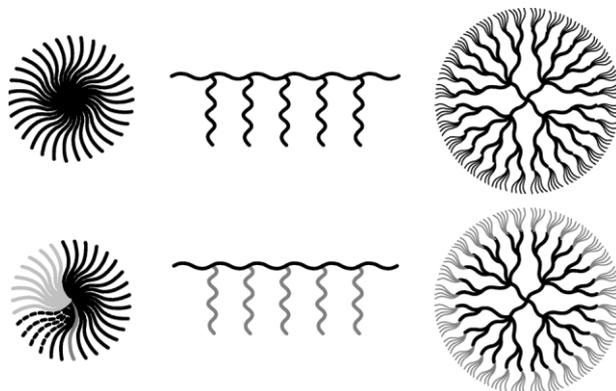


# Combining Living Anionic Polymerization with Branching Reactions in an Iterative Fashion to Design Branched Polymers

Tomoya Higashihara, Kenji Sugiyama, Hee-Soo Yoo, Mayumi Hayashi, Akira Hirao\*

This paper reviews the precise synthesis of many-armed and multi-compositional star-branched polymers, exact graft (co)polymers, and structurally well-defined dendrimer-like star-branched polymers, which are synthetically difficult, by a commonly-featured iterative methodology combining living anionic polymerization with branching reactions to design branched polymers. The methodology basically involves only two synthetic steps; (a) preparation of a polymeric building block corresponding to each branched polymer and (b) connection of the resulting building unit to another unit. The synthetic steps were repeated in a stepwise fashion several times to successively synthesize a series of well-defined target branched polymers.



## Introduction

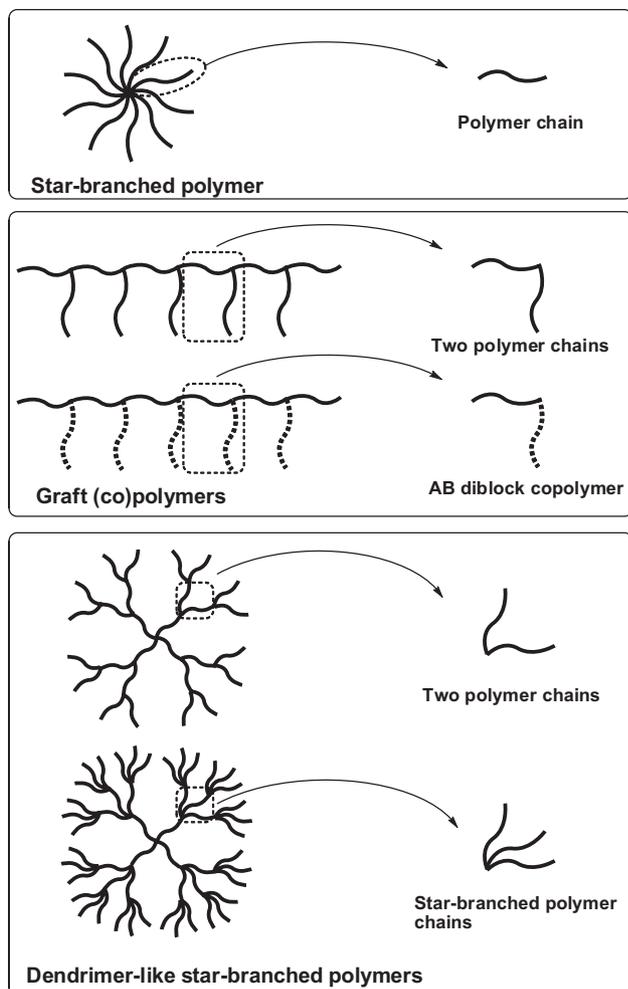
Star-branched polymers, graft (co)polymers, and dendrimer-like star-branched polymers are representative branched polymers and characterized by the number and position of the branch point. These polymers have been widely studied for a long time because of their interesting properties and behavior in the solution, melt, and solid states, different from corresponding linear polymers as well as their synthetic challenge.<sup>[1–6]</sup> In the case of branched polymers consisting of chemically different chains, these chains are generally thermodynamically immiscible to

exhibit unique phase and morphological behavior due to the characteristic branched architectures, resulting in the formation of periodically ordered nanostructures and molecular assemblies that have many potential applications in the fields of nanoscience and technology, similar to cases using block copolymers.<sup>[7–11]</sup>

In order to fundamentally understand the effect of chain branching on polymer properties, behavior, and morphology, the synthesis of branched polymers with well-defined structures and low degrees of compositional heterogeneity is essential. Unfortunately, however, the synthesis of well-defined branched polymers has been difficult even now and met limited success. Moreover, a variety of synthetic methodologies for such branched polymers so far developed are individually and specially designed on the basis of their own branched architecture.

The objective in this paper is to propose a novel commonly-featured methodology applicable to any of

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■ Scheme 1. Repeating units of branched polymers.

the three branched polymers and possibly other branched polymers with well-defined structures and to demonstrate the possible syntheses. From an architectural point of view, these polymers have their own polymeric building units and are made up of many units stretched throughout the polymer molecules as a common feature and, therefore, can possibly be synthesized by assembling them from their own building units in a stepwise iterative fashion. Let us consider the synthetic methodology of these branched polymers based on their building blocks. As shown in Scheme 1, a one-polymer chain, two-polymer chain (or AB diblock copolymer chain), and another two-polymer chain (or star-branched polymer chain) correspond exactly to the polymeric building units for star-branched polymers, graft (co)polymers, and dendrimer-like star-branched polymers, respectively. These units should have reactive functional groups capable of connecting to another unit at appropriate position(s), such as chain-end and in-chain positions. In order to synthesize branched polymers, the building unit is



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**Hee-Soo Yoo** was born in Seoul, Korea in October 29th, 1978. He received his Bachelor Degree (2005) in polymer Science and Engineering at Sungkyunkwan University, Korea, and Master Degree (2007) in Materials Science and Engineering under the supervision of Professor Jae-Suk Lee at Gwangju Institute of Science and Technology, Korea. He is currently a doctor course graduate student at Tokyo Institute of Technology, and doing research on precise synthesis of dendrimer-like star-branched polymers with well-defined structures via an iterative approach based on living anionic polymerization under the supervision of Professor Akira Hirao.



**Akira Hirao** received his Doctorate Degree from Tokyo Institute of Technology, Japan in 1975. During 1975–1977, he joined the group of Professor Charles U. Pittman, Jr. at the University of Alabama, USA, as a postdoctoral fellow. Then he became an Assistant Professor (1977), Associate Professor (1983), and Full Professor (1997) at Tokyo Institute of Technology. Therein, he has published more than 300 papers in refereed scientific journals and 35 books and reviews. His research covers living anionic polymerization of functional monomers and specially-shaped polymers including regular and asymmetric star-branched, comb-like, dendrimer-like star-branched, and exact graft polymers with well-defined structures.

first prepared and the resulting unit is connected to another unit in the second step. This synthetic sequence involving two steps, the so-called “*iterative process*,” is performed a number of times in a stepwise fashion to build-up the desired branched polymer. The reaction product synthesized by this iterative process automatically becomes the starting material of the next reaction product. Thus, the number of building units in the branched polymer increases simply by performing the same iterative process. As a result, a series of branched polymers composed of

many building units can be successively synthesized. Needless to say, highly reactive, selective, and quantitative reactions are required in the synthetic sequence to continue the iteration many times.

The choice of a living polymerization system is the other essential factor in order to synthesize branched polymers with well-defined structures. Although various living polymerization systems via different mechanisms have been developed, especially in the past 25 years,<sup>[12–25]</sup> the living anionic polymerization of styrene, 1,3-butadiene, isoprene, 2-vinylpyridine, methyl methacrylate (MMA),<sup>[26]</sup> and their derivatives with certain functional groups<sup>[27]</sup> are still the best systems due to the following features: (i) molecular weight can be precisely controlled in a wide range from  $10^2$  to even  $10^6 \text{ g} \cdot \text{mol}^{-1}$ , (ii) extremely narrow molecular weight distributions are attained, the  $\overline{M}_w/\overline{M}_n$  values being less than 1.05 or even smaller, and (iii) their living anionic polymers have highly reactive chain-end carbanions or enolate anions which are capable of reacting with various electrophiles in high yields, but stable enough for a long time under appropriate conditions. Even at the present time, such features have never been realized with any other living polymerization systems. These characteristics are ideally suited for the synthesis of branched polymers with well-defined structures. Thus, our description herein is confined to branched polymers built up by using the above-mentioned living anionic systems, unless otherwise stated.

In this paper, we report on the synthetic possibility of many-armed and multi-compositional star-branched polymers, exact graft (co)polymers, and structurally well-defined dendrimer-like star-branched polymers, which

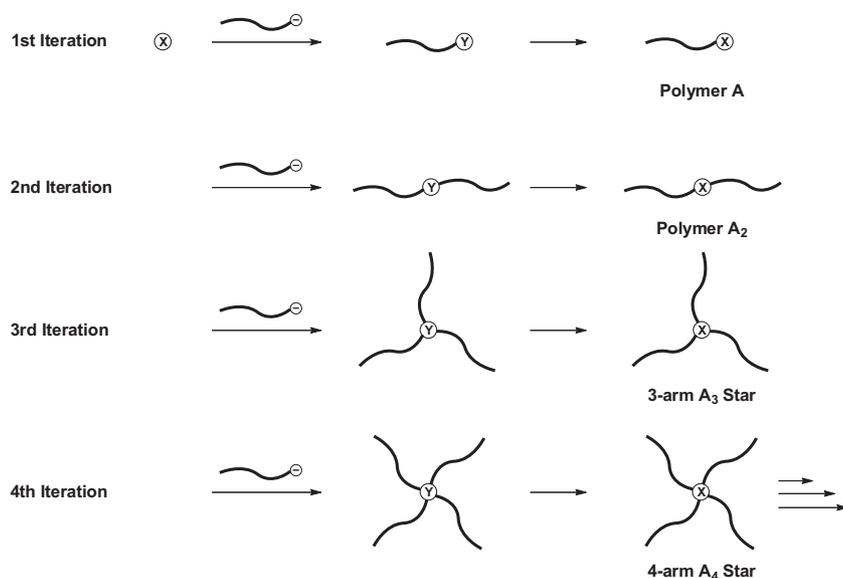
are synthetically difficult, by developing a novel commonly-featured methodology combining living anionic polymerization with branching reactions to in an iterative fashion to design branched polymers.

## Star-Branched Polymers

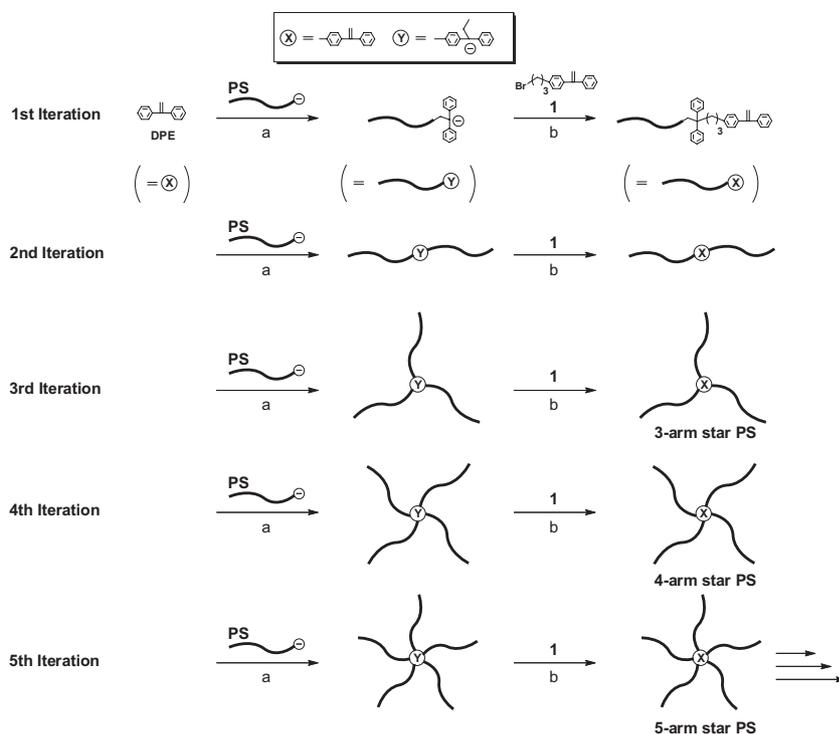
The physical properties, behavior, and morphologies of star-branched polymers are dominated and dramatically changed by the number of identical or different arm segments.<sup>[28–44]</sup> Although many star-branched polymers with well-defined structures have so far been synthesized,<sup>[28–39,45–87]</sup> most of them are composed of less than five arms in regular stars and less than three chemically different arms in asymmetric stars. Thus, the availability of many armed and compositional star-branched polymers is quite limited.

In order to efficiently synthesize a variety of many armed and compositional star-branched polymers, we have demonstrated a new methodology based on the iterative approach, which is very effective for such synthetic purposes.<sup>[88–90]</sup> Although we briefly mentioned in the introduction that one polymer chain with a functional group is a polymeric building unit of a star-branched polymer, a more detailed synthetic design is needed to realize the stepwise iterative methodology. As illustrated in Scheme 2, there are two functionalities, “X” and “Y,” which are designed as follows: in the first step of the synthetic sequence, X quantitatively reacts with a living anionic polymer to link the polymer chain, and X is changed to Y. The resulting Y is designed to be able to convert to X in the second step. The X thus regenerated can

be used as the next reaction site, capable of reacting with a living anionic polymer and, accordingly, the same iterative process involving the two reaction steps can be performed, resulting in 3-arm, 4-arm, and so on to many armed star-branched polymers with an increase one by one in the number of polymer chains to be linked. Thus, the regeneration of X is the key point to continue the iterative process in the methodology. The methodology also allows access to the synthesis of asymmetric star-branched polymers by linking a different living anionic polymer in each process. Accordingly, a variety of more complex star-branched polymers with many arms and/or compositions can be successively synthesized by performing the two reaction steps in the iterative process.



**Scheme 2.** Synthetic methodology for a series of star-branched polymers based on iterative approach.



**Scheme 3.** Synthesis of regular star PSs by iterative methodology using DPE functionality and DPE-derived anion as “X” and “Y” functionalities.

### Iterative Methodology Using 1-(4-(4-Bromobutyl)phenyl)-1-phenylethylene

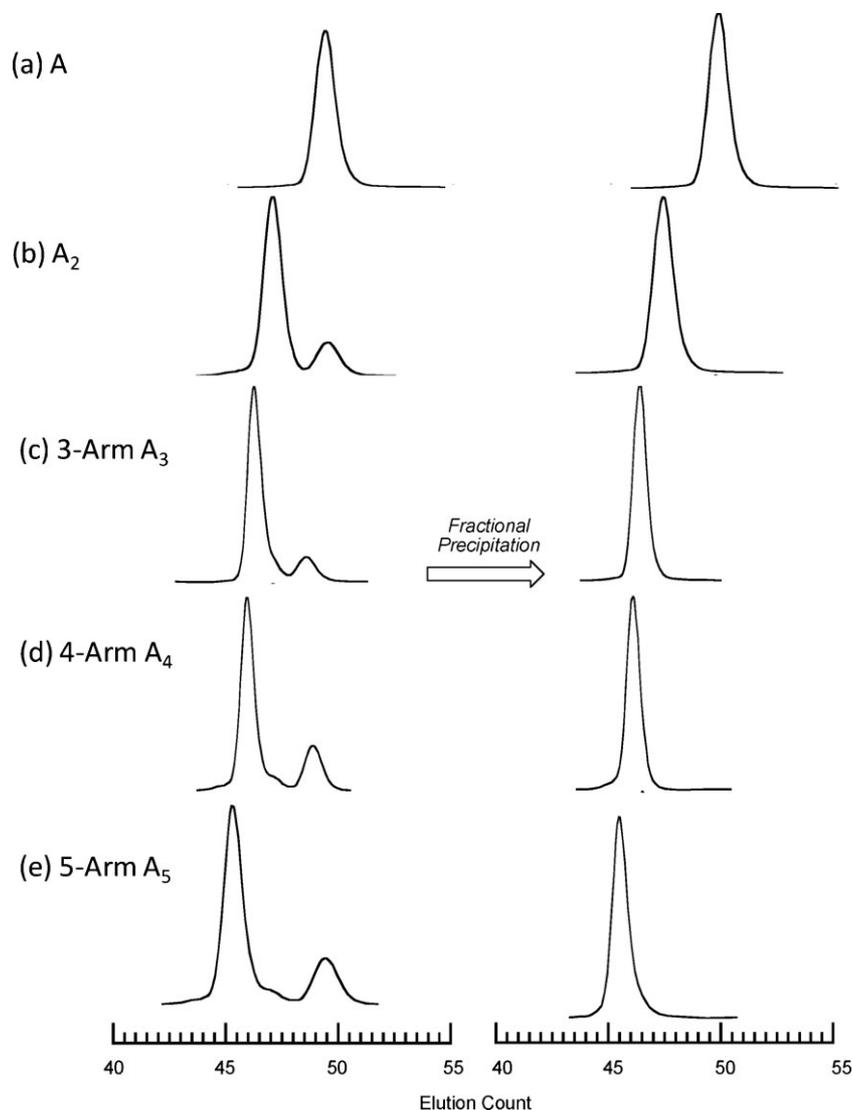
The first successful iterative methodology is illustrated in Scheme 3. This is based on the chemistry of 1,1-diphenylethylene (DPE) toward anionic species and 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene (**1**) is used as the key agent to regenerate the DPE functionality.<sup>[91–93]</sup> The following two reaction steps are employed for the iterative synthetic sequence: (a) a 1:1 addition reaction of a living anionic polymer to either DPE (first iteration) or a DPE-functionalized polymer to link the polymer chains, and (b) an in situ reaction of **1** with the DPE-derived anion produced at the linking point by the (a) step to regenerate the DPE functionality used as the next reaction site. By doing the iterative process involving the two reaction steps, the number of arms increases one by one. Accordingly, the DPE functionality and DPE-derived anion correspond to the X and Y functionalities shown in Scheme 2. In order to examine the effectiveness of this iterative methodology, the successive synthesis of regular star polystyrenes [(PS)s] was first carried out.

