6006 *Macromolecules* **2009**, *42*, 6006–6014
DOI: 10.1021/ma900750n

Macromolecules
ARTICLE

Successive Synthesis of Asymmetric Star-Branched Polymers Based on Iterative Methodology Using 1,1-Diphenylethylene Derivatives of Alternative Choice at Each Iteration

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Received April 7, 2009; Revised Manuscript Received May 23, 2009

ABSTRACT: We have demonstrated an advanced iterative methodology using specially designed 1-[4-(3-bromopropyl)phenyl]-1-phenylethylene (**1**) or 3,5-bis{3-[4-(1-phenylethenyl)phenyl]propoxy}benzyl bromide (**2**) of alternative choice at each iteration for the successive synthesis of asymmetric star polymers. The methodology involves only two sets of the following reaction conditions for the entire iterative reaction sequence: (a) a linking reaction of a living anionic polymer with a DPE-chain-functionalized polymer and (b) an in-situ reaction of **1** or **2** with the anion generated by the linking reaction to reintroduce the DPE functionality. The number of DPE moieties remains unchanged when **1** is used, whereas it doubles when **2** is used. In practice, various arrays of asymmetric star polymers could be successfully synthesized by repeating the iterative reaction sequence, (a) and (b), five times. The structural variation of the stars covers 3-arm AB_2, 5-arm AB_2C_2, 5-arm AB_2C_4, 7-arm $AB_2C_2D_2$, 9-arm $AB_2C_2D_4$, 11-arm $AB_2C_4D_4$, 15-arm $AB_2C_4D_8$, 9-arm $AB_2C_2D_2E_2$, 11-arm $AB_2C_2D_2E_4$, 13-arm $AB_2C_2D_4E_4$, 15-arm $AB_2C_4D_4E_4$, 17-arm $AB_2C_2D_4E_8$, 19-arm $AB_2C_4D_4E_8$, 23-arm $AB_2C_4D_8E_8$, and 31-arm $AB_2C_4D_8E_{16}$ types. The A, B, C, D, and E segments were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), and poly(4-trimethylsilylstyrene) segments, respectively. We have corroborated that all of the samples show a high degree of structural and compositional homogeneity by ^{1}H NMR and SEC-RALLS. The systematic synthesis of multicomponent and multiarmed stars supports the utility and universality of the proposed methodology.

Introduction

Asymmetric star polymers, whose arms differ in composition, so-called miktoarm (or heteroarm) star-branched polymers, have emerged as an important class of polymers due to their hierarchical structures over linear block copolymers.[1−15] These polymers have a possibility to create novel morphological nanostructures which are derived by self-assemblies of immiscible segments radiated from a core.[16−36] It has been, however, far more difficult to synthesize asymmetric star polymers than regular ones because the former requires multistep reactions corresponding to chemically different segments, together with isolation and purification of intermediate polymers. Indeed, the number of components of well-defined asymmetric star polymers synthesized so far has been limited to 4, especially only ABCD type for four-component stars.[37−42] In addition, there are few examples for asymmetric star polymers with more than 10 arms.[43−47] To break through this situation, the development of a general and effective methodology for multicomponent and multiarmed asymmetric star polymers is essential.

We have recently developed a novel iterative methodology based on living anionic polymerization using specially designed 1,1-diphenylethylene (DPE) derivatives to totally synthesize such star polymers.[13−15] The methodology involves only two sets of the following reaction conditions for the entire iterative reaction sequence: (a) a linking reaction of a living anionic polymer with a DPE-chain-functionalized polymer and (b) an in-situ reaction of DPE derivative with the anion generated by the linking reaction to reintroduce the DPE functionality usable at the next iteration. The key point of the iterative methodology is that reaction sites are always regenerated after each of the iterative processes, and hence the same reaction sequence can be, in principle, limitlessly repeated to successively synthesize star-branched polymers. Therefore, it is expected that similar or different arms in composition can be introduced into stars as many as possible until the reactions will be suppressed by the steric requirements.

As the simplest example shown in Scheme 1, a series of ABC, ABCD, and even ABCDE type asymmetric star polymers could be successfully synthesized by using 1-[4-(3-bromopropyl)phenyl]-1-phenylethylene (**1**) as a DPE derivative in the process (b).[48] By extending this procedure, we succeeded in synthesizing other series of 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ type as well as 6-arm A_3B_3 and 9-arm $A_3B_3C_3$ type asymmetric star polymers starting from 1,3-bis(1-phenylethenyl)benzene and 1,3-bis[3-(1-phenylethenyl)phenyl]ethylene, respectively.[49,50] On the other hand, the alternative functionality of a 1,3-butadienyl group could participate in this approach to successfully obtain quite new multicomponent 6-arm ABCDEF and 7-arm ABCDEFG type asymmetric star polymers where 1-bromo-3-methylene-5-pentene instead of a DPE derivative was used in the procedure (b).[51]

In order to increase the number of arms to be linked at each stage by less repetition of the iterative reaction sequence, we have newly synthesized DPE derivatives, 1-(3-chloromethylphenyl)-1-[3-(1-phenylethenyl)phenyl]ethylene and 3,5-bis{3-[4-(1-phenylethenyl)phenyl]propoxy}benzyl bromide (**2**), for employing in the process (b). These reagents are specially designed to be able to introduce two DPE moieties via one intermediate anion. Because of the superior performance of **2** for increasing the arm number, a quite novel series of 3-arm AB_2, 7-arm AB_2C_4, 15-arm $AB_2C_4D_8$,

