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Successive Synthesis of Regular and Asymmetric Star-Branched Polymers by Iterative Methodology Based on Living Anionic Polymerization Using Functionalized 1,1-Diphenylethylene Derivatives

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Summary: In order to achieve the successive synthesis of star-branched polymers, we have developed a new iterative methodology which involves only three sets of the reactions in each iterative process: (a) a coupling reaction of a living anionic polymer with 1,1-bis(3-chloromethylphenyl)ethylene to prepare a DPE-chain-functionalized polymer, (b) an addition reaction of *sec*-BuLi to the DPE-chain-functionalized polymer, followed by treatment with 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene to prepare a new DPE-chain-functionalized polymer whose DPE is separated by four methylene units from the main chain, and (c) a coupling reaction of 1,1-bis(3-chloromethylphenyl)ethylene with the polymer anion derived from the newly prepared DPE-chain-functionalized polymer and *sec*-BuLi. With this methodology, a series of well-defined 4-arm, 8-arm, and 16-arm regular star-branched polystyrenes as well as 4-arm A_2B_2, 8-arm A_4B_4, and 16-arm A_8B_8 asymmetric star-branched polymers comprising polystyrene and poly(α-methylstyrene) segments have been successively synthesized.

Keywords: anionic polymerization; iterative methodology; living polymerization; star polymers

Introduction

Star-branched polymers have been widely studied for a long time from both synthetic and theoretical viewpoints.[1–8] Among them, well-defined asymmetric type stars with different arms in chemical composition have recently received much attention because their arm segments may possibly phase-separate at molecular level, followed by self-organization to form complex periodic ordered nanoscopic objects potentially usable as nano-patterned devices. Indeed, new specific tetragonal and hexagonal morphologies have been observed in 3-arm ABC and the related asymmetric star-branched polymers by several research groups.[7–16] However, availability of such well-defined asymmetric star-branched polymers is rather limited because of two or more quantitative nature of reactions and the isolation of intermediate polymers are often required during the synthesis.[17–23] Therefore, a new development is still desired even at the present time to establish general and versatile methodologies usable for the synthesis of asymmetric stars with a variety of structural variables.

We have recently reported a novel iterative methodology, by which a variety of regular as well as asymmetric star-branched polymers can be successively synthesized.[24–27] The methodology involves only two reaction steps for the entire iterative synthetic sequence: (a) an addition reaction of a living anionic polymer to either the DPE derivative or

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DPE-chain-functionalized polymer to link the polymer chain *via* DPE function and (b) an *in-situ* coupling reaction of 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene (**1**) with the 1,1-diphenylalkyl anion generated by the above addition reaction to introduce a new DPE functionality. By repeating the reaction sequence, AB diblock copolymer, 3-arm ABC, 4-arm ABCD, followed by 5-arm ABCDE asymmetric stars can be successively synthesized.[24,25] The methodology has been extended to the synthesis of more complex asymmetric star-branched polymers. Using 1, 3-bis(1-phenylethenyl)benzene as a starting core compound, for example, the two reaction steps (a) and (b) were repeated three times to quantitatively afford A_2, 4-arm A_2B_2, followed by 6-arm $A_2B_2C_2$ asymmetric stars.[26] Similarly, a series of 3-arm A_3, 6-arm A_3B_3, and 9-arm $A_3B_3C_3$ asymmetric star-branched polymers were also successively synthesized by the same iterative methodology using 1,1-bis(3-(1-phenylethenyl)phenyl)ethylene as a core compound.[27] The key point of this iterative methodology is that the two reaction steps proceed cleanly and quantitatively and the DPE moiety used as a reaction site is always regenerated after each of the iterative processes and hence the same reaction sequence can be, in principle, limitlessly repeated to successively synthesize a variety of asymmetric star-branched polymers. It should be emphasized that the resulting star-branched polymers all were well-defined in branching architecture and precisely controlled in chain length, since the methodology is based on the "arm-first" termination method with pre-made living anionic polymers.

