Successive Synthesis of Well-Defined Star-Branched Polymers by "Convergent" Iterative Methodology Using Core-Functionalized 3-Arm Star-Branched Polymer and a Specially Designed 1,1-Diphenylethylene Derivative

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Summary: The synthesis of well-defined regular and miktoarm star-branched polymers by a convergent iterative methodology using core-functionalized 3-arm star-branched polymer with 1,1-diphenylethylene (DPE) moiety and a specially designed DPE derivative is described. The methodology involves the following two reaction steps in the entire iterative synthetic sequence: 1) a coupling reaction of a star-branched polymer having an anion at the core with a DPE derivative with two benzyl bromide moieties, 1-{4-[5,5-bis(3-bromomethylphenyl)-7-methylnonyl]phenyl}-1-phenylethylene, and 2) an addition reaction of the resulting core-DPE-functionalized star-branched polymer with *sec*-BuLi to convert the DPE moiety to a DPE-derived anion. The iterative synthetic sequence including these two reaction steps, 1) and 2), was repeated to successively synthesize star-branched polymers with more arms. Iteration of this synthetic sequence doubled the number of the arms in the star-branched polymer. With this methodology, 6-arm, 12-arm, and 14-arm regular star-branched polystyrenes as well as 6-arm $A_2B_2C_2$, A_4B_2, and 12-arm $A_4B_4C_4$ and A_8B_4 miktoarm star-branched polymers with well-defined structures have been successfully synthesized.

Keywords: convergent iterative methodology; living polymerization; specially designed 1,1-diphenylethylene derivative; star polymer; successive synthesis

Introduction

Star-branched polymers have been widely studied for a long time because of the synthetic challenges associated with preparing them and because they offer unique properties and behaviors in solution, melt, and solid states that are quite different from the corresponding linear polymers.[1–8] Among star-branched polymers, miktoarm star-branched polymers having chemically different arms have recently gained immense interest by their ability to change the morphological map of their linear block counterparts and to create novel nanostructured periodic domains with special shapes and suprastructural molecular assemblies potentially applicable to functional nano-devices.[9–17] Unfortunately, however, availability of well-defined miktoarm star-branched polymers composed of many arms and components is very limited because of the following synthetic difficulties:[9–11,18–25] 1) Two or more linking reactions with quantitative nature are required to introduce different arms, 2) Isolation of the intermediate polymers is often needed to obtain pure products, and 3) The combination of different arm segments is limited.

In order to overcome such difficulties to synthesize miktoarm star-branched polymers composed of many arms and components, we have been, for recent several years, developing novel iterative methodologies based on "divergent" approach using living anionic polymers in conjunction with specially designed 1,1-diphenylethylene (DPE) derivatives.[12,13,22,26–33] In these methodologies, only two reaction steps are basically employed in the entire iterative synthetic sequence as follows: 1) an addition reaction of living anionic polymer(s) with DPE-functionalized polymer(s) to link the polymer chains, and 2) a re-introduction reaction of DPE moiety(ies) used as the next reaction site(s). By repeating the iterative synthetic sequence, the same or different arm segment(s) is/are successively introduced into the stars, resulting in the formation of a series of miktoarm star-branched polymers with increasing arm segment(s) as iteration by iteration. With these methodologies, we have successfully synthesized a variety of miktoarm stars such as 3-arm ABC, 4-arm ABCD, 5-arm ABCDE, 6-arm ABCDEF, 7-arm ABCDEFG, 6-arm $A_2B_2C_2$, 6-arm A_3B_3, 9-arm $A_3B_3C_3$, 7-arm AB_2C_4, 15-arm $AB_2C_4D_8$, and 31-arm $AB_2C_4D_8E_{16}$ types. The resulting stars all were well-defined in branched architecture and precisely controlled in arm segment because best class living anionic polymers of styrene, 1,3-butadiene, isoprene, and their functional derivatives were used as arm segments. The successful synthesis of complex miktoarm star-branched polymers by these methodologies is also strongly attributed to the quantitative addition reaction of such living polymers with the DPE moiety(ies).