In the first step of the synthetic sequence, polystyryllithium (PSLi) reacted with chain-end-DPE-functionalized PS to link the two PS chains. As a new DPE-derived anion was produced by the linking reaction, **1** was in situ reacted with the anion in the second step. As is well known, a DPE-

derived anion cannot react with a DPE function at all under normal conditions because of steric hindrance and the high ceiling temperature. Therefore, the anion selectively reacted with the 4-bromobutyl substituent of **1** to introduce the DPE function between the two PS chains. Since the DPE functionality was thus regenerated, the same synthetic sequence involving (a) and (b) could be repeated. In practice, the synthetic sequence (or iterative process) was done three more times to successively synthesize 3-arm A<sub>3</sub>, 4-arm A<sub>4</sub>, and 5-arm A<sub>5</sub> star-branched (PS)s.

The SEC profiles of the reaction mixture and the isolated polymer at each iterative process are shown in Figure 1. As can be seen, the reaction mixture always shows two distinct peaks corresponding to the linked product and the PSLi used in excess in the reaction, and the linked product isolated by fractional precipitation exhibits a narrow monomodal distribution in each case. The linking efficiency in the (a) step in each iteration was

confirmed to be nearly quantitative by comparing the two peak areas in the SEC profile of the reaction mixture. A 1.5-fold excess of PSLi for the DPE function was used to drive the addition reaction to completion in THF at  $-78^\circ\text{C}$  and the linked product was always isolated in  $>80\%$  yields by fractional precipitation. The results are summarized in Table 1. The molecular weights measured by VPO and SLS agreed quite well with those calculated and narrow molecular weight distributions ( $\overline{M}_w/\overline{M}_n \leq 1.02$ ) were attained in all polymer samples. In order to evaluate the number of arm segments, their branching factors of  $g'$  values, defined as the ratio of  $[\eta]_{\text{linear}}$  to  $[\eta]_{\text{star}}$ , were determined and observed to be completely consistent with those calculated from the theoretical equation.<sup>[94]</sup> All of the analytical results clearly showed that the resulting polymers all possessed the expected and well-defined 3-, 4-, and 5-arm star-branched (PS)s. Thus, the iterative methodology works as desired to successively synthesize 3-, 4-, and 5-arm star (PS)s. Importantly, PSLi quantitatively undergoes the 1:1 addition reaction with the DPE-functionality and further more addition occurs at all. Moreover, the 4-bromobutyl group of **1** selectively and quantitatively reacts with the DPE-derived anion to regenerate the DPE functionality. Since the final 5-arm star PS had the same DPE functionality at the core, the same reaction sequence could be repeated to afford a 6-arm star and so on to stars with more arms.



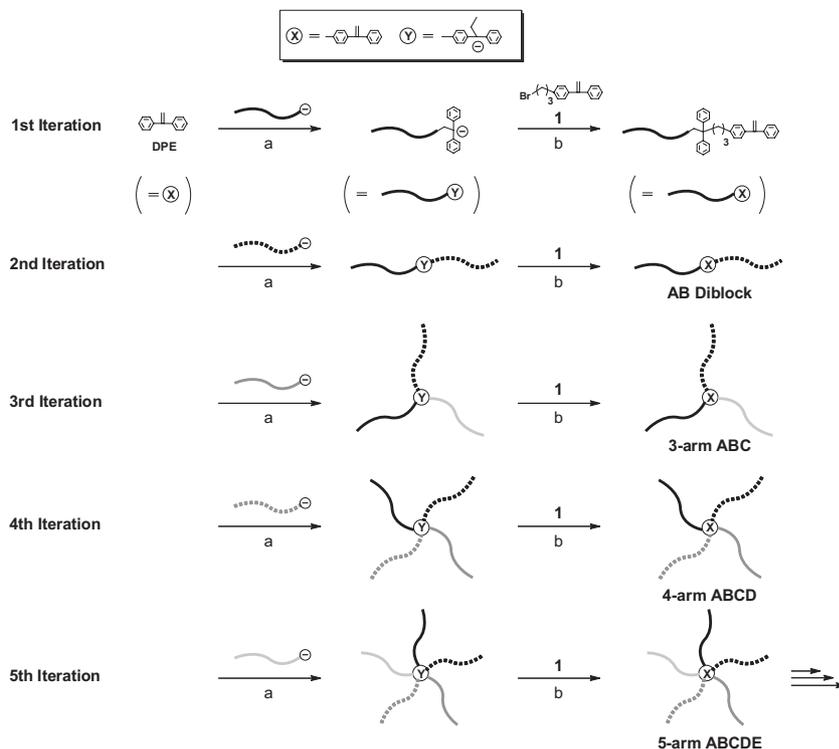
**Figure 1.** SEC profiles of the reaction mixtures and the isolated polymers: chain-end-DPE-functionalized PS (A) (a) and in-chain-DPE-functionalized PS ( $A_2$ ) (b), 3-arm  $A_3$  (c), 4-arm  $A_4$  (d), and 5-arm  $A_5$  (e) star-branched PSs.

**Table 1.** Synthesis of chain-end-DPE-functionalized PS (A), in-chain-DPE-functionalized PS ( $A_2$ ), 3-arm  $A_3$ , 4-arm  $A_4$ , and 5-arm  $A_5$  star-branched PSs by iterative methodology using **1**.

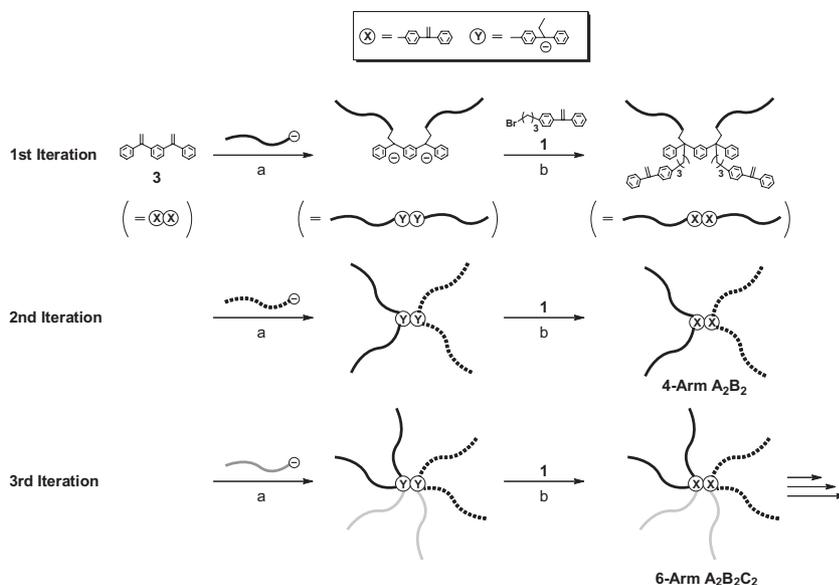
| Type  | $\bar{M}_n$                       |      |      | $\bar{M}_n$                       |                    | $\bar{M}_w/\bar{M}_n$ | DPE-Functionality |                   | $g'$  |       |
|-------|-----------------------------------|------|------|-----------------------------------|--------------------|-----------------------|-------------------|-------------------|-------|-------|
|       | $\text{kg} \cdot \text{mol}^{-1}$ |      |      | $\text{kg} \cdot \text{mol}^{-1}$ |                    |                       | Calcd             | $^1\text{H NMR}$  | Calcd | Exptl |
|       | Calcd                             | SEC  | VPO  | Calcd                             | SLS                | SEC                   |                   |                   |       |       |
| A     | 10.3                              | 10.4 | 10.5 | 10.5                              | 10.6 <sup>a)</sup> | 1.02                  | 1                 | 1.0 <sub>3</sub>  | –     | –     |
| $A_2$ | 21.5                              | 21.4 | 21.0 | 21.9                              | 21.8 <sup>a)</sup> | 1.02                  | 1                 | 0.96 <sub>6</sub> | –     | –     |
| $A_3$ | 30.9                              | 28.9 | 31.1 | 31.5                              | 34.7               | 1.02                  | 1                 | ca. 1             | 0.83  | 0.84  |
| $A_4$ | 42.4                              | 39.1 | 45.1 | 43.3                              | 44.1               | 1.02                  | 1                 | ca. 1             | 0.71  | 0.73  |
| $A_5$ | 53.0                              | 48.1 | 53.0 | 54.1                              | 55.0               | 1.02                  | 1                 | ca. 1             | 0.63  | 0.64  |

<sup>a)</sup>Measured by SEC.

On the basis of the successful synthesis of regular star PS, the methodology was applied to the successive synthesis of asymmetric star-branched polymers, as illustrated in Scheme 4, where a different living anionic polymer was used in step (a) of each iterative process. By performing the iterative process four times, an AB diblock copolymer plus 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE asymmetric stars were successively synthesized. Similar to the synthesis of regular star (PS), the asymmetric stars were almost quantitative in yield and isolated in >80% yields by fractional precipitation. Typically, the A, B, C, D, and E arms were poly(4-trimethylsilylstyrene) (PMSiS), poly(4-methoxystyrene) (PMOS), poly(4-methylstyrene) (PMS), PS, and poly(4-*tert*-butyldimethylsilyloxystyrene) (PTBDMSiOS), completely convertible to poly(4-vinylphenol). Excellent agreement between the molecular weights observed and calculated as well as the compositions observed and calculated clearly indicate that the iterative methodology also effectively works to successively synthesize a series of asymmetric star-branched polymers from 3-arm ABC to 4-arm ABCD and 5-arm ABCDE types. Living anionic polymers of isoprene and 1,3-butadiene can also be used in this iterative methodology. The 5-arm ABCDE star herein synthesized is the first successful asymmetric star-branched polymer composed of five different arms. Very recently, the



**Scheme 4.** Synthesis of asymmetric star-branched polymers by iterative methodology using DPE functionality (X) and DPE-derived anion (Y).



**Scheme 5.** Synthesis of asymmetric star-branched polymers by iterative methodology using **3** and **1**.

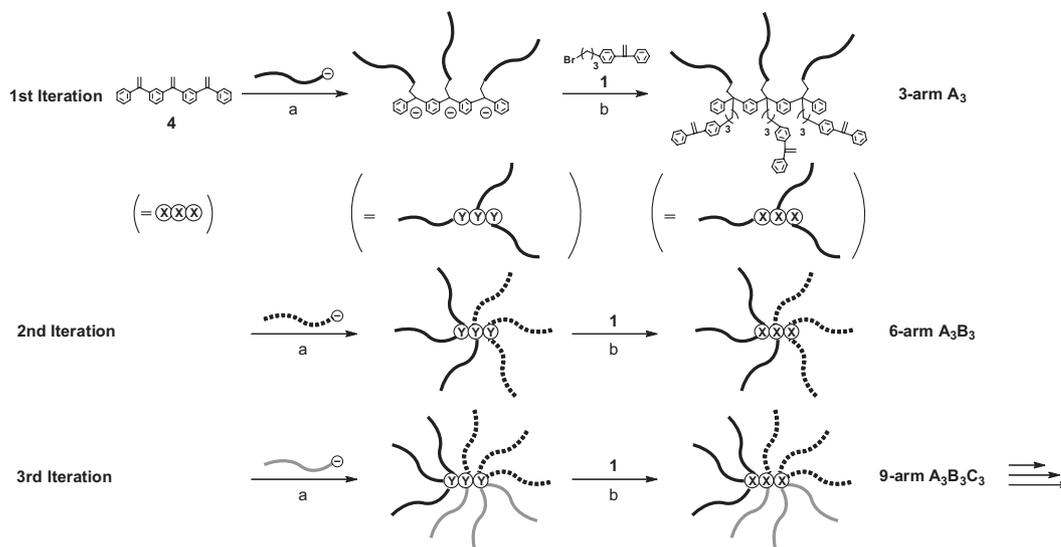
synthesis of a 6-arm ABCDEF asymmetric star was successfully synthesized by developing the same iterative methodology using 4-methylene-5-hexenyl bromide (**2**) instead of **1**.<sup>[95]</sup>

### Iterative Methodology Using 1,3-Bis(1-phenylethenyl)benzene and **1** or 1,1-Bis(3-(1-phenylethenyl)phenyl)ethylene and **1**

The number of arm segments increases one by one as the iterative process proceeds in the methodology, as mentioned above. Herein, the methodology designed in such a way that the number of arm segments increases two by two by performing the iterative process is described.<sup>[96,97]</sup> For this purpose, 1,3-bis(1-phenylethenyl)benzene (**3**) is used as the starting core compound, as illustrated in Scheme 5.

The addition reaction of two equivalents of a living anionic polymer to **3** resulted in the linking of two polymer chains with the production of two DPE-derived anions at the linking points. Two DPE functionalities were readily regenerated by the in situ reaction of **1** with the two DPE-derived anions. The in-chain-(DPE)<sub>2</sub>-functionalized polymer thus prepared was reacted with two equivalents of another living anionic polymer, followed by in situ treatment with **1**, to afford a 4-arm A<sub>2</sub>B<sub>2</sub> asymmetric star-branched polymer with two DPE functionalities at the core. The repetition of the same reaction sequence one more time resulted in a 6-arm A<sub>2</sub>B<sub>2</sub>C<sub>2</sub> star-branched polymer with two core-functionalized DPE moieties. Thus, the number of arm segments was increased two by two in each iterative process by using **3**.

With the use of 1,1-bis(3-(1-phenylethenyl)phenyl)ethylene (**4**) as the starting core compound in the same iterative methodology, it was possible to increase the number of arms three by three by performing the iterative process, as shown in Scheme 6.<sup>[98]</sup> 3-Arm A<sub>3</sub>, 6-arm A<sub>3</sub>B<sub>3</sub>, and more complex 9-arm A<sub>3</sub>B<sub>3</sub>C<sub>3</sub> asymmetric star-branched polymers were successfully synthesized. In addition, 3-, 6-, 9-, 12-, and even 15-arm regular star (PS)s could be successively synthesized by doing the iterative process five times with PSLi. This clearly indicates that there is no steric hindrance even with the introduction of up to 15 arms in the present system. All of



■ Scheme 6. Synthesis of asymmetric star-branched polymers by iterative methodology using **4** and **1**.

the star-branched polymers synthesized by the iterative methodology using either **3** or **4** in addition to **1** were confirmed by the characterization results to be well-defined in branch structure. Thus, the iterative methodology with either **3** or **4** as the core compound also works satisfactorily. Once again, the DPE functionality and DPE-derived anion are assigned to X and Y, illustrated in Scheme 2.