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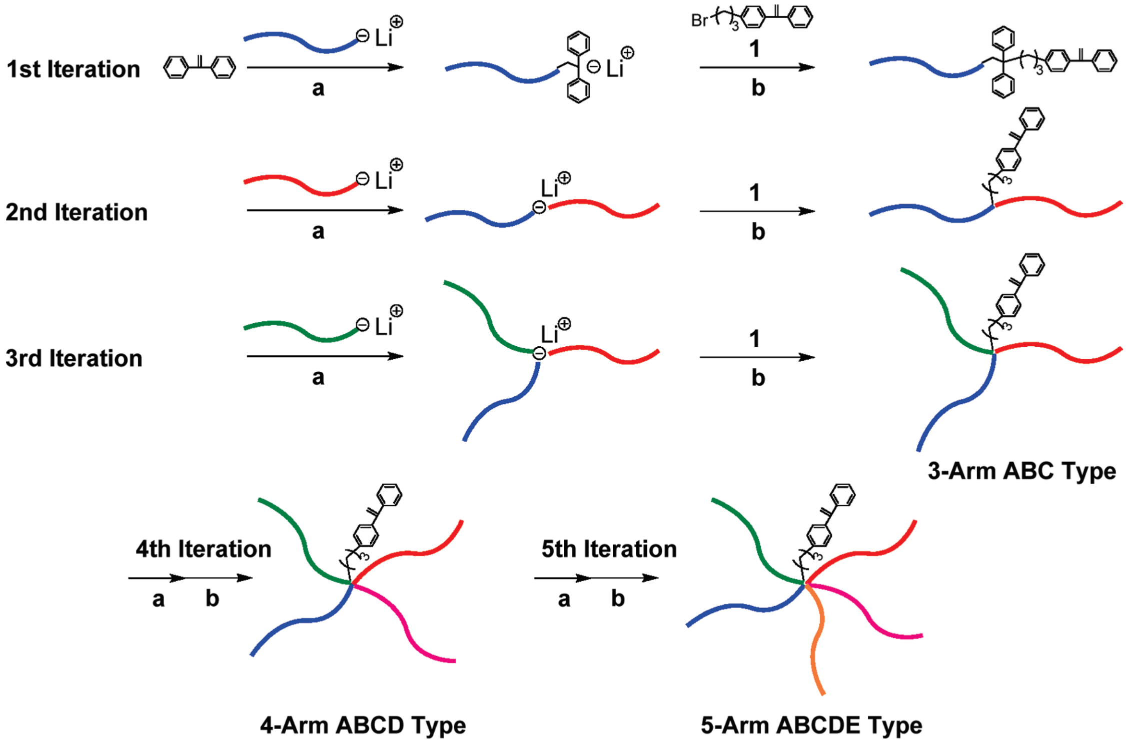
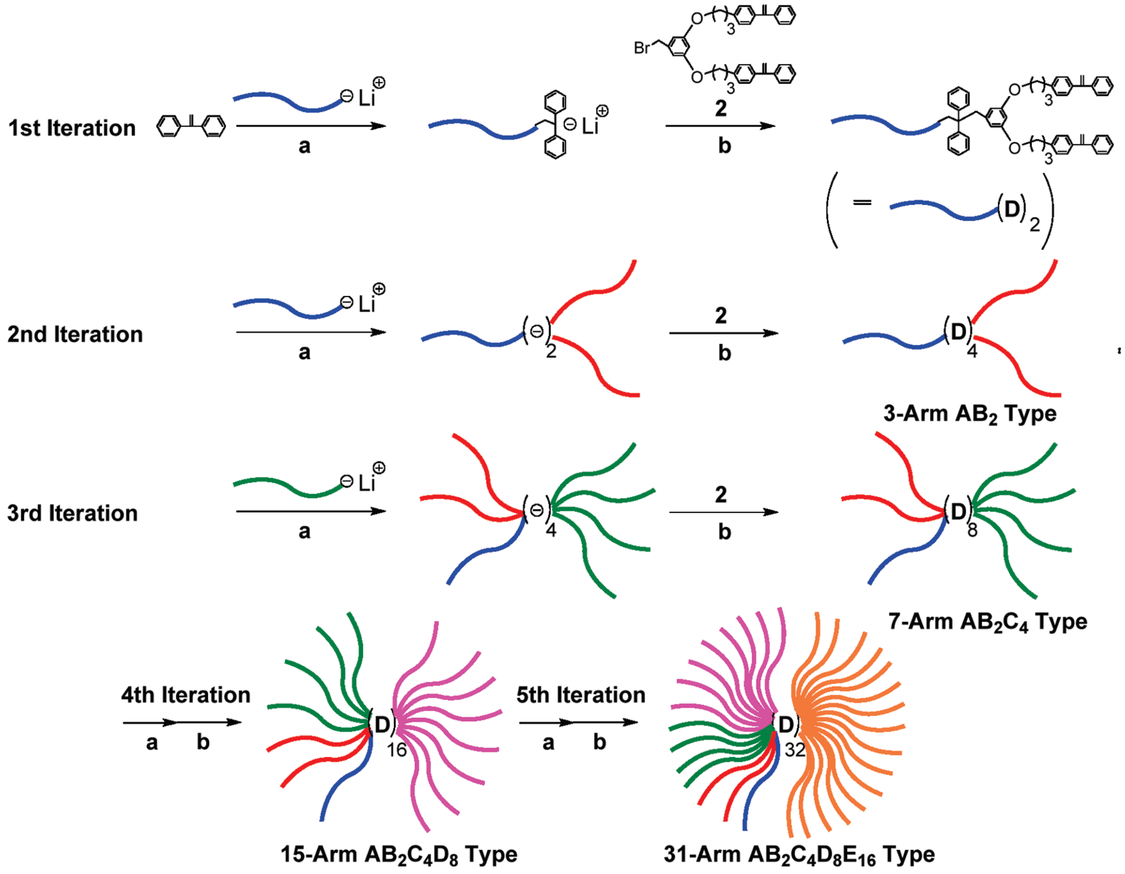
Scheme 1. Successive Synthesis of Asymmetric Star Polymers by Iterative Methodology Using 1



Scheme 2. Successive Synthesis of Asymmetric Star Polymers by Iterative Methodology Using 2



and even 31-arm $AB_2C_4D_8E_{16}$ types could be synthesized as shown in Scheme 2.[52]

Table 1 summarizes the types of asymmetric star polymers synthesized by our iterative methodology so far. As can be seen, the structural types are quite limited especially for more than 10-arm stars. The limitation comes from the rapid divergence of the number of arms formulated as $N = n^2 - 1$ (N = the number of arms, n = the number of iterations) when only **2** is used in the process (b). To infill intervals of the *N* values and pursue further new types of asymmetric star polymers, we report herein an advanced iterative methodology using **1** or **2** of alternative choice at each iteration. The advantageous feature of the proposed methodology is that the number of arms and components are controlled freely and simply by choosing **1** or **2** to be reacted at each iteration. For example, 16 types (see Figure 1) of stars can possibly be obtained at the fifth iteration by the proposed methodology, whereas only ABCDE (see Scheme 1) or $AB_2C_4D_8E_{16}$ type (see Scheme 2) stars are obtained at the fifth iteration by the previous one. In this article, the practical utility of this advanced iterative methodology has been examined.

Table 1. Asymmetric Star Polymers Synthesized by Our Iterative Methodologies

arm no.[a]	comp no.[b]	type	DPE derivative[c]	ref
3	2	AB_2	**2**	52, 53
3	3	ABC	**1**	45, 46, 48, 51, 53−55
4	2	A_2B_2	**1**	49, 55
4	4	ABCD	**1**	48, 51, 54, 55
5	3	AB_2C_2	**1**	44, 53
5	4	$ABCD_2$	**1**	53
5	5	ABCDE	**1**	48, 51, 54
6	2	A_3B_3	**1**	50
6	3	$A_2B_2C_2$	**1**	49
6	6	ABCDEF	Bd-Br[d]	51
7	3	AB_2C_4	**2**	52
7	4	$A_2B_2C_2D$	**1**	45, 46
7	5	$ABCD_2E_2$	**1**	53
7	7	ABCDEFG	Bd-Br[d]	51
9	3	$A_3B_3C_3$	**1**	50
13	4	$A_4B_4C_4D$	**1**	45, 46
15	4	$AB_2C_4D_8$	**2**	52
31	5	$AB_2C_4D_8E_{16}$	**2**	52

[a] The number of arm segments. [b] The number of components. [c] The DPE derivatives used at each iteration. [d] 1-Bromo-3-methylene-5-pentene instead of DPE derivatives was used at each iteration.

