

REVIEW ARTICLE

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

By Akira HIRAO,^{1,*} Kyouichi INOUE,¹ Tomoya HIGASHIHARA,¹ and Mayumi HAYASHI²

The subject of this review is to introduce a novel iterative methodology based on living anionic polymerization using specially designed 1,1-diphenylethylene (DPE) derivatives recently developed for the synthesis of well-defined many armed star-branched polymers with same or chemically different arm segments. The methodology basically involves only two sets of the following reaction conditions for the entire iterative synthetic sequence: (a) a linking reaction of a living anionic polymer with a DPE-chain-functionalized polymer, and (b) an *in situ* reaction of a DPE-functionalized agent with the anion generated by the linking reaction to reintroduce the DPE functionality usable for the next reaction. The number of arms to be linked by each stage of the iteration depends on the starting core and DPE-functionalized agents and can dramatically increase by the agent of choice. New functional asymmetric star-branched polymers involving conductive and rigid rod-like poly(acetylene) segment(s) have been synthesized by the methodology using the intermediate polymer anions produced by the linking reaction as macroinitiators to polymerize 4-methylphenyl vinyl sulfoxide, followed by thermal treatment of the resulting star-branched polymers.

KEY WORDS: Star-Branched Polystyrene / Asymmetric Star-Branched Polymer / Living Anionic Polymerization / Iterative Methodology / 1,1-Diphenylethylene Derivative / Poly(acetylene) /

Star-branched polymers have been widely investigated because of the synthetic challenges associated with preparing them and because they offer unique physical properties quite different from the linear counterparts.^{1–14} Among star-branched polymers, asymmetric star-branched polymers having chemically different arms have recently attracted much attention because such star polymers should exhibit unique and interesting morphologies as well as properties due to their branched architectures and heterophase structures. As expected, they have exhibited quite different morphological maps from those of linear block copolymers and created novel periodical nano-objects with special shapes that promise potential applications in the field of nanotechnology.^{15–35}

Although many star-branched polymers with well-defined structures have been so far synthesized, most of them are composed of less than five arms in regular star-branched polymer and less than three different arms in asymmetric star-branched polymer. The syntheses of regular star-branched polymers with many arms have been achieved only in a few cases even at the present time. With the most established methodology based on the linking reaction of living anionic polymers with multifunctional chlorosilane compounds, well-defined stars could be prepared with maximum arm numbers up to 18.^{10,36–39} It was also reported that advances in the synthesis of carbosilane dendrimers led to the successful synthesis of poly(1,3-butadiene) stars having 32, 64, and as high as 128 arms.^{40,41} Validity of the chlorosilane linking agents

throughout the synthesis of star-branched polymers with low molecular weight arms ($M_n \sim 10^3$) has recently been re-evaluated by NMR and MALDI-TOF MS techniques.^{42,43} For stars having theoretically 32 and 64 arms, the average functionalities of the chlorosilane linking agent were found to be 31 and 60 and the introduced arm numbers were 29 and 54, respectively. Obviously, these results demonstrate the steric requirements in the synthesis of regular star-branched polymers with many arms.

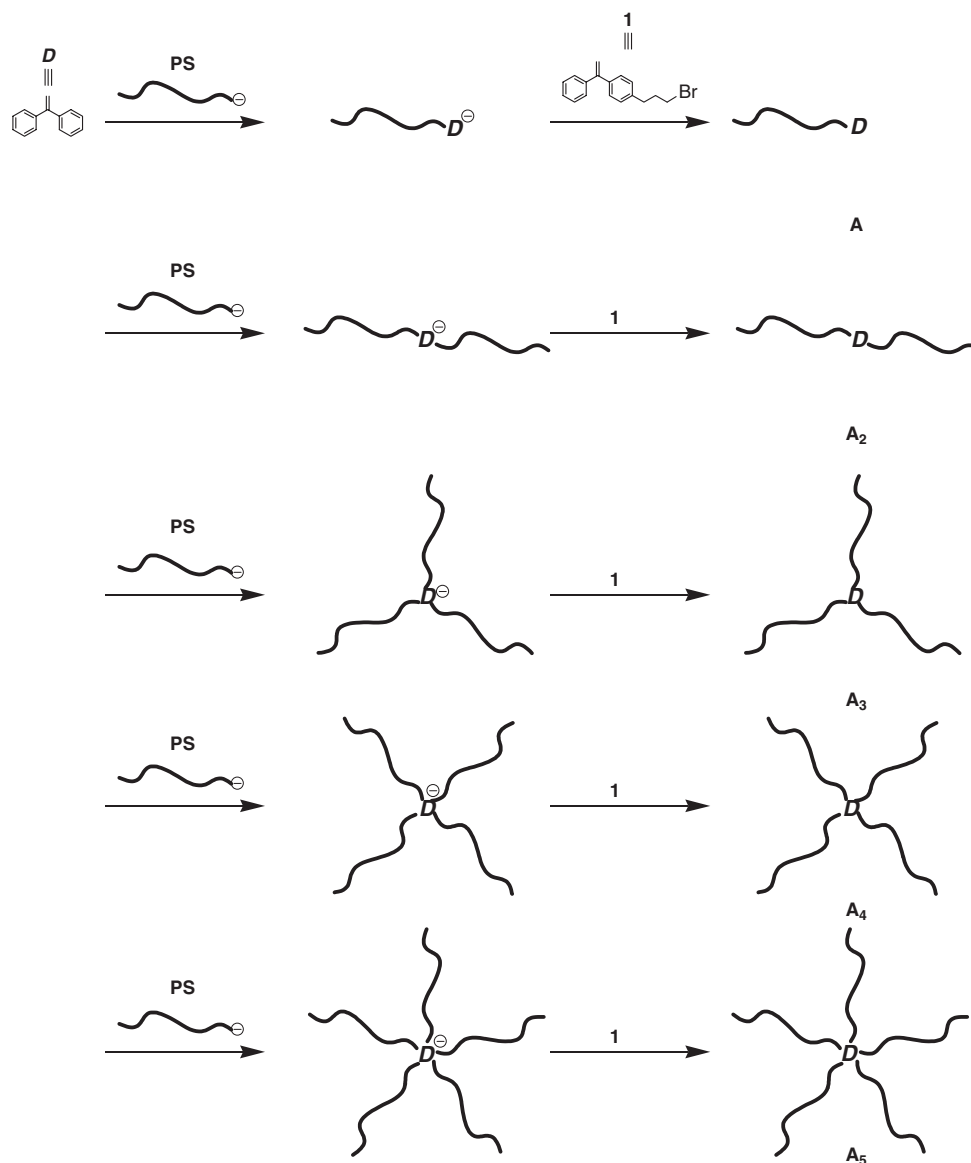
Many-armed star-branched polymers can also be prepared by an alternative procedure based on the reaction of living polymers with divinyl compounds represented as divinylbenzenes and α , ω -ethylene glycol dimethacrylates *via* the mechanism of polymerization followed by chain-branching. However, this methodology lacks the precision and control necessary for the synthesis of polymers with well-defined structures.^{11,44} Knauss and his coworkers reported a convenient synthesis of many-armed stars by the controlled addition of a dual-functionalized 4-(chlorodimethylsilyl)styrene to polystyryllithium to form star-branched polystyrene in a convergent fashion.⁴⁵ Again, the number of introduced arm could not be precisely controlled by this technique.

The introduction of different arms into star-branched polymers is also limited. As mentioned above, the well-defined asymmetric star-branched polymers so far reported are generally composed of less than three chemically different arms. Only a few examples of 4-arm ABCD star-branched polymers

¹Polymeric and Organic Materials Department, Graduate School of Science and Engineering, Tokyo Institute of Technology, H-127, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

²Petrochemicals Research Laboratory, Sumitomo Chemical Co., Ltd., 2-1, Kitasode, Sodegaura 299-0295, Japan

*To whom correspondence should be addressed (Tel: +81-3-5734-2131, Fax: +81-3-5734-2887, E-mail: ahirao@polymer.titech.ac.jp).



Scheme 1. Successive synthesis of star-branched polystyrenes by iterative methodology using 1.

have been synthesized even now, since the first successful synthesis reported by Hadjichristidis and his coworkers in 1993.^{46–51} The synthetic limitation is strongly attributed to the experimental difficulties in which multi-step synthetic routes accompanied by isolation of the intermediate products are required. For such situations, the development of the synthetic methodology for star-branched polymers with many same or different arms has been desired at the present time.

For the synthesis of the aforementioned many armed and component star-branched polymers, we have been, for a recent few years, developing a novel iterative methodology based on the living anionic polymerization using specially designed DPE derivatives.^{13,14} Basically, the methodology involves only two sets of reaction conditions for the entire iterative synthetic sequence: (a) a linking reaction of a living anionic polymer with a DPE-chain-functionalized polymer, and (b) an *in situ*

reaction of a specially designed DPE-functionalized agent with the anion generated by the linking reaction to reintroduce the DPE functionality usable for the next synthesis. If the two reaction sequence proceeds with excellent efficiencies close to 100%, the same process can be repeated, in principle, many times to successively synthesize a series of many armed star-branched polymers. The detailed reaction scheme will be described in the next section.

In this review, we report on the scope and limitation of the iterative methodology recently developed by us for the synthesis of well-defined star-branched polymers composed of many same or different arms. Throughout the synthesis of star-branched polymers, living anionic polymers of styrene, 1,3-butadiene, isoprene, and their derivatives have been used as arm segments.⁵² The choice of such living anionic polymers is based on the facts that they have precisely controlled molecular

weights, extremely narrow molecular weight distributions ($M_w/M_n < 1.05$), and highly reactive chain-end carbanions capable of reacting with the DPE functionalities used as reaction sites.

ITERATIVE METHODOLOGY USING 1-(4-(3-BROMOPROPYL)PHENYL)-1-PHENELETHYLENE

We have herein introduced the effectiveness of the iterative methodology through the synthesis of regular star-branched polystyrenes ((PS)s) as well as asymmetric star-branched polymers having chemically different arms.^{53–56} The synthetic procedure is illustrated in Scheme 1. 1-(4-(3-Bromopropyl)-phenyl)-1-phenylethylene (**1**) is used as a DPE-functionalized agent in this procedure to reintroduce the DPE functionality usable for the next synthesis. At first, the synthesis of a series of star-branched (PS)s by using this procedure was examined. As mentioned above, only two sets of the reaction conditions are employed as follows: (a) a linking reaction of polystyryllithium (PSLi) with a DPE-chain-functionalized PS, and (b) an *in situ* reaction of **1** with the anion generated by the linking reaction to reintroduce the DPE functionality. PSLi was adjusted to be *ca.* 10 kg/mol in M_n value. At the first stage of the iteration, PSLi reacted with a DPE-chain-end-functionalized PS to link two PS chains with generating a new DPE-derived anion at the linking point. Subsequently, **1** was *in situ* added to react with the generated anion to reintroduce DPE functionality. As a result, an in-chain-functionalized PS with DPE moiety was quantitatively obtained. Since the two reactions were very efficient reactions without side reactions, the same process was repeated one more time with the DPE-in-chain-functionalized PS as a precursor. As can be seen in Scheme 1, the polymer obtained by the second stage is a 3-arm star PS core-functionalized with DPE moiety and its well-defined structure is confirmed by the results listed in Table I.

The most important point of the iterative methodology is repeatability of the iterative synthetic sequence. Therefore, the same process involving the two reaction sequence was repeated two more times. The two reactions were always carried out in THF at -78°C for 1 h and 10 min, respectively. At each stage of the iteration, a 1.2-fold excess of PSLi toward the DPE moiety was used and a 2.0-fold excess of **1** reacted with the generated anion. Since PSLi was used in excess in the linking reaction, the crude product included the deactivated PS, which could be completely eliminated by fractional precipitation.

Table I. Synthesis of DPE-chain-end-functionalized PS (A), DPE-in-chain-functionalized PS (A₂), DPE-core-functionalized 3-arm A₃ and 4-arm A₄ star-branched (PS)s by iterative methodology using **1**

type	M_n (kg/mol)		M_n (kg/mol)		M_w/M_n	DPE-functionality		g'		
	calcd	SEC	VPO	SLS ^a		calcd	¹ H NMR	calcd	exptl	
A	10.3	10.4	10.5	10.5	10.6 ^b	1.02	1	1.0 ₃	—	—
A ₂	21.5	21.4	21.0	21.9	21.8 ^b	1.02	1	0.96 ₆	—	—
A ₃	30.9	28.9	31.1	31.5	34.7	1.02	1	<i>ca.</i> 1	0.83	0.84
A ₄	42.4	39.1	45.1	43.3	44.1	1.02	1	<i>ca.</i> 1	0.71	0.73

a In THF at 25°C. b Measured by SEC.