Herein, we propose an alternative iterative methodology for the successive synthesis of regular as well as asymmetric star-branched polymers. It involves two or three reaction steps in each iterative process using **1** or/and 1,1-bis(3-chloromethylphenyl)ethylene (**2**). A series of regular star-branched polystyrenes and asymmetric stars comprising polystyrene and poly(α-methylstyrene) segments will be synthesized by repeating the reaction sequence in each iteration.

Experimental Section

Materials

All chemicals (>98% purities) were purchased from Tokyo Kasei Co. Ltd. or Aldrich, Japan and used as received unless otherwise stated. THF, styrene, α-methylstyrene, and 1,1-diphenylethylene (DPE) were purified according to the procedures reported elsewhere.[27] 1-(4-(4-Bromobutyl)phenyl)-1-phenylethylene (1) and 1,1-bis(3-chloromethylphenyl)ethylene (2) were synthesized according to our procedures previously reported.[24]

Measurements

Size-exclusion chromatography (SEC) was performed on a TOSOH HLC 8020 instrument with UV (254 nm) and refractive index detection, THF being used as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Both ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured in $CDCl_3$ using a BRUKER DPX spectrometer. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instrument in benzene at 40 °C with a highly sensitive thermoelectric couple with equipment of very exact temperature control. Static light scattering (SLS) measurements were performed with an Ohotsuka Electronics DLS-7000 instrument equipped with a He-Ne laser (633 nm) in THF at 25 °C. The refractive index increment (d*n*/d*c*) in THF at 25 °C was determined for each star-branched polymer with an Ohotsuka Electronics DRM-1020 refractometer operating at 633 nm. Intrinsic viscosities were measured with an Ubbelohde viscometer in toluene at 35 °C.

Synthesis of Star-Branched Polystyrenes by Iterative Methodology Using 1 and 2

All polymerizations and reactions were carried out under a high vacuum condition (10^{-6} torr) in sealed glass reactors with break seals. Both polystyryllithium (PSLi) and poly(α-methylstyryl)lithium (PαMSLi) were prepared by the *sec*-BuLi-initiated polymerization of the corresponding monomers in THF at −78 °C for 20 min and 5 h, respectively.

First Iteration

To a mixture of THF (35.0 mL) and *tert*-butylbenzene (35.0 mL) including PSLi (11.0 g, 1.05 mmol, M_n (SEC) = 10.5 kg/mol) was added to DPE (1.55 mmol) in THF (6.16 mL) at −78 °C and the mixture was allowed to stir for 30 min at −78 °C, followed by addition of **2** (0.524 mmol) in THF (4.42 mL). After 1 h, the resulting polymer mixture was poured into a large amount of methanol to precipitate the polymer. The coupled polymer was isolated in 76% yield by fractional precipitation where hexane was slowly added into cyclohexane solution of the polymer at 25 °C and then the mixture was allowed to stand at 5 °C for 24 h. Reprecipitation of the polymer trice from THF to MeOH and freeze-drying from its dry benzene solution for 24 h afforded the expected DPE-in-chain-functionalized PS (A_2, M_n (SEC) = 20.7 kg/mol, M_w/M_n (SEC) = 1.01). The in-chain-functionalized PS with DPE moiety (8.39 g, 0.403 mmol) dissolved in THF (82.1 mL) was reacted with *sec*-BuLi (0.577 mmol) in hexane (4.44 mL) at −78 °C for 5 h, followed by addition of **1** (1.00 mmol) in THF (3.86 mL) to prepare a new in-chain-functionalized PS with the DPE moiety separated by four methylene units from the main chain. The polymer was precipitated in MeOH, reprecipitation twice from THF to MeOH, and freeze-dried from its dry benzene solution for 24 h. The polymer yield (M_n (SEC) = 20.8 kg/mol, M_w/M_n (SEC) = 1.02) was virtually quantitative.