Experimental Section

Materials. All chemicals (>98% purities) were purchased from Aldrich, Japan, and used as received unless otherwise noted. Tetrahydrofuran (THF) (99%, Mitsubishi Chemical Co., Ltd.) was refluxed over Na wire for 12 h and then distilled from lithium aluminum hydride under nitrogen. It was finally distilled from its sodium naphthalenide solution on a high-vacuum line (10^{-6} Torr). DPE, styrene, α-methylstyrene, 4-methylstyrene, and 4-methoxystyrene were washed with 10% NaOH aqueous solution, dried over $MgSO_4$, and distilled over CaH_2 under reduced pressure. 4-Trimethylsilylstyrene was synthesized and purified as previously reported.[56] All monomers were finally distilled over dibutylmagnesium (ca. 5 mol %) on the vacuum line into ampules equipped with break-seals that

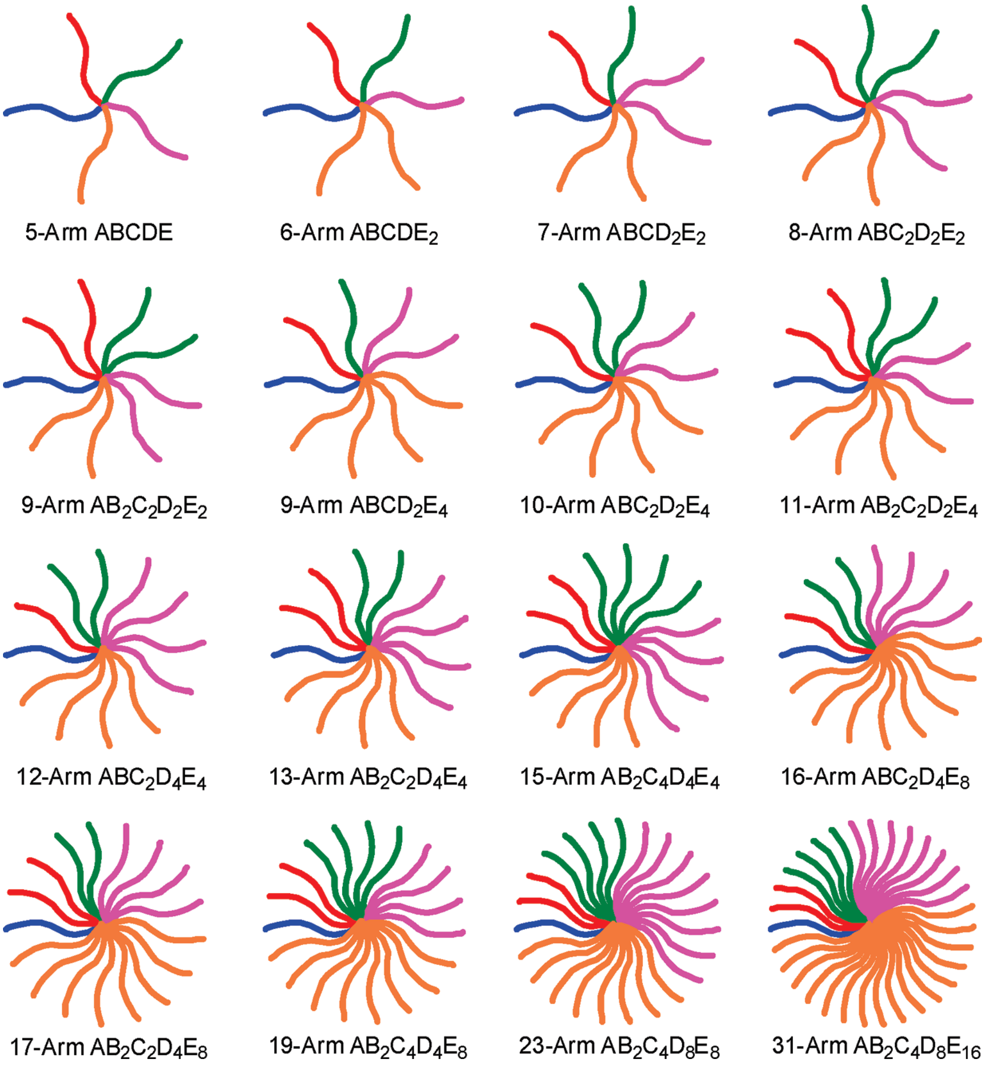

5-Arm ABCDE
6-Arm $ABCDE_2$
7-Arm $ABCD_2E_2$
8-Arm $ABC_2D_2E_2$
9-Arm $AB_2C_2D_2E_2$
9-Arm $ABCD_2E_4$
10-Arm $ABC_2D_2E_4$
11-Arm $AB_2C_2D_2E_4$
12-Arm $ABC_2D_4E_4$
13-Arm $AB_2C_2D_4E_4$
15-Arm $AB_2C_4D_4E_4$
16-Arm $ABC_2D_4E_8$
17-Arm $AB_2C_2D_4E_8$
19-Arm $AB_2C_4D_4E_8$
23-Arm $AB_2C_4D_8E_8$
31-Arm $AB_2C_4D_8E_{16}$

Figure 1. Possible structures of asymmetric star polymers obtained by the present iterative methodology using **1** or **2**.

were prewashed with the initiator solutions. 1-[4-(3-Bromopropyl)-phenyl]-1-phenylethylene (**1**)[57] and 3,5-bis{3-[4-(1-phenylethenyl)-phenyl]propoxy}benzyl bromide (**2**)[52] were synthesized and purified according to the previous papers.

Preparation of Living Anionic Polymers. All polymerizations and reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors with break-seals. The reactors were always prewashed with the initiator solutions after being sealed off from the vacuum line. Polystyryllithium (PSLi) was prepared by the *sec*-BuLi-initiated polymerization of styrene in THF at −78 °C for 20 min. Poly(α-methylstyryl)-lithium (PαMSLi), poly(4-methylstyryl)lithium (P4MSLi), poly-(4-methoxystyryl)lithium (P4MOSLi), and poly(4-trimethylsilyl-styryl)lithium (P4SiSLi) were prepared by the *sec*-BuLi-initiated polymerization of the corresponding monomers in THF at −78 °C for 3, 1, 1, and 1 h, respectively.

Synthesis of Two- and Three-Component Asymmetric Star Polymers. Two-component 3-arm AB_2 and three-component 5-arm AB_2C_2 and 7-arm AB_2C_4 type asymmetric star polymers were synthesized by repeating the iterative reaction sequence, (a) and (b). The A, B, and C segments of the stars were PS, PαMS, and P4MS, respectively. The typical synthetic procedures for 3-arm AB_2 and 5-arm AB_2C_2 type star polymers with two DPE moieties at the core are as follows.

First and Second Iterative Process. PSLi (0.201 mmol, M_n(obsd) = 10.3 kg/mol) in THF (20.4 mL) was reacted with DPE (0.269 mmol) in THF (3.72 mL) at −78 °C for 10 min. To the solution was added the mixture of **2** (0.235 mmol) and Bu_2Mg (0.203 mmol) in THF (7.24 mL). After 10 min, the resulting polymer was precipitated in methanol. The polymer was purified by reprecipitation twice using a THF/methanol system, followed by freeze-drying from its benzene solution to afford the objective chain-end-functionalized PS with two DPE moieties (2.05 g, 99% yield, M_n(obsd) = 10.6 kg/mol, PDI(SEC) = 1.03, DPE functionality (^{1}H NMR) = 1.9_9). Then, PαMSLi (0.147 mmol, M_n(obsd) = 11.6 kg/mol) in THF (20.9 mL) was reacted with the chain-end-functionalized PS (0.509 g, 0.0480 mmol, 0.0960 mmol for total two DPE moieties) in THF (6.78 mL) at −78 °C for 6 h. After adding DPE (0.155 mmol) in THF (2.15 mL) to end-cap the excess PαMSLi, the mixture was added in situ to **1** (0.187 mmol) prepurified with Bu_2Mg (0.177 mmol) in THF (9.31 mL). After 10 min, the resulting polymers were precipitated in methanol. The objective 3-arm AB_2 type asymmetric star polymer with two DPE moieties at the core was isolated by fractional precipitation with cyclohexane/hexanes and purified by reprecipitation using a THF/methanol system twice, followed by freeze-drying from its benzene solution to afford 1.41 g (90% isolated yield, M_n(RALLS) = 32.7 kg/mol, PDI (SEC) = 1.04).

