

## Successive Synthesis of Well-Defined Star-Branched Polymers by an Iterative Approach Based on Living Anionic Polymerization

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*Received October 11, 2005; Revised November 14, 2005*

**Abstract:** To successively synthesize star-branched polymers, we developed a new iterative methodology which involves only two sets of the reactions in each iterative process: (a) an addition reaction of DPE or DPE-functionalized polymer to a living anionic polymer, and (b) an *in-situ* reaction of 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene with the generated 1,1-diphenylalkyl anion to introduce one DPE functionality. With this methodology, 3-, 4-, and 5-arm, regular star-branched polystyrenes, as well as 3-arm ABC, 4-arm ABCD, and a new 5-arm ABCDE, asymmetric star-branched polymers, were successively synthesized. The A, B, C, D, and E arm segments were poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), polystyrene, and poly(4-*tert*-butyldimethylsilyloxystyrene), respectively. All of the resulting star-branched polymers were well-defined in architecture and precisely controlled in chain length, as confirmed by SEC, <sup>1</sup>H NMR, VPO, and SLS analyses. Furthermore, we extended the iterative methodology by the use of a new functionalized DPE derivative, 1-(3-chloromethylphenyl)-1-((3-(1-phenylethenyl)phenyl)ethylene, capable of introducing two DPE functionalities *via* one DPE anion reaction site in the reaction (b). The number of arm segments of the star-branched polymer synthesized by the methodology could be dramatically increased to 2, 6, and up to 14 by repeating the iterative process.

**Keywords:** star-branched polymers, living anionic polymerization, iterative methodology.

### Introduction

Star-branched polymers have been widely investigated from both experimental and theoretical viewpoints.<sup>1-10</sup> Among them, star-branched polymers in which more than two chemically different polymer segments are radially emanated from a single junction are termed heteroarm, miktoarm, or asymmetric star-branched polymers. Each different arm segment of asymmetric star-branched polymer may possibly phase-separate at molecular level followed by self-organization to form periodic specially shaped nanoscopic objects derived from both heterophase structure and branching architecture characteristic to asymmetric star-branched polymer.<sup>11-16</sup> Indeed, Sioura, Hadjichristidis, and Thomas have recently reported a new periodic hexagonal morphology formed by a 3-arm ABC asymmetric star-branched polymer comprised of polystyrene, polyisoprene, and poly(methyl methacrylate) segments.<sup>13</sup> Hückstädt, Göpfert, and Abetz have also observed new specific tetragonal and hexagonal morphologies with similar ABC stars.<sup>15</sup> The appearance of such new and complex morphologies first formed only by

asymmetric stars has provoked considerable interest in the synthesis of variety of well-defined asymmetric star-branched polymers. Availability of such asymmetric stars, however, is rather limited even at the present time because they are generally much more difficult in synthesis than the corresponding regular stars with the same number of arms, since two or more quantitative nature of reactions and the isolation of intermediate polymers are often required during the synthesis.<sup>15,17-41</sup> It is therefore essential to establish general, versatile, and systematic methodologies applicable to the synthesis of asymmetric star-branched polymers with a wide variety of compositions.

We have recently developed a novel iterative methodology by which a variety of regular as well as asymmetric star-branched polymers can be successively and systematically synthesized.<sup>42,43</sup> The methodology is based on living anionic polymerization with use of a specially designed 1,1-diphenylethylene (DPE) derivative, 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene (**1**), and involves only two sets of reactions for the entire iterative synthetic sequence: (a) an addition reaction of living anionic polymer to a DPE derivative or the produced DPE-chain-functionalized polymer and (b) an *in-situ* reaction of the newly generated 1,1-diphenylalkyl

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anion with **1** to introduce one DPE functionality. The iterative methodology starts from the addition reaction of a living anionic polymer to 1,3-bis(1-phenylethenyl)benzene (**2**) used as a core compound (reaction (a)), followed by treatment with **1** (reaction (b)). Subsequently, the two reactions, (a) and (b), are repeated two more times to successively synthesize a 4-arm A<sub>2</sub>B<sub>2</sub> asymmetric star, followed by a quite new 6-arm A<sub>2</sub>B<sub>2</sub>C<sub>2</sub> asymmetric star whose A, B, and C segments are polystyrene, poly( $\alpha$ -methylstyrene), and poly(4-methoxystyrene), respectively. Furthermore, the successive synthesis of a series of 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 stars could be achieved by using 1,1-bis(3-(1-phenylethenyl)phenyl)ethylene (**3**) as another starting core compound in the iterative methodology. The key point of this methodology is that reaction sites can be always regenerated after each of the iterative processes and hence the same reaction sequence can be, in principle, limitlessly repeated to be able to successively synthesize a variety of star-branched polymers.

Herein, we first report on the successive synthesis of asymmetric star-branched polymers with multi-component system such as 4-arm ABCD and even 5-arm ABCDE stars by making the iterative methodology possible to introduce one polymer segment at each iterative process, since only a few synthetic examples of ABCD stars<sup>20(b), 40, 41</sup> and ABCDE star<sup>44</sup> have been so far reported. Secondly, we report on a possible extension of the iterative methodology for the successive synthesis of different type star-branched polymers with many arms. For this purpose, we have synthesized 1-(3-chloromethylphenyl)-1-((3-(1-phenylethenyl)phenyl)ethylene (**4**) of a new functionalized DPE derivative capable of introducing two DPE functionalities *via* one reaction site in the reaction (b) and used in place of **1** in the iterative methodology. The number of arm segments of the star-branched polymer synthesized by the extended methodology could be dramatically increased to 2, 6, and so on to 14 by repeating the iterative process.

## Experimental

**Materials.** All chemicals (>98% purities) were purchased from Aldrich, Japan and used as received unless otherwise stated. Tetrahydrofuran (THF) (99%, Mitsubishi Chemical Co., Ltd.) was refluxed over Na wire for 12 h and then distilled over LiAlH<sub>4</sub> under nitrogen. It was finally distilled from its sodium naphthalenide solution on a high vacuum line (10<sup>-6</sup> torr). *tert*-Butylbenzene was washed with concentrated H<sub>2</sub>SO<sub>4</sub> and water and dried over CaCl<sub>2</sub> followed by P<sub>2</sub>O<sub>5</sub>. It was distilled twice from its BuLi solution under reduced pressure. 4-Trimethylsilylstyrene<sup>45</sup> and 4-*tert*-butyldimethylsilyloxystyrene<sup>46</sup> were synthesized and purified as previously reported. Styrene (99%), 4-methoxystyrene (99%), and 4-methylstyrene (99%) were washed with 10% NaOH aq, dried over MgSO<sub>4</sub>, and distilled over CaH<sub>2</sub> under reduced

pressures. The styrenes were finally distilled over Bu<sub>2</sub>Mg (*ca.* 5 mol%) on the vacuum line into ampoules equipped with break-seals that were pre-washed with potassium naphthalenide in THF. 1,1-Diphenylethylene was distilled over BuLi (*ca.* 5 mol%) on the vacuum line. 1,3-Bis(1-phenylethenyl)benzene (**2**)<sup>47</sup> and 1-(3-bromophenyl)-1-phenylethylene<sup>43</sup> were synthesized and purified as previously reported. 1-(4-(4-Bromobutyl)phenyl)-1-phenylethylene (**1**) was synthesized according to our procedures previously reported.<sup>42</sup> Acetic anhydride and carbon tetrachloride were distilled over CaH<sub>2</sub>.

**Measurements.** Size-exclusion chromatography (SEC) was performed on a TOSOH HLC 8020 instrument with UV (254 nm) and refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Three polystyrene gel columns (pore size (bead size): 650 Å (9  $\mu$ m), 200 Å (5  $\mu$ m), and 75 Å (5  $\mu$ m)) were used. Measurable molecular weight ranges are 10<sup>3</sup> ~ 4 × 10<sup>5</sup>. Calibration curves were made with polystyrene standards for determining both *M<sub>n</sub>* and *M<sub>w</sub>/M<sub>n</sub>* values. Both <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75 MHz) NMR spectra were measured in CDCl<sub>3</sub> 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 (TM-32K: Sensitivity; 35,000  $\mu$ V  $\pm$  10%/1 M) and 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 (*dn/dc*) 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.