#### Iterative Methodology Using 3,5-Bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide

For increasing the number of arms at each stage by less repetition of the process, 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide (**5**) was newly synthesized and employed in step (b) instead of **1** in the same iterative methodology.<sup>[99,100]</sup> This agent, **5**, is designed to be capable of regenerating two DPE reaction sites via one DPE-derived anion and therefore the reaction site increases exponentially with the iterative process. The synthesis of a series of many-armed star-branched (PS)s was carried out by the iterative methodology with the use of **5**, as outlined in Scheme 7. The methodology is the same as that developed above, which involves only two reaction steps for the linking of arm segments and regeneration of a DPE reaction site in each iteration process.

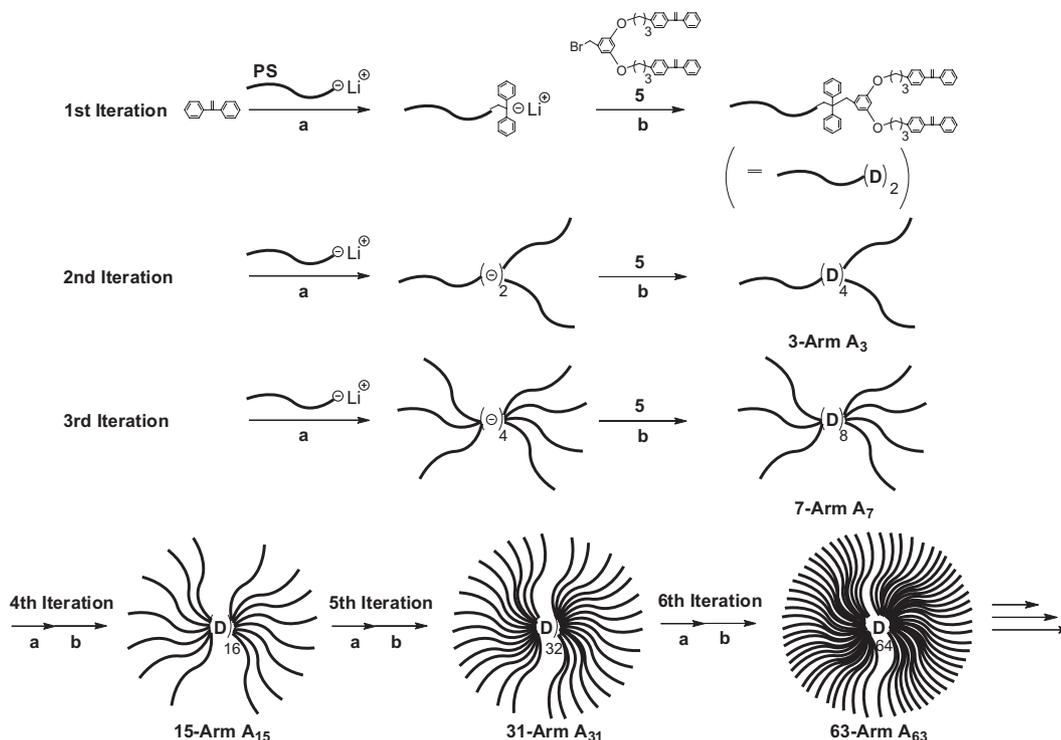
The starting chain-end-(DPE)<sub>2</sub>-functionalized PS was prepared by the reaction of **5** with PSLi end-capped with DPE and then reacted with two equivalents of PSLi to link two PS chains. Subsequently, **5** was in situ reacted with the two DPE-derived anions produced by the linking reaction to introduce four DPE moieties as the next reaction sites. Thus, the desired core-(DPE)<sub>4</sub>-functionalized 3-arm star PS was

quantitatively synthesized. The second and third iterative processes also proceeded essentially quantitatively to afford core-(DPE)<sub>8</sub>-functionalized 7-arm star PS and then core-(DPE)<sub>16</sub>-functionalized 15-arm star PS. Their well-defined structures were confirmed by the analytical results listed in Table 2. The iterative process was further performed to successively synthesize core-(DPE)<sub>32</sub>-functionalized 31-arm star PS and core-(DPE)<sub>64</sub>-functionalized 63-arm star PS. Figure 2 shows the SEC profiles of the reaction mixtures and the isolated polymers.

Since the synthetic ability of **5** to dramatically increase the number of arms was obvious, the same methodology was applied to the synthesis of many-armed asymmetric star-branched polymers (Scheme 8). The living anionic polymers used in the synthesis were PSLi, P $\alpha$ MSLi, PMSLi, PMOSLi, and PMSiSLi. All of the iterative processes could be done without any difficulty under the same conditions and the desired asymmetric stars were synthesized essentially quantitatively. The well-defined and expected structures of the desired 3-arm AB<sub>2</sub>, 7-arm AB<sub>2</sub>C<sub>4</sub>, 15-arm AB<sub>2</sub>C<sub>4</sub>D<sub>8</sub>, and 31-arm AB<sub>2</sub>C<sub>4</sub>D<sub>8</sub>E<sub>15</sub> stars with a high degree of homogeneity in molecular weight and composition were confirmed by all of the analytical results summarized in Table 6. Accordingly, the iterative methodology using **5** is also effective for the successive synthesis of a series of many-armed asymmetric star-branched polymers.

#### Iterative Methodology Using 1-(3-tert-Butyldimethylsilyloxymethylphenyl)-1-phenylethylene

In all of the iterative methodologies described above, the DPE functionality(ies) corresponded to X and could be



■ Scheme 7. Synthesis of star-branched PS with up to 63 arms by iterative methodology using 5.

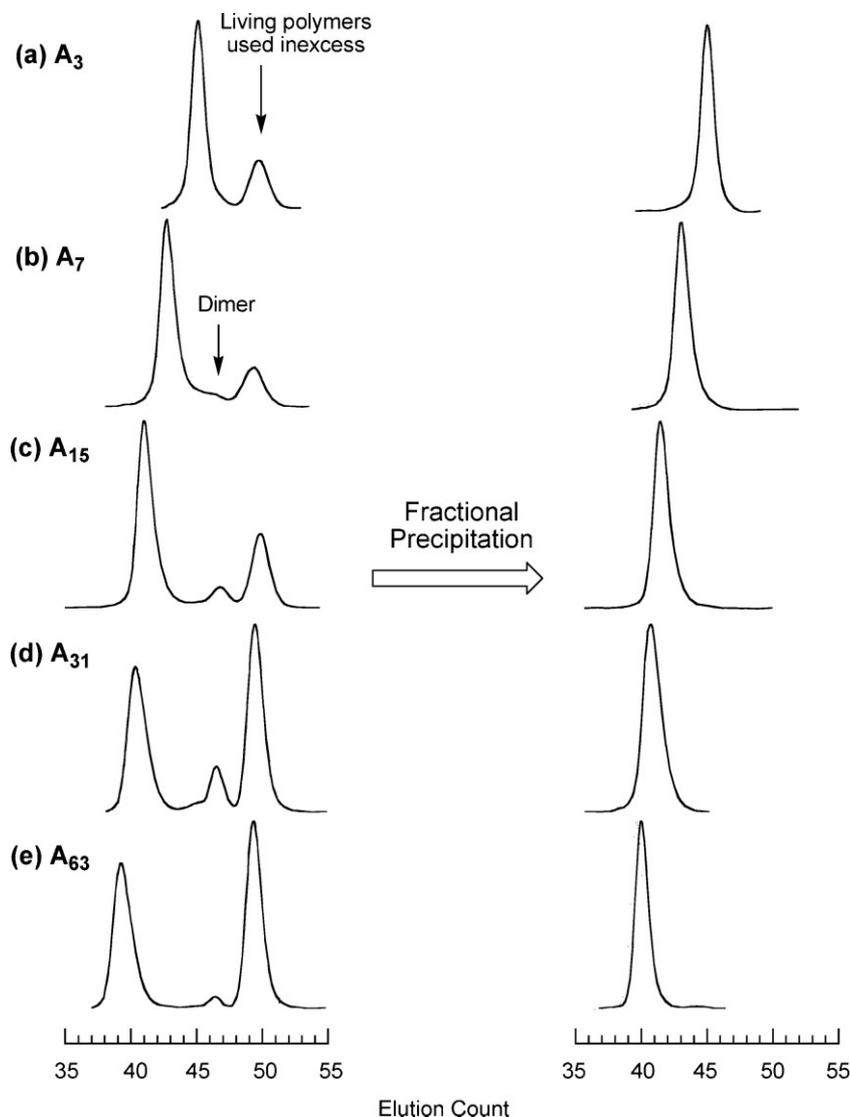
■ Table 2. Synthesis of star-branched PSs by iterative methodology using 5.

| Type            | $\bar{M}_n$                       |      | $\bar{M}_w$                       |      | $\frac{\bar{M}_w}{\bar{M}_n}$ | $g'$  |       |
|-----------------|-----------------------------------|------|-----------------------------------|------|-------------------------------|-------|-------|
|                 | $\text{kg} \cdot \text{mol}^{-1}$ |      | $\text{kg} \cdot \text{mol}^{-1}$ |      |                               | SEC   | Calcd |
|                 | Calcd                             | SEC  | Calcd                             | SLS  |                               |       |       |
| A <sub>3</sub>  | 31.1                              | 29.3 | 32.2                              | 33.7 | 1.03                          | 0.83  | 0.85  |
| A <sub>7</sub>  | 76.1                              | 59.1 | 79.4                              | 79.0 | 1.04                          | 0.51  | 0.53  |
| A <sub>15</sub> | 155                               | 75.4 | 163                               | 166  | 1.05                          | 0.27  | 0.28  |
| A <sub>31</sub> | 314                               | 104  | 330                               | 330  | 1.05                          | 0.15  | 0.16  |
| A <sub>63</sub> | 607                               | 129  | 625                               | 623  | 1.03                          | 0.083 | 0.10  |

regenerated by the reaction of a DPE-functionalized agent like **1** with the DPE-derived anion assigned to Y. Herein, an alternative iterative methodology using a different X and Y is introduced. This new methodology also involves the following two reaction steps which are repeatable in the process, as illustrated in Scheme 9:<sup>[101–104]</sup> (a) a coupling reaction between an  $\omega$ -terminal-functionalized living anionic polymer with a 3-*tert*-butyldimethylsilyloxymethylphenyl (SiOMP) group and a benzyl bromide (BnBr)-functionalized polymer and (b) a transformation reaction of the introduced SiOMP group into the BnBr function.<sup>[105]</sup> Since the BnBr function is regenerated by step

(b), it may be possible to repeat the two reaction steps in the process to successively synthesize a series of star-branched polymers. Accordingly, the BnBr and SiOMP groups correspond to X and Y, respectively. 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-phenylethylene (**6**) is the key agent in this methodology because it plays responsible roles in the two reaction steps.

The effectiveness of the new methodology was first examined by the possible synthesis of star PS.  $\omega$ -Terminal BnBr-functionalized PS was prepared by a 1:1 addition reaction of PSLi with **6** to introduce the SiOMP group at the chain-end, and subsequent treatment with a 1:1 mixture of



**Figure 2.** SEC profiles of the reaction mixtures and the isolated star-branched (PS)s,  $A_3$  (a),  $A_7$  (b),  $A_{15}$  (c),  $A_{31}$  (d), and  $A_{63}$  types (e).

$(\text{CH}_3)_3\text{SiCl}$  and LiBr to transform the SiOMP group into the BnBr function. The first iterative process involved a coupling reaction between the resulting chain-end-BnBr-functionalized PS and  $\omega$ -terminal SiOMP-functionalized living PS, prepared from PSLi and **6** in the same manner as that mentioned above, and the subsequent transformation of the SiOMP group into the BnBr function. The resulting in-chain-BnBr-functionalized PS was used as the starting material in the second iterative process, followed by the third process under the same conditions. The polymers obtained by this methodology were characterized by  $^1\text{H}$  NMR, SEC, and SLS to be the expected and well-defined 3- and 4-arm star (PS)s.

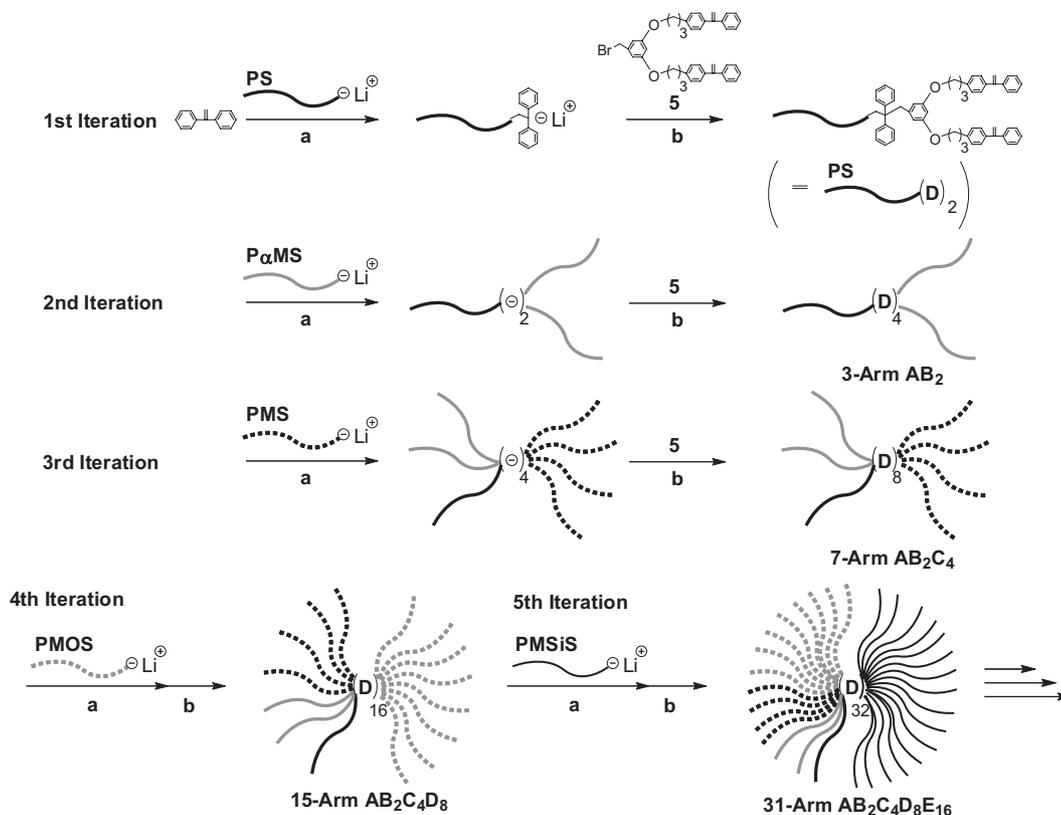
Next, the methodology using **6** was applied to the successive synthesis of asymmetric star-branched poly-

mers. As illustrated in Scheme 10, the synthesis starts from the same  $\omega$ -terminal-BnBr-functionalized PS.  $\text{P}\alpha\text{MSLi}$  and PMSLi were reacted with **6** and sequentially used in the second and third iterative processes, resulting in an in-chain-BnBr-functionalized AB diblock copolymer and a core-BnBr-functionalized 3-arm ABC star-branched polymer. Finally, a living anionic polymer of MMA was coupled with the core-BnBr-functionalized 3-arm ABC star to synthesize a 4-arm ABCD asymmetric star-branched polymer. The polymers all possessed sharp monomodal SEC distributions. Comparison of the compositions measured by  $^1\text{H}$  NMR with the calculated values gave excellent agreement in all polymer samples. All of the analytical results clearly showed that a series of symmetric star-branched polymers up to the 4-arm ABCD type was successively synthesized by the new methodology. The success is undoubtedly attributed to the facts that both the coupling and the transformation reactions cleanly and nearly quantitatively proceeded. Thus, the BnBr and SiOMP groups are demonstrated to be additional X and Y functionalities capable of being realized by the iterative methodology (Table 3).