Third Iterative Process. P4MSLi (0.058 mmol, M_n(obsd) = 10.5 kg/mol) in THF (7.05 mL) was reacted with the 3-arm AB_2 type asymmetric star polymer with two DPE moieties at the core (0.390 g, 0.0119 mmol, 0.0239 mmol for total two DPE moieties) in THF (5.48 mL) at −78 °C for 6 h. After adding DPE (0.112 mmol) in THF (1.55 mL) to end-cap the excess P4MSLi, the mixture was added in situ to **1** (0.186 mmol) prepurified with Bu_2Mg (0.104 mmol) in THF (5.35 mL). After 10 min, the resulting polymers were precipitated in methanol. The objective 5-arm AB_2C_2 type asymmetric star polymer with two DPE moieties at the core was isolated by fractional precipitation with cyclohexane/hexanes and purified by reprecipitation using a THF/methanol system twice, followed by freeze-drying from its benzene solution to afford 0.539 g (81% isolated yield, M_n(RALLS) = 55.9 kg/mol, PDI(SEC) = 1.02).

Synthesis of Four-Component Asymmetric Star Polymers. *Fourth Iterative Process*. Four-component 7-arm $AB_2C_2D_2$, 9-arm $AB_2C_2D_4$, 11-arm $AB_2C_4D_4$, and 15-arm $AB_2C_4D_8$ type asymmetric star polymers were synthesized by repeating the iterative reaction sequence, (a) and (b). The D segment newly employed was P4MOS. The typical synthetic procedure for a 7-arm $AB_2C_2D_2$ star polymer with two DPE moieties at the core is as follows. P4MOSLi (0.0344 mmol, M_n(obsd) = 10.4 kg/mol) in THF (2.89 mL) was reacted with the 5-arm AB_2C_2 type asymmetric star-branched polymer with two DPE moieties at the core (0.480 g, 0.008 59 mmol, 0.0172 mmol for total two DPE moieties) in THF (6.50 mL) at −78 °C for 18 h. After adding DPE (0.143 mmol) in THF (3.32 mL) to end-cap the excess P4MOSLi, the mixture was added in situ to **1** (0.219 mmol) prepurified with Bu_2Mg (0.139 mmol) in THF (5.95 mL). After 10 min, the resulting polymers were precipitated in methanol. The objective 7-arm $AB_2C_2D_2$ type asymmetric star polymer with two DPE moieties at the core was isolated by fractional precipitation with toluene/methanol and purified by reprecipitation using a THF/methanol system twice, followed by freeze-drying from its benzene solution to afford 0.503 g (75% isolated yield, M_n(RALLS) = 78.4 kg/mol, PDI(SEC) = 1.05).

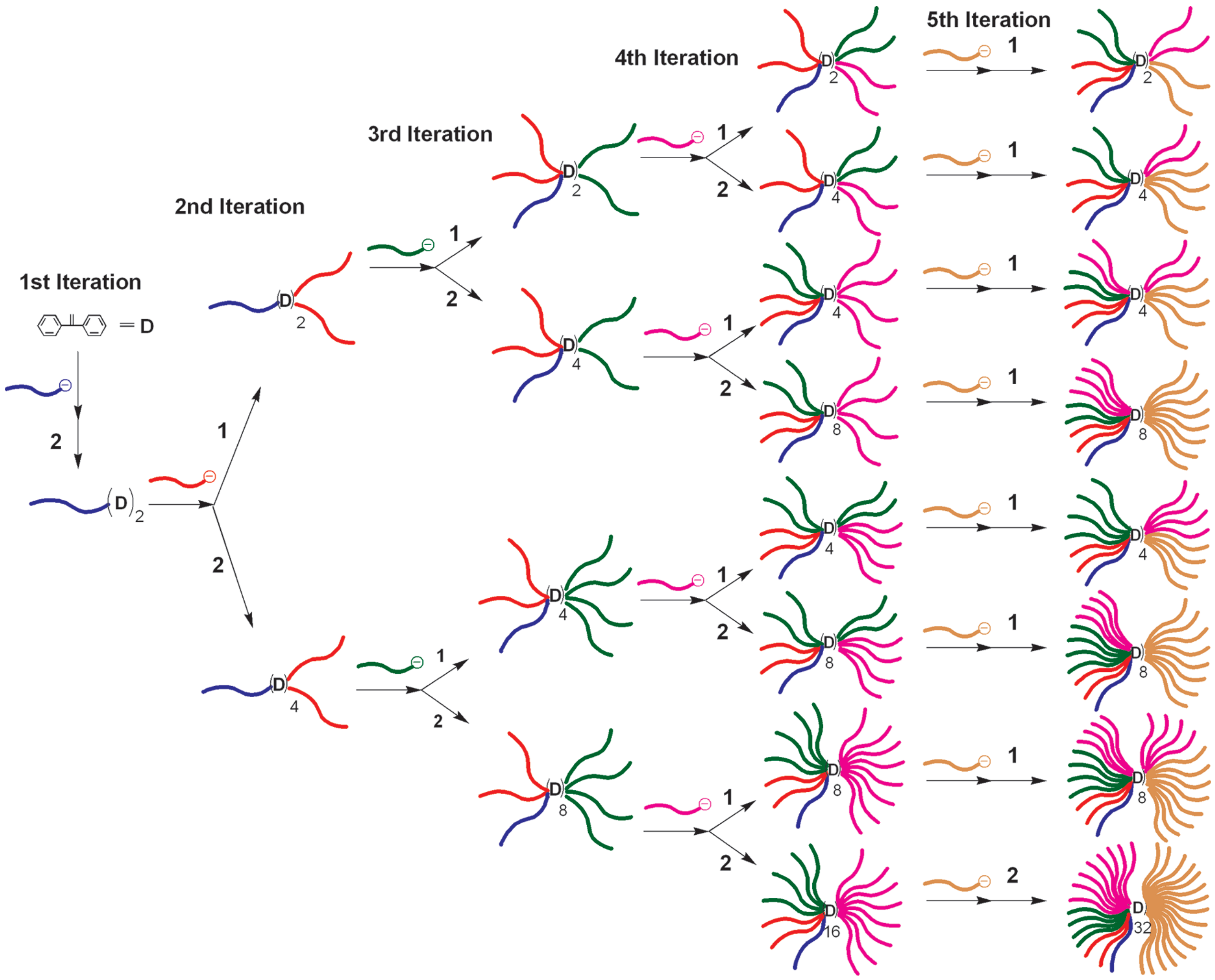
Synthesis of Five-Component Asymmetric Star Polymers. *Fifth Iterative Process*. Five-component 9-arm $AB_2C_2D_2E_2$, 11-arm $AB_2C_2D_2E_4$, 13-arm $AB_2C_2D_4E_4$, 15-arm $AB_2C_4D_4E_4$, 17-arm $AB_2C_2D_4E_8$, 19-arm $AB_2C_4D_4E_8$, 23-arm $AB_2C_4D_8E_8$, and 31-arm $AB_2C_4D_8E_{16}$ type asymmetric star polymers were synthesized by repeating the iterative reaction sequence, (a) and (b). The E segment newly employed was P4SiS. The typical synthetic procedure for a 9-arm $AB_2C_2D_2E_2$ star polymer with two DPE moieties at the core is as follows. P4SiSLi (0.0168 mmol, M_n(obsd) = 7.6 kg/mol) in THF (11.4 mL) was reacted with the 7-arm $AB_2C_2D_2$ asymmetric star-branched polymer with two DPE moieties at the core (0.220 g, 0.002 81 mmol, 0.005 61 mmol for total two DPE moieties) in THF (4.50 mL) at −78 °C for 18 h. After adding DPE (0.145 mmol) in THF (3.38 mL) to end-cap the excess P4SiSLi, the mixture was added in situ to **1** (0.216 mmol) prepurified with Bu_2Mg (0.106 mmol) in THF (4.92 mL). After 10 min, the resulting polymers were precipitated in methanol. The objective 9-arm $AB_2C_2D_2E_2$ asymmetric star-branched polymer with two DPE moieties at the core was isolated by fractional precipitation with toluene/methanol and purified by reprecipitation using a THF/methanol system twice, followed by freeze-drying from its benzene solution to afford 0.169 g (65% isolated yield, M_n(RALLS) = 92.9 kg/mol, PDI(SEC) = 1.05).

