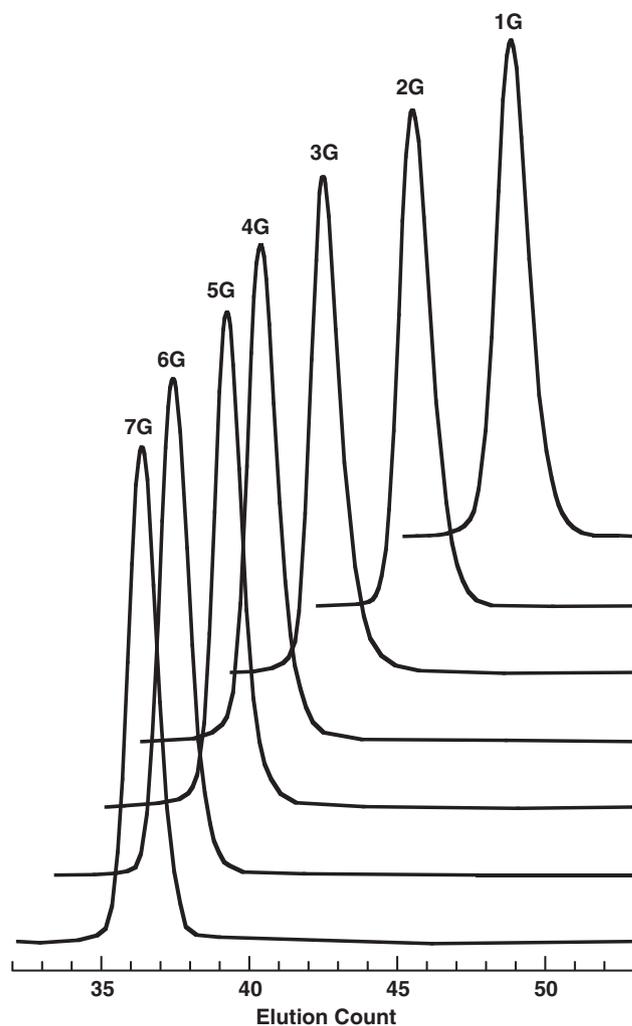
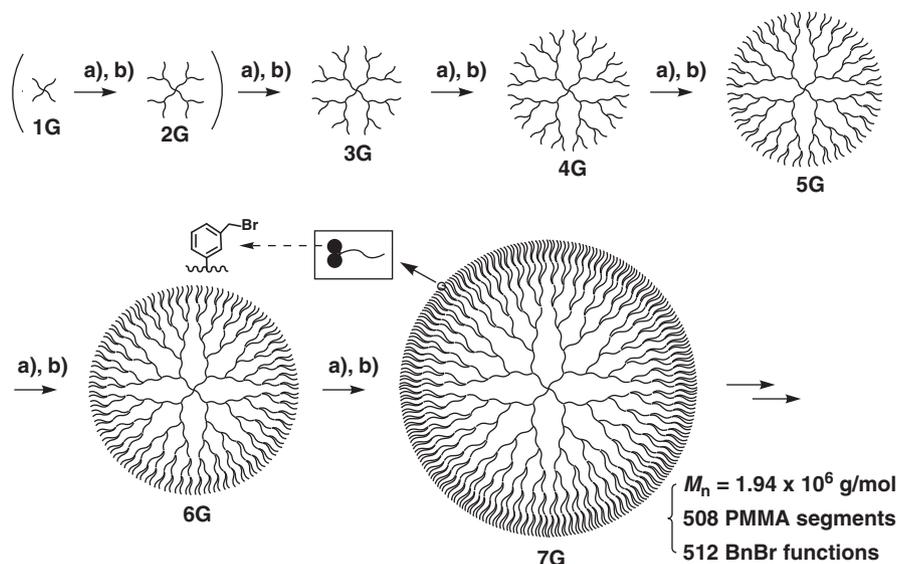


Figure 2 Size exclusion chromatography profiles of dendrimer-like star-branched poly(methyl methacrylate)s from first generation (1G) to seventh generation (7G).



Scheme 4 Synthesis of a series of dendrimer-like star-branched poly(methyl methacrylate)s (PMMAs) from 1 to 7G by a stepwise iterative methodology based on 'arm-first' divergent approach. 1G, first generation; 2G, second generation; 3G, third generation; 4G, fourth generation; 5G, generation; BnBr, benzyl bromide.

additional functionality. For example, a 3G DSPB was obtained by a reaction of a 2G brominated polymer with a living anionic poly (2-(*tert*-butyldimethylsilyloxy)ethyl methacrylate), yielding a 3G DSPB carrying many hydroxyl groups in the 3G layer after removal

Table 1 Synthesis of dendrimer-like star-branched PMMAs with four branches at the core and two branches at each junction

| Generation | Type | M_n (kg mol^{-1}) | | | M_w (kg mol^{-1}) | | |
|----------------|---|--------------------------------|------|------------------|--------------------------------|------|-----------|
| | | Calcd | SEC | $^1\text{H NMR}$ | Calcd | SLS | M_w/M_n |
| 1 ^a | (A ₄) | 14.6 | 13.8 | 14.2 | 14.9 | 14.8 | 1.02 |
| 2 ^a | (A-A ₂) ₄ | 43.0 | 36.9 | 42.9 | 43.9 | 44.2 | 1.02 |
| 3 ^a | (A-A ₂ -A ₄) ₄ | 97.3 | 66.1 | 98.4 | 99.2 | 105 | 1.02 |
| 4 ^a | (A-A ₂ -A ₄ -A ₈) ₄ | 219 | 115 | 219 | 223 | 230 | 1.02 |
| 5 ^a | (A-A ₂ -A ₄ -A ₈ -A ₁₆) ₄ | 452 | 178 | 449 | 462 | 472 | 1.03 |
| 6 ^a | (A-A ₂ -A ₄ -A ₈ -A ₁₆ -A ₃₂) ₄ | 980 | 282 | 974 | 1000 | 1060 | 1.02 |
| 7 ^a | (A-A ₂ -A ₄ -A ₈ -A ₁₆ -A ₃₂ -A ₆₄) ₄ | 1960 | 414 | 1940 | 1980 | 1970 | 1.02 |
| 1 ^b | (A ₄) | 44.4 | 36.2 | 44.9 | 45.3 | 45.3 | 1.02 |
| 2 ^b | (A-A ₂) ₄ | 131 | 93.1 | 131 | 134 | 134 | 1.02 |
| 3 ^b | (A-A ₂ -A ₄) ₄ | 298 | 171 | 300 | 304 | 305 | 1.02 |
| 4 ^b | (A-A ₂ -A ₄ -A ₈) ₄ | 639 | 301 | 649 | 658 | 661 | 1.03 |
| 5 ^b | (A-A ₂ -A ₄ -A ₈ -A ₁₆) ₄ | 1390 | 512 | 1430 | 1430 | 1500 | 1.03 |

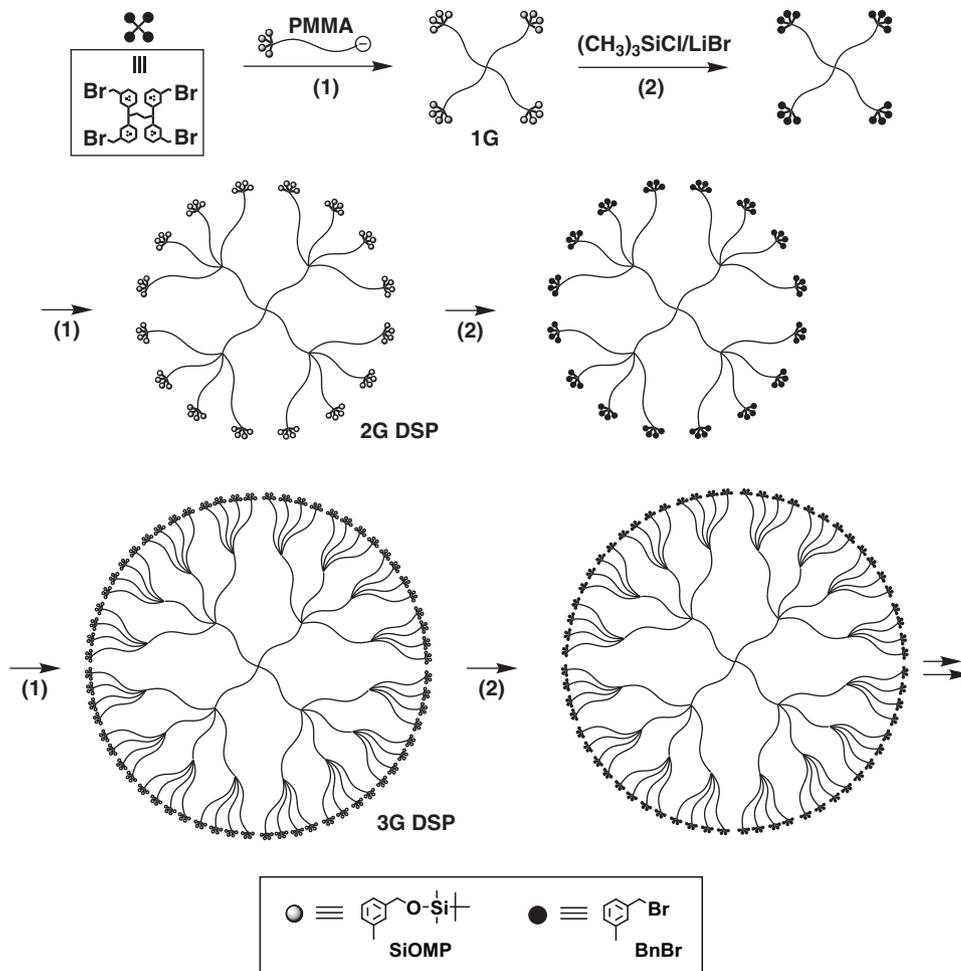
Abbreviations: NMR, nuclear magnetic resonance spectroscopy; PMMA, poly(methyl methacrylate); SEC, size exclusion chromatography.