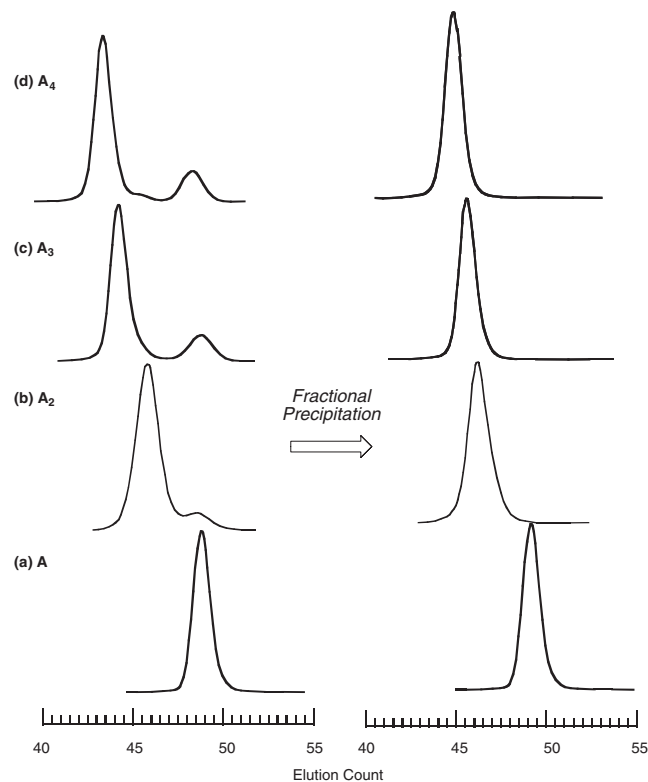


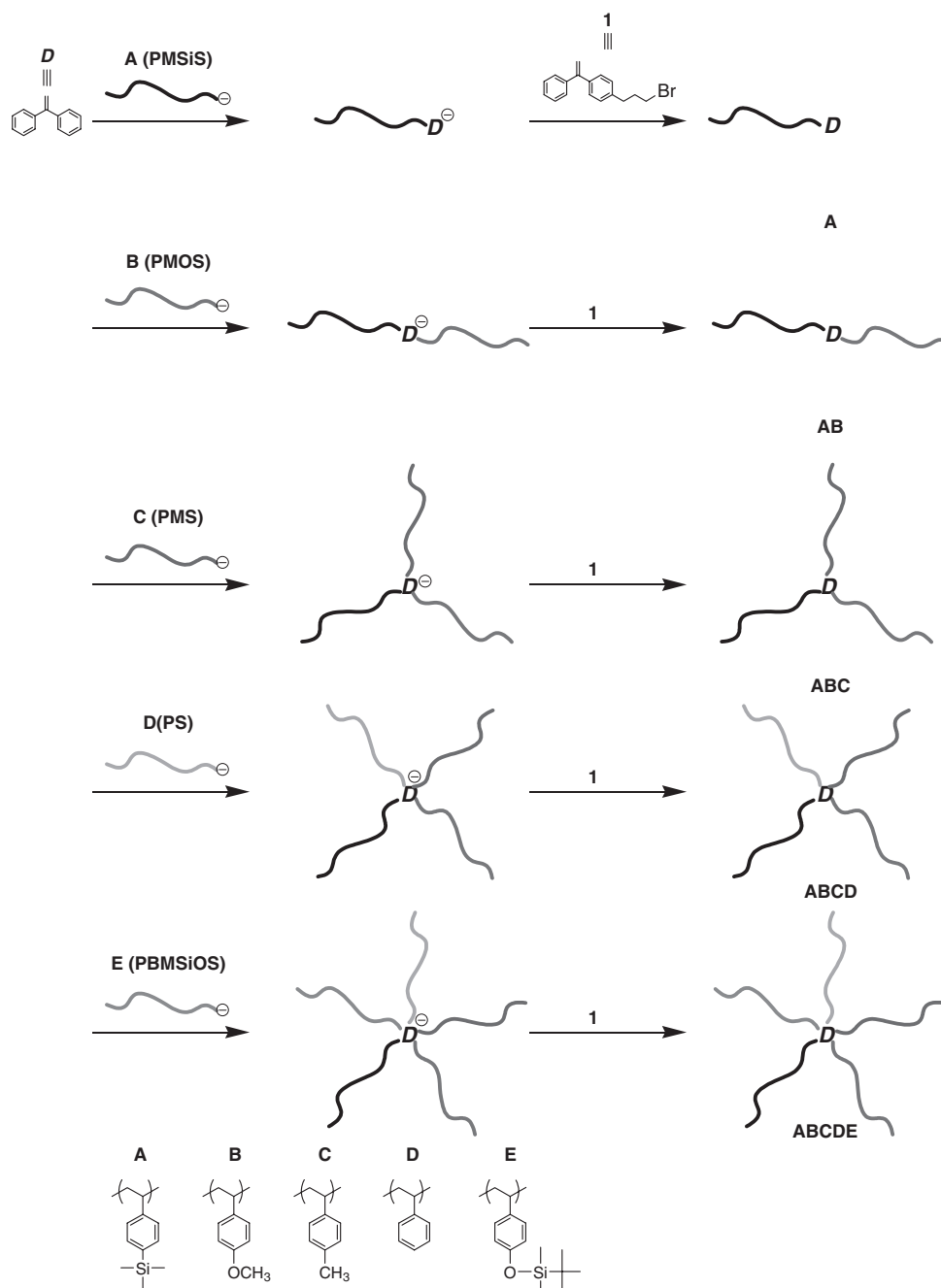
Figure 1. SEC profiles of DPE-chain-end-functionalized (a) and in-chain-functionalized (b) polystyrenes, core-functionalized 3-arm (c) and 4-arm (d) star-branched polystyrenes.

The SEC profiles of the polymerization mixtures and the isolated linked products obtained by all stages are summarized in Figure 1. As you can see, the isolated products all possess sharp monomodal distributions and no starting polymers and excess (PS)s remain at all. The M_n and M_w values measured by VPO and SLS agreed well with those calculated and narrow molecular weight distributions were attained in all polymers (see Table I). Star-branched architecture is demonstrated by comparing the g' value defined as $[\eta]_{\text{star}}/[\eta]_{\text{linear}}$ experimentally observed with that calculated from the following established equation (1) where “f” is the arm number.⁵⁷

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

Indeed, the g' values observed are in good agreement with those calculated as listed in Table I, clearly indicating that the resulting polymers possess 3-, 4-, and 5-arm star-branched architectures. Thus, all of the analytical results are consistent with the successful synthesis of well-defined 3-, 4-, followed by 5-arm star-branched (PS)s by the iterative methodology using **1**.

On the basis of the successful synthesis of star-branched (PS)s, the same iterative methodology has been applied to the synthesis of asymmetric star-branched polymers outlined in Scheme 2. Four different living anionic polymers in addition to PSLi were employed for this synthesis. They are poly(4-trimethylsilylstyryl)lithium (PMSiSLi), poly(4-methoxystyryl)lithium (PMOSLi), poly(4-methylstyryl)lithium (PMSLi), PSLi, and poly(3-*tert*-butyldimethylsilyloxystyryl)-



Scheme 2. Successive synthesis of asymmetric star-branched polymers by iterative methodology using **1**.

lithium (PBMSiOSLi) which correspond to the A, B, C, D, and E arm segments, respectively.^{55,56} As mentioned in introduction, the choice of such living polymers is based on the facts that they have well-controllable molecular weights, extremely narrow molecular weight distributions, and highly reactive chain-end carbanions capable of reacting with DPE functionality. The two reaction sequence was carried out under the same or very similar conditions as those used for the regular star PS synthesis.

At the first stage of the iteration, PMOSLi reacted with a chain-end-functionalized PMSiS with DPE moiety and sub-

sequently **1** reacted *in situ* with the DPE-derived anion to reintroduce the DPE functionality. The DPE-in-chain-functionalized AB diblock copolymer, PMSiS-*block*-PMOS, was thus obtained. By using the DPE-functionalized AB block copolymer as a precursor at the second stage, the same process was repeated three more times to synthesize 3-arm ABC, 4-arm ABCD, followed by 5-arm ABCDE asymmetric star-branched polymers.

Figure 2 shows the SEC profiles of the reaction mixtures obtained by all stages and the isolated linked polymers, *i.e.*, AB block, 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE stars.

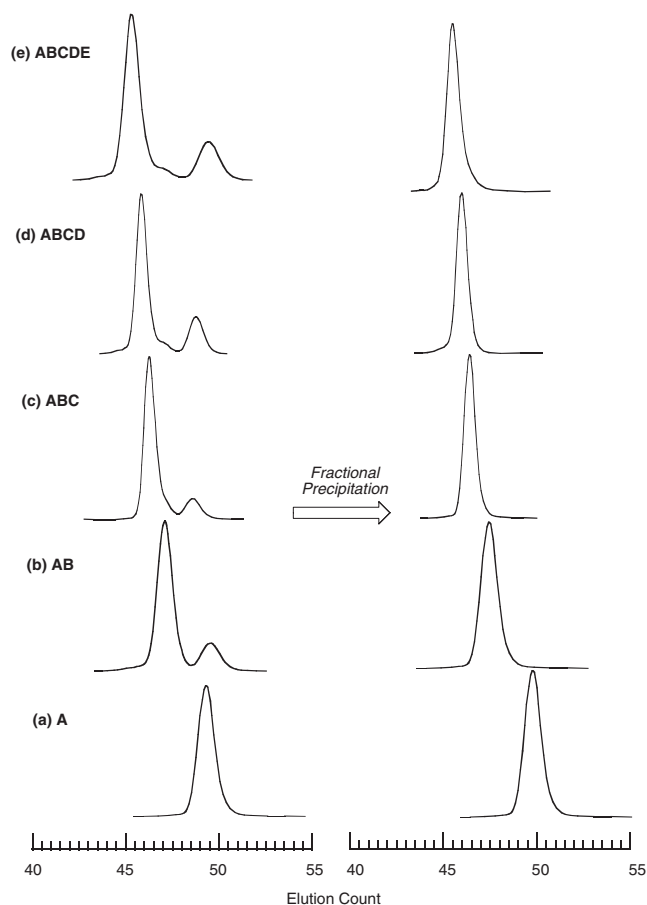


Figure 2. SEC profiles of DPE-chain-end-functionalized polymer (A) (a) and in-chain-functionalized diblock copolymer (AB) (b), core-functionalized 3-arm ABC (c), 4-arm ABCD (d), and 5-arm ABCDE (e) asymmetric star-branched polymers.

Overall, the isolated polymer at each stage exhibited a sharp monomodal SEC peak which shifted to a higher molecular weight side as the iteration proceeded. As summarized in Table II, the resulting polymers have M_n and M_w values determined by VPO, $^1\text{H NMR}$, and SLS which are in good agreement with those calculated from feed ratios. The $^1\text{H NMR}$ spectra of all these polymers are shown in Figure 3. The resonances characteristic to A (0.22 ppm for the silyl-methyl protons), B (3.72 ppm for the methoxy protons), C (2.26 ppm for the methyl protons), D (6.2–7.2 ppm for the phenyl protons), and E (0.94 ppm for the *tert*-butyl protons and 0.06 ppm for the silylmethyl protons) segments are clearly

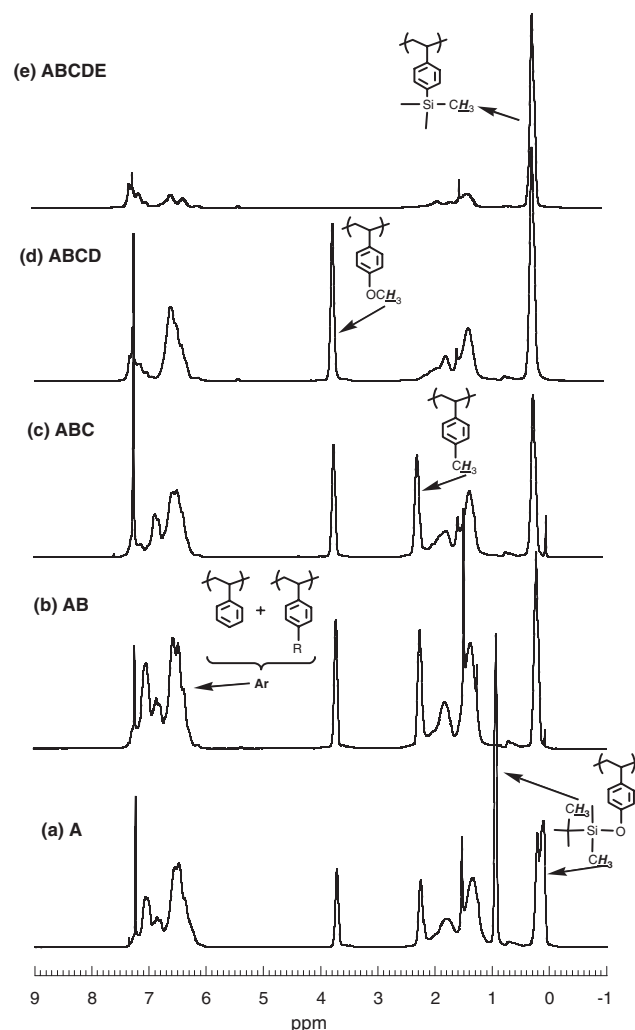


Figure 3. $^1\text{H NMR}$ spectra of poly(A) (a) and AB diblock copolymer (b), 3-arm ABC (c), 4-arm ABCD (d), and 5-arm ABCDE (e) asymmetric star-branched polymers.