Measurements. Molecular weights (MWs) and polydispersity indices (PDIs) were measured with a HPLC system (Viscotek model 302 TDA, Asahi Techneion Co., Ltd.) equipped with a pump, refractometer (RI), absorbance detector (UV, λ = 254 nm), online right angle laser light scattering (RALLS) detector (λ = 670 nm), sample processor, and three styragel size exclusion chromatography (SEC) columns (a TSKgel G2000HHR and two TSKgel GMHHR-H). THF was used as a carrier solvent at a flow rate of 1.0 mL/min at room temperature. MW and PDI data were calculated based on RALLS and RI with the software (omniSEC). Both ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured in $CDCl_3$ using a Bruker DPX spectrometer.

Results and Discussion

Synthesis of Two- and Three-Component Asymmetric Star Polymers. The synthetic outline of asymmetric star polymers is illustrated in Scheme 3. The methodology involves only two sets of the following reaction conditions for the entire iterative reaction sequence: (a) a linking reaction of a living anionic polymer with a DPE-chain-functionalized polymer and (b) an in-situ reaction of **1** or **2** with the anion generated by the linking reaction to reintroduce the DPE functionality. There is an important regulation such that the number of DPE moieties remains unchanged when **1** is used, whereas it doubles when **2** is used. In this article, we used **2** at the first iteration to synthesize a ω-chain-end-functionalized polymer

Scheme 3. Successive Synthesis of Asymmetric Star Polymers by Advanced Iterative Methodology Using 1 or 2



with two DPE moieties (A type); on the other hand, **1** or **2** was chosen and used at the second and third iteration to successively synthesize two- and three-component asymmetric star polymers with the following types: 3-arm AB_2 (2 or 4), 5-arm AB_2C_2 (2 or 4), and 7-arm AB_2C_4 (4 or 8), where the numbers inside parentheses indicate DPE moieties in number introduced at the core. Throughout the synthesis, living anionic polymers were adjusted to be around 10 kg/mol in an M_n value.

At the first iteration, polystyryllithium (PSLi) was reacted with DPE in THF at −78 °C followed by reacting with **2** to synthesize the ω-chain-end-functionalized polystyrene (PS) with two DPE moieties (A type) as described in detail elsewhere.[47] The second iterative process involves the addition reaction of a 3.0-fold excess of poly(α-methylstyryl)lithium (PαMSLi) to the ω-chain-end-functionalized PS (a 1.5-fold excess of PαMSLi over each DPE moiety) in THF at −78 °C for 6 h, followed by the treatment with **1** or **2** to introduce two or four DPE moieties for 10 min, respectively. Prior to the treatment with **1** or **2**, DPE was added to end-cap the excess PαMSLi in order to avoid the unwanted PαMSLi attack on the DPE moieties newly introduced into the polymer. After removal of the excess PαMS by fractional precipitation using cyclohexane/hexanes, two-component 3-arm AB_2 asymmetric star polymers with two or four DPE moieties at the core could be obtained in a 90% yield. At the third iteration, these polymers were then reacted with an excess of poly(4-methylstyryl)lithium (P4MSLi) in THF at −78 °C for 6 h, followed by treatment with **1** or **2** for 10 min. The excess P4MS could be easily removed by fractional precipitation using cyclohexane/hexanes in more than 80% yield. At this iteration, three-component 5-arm AB_2C_2 asymmetric star polymers with two or four DPE moieties and 7-arm AB_2C_4 asymmetric star polymers with four or eight DPE moieties were obtained as shown in Scheme 3.

SEC profiles of the representative reaction mixtures and isolated star polymers are shown in Figure 2A−C. There are always two distinct sharp peaks corresponding to a star polymer and a original living polymer used in excess, together with a minor peak for a dimer of the living polymer between the two peaks. The dimer may be formed by the elimination of β-proton from the living polymer, followed by the addition reaction of the resulting vinyl terminus with another living polymer as reported previously.[58,59] The SEC profile of the star polymer isolated at each stage exhibits a sharp monomodal peak (see Figure 2D−F). The characterization results are summarized in Table 2. The M_n and M_w values determined by ^{1}H NMR and RALLS agreed with those predicted. The PDIs were quite low (< 1.04) in all cases. It was found that agreement of the compositions between determined by ^{1}H NMR and calculated from the feed ratios was excellent by comparing each resonance corresponding to PS, PαMS, and P4MS polymer segments. The same ^{1}H NMR spectra also showed the quantitative introduction of the prescribed number of DPE moieties. Thus, we could successfully synthesize the expected two- and three-component 3-arm AB_2, 5-arm AB_2C_2, and 7-arm AB_2C_4 asymmetric star polymers.

Synthesis of Four-Component Asymmetric Star Polymers. As mentioned in the Introduction, the synthesis of asymmetric star polymers is much more difficult than that of simple regular star polymers or linear block copolymers. Especially, the synthetic examples for complex four-component star polymers are very few and limited to only one structure of ABCD type so far.[37−42] In this section, various four-component star polymers with $AB_2C_xD_y$ type would be synthesized by further repeating the same reaction sequence (a) and (b) as that in the previous section. As shown in Scheme 3, it is possible to prepare four-component 7-arm $AB_2C_2D_2$ (2 or 4), 9-arm $AB_2C_2D_4$ (4 or 8), 11-arm $AB_2C_4D_4$ (4 or 8), and 15-arm $AB_2C_4D_8$ (8 or 16) type asymmetric star polymers.

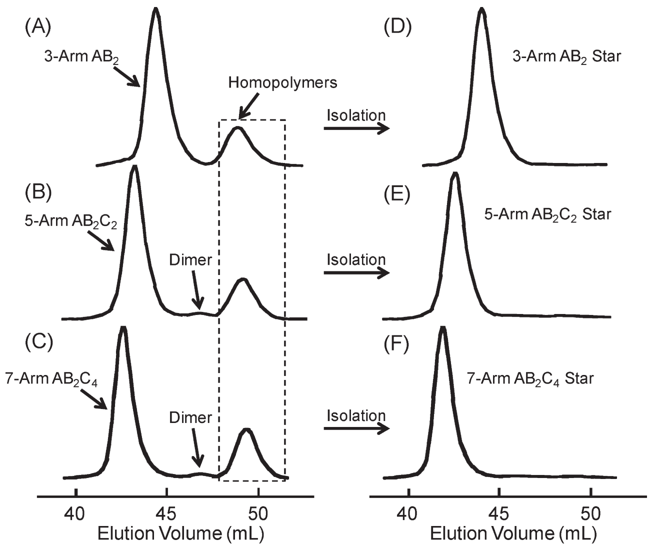


Figure 2. SEC RI traces of the reaction mixtures and the isolated asymmetric star polymers.