^aMolecular weight of arm polymer, $M_n \sim 4000 \text{ g mol}^{-1}$.

^bMolecular weight of arm polymer, $M_n \sim 10000 \text{ g mol}^{-1}$.

of the silyl protective groups. Various 4G DSPBs, whose 4G layer was functionalized with carboxylic acid, 1,2-diol, 2-vinylpyridine or pyridinium ions, could also be synthesized by reacting the 3G brominated polymer with a living anionic polymer of *tert*-butyl methacrylate, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate or 2-vinylpyridine followed by deprotection or quaternarization. Thus, the introduction of various functional groups into the outer generation of the DSP is of particular importance in broadening the synthetic range of functional DSPs with many potential applications. Furthermore, the many highly reactive BnBr termini present at the periphery could be transformed into a variety of useful functional groups, such as COOH, OH, SH, NH₂, CHO, N₃ and C≡CH. The latter two functions are often used in the Click reaction that was developed recently.

Dendrimer-like star-branched polystyrenes. As mentioned above, α -(SiOMP)₂-functionalized living PMMA, used as a reactive building block, is prepared by the living anionic polymerization of MMA with the functionalized DPE-derived anion from **1** and *sec*-BuLi. For this preparation, a 1.5 or more excess of **1** with *sec*-BuLi is usually employed to completely convert *sec*-BuLi into the anion. The unreacted remaining **1** has no influence on the subsequent anionic polymerization of the MMA because **1** cannot react with the PMMA growing chain-end enolate anion and remains intact during and after the polymerization.



Scheme 5 Synthesis of a series of dendrimer-like star-branched poly(methyl methacrylate)s (PMMAs) having four branches at the core as well as at the junctions. 1G, first generation; 2G, second generation; 3G, third generation; DSP, dendrimer-like star-branched polymer.

In contrast to the polymerization of MMA, the presence of an excess of **1** is problematic in the anionic polymerization of styrene, because **1** reacts readily with the chain-end styrylanion

Table 2 Synthesis of dendrimer-like star-branched PMMAs with four branches at the core as well as all junctions

| Generation | Type | M_n (kg mol^{-1}) | | | M_w (kg mol^{-1}) | | |
|------------|---|--------------------------------|------|------------------|--------------------------------|------|-----------|
| | | Calcd | SEC | $^1\text{H NMR}$ | Calcd | SLS | M_w/M_n |
| 1 | (A ₄) | 52.8 | 46.5 | 52.2 | 53.9 | 51.6 | 1.02 |
| 2 | (A-A ₄) ₄ | 260 | 156 | 163 | 268 | 272 | 1.03 |
| 3 | (A-A ₄ -A ₁₆) ₄ | 1300 | 522 | 1340 | 1340 | 1390 | 1.03 |

Abbreviations: NMR, nuclear magnetic resonance spectroscopy; PMMA, poly(methyl methacrylate); SEC, size exclusion chromatography.

to be incorporated in the polystyrene (PS) chain, which results in the introduction of the SiOMP group not only at the target α -terminal chain-end, but also randomly into the PS chain. On the other hand, when less than the stoichiometric amount of **1** is used in the reaction with *sec*-BuLi, nonfunctionalized living PS is produced by the polymerization of styrene with the residual *sec*-BuLi. After the transformation reaction of the SiOMP groups, either more than two or less than two PS chains are introduced at the next linking reaction, which results in the formation of imperfect or defective structures. Accordingly, a rigid stoichiometry between **1** and *sec*-BuLi is required, but this is almost impossible to achieve in experimental practice using the highly reactive *sec*-BuLi and the functional anion. More important, such rigid stoichiometry is needed a number of times to synthesize high-generation dendrimer-like star-branched PSs. Thus, the protocol effective for the preparation of α -(SiOMP)₂-functionalized living

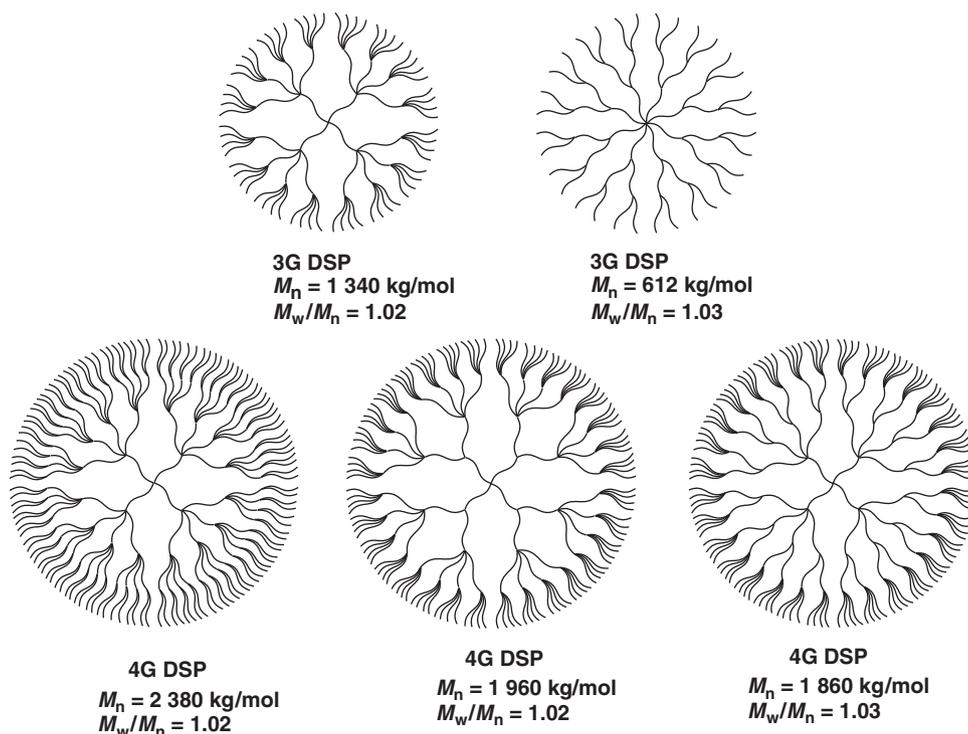
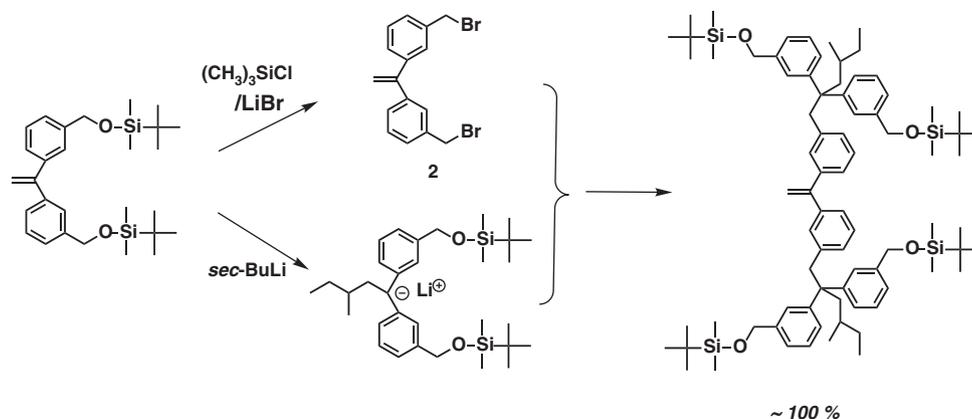
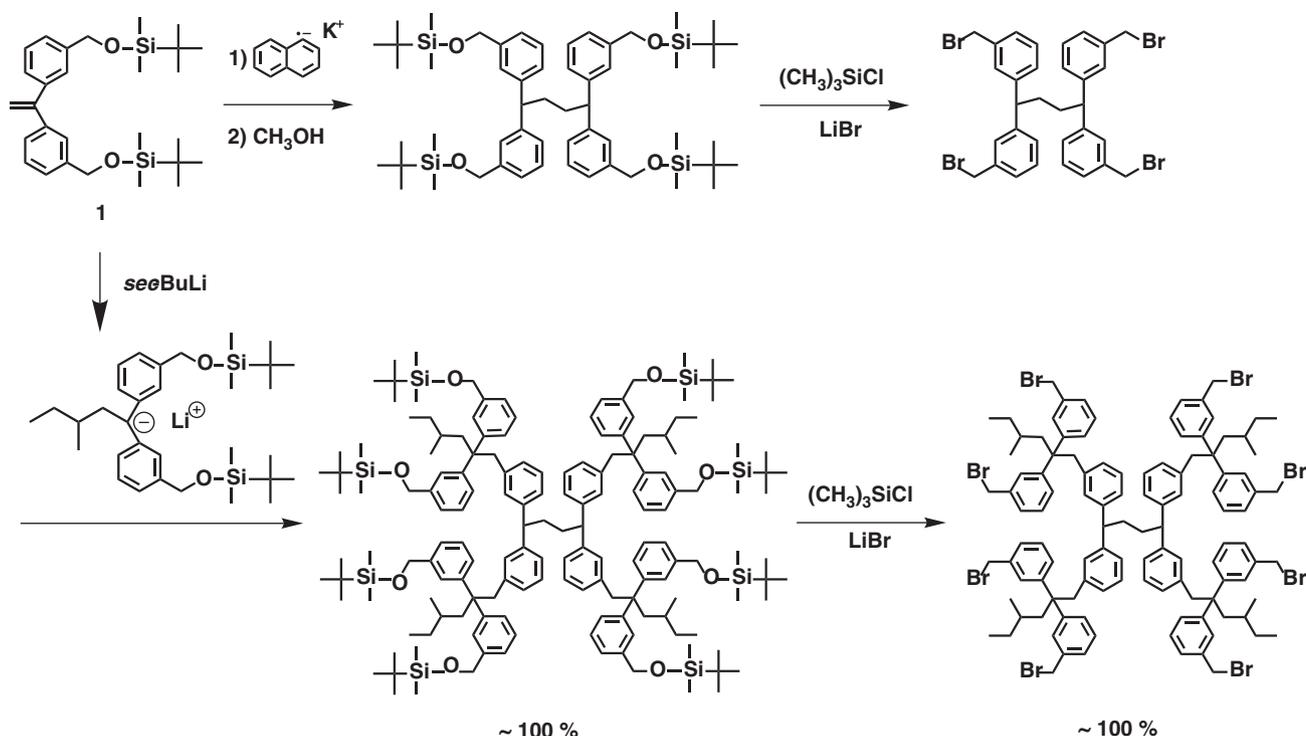