More recently, we have also developed an alternative iterative methodology based on ‘‘convergent’’ approach for the synthesis of similar miktoarm star-branched polymers composed of many arms and components.[34] The methodology involves the following two reaction steps in the iterative synthetic sequence: 1) a coupling reaction of a polymer anion with 1,1-bis(3-chloromethylphenyl)ethylene to link the polymer chains with the introduction of the DPE moiety, and 2) an addition reaction of the resulting DPE-functionalized polymer with *sec*-BuLi to convert the DPE moiety to a DPE-derived anion. By repeating the two reaction steps, the successive synthesis of well-defined 4-arm, 8-arm, followed by16-arm regular star-branched polystyrenes as well as 4-arm A_2B_2, 8-arm A_4B_4, followed by 16-arm A_8B_8 miktoarm stars has been successfully achieved. Based on the convergent approach, the number of arms in such stars were extremely presice free of any defects.

Herein, we extend the ‘‘convergent’’ iterative methodology to the successive synthesis of a series of miktoarm star-branched polymers composed of three chemically different arms. In this synthesis, a 3-arm ABC star-branched polymer core-functionalized with DPE moiety and a new specially designed DPE derivative, 1-{4-[5,5-bis(3-bromomethylphenyl)-7-methylnonyl]-phenyl}-1-phenylethylene (**3**) are used.

Experimental Part

Materials

All chemicals (> 98% purity) were purchased from Aldrich Japan or Tokyo Kasei Co. Ltd., and used as received unless otherwise noted. Tetrahydrofuran (THF), heptane, styrene, DPE, α-methylstyrene, 4-methylstyrene, and isoprene were purified according to the procedures reported elsewhere.[26] 1-[4-(4-Bromobutyl)phenyl]-1-phenylethylene (**1**) and **3** were synthesized by our procedure previously reported.[26,29]

Measurements

Size exclusion chromatography (SEC) was performed on an Asahi Techneion AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL/min at 30 °C. Three PS gel columns were used. Their pore sizes (bead size) were as follows: 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm). The relative molecular weight of a polymer was calculated by RI detection using standard polystyrene calibration. The combination of viscometer, right angle laser light scattering (RALLS) detection, and RI detection was applied for the online SEC system in order to determine the absolute molecular weight of branched polymers. Both ^1H and ^{13}C NMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $CHCl_3$ (δ 7.26) and $CDCl_3$ (δ 77.1) for ^1H and ^{13}C NMR as standard, respectively.

Synthetic Procedures

All the polymerizations and reactions were carried out under high vacuum conditions ($\sim 10^{-6}$ torr) in sealed glass reactors with breakable seals. Polystyryllithium (PSLi), poly(α-methylstyryl)lithium (PαMSLi), and poly(4-methylstyryl)lithium (PMSLi) were prepared by the *sec*-BuLi-initiated polymerization of the corresponding monomers in THF at −78 °C for 20 min, 3 h, and 30 min, respectively. Poly(isoprenyl)lithium (PILi) was prepared by the *sec*-BuLi-initiated polymerization of isoprene in heptane at 30 °C for 5 h.

Preparation of 3-Arm ABC Miktoarm Star-Branched Polymer Core-Functionalized with DPE Moiety

Under high vacuum conditions, DPE (0.765 mmol) in THF (5.05 mL) was added to PSLi (0.500 mmol, $M_n = 10\,300$ g/mol) in THF (58.5 mL) at −78 °C and the mixture was allowed to stand for an additional 1 h. The resulting PSLi end-capped with DPE was *in-situ* reacted with **1** (0.622 mmol) in THF (5.50 mL) at −78 °C for 10 min. The reaction mixture was poured into a large amount of methanol to precipitate the polymer. It was purified by reprecipitation twice, followed by freeze-drying from its absolute benzene solution for 24 h. The chain-end-DPE-functionalized PS was obtained (4.99 g, 95%, $M_n = 10\,500$ g/mol, $M_w/M_n = 1.02$). The degree of DPE end-functionality was observed by ^1H NMR analysis to be quantitative (>99%).