**1-(3-Chloromethylphenyl)-1-(3-(1-phenylethenyl)phenyl)ethylene (**4**).** Under nitrogen, a solution of 3-methoxymethylphenylmagnesium bromide prepared from 3-methoxymethylphenyl bromide (8.68 g, 43.2 mmol) and Mg (1.53 g, 62.9 mmol) in dry THF (130 mL) was added dropwise to an ice-cooled dry THF solution (30 mL) containing acetic anhydride (14.6 g, 143 mmol) over a period of 30 min. The resulting mixture was then stirred at 25 °C for 18 h. It was acidified with 2 N HCl, extracted with ether, and dried over MgSO<sub>4</sub>. After removal of the solvent, the residue was purified by flash column chromatography on silica gel eluting a mixed solvent of hexane and ethyl acetate (5/1 to 3/1, *v/v*) to afford 3-methoxymethylacetophenone as a colorless oil (3.79 g, 23.1 mmol, 54%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.89–7.24 (4H, m, ArH), 4.48 (2H, s, ArCH<sub>2</sub>O-), 3.39 (3H, s, -CH<sub>2</sub>OCH<sub>3</sub>), 2.58 (-CO-CH<sub>3</sub>)

3-Methoxymethylacetophenone (2.02 g, 12.3 mmol) dried in vacuo for 6 h was dissolved in dry THF (10 mL) and then added dropwise to an ice-cooled dry THF solution (45 mL) of 3-(1-phenylethenyl)phenylmagnesium bromide prepared

from 1-(3-bromophenyl)-1-phenylethylene (2.93 g, 11.3 mmol) and Mg (0.41 g, 16.9 mmol) under nitrogen over a period of 10 min. The resulting mixture was stirred at 25 °C for 12 h. It was acidified with 2 N HCl (60 mL), extracted with ether, and dried over MgSO<sub>4</sub>. Removal of the solvent under reduced pressure yielded crude 1-(3-methoxymethylphenyl)-1-(3-(1-phenylethenyl)phenyl)ethanol as a viscose yellow oil (3.87 g, 11.3 mmol, 100%). It was then dehydrated with *p*-toluenesulfonic acid in benzene (80 mL) at 80 °C for 6 h. After cooling to room temperature, saturated aqueous NaHCO<sub>3</sub> (80 mL) was added to the solution and the resulting mixture was extracted with ether and dried over MgSO<sub>4</sub>. After evaporation, the residue was purified by flash column chromatography on silica gel eluting with hexane/ethyl acetate (15/1, *v/v*) to afford 1-(3-methoxymethylphenyl)-1-(3-(1-phenylethenyl)phenyl)ethylene as a colorless syrup (1.06 g, 3.25 mmol, 28%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ=7.36–7.24 (13H, m, ArH), 5.46 and 5.44 (2H, ss, CH<sub>2</sub>=), 4.44 (2H, s, ArCH<sub>2</sub>O-), 3.38 (3H, s, OCH<sub>3</sub>)

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ=149.9 (Ar-C(=CH<sub>2</sub>)-Ar-), 149.7 (-Ar-C(=CH<sub>2</sub>)-Ar-), 141.5, 141.4 (2C, C-C-C=H<sub>2</sub>), 138.7 (C-CH<sub>2</sub>Cl), 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.3 (13C, Ar), 114.7 (Ar-C(=CH<sub>2</sub>)-Ar-), 114.5 (-Ar-C(=CH<sub>2</sub>)-Ar-), 74.7 (-CH<sub>2</sub>O), 58.2 (OCH<sub>3</sub>)

Under nitrogen, to a dry carbon tetrachloride solution (5.0 mL) of 1-(3-methoxymethylphenyl)-1-(3-(1-phenylethenyl)phenyl)ethylene (1.06 g, 3.25 mmol) was added dropwise a 1.0 M methylene dichloride solution (5.0 mL) of boron trichloride (5.0 mmol) at 0 °C. After stirring for 2.5 h, the mixture was quenched with methanol (20 mL). It was neutralized with 10% NaOH aq (40 mL), extracted with carbon tetrachloride, washed with water, dried over MgSO<sub>4</sub>, and evaporated. Flash column chromatography on silica gel eluting a mixed solvent of hexane and ethyl acetate (50/1 to 30/1, *v/v*) afforded the title compound, **4**, as a colorless syrup (0.32 g, 0.967 mmol, 30%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ=7.35–7.24 (13H, m, ArH), 5.47 and 5.44 (2H, ss, CH<sub>2</sub>=), 4.56 (2H, s, ArCH<sub>2</sub>Cl)

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ=149.8 (Ar-C(=CH<sub>2</sub>)-Ar-), 149.4 (-Ar-C(=CH<sub>2</sub>)-Ar-), 141.9, 141.6, 141.3, 141.1 (4C, C-C-C=H<sub>2</sub>), 137.4 (C-CH<sub>2</sub>Cl), 128.7, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8 (11C, Ar), 115.0 (Ar-C(=CH<sub>2</sub>)-Ar-), 114.6 (-Ar-C(=CH<sub>2</sub>)-Ar-), 46.2 (CH<sub>2</sub>Cl)

**Preparation of Living Anionic Polymers.** All polymerizations were carried out under a high vacuum condition (< 10<sup>-6</sup> torr) in sealed glass reactors with break seals. The reactors were always pre-washed with the initiator solutions after being sealed off from the vacuum line. Polystyryllithium, poly(4-trimethylsilylstyryl)lithium, poly(4-methoxystyryl)lithium, poly(4-methylstyryl)lithium, and poly(4-*tert*-butyldimethylsilyloxystyryl)lithium were prepared by the *sec*-BuLi-initiated polymerization of the corresponding styrenes in THF at -78 °C for 20 min, 1, 1, 1, and 2 h, respectively.

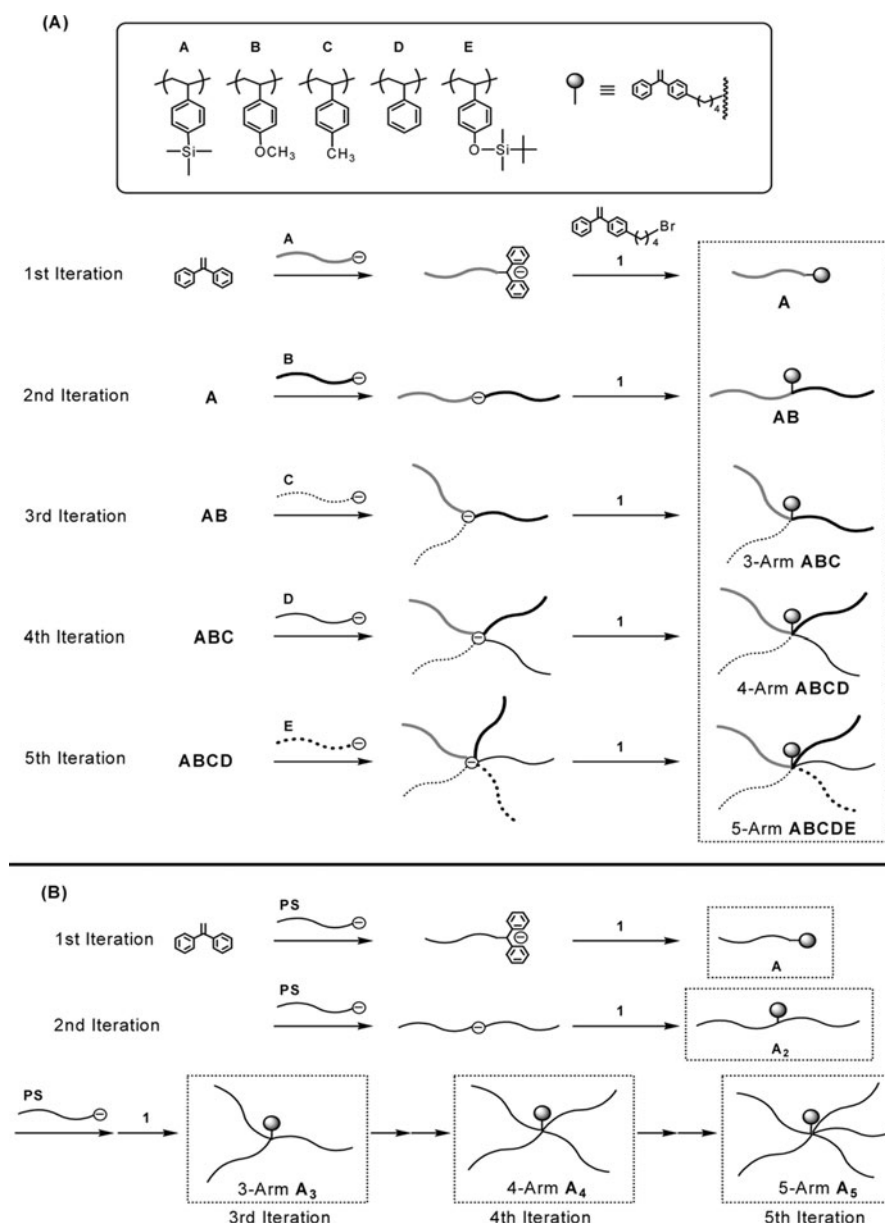
Monomers and initiators were used in the concentration ranges of *ca.* 0.5~0.8 M and *ca.* 0.04~0.06 M, respectively. In the iterative methodology using **4**, each polystyryllithium was prepared by the *sec*-BuLi-initiated polymerization of styrene in *tert*-butylbenzene at 25 °C for 2 h where the concentration of styrene is conducted to be around 3.0 M.