Figure 3 Third generation (3G) and fourth generation (4G) dendrimer-like star-branched polymers (DSPs) with different branch densities.





Scheme 7 Synthesis of a core compound substituted with four benzyl bromide functions.

PMMA cannot be used for the preparation of α -(SiOMP)₂-functionalized living PS.

An alternative strategy has been proposed to synthesize well-defined dendrimer-like star-branched PSs, as illustrated in Scheme 8, where a new functional anionic initiator, 3-*tert*-butyldimethylsilyloxy-1-propyllithium (**3**), is employed instead of the functional DPE-derived anion.²⁶ Although the alternative strategy is based on the same ‘arm-first’ divergent approach as that mentioned above, more reaction steps from the introduced 3-(*tert*-butyldimethylsilyloxy)propyl (SiOP) group to two SiOMP termini are needed to avoid the above drawback. As can be seen, styrene is first polymerized with **3** to afford an α -SiOP-functionalized living PS. Throughout the synthesis, living PS was adjusted to be *ca.* 10 000 g mol⁻¹ in *M_n* value. The resulting α -SiOP-functionalized living PS was end-capped with DPE and subsequently reacted with a core substituted with four BnBr functions, which results in a four-arm star PS. Then, the SiOP terminus of each PS arm segment was deprotected with (C₄H₉)₄NF, followed by bromination with CBr₄ and Ph₃P to convert the generated 3-hydroxypropyl group to a 3-bromopropyl function. A functional DPE-derived anion was prepared from **1** and *sec*-BuLi and reacted with this brominated four-arm star PS to introduce two SiOMP groups at each chain-end. The end-functionalized PS star prepared in this way corresponds to a brominated 1G polymer in this synthesis.

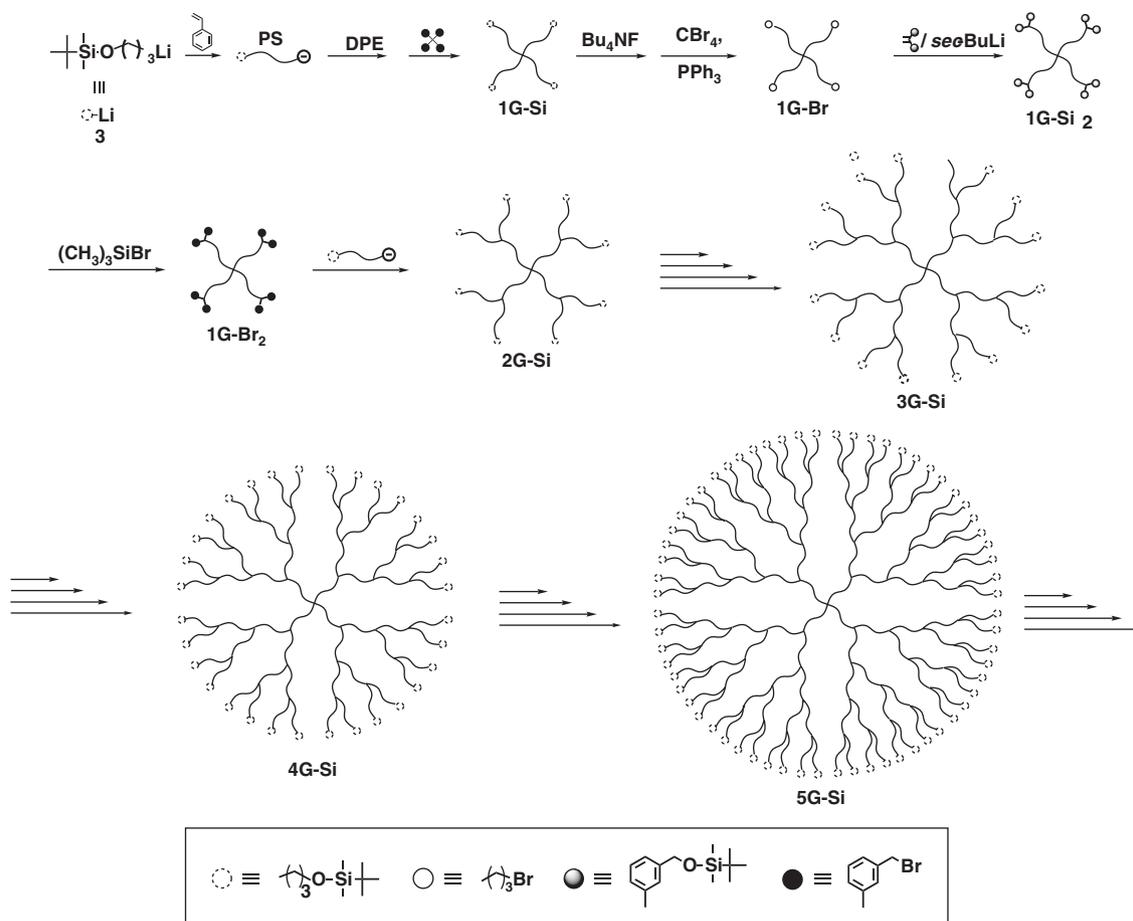
The same reaction sequence was repeated as follows. A new α -SiOP-functionalized living PS end-capped with DPE was prepared in a similar manner and subsequently reacted with the brominated 1G polymer. The reaction was observed to proceed quantitatively to yield the target 2G dendrimer-like star-branched PS having a minimum dendrimer-like star-branched architecture. The SiOP terminus at each chain-end was deprotected, brominated and converted into two SiOMP groups by the reaction with the functionalized DPE-derived anion. Because the reaction sequence involving the linking reaction, deprotection and bromination followed by the introduction of two

SiOMP termini at each chain-end proceeded efficiently and quantitatively, it could be repeated three more times without any difficulty, which would result in 3G, 4G and 5G dendrimer-like star-branched PSs. The results are summarized in Table 3. The agreement between the observed and calculated *M_n* values and a narrow molecular weight distribution in each of all polymer samples clearly demonstrated that each iterative process proceeded as desired and that the resulting polymers were well defined and requisite in structure. Thus, the new methodology works quite satisfactorily.