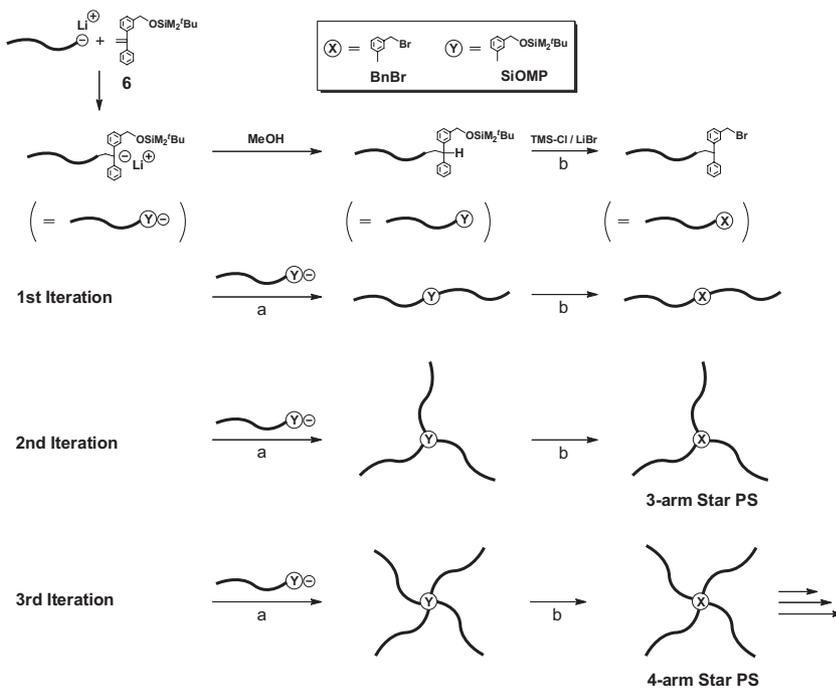
### Iterative Methodology Using Polymer Anions as Building Blocks

The successive synthesis of star-branched polymers by the iterative methodology using a polymer anion as a building block was recently reported by us.<sup>[106,107]</sup> As illustrated in Scheme 11, in-chain-DPE-functionalized PS was prepared in the first step by a coupling reaction between PSLi end-capped with DPE and 1,1-bis(3-chloromethylphenyl)ethylene (**7**). In the second step, the resulting in-chain-DPE-functionalized PS was treated with *sec*-BuLi to convert it to a DPE-derived anion, followed by coupling with **7**, resulting in a 4-arm star PS. The successful syntheses of the expected 4-, 8-, and 16-arm star (PS)s were confirmed by the results listed in Table 4.

Very recently, we reported the successful use of in-chain-DPE-functionalized AB block copolymers, 3-arm core-DPE-functionalized  $A_2B$ , or ABC asymmetric star-branched polymers as the starting polymers in the same

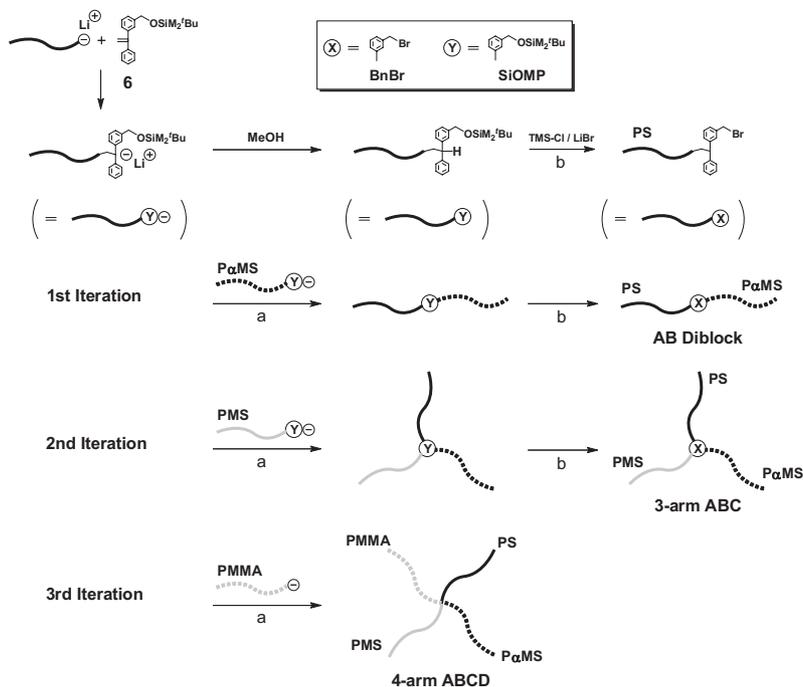


■ Scheme 8. Synthesis of asymmetric star-branched polymers by iterative methodology using 5.

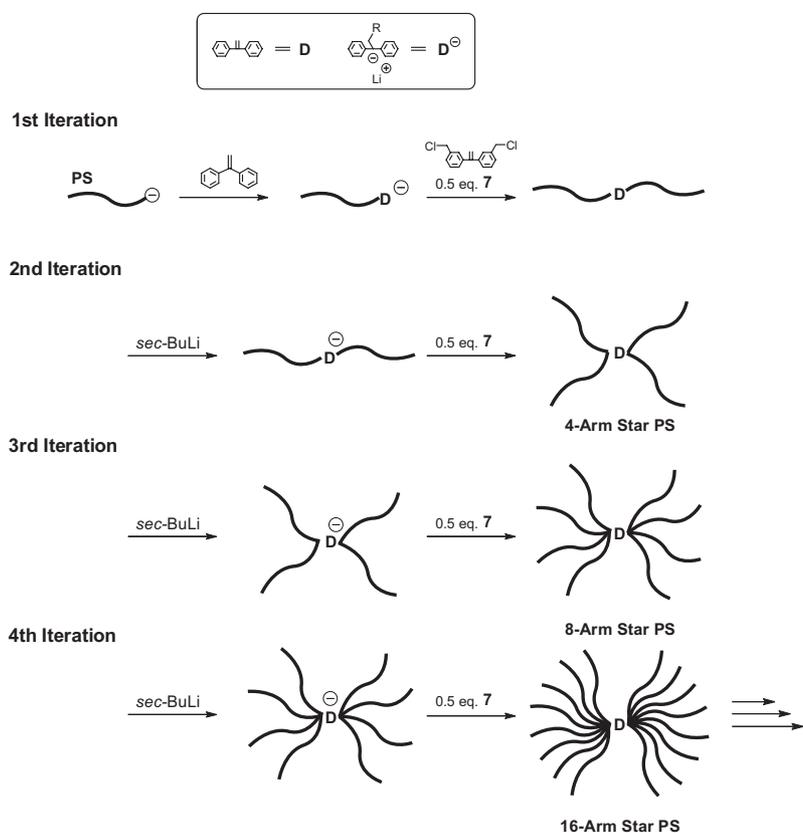


■ Scheme 9. Synthesis of star-branched (PS)s by iterative methodology using BnBr and SiOMP groups as “X” and “Y” functionalities.

methodology.<sup>[107]</sup> With this methodology, as illustrated in Scheme 12, 4-arm A<sub>2</sub>B<sub>2</sub>, 8-arm A<sub>4</sub>B<sub>4</sub>, 16-arm A<sub>8</sub>B<sub>8</sub>, 6-arm A<sub>4</sub>B<sub>2</sub>, 12-arm A<sub>8</sub>B<sub>4</sub>, 6-arm A<sub>2</sub>B<sub>2</sub>C<sub>2</sub>, and 12-arm A<sub>4</sub>B<sub>4</sub>C<sub>4</sub> asymmetric star-branched polymers were successfully synthesized. A new DPE-functionalized agent, 1-(4-(5,5-bis(3-bromomethylphenyl)-7-methylnonyl)phenyl)-1-phenylethylene (**8**), was also synthesized in order to reduce the steric hindrance in the coupling reaction between the polymer anions. Since the contribution of the DPE-derived anion to the mass of the product dramatically decreased as the number of iterative processes increased, the coupling yields were significantly reduced with the iteration. In general, isolation of the desired polymer became more difficult by increasing the number of arms. For these reasons, the iterative methodology presently developed works only at the synthetic stage of star-branched polymers having up to 12–16 arms.



**Scheme 10.** Synthesis of asymmetric star-branched polymers by iterative methodology using **6**.



**Scheme 11.** Synthesis of star-branched (PS)s by iterative methodology using **7** based on "convergent" approach.

## Exact Graft (co)Polymers

A graft copolymer is a branched polymer consisting of two or more branch (grafted) chains connected to the backbone chain and the same number of branch points is present along the backbone chain. Since the backbone and branch chains are in general thermodynamically incompatible, most graft copolymers are multiphase materials which exhibit unique and interesting composition-sensitive behavior and morphologies.<sup>[108,109]</sup>

The structure of a graft copolymer can be defined by the following four points: (i) molecular weight of the backbone chain, (ii) molecular weight of the branch chain, (iii) distance (or molecular weight) between the branch points, and (iv) number of the branch points along the backbone chain. An ideal graft copolymer, in which all of the above points are perfectly controlled, is called as "an exact graft copolymer" by Paraskeva and Hadjichristidis.<sup>[110]</sup> Although several attempts have been made to synthesize such exact graft copolymers, most graft copolymers so far synthesized were not completely controlled in structure with respect to such features.<sup>[111–121]</sup> As mentioned in the introduction, exact graft (co)polymers can be synthesized by first preparing a polymeric building block unit with functional groups, followed by connecting the unit to other units in a stepwise iterative fashion to build up the graft architecture.

### Iterative Methodology Using Initiation Reaction for Chain Growth

Hadjichristidis and Paraskeva reported the first successful synthesis of an exact graft copolymer composed of a poly(isoprene) (PI) backbone chain and two PS branch chains by a stepwise iterative methodology, as illustrated in Scheme 13.<sup>[110]</sup> The first step was the addition reaction of poly(isoprenyl)lithium (PILi) to 1,4-bis(phenylethenyl)benzene (**9**) to introduce the DPE moiety at the chain end. The resulting  $\omega$ -terminal DPE-functionalized PI was reacted with a stoichiometric amount of PSLi in a 1:1 addition manner to link PS to the PI chain in the second step. The resulting AB diblock copolymer with the DPE-derived anion between the two

Table 3. Synthesis of asymmetric star-branched polymers by iterative methodology using 5.

| Type <sup>a)</sup>   | $\bar{M}_n$                       |      |                    | $\bar{M}_w$                       |      | $\bar{M}_w/\bar{M}_n$ | Composition  |                    |
|--|-----------------------------------|------|--------------------|-----------------------------------|------|-----------------------|--------------|--------------------|
|  | $\text{kg} \cdot \text{mol}^{-1}$ |      |                    | $\text{kg} \cdot \text{mol}^{-1}$ |      |                       | wt.-%        |                    |
|  | Calcd                             | SEC  | <sup>1</sup> H NMR | Calcd                             | SLS  | SEC                   | Calcd        | <sup>1</sup> H NMR |
| A  | 11.9                              | 11.6 | 11.7               | 12.3                              | 11.9 | 1.02                  | 100          | 100                |
| 3-Arm AB <sub>2</sub>  | 31.5                              | 26.4 | 31.3               | 32.1                              | 35.7 | 1.02                  | 36/64        | 38/62              |
| 7-Arm AB <sub>2</sub> C <sub>4</sub>                                 | 75.5                              | 55.5 | 73.3               | 77.0                              | 79.2 | 1.02                  | 16/28/56     | 17/27/56           |
| 15-Arm AB <sub>2</sub> C <sub>4</sub> D <sub>8</sub>                 | 139                               | 67.6 | 161                | 162                               | 172  | 1.02                  | 8/12/27/53   | 8/10/30/52         |
| 31-Arm AB <sub>2</sub> C <sub>4</sub> D <sub>8</sub> E <sub>16</sub> | 332                               | 97.9 | 309                | 339                               | 363  | 1.02                  | 4/6/13/27/50 | 4/7/15/29/46       |

<sup>a)</sup>A, B, C, D, and E were PS, P $\alpha$ MS, PMS, PMOS, and PMSiS, respectively.

Table 4. Synthesis of in-chain-DPE-functionalized PS (A<sub>2</sub>), 4-arm A<sub>4</sub>, 8-arm A<sub>8</sub>, and 16-arm A<sub>16</sub> star-branched PSs by iterative methodology using 7 based on "convergent" approach.

| Type            | $\bar{M}_n$                       |      |                   | $\bar{M}_n$                       |      | $\bar{M}_w/\bar{M}_n$ | DPE-Functionality |                    | $g'$  |       |
|-----------------|-----------------------------------|------|-------------------|-----------------------------------|------|-----------------------|-------------------|--------------------|-------|-------|
|                 | $\text{kg} \cdot \text{mol}^{-1}$ |      |                   | $\text{kg} \cdot \text{mol}^{-1}$ |      | SEC                   | Calcd             | <sup>1</sup> H NMR | Calcd | Exptl |
|                 | Calcd                             | SEC  | VPO               | Calcd                             | SLS  |                       |                   |                    |       |       |
| A <sub>2</sub>  | 21.1                              | 20.8 | 19.8              | 21.5                              | 21.1 | 1.02                  | 1                 | 0.99 <sub>0</sub>  | –     | –     |
| A <sub>4</sub>  | 41.2                              | 35.1 | 40.0              | 41.6                              | 41.7 | 1.01                  | 1                 | ca. 1              | 0.71  | 0.72  |
| A <sub>8</sub>  | 80.8                              | 55.3 | 79.1              | 84.0                              | 84.7 | 1.04                  | 1                 | ca. 1              | 0.46  | 0.46  |
| A <sub>16</sub> | 168                               | 85.2 | 168 <sup>a)</sup> | 170                               | 170  | 1.01                  | 1                 | ca. 1              | –     | –     |

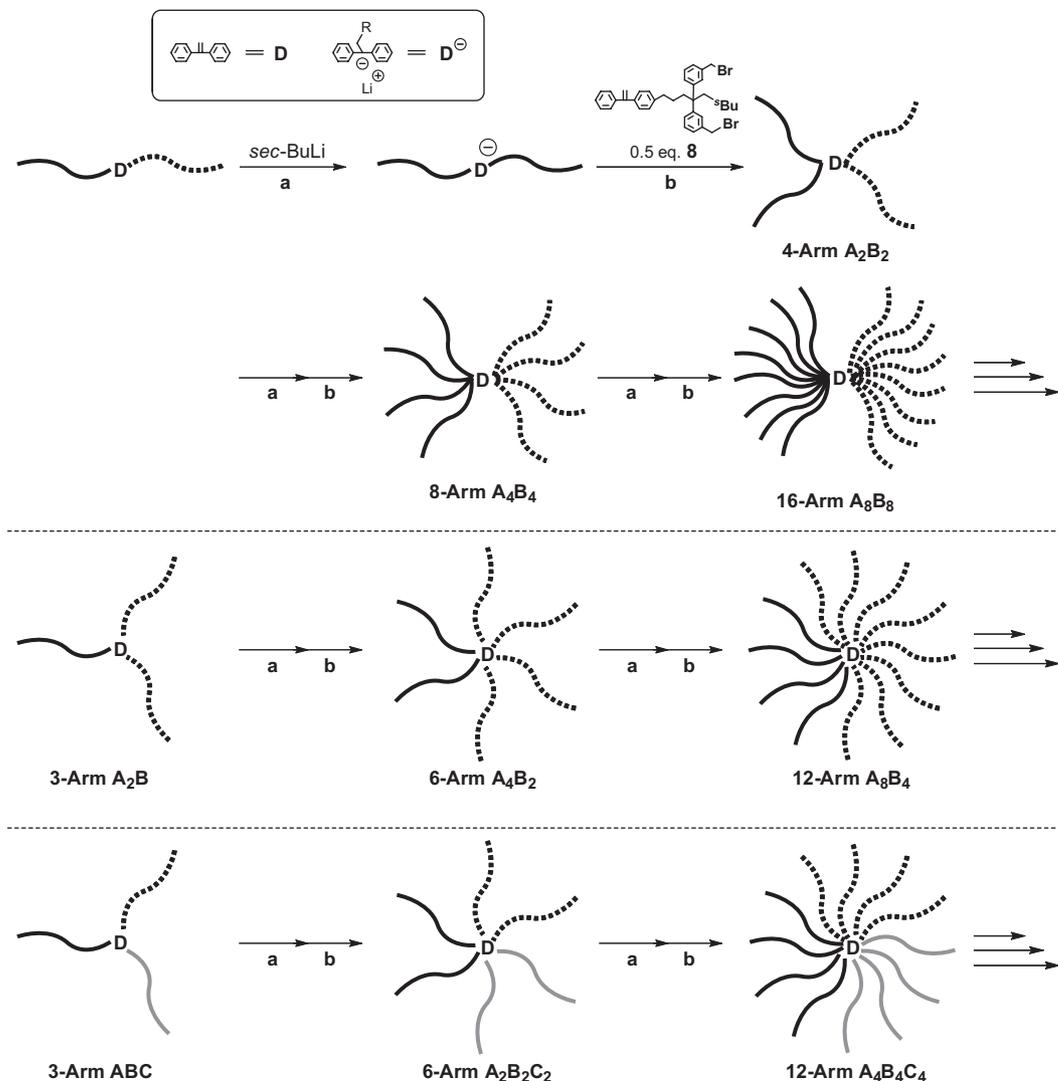
<sup>a)</sup>Determined by  $\bar{M}_w$  (SLS) and  $\bar{M}_w/\bar{M}_n$  (SEC).

blocks is a building unit in this synthesis. In the second iteration, isoprene was in situ polymerized with this DPE-derived anion to prepare a living 3-arm A<sub>2</sub>B star-branched copolymer, followed by reacting with 9 to introduce the DPE moiety at the chain end. A stoichiometric amount of PSLi toward the DPE moiety at the chain-end was reacted to introduce the second branch. Finally, isoprene was polymerized with the DPE-derived anion to afford the desired graft copolymer composed of two PS branch chains.