Second Iteration

To a THF solution (78.5 mL) of the new in-chain-functionalized PS with DPE moiety (8.20 g, 0.394 mmol, M_n (SEC) = 20.8 kg/mol) cooled at −78 °C was added *sec*-BuLi (0.394 mmol) in hexane (4.78 mL) and the mixture was allowed to stand at −78 °C for 1 h. The resulting in-chain-functionalized PS anion was *in-situ* coupled with **2** (0.197 mmol) in THF (4.55 mL) at −78 °C for 1 h. After termination with degassed MeOH, the coupled polymer was isolated in 90% yield by fractional precipitation. Reprecipitation of the polymer twice from THF to MeOH, followed by freeze-drying from its dry benzene solution for 24 h afforded the expected 4-arm A_4 star-branched PS (A_4, M_n (VPO) = 40.0 kg/mol, M_w/M_n (SEC) = 1.01). To a THF (51.4 mL) solution of the 4-arm star PS (4.96 g, 0.124 mmol) was added *sec*-BuLi (0.189 mmol) in hexane (3.28 mL) at −78 °C and the mixture was allowed to stir at −78 °C for 5 h. Then, **1** (0.258 mmol) in THF (3.67 mL) was added to the resulting star polymer anion and the mixture was stirring at −78 °C for an additional 1 h. Thus, the new 4-arm A_4 star-branched PS core-functionalized with the DPE moiety separated by four methylene units from the main chain was obtained in 100% yield.

Third Iteration

The same procedures were repeated as those used in the second iteration mentioned above.

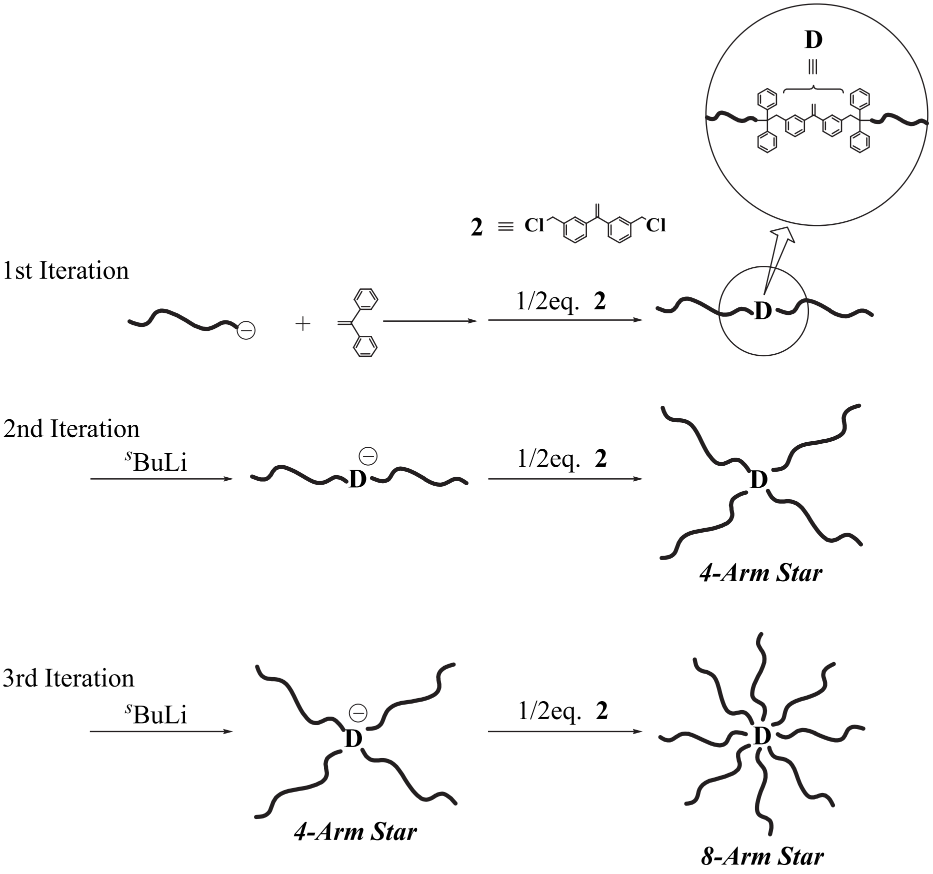
Successive Synthesis of Asymmetric Star-Branched Polymers by Iterative Methodology Using 1 and 2