By combining the two methodologies introduced in the preceding and present sections, it is possible to synthesize new generation-alternative 3G DSBPs composed of PS (1G), PMMA (2G) and PS (3G), as well as PMMA (1G), PS (2G) and PMMA (3G). Moreover, a 3G DSBP composed of PS (1G), PMMA (2G) and poly(2-vinylpyridine) (3G) was also synthesized by sequentially reacting living PS, living PMMA and living poly(2-vinylpyridine), in this order (Yoo and Hirao, unpublished results). Thus, the combination of the two methodologies allows for a general and versatile synthetic procedure with which either PS or PMMA segments can be introduced at any generation. This strongly indicates the possible use of living anionic polymers with different reactivities, ranging from highly reactive living polymers of styrene, and possibly 1,3-butadiene and isoprene, to less reactive living polymers of 2-vinylpyridine, followed by various alkyl methacrylate monomers. It is surprising that well-defined huge macromolecules with regulated hyperbranched structures having *M_n* values in the millions or greater can be synthesized simply by repeating the synthetic sequence involving two or even more reaction steps.

Methodology using living AB diblock copolymers as building blocks

As mentioned in the preceding section, a highly branched 3G DSP having four branches at the core, as well as at all junctions, was synthesized by using α -(SiOMP)₄-functionalized living PMMA.



Scheme 8 Synthesis of a series of dendrimer-like star-branched PSs from 1G to 5G by a stepwise iterative methodology based on the ‘arm-first’ divergent approach. 1G, first generation; 2G, second generation; 3G, third generation; 4G, fourth generation; 5G, generation; DPE, 1,1-diphenylethylene.

Table 3 Synthesis of dendrimer-like star-branched PSs

| Generation | Type | M_n (kg mol^{-1}) | | | M_w (kg mol^{-1}) | | |
|------------|---|--------------------------------|------|------------------|--------------------------------|------|-----------|
| | | Calcd | SEC | $^1\text{H NMR}$ | Calcd | SLS | M_w/M_n |
| 1 | (A ₄) | 39.7 | 34.7 | 39.5 | 40.5 | 39.4 | 1.02 |
| 2 | (A-A ₂) ₄ | 113 | 102 | 123 | 116 | 128 | 1.03 |
| 3 | (A-A ₂ -A ₄) ₄ | 305 | 209 | 300 | 320 | 311 | 1.05 |
| 4 | (A-A ₂ -A ₄ -A ₈) ₄ | 688 | 314 | 667 | 722 | 704 | 1.05 |
| 5 | (A-A ₂ -A ₄ -A ₈ -A ₁₆) ₄ | 1730 | 542 | 1800 | 1820 | 1880 | 1.05 |

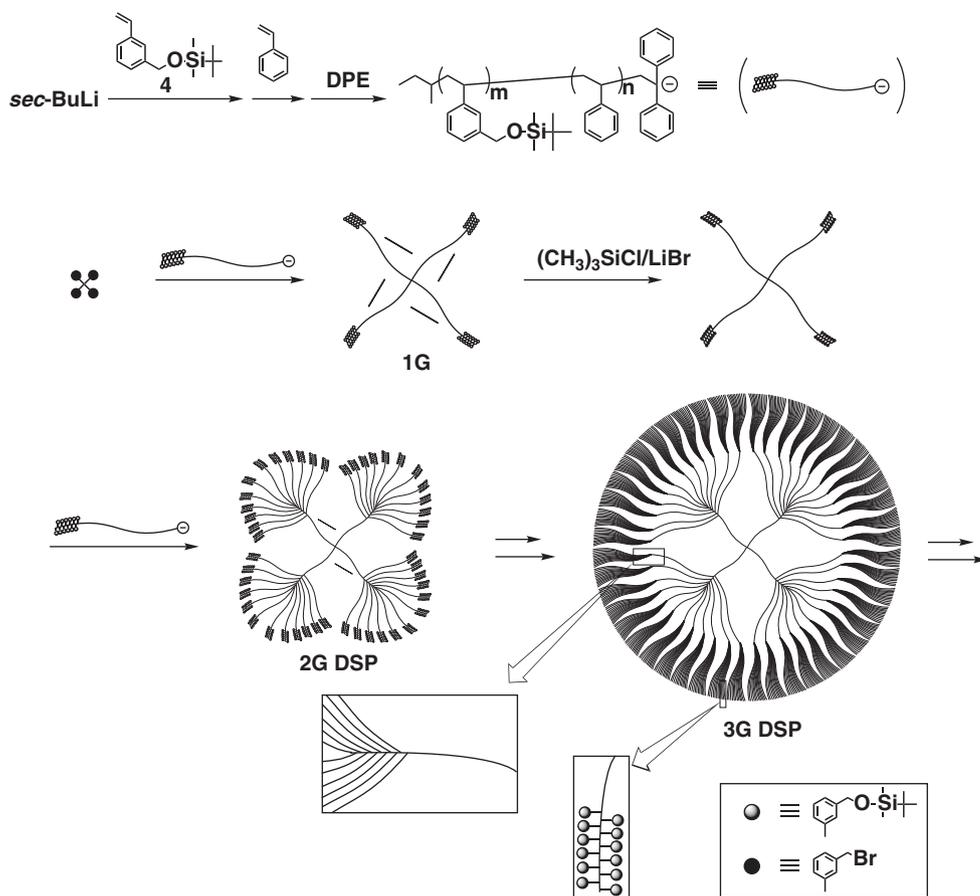
Abbreviations: NMR, nuclear magnetic resonance spectroscopy; SEC, size exclusion chromatography.

Unfortunately, a 4G DSP with the same branch density could not be synthesized by repeating the same synthetic sequence one more time. Although a high-molecular-weight DSP was obtained ($M_n=3.96 \times 10^6 \text{ g mol}^{-1}$, $M_w/M_n=1.08$), the linking reaction between the brominated 3G polymer and living PMMA was saturated around 75% due to steric hindrance. Several attempts were not successful at synthesizing the 4G polymer.^{23,24}

In this section, a new methodology using a living anionic AB diblock copolymer as a building block is proposed for the synthesis of higher molecular weight and more densely branched DSPs, as illustrated in Scheme 9.²⁷ Similar to the methodologies introduced in the preceding sections, the new methodology is based on the ‘arm-first’

divergent approach. It involves three sequential reaction steps: (1) anionic block copolymerization to prepare a living AB diblock copolymer composed of styrene and 3-*tert*-butyldimethylsilyloxy-methylstyrene (4), (2) a linking reaction of the living AB block copolymer with either a core substituted with four BnBr functions or chain-(BnBr)_n-multifunctionalized polymers attached to the core or repeating unit and (3) a transformation reaction of the SiOMP groups into BnBr functions. The living AB diblock copolymer that is used as a building block is purposely designed in such a way to reduce the steric hindrance in the linking reaction and to increase the branch density.

In the first iteration, living anionic block copolymerization was conducted by the sequential addition of 4 and styrene followed by the addition of DPE for end capping. The resulting living AB diblock copolymer ($M_n=25\,300 \text{ g mol}^{-1}$, $M_w/M_n=1.02$, $\text{DP}_{\text{P(4)}}/\text{DP}_{\text{PS}}=12.3/216$) was *in situ* reacted with a core compound substituted with four BnBr functions. The reaction proceeded quantitatively to yield a four-arm star block copolymer. This polymer was a 1G polymer having a M_n value of $1.02 \times 10^5 \text{ g mol}^{-1}$, which agrees with the calculated value of $M_n=1.03 \times 10^5 \text{ g mol}^{-1}$. In the second iteration, the resulting 1G polymer was brominated with $\text{Me}_3\text{SiCl/LiBr}$ to transform the SiOMP groups into BnBr functions and then reacted with a living anionic block copolymer end-capped with DPE ($M_n=23\,400 \text{ g mol}^{-1}$, $M_w/M_n=1.02$, $\text{DP}_{\text{P(1)}}/\text{DP}_{\text{PS}}=12.4/195$). The reaction was observed to proceed virtually quantitatively.



Scheme 9 Synthesis of a series of high-molecular-weight and more densely branched dendrimer-like star-branched PSs from 1G to 3G. 1G, first generation; 2G, second generation; DPE, 1,1-diphenylethylene; DSP, dendrimer-like star-branched polymer.