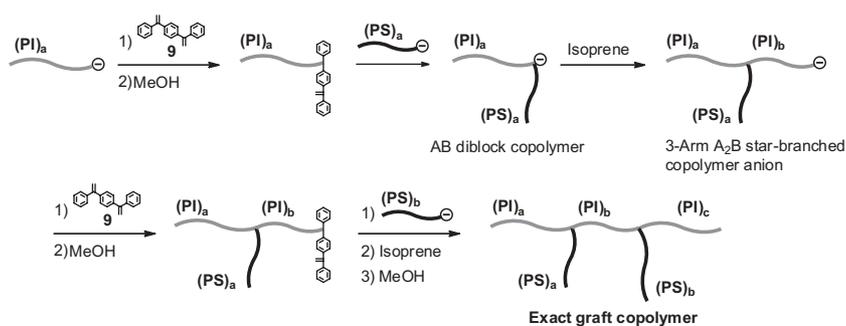
The narrow molecular weight distribution ( $\bar{M}_w/\bar{M}_n = 1.08$ ) and predictable molecular weights ( $\bar{M}_n = 233 \text{ kg} \cdot \text{mol}^{-1}$ ) and compositions were confirmed by SEC, <sup>1</sup>H NMR, and RALLS, respectively. The distances from the  $\alpha$ -terminal chain end to the first PS branch, between the first and the second PS branches, and from the second PS branch to the opposite  $\omega$ -terminal chain end are individually controlled by the molecular weights of the living (PI)s, shown as (PI)<sub>a</sub>, (PI)<sub>b</sub>, and (PI)<sub>c</sub> in Scheme 13. The backbone and branch chains are constructed by (PILi)s and (PSLi)s and therefore precisely controlled in molecular weight. Thus, all of the four factors are perfectly controlled in the resulting graft polymer.

This iterative methodology can offer potential for providing a general procedure for exact graft copolymers with more branch chains by repeating the same reaction sequence. However, the synthesis worked only at the introduction stage of the two branch chains. This is probably because a perfect 1:1 stoichiometry, experimentally very difficult, is always required in each addition reaction of PSLi to the DPE moiety in the polymer chain.

Very recently, Hadjichristidis and his coworkers synthesized an exact graft poly(1,3-butadiene) (PB) having three PB branch chains.<sup>[122]</sup> As illustrated in Scheme 14, a living star PB with an anion at the  $\omega$ -terminus was first prepared in the same manner mentioned above and then coupled with either MeSiCl<sub>3</sub> or 1-(4-dichloromethylsilyl)phenyl-1-phenylethylene. The resulting coupled product having one residual Si–Cl bond was reacted with PBLi to give an exact graft PB having three PB branches. Similarly, the same exact graft PB was synthesized by treatment of the above coupled polymer having a DPE moiety with an exact amount of *sec*-BuLi, followed by the polymerization of 1,3-butadiene with the generated DPE-derived anion.



■ Scheme 12. Synthesis of asymmetric star-branched polymers by iterative methodology using **8** based on “convergent” approach.



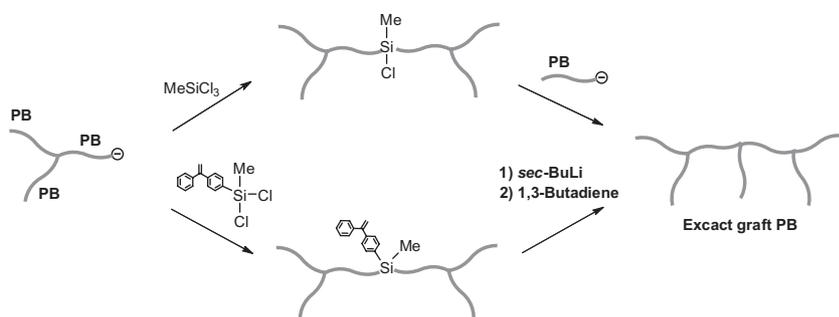
■ Scheme 13. Synthesis of exact graft copolymers composed of PI backbone and PS branches.

### Iterative Methodology Using Termination Reaction for Chain Growth

We recently demonstrated the successful synthesis of a series of exact graft (PS) having up to five PS branch chains by a new iterative methodology.<sup>[123]</sup> In contrast to the methodology introduced above, a termination reaction is used for chain growth in this methodology, as illustrated in Scheme 15. The following three reaction steps are employed in each iterative synthetic sequence: (a) a transformation reaction of the  $\alpha$ -terminal 3-*tert*-butyldimethylsilyloxypropyl (SiOP) group into a 3-bromopropyl function via deprotection of the SiOP group, (b) a coupling reaction of the resulting

Unfortunately, this procedure is not based on the iterative approach and therefore it is not possible to apply it to the successive synthesis of graft polymers with more branches.

iterative synthetic sequence: (a) a transformation reaction of the  $\alpha$ -terminal 3-*tert*-butyldimethylsilyloxypropyl (SiOP) group into a 3-bromopropyl function via deprotection of the SiOP group, (b) a coupling reaction of the resulting



■ Scheme 14. Synthesis of exact graft PB having up to three branches.

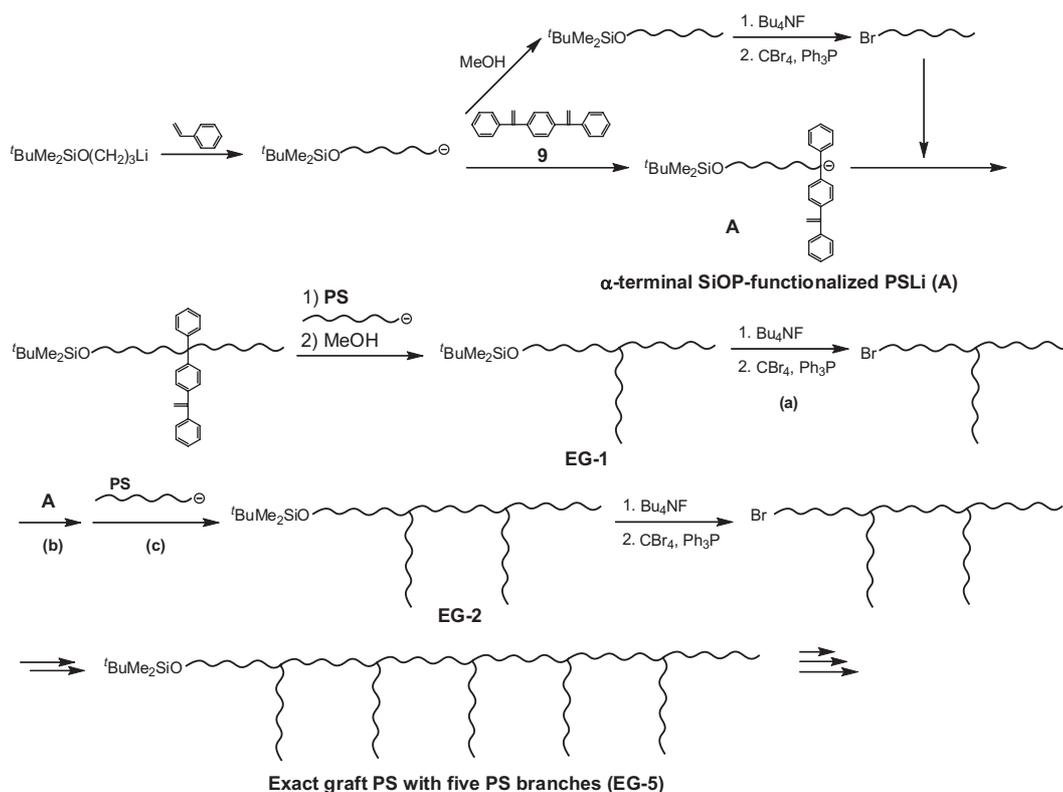
$\alpha$ -terminal 3-bromopropyl-functionalized PS with an  $\alpha$ -SiOP- $\omega$ -DPE-functionalized living PS, resulting in an  $\alpha$ -terminal SiOP-in-chain-DPE-functionalized PS, and (c) an addition reaction of PSLi with the DPE moiety to introduce the PS branch chain. The polymeric building unit with a functional group is prepared by the three steps and the iterative process can be done by regeneration of the 3-bromopropyl reaction site from the  $\alpha$ -SiOP terminus by step (a). A series of the desired exact graft (PS)s was actually synthesized by performing the iterative process five times.

At first,  $\alpha$ -terminal 3-bromopropyl-functionalized PS was prepared by living anionic polymerization of styrene with

3-(*tert*-butyldimethylsilyloxy)-1-propyl-lithium (SiOPLi), followed by transformation of the  $\alpha$ -terminal SiOP group into the 3-bromopropyl reaction site by treatment first with  $(C_4H_9)_4NF$  and then with  $Ph_3P$  and  $CBr_4$ . Next, the same  $\alpha$ -terminal SiOP-functionalized PSLi was prepared by SiOPLi-initiated polymerization of styrene as above and then reacted with **9**, resulting in  $\alpha$ -SiOP- $\omega$ -DPE-functionalized living PS. Similar to the addition reaction of **9** to PSLi, only one of the two double bonds of **9** reacted with the  $\alpha$ -terminal SiOP-functionalized PSLi in a 1:1

addition manner. In the second step, the resulting  $\alpha$ -SiOP- $\omega$ -DPE functionalized living PS was in situ reacted with  $\alpha$ -terminal 3-bromopropyl-functionalized PS to link the two PS chains, resulting in  $\alpha$ -terminal SiOP-in-chain-DPE-functionalized PS. Finally, PSLi was reacted with the DPE functionality in PS to introduce a PS branch by step (c). Thus, one building unit with the  $\alpha$ -terminal SiOP group converted to the 3-bromopropyl group for the next reaction site was prepared.

Since the above-mentioned three reaction steps proceeded with essentially quantitative efficiency and the final product had the same  $\alpha$ -terminal SiOP group, the same



■ Scheme 15. Synthesis of a series of exact graft (PS)s with up to five branches by iterative methodology.

**Table 5.** Synthesis of an series of exact graft PSs by iterative methodology.

| Type <sup>a)</sup> | $\bar{M}_n$            |      |       | $\bar{M}_w$            |       | $\bar{M}_w/\bar{M}_n$ |
|--------------------|------------------------|------|-------|------------------------|-------|-----------------------|
|                    | kg · mol <sup>-1</sup> |      |       | kg · mol <sup>-1</sup> |       |                       |
|                    | Calcd                  | SEC  | RALLS | Calcd                  | RALLS | SEC                   |
| EG-1               | 29.1                   | 26.9 | 29.2  | 29.7                   | 29.8  | 1.02                  |
| EG-2               | 51.2                   | 45.0 | 54.3  | 52.2                   | 55.4  | 1.02                  |
| EG-3               | 83.5                   | 65.1 | 84.1  | 85.2                   | 85.8  | 1.02                  |
| EG-4               | 102                    | 78.5 | 103   | 105                    | 106   | 1.03                  |
| EG-5               | 125                    | 94.7 | 124   | 129                    | 128   | 1.03                  |

<sup>a)</sup>EG-n indicates an exact graft PS with n branches.

iterative process involving the three reaction steps could be performed. Actually, an exact graft PS having two PS branches could be synthesized by the iterative process, as shown in the same scheme. Thus, the iterative process results in an increase in the graft repeating units one by one to buildup exact graft (PS)s with a number of PS branches. The same iterative process were done four more times to successively synthesize a series of exact graft (PS)s having up to five PS branches. Needless to say, the four points are perfectly controlled in all resulting graft (PS)s. The results are summarized in Table 5.

When the reaction processes were monitored by SEC, it was noticed that all graft (PS)s exhibited sharp monomodal SEC distributions and their peaks were gradually moved to higher molecular weight sides, as shown in Figure 3. Agreement of the molecular weights between those calculated and those determined by SEC-RALLS was quite satisfactory in all polymer samples. Their molecular weight distributions were very narrow, the  $\bar{M}_w/\bar{M}_n$  values being 1.03 or even smaller, as estimated by SEC. Thus, the expected structures and high degrees of molecular homogeneity of the resulting graft (PS)s were confirmed by these characterization results. The position of the branch and distance between the branches were precisely controlled by the molecular weight of  $\alpha$ -terminal SiOP-functionalized living PS used in step (b) in each process and can be intentionally changed by changing the molecular weight. In order to examine the possible control of distance between branches, the distances between the third and fourth branch points and the fourth and fifth branch points in the final product were set to be 20 000 and 6 000 g · mol<sup>-1</sup>, respectively, while others were adjusted to be around 10 000 g · mol<sup>-1</sup>. The results clearly showed such architectures.

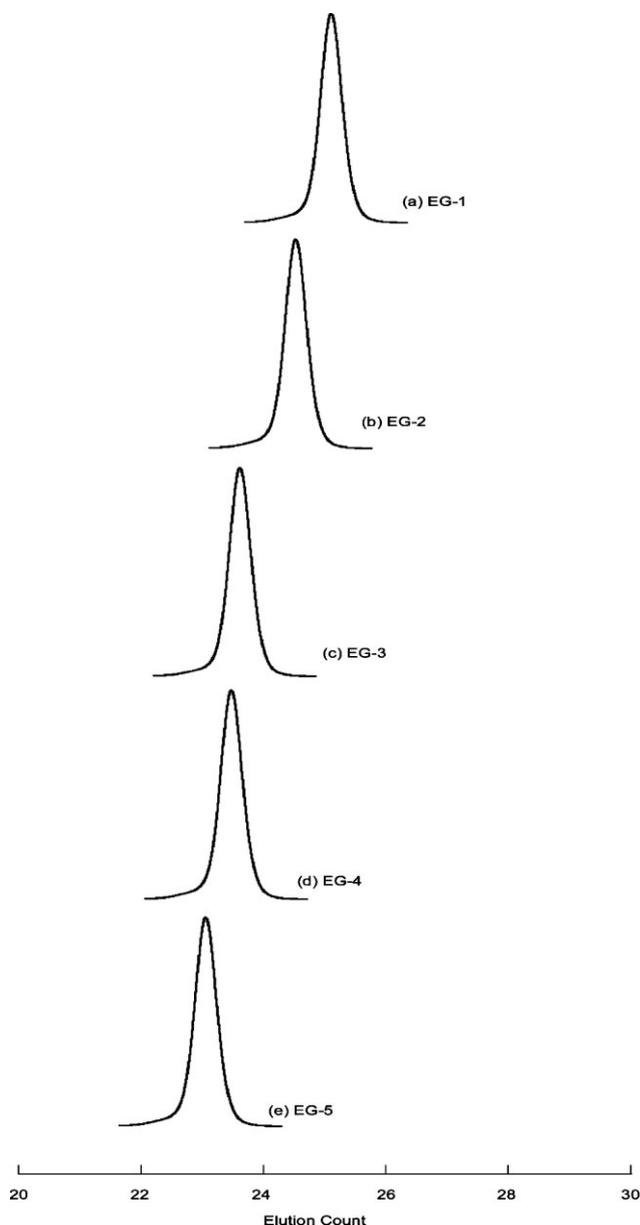
The iterative methodology was successfully applied to the synthesis of an exact graft copolymer composed of a PS backbone and PI branches. The same iterative process, except for the use of PILi in step (c), was performed as shown

in Scheme 16. The end-capping of PILi with a few units of styrene was required in order to react quantitatively with the DPE functionality incorporated in the PS main chain.