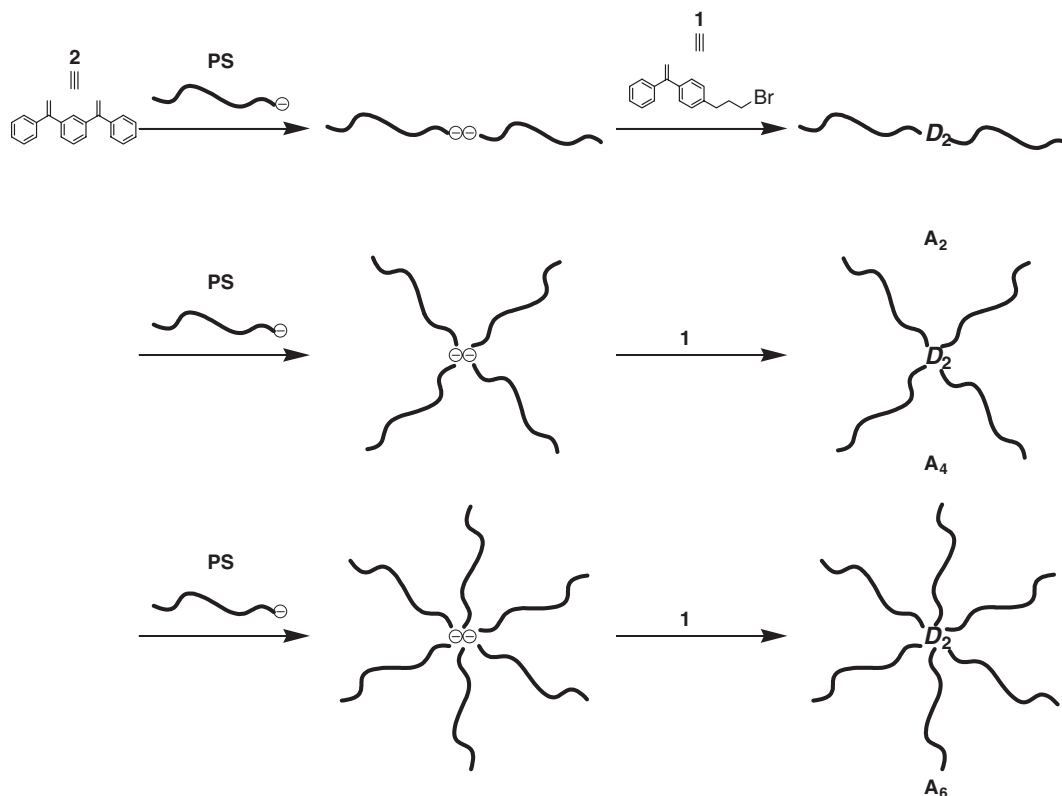
observed in expected intensities. All of these results clearly show that the resulting polymers are the expected 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE asymmetric star-branched polymers with well-defined structures.⁵⁶ Thus, the iterative methodology could also be successfully applied to the synthesis of asymmetric star-branched polymers.

To the best of our knowledge, the 5-arm ABCDE star herein synthesized is the first successful asymmetric star-branched

Table II. Synthesis of DPE-chain-end-functionalized PMSiS (A), DPE-in-chain-functionalized AB diblock copolymer (AB), DPE-core-functionalized 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE asymmetric star-branched polymers by iterative methodology using 1

type ^a	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt %)	
	calcd	VPO	$^1\text{H NMR}$	calcd	SLS ^b		calcd	$^1\text{H NMR}$
A	10.2	10.7	10.0	—	—	1.03	—	—
AB	20.9	21.2	20.8	—	—	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

a A, B, C, D, and E were PMSiS, PMOS, PMS, PS, and PBMSIOS respectively. b In THF at 25 °C.



Scheme 3. Successive synthesis of star-branched polystyrenes by iterative methodology using **2** and **1**.

polymer having chemically different five arms.^{52,58,59} Since the E segment is readily and quantitatively converted to poly(4-vinylphenol) by treatment with $(C_4H_9)_4NF$ under neutral conditions,⁵³ the 5-arm ABCDE star can be changed to a new functional star-branched polymer having poly(4-vinylphenol) segment. This segment is acidic and hydrophilic and becomes water-soluble in basic media. Importantly, the two reactions proceed with efficiencies close to 100% and can be repeated at least four and possibly more times to result in a series of well-defined star-branched polymers with same or different arms. It should be noted that each DPE-core-functionalized star-branched polymer synthesized at the preceding stage can always become the precursory polymer for the star-branched polymer obtained at the next stage.

ITERATIVE METHODOLOGY USING 1,3-BIS-(1-PHENYLETHENYL)BENZENE AND **1**

The number of polymer chains to be linked increases one by one as the iteration proceeds in the methodology mentioned above. If 1,3-bis(1-phenylethenyl)benzene (**2**) composed of two DPE skeletons is used as a starting core agent, two DPE-derived anions are generated by the linking reaction with two equivalents of living anionic polymer as illustrated in Scheme 3.⁶⁰ By the subsequent reaction of **1** with the generated two anions, two DPE moieties may be reintroduced, followed by linking two polymer chains at the next stage.

The first addition of PSLi to **2** proceeded in a facile manner,

but a further addition was very sluggish in THF at $-78^\circ C$ and even at $-40^\circ C$ for 24 h. This can be explained by the ionic repulsion between the delocalized negative charge in the monoadduct anion and negatively charged PSLi dissociated in THF. On the other hand, the addition reaction of PSLi to **2** was found to quantitatively proceed in *tert*-butylbenzene at room temperature for 24 h. Thus, the solvent effect on the addition reaction is obvious. In non-polar *tert*-butylbenzene, the intermediate monoadduct anion as well as PSLi would remain as the contact ion pairs to prevent from delocalizing the negative charges. As a result, the ionic repulsion in polar solvents like THF may be considerably suppressed to facilitate the addition of PSLi to the monoadduct anion. Thus, two DPE functionalities were then introduced exactly between two PS chains by reacting **1** *in situ* with the two generated anions. At the first stage of the iteration, the linking reaction of PSLi with the DPE-in-chain-functionalized PS was carried out and subsequently **1** was added to react with the generated two anions to reintroduce two DPE functionalities. The two reactions efficiently proceeded to result in the formation of a 4-arm star-branched PS core functionalized with two DPE moieties. Furthermore, a DPE-core-functionalized 6-arm PS star was further obtained by repeating the same reaction sequence one more time. The 1H NMR analysis showed that the resonance at 5.4 ppm assigned to vinylene protons of the DPE moiety was always present at the reasonable intensity in each polymer sample. The results are summarized in Table III. The good agreement among the molecular weights determined

Table III. Synthesis of DPE-in-chain-functionalized PS (A_2), DPE-core-functionalized 4-arm, and 6-arm star-branched (PS)s by iterative methodology using **2** and **1**

type	M_n (kg/mol)			M_n (kg/mol)		M_w/M_n	DPE-functionality		g'	
	calcd	SEC	VPO	calcd	SLS ^a	SEC	calcd	¹ H NMR	calcd	expt
A_2	21.2	22.1	21.0	21.6	22.5 ^b	1.02	2	2.0 ₃	—	—
A_4	41.2	36.4	42.1	42.0	41.4	1.02	2	ca.2	0.71	0.71
A_6	61.1	44.9	60.3	63.5	64.4	1.04	2	ca.2	0.56	0.56

a In THF at 25 °C. b Measured by SEC.

Table IV. Synthesis of DPE-core-functionalized 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ asymmetric star-branched polymers by iterative methodology using **2** and **1**

type	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt%)	
	calcd	SEC	¹ H NMR	calcd	SLS ^c	SEC	calcd	¹ H NMR
A_2B_2 ^a	40.5	34.1	42.1	41.1	41.8	1.02	55/45	54/46
$A_2B_2C_2$ ^a	60.5	41.1	58.5	61.7	62.4	1.02	37/30/33	38/30/32
$A_2B_2C_2$ ^b	32.8	25.6	32.5	34.8	31.8	1.06	32/30/38	31/30/39

a A, B, and C were PS, P α MS, and PMOS, respectively. b A, B, and C were PI, P α MS, PS, respectively. c In THF at 25 °C.

by VPO and SLS and calculated from the feed ratios and the narrow molecular weight distributions ($M_w/M_n < 1.05$) clearly show the successful synthesis of the well-defined 4-arm A_4 followed by 6-arm A_6 star-branched (PS)s.

In order to investigate the usefulness of this iterative methodology for the asymmetric star polymer synthesis, two series of 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ stars were synthesized using the same methodology with different living anionic polymers. Their A, B, and C segments were PS, poly(α -methylstyrene) (P α MS), PMOS and polyisoprene (PI), P α MS, PS, respectively. The SEC profiles of both asymmetric star series all showed narrow monomodal distributions. The molecular weights (M_n and M_w), molecular weight distributions, compositions, and DPE functionalities are summarized in Table IV. All of these results clearly indicate that the resulting polymers are the targeted 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ asymmetric stars with expected structures. Thus, the starting core compound of **2** is a very effective agent to increase the number of arm segments two by two at each stage in the synthesis of both regular and asymmetric stars.

ITERATIVE METHODOLOGY USING 1,1-BIS(3-(1-PHENYLETHENYL)PHENYL)ETHYLENE AND **1**

In order to increase the number of arms to be linked three by three at each stage, 1,1-bis(3-(1-phenylethenyl)phenyl)ethylene (**3**) composed of three DPE skeletons has been used as a starting core agent in the iterative methodology.⁶¹ The iterative methodology herein used is completely the same as that using **2** and **1** except for the use of **3**. Since the steric requirement around the core part using **3** may be more cumulated than the case using **2** as the iteration proceeds as outlined in Scheme 4, we have first focused on how many times the same iterative process can be practically repeated.

Similar to the reaction of PSLi with **2**, the addition reaction of PSLi to **3** proceeded inefficiently in THF at -78 °C even

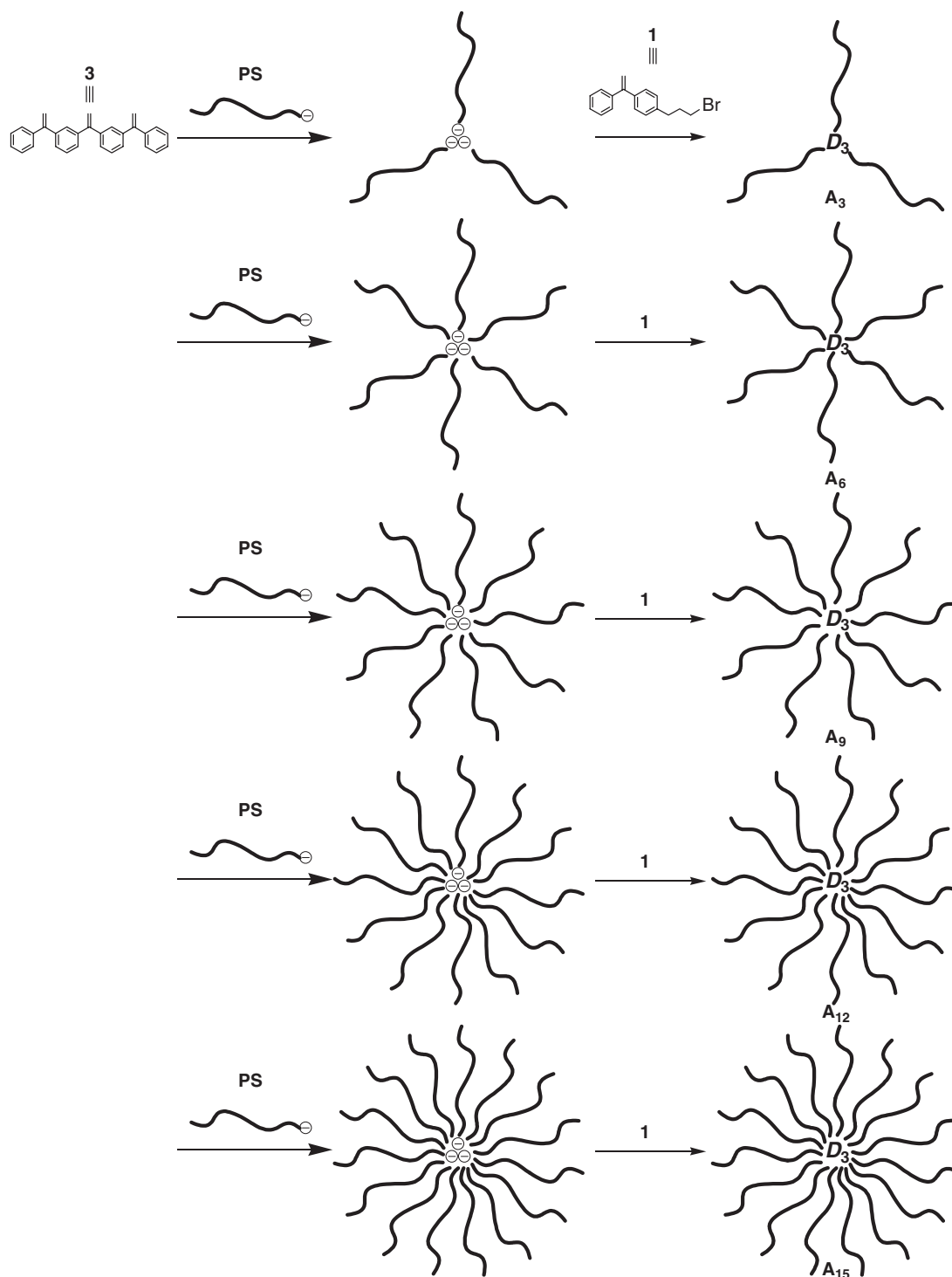
for a longer reaction time of 48 h, whereas underwent very efficiently under the conditions in *tert*-butylbenzene at 25 °C within 1 h. The subsequent *in situ* reaction of **1** with the three DPE-derived anions generated by the linking reaction produced the core-functionalized 3-arm star PS with three DPE moieties. At the first stage of the iteration, PSLi reacted with the DPE-core-functionalized 3-arm star and then **1** reacted *in situ* to reintroduce three DPE functionalities. The efficiency of the linking reaction was essentially quantitative as evidenced in the SEC profile of the reaction mixture. The M_n and M_w values of the resulting polymer determined by VPO and SLS agreed well with those calculated and a narrow molecular weight distribution was attained as was seen in Table V. Thus, a core-functionalized 6-arm star PS with three DPE moieties could be synthesized only by repeating the two reaction sequence one time.