The M_n value of the resulting polymer by right angle laser light scattering (RALLS) was $1.23 \times 10^6 \text{ g mol}^{-1}$, which is in good agreement with the calculated value of $1.25 \times 10^6 \text{ g mol}^{-1}$. A sharp monomodal size exclusion chromatography distribution was attained ($M_w/M_n=1.05$). The resulting polymer was a 2G dendrimer-like star-branched PS possessing four branches at the core and an average of 12.3 branches at the junction. The third iteration involved the bromination of the 2G polymer and a subsequent linking reaction with a living anionic AB diblock copolymer end-capped with DPE ($M_n=23\,300 \text{ g mol}^{-1}$, $M_w/M_n=1.02$, $\text{DP}_{\text{P}(1)}/\text{DP}_{\text{P}(5)}=12.5/192$). When placed in THF at -40°C for 6 h, the living diblock polymer underwent a linking reaction with the brominated 2G polymer to produce an $\sim 100\%$ yield. The M_n value of the resulting 3G polymer determined by RALLS was $1.43 \times 10^7 \text{ g mol}^{-1}$, very close to the calculated value of $1.49 \times 10^7 \text{ g mol}^{-1}$. The 3G polymer synthesized in this way expectedly had four branches at the core and 12.3 and 12.4 branches at the junctions of the 2G and 3G layers, respectively, and was composed of 668 ($4+4 \times 12.3+4 \times 12.3 \times 12.4$) branches carrying 7688 ($4 \times 12.3 \times 12.4 \times 12.5$) SiOMP termini.

Similarly, two different 3G dendrimer-like star-branched PSs could be synthesized by the same methodology using core compounds substituted with either two or three BnBr functions. The methodology works well to yield target 3G polymers possessing 2 and 3 branches at the cores and 12 branches at the junctions, as shown in Figure 4 (Watanabe and Hirao, unpublished results). These polymers had predictable molecular weights ($(M_n)_s=7.15 \times 10^6$ and $1.00 \times 10^7 \text{ g mol}^{-1}$) and narrow molecular weight distributions

($(M_w/M_n)_s=1.04$ and 1.05). Because it was possible to prepare an AB block copolymer anion composed of poly(**4**) and PMMA segments, a more densely branched 3G DSBP could also be synthesized (see also Figure 4; Watanabe and Hirao, unpublished results). It should be mentioned that the number of branch segments in these polymers synthesized by this methodology was not exact, but was defined on average by the living anionic polymerization of **4**. Thus, the methodology readily allows for the synthesis of much higher molecular weight and more densely branched DSPs.

MOLECULAR SIZES OF THE DSPS

To estimate the molecular sizes of the DSPs synthesized according to the methods discussed above, the hydrodynamic radii, (R_h), of a second series of dendrimer-like star-branched PMMAs from 1G to 5G (see Table 1) were measured by RALLS in THF.^{2,24} The results are summarized in Table 4. These polymers are four branched at the core and two branched at each junction and are abbreviated as A_4 (1G), $(A-A_2)_4$ (2G), $(A-A_2-A_4)_4$ (3G), $(A-A_2-A_4-A_8)_4$ (4G) and $(A-A_2-A_4-A_8-A_{16})_4$ (5G). The M_n value of the PMMA branch is adjusted to be *ca.* $10\,000 \text{ g mol}^{-1}$. As expected, the R_h value increases with the molecular weight; therefore, generation and a good linear relationship is observed between $\log R_h$ and $\log M_w$, as shown in Figure 5. Accordingly, the molecular size estimated from the R_h value was strongly correlated with the M_w value. The diameter of the 5G PMMA ($M_w=1.50 \times 10^6 \text{ g mol}^{-1}$) was 38.8 (19.4 \times 2) nm.

Next, the effect of branched architecture on molecular size was examined. As mentioned before, the branch number between

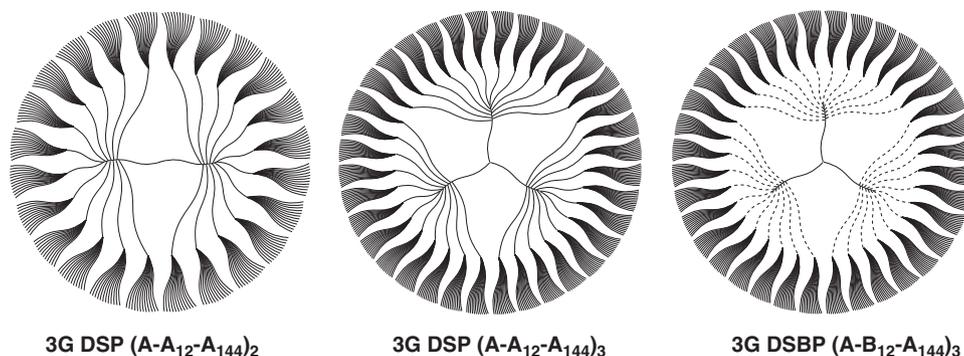


Figure 4 High-molecular-weight and more densely branched third generation (3G) DSPs and 3G dendrimer-like star-branched block copolymers (DSBPs).

Table 4 Hydrodynamic radii of dendrimer-like star-branched PMMAs with four branches at the core and two branches at each junction

| Generation | Type | M_w (kg mol ⁻¹) ^a | R_h (nm) ^a |
|------------|---|--|-------------------------|
| 1G | (A ₄) | 47.0 | 4.72 |
| 2G | (A-A ₂) ₄ | 136 | 7.84 |
| 3G | (A-A ₂ -A ₄) ₄ | 295 | 10.2 |
| 4G | (A-A ₂ -A ₄ -A ₈) ₄ | 661 | 13.9 |
| 5G | (A-A ₂ -A ₄ -A ₈ -A ₁₆) ₄ | 1500 | 19.4 |

Abbreviations: PMMA, poly(methyl methacrylate); THF, tetrahydrofuran.
^aMeasured by RALLS in THF.

Table 5 Hydrodynamic radii and radii of gyration of 3G and 4G dendrimer-like star-branched PMMAs with four branches at the core and either two or four branches at each junction

| Generation | Type | M_w (kg mol ⁻¹) ^a | R_h (nm) ^a | R_g (nm) ^b | R_g/R_h |
|------------|--|--|-------------------------|-------------------------|-----------|
| 3 | (A-A ₂ -A ₄) ₄ | 295 | 10.2 | 11.9 | 1.16 |
| | (A-A ₂ -A ₈) ₄ | 514 | 14.7 | 12.8 | 0.871 |
| | (A-A ₄ -A ₈) ₄ | 568 | 14.9 | 12.5 | 0.839 |
| | (A-A ₄ -A ₁₆) ₄ | 939 | 17.2 | 17.3 | 1.01 |
| 4 | (A-A ₂ -A ₄ -A ₈) ₄ | 661 | 13.9 | 13.6 | 0.978 |
| | (A-A ₂ -A ₈ -A ₃₂) ₄ | 1960 | 18.1 | 18.8 | 1.04 |
| | (A-A ₄ -A ₈ -A ₃₂) ₄ | 1920 | 20.1 | 19.3 | 0.960 |
| | (A-A ₄ -A ₁₆ -A ₃₂) ₄ | 2360 | 24.6 | 20.4 | 0.829 |
| | (A-A ₄ -A ₁₆ -A ₄₆) ₄ | 3960 | 30.2 | | |

Abbreviations: 3G, third generation; 4G, fourth generation; PMMA, poly(methyl methacrylate); SAX, small-angle X-ray scattering; THF, tetrahydrofuran.
^aMeasured by RALLS in THF.
^bMeasured by SAX in THF.