The same procedures were similarly carried out as those used for the synthesis of regular star-branched polystyrenes mentioned above. Only the difference is to use DPE-in-chain-functionalized diblock copolymer of styrene and α-methylstyrene as a starting polymer at the second and third iterative processes.

Results and Discussion

First Iterative Methodology Using 2 for Successive Synthesis of Regular Star-Branched Polystyrenes

The first iterative methodology herein proposed is illustrated in Scheme 1. The compound, **2**, was used as a core compound in each iterative process. The synthesis of regular star polystyrenes (PS)s was carried out to examine the effectiveness of the methodology. In the first iteration, an in-chain-functionalized PS with DPE moiety was prepared by the coupling reaction of **2** with polystyryllithium (PSLi). Prior to the



Scheme 1.
Successive synthesis of in-chain-functionalized polystyrene with one DPE moiety and core-functionalized 4- and 8-arm star-branched polystyrenes with one DPE moiety by an iterative methodology using **2**.

coupling reaction, PSLi was end-capped with DPE to avoid the further addition of PSLi with the DPE moiety introduced into PS. A 2.2-fold excess of PSLi toward the DPE functionality was used to complete the reaction. SEC profile of the reaction mixture showed two distinct peaks corresponding to the coupled polymer and the deactivated PSLi used in excess. The coupling efficiency was estimated to be quantitative by comparing the two peak areas. The coupled polymer was isolated in 90% yield by fractional precipitation. In the second iteration, the DPE-in-chain-functionalized PS thus synthesized was converted to the corresponding in-chain-functionalized PS anion with *sec*-BuLi, followed by coupling with **2** to result in the formation of a 4-arm A_4 star-branched PS core-functionalized with DPE moiety. SEC profile of the reaction mixture exhibited only two peaks for the coupled polymer and the deactivated in-chain PS anion used in excess. The coupling efficiency of this reaction was also quantitative based on the two peak areas. The coupled polymer was isolated in 85% yield by fractional precipitation. The results are summarized in Table 1.

As expected from its branched architecture, the M_n value estimated by SEC was somewhat smaller than the expected value. On the other hand, the M_n value determined by VPO is in good agreement with

Table 1.
Synthesis of in-chain-functionalized polystyrene with one DPE moiety and core-functionalized 4-, 8-, and 16-arm star-branched polystyrenes with one DPE moiety.

Type	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	$g' = [\eta]_{star}/[\eta]_{linear}$[c]	
	calcd	SEC	VPO	calcd[a]	SLS[b]	SEC	calcd[d]	exptl
in-chain[e]	20.8	20.7	20.0	21.2	21.1[g]	1.01		
4-arm[e]	42.1	37.0	41.1	42.9	42.2	1.02	0.71	0.71
8-arm[e]	83.4	59.6	81.3	85.1	85.1	1.02	0.46	0.47
in-chain[f]	21.1	20.8	19.8	21.5	21.1[g]	1.02		
4-arm[f]	41.2	35.1	40.0	41.6	41.7	1.01	0.71	0.72
8-arm[f]	80.8	55.3	79.1	84.0	84.7	1.04	0.46	0.46
16-arm[f]	168	85.2	nd	170	170	1.01		