PαMSLi (0.427 mmol, $M_n = 10\,700$ g/mol, $M_w/M_n = 1.02$) in THF (41.9 mL) was added to a THF solution (36.0 mL) containing chain-end-DPE-functionalized PS (0.385 mmol) at −78 °C and the reaction mixture was allowed to stand for 2 h. Then, DPE (0.126 mmol) in THF (2.02 mL) was added to end-cap the excess unreacted PαMSLi to avoid the unwanted attack of PαMSLi to the DPE moiety of **1** prior to the addition reaction, followed by *in-situ* addition of **1** (0.560 mmol) in THF (5.33 mL) in THF at −78 °C for 10 min. The reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymer was isolated by fractional precipitation using cyclohexane-hexane system and purified by reprecipitation twice, followed by freeze-drying from its absolute benzene solution for 24 h. Thus, the in-chain-DPE-functionalized PS-*block*-PαMS was prepared (6.74 g, 80%, $M_n = 21\,900$ g/mol, $M_w/M_n = 1.04$).

Finally, PMSLi (0.304 mmol, $M_n = 10\,800$ g/mol, $M_w/M_n = 1.02$) in THF (33.8 mL) was added to a THF solution (50.0 mL) containing in-chain-DPE-functionalized PS-*block*-PαMS (0.268 mmol) at −78 °C and the reaction mixture was allowed to stand for 5 h. Then, DPE (0.127 mmol) in THF (2.12 mL) was added to end-cap the excess unreacted PMSLi to avoid the unwanted attack of PMSLi with the DPE moiety of **1**, followed by *in-situ* addition of **1** (0.442 mmol) in THF (2.70 mL) at −78 °C for 10 min. The reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymer was isolated by fractional precipitation using cyclohexane-hexane system and purified by reprecipitation twice, followed by freeze-drying from its absolute benzene solution for 24 h. The 3-arm ABC miktoarm star-branched polymer core-functionalized with DPE moiety was obtained (6.46 g, 74%, $M_n = 33\,400$ g/mol, $M_w/M_n = 1.02$).

Both the core-DPE-functionalized 3-arm A_3 and A_2B star-branched polymers, where A and B are PS and PI segments, were prepared in a similar manner. Their M_n values and M_w/M_n were 30 700 g/mol, 35 300 g/mol, and 1.04, 1.03, respectively.

Successive Synthesis of 6-Arm $A_2B_2C_2$ and 12-Arm $A_4B_4C_4$ Miktoarm Star-Branched Polymers by Convergent Iterative Methodology

A core-DPE-functionalized 3-arm ABC miktoarm star-branched polymer (0.0938 mmol, 3.04 g) in THF (32.5 mL) pre-cooled at −78 °C was mixed with *sec*-BuLi (0.0944 mmol) in heptane (2.05 mL) at −78 °C. The reaction mixture was immediately changed to a dark red in color and allowed at −78 °C for an additional 1 h. Then, a THF (1.50 mL) solution containing **3** (0.0391 mmol) was added slowly to the dark red solution at −78 °C and the reaction mixture was allowed to react for 1 h. The reaction was terminated with degassed methanol and the resulting mixture was poured into a large amount of methanol to precipitate the polymers. The objective coupled polymer was isolated by fractional precipitation using cyclohexane-hexane system. The isolated polymer was purified by reprecipitation twice, followed by freeze-drying from its absolute benzene solution for 24 h. The 6-arm $A_2B_2C_2$ miktoarm star-branched polymer core-functionalized with DPE moiety was obtained (1.82 g, 60%, $M_n = 66\,600$ g/mol, $M_w/M_n = 1.02$).