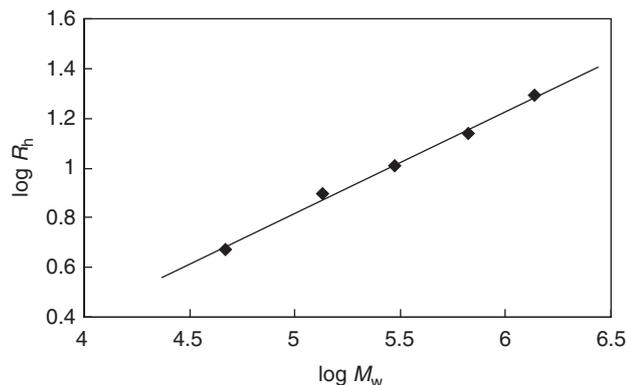


Figure 5 Relationship between $\log M_w$ and $\log R_h$ in a series of DSPs from first generation to fifth generation.

junctions can be altered by adjusting the number of α -SiOMP termini of living PMMA used as the building blocks. The R_h values of the four 3G polymers, (A-A₂-A₄)₄, (A-A₂-A₈)₄, (A-A₄-A₈)₄ and (A-A₄-A₁₆)₄, and the five 4G polymers, (A-A₂-A₄-A₈)₄, (A-A₂-A₈-A₃₂)₄, (A-A₄-A₈-A₃₂)₄, (A-A₄-A₁₆-A₃₂)₄ and (A-A₄-A₁₆-A₄₆)₄ measured by RALLS are listed in Table 5. These polymers are composed of four branches at the cores and either two or four branches between the junctions, and therefore have different M_w values even in the same generation. It was also observed in these polymers that the molecular size increased by increasing the M_w value. As shown in Figure 6, a good linear relationship is obtained by plotting $\log R_h$ against $\log M_w$. Interestingly, the data plotted in Figure 5 fell on the same line. Moreover, the results ($M_w=1.50 \times 10^7$ g mol⁻¹ and $R_h=46.5$ nm) of the 3G higher molecular weight and more densely branched polymer, (A-A_{12,3}-A₁₅₃)₄, also fit well with this line.²⁷ Although the M_w value changes

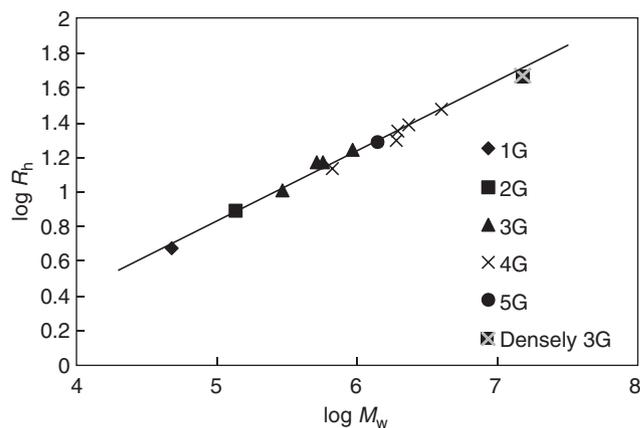


Figure 6 Relationship between $\log M_w$ and $\log R_h$ in DSPs having different branch densities. 1G, first generation; 2G, second generation; 3G, third generation; 4G, fourth generation; 5G, fifth generation.

according to the branched architecture and/or generation, the results shown in both Figures 5 and 6 clearly indicate that the R_h value is strongly correlated with the M_w value, but is not directly reflected in the branched architecture and generation.

The radii of gyration, (R_g), of the 3G and 4G polymers were measured with small-angle X-ray scattering. Similar to the relationship between the R_h and M_w values, it was observed that the R_g value

increased as the M_w value increased (see also Table 5). The ratios of R_g/R_h were between 0.83 and 1.16, which were relatively higher than the value of 0.775 of the Pyun–Fixman prediction, which theoretically represents a compact spherical shape. Curiously, these data are similar to those of previously reported multiarmed star-branched polymers with high segment densities near the cores,^{28,29} although the 3G and 4G DSPs are considered to possess the most shell-weighted density distribution, as estimated from their branched architectures.

SOLUTION VISCOSITY AND BRANCHING FACTOR

To study the solution behavior of DSP, the intrinsic viscosity values, $[\eta]_{\text{DSP}}$ of the two series of dendrimer-like star-branched PMMAs mentioned above were measured in THF at 25 °C.^{2,24} Their $[\eta]_{\text{DSP}}$ values are summarized in Table 6. For comparison, the intrinsic viscosities of linear PMMAs, $[\eta]_{\text{linear}}$ calculated from the Equation $[\eta]_{\text{linear}}=1.11 \times 10^{-2} M_w^{0.695}$, were added in the same table.³⁰ Although both viscosities increased by increasing the molecular weight, the $[\eta]_{\text{DSP}}$ values were always smaller than those of linear polymers with the same molecular weights. As shown in Figure 7, $\log [\eta]_{\text{DSP}}$ gradually increases with $\log M_w$. This trend is rather different from the bell-shaped curves previously reported in dendrimers³¹ and dendrimer-like star-branched PSs.¹⁴

Surprisingly, the $[\eta]_{\text{DSP}}$ values of the four 3G DSPs were close to each other (between 32.2 and 35.2 ml g⁻¹), although their M_w values varied considerably from 2.95×10^5 to 9.39×10^5 g mol⁻¹. For instance, the (A-A₄-A₁₆)₄ polymer was almost equal in $[\eta]$ value to the

(A-A₂-A₄)₄ polymer, whereas the former was three times higher in M_w value than the latter. A similar trend was observed among the 4G DSPs. The $[\eta]$ value of the (A-A₄-A₁₆-A₄₆)₄ polymer was the same as that of the (A-A₂-A₄-A₈)₄ polymer, but the latter sample had only one-sixth of the M_w value of the former sample. Thus, the insensitivity of molecular weight to viscosity seems to be apparent among same generation polymers. This means that the M_w value and branched architecture do not depend on the $[\eta]$ value in the same generation. On the other hand, the dependence of molecular weight as well as generation on viscosity was clearly observed in the polymer series ranging from 1G to 7G, as mentioned above. Even among the 3G and 4G polymers, the intrinsic viscosity shows a discernible increase from the 3G to the 4G polymers, and the 4G polymers 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 structural differences in the DSPs. To understand the relationship between intrinsic viscosity and molecular weight, the viscosities of a series of identically branched architectural DSPs composed of arm segments with different molecular weights should first be measured and compared.

In regular type star-branched polymers, the g' value (the branching factor), defined as $[\eta]_{\text{star}}/[\eta]_{\text{linear}}$ is an important factor in estimating the volume extended in solution by the number of arm segments. The g' value correlates with the number of arm segments and decreases rapidly by increasing the arm number according to the following well-established equation: $g'=[(3f-2)/f^2]^{0.58}[0.724-0.015(f-1)]/0.724$ (f =arm number ($3 < f < 18$)).³² In the case of stars with more than 18 arms, the empirical equation is $\log g'=0.36-0.80 \log f$.³³ Because the $[\eta]_{\text{DSP}}$ values were measured in several DSPs, the g' value was determined in each DSP sample. The results are also summarized in Table 6. As mentioned above, the $[\eta]_{\text{DSP}}$ values were always smaller than those of the corresponding linear polymers because of their branched architectures; therefore, the g' values were less than unity for all polymer samples. In the same polymer series from 1G to 7G, the g' value decreased by increasing the generation from 1G to 7G, indicating that the DSPs are smaller in volume in solution than the corresponding linear polymers, and the trend is emphasized more by increasing the generation. Interestingly, a star-branched polymer is always somewhat smaller in g' value than that of a DSP having the same number of outermost arm segments (see also Table 6). Thus, it seems reasonable to consider that star-branched polymers possess single-branch points, whereas DSPs with generation-based hyper-branched architecture has many branch points.

Table 6 Intrinsic viscosities and g' values of dendrimer-like star-branched PMMAs

| Generation | Type | $M_w(\text{kg mol}^{-1})^a$ | $[\eta] (\text{ml g}^{-1})$ | | g' | |
|----------------|---|-----------------------------|-----------------------------|----------------------------|------------------|--------------------|
| | | | $[\eta]_{\text{DSP}}^b$ | $[\eta]_{\text{linear}}^c$ | DSP ^d | Star |
| 1 ^e | (A ₄) | 14.8 | 6.76 | 8.78 | 0.77 | 0.71 ^g |
| 2 ^e | (A-A ₂) ₄ | 44.2 | 12.5 | 18.8 | 0.66 | 0.46 ^g |
| 3 ^e | (A-A ₂ -A ₄) ₄ | 105 | 16.3 | 34.3 | 0.48 | 0.25 ^g |
| 4 ^e | (A-A ₂ -A ₄ -A ₈) ₄ | 230 | 18.9 | 59.1 | 0.32 | 0.14 ^h |
| 5 ^e | (A-A ₂ -A ₄ -A ₈ -A ₁₆) ₄ | 472 | 22.5 | 97.4 | 0.23 | 0.083 ^h |
| 6 ^e | (A-A ₂ -A ₄ -A ₈ -A ₁₆ -A ₃₂) ₄ | 1060 | 24.0 | 171 | 0.14 | 0.048 ^h |
| 7 ^e | (A-A ₂ -A ₄ -A ₈ -A ₁₆ -A ₃₂ -A ₆₄) ₄ | 1970 | 26.3 | 263 | 0.10 | 0.027 ^h |
| 1 ^f | (A ₄) | 7.0 | 16.7 | 19.6 | 0.85 | 0.71 |
| 2 ^f | (A-A ₂) ₄ | 136 | 26.1 | 41.0 | 0.64 | 0.46 |
| 3 ^f | (A-A ₂ -A ₄) ₄ | 295 | 35.2 | 70.3 | 0.50 | 0.25 |
| 4 ^f | (A-A ₂ -A ₄ -A ₈) ₄ | 661 | 42.2 | 123 | 0.34 | 0.083 |
| 5 ^f | (A-A ₂ -A ₄ -A ₈ -A ₁₆) ₄ | 1500 | 48.6 | 218 | 0.24 | 0.048 |
| 3 ^f | (A-A ₂ -A ₄) ₄ | 295 | 35.2 | 70.3 | 0.50 | 0.25 |
| | (A-A ₂ -A ₈) ₄ | 514 | 33.2 | 103 | 0.32 | 0.14 |
| | (A-A ₄ -A ₈) ₄ | 568 | 32.3 | 111 | 0.29 | 0.14 |
| | (A-A ₄ -A ₁₆) ₄ | 939 | 35.1 | 157 | 0.22 | 0.083 |
| 4 ^f | (A-A ₂ -A ₄ -A ₈) ₄ | 661 | 42.2 | 123 | 0.34 | 0.14 |
| | (A-A ₂ -A ₈ -A ₃₂) ₄ | 1960 | 39.1 | 262 | 0.15 | 0.048 |
| | (A-A ₄ -A ₈ -A ₃₂) ₄ | 1920 | 43.3 | 258 | 0.17 | 0.048 |
| | (A-A ₄ -A ₁₆ -A ₃₂) ₄ | 2360 | 38.1 | 298 | 0.13 | 0.048 |
| | (A-A ₄ -A ₁₆ -A ₄₆) ₄ | 3960 | 42.1 | 427 | 0.099 | 0.023 |