[a] Calculated from M_n (calcd) and M_w/M_n (SEC) values.
[b] Measured in THF at 25 °C. $dn/dc = 0.182 - 0.189$ (mL/g).
[c] Intrinsic viscosities of star-branched polystyrenes ($[\eta]_{star}$) were measured in toluene at 35 °C. Intrinsic viscosities of linear polystyrenes with the same molecular weights ($[\eta]_{linear}$) were calculated from the equation: $[\eta] = 1.29 \times 10^{-4} M_w(\mathrm{SLS})^{0.71}$ values (ref 29).
[d] Calculated from $g' = [(3f - 2)/f^2]^{0.58}[0.724 - 0.015(f - 1)]/0.724$. f = arm number ($3 \le f \le 18$) (ref.28).
[e] Synthesis of star-branched polystyrenes using **2**.
[f] Synthesis of star-branched polystyrenes using **1** and **2**.
[g] Measured by SEC.

that expected. The absolute value of M_w measured by SLS also agreed well with the predicted value. Furthermore, the g′ value was consistent with the predicted value determined by the established equation.[28] All of these analytical results clearly indicate the resulting polymer to be the objective 4-arm A_4 star-branched PS. Thus, the star polymer synthesis by the second iterative process is successful.

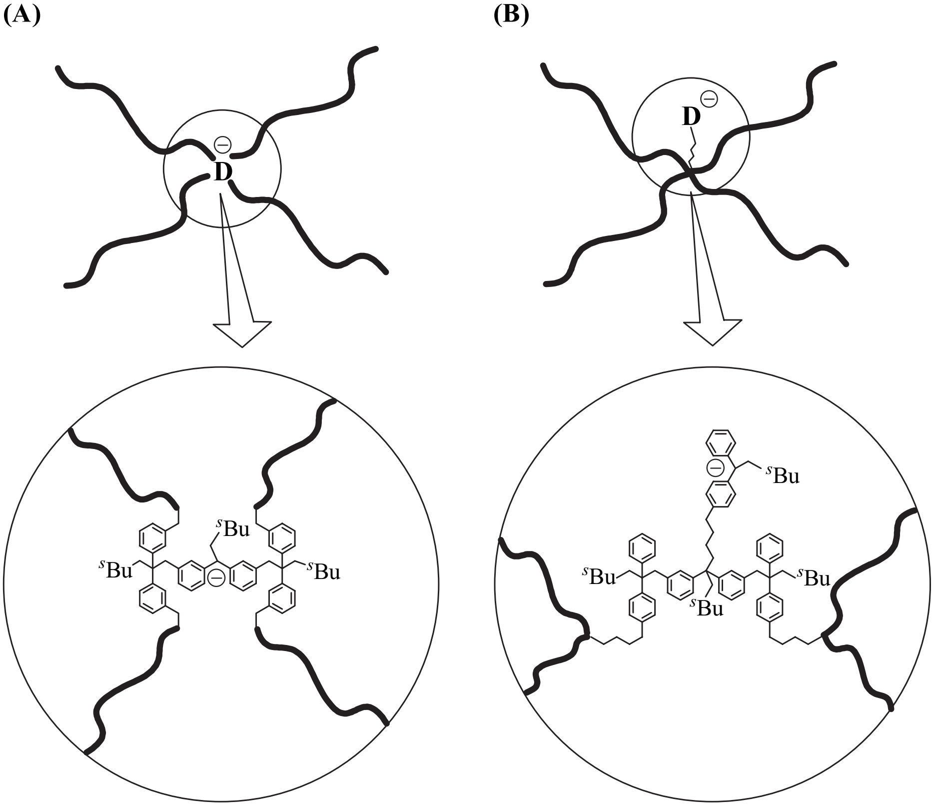
With use of the synthesized 4-arm star-branched PS as a starting polymer, the third iterative process was carried out by treatment of the 4-arm star with *sec*-BuLi, followed by coupling with **2**. The requisite 8-arm A_8 star-branched PS was synthesized as shown in Table 1. However, the polymer yield was not quantitative, but 62% on the basis of SEC profile of the reaction mixture. Accordingly, it is considered that the successive synthesis of 16-arm star-branched PS and so on to 32-arm star by this iterative methodology may be difficult.