The further synthesis of 9-, 12-, and 15-arm star-branched (PS)s were performed by repeating the same process three more times under the same conditions. The SEC profiles of 9-, 12-, and 15-arm star-branched (PS)s in addition to 3- and 6-arm star (PS)s showed sharp monomodal distributions, the M_w/M_n values being less than 1.05. The agreement among the molecular weights determined by VPO and SLS and those calculated is quite satisfactory in all polymer samples (see Table V). The successful formation of the expected star-branched (PS)s by this procedure is further documented by the fact that they have g' values which are in good agreement with calculated values by eq (1) mentioned above. Since the 15-arm A_{15} star PS possesses the same three DPE functionalities at the core, it may be possible to continue the same iterative process to synthesize 18- or more armed star polymers.

In order to investigate the best conditions by this procedure using **3** and **1**, the synthetic conditions were further examined in detail. Very surprisingly, it has been observed that the linking reaction is unexpectedly rapid and complete within 10 min in THF at -78 °C in each of the all stages. Thus, it appears that no steric limitation is encountered even in the reaction of PSLi ($M_n = 11\ 000$) with the core-functionalized 12-arm star PS with three DPE moieties ($M_n = 126\ 000$) at the fourth stage of the iteration.

Next, the present iterative methodology has been applied to the synthesis of asymmetric star-branched polymers. Three series of asymmetric star-branched polymers were synthesized using the method outlined in Scheme 5. The living anionic polymers used for the synthesis were PSLi and PMOSLi as A and B segments and PILi, PMSiSLi, or PBMSiOSLi as a C segment. All of the reactions proceeded very efficiently under the same conditions as evidenced by the SEC profiles of the resulting polymers. The successful synthesis of the targeted 6-arm A_3B_3 and three series of 9-arm $A_3B_3C_3$ asymmetric star-branched polymers by the methodology using **3** and **1** has been clearly confirmed by the characterization results listed in Table VI.

With use of **3** as a core agent, the number of arms successfully increased three by three at each stage. Thus, the



Scheme 4. Successive synthesis of asymmetric star-branched polymers by iterative methodology using **3** and **1**.

number of DPE skeletons in the core agent exactly corresponds to the number of arms by each stage. Accordingly, the appropriate DPE derivative of choice can offer the potential of increasing the number of arms to be linked at each stage of the iteration. Importantly, it appears no steric limitation at all at least by four repetition of the same iterative process.

ITERATIVE METHODOLOGY USING 3,5-BIS(3-(4-(1-PHENYLETHENYL)PHENYL)PROPOXY)BENZYL BROMIDE

For increasing the number of arms to be linked at each stage by less repetition of the iterative synthetic sequence, we have

Table V. Synthesis of DPE-core-functionalized 3-arm A_3 , 6-arm A_6 , 9-arm A_9 , 12-arm A_{12} , and 15-arm A_{15} star-branched (PS)s by iterative methodology using **3** and **1**

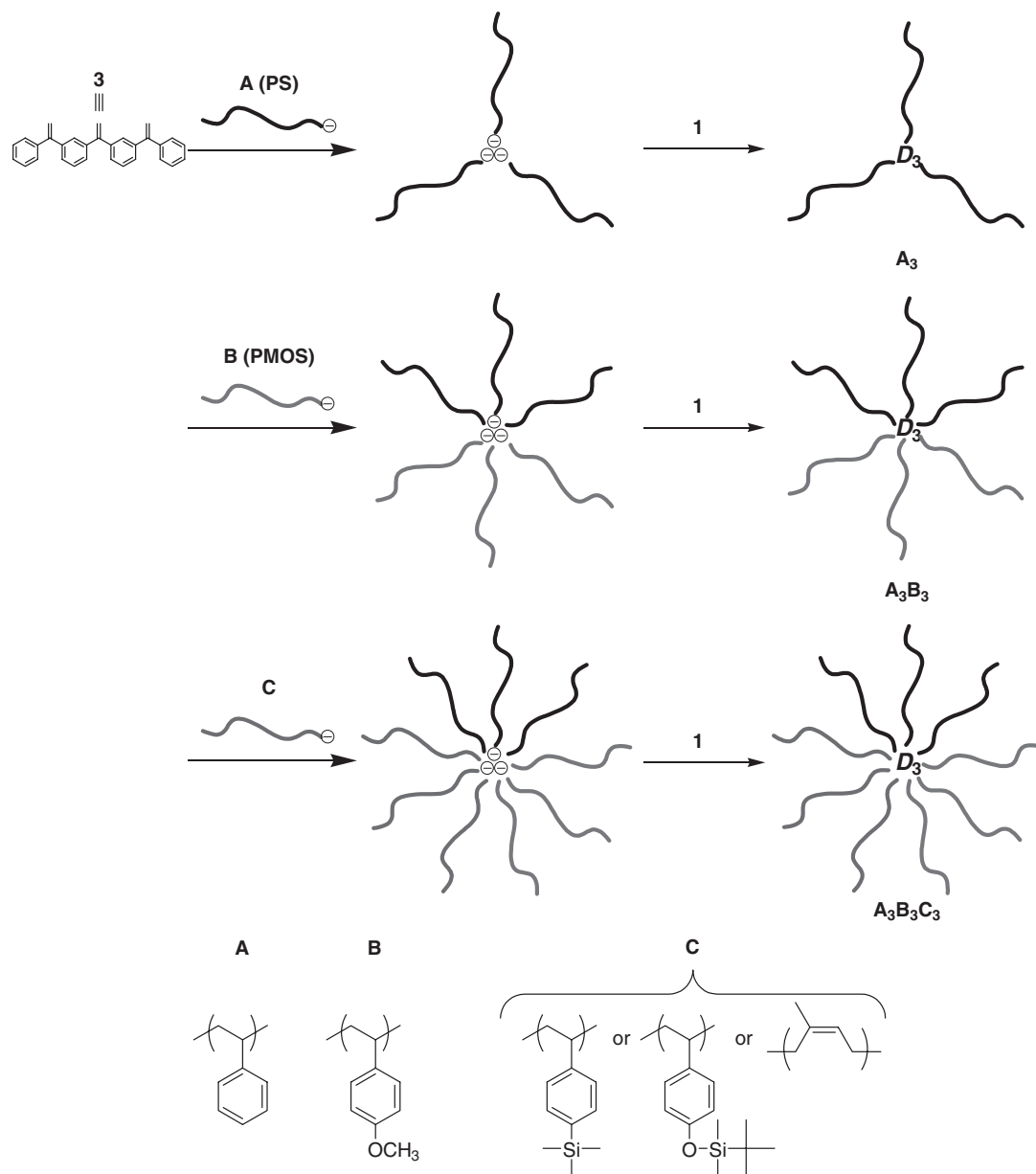
type	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	DPE-functionality		g'	
	calcd	SEC	VPO	calcd	SLS ^a		calcd	¹ H NMR	calcd	exptl
A_3	32.9	27.5	31.8	33.6	32.2	1.02	3	3.0 ₁	0.83	0.85
A_6	66.9	43.8	66.2	68.9	69.7	1.03	3	3.0 ₃	0.56	0.55
A_9	99.4	63.2	98.2	103	102	1.04	3	ca.3	0.42	0.43
A_{12}	134	74.2	—	141	142	1.05	3	ca.3	0.33	0.34
A_{15}	166	82.3	—	173	175	1.04	3	ca.3	0.27	0.29

^a In THF at 25 °C.

Table VI. Synthesis of DPE-core-functionalized 6-arm A_3B_3 and 9-arm $A_3B_3C_3$ asymmetric star-branched polymers by iterative methodology using **3** and **1**

type ^a	C	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt %)	
		calcd	SEC	VPO	calcd	SLS		SEC	calcd
A_3B_3	—	65.8	44.2	64.2	67.8	66.7	1.03	50/50	52/48
$A_3B_3C_3$	PMSiS	95.1	51.6	94.4	97.0	97.1	1.02	34/35/31	35/34/31
$A_3B_3C_3$	PI	96.7	59.2	95.0	101	103	1.04	—	—
$A_3B_3C_3$	PBMSiOS	95.4	49.2	93.9	98.3	97.2	1.03	34/35/31	33/35/32

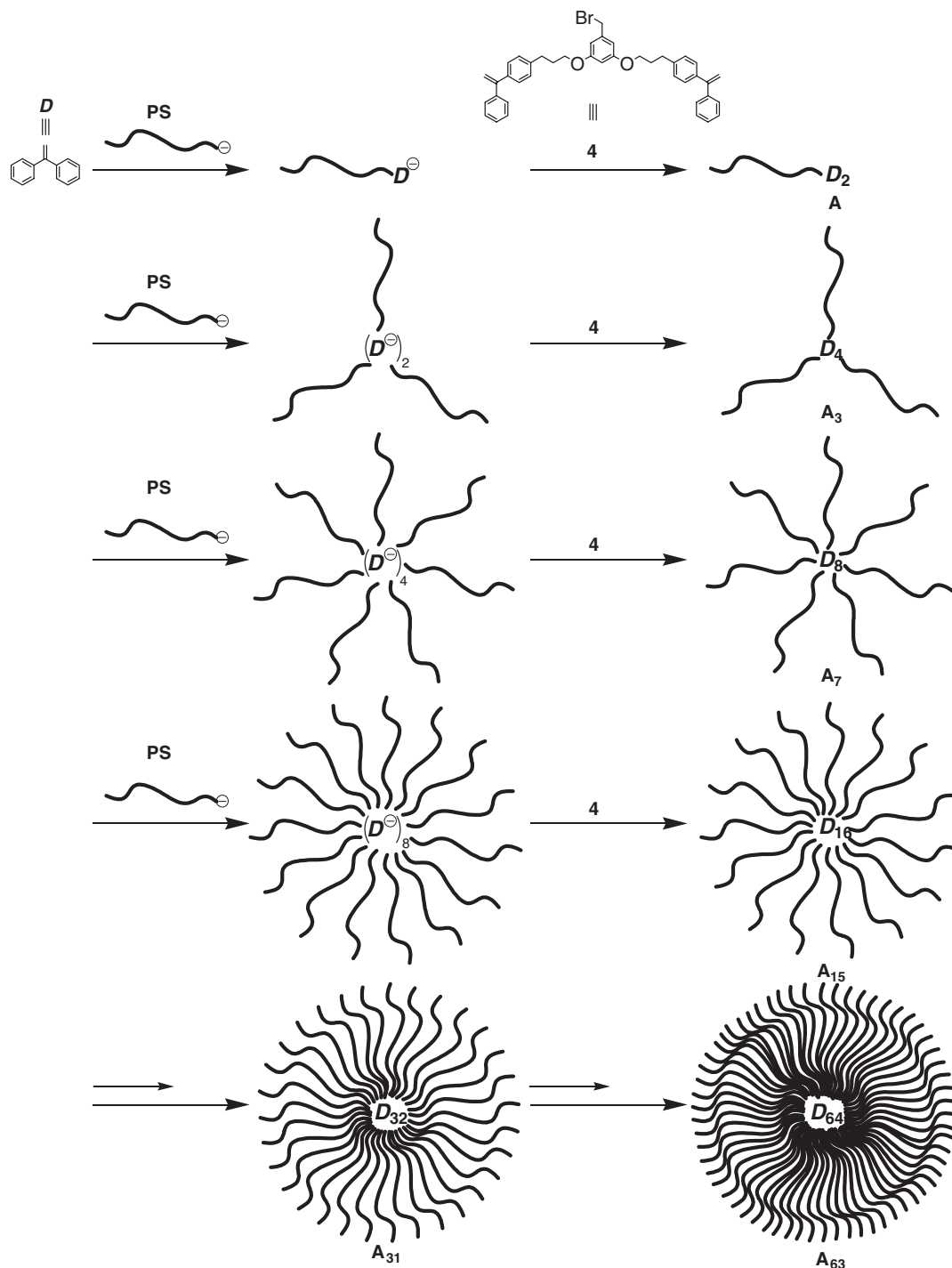
^a A and B were PS and PMOS, respectively. Their M_n values were 10.6 and 10.7 kg/mol, respectively, in all cases.