Abbreviations: DSP, dendrimer-like star-branched polymer; PMMA, poly(methyl methacrylate); THF, tetrahydrofuran.

^aMeasured by RALLS in THF.

^bMeasured in THF.

^cCalculated from $[\eta]_{\text{linear}}=1.11 \times M_w^{0.695}$.

^dCalculated from $g'=[\eta]_{\text{DSP}}/[\eta]_{\text{linear}}$.

^eMolecular weight of arm polymer, $M_n \sim 4000$ g mol⁻¹.

^fMolecular weight of arm polymer, $M_n \sim 10\,000$ g mol⁻¹.

^gCalculated from $g'_{\text{star}}=[(3f-2)/f^2]^{0.58}[0.724-0.015 \times (f-1)]/0.724$; f =number of arms ($3 < f < 18$) (Douglas, Roovers and Freed, 1990).

^hCalculated from $\log g'_{\text{star}}=0.36-0.80 \times \log f$; f =number of arms ($6 < f$) (Roovers, 1999).

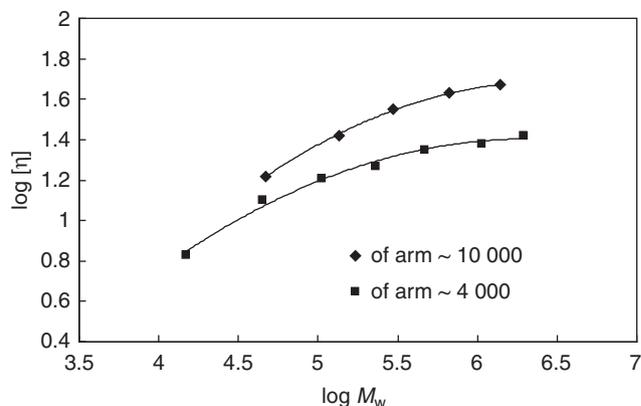


Figure 7 Relationship between $\log M_w$ and $\log [\eta]$ in two series of DSPs.

The relationship between the g' value and the branched architecture (and/or, therefore, molecular weight) is also interesting. As expected, the g' value strongly depends on the branched architecture, even in the same generation, and decreases by increasing the branch density. For instance, the g' value of $(A-A_4)_4$ was found to be smallest among the 2G polymers, $(A-A_2)_2$, $(A-A_2)_4$ and $(A-A_4)_4$. Similarly, increasing the branch density from $(A-A_2-A_4)_2$ to $(A-A_2-A_4)_4$ to $(A-A_4-A_{16})_4$ in the 3G polymers decreased the g' value. The same trend was observed among the 4G polymers. More interesting, the g' value evidently appears to be strongly correlated with the number of branch segments in the outermost layer, even in different generations. For instance, two 3G polymers with 32 outermost branch segments, $(A-A_2-A_8)_4$ and $(A-A_4-A_8)_4$, were close in g' value to a 4G polymer, $(A-A_2-A_4-A_8)_4$, which had the same number of 32 branches in the 4G layer. In fact, these g' values were between 0.29 and 0.34. Moreover, by increasing the outermost branches to 64 in number, the g' value of a 3G polymer, $(A-A_4-A_{16})_4$, was reduced to 0.22 and was consistent even with that ($g'=0.23$) of a 5G polymer, $(A-A_2-A_4-A_8-A_{16})_4$.

Overall, the g' value decreased significantly by increasing the branch density, but it was comparable among polymers having the same number of branches in the outermost layer, even in different generations. Accordingly, most of the data fit well on a curve made by plotting the g' value as a function of the logarithmic outermost branch number, as shown in Figure 8. Although the relationship is not theoretically understood at the moment, the g' value can be readily predicted only by the outermost branch number of DSPs. This suggests that the g' value depends strongly on the branch density at the periphery more than the inside branch density.

MOLECULAR SHAPE OF DSPS

DSPs are believed to be nanosize globular molecules, as estimated by their generation-based branched architectures, molecular models and some analytical results. Recently, high-molecular-weight architectural polymers, such as combs, dendrigrafts, comb-on-stars and comb-on-cyclic polymers, have been successfully visualized by atomic force microscopy (AFM) measurements.^{34–39} The shapes observed by AFM imaging are actually similar to those that were expected or imagined. More interesting, the presence of several byproducts could be observed by their AFM images. Dendrimers have also been visualized as spherical dome-shaped molecules by AFM and STM.^{40,41} Thus, AFM has currently become a valuable tool for directly visualizing molecular shapes of structurally complex architectural polymers.

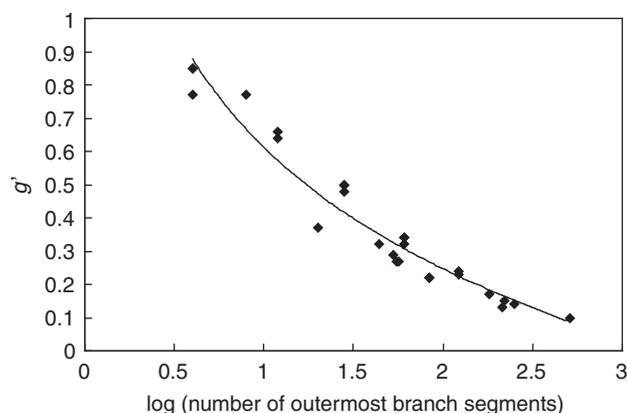


Figure 8 Relationship between log (number of outermost branch segments) and log g' .

Because some samples of high-molecular-weight DSPs that are synthesized in this study have AFM-measurable sizes, Deffieux and colleagues attempted to visualize the 4G dendrimer-like star-branched PMMA, $(A-A_4-A_{16}-A_{46})_4$ ($M_n=3.96 \times 10^6 \text{ g mol}^{-1}$, $M_w/M_n=1.08$), by AFM tapping mode on highly ordered graft.²⁴ This polymer possesses four branches at the core, as well as in the 2G and 3G layers, but has three branches on average in the 4G layer. Contrary to the expectation, however, flattened objects with an average square size close to 100 nm and a height of only 1.6 nm were observed as isolated molecules on the AFM image. Because this polymer was estimated to have a diameter of 60 nm in THF from the R_h value, the average size observed by the AFM is too large and the height is too small. Such a difference may be explained by the speculation that the polymer molecule is spread out on the highly ordered graft and sticks flatly on the graphite surface due to the low polymer compactness and strong interaction between the polymer and the surface, as is often observed in vinyl polymers by AFM measurements. It is thus considered that the synthesis of a DSP having more compactness is needed to visualize the real shape of the DSP with AFM.

Recently, we developed a new ready-made procedure by employing a SiOMP-functionalized living AB diblock copolymer as a building block. With this procedure, a higher molecular weight ($1.43 \times 10^7 \text{ g mol}^{-1}$) dendrimer-like star-branched PS with more branches (12 branches, which makes it denser and tougher) was successfully synthesized.²⁷ The R_g and R_h values were determined to be 46.7 and 46.5 nm, respectively. Direct visualization of this polymer sample was conducted by similar AFM analysis on highly ordered graft in the light-tapping mode. Deposits of the sample were obtained by spin casting their CH_2Cl_2 solution on graphite plates.