Second Iterative Methodology Using 1 and 2

The insufficient yield of 8-arm star-branched PS is undoubtedly attributed to the steric hindrance between the reaction sites of intermediates in the coupling reaction as illustrated in Scheme 2(A). In particular, the microstructure around the 1,1-diphenylalkyl anion generated at the core of 4-arm star PS seems to be sterically hindered due to the fixation at the both sides by polymer chains. In order to reduce the steric hindrance, we have separated the anion by four methylene units from the main polymer chain as illustrated in Scheme 2(B) with the hope that the coupling reaction proceeds more smoothly.

To realize such an idea, one more reaction step was added in the iterative reaction sequence as illustrated in Scheme 3. By using the same procedures as those mentioned before, a DPE-in-chain-functionalized PS was prepared, followed by treatment with *sec*-BuLi to convert to the corresponding in-chain-functionalized PS anion. Then, **1** was reacted with the polymer anion to introduce the DPE moiety separated by four methylene units from the main chain. Accordingly, the anion generated in the next reaction step is also separated by four methylene units from the main chain.

In the second iteration, the DPE-in-chain-functionalized PS newly synthesized

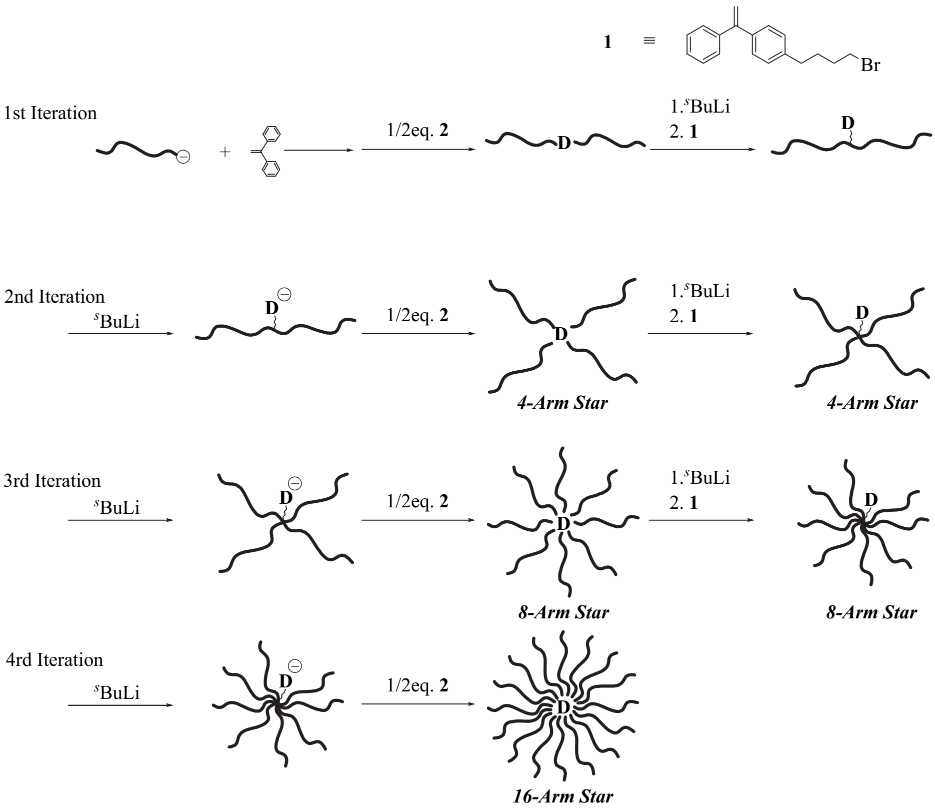


Scheme 2.
Steric hindrance around reaction sites using **2** (A) and using **1** and **2** (B).