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

synthesized a new DPE-functionalized agent, 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide (**4**).⁶² This agent is designed to be capable of introducing two DPE

reaction sites *via* one anion. In order to examine the possible utility of **4**, a series of many armed star-branched (PS)s were synthesized using the methodology outlined in Scheme 6. The



Scheme 6. Successive synthesis of star-branched polystyrenes by iterative methodology using **4**.

methodology is the same as those developed above which involve only two sets of the reaction conditions at each stage of the iteration. If the methodology using **4** works as expected, the number of PS arms dramatically increases from 3, 7, 15, and so on to 31 as the iteration proceeds.

The starting chain-end-functionalized PS with two DPE moieties was prepared by the reaction of **4** with PSLi end-capped with DPE. At the first stage of the iteration, PSLi

reacted with the DPE-chain-end-functionalized PS and the subsequent reaction of **4** with the two anions generated by the linking reaction to reintroduce four DPE functionalities. The two reactions efficiently proceeded under the conditions in THF at -78°C . The linked product isolated by fractional precipitation exhibits a sharp monomodal SEC distribution and the M_w value determined by SLS agreed with that predicted as listed in Table VII. The ^1H NMR spectrum showed the

Table VII. Synthesis of star-branched (PS)s by iterative methodology using **4**

type	reaction conditions		M_n (kg/mol)		M_w (kg/mol)		M_w/M_n	g'	
	solvent	time (h)	calcd	SEC	calcd	SLS ^a		SEC	calcd
A	THF	—	11.5	11.5	11.8	11.8 ^c	1.03	—	—
A ₃	THF	1	31.1	29.3	32.2	33.7	1.03	0.83 ^d	0.85
A ₇	THF	24	76.1	59.1	79.4	79.0	1.04	0.51 ^d	0.53
A ₁₅	THF	24	155	75.4	163	166	1.05	0.27 ^d	0.28
A ₃₁	^t BuBz	168	314	104	330	330	1.05	0.15 ^e	0.16
A ₆₃	^t BuBz ^b	72	607	129	625	623	1.03	0.083 ^e	0.10
A ₁₁₃	^t BuBz ^b	72	1220	156	1280	1130	1.05	—	—

a In toluene at 25 °C. b A 2-fold excess of TMEDA toward PSLi was added. c Measured by SEC. d Calculated from eq 1. e Calculated from eq 2.

resonances at 5.4 ppm corresponding to vinylene protons of the DPE moieties at the expected intensity. Thus, the first stage of the iteration produced the expected 3-arm A₃ star-branched PS core-functionalized with four DPE moieties.

The second and third stages of the iteration were carried out under the similar conditions. Both iterative synthetic sequences proceeded virtually quantitatively as evidenced by the SEC profiles shown in Figure 4(b) and 4(c).⁶³ Their well-defined structures are confirmed by the results listed in Table VII. Moreover, these polymers have g' values which are in good agreement with both observed and calculated values, strongly indicating 7- and 15-arm star-branched architectures.

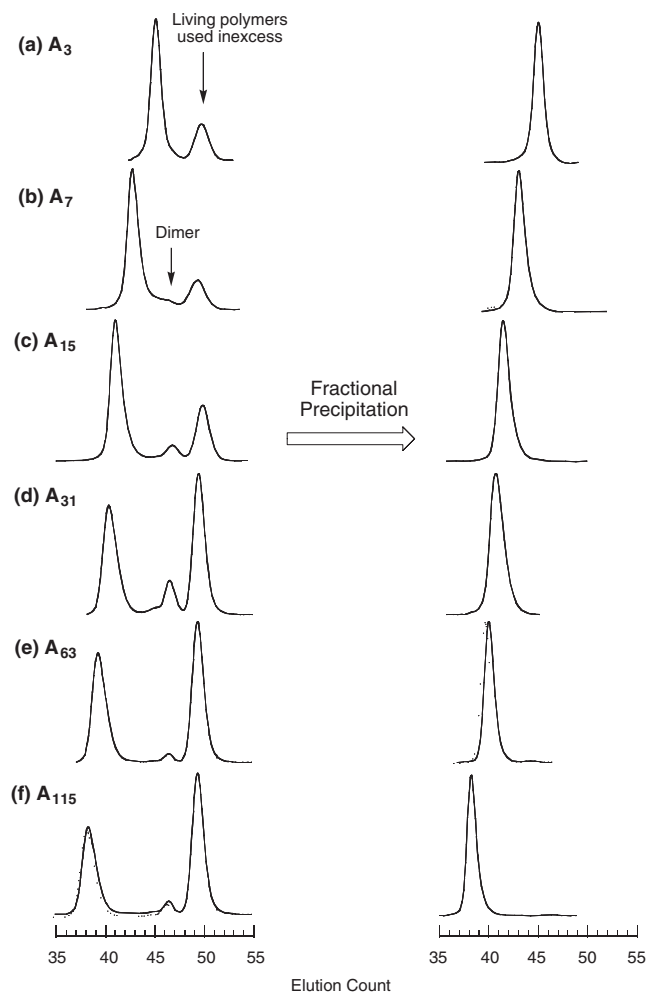
It was however observed that PSLi reacted with the 16 DPE moieties of 15-arm star PS at the fourth stage but not quantitatively in THF at -78 °C even for a longer reaction time of 48 h. Averagely 10 arms were linked to result in a 25-arm star (target: a 31-arm star). On the other hand, the linking reaction proceeded completely by changing the reaction conditions to those in *tert*-butylbenzene at 30 °C for 168 h. Moreover, a 3-fold excess of PSLi was used toward the DPE moiety in this reaction. Indeed, the M_w value of the resulting polymer determined by SLS agreed with that predicted (see Table VII). The observed g' value was very close to that calculated by the following eq (2),⁶⁴ since the above-mentioned equation (1) is not suitable for star-branched polymers having more than 17 arms:

$$\log g' = 0.36 - 0.80 \log f \quad (f: \text{arm number}) \quad (2)$$

Thus, the objective 31-arm star-branched PS could be synthesized by changing the reaction conditions.

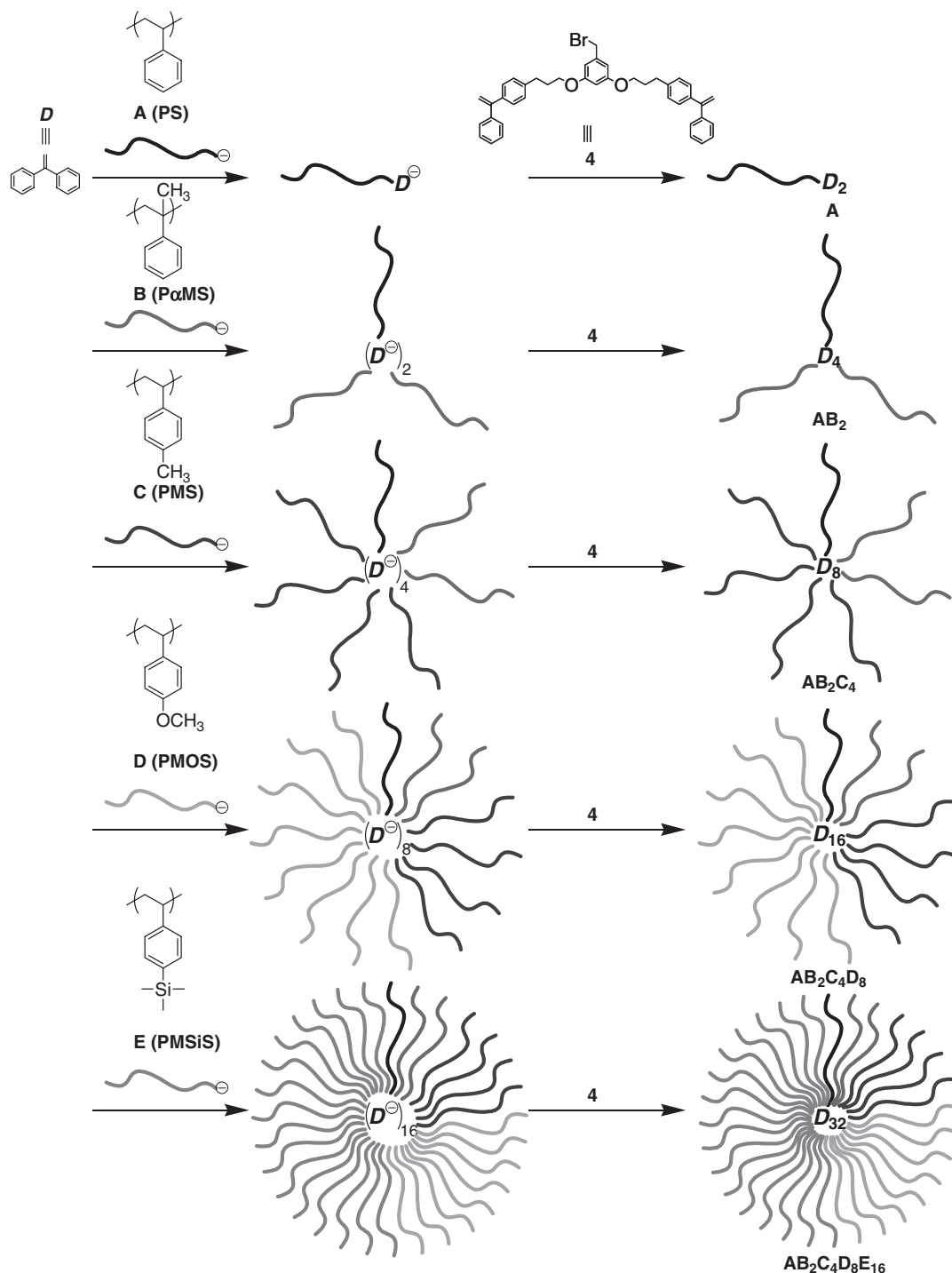
The linking reaction at the fifth stage of the iteration was carried out in *tert*-butylbenzene at 30 °C effective for the synthesis of 31-arm star PS, but the reaction proceeded only to a little extent. In order to facilitate the reaction, two equivalents of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to PSLi was added and the reaction temperature was raised to 40 °C. In this manner, the linking reaction proceeded completely for 72 h to result in the targeted 63-arm star-branched PS with 64 DPE moieties at the core.

With use of the DPE-core-functionalized 63-arm star-branched PS, the sixth iteration was attempted under the same conditions. Although the linking reaction proceeded, the


Figure 4. SEC profiles of DPE-core-functionalized A₃ (a), A₇ (b), A₁₅ (c), A₃₁ (d), A₆₃ (e), and A₁₁₃ (f) star-branched polystyrenes.

resulting polymer possessed averagely 113 arms, but not the targeted 127 arms (see Table VII). This may possibly be attributed to the increase of steric hindrance around the reaction sites as well as the negative charge repulsion among PSLi and many 1,1-diphenylalkyl anions generated around the core. As discussed in the methodology using **3** and **1**, no steric requirement was observed for the synthesis of the 15-arm star PS, but steric hindering effect appeared with increasing the number of arms to be linked. It should be therefore kept in mind that the reaction condition of choice is very important and critical for the synthesis of many armed star-branched polymers.

The synthetic utility of **4** in the iterative methodology becomes apparent for the synthesis of star-branched PS having as many as 63 arms. On the basis of such results, many armed asymmetric star-branched polymers have been synthesized by the methodology as illustrated in Scheme 7. The living polymers used for the synthesis were PSLi, P α MSLi, PMSLi, PMOSLi, and PMSiSLi, respectively. With this methodology, the successive synthesis of 3-arm AB₂, 7-arm AB₂C₄, 15-arm AB₂C₄D₈, and 31-arm AB₂C₄D₈E₁₆ stars would be expected



Scheme 7. Successive synthesis of asymmetric star-branched polymers by iterative methodology using 4.

by repeating the two reaction sequence four times. The reaction conditions were followed by those employed for the regular star (PS)s mentioned above.