#### Successive Synthesis of 3-, 4-, and 5-Arm Regular Star-Branched Polystyrenes by Iterative Methodology Using **1** (see Scheme I(B)).

**First Iterative Process:** Under the high vacuum conditions (<10<sup>-6</sup> torr), polystyryllithium (2.12 g, 0.210 mmol, *M<sub>n</sub>* (SEC)=10.1 kg/mol) in THF (21.4 mL) was added to a THF (3.58 mL) solution of DPE (0.250 mmol) at -78 °C and the mixture was allowed to stir for 30 min at -78 °C. The mixture was then added to a THF (5.41 mL) solution of **1** (0.252 mmol) pre-purified with Bu<sub>2</sub>Mg (0.0879 mmol). After 1 h, the resulting polymer was poured into a large amount of MeOH (200 mL) to precipitate the polymer. It was reprecipitated two times from THF to MeOH and freeze-dried from its benzene solution for 24 h to afford the expected DPE-chain-end-functionalized polystyrene (**A**, 2.15 g, 99%, *M<sub>n</sub>* (SEC)=10.4 kg/mol, *M<sub>w</sub>*/*M<sub>n</sub>* (SEC)=1.02, and the degree of functionalization determined by <sup>1</sup>H NMR =1.0<sub>3</sub>).

**Second Iterative Process:** Polystyryllithium (2.16 g, 0.198 mmol, *M<sub>n</sub>* (SEC)=10.9 kg/mol) in THF (20.8 mL) was added to a THF (18.8 mL) solution of **A** (1.72 g, 0.165 mmol) at -78 °C and the mixture was allowed to stand for 10 min. After adding DPE (0.244 mmol) in THF (3.71 mL), the mixture was *in-situ* reacted with **1** (0.237 mmol) pre-purified with Bu<sub>2</sub>Mg (0.0879 mmol) in THF (5.25 mL) at -78 °C for 1 h. The resulting polymer was poured into a large amount of MeOH (400 mL) to precipitate the polymer. The coupled polymer was isolated in 75% yield (2.65 g) 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 for 24 h at 5 °C to precipitate the polymer. Reprecipitation of the polymer two times from THF to MeOH followed by freeze-drying from its benzene solution for 24 h afforded the expected DPE-in-chain-functionalized polystyrene (**A**<sub>2</sub>, *M<sub>n</sub>* (SEC)=21.4 kg/mol, *M<sub>w</sub>*/*M<sub>n</sub>* (SEC)=1.02, and the degree of functionalization determined by <sup>1</sup>H NMR=0.96<sub>6</sub>).

**Third Iterative Process:** Polystyryllithium (1.26 g, 0.136 mmol, *M<sub>n</sub>* (SEC)=9.26 kg/mol) was reacted with **A**<sub>2</sub> (2.11 g, 0.0986 mmol) in THF (33.8 mL) at -78 °C and the mixture was allowed to stand for 10 min. After adding DPE (0.166 mmol) in THF (5.14 mL), the mixture was *in-situ* reacted with **1** (0.154 mmol) pre-purified with Bu<sub>2</sub>Mg (0.0691 mmol) in THF (3.85 mL) at -78 °C for 1 h. The resulting polymer was poured into a large amount of MeOH (300 mL) to precipitate the polymer. The expected core-functionalized 3-arm regular star-branched polystyrene with DPE moiety (**A**<sub>3</sub>) was isolated in 81% yield (2.49 g) by fractional precipitation



**Scheme I.** Successive synthesis of 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE asymmetric star-branched polymers by an iterative methodology using DPE and **1**.

using hexane and cyclohexane ( $M_n$  (VPO)=31.1 kg/mol,  $M_w/M_n$  (SEC)=1.02, and the degree of functionalization determined by  $^1\text{H NMR}$ =1.0<sub>0</sub>).

**Fourth and Fifth Iterative Processes:** Similarly, the fourth and fifth iterations were carried out to successively synthesize 4-, followed by 5-arm regular star-branched polystyrenes (**A<sub>4</sub>** and **A<sub>5</sub>**), respectively. A 1.5-fold excess of PSLi toward DPE functionality was always employed in each addition reaction. The resulting star-branched polystyrenes were isolated by fractional precipitation using hexane and cyclohexane. Both **A<sub>4</sub>** and **A<sub>5</sub>** were obtained in 88 and 95% yields, respectively. Their detailed results are listed in

Table I.

**Successive Synthesis of 3-Arm ABC, 4-Arm ABCD, and 5-Arm ABCDE Asymmetric Star-Branched Polymers by Iterative Methodology Using **1**** (see Scheme I(A)).

Similarly, 3-arm ABC, 4-arm ABCD, followed by 5-arm ABCDE asymmetric star-branched polymers were successively synthesized by the iterative methodology. The A, B, C, D, and E segments were poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), polystyrene, and poly(4-*tert*-butyldimethylsilyloxystyrene) segments, respectively. Detailed procedures and conditions are as follows:

**Table I. Synthesis of DPE-Chain-End (A) and DPE-In-Chain-Functionalized Polystyrenes (A<sub>2</sub>), 3-Arm A<sub>3</sub>, 4-Arm A<sub>4</sub>, and 5-Arm A<sub>5</sub> Star-Branched Polystyrenes Using DPE and 1 in THF at -78 °C<sup>a</sup>**

Type	$M_n$ (kg/mol)			$M_w$ (kg/mol)		$M_w/M_n$	Functionality <sup>d</sup>		$g' = [\eta]_{star}/[\eta]_{linear}$ <sup>e</sup>	
	Calcd	SEC	VPO	Calcd <sup>b</sup>	SLS <sup>c</sup>	SEC	Calcd	<sup>1</sup> H NMR	Calcd <sup>f</sup>	Expml
A	10.3	10.4	10.5	10.4	10.6 <sup>g</sup>	1.02	1	1.03	–	–
A <sub>2</sub>	21.5	21.4	21.0	21.9	21.8 <sup>g</sup>	1.02	1	0.96 <sub>6</sub>	–	–
A <sub>3</sub>	30.9	28.9	31.1	31.5	34.7	1.02	1	1.00	0.83	0.84
A <sub>4</sub>	42.4	38.1	45.1	43.3	44.1	1.02	1	1.02	0.71	0.73
A <sub>5</sub>	52.9	–	53.4	–	–	–	1	–	–	–

<sup>a</sup>Yields of the isolated polymers were always more than 75%. <sup>b</sup>Calculated from  $M_n$  (calcd) and  $M_w/M_n$  (SEC) values. <sup>c</sup>Measured in THF at 25 °C.  $dn/dc = 0.185\text{--}0.189$  (mL/g). <sup>d</sup>Functionality of DPE moiety. <sup>e</sup>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;  $[\eta] = 1.2910^{-4}M_w$  (SLS)<sup>0.71</sup> values (ref. 49). <sup>f</sup>Calculated from the eq. (1);  $g' = [(3f-2)/f^2]^{0.58}[0.724-0.015(f-1)]/0.724$ ;  $f = \text{arm number}$  ( $3 \leq f \leq 18$ ) (ref. 48). <sup>g</sup>Measured by SEC.

**First Iterative Process:** Under the high vacuum conditions ( $<10^{-6}$  torr), poly(4-trimethylsilylstyryl)lithium (2.15 g, 0.219 mmol) in THF (23.3 mL) was added to a THF solution (3.76 mL) of DPE (0.263 mmol) at -78 °C and the mixture was allowed to stir for 1 h at -78 °C. The polymer mixture was reacted with **1** (0.307 mmol) pre-purified with Bu<sub>2</sub>Mg (0.108 mmol) in THF (6.58 mL). After 1 h, the resulting polymer was poured into a large amount of MeOH (200 mL) to precipitate the polymer. It was reprecipitated two times from THF to MeOH and freeze-dried from its benzene solution for 24 h to afford the expected DPE-chain-end-functionalized poly(4-trimethylsilylstyrene) (**A**, 2.19 g, 98%,  $M_n$  (<sup>1</sup>H NMR)=10.0 kg/mol,  $M_w/M_n$  (SEC)=1.03, and the degree of functionalization determined by <sup>1</sup>H NMR=0.99<sub>5</sub>).