was converted to the polymer anion with *sec*-BuLi, followed by coupling with **2** under the same conditions. As expected, a 4-arm star-branched PS was obtained in 100% yield. The results are also summarized in Table 1. Then, the resulting star PS was reacted with *sec*- BuLi and subsequently with **1** to afford a new core-functionalized 4-arm star PS with the DPE moiety separated by four methylene unit from the core. The third iteration was performed by treatment of the new 4-arm star with *sec*-BuLi, followed by coupling with **2** for the synthesis of 8-arm star PS. Very importantly, the polymer yield was found to be virtually quantitative in this synthesis. Furthermore, 16-arm star-branched PS could be synthesized in 70% yield by repeating the same reaction sequence. Thus, the new methodology with an additional reaction step in the iterative reaction sequence is more effective in the star polymer synthesis than the methodology proposed before. With this improved methodology, repeating the iterative reaction sequence four times is actually possible. However, more suitable design in the methodology is required for the further synthesis of star-branched PS with 32 arms and so on to more arm segments.

Synthesis of Asymmetric Star-Branched Polymers by Second Iterative Methodology Using 1 and 2

The improved methodology using **1** and **2** was applied to the successive synthesis of asymmetric star-branched polymers comprising PS and poly(α-methylstyrene) (PαMS)



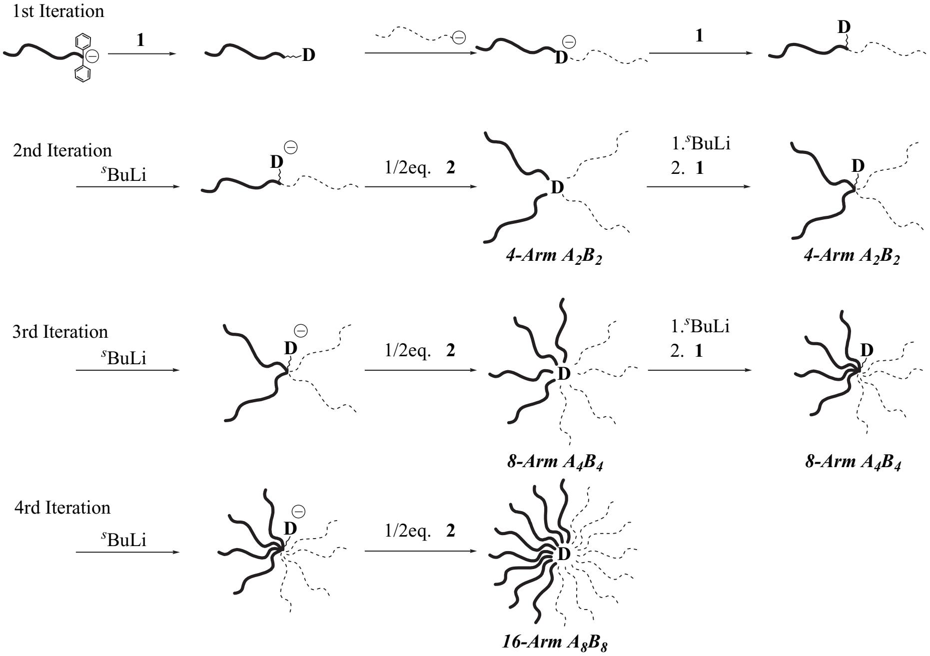
Scheme 3.

Successive synthesis of in-chain-functionalized polystyrene with one DPE moiety and core-functionalized 4- , 8-, and 16-arm star-branched polystyrenes with one DPE moiety by an iterative methodology using **1** and **2**.

segments. The synthetic route is illustrated in Scheme 4.