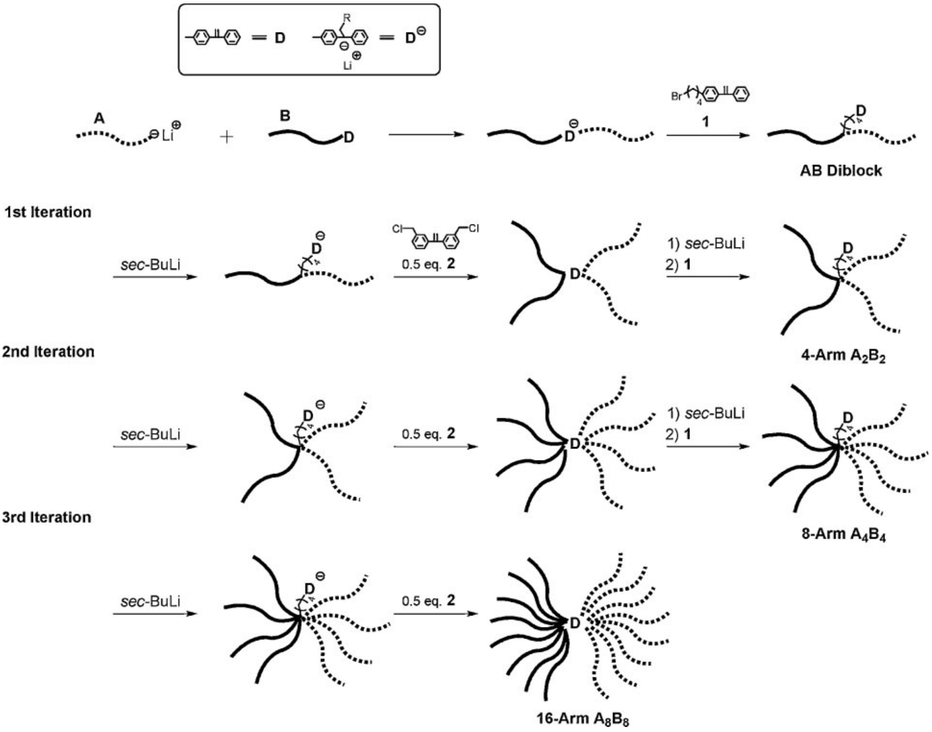
The core-DPE-functionalized 6-arm $A_2B_2C_2$ miktoarm star-branched polymer thus synthesized (1.33 g, 0.0500 mmol) in THF (14.0 mL) pre-cooled at −78 °C was mixed with *sec*-BuLi (0.0505 mmol) in heptane (1.20 mL) at −78 °C and the reaction mixture was allowed to react at −78 °C for an additional 1 h. Then, a THF (1.50 mL) solution containing **3** (0.0209 mmol) was added slowly to the reaction mixture at −78 °C and allowed to react for 3 h. The reaction was terminated with degassed methanol and the resulting reaction mixture poured into a large amount of methanol to precipitate the polymers. The reaction efficiency was estimated by SEC profile of the reaction mixture to be 70%. The coupled polymer was isolated by SEC. The isolated polymer was purified by reprecipitation twice, followed by freeze-drying from its absolute benzene solution for 24 h. The 12-arm $A_4B_4C_4$ miktoarm star-branched polymer core-functionalized with DPE moiety was obtained ($M_n = 134\,000$ g/mol, $M_w/M_n = 1.02$).

Similarly, 6-arm, 12-arm, and 14-arm regular star-branched (PS)s as well as 6-arm A_4B_2 and 12-arm A_8B_4 miktoarm star-branched polymers were synthesized by the same convergent iterative methodology using either the core-DPE-functionalized 3-arm A_3 or A_2B star-branched polymer as a starting material. The yields of the 6-arm stars were always quantitative, while the 12-arm and 14-arm star-branched polymers were obtained in 70–76% yields.

Results and Discussion

Successive Synthesis of Regular Star Polystyrenes by "Convergent" Iterative Methodology

As mentioned in introduction, we previously reported the successive synthesis of miktoarm star-branched polymers by developing the iterative methodology based on "convergent" approach as illustrated in Scheme 1.[34] In-chain-DPE-functionalized AB diblock copolymer was first synthesized by the addition reaction of living polymer A to chain-end-DPE-functionalized polymer B, followed by reacting with **1** to introduce the DPE moiety between the two blocks separated by four methylene units from the linking point to reduce the steric hindrance. The in-chain-DPE-functionalized AB diblock polymer thus prepared was treated with *sec*-BuLi to convert the DPE moiety to a DPE-derived anion, followed by reacting with 1,1-bis(3-chloromethylphenyl)ethylene (**2**) to afford a 4-arm A_2B_2 miktoarm star-branched polymer core-functionalized with DPE moiety. The reaction efficiency was quantitative in this coupling reaction. In the second iterative synthetic sequence, the resulting 4-arm A_2B_2 star core-functionalized with DPE moiety was treated in the same manner as that mentioned above, followed by reacting with **2** to afford a 8-arm A_4B_4 miktoarm star-branched polymer core-functionalized with DPE moiety. Further iteration of this synthetic sequence gave a more complex 16-arm A_8B_8 miktoarm star. Although the coupling reaction smoothly proceeded, the efficiency was not quantitative as expected, but 65% in this stage.