**Second Iterative Process:** Poly(4-methoxystyryl)lithium (1.99 g, 0.188 mmol) in THF (21.3 mL) was added to a THF (18.8 mL) solution of **A** (1.57 g, 0.157 mmol) at -78 °C and the mixture was allowed to stand for 1 h. After adding DPE (0.201 mmol) in THF (3.45 mL), the mixture was *in-situ* reacted with **1** (0.263 mmol) pre-purified with Bu<sub>2</sub>Mg (0.0995 mmol) in THF (5.74 mL) at -78 °C for 1 h. The resulting polymer was poured into a large amount of MeOH (400 mL) to precipitate the polymer. The expected DPE-in-chain-functionalized AB diblock copolymer (**AB**) was isolated in 92% yield (3.01 g) by fractional precipitation using hexane/ethanol (1/1, v/v) ( $M_n$  (<sup>1</sup>H NMR)=20.8 kg/mol,  $M_w/M_n$  (SEC)=1.02, and the degree of functionalization determined by <sup>1</sup>H NMR=1.0<sub>5</sub>).

**Third Iterative Process:** Poly(4-methylstyryl)lithium (1.12 g, 0.109 mmol) was reacted with **AB** (1.74 g, 0.0837 mmol) in THF (35.8 mL) at -78 °C and the mixture was allowed to stand for 1 h. After adding DPE (0.125 mmol) in THF (3.32 mL), the mixture was *in-situ* reacted with **1**

(0.159 mmol) pre-purified with Bu<sub>2</sub>Mg (0.0755 mmol) in THF (3.48 mL) at -78 °C for 1 h. The resulting polymer was poured into a large amount of MeOH (300 mL) to precipitate the polymer. The expected core-functionalized 3-arm ABC asymmetric star-branched polymer with DPE moiety (**ABC**) was isolated in 72% yield (1.89 g) by fractional precipitation using benzene and methanol (5/4, v/v) ( $M_n$  (<sup>1</sup>H NMR)=31.8 kg/mol,  $M_w/M_n$  (SEC)=1.02, and the degree of functionalization determined by <sup>1</sup>H NMR=0.97<sub>2</sub>).

**Fourth and Fifth Iterative Processes:** Similarly, the fourth and fifth iterations were carried out to successively synthesize 4-arm ABCD, followed by 5-arm ABCDE asymmetric star-branched polymers (**ABCD** and **ABCDE**), by using polystyryllithium and poly(4-*tert*-butyldimethylsilyloxystyryl)lithium, respectively. A 1.5-fold excess of living anionic polymer toward DPE functionality was always employed in each addition reaction. The resulting star-branched polymers were isolated by fractional precipitation as described later. Both **ABCD** and **ABCDE** were obtained in 85 and 90% yields, respectively. Their detailed results are listed in Table II.

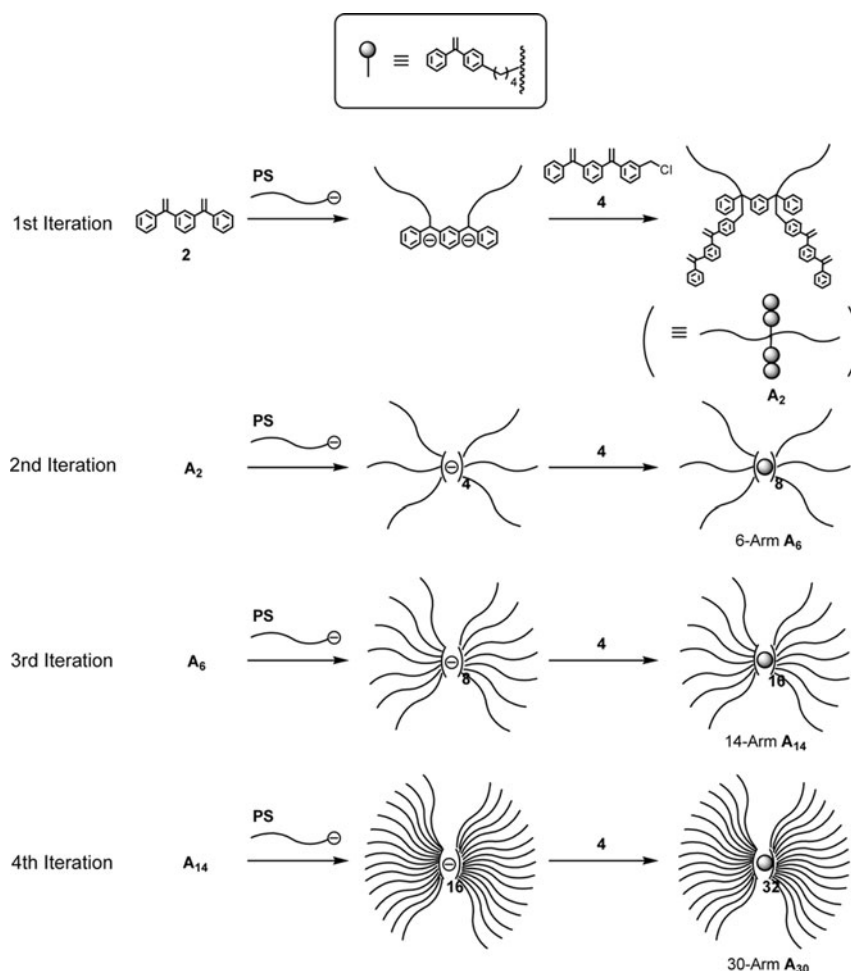
**Deprotection of E Segment in 5-Arm ABCDE Asymmetric Star-Branched Polymer.** The deprotection was carried out by treating 5-arm ABCDE star-branched polymer (0.450 g) with Bu<sub>4</sub>NF (2.70 mmol) in THF (10.0 mL) and the mixture was stirred at 25 °C for 5 h under nitrogen. It was then poured into MeOH (50 mL) to precipitate the polymer (0.395 g, 100% yield). The polymer was reprecipitated twice from the THF solution to MeOH and freeze-dried from its benzene solution for 24 h. Complete deprotection of the *tert*-butyldimethylsilyl group was confirmed by <sup>1</sup>H NMR and IR analyses.

**Successive Synthesis of Star-Branched Polystyrenes by Iterative Methodology Using 4 (see Scheme II).**

**Table II. Synthesis of DPE-Chain-End-Functionalized Poly(4-trimethylsilylstyrene) (A), AB Diblock Copolymer, 3-Arm ABC, 4-Arm ABCD, and 5-Arm ABCDE Asymmetric Star-Branched Polymers Using DPE and 1 in THF at -78 °C<sup>a</sup>**

Type	$M_n$ (kg/mol)			$M_w$ (kg/mol)		$M_w/M_n$	Composition (wt%) <sup>d</sup>	
	Calcd	VPO	<sup>1</sup> H NMR	Calcd <sup>b</sup>	SLS <sup>c</sup>		Calcd	<sup>1</sup> H NMR
A	10.2	10.7	10.0	10.5	10.3 <sup>e</sup>	1.03	100	100
AB	20.9	21.2	20.8	21.3	21.2 <sup>e</sup>	1.02	48/52	48/52
ABC	31.3	30.5	31.8	32.0	34.4	1.02	32/35/33	31/35/34
ABCD	42.0	43.8	42.8	42.8	43.0	1.02	24/29/23/24	23/28/23/26
ABCDE	57.6	55.5	59.3	59.3	57.0	1.03	17/21/17/19/26	17/19/18/19/27

<sup>a</sup>Yields of the isolated polymers were always more than 72%. A, B, C, D, E segments were poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), polystyrene, and poly(4-*tert*-butyldimethylsilyloxystyrene), respectively. <sup>b</sup>Calculated from  $M_n$  (calcd) and  $M_w/M_n$  (SEC) values. <sup>c</sup>In THF at 25 °C. The  $dn/dc$  values were 0.179, 0.181, and 0.176 mL/g for ABC, ABCD, and ABCDE stars, respectively. <sup>d</sup>A/B, A/B/C, A/B/C/D, and A/B/C/D/E, respectively. <sup>e</sup>Calculated from  $M_n$  (<sup>1</sup>H NMR) and  $M_w/M_n$  (SEC) values.