All of the iterative processes proceeded efficiently without any difficulty and the resulting polymers could be isolated in more than 80% yields by fractional precipitation. The SEC profiles shown in Figure 5 exhibit that the isolated polymers possess sharp monomodal distributions and neither precursors

nor living anionic polymers remains at all. The results are summarized in Table VIII. The good agreement among the molecular weights determined by ^1H NMR and RALLS and those calculated and narrow molecular weight distributions ($M_w/M_n < 1.02$) clearly indicate the expected structures of 3-arm AB_2 , 7-arm AB_2C_4 , 15-arm $\text{AB}_2\text{C}_4\text{D}_8$, and 31-arm $\text{AB}_2\text{C}_4\text{D}_8\text{E}_{16}$ stars with a high degree of homogeneity in molecular weight and composition. This is also supported by

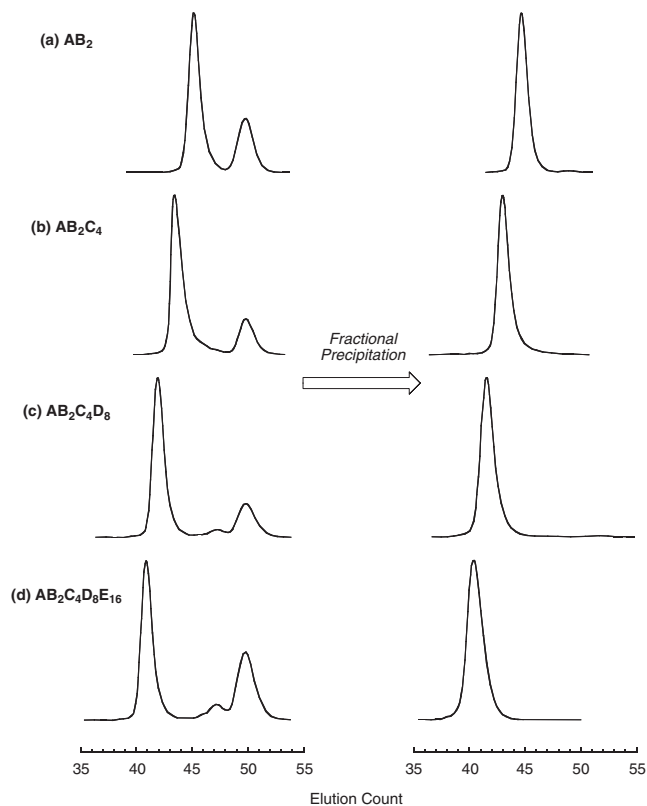


Figure 5. SEC profiles of DPE-core-functionalized 3-arm AB_2 (a), 7- AB_2C_4 (b), 15-arm $AB_2C_4D_8$ (c), and 31-arm $AB_2C_4D_8E_{16}$ (d) star-branched polymers.

the agreement between the compositions calculated from the feed ratio and observed by 1H NMR shown in Figure 6. Incompatibility of different polymer segments seems not to be affected on the synthesis under the conditions. Thus, the iterative methodology using **4** can also be effective for the successive synthesis of a series of asymmetric star-branched polymers having many arms and compositions.

In conclusion, we have successfully developed the iterative methodology for the synthesis of asymmetric star-branched polymers having chemically different arms as well as the corresponding regular star (PS)s. The use of specially designed DPE derivatives such as **1**, **2**, **3**, and **4** makes the methodology possible to dramatically increase the number of arms to be linked by each stage of the iteration. The star-branched polymers herein obtained by the iterative methodology are

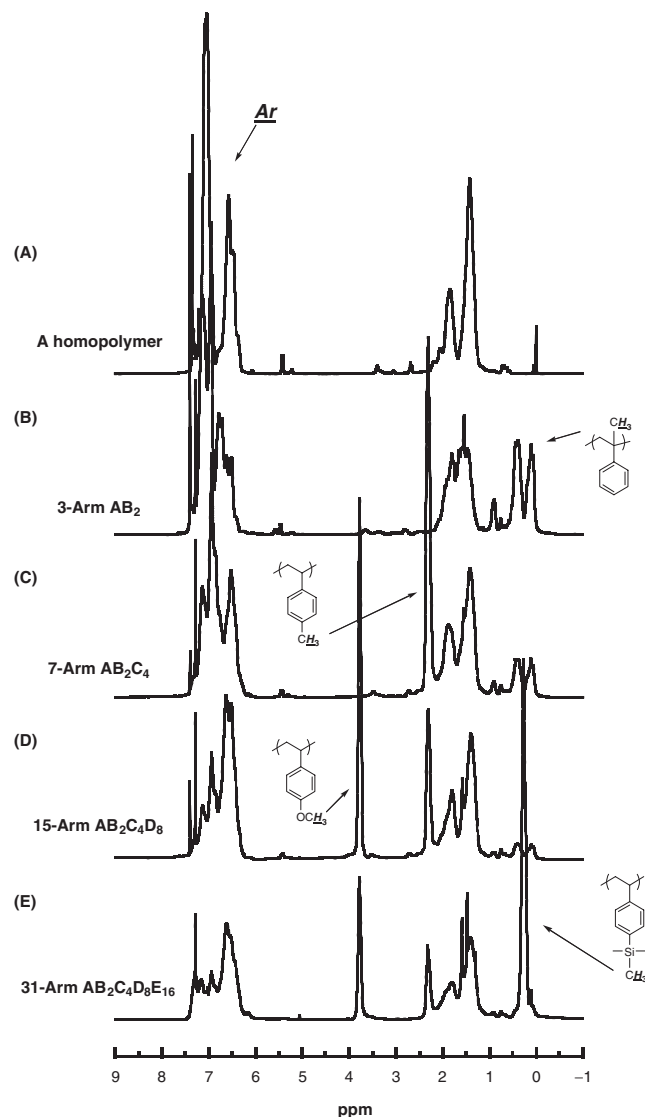


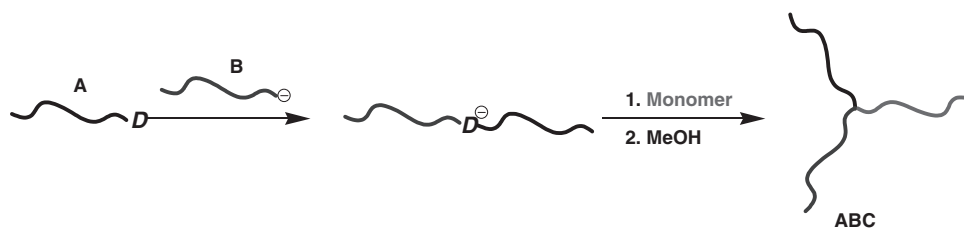
Figure 6. 1H NMR spectra of DPE-chain-end functionalized A (A), DPE-core-functionalized 3-arm AB_2 (B), 7- AB_2C_4 (C), 15-arm $AB_2C_4D_8$ (D), and 31-arm $AB_2C_4D_8E_{16}$ (E) star-branched polymers.

well-defined in branched architecture and precisely controlled in chain length because of the efficient iterative reaction sequences and the use of pre-made living anionic polymers. However, one of the limitations is that there is a restriction on living anionic polymers that can be used in this methodology.

Table VIII. Synthesis of DPE-chain-end-functionalized PS (A), core-functionalized 3-arm AB_2 , 7-arm AB_2C_4 , 15-arm $AB_2C_4D_8$, and 31-arm $AB_2C_4D_8E_{16}$ asymmetric star-branched polymers by iterative methodology using **4**

type ^a	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt %)	
	calcd	SEC	1H NMR	calcd	SLS		calcd	1H NMR
A	11.9	11.6	11.7	12.3	11.9 ^b	1.02	100	100
AB_2	31.5	26.4	31.3	32.1	35.7	1.02	36/64	38/62
AB_2C_4	75.5	55.5	73.3	77.0	79.2	1.02	16/28/56	17/27/56
$AB_2C_4D_8$	139	67.6	161	162	172	1.02	8/12/27/53	8/10/30/52
$AB_2C_4D_8E_{16}$	332	97.9	309	339	363	1.02	4/6/13/27/50	4/7/15/29/46

a A, B, C, D, and E were PS, P α MS, PMS, PMOS, and PMSiS, respectively. b Measured by SEC.



Scheme 8. Synthesis of 3-arm asymmetric star-branched polymers.

Living anionic polymers of styrene, 1,3-diene monomers such as 1,3-butadiene and isoprene, and the related derivatives are usable because of their reactive chain-end carbanions capable of reacting with the DPE moieties, while less reactive living anionic polymers of (meth)acrylates, ethylene oxide, cyclic siloxanes, and NCA can not be used at the present time.

SYNTHESIS OF ASYMMETRIC STAR-BRANCHED POLYMERS BY USING INTERMEDIATE POLYMER ANIONS AS MACROINITIATORS

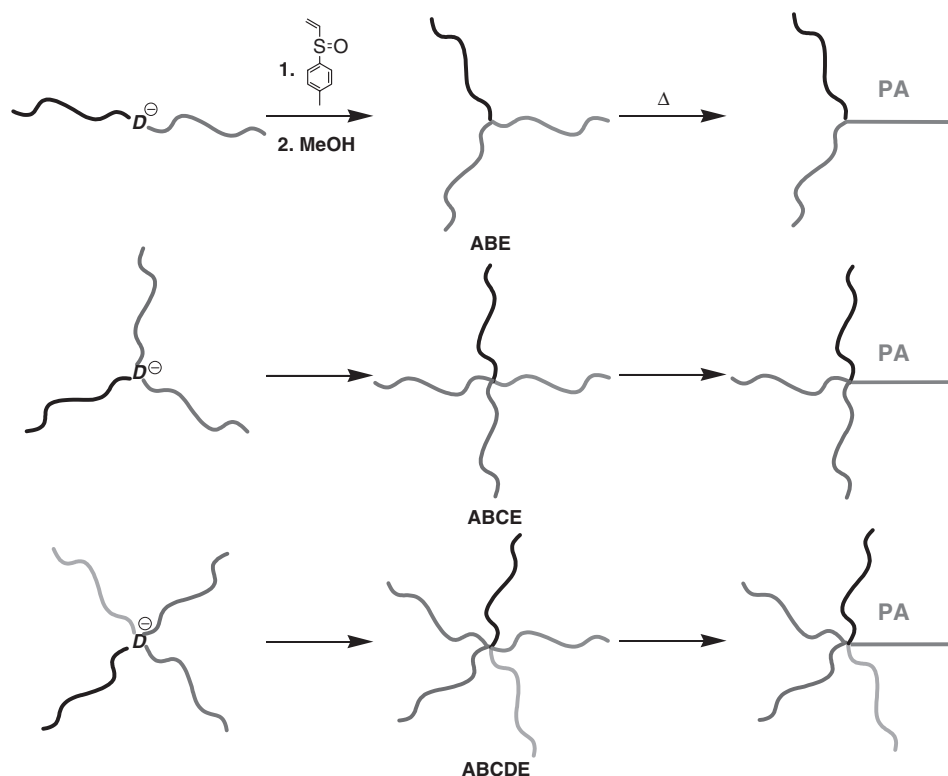
The linking reaction of a living anionic polymer with a DPE-end-functionalized polymer, followed by the polymerization of an additional monomer outlined in Scheme 8, has been known as one of the most established procedure for the synthesis of 3-arm ABC asymmetric star-branched polymers. In this procedure, the intermediate polymer anion is used as a macroinitiator to polymerize the additional monomer to make the third arm. In fact, several synthetic examples of 3-arm ABC asymmetric stars by this procedure have been reported so far.^{20,24,29,65–71}

In all of the iterative methodologies herein developed, similar but much more complex intermediate polymer anions are produced as can be seen in Schemes 1–7. Accordingly, one can readily imagine the synthetic procedure using such polymer anions accessible to various asymmetric star-branched polymers. The advantage of this procedure is to be able to use any monomer which undergoes living anionic polymerization at the final polymerization step.

Poly(4-methylphenyl vinyl sulfoxide) is of particularly interest in this regard that it is readily and quantitatively converted to conductive and rigid rod-like poly(acetylene) segment simply by thermal treatment at 150 °C for a few hours.^{72–74} Although 4-methylphenyl vinyl sulfoxide undergoes living anionic polymerization, the resulting living polymer can not be used in the iterative methodology because of its low reactive chain-end anion incapable of reacting with the DPE functionality. For synthesizing the asymmetric star-branched polymers having poly(4-methylphenyl vinyl sulfoxide) segments convertible to poly(acetylene) chains, we have adapted the above-mentioned methodology in which 4-methylphenyl vinyl sulfoxide is anionically polymerized with either of the intermediate polymer anions followed by thermal treatment.⁵⁵ As outlined in Scheme 9, 3-arm ABC and 4-arm ABCD star-

branched polymer anions as well as an AB diblock copolymer anion were first prepared according to the procedure illustrated in Scheme 2 and 4-methylphenyl vinyl sulfoxide was then added *in situ* to each polymer anion to polymerize in a living manner. Since a slight excess of living polymer was usually employed in each linking reaction, the objective star-branched polymer was synthesized along with the formation of the unwanted diblock copolymer and, accordingly, the objective star was isolated by fractional precipitation. The characterization results are summarized in Table IX. The agreement between the molecular weights determined and predicted is excellent. In addition, the molecular weight distributions are narrow. These results strongly indicate that the procedure works as desired to synthesize the targeted 3-arm ABE, 4-arm ABCE, and 5-arm ABCDE asymmetric star-branched polymers. Herein, the A, B, C, D, and E corresponded to PS, P α MS, PMOS, PMSiS or PMS, and poly(4-methylphenyl vinyl sulfoxide) segments, respectively.⁵⁵ Finally, the resulting polymers were thermally treated to quantitatively convert to new functional asymmetric stars consisting of one conductive rigid rod-like poly(acetylene) and other coil segments.