The samples appear on topographic AFM images as completely flattened objects with a homogeneous and symmetrically square or rectangular shape, as shown in Figure 9. These were similar in shape to those of the previous sample just mentioned above. The sample shows an average diagonal size of 250 nm and a height of <1 nm. The low value for the height is consistent with the spreading out of the polymer molecule as a monolayer on the highly ordered graft, which suggests that most of the PS aromatic rings are lying flat on the graphite surface because of their still low compactness and strong interactions. A rough calculation of the diameter of the 3G polymer in a fully extended conformation, considering the sum of the polymerization degrees of different generations, that is, $D=0.25 \times 2(243+225+224)=346$ nm, is in agreement with the

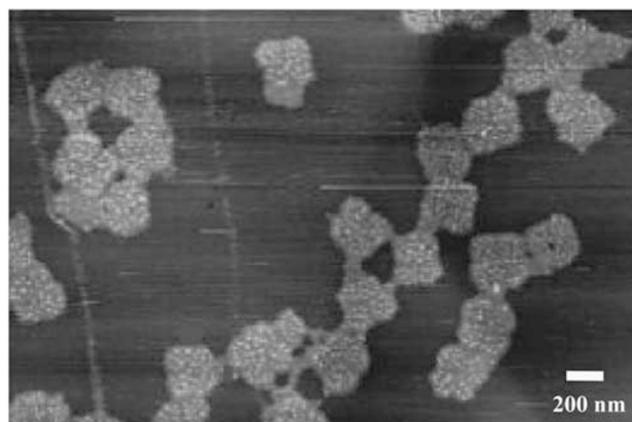


Figure 9 Atomic force microscopy images of a third generation dendrimer-like star-branched PS. General view.

measured value, which strongly confirms the spreading of the polymer molecule.

Among the polymer molecules observed, a large number clearly appear to consist of four interconnected lobes. This corresponds to the building of the DSP in four substructures issued from the tetrafunctional core. Interestingly, an image of the magnified polymer molecules, as shown in Figure 10, shows the presence inside the object of a large number of regularly distributed white spots that correspond to more compact and harder zones in the polymer molecule. Their numbers, around 50 per polymer, closely correspond to the calculated 52 connecting domains between the 1G and 2G (4) and 2G and 3G (48) layers. In the cross-section given as an inset in the same figure, the harder domains appear as a series of peaks of about two times the height of the less dense and softer domains constituted by the PS branches. This particular topology is highlighted in three-dimensional image in Figure 11, in which the harder domains appear as white peaks in contrast to the less dense and softer PS domains. This represents one of the first examples of direct visualization of the internal structure of a macromolecular dendrimer. Thus, even the high-molecular-weight and more densely branched dendrimer-like star-branched PS is still too soft; therefore, tougher polymers with cross-linking or the introduction of rigid polymer segments are needed for AFM analysis.

Two more 3G dendrimer-like star-branched PSs were synthesized by developing the same methodology with the use of either difunctional or trifunctional core compounds, as mentioned above in the preceding section. AFM images of such polymers under the tapping same mode are shown in Figure 12. As one can see, either two or three lobes interconnected to each other are clearly observed. This provides additional evidence that these lobes correspond to the substructures issuing from the difunctional and trifunctional cores.

Ree and colleagues recently reported synchrotron small-angle X-ray scattering studies of 3G $(A-A_2-A_4)_4$ and 4G $(A-A_2-A_8-A_{32})_4$ polymers, showing that these polymers have ellipsoidal shapes composed of a core and a shell, where the core has a higher density than the shell.⁴² This indication is also quite different from the molecular shapes that would be imagined. Detailed small-angle X-ray scattering studies are expected to characterize the shapes of DSPs, and such investigations are currently underway.

CONCLUSIONS

This article reviews the precise synthesis of a variety of DSPs and DSBPs by stepwise iterative methodologies in conjunction with pre-made living anionic polymers based on the 'arm-first' divergent

approach focusing on the control of synthetic factors necessary for well-defined and precisely controlled structures of the polymers, that is, molecular weight, molecular weight distribution, number of arm segments and composition. With the first developed methodology, well-defined and well-characterized DSPs up to the 7G stage with M_n values of a few million and with M_w/M_n values of < 1.05 have been successfully synthesized. Their branched architectures can be varied to a certain extent, and a variety of functional polymer segments can be introduced into any generation to add desirable functionalities. Moreover, intermediate and/or final polymers usually have numerous

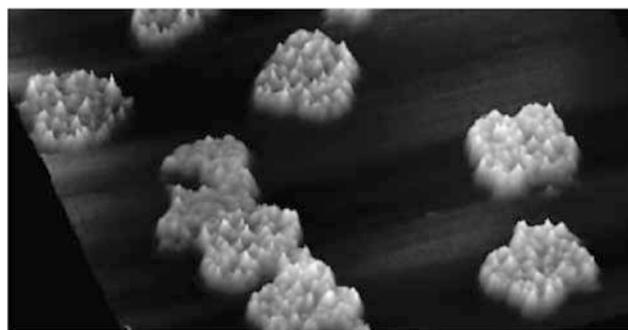


Figure 11 Atomic force microscopy image of a third generation dendrimer-like star-branched PS. Three-dimensional image showing the presence and distribution of hard (higher part) and soft (lower part) domains.

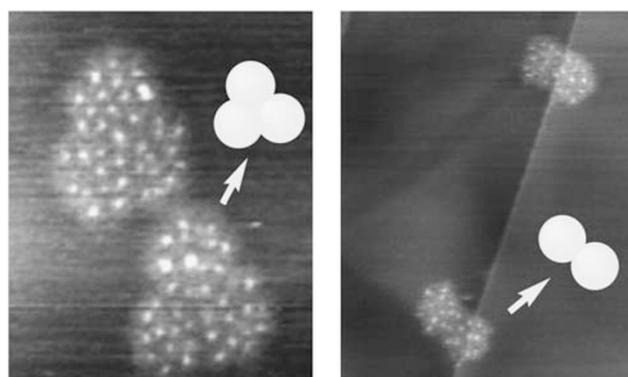


Figure 12 Atomic force microscopy image of a third generation dendrimer-like star-branched PSs with either three- or two-branched cores.

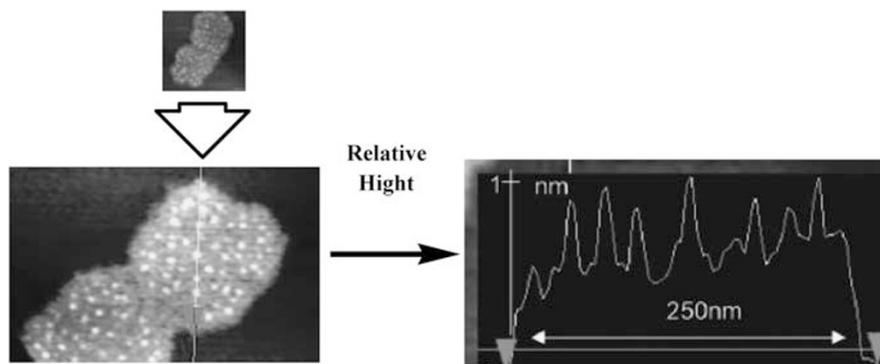


Figure 10 Atomic force microscopy image of a third generation dendrimer-like star-branched PS. Magnified objects and cross-section of the DSP showing the relative height.

highly reactive BnBr termini at their peripheries that are capable of continuing the next iterative reaction step, and it is also possible to introduce many useful functional groups and molecules via such BnBr termini. The second developed methodology, which uses a SiOMP-functionalized living AB diblock copolymer as the building block, allows for the successful synthesis of DSPs with higher molecular weights (up to $1.43 \times 10^7 \text{ g mol}^{-1}$) and with more branches (12 in this case) than were achievable with the first methodology, although the number of branch segments is not exact, rather it is defined on average by the living anionic polymerization of the B segment.

DSPs are well-defined large macromolecules with regulated hyperbranched architectures, specific nanosize shapes, many controllable structural variables and appropriately functionalized segments in any generation and at the peripheries (or termini). Different segments and functional groups may be phase separated at the molecular level, then self-organized, to form quite new nanosize ordered suprastructures and supramolecular assemblies. Thus, such functionalized DSPs and DSBP are anticipated to have many practical applications, especially in nanoscience and nanotechnology. Several preliminary applications have appeared in papers by Gnanou and colleagues⁴ and Hedrick *et al.*⁴³ The basic properties and behavior of DSPs have not been characterized thoroughly enough, and related morphological and rheological studies have just begun at the present time.^{44–46} As mentioned above, the direct visualization by AFM of the real shapes of the DSPs has not been successful yet, although important information on the internal structure has been obtained. Accordingly, it is time to clarify the whole image of DSPs by developing further analytical and physical studies.

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