#### Iterative Methodology Using In-Chain-Functionalized AB Diblock Copolymer Anion

The successful synthesis of an exact graft (PS)s having up to five PS branches by the iterative methodology was described, as stated in the preceding section. As was seen in Scheme 15, the backbone and branch chains were individually introduced to prepare one building unit and the resulting unit was connected in a stepwise iterative fashion by a functional group pre-introduced to buildup a series of exact graft (PS)s. Very recently, we successfully synthesized another series of exact graft copolymers composed of poly(methyl methacrylate) (PMMA) backbone chains and PS branches by developing a new iterative methodology using in-chain-functionalized AB diblock copolymer anions.<sup>[124]</sup>

In the new methodology, a specially designed AB diblock copolymer (PS-*block*-PMMA) anion, in-chain-functionalized with a SiOMP group between the PS and PMMA blocks, is employed as the key polymeric building block unit, as illustrated in Scheme 17. This unit with the SiOMP functional group is designed to place both the backbone and branch chains together and connect them to other units via the SiOMP group. The following three steps were needed for the iterative synthetic sequence: (a) living anionic block copolymerization to prepare in-chain-SiOMP-functionalized PS-*block*-PMMA anions, (b) a transformation reaction of the SiOMP group to the BnBr reaction site, and (c) a coupling reaction of the in-chain-SiOMP-functionalized PS-*block*-PMMA anions obtained by step (a) with in-chain-BnBr-functionalized PS-*block*-PMMA prepared by step (b). The  $\alpha$ -terminal SiOMP-functionalized repeating unit can be



**Figure 3.** SEC profiles of a series of exact graft PSs with one (a, EG-1), two (b, EG-2), three (c, EG-3), four (d, EG-4), and five (e, EG-5) PS branches.

prepared by step (a) and can be connected to other units by step (c). Since the BnBr reaction site is regenerated by step (b), the same iterative process involving the three steps can be performed, resulting in an increase in the number of building units.

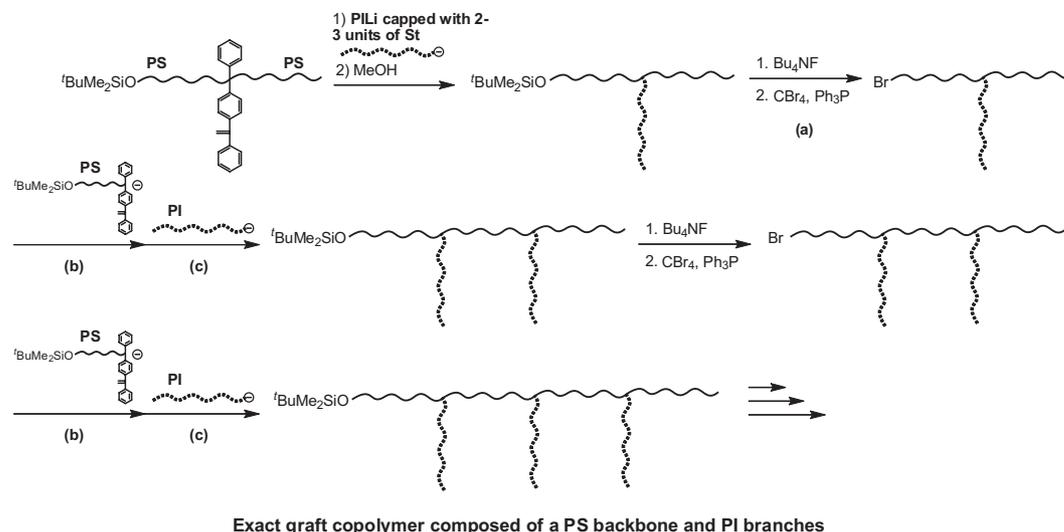
In the first step of the reaction sequence, in-chain-SiOMP-functionalized PS-*block*-PMMA anions were prepared by living anionic block copolymerization where styrene, 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-phenylethylene (**10**), and MMA were sequentially reacted in that order in THF at  $-78^{\circ}\text{C}$  with *sec*-BuLi as the initiator. A three-fold

excess of LiCl to PSLi was added prior to the polymerization of MMA to narrow the molecular weight distribution. Unless otherwise stated, the  $\bar{M}_n$  value of the block copolymer [PS ( $\bar{M}_n$ )/PMMA ( $\bar{M}_n$ )] was adjusted to be around  $10\,000\text{ g}\cdot\text{mol}^{-1}$  (5 000/5 000). The block copolymer thus prepared was treated with a 1:1 mixture of  $(\text{CH}_3)_3\text{SiCl}$  and LiBr to quantitatively transform the SiOMP group into the BnBr function. Finally, in-chain-SiOMP-functionalized PS-*block*-PMMA anions separately prepared in the same manner were coupled with the resulting in-chain-BnBr-functionalized PS-*block*-PMMA in THF at  $-40^{\circ}\text{C}$  for 24 h. The coupling efficiency was nearly quantitative under such conditions. The coupled product, isolated in 85% yield by fractional precipitation, exhibited a narrow molecular weight distribution ( $\bar{M}_w/\bar{M}_n = 1.03$ ) and a  $\bar{M}_n$  value that agreed well with the calculated value, as listed in Table 6. The composition ratio of PS and PMMA segments observed by  $^1\text{H}$  NMR was consistent with that calculated from the both block copolymers. Thus, all of the analytical results clearly indicate that the coupling reaction was efficiently carried out to afford the expected graft copolymers with two PS branches.

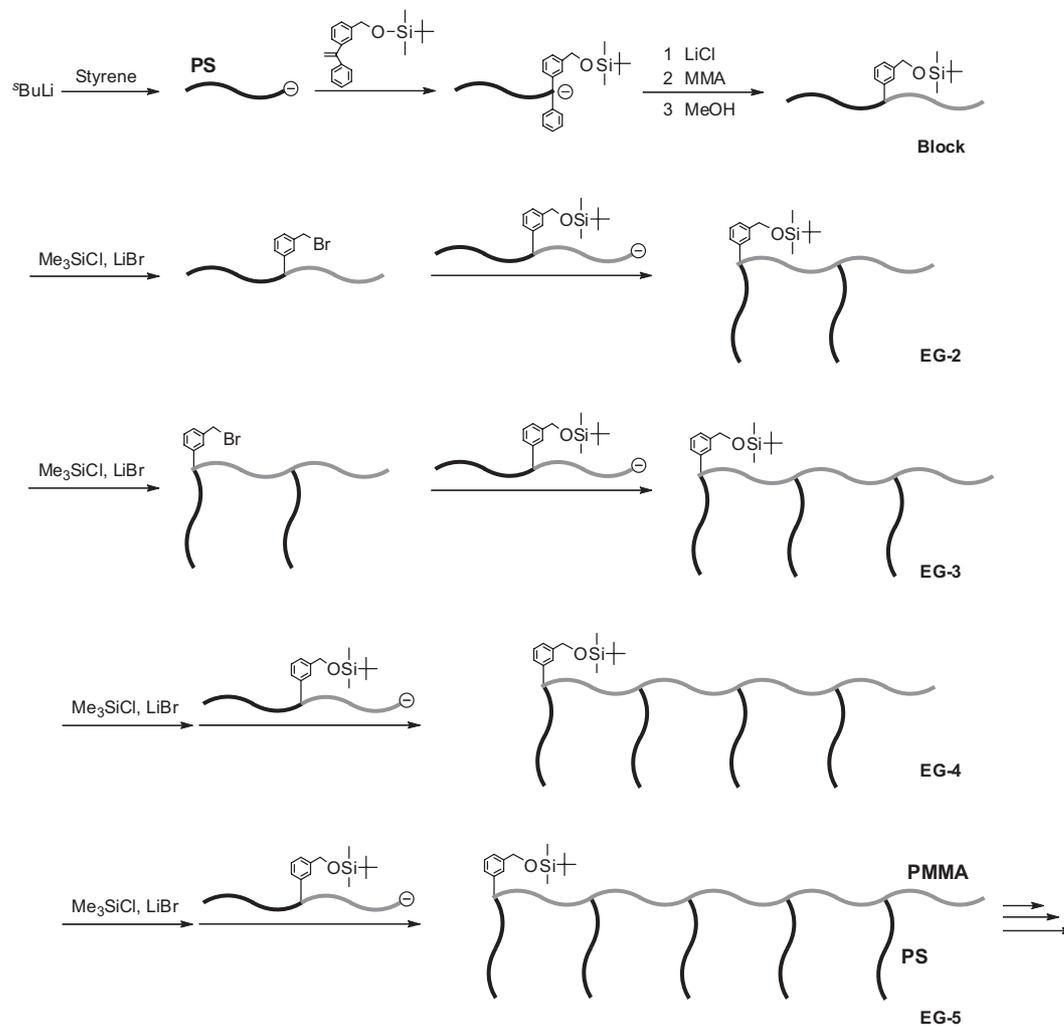
Likewise, a series of exact graft copolymers with three, four, and five PS branches was successively synthesized by performing the same iterative process involving the three reaction steps, (a)–(c), starting from a graft copolymer with two PS branches. The successful formation of such graft copolymers was confirmed by the analytical results listed in Table 6. All reactions were monitored by SEC and found to proceed cleanly and quantitatively. Figure 4 shows the SEC peaks of all graft copolymers in addition to that of the starting AB diblock copolymer. As seen, all polymers possess sharp monomodal distributions without shoulders or tailings.

Thus, the new iterative methodology satisfactorily works to successively synthesize a series of well-defined exact graft copolymers with two, three, four, and five PS branches. The distance between PS branches can be controlled by the molecular weight of the PMMA block. The molecular weights of the backbone and branch chains respectively correspond to those of the PS and PMMA blocks and are readily controlled by living anionic block copolymerization. The number of building units increases with the performance of the iterative process. Thus, obviously, the four features are perfectly and intentionally controlled in the graft copolymers synthesized by this iterative methodology.

Since it is possible to prepare several in-chain-SiOMP-functionalized AB diblock copolymers by living anionic block copolymerization, a variety of exact graft copolymers may be synthesized by developing the same iterative methodology. For example, two different exact graft copolymers having two branches composed of either poly(2-vinylpyridine) (P2VP) or poly(2-perfluorooctylethyl



■ Scheme 16. Synthesis of a series of exact graft copolymers composed of PS backbone and PI branches.



■ Scheme 17. Synthesis of a series of exact graft copolymers composed of PMMA backbone and PS branches by iterative methodology using in-chain-functionalized AB diblock copolymer anion.

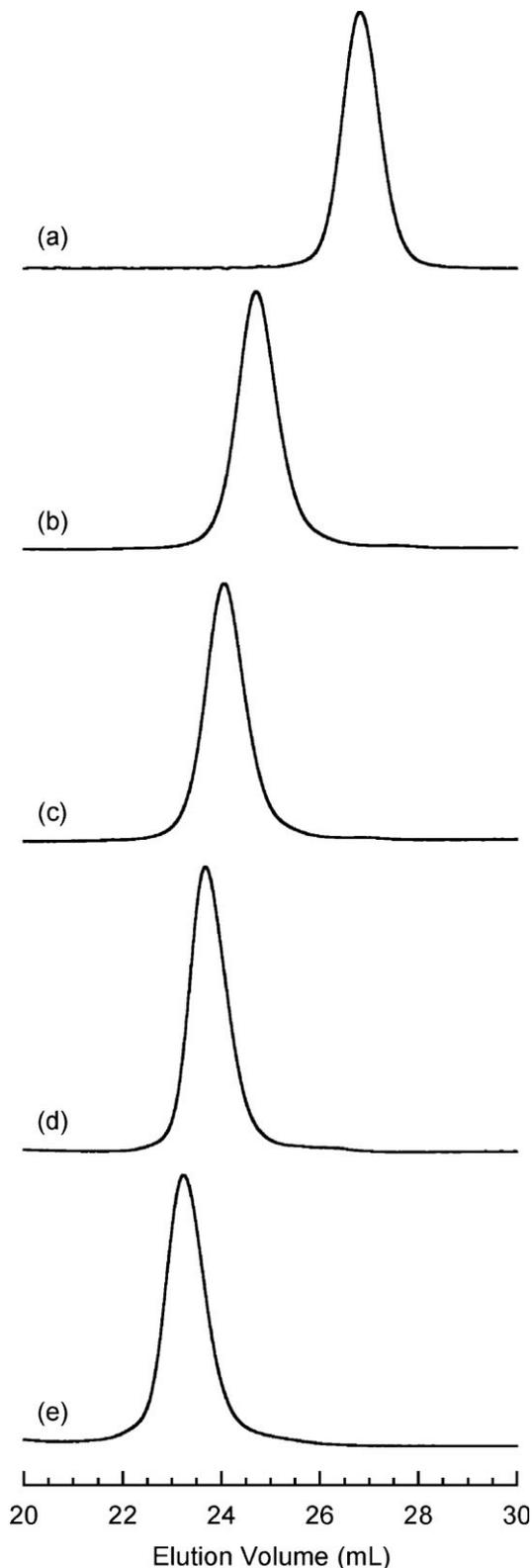


Figure 4. SEC profiles of in-chain-functionalized PMMA-*block*-PS (a) and a series of exact graft copolymers composed of PMMA and PS having one (b), two (c), three (d), and four (e) PS grafts.

methacrylate) (PF17MA) as the backbone chain, and PS as the branch, were successfully synthesized by using in-chain-SiOMP-functionalized PS-*block*-P(2VP) or PS-*block*-PF17MA) anions.

Thus, the excellence as well as the versatility of the present iterative methodology using the AB diblock copolymer anions as a polymeric building block has been demonstrated. The choice and setting of the three reaction conditions used in the iterative process are critical to achieve successive synthesis. Since the final products have the same SiOMP groups in the polymer chains, the same process can be further repeated to increase the number of building units.

### Dendrimer-Like Star-Branched Polymers

Dendrimer-like star-branched polymers, recently appeared as a new class of hyperbranched polymers, resembling dendrimers in branch architecture, but comprising dendritically branched polymer chains emanating from a central core, and two or more branches at every junction as repeating units.<sup>[89,125–128]</sup> Moreover, they can be differentiated from usual hyperbranched polymers by their structural perfection. Since dendrimer-like star-branched polymers are composed of many polymer chains which are regularly branched in their architecture, they are much higher in molecular weight and much larger in molecular size than dendrimers. Therefore, they are recognized as nano-ordered globular macromolecules from their branched architectural models and some analytical results. In order to make the image of dendrimer-like star-branched polymer clear, a fifth-generation (5G) dendrimer-like star-branched polymer is shown as a representative example (Figure 5).

Because of such branched architectures, dendrimer-like star-branched polymers have many characteristic features

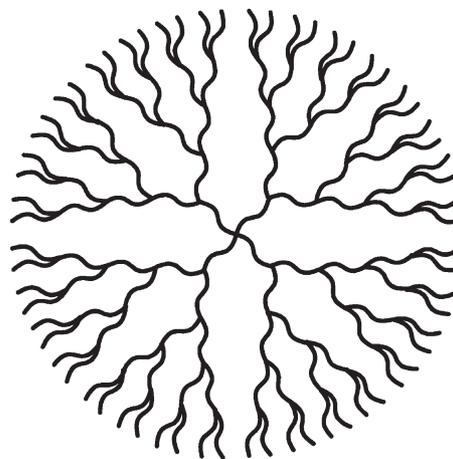
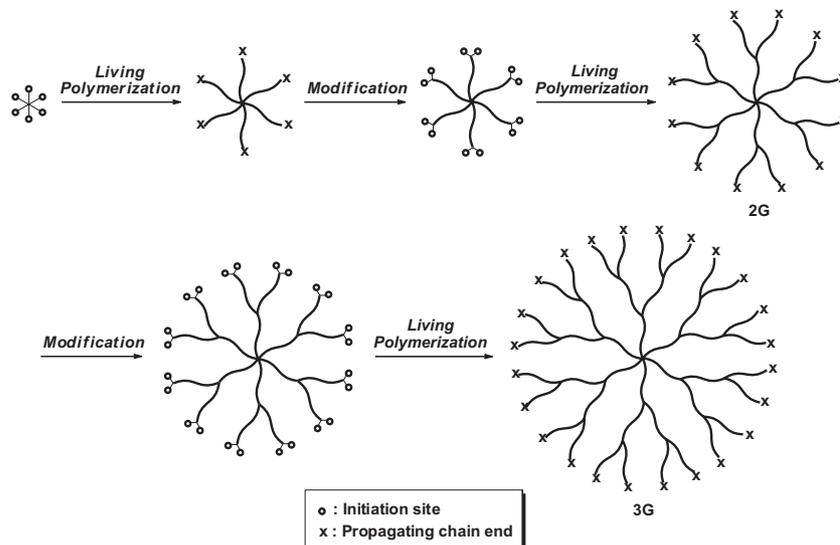


Figure 5. 5G Dendrimer-like star-branched polymer.

such as hierarchic hyperbranched and generation-based radial structures, layers composed of branched repeating units, different branch densities between the core and outer layer, and many branch points and end groups. It is also possible to synthesize a variety of block copolymers with the same branched architectures by introducing different polymer segments at each generation. These block copolymers are expected to be phase-separated at the molecular level, followed by self-organizing, generating unique and characteristic nanostructured domains, and supramolecular assemblies. The formation of alternative or several separated layer structures is highly probable.