By using poly(4-methoxystyrene) (P4MOS) as a D segment, the fourth iterative process was performed with 5-arm AB_2C_2 (2 or 4) or 7-arm AB_2C_4 (2 or 4) type asymmetric star polymers. The linking reaction and the treatment with **1** or **2** were carried out in THF at −78 °C for 18 h and 10 min, respectively. Each SEC profile of the reaction mixtures shows two major peaks for the expected star polymers and an original living polymer used in excess, similar to the results obtained at the preceding iteration. The star polymers were isolated by fractional precipitation using toluene/methanol in more than 75% yield and displayed a sharp monomodal SEC distribution shifting to high molecular weight region as the total number of arms increases. The characterization results are summarized in Table 3. The M_n and M_w values determined by ^1H NMR and RALLS agreed well with those targeted. As representatively shown in Figure 3, the ^1H NMR signals characteristic of A (6.2−7.2 ppm, Ar), B (−0.95 to −0.5 ppm, α-CH_3), C (2.35 ppm, Ar−CH_3), and D (3.73 ppm, OCH_3) segments are clearly observed for the 7-arm $AB_2C_2D_2$ type. The compositions of A/B/C/D determined by ^1H NMR were quite close to those calculated in all cases. Furthermore, the quantitative introduction of a definite number of DPE moieties could be corroborated in the same ^1H NMR spectra. Thus, the fourth iterative process successfully results in the formation of the expected four-component 7-arm $AB_2C_2D_2$ (2 or 4), 9-arm $AB_2C_2D_4$ (4 or 8), 11-arm $AB_2C_4D_4$ (4 or 8), and 15-arm $AB_2C_4D_8$ (8 or 16) asymmetric star polymers.

Synthesis of Five-Component Asymmetric Star Polymers. The examples for more complex five-component asymmetric star polymers have so far been synthesized only by our group and limited to two structures of 5-arm ABCDE[48,51,54] and 31-arm $AB_2C_4D_8E_{16}$ types.[47] In this section, a wide variety of five-component asymmetric star polymers would be synthesized by repeating the same iterative process as shown in Scheme 3. We have used **1** in order to synthesize seven types (9-arm $AB_2C_2D_2E_2$, 11-arm $AB_2C_2D_2E_4$, 13-arm $AB_2C_2D_4E_4$, 15-arm $AB_2C_4D_4E_4$, 17-arm $AB_2C_2D_4E_8$, 19-arm $AB_2C_4D_4E_8$, 23-arm $AB_2C_4D_8E_8$) and used **2** for the synthesis of 31-arm $AB_2C_4D_8E_{16}$ type at the fifth iteration. These structures are

Table 2. Characterization Results of Two- and Three-Component Asymmetric Star Polymers

			M_n (kg/mol)			M_w/M_n	composition[d]	
arm no.[a]	type[b]	DPE no.[c]	calcd	RALLS	^1H NMR	SEC	calcd	^1H NMR
3	AB_2	2	33.7	32.6	35.0	1.04	31/69	30/70
3	AB_2	4	31.5	35.0	31.3	1.02	36/64	38/62
5	AB_2C_2	2	54.9	55.9	56.2	1.04	19/42/39	21/39/40
5	AB_2C_2	4	56.5	58.0	57.1	1.02	19/41/40	17/42/41
7	AB_2C_4	4	74.4	74.4	75.0	1.02	15/27/58	16/26/58
7	AB_2C_4	8	75.5	77.6	73.3	1.04	16/28/56	17/27/56

[a] The number of arm segments. [b] A, B, and C segments correspond to polystyrene, poly(α-methylstyrene), and poly(4-methylstyrene), respectively. [c] The number of DPE moieties introduced at the core of asymmetric star polymers. [d] The composition represents A/B and A/B/C by weight, respectively.

Table 3. Characterization Results of Four-Component Asymmetric Star Polymers

			M_n (kg/mol)			M_w/M_n	composition[d]	
arm no.[a]	type[b]	DPE no.[c]	calcd	RALLS	^1H NMR	SEC	calcd	^1H NMR
7	$AB_2C_2D_2$	2	72.3	78.4	70.4	1.05	14/32/30/24	20/29/29/22
7	$AB_2C_2D_2$	4	73.1	83.1	74.2	1.05	14/32/29/25	17/28/29/26
9	$AB_2C_2D_4$	4	98.4	100	99.1	1.02	10/24/23/43	10/25/23/42
9	$AB_2C_2D_4$	8	98.2	106	99.1	1.05	11/24/23/42	10/25/22/43
11	$AB_2C_4D_4$	4	116	119	116	1.02	10/17/37/36	10/17/37/36
11	$AB_2C_4D_4$	8	118	121	126	1.04	9/17/37/37	10/16/33/41
15	$AB_2C_4D_8$	8	159	163	161	1.04	7/9/27/57	6/9/28/57
15	$AB_2C_4D_8$	16	159	168	161	1.02	8/12/27/53	7/10/31/52

[a] The number of arm segments. [b] A, B, C, and D segments correspond to polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), and poly(4-methoxystyrene), respectively. [c] The number of DPE moieties introduced at the core of asymmetric star polymers. [d] The composition represents A/B/C/D by weight.

totally new except for 31-arm $AB_2C_4D_8E_{16}$ type. In this synthesis, poly(4-trimethylsilylstyrene) (P4SiS) is used as the E segment of choice in the linking reaction. A 3.0-fold excess of PSiSLi over each DPE function of precursors was always employed in the process (a) to go to completion. As shown in Figure 4, each of SEC profiles of the isolated stars by fractionation using hexane/ethanol shows a sharp symmetrical peak. All of the characterization results (M_n, PDI, and composition) clearly indicate the successful formation of the expected five-component asymmetric star polymers (see Table 4). Figure 5 representatively shows the ^{1}H NMR spectra of star polymers with 9-arm $AB_2C_2D_2E_2$ and 23-arm $AB_2C_4D_8E_8$ types, in which the presence of characteristic resonances of A, B, C, D, and E segments and their reasonable intensity ratios are confirmed. Thus, the desired five-component asymmetric star polymers were successively synthesized by repeating the iterative processes five times. The virtually quantitative reactions of both (a) and (b) could again be revealed. The crowding effect at the core of stars does not effect on the reactivity at all between DPE functional polymers and incoming living anionic polymers even in the fifth iteration, probably because of methylene spacers of **1** and **2** to release the steric hindrance. Obviously, the iterative methodology developed in this study is quite effective for the versatile synthesis of multicomponent and multiarmed asymmetric star polymers as many as five different segments.

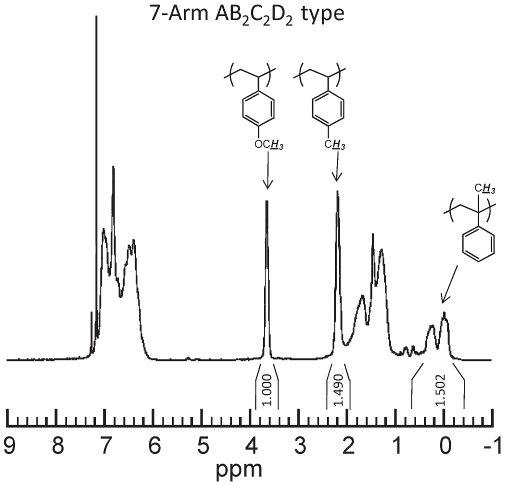


Figure 3. ^{1}H NMR spectrum of 7-arm $AB_2C_2D_2$-type asymmetric star polymer.