**Scheme II.** Successive synthesis of star-branched polystyrenes with many arm segments by an iterative methodology using **2** and **4**.

**First Iterative Process:** Under the high vacuum conditions ( $<10^{-6}$  torr), polystyryllithium (2.56 g, 0.239 mmol,  $M_n$  (SEC)=10.7 kg/mol) in *tert*-butylbenzene (8.90 mL) was added to a *tert*-butylbenzene (2.95 mL) solution of 1,3-bis(1-phenylethenyl)benzene (**2**, 0.126 mmol) at 25 °C and the

mixture was allowed to stir for 12 h at 25 °C. After adding THF (10.2 mL) chilled at -78 °C, the polymer mixture was reacted with **4** (0.267 mmol) pre-purified with Bu<sub>2</sub>Mg (0.0949 mmol) in THF (5.23 mL) at -78 °C. After 1 h, the resulting polymer was poured into a large amount of MeOH

(250 mL) to precipitate the polymer. The expected in-chain-end-functionalized polystyrene with four DPE moieties (2.51 g) was isolated in 90% yield by fractional precipitation using hexane/cyclohexane ( $M_n$  (SEC)=22.1 kg/mol,  $M_w/M_n$  (SEC)=1.01, and the degree of functionalization determined by  $^1\text{H NMR}$ =3.99).

**Second and Third Iterative Processes:** Similarly, the successive synthesis of 6- and 14-arm star-branched polystyrenes ( $\mathbf{A}_6$  and  $\mathbf{A}_{14}$ ) were performed in the second and third iterations. A 1.5-fold excess of living anionic polymer toward DPE functionality was always employed in each addition reaction. Both  $\mathbf{A}_6$  and  $\mathbf{A}_{14}$  were isolated by fractional precipitation in 81 and 85%, respectively. Their detailed results are listed in Table III.

**Fourth Iterative Process:** The fourth iteration was attempted under various conditions for the synthesis of 30-arm star-branched polystyrenes. A 1.5-fold excess of PSLi toward DPE functionality was always employed in each coupling reaction. The addition reactions (a) were carried out in *tert*-butylbenzene at 30, 40, 50 °C for 24, 168, and 336 h in the presence and absence of THF or TMEDA as additives or in THF at -40 °C for 168 h.

**Isolation and Purification of Polymers.** The objective star-branched polystyrenes were effectively isolated from the resulting polymer mixtures by fractional precipitation using hexane/cyclohexane (2/3~1/4, v/v) at 5 °C. Hexane was added slowly to a cyclohexane solution of polystyrene (*ca.* 1 g/150 mL) at 25 °C until the mixture became turbid and the mixture was stirred at 5 °C for 1 h. The precipitated polymer was recovered by carefully decanting the supernatant solution. Similarly, the 3-arm ABC and 4-arm ABCD stars were isolated in 72 and 76% yields by fractional precipitation using benzene/methanol (5/4 and 2/1, v/v), respectively. Both AB diblock copolymer and 5-arm ABCDE

star were also isolated by pouring their THF solutions to hexane / ethanol (1/1, v/v). The polymers all were purified by reprecipitating twice from THF into MeOH and then freeze-drying from their absolute benzene solutions for 8 h thrice.

## Results and Discussions

### Successive Synthesis of 3-, 4-, and 5-Arm Regular Star-Branched Polystyrenes by Iterative Methodology Using 1-(4-(4-Bromobutyl)phenyl)-1-phenylethylene (1).

As mentioned in introduction, we have been developing a novel iterative methodology for the synthesis of asymmetric star-branched polymers. Indeed, a series of  $\mathbf{A}_2\mathbf{B}_2$ ,  $\mathbf{A}_2\mathbf{B}_2\mathbf{C}_2$  and  $\mathbf{A}_3$ ,  $\mathbf{A}_3\mathbf{B}_3$ , and  $\mathbf{A}_3\mathbf{B}_3\mathbf{C}_3$  asymmetric stars could be successively synthesized by this methodology with either **2** or **3** as a starting core compound.<sup>42,43</sup> In order to successively synthesize the objective asymmetric star-branched polymers comprised of multi-component arm segments in this study, in place of **2** or **3** DPE was used as a starting core compound in the same iterative methodology and the iteration process was repeated. Scheme I(A) shows the present iterative methodology with DPE. As can be seen, one polymer segment is introduced at each iteration stage to successively synthesize 3-arm ABC, 4-arm ABCD, and so on to 5-arm ABCDE asymmetric stars. As shown in Scheme I(B), we have first intended to synthesize regular star-branched polystyrenes in order to examine whether the iterative methodology does work satisfactorily in terms of the successive star-branched polymer synthesis. The scheme illustrates the same synthetic routs as Scheme I(A) except for only using of polystyryllithium at each iteration. Throughout the synthesis, the arm segment was designated to be *ca.* 10 kg/mol in  $M_n$  value.

**Table III. Synthesis of Star-Branched Polystyrenes by an Iterative Methodology Using 2 and 4**

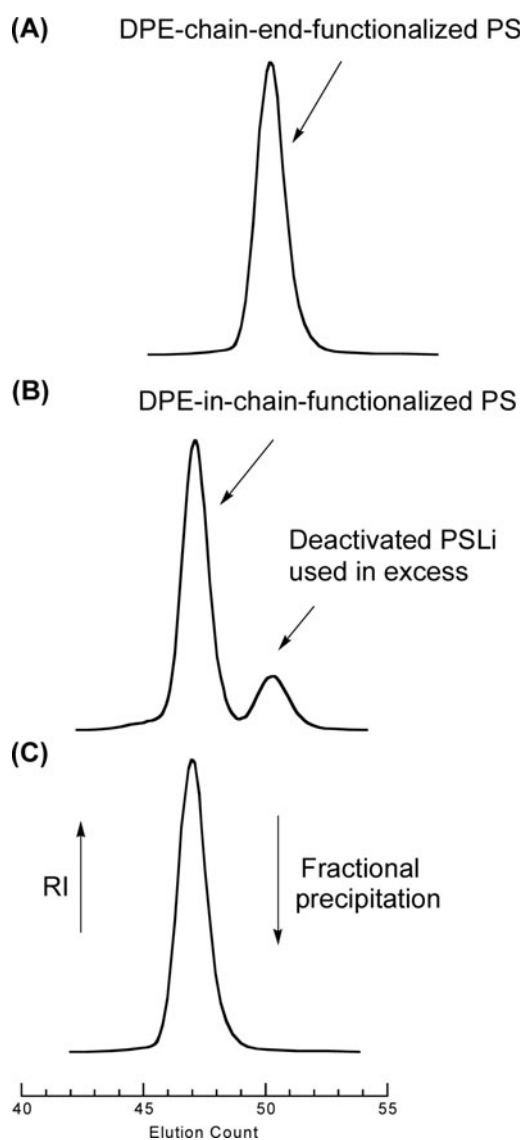
Type	Conditions <sup>a</sup>	$M_n$ (kg/mol)		$M_w$ (kg/mol)		$M_w/M_n$	Yield (%)	Functionality <sup>d</sup>		$g^{*e}$	
	Temp / Time	Calcd	SEC	Calcd <sup>b</sup>	SLS <sup>c</sup>			calcd	$^1\text{H NMR}$	Calcd <sup>f</sup>	Expml
In-chain <sup>g</sup>	25 °C/12 h	20.9	22.1	21.1	22.3 <sup>g</sup>	1.01	100	4	3.99	–	–
6-arm	25 °C/96 h	62.2	43.7	64.5	65.1	1.04	100	8	7.62	0.55	0.56
14-arm	25 °C/240 h	141	72.9	145	145	1.03	100	16	16.0	0.28	0.29
24-arm	25 °C/240 h	290	94.1	298	237	1.03	80	32	–	–	–
25-arm	40 °C/240 h	297	93.5	307	255	1.03	83	32	–	–	–
25-arm <sup>i</sup>	40 °C/336 h <sup>h</sup>	299	93.4	309	257	1.04	83	32	–	–	–

<sup>a</sup>In the addition reactions (a), *tert*-Butylbenzene was always employed as a solvent. <sup>b</sup>Calculated from  $M_n$  (calcd) and  $M_w/M_n$  (SEC) values.