As can be seen in Figure 5, dendrimer-like star-branched polymers are made up of a number of generation-based layers of branched units emanating from a core.

Similar to the synthesis of star-branched polymers and exact graft (co)polymers, there are two reaction steps in the synthesis, as follows: a polymeric building unit with appropriate functional group(s) is prepared in the first step and then connected to other units via the functional group(s) in the second step. By repeating the two steps, a series of dendrimer-like star-branched polymers is successively synthesized. At the present time, several examples of dendrimer-like star-branched polymers have been synthesized by two complementary iterative methodologies based on “divergent” and “convergent” approaches, similar to dendrimer synthesis.<sup>[129]</sup> The use of living polymer(s) as well-defined polymer chain(s) linked between the junctions is required in order to synthesize well-defined dendrimer-like star-branched polymers. Accordingly, either a core-first



**Scheme 18.** Synthesis of dendrimer-like star-branched polymers by iterative divergent methodology using initiation reaction for chain growth.

initiation or an arm-first termination reaction is used for chain growth.

#### Iterative Divergent Methodology Using Initiation Reaction for Chain Growth

The synthesis of dendrimer-like star-branched polymers by the iterative divergent methodology using an initiation reaction for chain growth was reported first by Gnanou and coworkers,<sup>[130–139]</sup> and soon after by Hedrick and coworkers,<sup>[140–148]</sup> and Percec et al.<sup>[149–151]</sup> As shown in Scheme 18, a multifunctional initiator is first prepared as the core, with which an appropriate monomer is polymerized in a living manner, and then each of the propagating chain-ends is modified to convert them to

**Table 6.** Synthesis of a series of exact graft copolymers composed of PMMA and PS having up to five PS grafts.

| Type <sup>a)</sup>  | $\bar{M}_n$                       |      |      |       | $\bar{M}_w/\bar{M}_n$ | Composition |       |
|---------------------|-----------------------------------|------|------|-------|-----------------------|-------------|-------|
|                     | $\text{kg} \cdot \text{mol}^{-1}$ |      |      |       |                       | wt.-%       |       |
|                     | Calcd                             | SEC  | NMR  | RALLS |                       | SEC         | Calcd |
| Block <sup>b)</sup> | 12.5                              | 11.7 | 12.6 | 12.6  | 1.03                  | 50/50       | 48/52 |
| EGC-1               | 22.2                              | 17.9 | 22.5 | 23.6  | 1.03                  | 51/49       | 50/50 |
| EGC-2               | 33.8                              | 31.9 | 35.4 | 34.6  | 1.02                  | 50/50       | 49/51 |
| EGC-3               | 43.5                              | 33.5 | 46.1 | 45.6  | 1.04                  | 49/51       | 50/50 |
| EGC-4               | 56.2                              | 41.3 | 56.0 | 55.0  | 1.04                  | 50/50       | 50/50 |

<sup>a)</sup>EGC-n indicates an exact graft copolymer with n branches; <sup>b)</sup>the starting in-chain-SiOMP-functionalized PMMA-block-PS.

**Table 7.** Representative dendrimer-like star-branched polymers synthesized by iterative divergent methodology using initiation reaction for chain growth.

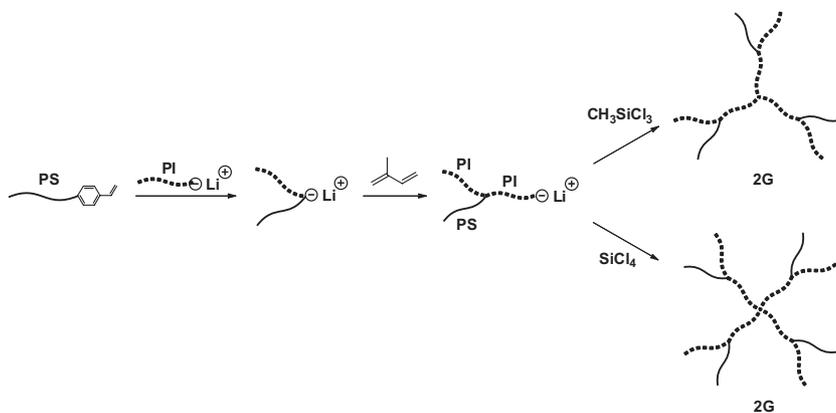
| Polymer segment   | Generation | Number of branch |               | Number of total segment | $\bar{M}_n$<br>kg · mol <sup>-1</sup> | $\bar{M}_w/\bar{M}_n$ | Literature |
|---|------------|------------------|---------------|-------------------------|---------------------------------------|-----------------------|------------|
|   |            | Core             | Layer         |                         |                                       |                       |            |
|   |            |                  |               |                         |                                       |                       |            |
| PEO   | 2          | 3                | 2             | 9                       | 28.0                                  | 1.30                  | 130        |
|   | 8          | 3                | 2,2,2,2,2,2,2 | 765                     | 650                                   | 1.18                  | 135        |
| PS  | 3          | 8                | 2,2           | 56                      | 141                                   | 1.27                  | 136        |
|   | 7          | 4                | 2,2,2,2,2,2   | 508                     | 1920                                  | 1.04                  | 139        |
| poly( $\epsilon$ -caprolactone)                                     | 2          | 6                | 8             | 54                      | 221                                   | 1.12                  | 140        |
|   | 3          | 6                | 2,2           | 42                      | 158                                   | 1.14                  | 141        |
| Poly(L-lactide)   | 3          | 6                | 2,2           | 42                      | 101                                   | 1.26                  | 148        |
| PMMA  | 4          | 3                | 2,2,2         | 45                      | 456                                   | 1.23                  | 149        |
| PEO- <i>b</i> -PS   | 2          | 4                | 2             | 12                      | 117                                   | –                     | 131        |
| PEO- <i>b</i> -P <sup>t</sup> BA                                    | 2          | 3                | 2             | 9                       | 17.5                                  | 1.28                  | 133        |
| poly( $\epsilon$ -caprolactone)- <i>b</i> -(PMMA- <i>co</i> -PHEMA) | 2          | 6                | 4             | 30                      | 76.0                                  | 1.19                  | 142        |

two or more initiation sites in the second step. Thus, this methodology involves the following two reaction steps: (a) living polymerization of an appropriate monomer and (b) chain-end modification. The building block unit is prepared in step (a) and the reaction sites are regenerated in step (b). The iterative synthetic sequence involving steps (a) and (b) is performed to successively synthesize a series of dendrimer-like star-branched polymers in an outward direction.

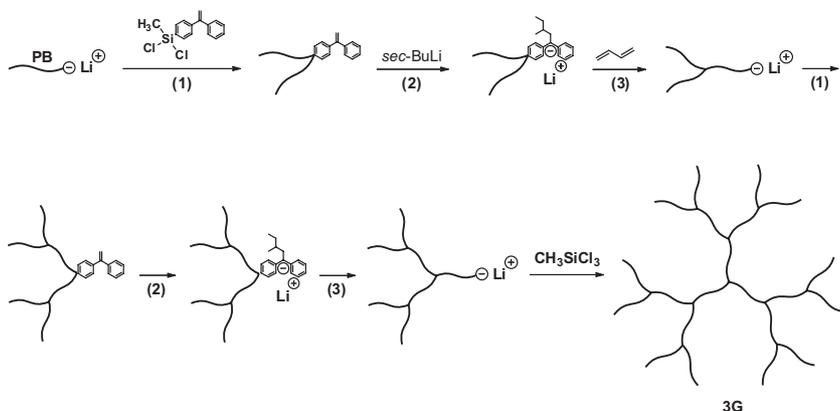
A variety of dendrimer-like star-branched polymers and their structural analogous amphiphilic block copolymers have been synthesized by this methodology in conjunction with living/controlled radical polymerizations and/or living anionic polymerization of vinyl and cyclic monomers. Some representative synthetic examples are summarized in Table 7 (core and branching number). Most of the samples so far synthesized are limited to 4G stages except for the two cases (7G and 8G) reported by Gnanou et al., and 10<sup>5</sup> g · mol<sup>-1</sup> orders in molecular weight because of practical difficulties in repeating the living polymerization generation by generation. The synthesis of the 7G dendrimer-like star-branched PS was recently reported by Matmour and Gnanou.<sup>[139]</sup> Since the resulting polymers have predictable high molecular weights and extremely narrow molecular weight distributions ( $\bar{M}_w/\bar{M}_n \leq 1.05$ ) and the

synthetic potential seems very attractive, once again there is no description of the uniformity of the branch segment.

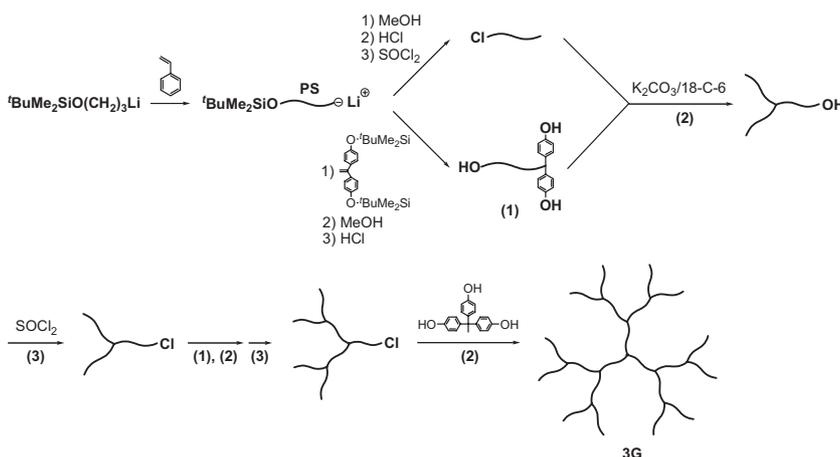
Although the defined structures are generally suggested in most of the polymers so far reported, there always remains a serious problem with the uniformity of all polymer chains propagated from multi-initiation sites at each generation. Furthermore, as the number of initiation sites increases exponentially with generation, it is not possible to accurately determine how many reaction sites work, especially at higher generation. Gnanou and co-workers have demonstrated that MALDI-TOF mass spectroscopy is a powerful technique for monitoring the structural imperfection.<sup>[152]</sup> Detailed analysis of several



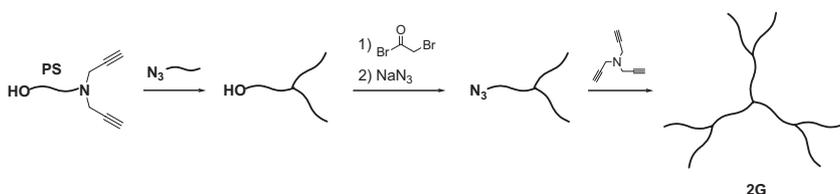
**Scheme 19.** Synthesis of dendrimer-like star-branched polymers by iterative divergent methodology using termination reaction for chain growth.



**Scheme 20.** Synthesis of 3G dendrimer-like star-branched PB by iterative convergent methodology.



**Scheme 21.** Synthesis of 3G dendrimer-like star-branched PS by iterative convergent methodology using  $\alpha, \omega$ -XY<sub>2</sub> PS macromonomers.



**Scheme 22.** Synthesis of 2G dendrimer-like star-branched PS by means of click reaction.

low-molecular-weight poly(ethylene oxide) (PEO) samples clearly shows that the hydroxyl termini could be quantitatively modified and uniform growth of PEO was performed, strongly indicating that the polymerization of ethylene oxide and chain-end-modification reaction worked satisfactorily. However, the problems still remain in the synthesis of high-generation and high-molecular-weight polymers.

Given an appropriate choice of living polymerization and chain-end modification, the isolation step in each iterative

process is not necessary and therefore this methodology is suited for easy and large-scale preparation. However, because of the incomplete initiation and heterogeneous propagation mentioned above, structural defects increase significantly with generation.

### Iterative Convergent Methodology Using Termination Reaction for Chain Growth

In order to overcome the above-mentioned problem, Chalari and Hadjichristidis developed an alternative iterative methodology based on a convergent approach for the synthesis of dendrimer-like star-branched polymers.<sup>[153]</sup> A termination reaction was used for chain growth. The synthetic outline is illustrated in Scheme 19. A living anionic off-center graft copolymer used as the building block unit was first prepared by the linking of an  $\omega$ -styryl macromonomer with a living anionic polymer of styrene or isoprene, followed by living polymerization of isoprene with anions produced in the linking reaction. Then, the resulting living off-center graft copolymer anions were coupled in situ with either MeSiCl<sub>3</sub> or SiCl<sub>4</sub>, resulting in the formation of 2G polymers. Also, 3G polymers have been synthesized by extending the above-mentioned methodology, as illustrated in Scheme 20.<sup>[154]</sup>

Similarly, a 3G dendrimer-like star-branched PS was synthesized by Hutchings and his coworkers with use of  $\alpha, \omega$ -XY<sub>2</sub> PS macromonomers (X and Y were different functionalities), as illustrated in Scheme 21.<sup>[155]</sup> The 3G polymer was built up into dendritic structures by a series of Williamson reactions and subsequent end-group modification reactions. Recently,

Monteiro and coworkers reported that 2G dendrimer-like star-branched polymers could be synthesized by a combination of atom-transfer radical polymerization and “click” reactions (see Scheme 22).<sup>[156]</sup>

The structure of the dendrimer-like star-branched polymer synthesized by the iterative convergent methodology herein employed can be readily checked by comparing the molecular weight of the final product with that of the building unit prepared by pre-made living polymers of known molecular weights. The results of some

**Table 8.** Representative dendrimer-like star-branched polymers synthesized by iterative convergent methodology using termination reaction for chain growth.

| Polymer segment                 | Generation | Number of branch |       | Number of total segment | $\bar{M}_n$                       |      | Literature |
|---------------------------------|------------|------------------|-------|-------------------------|-----------------------------------|------|------------|
|                                 |            | Core             | Layer |                         | $\text{kg} \cdot \text{mol}^{-1}$ |      |            |
|                                 |            |                  |       |                         | RALLS                             | SEC  |            |
| PI                              | 2          | 4                | 2     | 12                      | 245                               | 1.07 | 153        |
| PB                              | 3          | 3                | 2,2   | 21                      | 380                               | 1.09 | 154        |
| PS                              | 3          | 3                | 2,2   | 21                      | 299                               | 1.05 | 155        |
| PS- <i>b</i> -PI                | 2          | 3                | 2     | 9                       | 167                               | 1.07 | 153        |
| PS- <i>b</i> -P <sup>t</sup> BA | 2          | 3                | 2     | 6                       | 57.0                              | 1.19 | 156        |

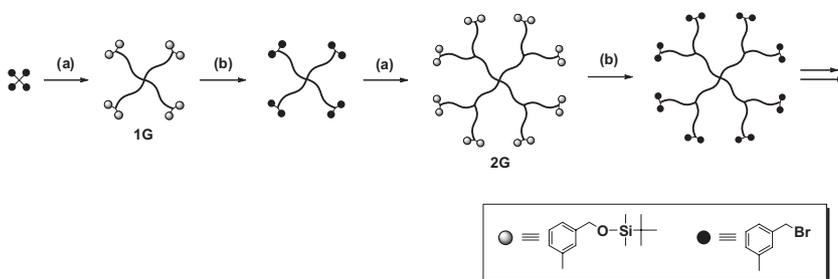
synthetic examples by this methodology are listed in Table 8. Their structures are completely verified by good agreement of the molecular weights between those calculated from the building unit and those observed. The agreement also clearly indicates the structural perfection of the resulting polymers.

The linking reaction among the building units is required at the final stage in this methodology, but becomes increasingly difficult with each generation increment because the molecular weight of the unit essentially multiplies. This means that the iterative convergent methodology is not suited for the synthesis of high-generation dendrimer-like star-branched polymers, especially those with high molecular weights.