In this synthesis, an in-chain-functionalized diblock copolymer, PS-*b*-PαMS, with DPE moiety is used as a starting material. PSLi end-capped with DPE was reacted with a 1.5-fold excess of **2** to prepare a chain-end-functionalized PS with DPE and benzyl chloride moieties in 75% yield. It was then reacted with a 1.2-fold excess of poly(α-methylstyryl)lithium (PαMSLi) end-capped with DPE, resulting in the formation of in-chain-functionalized PS-*b*-PαMS with DPE moiety in 100% yield. The resulting DPE-in-chain-functionalized diblock polymer was reacted with *sec*-BuLi and then with **1** to introduce the DPE moiety separated by four methylene units from the main chain. A 4-arm asymmetric star-branched polymer was synthesized by treatment of the new DPE-in-chain-functionalized diblock copolymer with *sec*-BuLi, followed by coupling with **2**. Similar to the synthesis of 4-arm regular star-branched PS mentioned above , two distinct sharp peaks corresponding to the coupled polymer and the deactivated block copolymer anion used in excess were observed in SEC profile of the reaction mixture. The polymer yield was estimated to be quantitative by comparing the two peak areas. After fractional precipitation, the star-branched polymer was isolated in 85% yield. The results are also summarized in Table 2.

The calculated molecular weight values are in good agreement with those determined by ^{1}H NMR and SLS, respectively. Comparison of the composition expected and determined by ^{1}H NMR gave excellent



Scheme 4.

Successive synthesis of in-chain-functionalized AB diblock copolymer with one DPE moiety and core-functionalized 4-arm A_2B_2, 8-arm A_4B_4, 16-arm A_8B_8 asymmetric star-branched polymers with one DPE moiety by an iterative methodology using **1** and **2**.

agreement. Thus, the objective 4-arm A_2B_2 asymmetric star-branched polymer was successfully synthesized. Furthermore, an 8-arm A_4B_4 star could be synthesized in 100% yield from the 4-arm A_2B_2 star. Thus, the improved methodology is also effective for the synthesis of 4- and 8-arm asymmetric star-branched polymers. It was also possible to synthesize a more complex 16-arm A_8B_8 asymmetric star-branched polymer. Unfortunately, the polymer yield was 65%, but not quantitative as expected.

In conclusion, we have developed a new iterative methodology, by which 4-arm,

Table 2.

Synthesis of chain-end-functionalized polystyrene (A), in-chain-functionalized poly(styrene)-*b*-poly(α-methylstyrene)(AB) with one DPE moiety, and core-functionalized 4-arm A_2B_2, 8 - arm A_4B_4, and 16-arm A_8B_8 asymmetric star-branched polymers[a].

Type	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt%)	
	calcd	SEC	^{1}H NMR	calcd[b]	SLS[c]	SEC	calcd	^{1}H NMR
A	10.6	10.7	10.5	10.8	10.9[d]	1.02	100	100
AB	21.5	22.0	20.1	22.1	23.2	1.03	52/48	52/48
A_2B_2	45.4	36.5	42.1	46.6	48.3	1.03	52/48	51/49
A_4B_4	94.8	66.6	90.3	99.0	108	1.04	52/48	52/48
A_8B_8	204	83.3	nd	208	199	1.02	52/48	nd

[a] A and B segments were polystyrene and poly(α-methylstyrene), respectively.
[b] Calculated from M_n (calcd) and M_w/M_n (SEC) values.
[c] Measured in THF at 25 °C. $dn/dc = 0.181 - 0.187$ (mL/g).
[d] Measured by SEC.

8-arm, 16-arm regular star-branched polystyrenes as well as 4-arm A_2B_2, 8-arm A_4B_4, and 16-arm A_8B_8 asymmetric star-branched polymers comprising PS and PαMS segments were successively synthesized. The methodology appears to be attractive in star-branched polymer synthesis from the following viewpoints. At first, a series of not only well-defined regular but asymmetric star-branched polymers can be successively synthesized by repeating the same reaction sequence involving three simple reaction steps. Secondly, stars with many arms like 16 arms can be actually synthesized by repeating the reaction sequence only four times. However, stars having 16 arms could be synthesized in 65 ~ 70% yields and, therefore, changing the design in the iterative methodology is needed for a further synthetic development leading to star-branched polymers with 32 or more arms.

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