<sup>c</sup>Measured in THF at 25 °C.  $dn/dc=0.188\sim 0.190$  (mL/g). <sup>d</sup>Functionality of DPE moieties. <sup>e</sup> $[\eta]_{\text{star}}$  was measured in toluene at 35 °C.  $[\eta]_{\text{linear}}$  was calculated from the equation;  $[\eta]=1.29\cdot 10^{-4}M_w$  (SLS)<sup>0.71</sup> (ref. 49). <sup>f</sup>Calculated from the equation;  $g^*=[(3f-2)/f^2]^{0.58}[0.724-0.015(f-1)]/0.724$ ;  $f$ =arm number ( $3\leq f\leq 18$ ) (ref. 48). <sup>g</sup>Measured by SEC. <sup>h</sup>6-Arm star-branched polystyrene with eight BnBr moieties was used as a precursor.

<sup>i</sup>A 3.0-fold excess of TMEDA toward polystyryllithium was added.

The first iterative process involves the addition reaction of polystyryllithium (PSLi) to a 1.2-fold excess of DPE in THF at  $-78^{\circ}\text{C}$  for 10 min, followed by an *in-situ* reaction with a 1.5-fold excess of **1** to introduce the DPE moiety at the chain-end. As expected, SEC profile of the resulting polymer showed a sharp monomodal peak without any shoulder and tailing (see Figure 1(A)). The  $M_n$  values measured by SEC (10.4 kg/mol) and VPO (10.5 kg/mol) agreed well with the predicted value (10.3 kg/mol), the  $M_w/M_n$  value being 1.02. The degree of chain-end functionality of DPE was determined to be quantitative ( $f=1.03$ ) by  $^1\text{H}$  NMR using two resonances at 5.40 and 0.6~0.8 ppm assigned to vinylene protons of the DPE moiety and methyl protons of the initiator fragment. Thus, a DPE-chain-end-functionalized



**Figure 1.** SEC profiles of the resulting polymers obtained after (A) first and (B) second iterative reaction processes and (C) the isolated DPE-in-chain-functionalized polystyrene.

polystyrene was obtained by the first iteration. The results are summarized in Table I. In the second iteration, the addition reaction of a 1.2-fold excess of PSLi to the DPE-chain-end-functionalized polystyrene was carried out in THF at  $-78^{\circ}\text{C}$  for 10 min to couple the two polystyrene chains. The DPE functionality was introduced by the subsequent *in-situ* reaction of **1** with the 1,1-diphenylalkyl anion generated at the junction of the two polystyrene chains under the same conditions. Figure 1(B) shows SEC profile of the resulting mixture obtained after the second iteration. There are only two distinct sharp peaks corresponding to the coupled product and the deactivated PSLi used in excess in the reaction. The reaction efficiency was essentially quantitative on the basis of the two peak areas. The coupled product was isolated in 75% yield by fractional precipitation. The isolated polymer exhibits a monomodal SEC distribution (see Figure 1(C)). Again, the  $M_n$  value measured by either SEC or VPO agreed with that predicted and the quantitative introduction of DPE moiety was confirmed by  $^1\text{H}$  NMR measurement. Thus, an DPE-in-chain-functionalized polystyrene was successfully synthesized by repeating the iteration two times.

In order to synthesize an array of 3-, 4-, followed by 5-arm star-branched polystyrenes, the iteration involving the two reactions, (a) and (b), was repeated three more times under the identical conditions. In each of the iterations, the resulting star-branched polymer ( $\mathbf{A}_n$ ) was always used as a starting polymer for the synthesis of the following star ( $\mathbf{A}_{n+1}$ ) in the next iteration. Fortunately, all of the addition reactions were very fast and complete within 10 min even at the fifth iteration in THF at  $-78^{\circ}\text{C}$ . The SEC profile of the polymer isolated at each reaction stage exhibits a sharp monomodal peak and shifts to a higher molecular weight side as the iteration proceeded. In each case, the reaction efficiency was virtually quantitative based on the SEC profile. The characterization results are also summarized in Table I. The  $M_n$  values of the polymers,  $\mathbf{A}_3$ ,  $\mathbf{A}_4$ , and  $\mathbf{A}_5$ , obtained by third, fourth, and fifth iterations estimated by SEC were somewhat smaller than the predicted values as expected from smaller hydrodynamic volumes due to their star-branched structures. On the other hand, both  $M_n$  and  $M_w$  values determined by VPO and SLS were in good agreement with those predicted. Star-branched architectures of the resulting polymers could be supported by good agreement between the  $g'$  values defined as  $[\eta]_{\text{star}}/[\eta]_{\text{linear}}$  experimentally determined and those predicted from the established eq. (1) where  $f$  is arm number for regular star-branched polymers.<sup>48</sup>

$$g' = [(3f - 2)/f^2]^{0.58} [0.724 - 0.015(f - 1)] / 0.724 \quad (1)$$

Overall, the successive synthesis of an array of 3-, 4-, followed by 5-arm star-branched polystyrenes,  $\mathbf{A}_3$ ,  $\mathbf{A}_4$ , and  $\mathbf{A}_5$ , was successfully achieved without difficulty by repeating

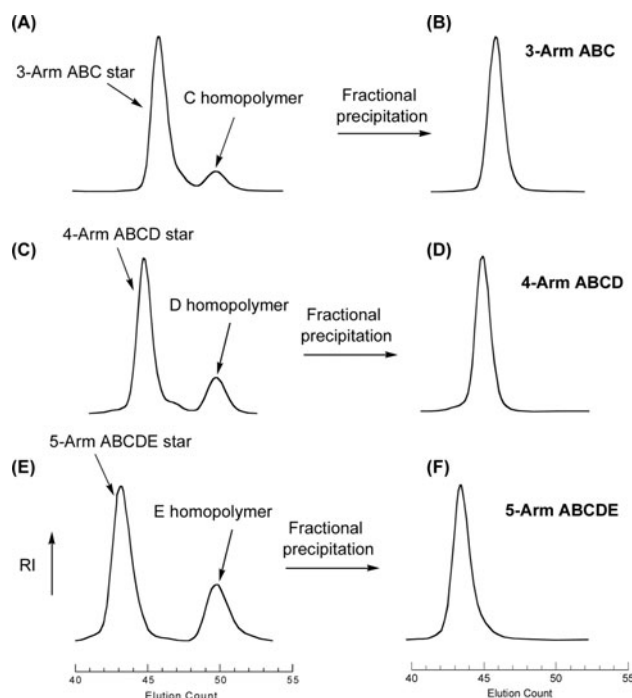


the iterative processes five times. Thus, the proposed methodology works satisfactorily and therefore may possible to apply the synthesis of the objective asymmetric star-branched polymers.

**Successive Synthesis of 3-Arm ABC, 4-Arm ABCD, and 5-Arm ABCDE Asymmetric Star-Branched Polymers by Iterative Methodology Using 1.** Based on the successive synthesis of regular star-branched polystyrenes successfully achieved, the iterative methodology has been applied to the successive synthesis of asymmetric star-branched polymers. As illustrated in Scheme I(A) in the preceding section, a series of living anionic polymers of styrene derivatives, poly(4-trimethylsilylstyryl)lithium, poly(4-methoxystyryl)lithium, poly(4-methylstyryl)lithium, polystyryllithium, and poly(4-*tert*-butyldimethylsilyloxystyryl)lithium were successively added in the iterations going from first to fifth. Accordingly, the A, B, C, D, and E segments corresponded to poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), polystyrene, and poly(4-*tert*-butyldimethylsilyloxystyrene) chains, respectively. The reason for the poly(4-*tert*-butyldimethylsilyloxystyrene) segment of choice is that this segment can be readily and quantitatively converted to poly(4-vinylphenol) (*E'*) by deprotection under mild conditions. The resulting ABCDE' star, if synthesized, is expected to have a variety of potential applications because of its amphiphilic character and the presence of many reactive phenol functionalities.

At the first and second iterations, a DPE-chain-end-functionalized poly(4-trimethylsilylstyrene) (A), followed by a DPE-in-chain-functionalized AB diblock copolymer was synthesized by the addition reaction of a 1.2-fold excess of the corresponding living anionic polymer to DPE or A and the subsequent *in-situ* treatment with a 1.4-fold excess of **1** in THF at  $-78^{\circ}\text{C}$ . SEC profiles of the resulting polymer mixtures were similar to those observed in the regular star-branched polymer synthesis at the first and second iterations, respectively. The AB diblock copolymer could be isolated in 92% yield by fractional precipitation using a mixture of hexane and ethanol (1/1, by vol). The results were summarized in Table II. The  $M_n$  values determined by both  $^1\text{H}$  NMR and VPO agreed well with that calculated. The degree of DPE-functionalization was determined to be quantitative in each sample.