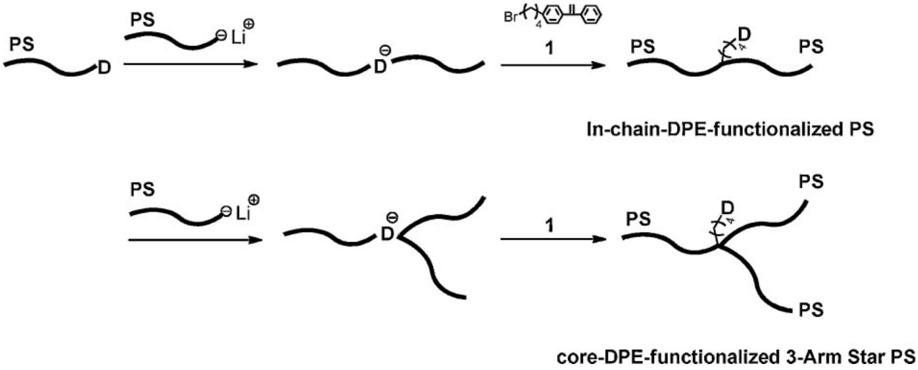


Scheme 1.
Synthetic routes for 4-arm A_2B_2, 8-arm A_4B_4, and 16-arm A_8B_8 miktoarm star-branched polymers based on convergent iterative methodology.

As was seen in Scheme 1, the number of the arm segments exactly doubled as repeating the iterative synthetic sequence to result in the formation of 4-arm, 8-arm, followed by even 16-arm star-branched polymers. This result strongly indicates that the convergent iterative methodology shown in Scheme 1 is worth of further study as one of the general synthetic procedures for miktoarm star-branched polymers composed of many arms.

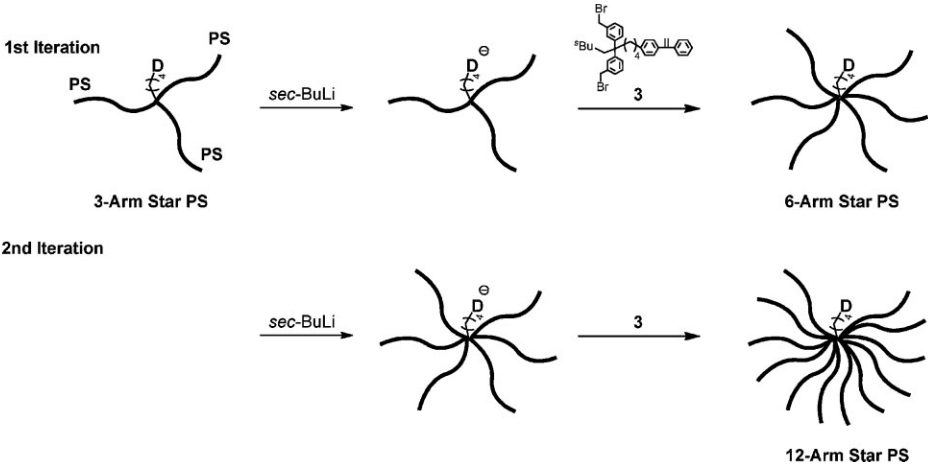
In this study, we have extended the above mentioned methodology to the successive synthesis of miktoarm star-branched polymers having three chemically different arms in order to demonstrate the utility and versatility of the methodology. In this methodology, 3-arm ABC miktoarm star-branched polymer core-functionalized with DPE moiety is employed as a starting material. To examine the possible use of 3-arm star-branched polymer, the successive synthesis of regular star (PS)s was first carried out by using the core-DPE-functionalized 3-arm star-branched PS as a starting material. This star PS was prepared by our procedure previously reported as illustrated in Scheme 2.[27] PSLi was reacted with chain-end-DPE-functionalized PS, followed by reacting with **1** to introduce the DPE moiety between the two PS chains. The resulting in-chain-DPE-functionalized PS further reacted with PSLi to link PS chain and then *in-situ* with **1** to introduce the DPE moiety at the core of the resulting 3-arm star PS. Since each of all the reactions was always carried out with almost 100% efficiencies, the yield of the 3-arm star PS was nearly quantitative.