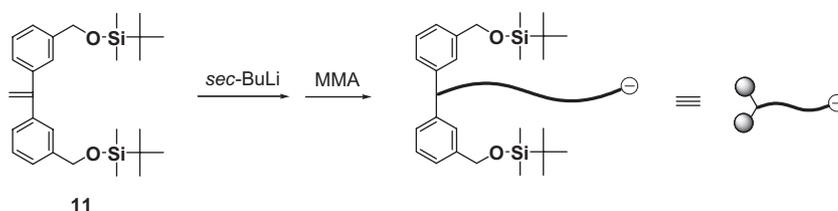
### Iterative Divergent Methodology Using Termination Reaction for Chain Growth

Several difficulties arose in the synthesis of dendrimer-like star-branched polymers by the aforementioned two methodologies. To overcome such difficulties in synthesizing high-generation and high-molecular-weight dendrimer-like star-branched polymers with well-characterized structures, we recently developed a new iterative methodology.<sup>[89,125,128,157–162]</sup> In this methodology, a divergent approach was adopted and a termination reaction with a pre-made living anionic polymer of known molecular weight was employed for chain growth to prepare the building block unit, like the iterative convergent methodology described in the preceding section.

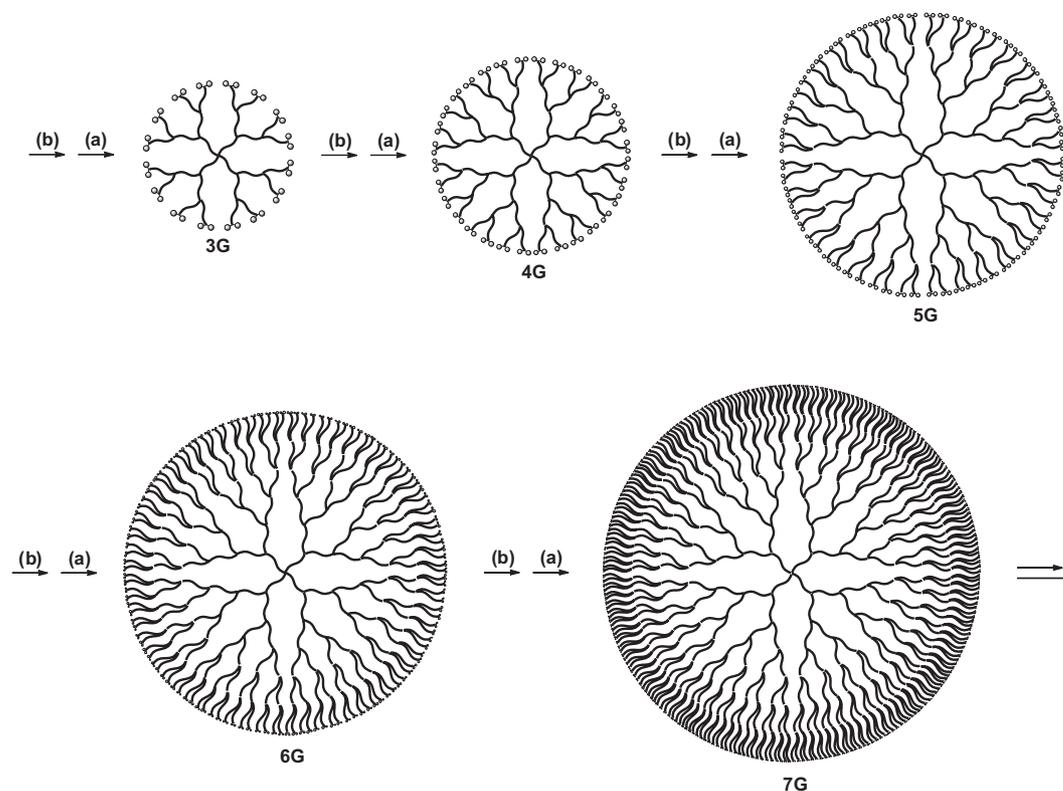
The synthetic outline is illustrated in Scheme 23.<sup>[158]</sup> Basically, two reaction steps are needed for the iterative synthetic sequence: (a) a linking reaction between an  $\alpha$ -terminal (SiOMP)<sub>2</sub>-functionalized living anionic polymer and either a core compound having four BnBr functions (only for the first iterative process) or an  $\alpha$ -terminal (BnBr)<sub>2</sub>-functionalized polymer and (b) a transformation reaction of the SiOMP groups into BnBr functions. Typically,  $\alpha$ -terminal (SiOMP)<sub>2</sub>-functionalized living anionic PMMA was used as a well-defined polymer chain linked between the junction, which was prepared in THF at  $-78^\circ\text{C}$  by living anionic polymerization of MMA with the initiator from 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**11**) and *sec*-BuLi, as illustrated in Scheme 24. A three-fold excess of LiCl was added prior to the polymerization to



**Scheme 23.** Synthesis of 2G dendrimer-like star-branched PMMA by iterative divergent methodology using termination reaction for chain growth.



**Scheme 24.** Preparation of  $\alpha$ -terminal (SiOMP)<sub>2</sub>-functionalized living anionic PMMA.



**Scheme 25.** Synthesis of a series of dendrimer-like star-branched (PMMA)s up to 7G by iterative divergent methodology using termination reaction for chain growth.

narrow the molecular weight distribution. In step (b), the resulting PMMA was treated with  $(\text{CH}_3)_3\text{SiCl-LiBr}$  to transform the two  $\alpha$ -terminal SiOMP groups into two BnBr reaction sites.<sup>[105]</sup> Then, a 1.5-fold excess of  $\alpha$ -terminal  $(\text{SiOMP})_2$ -functionalized living anionic PMMA was reacted with the resulting  $\alpha$ -terminal  $(\text{BnBr})_2$ -functionalized PMMA in THF at  $-40^\circ\text{C}$  for 24 h. Thus, the building unit was prepared by step (a). Since both steps proceeded nearly quantitatively, they could be repeated at least seven times to afford a series of well-defined dendrimer-like star-branched (PMMA)s up to 7G in nearly 100% yields, as illustrated in Scheme 25.

The resulting polymers all have four branch chains emanating from the core and two branch points in all of the layers from 1G to 7G. As can be seen in step (a), in each of the iterative processes where the termination reaction is used for chain growth, incomplete initiation, and heterogeneous propagation from multi-initiation sites and linking reactions among high-molecular-weight repeating units are completely avoided. Accordingly, high-generation and high-molecular-weight polymers with well-defined structures were successfully synthesized. Furthermore, the expected and well-defined structures of the resulting polymers from 1G to 7G were completely verified by agreement of the molecular weights between the building

unit prepared from the starting pre-made living PMMA and the final polymer obtained at each generation.

As shown in Figure 6, all of the polymers from 1G to 7G exhibit sharp monomodal SEC distributions. The characterization results are summarized in Table 9. Two series of polymers were synthesized and their branch chains, composed at each generation, were around 4000 and 10000  $\text{g}\cdot\text{mol}^{-1}$  in molecular weight. Good agreement of the molecular weights between those calculated and observed, and narrow molecular weight distributions ( $\overline{M}_w/\overline{M}_n \leq 1.03$ ) were attained in all polymer samples. The 7G polymer in the first series was a huge macromolecule possessing a predictable  $\overline{M}_n$  value of 2 million  $\text{g}\cdot\text{mol}^{-1}$  and consisting of 508 polymer segments with 512 termini.<sup>[158]</sup> In the case of the second polymer series, the molecular weight reached 1.4 million  $\text{g}\cdot\text{mol}^{-1}$  even in the 5G polymer.<sup>[161]</sup>

A series of highly branched dendrimer-like star-branched (PMMA)s were also successfully synthesized by the same methodology using  $\alpha$ -terminal  $(\text{SiOMP})_4$ -functionalized living PMMA as the new building block, as illustrated in Scheme 26.<sup>[159,162]</sup> The final 3G polymer possesses four polymer segments branched from the cores as well as from all branch points, and a loading capacity of 256 BnBr termini, which is exactly equal to the number of BnBr

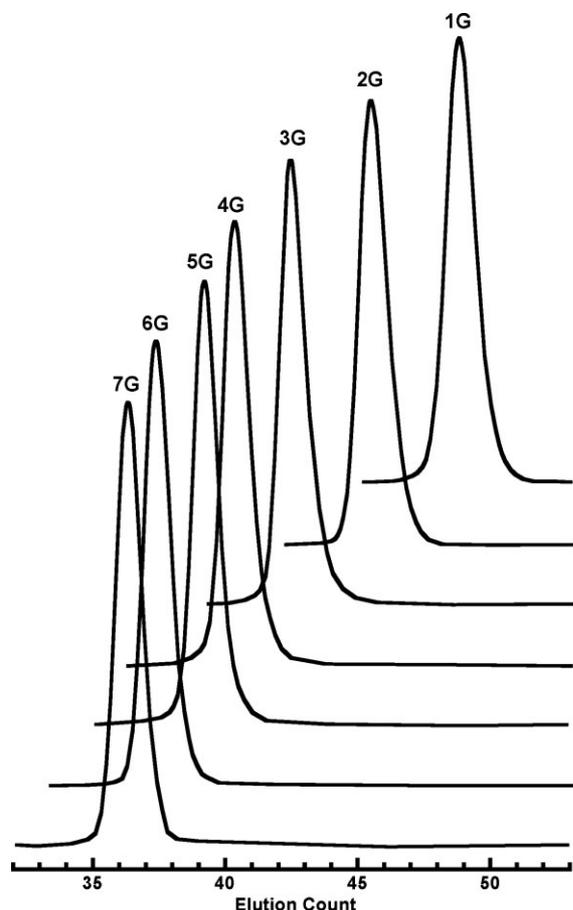


Figure 6. SEC profiles of dendrimer-like star-branched (PMMA)s from 1G to 7G.

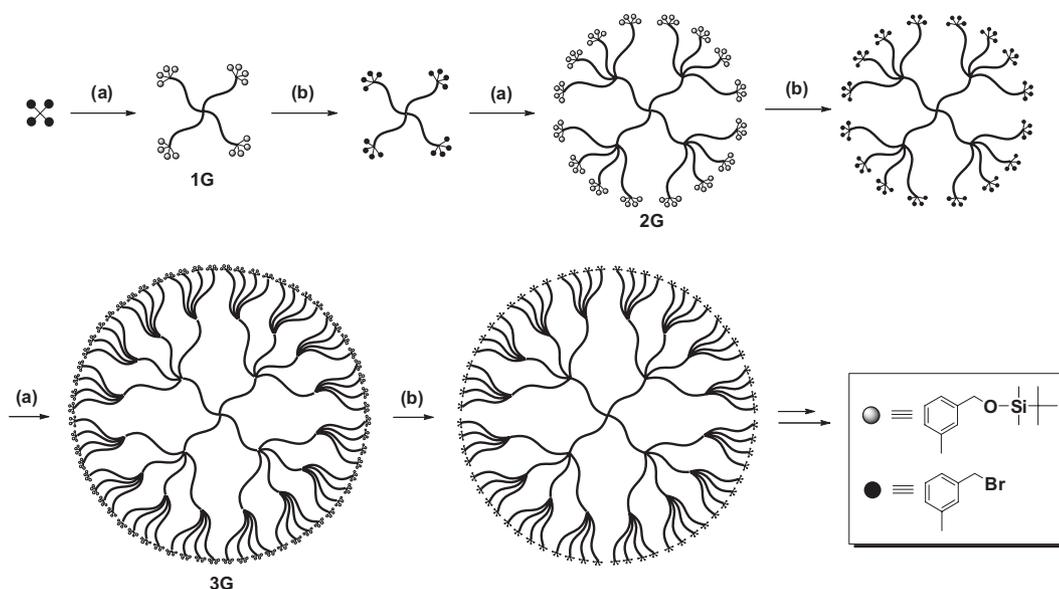
Table 9. Synthesis of dendrimer-like star-branched (PMMA)s by iterative divergent methodology using termination reaction for chain growth.

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

<sup>a)</sup>Molecular weights of arm polymers is  $\approx 4.00$  (kg · mol<sup>-1</sup>); <sup>b)</sup>Molecular weights of arm polymers is  $\approx 10.0$  (kg · mol<sup>-1</sup>).

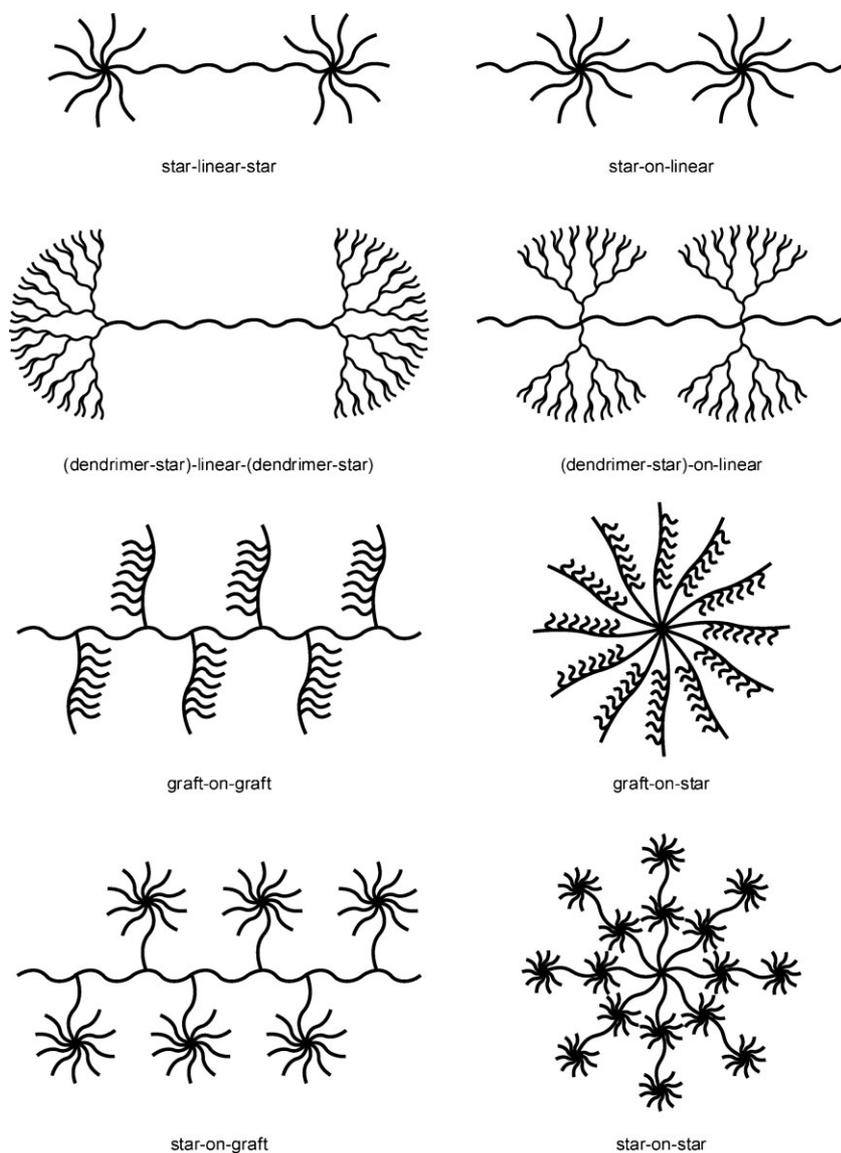
termini of the 6G polymer mentioned above. Furthermore, by appropriately choosing  $\alpha$ -functionalized living anionic PMMA with either two or four SiOMP groups in each iterative process, three 4G polymers with different branched architectures could also be synthesized, as shown in Figure 7.<sup>[160,162]</sup> Their well-defined and characterized structures were confirmed by the analytical results of all polymer samples.

Very recently, the successful synthesis of a series of dendrimer-like star-branched (PS)s and block copolymers



Scheme 26. Synthesis of highly branched dendrimer-like star-branched (PMMA)s using  $\alpha$ -terminal (SiOMP)<sub>4</sub>-functionalized living anionic PMMA.





■ Figure 8. Branched polymers with complex architectures.

received much attention. Branched polymers will have more possibility in this respect in the same fields because of their complexity, branched architectures, and more structural variables. However, their utility has been necked by their synthetic difficulties. Throughout this paper, we have demonstrated that the commonly-featured methodology herein introduced is applicable to a variety of branched polymers and, in fact, many-armed and multi-compositional star polymers, exact graft (co)polymers, and structurally well-defined dendrimer-like star-branched polymers, which are synthetically difficult, are successfully synthesized by this methodology. Such branched polymers may be utilized as next generation polymers leading to nanomaterials. For instance, it may be expected that these

polymers will be used as enzyme and catalyst carrying nanoreactors, multi-compartment micelles, carriers of drugs and genetic materials, shape-persistent nanodevices, biomimetic molecules, nanosurface modifiers, etc.

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