With use of the AB diblock copolymer thus synthesized, the same iterative reaction sequence was repeated three more times to synthesize 3-arm ABC and 4-arm ABCD, followed by 5-arm ABCDE asymmetric star-branched polymers. In the third iteration, a 1.3-fold excess of poly(4-methylstyryl)lithium was reacted with the AB diblock copolymer in THF at  $-78^{\circ}\text{C}$  for 1 h, followed by the reacting with **1** for 1 h. SEC profile of the reaction mixture is shown in Figure 2(A). The coupled product was eluted as a higher molecular weight major peak and isolated in 72% yield by fractional precipitation (see experimental section and Figure

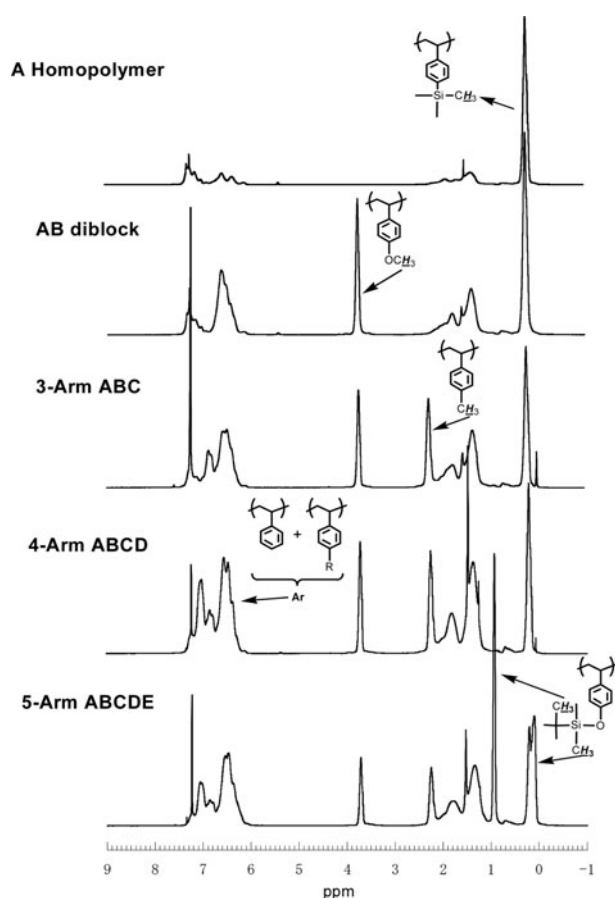


**Figure 2.** SEC profiles of the resulting reaction mixtures and the isolated polymers in the synthesis of 3-arm ABC ((A) and (B)), 4-arm ABCD ((C) and (D)), and 5-arm ABCDE ((E) and (F)) asymmetric star-branched polymers, respectively.

2(B)). The  $M_n$  value determined by either  $^1\text{H}$  NMR (31.8 kg/mol) or VPO (30.5 kg/mol) agreed with the calculated value (31.3 kg/mol) as was seen in Table II. Furthermore, the  $M_w$  value (34.4 kg/mol) measured by SLS is consistent with that calculated (32.0 kg/mol). The introduction of one DPE functionality was confirmed by  $^1\text{H}$  NMR. Thus, the expected 3-arm ABC asymmetric star-branched polymer was obtained. In the fourth iteration, a 1.5-fold excess of PSLi was reacted with the 3-arm ABC star in THF at  $-78^{\circ}\text{C}$  for 1 h, followed by treatment with **1** under the same condition. SEC profile of the reaction mixture shown in Figure 2(C) exhibits only two sharp peaks corresponding to the coupled product and the deactivated PSLi used in excess in the reaction. The coupled product was isolated in 85% yield by fractional precipitation (see experimental section and Figure 2(D)). The  $M_n$  and  $M_w$  values of the resulting polymer determined by  $^1\text{H}$  NMR, VPO, and SLS agreed well with those predicted. Thus obviously, the resulting polymer proved to be the expected 4-arm ABCD asymmetric star-branched polymer with one DPE moiety at the core.

Finally, a 5-arm ABCDE asymmetric star was synthesized by the reacting of a 1.5-fold excess of poly(4-*tert*-butyldimethylsilyloxystyryl)lithium with the 4-arm ABCD star in THF at  $-78^{\circ}\text{C}$  for a longer reaction time to 12 h. As can be seen in SEC profile of the reaction mixture (see Figure 2(E)), the coupling reaction proceeded satisfactorily. The excess poly(4-*tert*-butyldimethylsilyloxystyrene) was readily

removed by fractional precipitation (see experimental section). The isolated polymer exhibits a sharp monomodal SEC distribution as shown in Figure 2(F). Both  $M_n$  and  $M_w$  values determined by  $^1\text{H}$  NMR, VPO, SLS are in good agreement with those calculated. Overall SEC profiles of the resulting polymers clearly demonstrate that each peak of the coupled polymer is narrow and monomodal and shifts to a higher molecular side as the iteration process proceeds. Figure 3 shows  $^1\text{H}$  NMR spectra of all these polymers. The resonances characteristic to poly(4-trimethylsilylstyrene) (A) (0.22 ppm for the silylmethyl protons), poly(4-methoxystyrene) (B) (3.72 ppm for the methoxy protons), poly(4-methylstyrene) (C) (2.26 ppm for the 4-methyl protons), polystyrene (D) (6.2–7.2 ppm for the phenyl protons), and poly(4-*tert*-butyldimethylsilyloxystyrene) (E) (0.94 ppm for the *tert*-butyl protons, 0.06 ppm for the silylmethyl protons) segments are clearly observed in expected intensities. Accordingly, the compositions estimated from  $^1\text{H}$  NMR using these resonances agreed well with those predicted all over the five samples, A, AB, ABC, ABCD, and ABCDE types, as listed in Table II. Thus, the proposed methodology could allow to



**Figure 3.**  $^1\text{H}$  NMR spectra of A homopolymer, AB diblock copolymer, 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE asymmetric star-branched polymers.

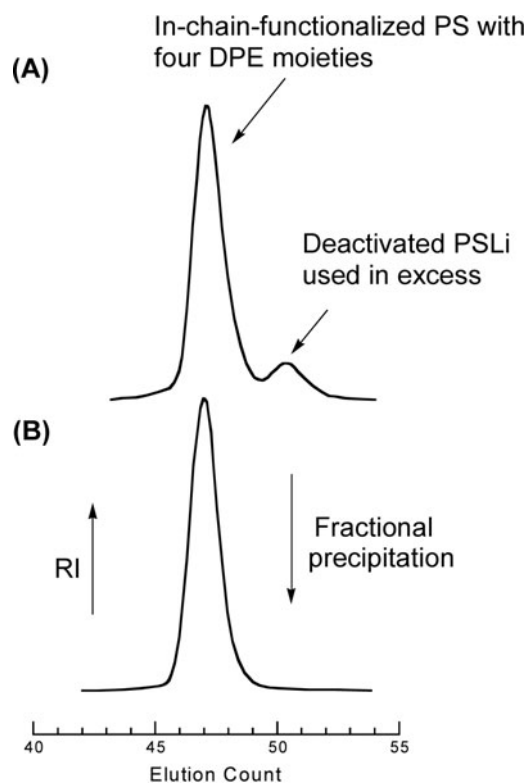
readily access to the successive synthesis of asymmetric star-branched polymers as well as that of regular star-branched polystyrenes. Incompatibility of the different polymer segments seemed not to be affected in the synthesis under the conditions employed here. Importantly, the coupling efficiency was always virtually quantitative in each of the reactions and the resulting polymers all were well-defined in architecture and precisely controlled in chain length. Therefore, these polymers have a high molecular and structural homogeneity.

The 5-arm ABCDE star-branched polymer could be readily and quantitatively converted to a new amphiphilic ABCDE' star by hydrolyzing the poly(4-*tert*-butyldimethylsilyloxystyrene) segment to poly(4-hydroxystyrene) one (E') with  $\text{Bu}_4\text{NF}$  in THF. The resulting star-branched polymer is expected to exhibit unique behaviors and morphologies derived from its hybrid structures of heterophase, branching, and multicomponent systems. It should be mentioned that 4-arm ABCD, 5-arm ABCDE, and ABCDE' asymmetric star-branched polymers have been very rare or not synthesized yet so far.<sup>50</sup>

**Successive Synthesis of Star-Branched Polymers by Iterative Methodology Using 1-(3-Chloromethylphenyl)-1-((3-(1-phenylethenyl)phenyl)ethylene) (4).** In the iterative methodologies as illustrated in Schemes I(A) and I(B), one polymer segment is basically linked *via* one DPE functionality introduced in the reaction (a). If two or more DPE functionalities were introduced *via* one reaction site in the reaction (b), the number of arm segment linked would dramatically increase.