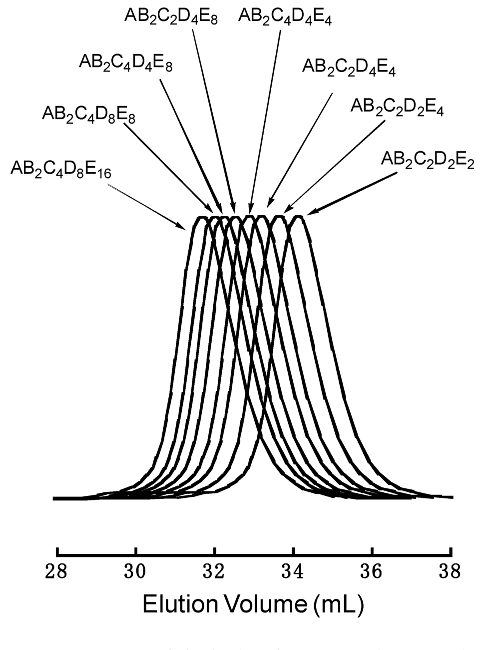


Figure 4. SEC RI traces of the isolated asymmetric star polymers.

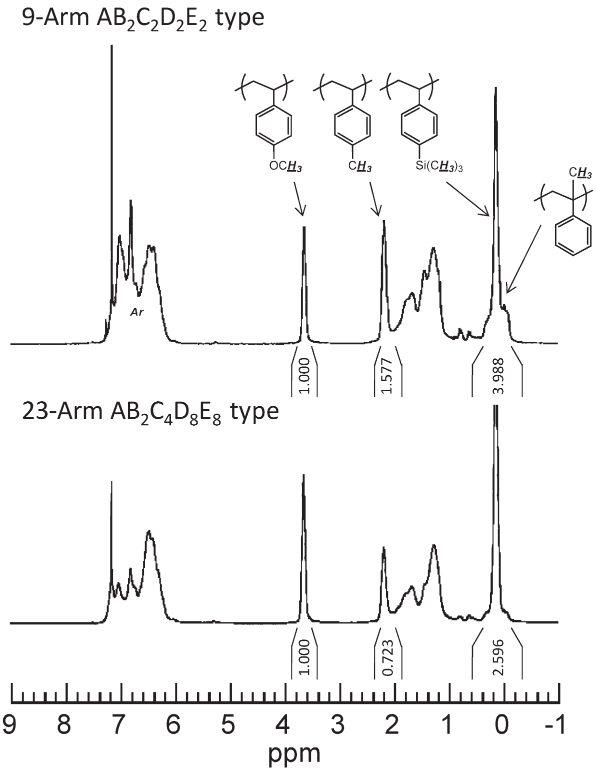


Figure 5. ^{1}H NMR spectra of 9-arm $AB_2C_2D_2E_2$ type and 23-arm $AB_2C_4D_8E_8$ type asymmetric star polymers.

Table 4. Characterization Results of Five-Component Asymmetric Star Polymers

			M_n (kg/mol)			M_w/M_n	composition[d]	
arm no.[a]	type[b]	DPE no.[c]	calcd	RALLS	^{1}H NMR	SEC	calcd	^{1}H NMR
9	$AB_2C_2D_2E_2$	2	87.5	92.9	91.5	1.05	12/26/24/20/18	14/23/25/18/20
11	$AB_2C_2D_2E_4$	4	116	109	123	1.04	9/20/18/16/37	7/18/18/16/41
13	$AB_2C_2D_4E_4$	4	136	150	137	1.05	8/17/17/29/29	6/19/19/28/28
15	$AB_2C_4D_4E_4$	4	158	154	159	1.04	7/13/27/26/27	7/13/27/26/27
17	$AB_2C_2D_4E_8$	8	171	178	156	1.04	6/14/13/24/43	9/15/15/24/37
19	$AB_2C_4D_4E_8$	8	188	181	179	1.04	6/11/23/23/37	7/14/25/20/34
23	$AB_2C_4D_8E_8$	8	243	260	234	1.04	4/6/18/37/35	3/11/21/33/32
31	$AB_2C_4D_8E_{16}$	32	332	356	309	1.02	4/6/13/27/50	4/7/15/28/46

[a] The number of arm segments. [b] A, B, C, D, and E segments correspond to polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), and poly(4-trimethylsilylstyrene), respectively. [c] The number of DPE moieties introduced at the core of asymmetric star polymers. [d] The composition represents A/B/C/D/E by weight.

Conclusions

An advanced iterative methodology using **1** or **2** of alternative choice at each iteration for the versatile synthesis of asymmetric star polymers has been demonstrated. The key point of this methodology is the facile control of arm numbers and components by choosing **1** or **2** to be reacted at each iteration. In practice, the iterative process could be satisfactorily repeated five times to successively synthesize two-, three-, four-, and even five-component asymmetric star polymers. As the iteration proceeds, the structures of stars widely spread. Indeed, 3-arm AB_2, 5-arm AB_2C_2, and 7-arm AB_2C_4 type stars were readily obtained by the third iteration. Furthermore, four-component 7-arm $AB_2C_2D_2$, 9-arm $AB_2C_2D_4$, 11-arm $AB_2C_4D_4$, and 15-arm $AB_2C_4D_8$ type stars could be obtained at the fourth iteration. We also successfully synthesized an array of 9-arm $AB_2C_2D_2E_2$, 11-arm $AB_2C_2D_2E_4$, 13-arm $AB_2C_2D_4E_4$, 15-arm $AB_2C_4D_4E_4$, 17-arm $AB_2C_2D_4E_8$, 19-arm $AB_2C_4D_4E_8$, 23-arm $AB_2C_4D_8E_8$, and 31-arm $AB_2C_4D_8E_{16}$ type stars at the fifth iteration. The A, B, C, D, and E segments were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), and poly(4-trimethylsilylstyrene) segments, respectively. A high degree of structural and compositional homogeneity in each of all the samples is confirmed by analytical results with ^{1}H NMR and SEC-RALLS. The effectiveness of the proposed iterative method is attributed to the design of **1** or **2** whose DPE and halide moieties are separated by alkyl spacers to reduce steric requirement and electric repulsion between intermediate polymer anions and incoming living anionic polymers. Since all of the stars synthesized herein still possess DPE moieties, further iterative process can possibly continue to obtain six-, seven-, and more-component stars. It should be mentioned that the styrenic monomers have been always used here for facile characterization of stars by ^{1}H NMR; however, polymers derived from 1,3-dienes may possibly participate in the proposed methodology as well.

References and Notes

(1) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978**, *51*, 406–436.

(2) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 89–116.

(3) Roovers, J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1985; Suppl. Vol. *2*, pp 478−499.

(4) Rempp, P.; Herz, J. E. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1989; Suppl. Vol, pp 493−510.

(5) Fetters, L. J.; Thomas, E. L. *Material Science and Technology*; VCH Verlangesellschaft: Weinheim, Germany, 1993; Vol. *12*, pp 1−31.

(6) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Applications*; Marcel Dekker: New York, 1996; pp 333−368.

(7) Grest, G. S.; Fetters, L. J.; Huang, J. S. *Adv. Chem. Phys.* **1996**, *94*, 67–163.

(8) Lutz, P. J.; Rein, D. In *Star and Hyperbranched Polymers*; Mishra, M. K., Kobayashi, S., Eds.; Marcel Dekker: New York, 1999; pp 27−57.

(9) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857–871.