Two poly(acetylene) segments could also be introduced by the living anionic polymerization of 4-methylphenyl vinyl sulfoxide with the following polymers having two anions at the chain-end, in-chain, or at the core as shown in Scheme 10.⁷⁵ A variety of asymmetric star-branched polymers have been successfully synthesized. They involve two series of 3-arm AE₂, 4-arm ABE₂, 5-arm ABCE₂, and 5-arm AD₂E₂, 6-arm ABD₂E₂, 7-arm ABCD₂E₂ asymmetric star-branched polymers where the A, B, C, D, and E segments are PS, P α MS, PMOS, PMSiS, and poly(4-methylphenyl vinyl sulfoxide) chains, respectively. The resulting star-branched polymers were observed to have the expected structures with well-defined branched architectures as shown in Table X. After thermal treatment at 150 °C for a few hours, these star polymers were quantitatively converted to new functional asymmetric star-branched polymers having two poly(acetylene) segments. In these star-branched polymers, it is expected that phase-separation at molecular level, followed by self-organization would occur to create new and unique nano-ordered suprastructures and molecular assemblies involving conductive poly(acetylene) segments. The physical properties as well as solution behaviors of such star-branched polymers may also be very interesting because they are composed of rigid rod-like poly(acetylene) segments and usual coil segments.



Scheme 9. Synthesis of 3-arm ACE, 4-arm ABCE, and 5-arm ABCDE asymmetric star-branched polymers having poly(4-methylphenyl vinyl sulfoxide) or poly(acetylene).

Table IX. Synthesis of 3-arm ACE, 4-arm ABCE, and 5-arm ABCDE asymmetric star-branched polymers having poly(4-methylphenyl vinyl sulfoxide)

type ^a	C	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt %) ^c	
		calcd	SEC	¹ H NMR	calcd	SLS ^b		calcd	¹ H NMR
ACE	P α MS	31.2	20.5	31.5	31.8	32.7	1.02	31/31/38	31/31/38
ACE	PMSiS	29.8	21.9	30.1	30.7	31.8	1.03	32/33/35	32/34/34
ACE	PMOS	31.2	23.0	32.0	31.8	34.6	1.02	31/35/34	30/35/35
ACE	PMS	30.6	23.3	31.2	31.2	33.5	1.02	31/34/35	31/34/35
ABCE	PMOS	41.9	31.0	43.3	42.7	44.6	1.02	24/24/25/27	23/23/25/29
ABCE	PMSiS	42.0	29.3	43.2	43.3	43.6	1.03	24/24/26/26	23/23/24/29
ABCE	PMS	42.6	33.5	43.9	43.5	44.9	1.02	23/23/24/30	23/23/24/30
ABCDE	PMSiS	50.0	38.6	50.4	51.5	53.6	1.03	19/20/23/21/17	19/20/23/20/18

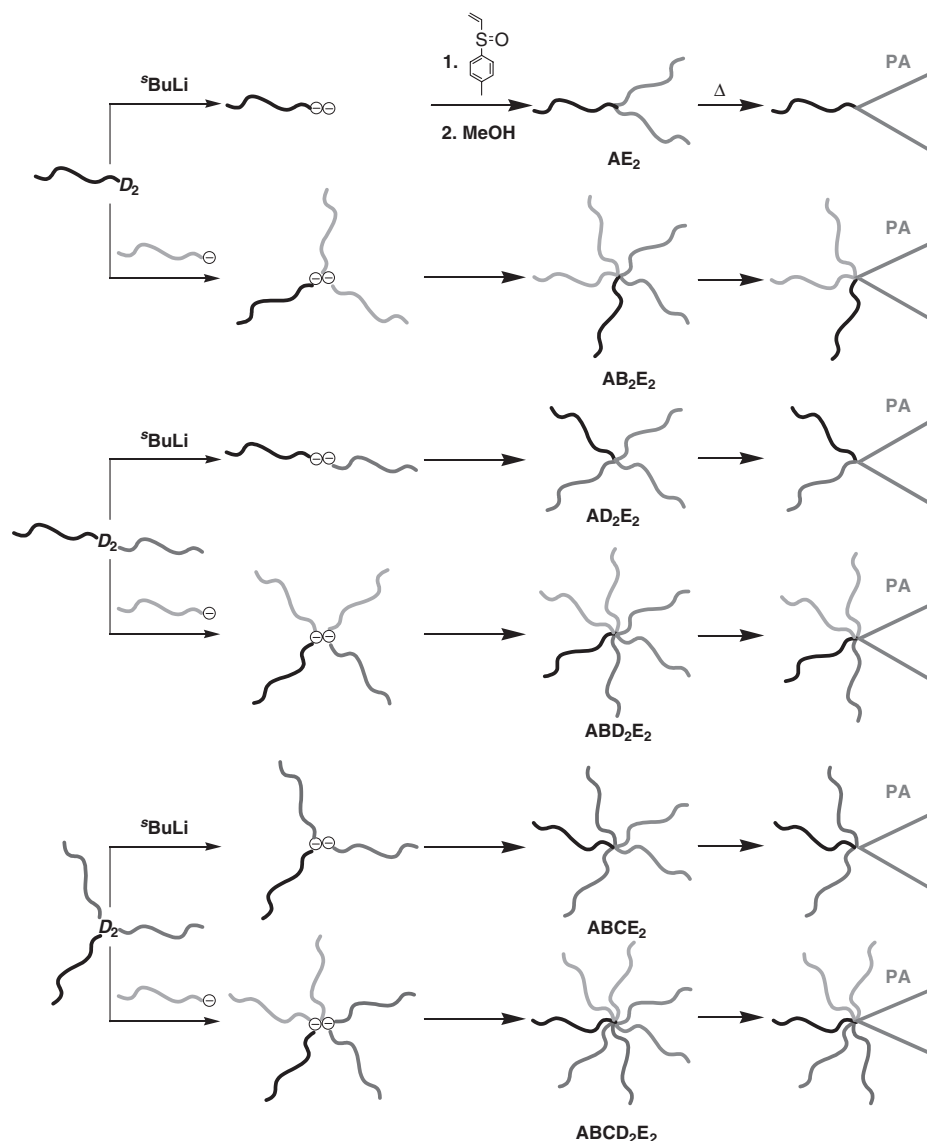
a A, B, D, and E were PS, P α MS, PMOS, and Poly(4-methylphenyl vinyl sulfoxide), respectively. b In THF at 25 °C.

MORPHOLOGICAL STUDIES OF ASYMMETRIC STAR-BRANCHED POLYMERS

A number of morphological studies have been so far reported with respect to linear block copolymers, but those of asymmetric star-branched polymers have been much less focused on possibly due to the difficulty and limitation in systematic syntheses of complex asymmetric stars, although unique and unusual morphological behaviors must be expected for such new type stars originating from their heterophase in addition to nonlinear architectures.

For 3-arm ABC star-branched polymers, however, their morphologies have been studied by several research groups.^{15–35} Unlike the corresponding linear ABC block

terpolymers, these star polymers generally tend to form characteristic cylinder-based morphologies because three different polymer chains connected at one junction must be aligned one-dimensionally due to the geometrical restriction. For instance, Abetz and coworkers reported that ABC asymmetric star-branched polymers (A = PS, B = poly(2-vinylpyridine) (P2VP), and C = poly(1,3-butadiene)) showed new hexagonal packed cylinders (see Figure 7(A)) which could be changed to other new cylindrical morphologies (tetragonal, cylinders-in-lamellar) simply by varying molecular weight of each arm.²⁰ Hasegawa, Hadjichristidis, and their coworkers reported on the detailed morphologies of ABC asymmetric star-branched polymers (A = polyisoprene (PI), B = PS, and C = poly(dimethylsiloxane)) with almost the same molecular weights of arms. Combined energy-filtering transmission



Scheme 10. Synthesis of 3-arm AE_2 , 4-arm ABE_2 , 5-arm $ABCE_2$, 5-arm AD_2E_2 , 6-arm ABD_2E_2 , and 7-arm $ABCD_2E_2$ asymmetric star-branched polymers having two poly(4-methylphenyl vinyl sulfoxide) or poly(acetylene).

Table X. Synthesis of 3-arm AE_2 , 4-arm ABE_2 , 5-arm $ABCE_2$, 5-arm AD_2E_2 , 6-arm ABD_2E_2 , 7-arm $ABCD_2E_2$ asymmetric star-branched polymers having two poly(4-methylphenyl vinyl sulfoxide)

type ^a	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt %)	
	calcd	SEC	¹ H NMR	calcd	SLS ^b		calcd	¹ H NMR
AE_2	32.3	21.8	28.6	33.6	29.7	1.04	27/73	30/70
ABE_2	42.3	29.2	42.5	43.1	44.5	1.02	23/24/53	23/24/53
$ABCE_2$	51.0	27.2	52.7	52.5	54.3	1.03	21/19/19/41	21/18/18/43
AD_2E_2	50.0	30.8	45.8	51.5	52.8	1.03	17/41/42	19/37/44
ABD_2E_2	60.8	40.5	58.0	62.6	63.4	1.03	17/16/32/35	18/17/43/22
$ABCD_2E_2$	73.4	47.2	69.8	75.6	75.9	1.03	16/13/13/27/31	15/14/14/25/32

a A, B, C, D, and E were PS, P α MS, PMOS, PMSiS, and Poly(4-methylphenyl vinyl sulfoxide), respectively. b In THF at 25 °C.

electron microscopy and 3D electron tomography clearly revealed that three kinds of cylindrical structures, composed of three different arms, joined to fill the space and that these cylinders were curved collectively into an arc as shown in Figure 7(B).²⁴ Very recently, Matsushita and his coworkers

have first identified three types of hierarchical morphologies, *i.e.*, a new series of lamellae-in-cylinder (see Figure 7(C)), lamellae-in-sphere, and cylinders-in-lamella morphologies, for ABC asymmetric stars (A = PI, B = PS, and C = P2VP) by TEM and SAXS.³⁵

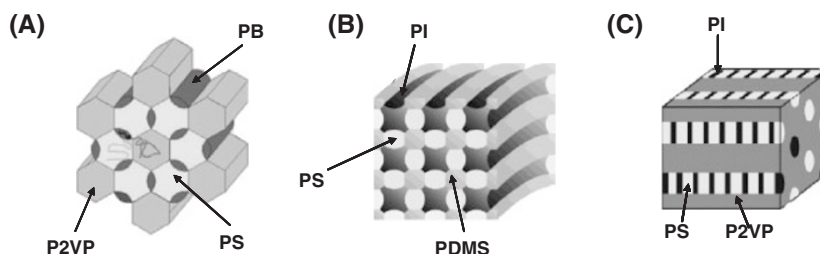


Figure 7. Morphological illustrations of ABC asymmetric star-branched polymers (A) A = polystyrene (PS, 34 wt%), B = poly(2-vinylpyridine) (P2VP, 55 wt%), and C = polybutadiene (PB, wt%), (B) A = polyisoprene (PI, 34 wt%), B = PS (33 wt%), and C = poly(dimethylsiloxane) (PDMS, 33 wt%), (C) A = PI (3.3 wt%), B = PS (6.8 wt%), and C = P2VP (89.9 wt%).

Thus, phase-separated morphologies of 3-arm ABC asymmetric stars have been clarified to certain extents, but there has been no information about the morphologies of more complex stars with many arms defined as $A_1B_mC_n$... types which have been developing by us. The exploration about the dependence of arm number on morphologies would be challenging topics in the future.

CONCLUDING REMARKS

We have demonstrated the effectiveness of the iterative methodology for the synthesis of many armed star-branched polymers with same or chemically different arm segments. In fact, a wide variety of many armed star-branched polymers with well-defined branched architectures and precisely controlled chain lengths have been successfully synthesized. Most of such complex architectural star-branched polymers herein synthesized are quite new and difficult to be synthesized by any other methods. The number of arms to be linked by each stage of the iteration can be controlled by appropriately choosing the starting core and DPE-functionalized agents such as **1**, **2**, **3**, and **4**, respectively, shown in each section. It may be possible to synthesize more variety of star-branched polymers by combining the two agents in different way, for example, **2** and **4** or **3** and **4**. Another type star-branched polymer can be synthesized by utilizing either of the intermediate polymer anions produced by the linking reaction as a macroinitiator to polymerize an additional monomer. In this way, new functional asymmetric star-branched polymers involving conductive and rigid rod-like poly(acetylene) segment(s) have been successfully synthesized by the polymerization of 4-methylphenyl vinyl sulfonate with the polymer anion, followed by thermal treatment. Since various (meth)acrylate monomers, ethylene oxide, and cyclic siloxane, similar to 4-methylphenyl vinyl sulfonate, can be polymerized with either of the above-mentioned polymer anions, it may be possible to introduce their polymer segments into the original star-branched polymers as additional arms to synthesize other many armed asymmetric star-branched polymers.

Acknowledgment. A.H. gratefully acknowledges both Sumitomo Chemical Co. Ltd. and Denki Chemical Co. Ltd. for providing the financial support.