As a possible extension of the iterative methodology for realizing the successive synthesis of stars with many arms, we introduce herein 1-(3-chloromethylphenyl)-1-((3-(1-phenylethenyl)phenyl)ethylene) (4), comprised of a double DPE skeleton substituted with benzyl chloride moiety as a new DPE functionalized compound used in the reaction step (b). The synthetic outline of the extended iterative methodology using 4 is illustrated in Scheme II. Only the exception is that two DPE functionalities may be introduced *via* one reaction site by using 4 in place of 1 in the reaction step (b). As a result, the drastic increment of the number of arm segments going from 2, 6, 14, and so on to 30 can be expected by repeating the iterative process. Furthermore, the DPE functionality introduced also rapidly increases from 4, 8, 16, and so on to 32 in number.

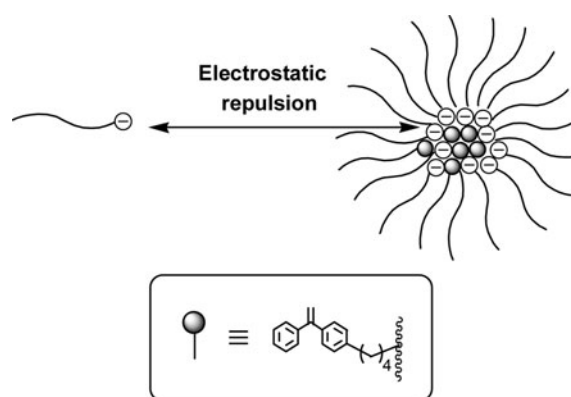
In the first iteration, an in-chain-functionalized polystyrene with four DPE moieties was prepared by the reaction of 2 with two equivalents of PSLi, followed by treatment with 4. As shown in Figure 4(A), SEC profile of the reaction mixture exhibits a sharp monomodal peak corresponding to the coupled product along with a small peak for the deactivated PSLi used in excess in the reaction. The reaction efficiency was estimated to be quantitative based on the two peak areas and the higher molecular weight fraction was isolated



**Figure 4.** SEC profiles of the resulting polymers obtained by the addition reaction of PSLi to **2**, followed by the *in-situ* reacting of **4**, (A) before and (B) after fractionation.

by fractional precipitation in 90% yield (see Figure 4(B)). The resulting polymer possessed a predictable molecular weight and a narrow molecular weight distribution. The degree of DPE functionality was determined by  $^1\text{H}$  NMR to be quantitative ( $f=3.99$ ). The results are summarized in Table III.

In the second iteration, the resulting in-chain-functionalized polystyrene with four DPE moieties was reacted with four equivalents of PSLi, followed by treatment with **4** under the similar conditions employed in the first iteration. The resulting polymer was confirmed by  $^1\text{H}$  NMR, SEC, and SLS to be a core functionalized 6-arm star-branched polystyrene with eight DPE moieties. With use of the 6-arm star-branched polystyrene, the third iterative process involving the addition reaction of PSLi, followed by treatment with **4**, was similarly carried out to afford a core-functionalized 14-arm star-polystyrene with sixteen DPE functionalities. Agreement between  $g'$  values experimentally determined and those predicted from eq. (1) was very satisfactory in each star, strongly supporting that the resulting polymers possessed 6- and 14-arm star-branched architectures. The characterization results obtained by  $^1\text{H}$  NMR, SEC, SLS, and viscosity measurements are also summarized in Table III. Thus, the extended iterative methodology using **4** does successfully work to successively synthesize 6-arm,



**Scheme III.** Electrostatic repulsion between PSLi and the intermediate star-branched polystyrene having many 1,1-diphenylalkyl anions.

followed by 14-arm star-branched polystyrenes. Yields of both stars were found to be almost quantitative.

In the fourth iteration, however, difficulty was encountered in the reaction of PSLi between the 14-arm star-branched polystyrene with sixteen DPE moieties. The reaction efficiently proceeded to afford a star with average 25 arms, but not a star with the targeted 30 arms in THF at  $-78^\circ\text{C}$  even for a longer reaction time up to 168 h (one week). Several attempts were unsuccessful by changing the reaction conditions (in *tert*-butylbenzene at 30, 40, and  $50^\circ\text{C}$  for 240 and 336 h in the absence and presence of THF or TMEDA and in THF at  $-40^\circ\text{C}$  for 168 h). The representative results were also listed in Table III. The difficulty may be resulted from the steric hindrance and/or the electrostatic repulsion between PSLi and the intermediate star having many 1,1-diphenylalkyl anions generated by the addition reaction, as one can imagine in Scheme III. Therefore, the structure of **4** should be modified in such a way that steric hindrance around the reaction sites is reduced.

Since the iterative methodology using **4** is effectively achieved until the third iteration process as mentioned above, it may be possible to synthesize  $A_2$ , 6-arm  $A_2B_4$  star, followed by a new type 14-arm  $A_2B_4C_8$  star by repeating the iterative process. The successive synthesis of such asymmetric star-branched polymers is now undertaken.

## Conclusions

We have achieved the successive synthesis of multi-component 3-arm ABC, 4-arm ABCD, followed by 5-arm ABCDE asymmetric stars as well as 3-, 4-, and 5-arm star-branched polystyrenes by developing the iterative methodology involving only two sets of reactions in each iterative process: (a) an addition reaction of living anionic polymer to DPE or the DPE-functionalized polymer and (b) an *in-situ* reaction with **1** to introduce one DPE functionality via the generated 1,1-diphenylalkyl anion. The A, B, C, D, and

E segments are poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), polystyrene, and poly(4-*tert*-butyldimethylsilyloxystyrene) chains, respectively. All of the resulting star-branched polymers were well-defined in architecture and precisely controlled in chain length as confirmed by SEC, <sup>1</sup>H NMR, VPO, and SLS analyses. A new creation of periodic ordered nano-objects is expected by the phase separation at molecular level, followed by self-organization of new multi-component star-branched polymers synthesized in this study.

In order to dramatically increase the number of arm segment, a possible extension of the iterative methodology has been carried out by using a new functionalized DPE derivative, 4, capable of introducing two DPE functionalities *via* one reaction site in the reaction (b). By repeating the iteration only three times 2- and 6-, followed by 14-arm star-branched polystyrenes were readily obtained. Thus, the rapid increment of the number of arms was achieved. In the fourth iteration, however, the reaction (a) proceeded efficiently but not completely under the conditions even for a longer reaction time to afford a star with average 25-arms (target: 30 arms). The incomplete introduction of arm segment may be resulted from the steric hindrance and/or the electrostatic repulsion between PSLi and the intermediate star having many 1,1-dihphenylalkyl anions generated by the addition reaction. Further optimization of the reaction conditions in addition to a new molecular design of 4 is required to achieve the fourth and higher iterative processes.

**Acknowledgements.** The financial support of a Grant-in-Aid for Scientific Research (No 00164351) from the Ministry of Education, Science, Sports, and Culture of Japan is gratefully acknowledged by the authors. This research was supported in part by Sumitomo Chemical Co. Ltd and Denki Kagaku Kogyo Co. Ltd. T.H. is also thankful for support from the Japan Society for the Promotion of Science Research Fellowships for Young Scientists (JSPS).

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- (50) The first successful synthesis of 4-arm ABCD asymmetric star-branched polymer by the coupling of living anionic polymers with SiCl<sub>4</sub> was reported by Hadjichristidis's group in 1993 (ref. 20(b)). In this star, the A, B, C, and D segments were polystyrene, poly(4-methylstyrene), polyisoprene, and poly(1,3-butadiene), respectively. We have recently synthesized two structural similar 4-arm ABCD asymmetric star-branched polymers whose A, B, C, and D segments are polyisoprene, poly(4-methoxystyrene), polystyrene, and poly(4-trimethylsilylstyrene) (ref. 40), and polystyrene, poly( $\alpha$ -methylstyrene), poly(4-methylstyrene), and poly(methyl methacrylate) (ref. 41). Furthermore, the synthesis of more complex well-defined 7-arm A<sub>2</sub>B<sub>2</sub>C<sub>2</sub>D and 13-arm A<sub>4</sub>B<sub>4</sub>C<sub>4</sub>D asymmetric stars has also been successfully achieved by our research group (refs. 37 and 38). Very recently, we have successfully synthesized a 5-arm ABCDE asymmetric star-branched polymer for the first time. The A,B,C,D, and E segments in this star are polystyrene, poly( $\alpha$ -methylstyrene), poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), and poly(4-methylphenyl vinyl sulfoxide), respectively (ref. 44).