The successive synthesis of star-branched (PS)s was performed by the convergent iterative methodology using the core-DPE-functionalized 3-arm star PS as illustrated in Scheme 3. In the present



Scheme 2.
Synthetic routes for core-DPE-functionalized 3-arm star-branched PS.

methodology, a new specially designed DPE derivative, **3**, was used in order to introduce the DPE moiety separated by four methylene units from the linking point. With use of **3**, the reaction steps involving the *sec*-BuLi treatment and the reaction of the DPE-derived anion with **1** in the previous methodology shown in Scheme 1 could be avoided. The core-DPE-functionalized 3-arm star PS was treated with a nearly equal amount of *sec*-BuLi to convert the DPE moiety to a DPE-derived anion, followed by reacting with **3** in THF at −78 °C to couple the 3-arm star-branched PS anion each other. A 1.2-fold excess of the star PS anion toward each of the two benzyl bromide (BnBr) moieties was used to complete the reaction. The SEC profile of the reaction mixture shown in Figure 1 exhibits only two peaks corresponding to the coupled product and the unreacted star PS anion used in excess in the reaction. The coupling reaction was estimated to proceed virtually quantitatively by comparing the two peak areas. The coupled product isolated by fractional precipitation exhibited a sharp monomodal SEC distribution (see also Figure 1).



Scheme 3.
Synthetic routes for 6-arm and 12-arm star-branched polystyrenes based on convergent iterative methodology using **3**.

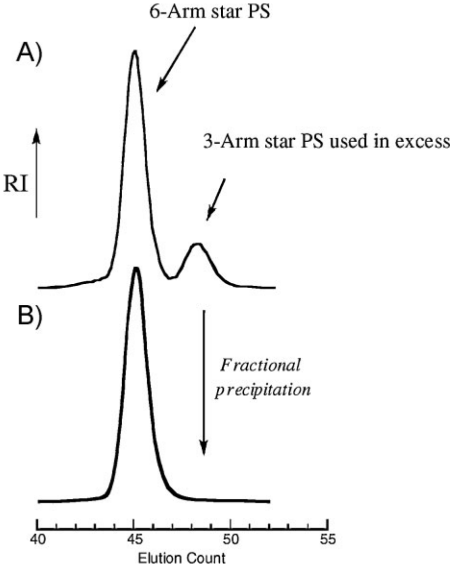


Figure 1.
SEC profiles of the resulting polymers obtained by the coupling reaction of 3-arm star-branched PS anion with **3**; (A) before and (B) after fractional precipitation.

The results are summarized in Table 1. Although the M_n value estimated by SEC was smaller than that predicted as expected from its star-branched architecture, either the M_n or M_w value determined by RALLS was in good agreement with that calculated. Moreover, the g' value measured was almost the same as that calculated from the theoretical equation previously established.[35] These results clearly indicate that the resulting polymer is the expected 6-arm star-branched PS with well-defined structure. Thus, the first iteration works satisfactorily.

At the second iteration, the core-DPE-functionalized 6-arm star-branched PS obtained by the first iteration was treated with *sec*-BuLi, followed by coupling with **3** under the similar conditions to those employed for 6-arm star PS synthesis. The coupling reaction was observed to proceed with the efficiency of 75% by estimating from the SEC profile of the reaction mixture. The efficiency was not improved by changing the reaction conditions and the ratio of the star PS anion with 3. This may be attributed to the steric hindrance between the 6-arm star PS anion and the intermediate 6-arm star PS core-functionalized with BnBr moiety.

In order to examine the steric hindering effect and to explore the more possibility of the coupling reaction, the 6-arm core-DPE-functionalized star PS was reacted with 0.95 equivalents of PSLi to link one more PS chain, followed by reacting with **1** to introduce the DPE moiety. Then, the core-functionalized 7-arm star PS thus synthesized was treated with *sec*-BuLi then coupled with **3** to afford a 14-arm star PS. The SEC profile of the reaction mixture was very similar to that observed in the synthesis of 12-arm star-branched PS. The coupling efficiency was estimated by the SEC profile to be 76%. The characterization results listed in Table 1 clearly show that the resulting polymer is the expected 14-arm star-branched PS.