(10) Hadjichristidis, N.; Pitsikalis, M.; Iatrou, H.; Vlahos, C. *Adv. Polym. Sci.* **1999**, *142*, 72–127.

(11) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792.

(12) Hadjichristidis, N.; Pitsikalis, M.; Iatrou, H.; Pispas, S. *Macromol. Rapid Commun.* **2003**, *24*, 979–1013.

(13) Hirao, A.; Hayashi, M.; Tokuda, Y.; Haraguchi, N.; Higashihara, T.; Ryu, S. W. *Polym. J.* **2002**, *34*, 1–26.

(14) Hirao, A.; Hayashi, M.; Lokulnant, S.; Sugiyama, K.; Ryu, S. W.; Haraguchi, N.; Matsuo, A.; Higashihara, T. *Prog. Polym. Sci.* **2005**, *30*, 111–182.

(15) Hirao, A.; Inoue, K.; Higashihara, T.; Hayashi, M. *Polym. J.* **2008**, *40*, 923–941.

(16) Milner, S. T. *Macromolecules* **1994**, *27*, 2333–2335.

(17) Okamoto, S.; Hasegawa, H.; Hashimoto, T.; Fujimoto, T.; Zhang, H.; Kazama, T.; Takano, A.; Isono, Y. *Polymer* **1997**, *38*, 5275–5281.

(18) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1998**, *31*, 5272–5277.

(19) Hadjichristidis, N.; Iatrou, H.; Behal, S. K.; Chludznski, J. J.; Disko, M. M.; Garner, R. T.; Liang, K. S.; Lohse, D. J.; Milner, S. T. *Macromolecules* **1993**, *31*, 5812–5815.

(20) Sioula, S.; Hadjichristidis, N.; E. Thomas, L. *Macromolecules* **1998**, *31*, 8429–8432.

(21) Hückstädt, H.; Göpfert, A.; Abetz, V. *Macromol. Chem. Phys.* **2000**, *201*, 296–307.

(22) Bohbot-Raviv, Y.; Wang, Z.-G. *Phys. Rev. Lett.* **2000**, *85*, 3428–307.

(23) He, X.; Huang, L.; Pan, C. *J. Chem. Phys.* **2002**, *116*, 10508–10513.

(24) Gemma, T.; Hatano, A.; Dotera, T. *Macromolecules* **2002**, *35*, 3225–3237.

(25) Yamauchi, K.; Takahashi, K.; Hasegawa, H.; Iatrou, H.; Hadjichristidis, N.; Kaneko, T.; Nishikawa, Y.; Jinnai, H.; Matsui, T.; Nishioka, H.; Shimizu, M.; Furukawa, H. *Macromolecules* **2003**, *36*, 6962–6966.

(26) He, X.; Huang, L.; Liang, H.; Pan, C. *J. Chem. Phys.* **2003**, *118*, 9861–9863.

(27) Lu, T.; He, X.; Liang, H. *J. Chem. Phys.* **2004**, *121*, 9702–9707.

(28) Birshtein, T. M.; Polotsky, A. A.; Abetz, V. *Macromol. Theory Simul.* **2004**, *13*, 512–519.

(29) Tang, P.; Qiu, F.; Zhang, H.; Yang, Y. *J. Phys. Chem. B* **2004**, *108*, 8434–8438.

(30) Takano, A.; Wada, S.; Sato, S.; Araki, T.; Hirahara, K.; Kazama, T.; Kawahara, S.; Isono, Y.; Ohono, A.; Tanaka, N.; Matsushita, Y. *Macromolecules* **2004**, *37*, 9941–9946.

(31) Takano, A.; Kawashima, W.; Noro, A.; Isono, Y.; Tanaka, N.; Dotera, T.; Matsushita, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 2427–2432.

(32) Yamauchi, K.; Akasaka, S.; Hasegawa, H.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **2005**, *38*, 8022–8027.

(33) Li, Z.; Hillmyer, M. A.; Lodge, T. P. *Macromolecules* **2006**, *39*, 765–771.

(34) Hayashida, K.; Kawashima, W.; Takano, A.; Shinohara, Y.; Amemiya, Y.; Nozue, Y.; Matsushita, Y. *Macromolecules* **2006**, *39*, 4869–4872.

(35) Hayashida, K.; Takano, A.; Arai, S.; Shinohara, Y.; Amemiya, Y.; Matsushita, Y. *Macromolecules* **2006**, *39*, 9402–9408.

(36) Hayashida, K.; Saito, N.; Arai, S.; Takano, A.; Tanaka, N.; Matsushita, Y. *Macromolecules* **2007**, *40*, 3695–3699.

(37) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 2479–2484.

(38) Higashihara, T.; Hirao, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4535–4547.

(39) Higashihara, T.; Nagura, M.; Inoue, K.; Haraguchi, N.; Hirao, A. *Macromolecules* **2005**, *38*, 4577–4587.

(40) Mavroudis, A.; Hadjichristidis, N. *Macromolecules* **2006**, *39*, 535–540.

(41) Wang, X.; He, J.; Yang, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4818–4828.

(42) Altintas, O.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1218–1228.

(43) Avgeropoulos, A.; Poulos, Y.; Hadjichristidis, N.; Roovers, J. *Macromolecules* **1996**, *29*, 6076–6078.

(44) Hirao, A.; Tokuda, Y. *Macromolecules* **2003**, *36*, 6081–6086.

(45) Hirao, A.; Kawasaki, K.; Higashihara, T. *Macromolecules* **2004**, *37*, 5179–5189.

(46) Hirao, A.; Kawasaki, K.; Higashihara, T. *Sci. Technol. Adv. Mater.* **2004**, *5*, 469–477.

(47) Hirao, A.; Higashihara, T.; Sakurai, T. *Macromolecules* **2006**, *39*, 6081–6091.

(48) Higashihara, T.; Inoue, K.; Nagura, M.; Hirao, A. *Macromol. Res.* **2006**, *14*, 287–299.

(49) Hirao, A.; Hayashi, M.; Higashihara, T. *Macromol. Chem. Phys.* **2001**, *202*, 3165–3173.

(50) Hirao, A.; Higashihara, T. *Macromolecules* **2002**, *35*, 7238–7245.

(51) Hirao, A.; Higashihara, T.; Inoue, K. *Macromolecules* **2008**, *41*, 3579–3587.

(52) Hirao, A.; Higashihara, T.; Nagura, M.; Sakurai, T. *Macromolecules* **2006**, *39*, 6081–6091.

(53) Zhao, Y.; Higashihara, T.; Sugiyama, K.; Hirao, A. *Macromolecules* **2007**, *40*, 228–238.

(54) Zhao, Y.; Higashihara, T.; Sugiyama, K.; Hirao, A. *J. Am. Chem. Soc.* **2005**, *127*, 14158–14159.
(55) Higashihara, T.; Nagura, M.; Inoue, K.; Haraguchi, N.; Hirao, A. *Macromolecules* **2005**, *38*, 4577–4587.
(56) Pike, R. M. *J. Polym. Sci.* **1959**, *40*, 577–578.
(57) Sugiyama, K.; Karasawa, Y.; Higashihara, T.; Zhao, Y.; Hirao, A. *Monatsh. Chem.* **2006**, *137*, 869–880.
(58) Glasse, M. D. *Prog. Polym. Sci.* **1983**, *9*, 133–195.
(59) Hsieh, H. L.; Quirk, R. P. In *Anionic Polymerization: Principles and Applications*; Marcel Dekker: New York, 1996; pp 175−176.