Received: March 6, 2008

Accepted: April 12, 2008

Published: June 4, 2008

REFERENCES

- B. J. Bauer and L. J. Fetters, *Rubber Chem. Technol.*, **51**, 406 (1978).
- S. Bywater, *Adv. Polym. Sci.*, **30**, 89 (1979).
- J. Roovers, "Encyclopedia of Polymer Science and Engineering" 2nd ed., J. I. Kroschwitz, Ed., Wiley-Interscience, New York, 1985, Suppl. vol. 2, pp 478–499.
- P. Rempp and J. E. Herz, "Encyclopedia of Polymer Science and Engineering" 2nd ed., J. I. Kroschwitz, Ed., Wiley-Interscience, New York, 1989, Suppl., pp 493–510.
- L. J. Fetters and E. L. Thomas, "Material Science and Technology" VCH Verlagsgesellschaft, Weinheim, Germany, 1993, vol. 12, pp 1–31.
- H. L. Hsieh and R. P. Quirk, "Anionic Polymerization: Principles and Applications" Marcel Dekker, New York, 1996, pp 333–368.
- G. S. Grest, L. J. Fetters, and J. S. Huang, *Adv. Chem. Phys.*, **XCIV**, 67 (1996).
- P. J. Lutz and D. Rein, in "Star and Hyperbranched Polymers" M. K. Mishra and S. Kobayashi, Ed., Marcel Dekker, New York, 1999, pp 27–57.
- N. Hadjichristidis, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 857 (1999).
- N. Hadjichristidis, M. Pitsikalis, H. Iatrou, and C. Vlahos, *Adv. Polym. Sci.*, **142**, 72 (1999).
- N. Hadjichristidis, M. Pitsikalis, S. Pispas, and H. Iatrou, *Chem. Rev.*, **101**, 3747 (2001).
- N. Hadjichristidis, M. Pitsikalis, H. Iatrou, and S. Pispas, *Macromol. Rapid Commun.*, **24**, 979 (2003).
- A. Hirao, M. Hayashi, Y. Tokuda, N. Haraguchi, T. Higashihara, and S.-W. Ryu, *Polym. J.*, **34**, 633 (2002).
- A. Hirao, M. Hayashi, S. Lokulnant, K. Sugiyama, S.-W. Ryu, N. Haraguchi, A. Matsuo, and T. Higashihara, *Prog. Polym. Sci.*, **30**, 111 (2005).
- S. T. Milner, *Macromolecules*, **27**, 2333 (1994).
- S. Okamoto, H. Hasegawa, T. Hashimoto, T. Fujimoto, H. Zhang, T. Kazama, A. Takano, and Y. Isono, *Polymer*, **38**, 5275 (1997).
- S. Sioula, N. Hadjichristidis, and E. L. Thomas, *Macromolecules*, **31**, 5272 (1998).
- N. Hadjichristidis, H. Iatrou, S. K. Behal, J. J. Chludznski, M. M. Disko, R. T. Garner, K. S. Liang, D. J. Lohse, and S. T. Milner, *Macromolecules*, **31**, 5812 (1993).
- S. Sioula, N. Hadjichristidis, and E. L. Thomas, *Macromolecules*, **31**, 8429 (1998).
- H. Hückstädt, A. Göpfert, and V. Abetz, *Macromol. Chem. Phys.*, **201**, 296 (2000).
- Y. Bohbot-Raviv and Z.-G. Wang, *Phys. Rev. Lett.*, **85**, 3428 (2000).
- X. He, L. Huang, and C. Pan, *J. Chem. Phys.*, **116**, 10508 (2002).
- T. Gemma, A. Hatano, and T. Dotera, *Macromolecules*, **35**, 3225 (2002).

- (2002).
24. K. Yamauchi, K. Takahashi, H. Hasegawa, H. Iatrou, N. Hadjichristidis, T. Kaneko, Y. Nishikawa, H. Jinnai, T. Matsui, H. Nishioka, M. Shimizu, and H. Furukawa, *Macromolecules*, **36**, 6962 (2003).
 25. X. He, L. Huang, H. Liang, and C. Pan, *J. Chem. Phys.*, **118**, 9861 (2003).
 26. T. Lu, X. He, and H. Liang, *J. Chem. Phys.*, **121**, 9702 (2004).
 27. T. M. Birshtein, A. A. Polotsky, and V. Abetz, *Macromol. Theory Simul.*, **13**, 512 (2004).
 28. P. Tang, F. Qiu, H. Zhang, and Y. Yang, *J. Phys. Chem. B*, **108**, 8434 (2004).
 29. A. Takano, S. Wada, S. Sato, T. Araki, K. Hirahara, T. Kazama, S. Kawahara, Y. Isono, A. Ohono, N. Tanaka, and Y. Matsushita, *Macromolecules*, **37**, 9941 (2004).
 30. A. Takano, W. Kawashima, A. Noro, Y. Isono, N. Tanaka, T. Dotera, and Y. Matsushita, *J. Polym. Sci., Part B: Polym. Phys.*, **43**, 2427 (2005).
 31. K. Yamauchi, S. Akasaka, H. Hasegawa, H. Iatrou, and N. Hadjichristidis, *Macromolecules*, **38**, 8022 (2005).
 32. Z. Li, M. A. Hillmyer, and T. P. Lodge, *Macromolecules*, **39**, 765 (2006).
 33. K. Hayashida, W. Kawashima, A. Takano, Y. Shinohara, Y. Amemiya, Y. Nozue, and Y. Matsushita, *Macromolecules*, **39**, 4869 (2006).
 34. K. Hayashida, A. Takano, S. Arai, Y. Shinohara, Y. Amemiya, and Y. Matsushita, *Macromolecules*, **39**, 9402 (2006).
 35. K. Hayashida, N. Saito, S. Arai, A. Takano, N. Tanaka, and Y. Matsushita, *Macromolecules*, **40**, 3695 (2007).
 36. N. Hadjichristidis, A. Guyot, and L. J. Fetters, *Macromolecules*, **11**, 668 (1978).
 37. N. Hadjichristidis and L. J. Fetters, *Macromolecules*, **13**, 191 (1980).
 38. J. Roovers, N. Hadjichristidis, and L. J. Fetters, *Macromolecules*, **16**, 214 (1983).
 39. P. M. Toporowski and J. Roovers, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 3009 (1986).
 40. L.-L. Zhou, N. Hadjichristidis, P. M. Toporowski, and J. Roovers, *Rubberr Chem. Technol.*, **65**, 303 (1992).
 41. J. Roovers, L.-L. Zhou, P. M. Toporowski, M. van der Zwan, H. Iatrou, and N. Hadjichristidis, *Macromolecules*, **26**, 4324 (1993).
 42. M. Pitsikalis, N. Hadjichristidis, G. Di Silvestro, and P. Sozzani, *Macromol. Chem. Phys.*, **196**, 2767 (1995).
 43. J. Allgaier, K. Martin, H. J. Räder, and K. Müllen, *Macromolecules*, **32**, 3190 (1999).
 44. H. L. Hsieh and R. P. Quirk, "Anionic Polymerization: Principles and Applications" Marcel Dekker, New York, 1996, pp 335–347.
 45. D. M. Knauss, H. A. Al-Muallem, T. Huang, and D. T. Wu, *Macromolecules*, **33**, 3557 (2000).
 46. H. Iatrou and N. Hadjichristidis, *Macromolecules*, **26**, 2479 (1993).
 47. T. Higashihara and Hirao, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 4535 (2004).
 48. T. Higashihara, M. Nagura, K. Inoue, N. Haraguchi, and A. Hirao, *Macromolecules*, **38**, 4577 (2005).
 49. A. Mavroudis and N. Hadjichristidis, *Macromolecules*, **39**, 535 (2006).
 50. X. Wang, J. He, and Y. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 4818 (2007).
 51. O. Altintas, G. Hizal, and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, **46**, 1218 (2008).
 52. A. Hirao, S. Loykulant, and T. Ishizone, *Prog. Polym. Sci.*, **27**, 1399 (2002).
 53. A. Hirao, K. Kawasaki, and T. Higashihara, *Sci. Tech. Adv. Mater.*, **5**, 469 (2004).
 54. A. Hirao, K. Kawasaki, and T. Higashihara, *Macromolecules*, **37**, 5179 (2004).
 55. Y. Zhao, T. Higashihara, K. Sugiyama, and A. Hirao, *J. Am. Chem. Soc.*, **127**, 14158 (2005).
 56. T. Higashihara, K. Inoue, M. Nagura, and A. Hirao, *Macromol. Res.*, **14**, 287 (2006).
 57. J. F. Douglas, J. Roovers, and K. F. Freed, *Macromolecules*, **23**, 4168 (1990).
 58. A. Hirao, K. Yamaguchi, K. Takenaka, K. Suzuki, S. Nakahama, and N. Yamazaki, *Makromol. Chem., Rapid Commun.*, **3**, 941 (1982).
 59. A. Hirao, K. Kitamura, K. Takenaka, and S. Nakahama, *Macromolecules*, **26**, 4995 (1993).
 60. A. Hirao, M. Hayashi, and T. Higashihara, *Macromol. Chem. Phys.*, **202**, 3165 (2001).
 61. A. Hirao and T. Higashihara, *Macromolecules*, **35**, 7238 (2002).
 62. A. Hirao, T. Higashihara, M. Nagura, and T. Sakurai, *Macromolecules*, **39**, 6081 (2006).
 63. In addition, small peaks corresponding to dimmers of the original (PSLi)s were always observed between two peaks. They may be formed by the elimination of LiH from PSLi, followed by the addition reaction of another PSLi to the resulting styryl terminus. Such a dimer formation is usually observed by allowing PSLi to stand longer times of 24 h or more times.
 64. J. Roovers, in "Star and Hyperbranched Polymers" M. K. Mishra and S. Kobayashi, Ed., Marcel Dekker, New York, 1999, pp 285–341.
 65. T. Fujimoto, H. Zhang, T. Kazama, Y. Isono, H. Hasegawa, and T. Hashimoto, *Polymer*, **33**, 2208 (1992).
 66. H. Hückstädt, V. Abetz, and R. Stadler, *Macromol. Rapid Commun.*, **17**, 599 (1996).
 67. S. Sioula, Y. Tselikas, and N. Hadjichristidis, *Macromolecules*, **30**, 1518 (1997).
 68. R. P. Quirk, T. Yoo, Y. Lee, J. Kim, and B. Lee, *Adv. Polym. Sci.*, **153**, 67 (2000).
 69. A. Zioga, S. Sioula, and N. Hadjichristidis, *Macromol. Symp.*, **157**, 239 (2000).
 70. S. Reutenauer, G. Hurtrez, and P. Dumas, *Macromolecules*, **34**, 755 (2001).
 71. M. Nasser-Eddine, S. Reutenauer, C. Delaite, G. Hurtrez, and P. Dumas, *J. Polym. Sci., Part A: Polym. Chem. Ed.*, **42**, 1745 (2004).
 72. R. S. Kanga, T. E. Hogen-Esch, E. Randrianalimanana, A. Soum, and M. Fontanille, *Macromolecules*, **23**, 4235 (1990).
 73. R. S. Kanga, T. E. Hogen-Esch, E. Randrianalimanana, A. Soum, and M. Fontanille, *Macromolecules*, **23**, 4241 (1990).
 74. D. Reibel, R. Nuffer, and C. Mathis, *Macromolecules*, **25**, 7090 (1992).
 75. Y. Zhao, T. Higashihara, K. Sugiyama, and A. Hirao, *Macromolecules*, **40**, 228 (2007).



Akira Hirao was born in Tokushima, Japan in December 4th, 1947. He received his Doctorate Degree from Tokyo Institute of Technology, Japan in 1975. During 1975–1977, he joined the group of Professor Charles U. Pittman, Jr. as a postdoctoral research fellow at the University of Alabama, USA. His career at Tokyo Institute of Technology has included being Assistant Professor (1977), Associate Professor (1983), and Full Professor (1997). His research covers living anionic polymerization of functional monomers, precise synthesis of chain-end or in-chain multi-functionalized polymers, and precise synthesized specially shaped polymers including regular and asymmetric star-branched, comb-like, dendrimer-like star-branched, exact graft polymers by means of living anionic polymerization.



Tomoya Higashihara was born in Kagawa, Japan in March 10th, 1977. He received his Bachelor (2000), Master (2002), and Doctorate Degrees (2005) in polymer chemistry under the supervision of Professor Akira Hirao at Tokyo Institute of Technology, Japan. During 2004–2006, he received a Japan Society for Promotion of Science (JSPS) fellowship. During 2005–2008, he joined the group of Professor Rudolf Faust as a postdoctoral research fellow at University of Massachusetts Lowell, USA. Then he became Assistant Professor at Tokyo Institute of Technology in 2008. His research covers precise synthesis of regular and asymmetric star-branched polymers with well-defined structures *via* an iterative approach based on living anionic polymerization and novel block copolymers for medical applications by combination of living anionic and living cationic polymerizations.



Kyouichi Inoue was born in Gunma, Japan in April 24th, 1981. He received his Bachelor (2004) and Master Degrees (2006) in polymer chemistry under the supervision of Professor Akira Hirao at Tokyo Institute of Technology, Japan. He is currently a doctor course graduate student at Tokyo Institute of Technology, and doing research on precise synthesis of multi-component asymmetric star-branched polymers with well-defined structures *via* an iterative approach based on living anionic polymerization under the supervision of Professor Akira Hirao.



Mayumi Hayashi was born in Kanagawa, Japan, in September 10th, 1971. She received her Bachelor (1995), Master (1997), and Doctorate degrees (2000) in polymer chemistry under the supervision of Professor Akira Hirao at Tokyo Institute of Technology, Japan, where she received a Research Fellowship for Young Scientists of the Japan Society for the Promotion of Science (1998–2000). She joined Sumitomo Chemical Co., Ltd. in Japan and is now a Research Associate in Petrochemical Research Laboratory. Her current research subject is the development of new S-SBR for energy-saving tires.