Table 1.
Synthesis of 3-, 6-, 7-, and 14-arm star-branched polystyrenes.

	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	$g' = [\eta]_{star}/[\eta]_{linear}$ b)	
Type	Calcd	SEC	RALLS	Calcd a)	RALLS	SEC	Calcd c)	Expml
3-Arm	30.3	27.9	30.7	31.5	31.9	1.04	0.82	0.84
6-Arm	61.1	42.9	64.2	63.5	66.8	1.04	0.57	0.56
7-Arm	72.2	48.8	72.0	75.1	74.2	1.04	0.51	0.52
14-Arm	145	69.9	149	150	153	1.03	0.29	0.30

a) Calculated from M_n (calcd) and M_w/M_n (SEC) values.
b) Intrinsic viscosities of star-branched PSs ($[\eta]_{star}$) were measured in toluene at 35 °C. Intrinsic viscosities of linear PSs with the same molecular weights ($[\eta]_{linear}$) were calculated from the equation; $[\eta] = 1.29 \cdot 10^{-4} M_w (\mathrm{RALLS})^{0.71}$ values.
c) Calculated from the equation; $g' = [(3f - 2)/f^2]^{0.58}[0.724 - 0.015(f - 1)]/0.724$.

The coupling reaction of either 6-arm or 7-arm star PS anion with **3** proceeded with efficiencies of around 75%, but not quantitatively, possibly due to the steric hindering effect between the star polymer anion and the intermediate core-BnBr-functionalized star polymer. They are similar to the previous result obtained in the synthesis of 16-arm star-branched polymer as shown in Scheme 1. This strongly suggests that molecular design to reduce the steric hindrance around the core is needed to synthesize star-branched polymers with more than 12 arms by the convergent iterative methodology. Nevertheless, rather surprising was that the coupling reaction proceeded with high efficiencies of around 75% between high molecular weight polymers having M_n values of around 70 000 g/mol. Based on such synthetic results, the synthesis of miktoarm star-branched polymers by the convergent iterative methodology using core-DPE-functionalized 3-arm ABC star-branched polymer are carried out in the next section.

Synthesis of Miktoarm Star-Branched Polymers Composed of Three Chemically Different Arms by "Convergent" Iterative Methodology

As mentioned above, the core-DPE-functionalized 3-arm ABC miktoarm star-branched polymer is needed as a starting polymer to synthesize the miktoarm star-branched polymers composed of three different arm segments by the convergent iterative methodology. The 3-arm ABC star was readily prepared by the procedure similar to that used for the preparation of 3-arm star PS shown in Scheme 1. Instead of the use of PSLi in each of the three reaction steps, PSLi, PαMSLi, and PMSLi were sequentially reacted in the linking reaction steps. The 3-arm core-DPE-functionalized ABC star-branched polymer was nearly quantitatively yielded and well-defined in structure as listed in Table 2.

The synthetic outline of miktoarm star-branched polymers composed of three different arms by the convergent iterative methodology is illustrated in Scheme 4. At the first iteration, the 3-arm ABC star was treated with *sec*-BuLi to convert the DPE moiety to a DPE-derived anion and then reacted with **3** under the same conditions as those used for the synthesis of 6-arm star PS. A 1.2-fold excess of the 3-arm ABC asymmetric star polymer anion was also used in this coupling reaction. The reaction quantitatively underwent as expected. In the SEC profile of the isolated product, a sharp monomodal peak was obtained and the peak position was completely sifted to higher molecular weight region.

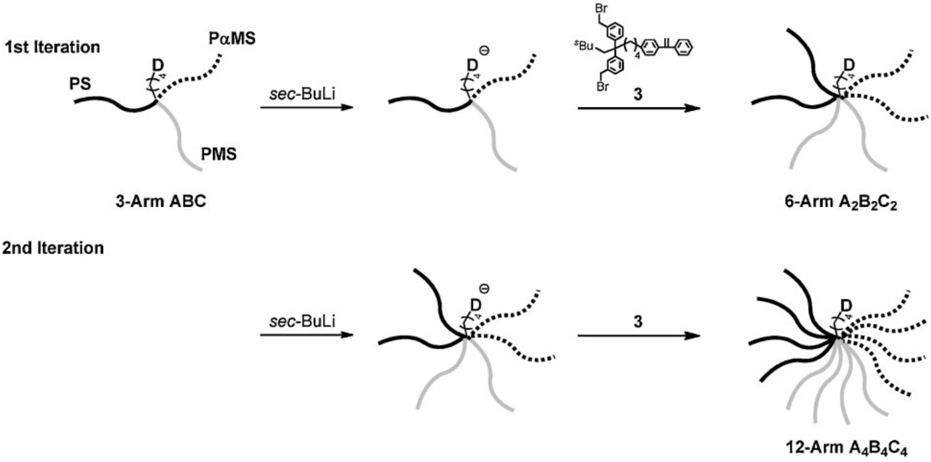
As listed in Table 2, good agreement of the molecular weights as well as the compositions between calculated and observed is observed, and a narrow molecular weight distribution is attained. Thus, all of the analytical results are consistent with the successful formation of the expected and well-defined 6-arm $A_2B_2C_2$ miktoarm star core-functionalized with DPE moiety.

Since the resulting 6-arm star possessed the same DPE moiety at the core, the same iterative synthetic sequence was repeated. The coupling reaction could proceed with the efficiency of 70% similar to that observed in the synthesis of 12-arm star-

Table 2.
Synthesis of 3-arm ABC, 6-arm $A_2B_2C_2$, and 12-arm $A_4B_4C_4$ miktoarm star-branched polymers.

	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	Composition (A/B/C wt%)	
Type	Calcd	SEC	RALLS	Calcd$^{a)}$	RALLS	SEC	Calcd	Expml
ABC	32.0	27.9	33.4	32.6	34.1	1.02	35/32/33	37/32/31
$A_2B_2C_2$	67.1	51.9	66.6	68.4	67.9	1.02	35/32/33	32/33/35
$A_4B_4C_4$	134	74.3	134	137	137	1.02	35/32/33	35/32/33

a)Calculated from M_n (calcd) and M_w/M_n (SEC) values.



Scheme 4.
Synthetic routes for 6-arm $A_2B_2C_2$ and 12-arm $A_4B_4C_4$ miktoarm star-branched polymers based on convergent iterative methodology using **3**

branched PS. Several attempts by changing the reaction variables to improve the efficiency were not successful. Since the pure polymer was not obtained by fractional precipitation, the coupled product was isolated by SEC and characterized by SEC, ^{1}H NMR, and RALLS, respectively. As was seen in Table 2, the isolated polymer was confirmed by all of the analytical results to be the expected and well-defined 12-arm $A_4B_4C_4$ miktoarm star-branched polymer. This 12-arm miktoarm star composed of three different arms is the first successful example and difficult by other methodologies so far reported.

Similarly, we have successfully synthesized well-defined 6-arm A_4B_2 and 12-arm A_8B_4 miktoarm star-branched polymers, in which A and B are PS and poly(isoprene) (92% cis-1,4) segments, by twice repeating the iterative synthetic sequence in the same methodology using the core-DPE-functionalized 3-arm A_2B star polymer as a starting polymer.

In conclusion, the convergent iterative methodology herein proposed works satisfactorily for the synthesis of 6- followed by 12-arm regular and miktoarm star-branched polymers. In particular, the successful synthesis of the 12-arm $A_4B_4C_4$ miktoarm star-branched polymer is of great value because it is difficult by other methodologies. Initially, we thought that the successive synthesis of star-branched polymers up to those having even more than 12 arms would be achieved by the convergent iterative procedure. It was however difficult to repeat the iterative synthetic sequence one more time for the synthesis of 24-arm star-branched polymers. In practice, the coupling reaction of the12-arm $A_4B_4C_4$ star anion with **3** could have occurred only to an extent of *ca.* 10% under the same conditions with a longer reaction time. As mentioned above, changing the molecular design to reduce the steric hindrance aorund the core is strongly desired for a further synthetic development affording 24-arm or more arm star-branched polymers.

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