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Precise Synthesis of Star-Branched Polymers by Means of Living Anionic Polymerization Using 1,1-Bis(3-chloromethylphenyl)ethylene

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Summary: The syntheses of three- and four-arm star-branched polymers by a new convenient methodology using 1,1-bis(3-chloromethylphenyl)ethylene are described. The methodology involves only two sets of reactions: an addition reaction of living anionic polymer to 1,1-bis(3-chloromethylphenyl)ethylene and a linking reaction of the intermediate polymer anion with ω-4-bromobutyl-functionalized polymer. All combinations of well-defined three- and four-arm stars comprised of polystyrene and polyisoprene segments were successfully synthesized by this methodology.

Keywords: anionic polymerization; benzyl halide; 1,1-diphenylethylene; star polymers; well-defined architectures

Introduction

In recent years, we have developed new methodologies for the synthesis of regular and, in particular, asymmetric star-branched polymers based on living anionic polymerization in combination with functionalized 1,1-diphenylethylene (DPE) derivatives.[1-12] The first example is 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**).[9] Its *tert*-butyldimethylsilyloxymethylphenyl group is stable toward carbanionic species such as organolithiums and living anionic polymers of styrene and 1,3-diene monomers and quantitatively transformable into highly reactive benzyl halides. By reacting living anionic polymers with **1**, followed by transformation to benzyl halides, novel chain-functionalized polymers with a definite number of benzyl halide moieties have been successfully synthesized. A variety of star-branched polymers with well-defined structures could be synthesized by coupling such benzyl halide-chain-functionalized polymers with living anionic polymers.

The second DPE derivative useful for the synthesis of star-branched polymer is 1-[4-(4-

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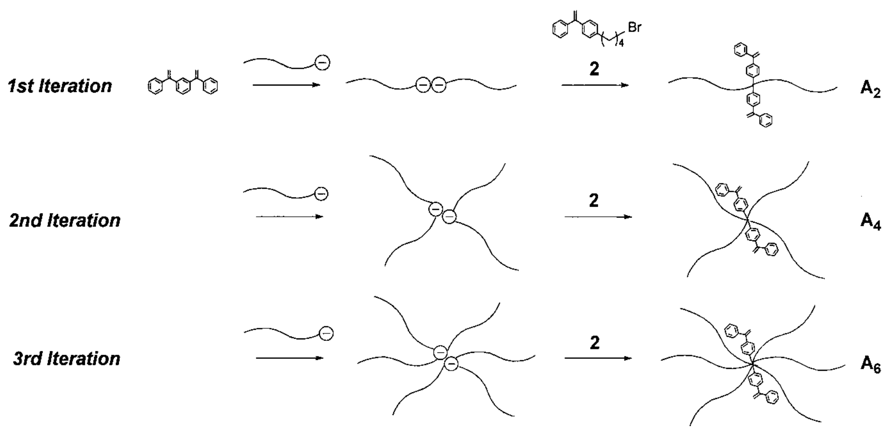
bromobutyl)phenyl]-1-phenylethylene (**2**).[6,10] The DPE function is readily introduced either at chain-ends or in chains by the reaction of **2** with living anionic polymers and polymer anions. The resulting DPE-chain-functionalized polymers have been utilized as precursor polymers to synthesize star-branched polymers. Furthermore, we have demonstrated that regular as well as asymmetric star-branched polymers can be successively synthesized by repeating the reaction of DPE-chain-functionalized polymer with living anionic polymer and the subsequent introduction of DPE function by the reaction of **2** with the generated anion as illustrated in Scheme 1.



Scheme 1. Synthesis of A_2, A_4, and A_6 star-branched polymers based on an iterative methodology by using **2**.

Herein, we report on a new convenient methodology based on living anionic polymerization in combination with a new DPE derivative, 1,1-bis(3-chloromethylphenyl)ethylene (**3**), developed for the synthesis of three- and four-arm star-branched polymers comprised of two kinds of polymer segments.

Experimental Section

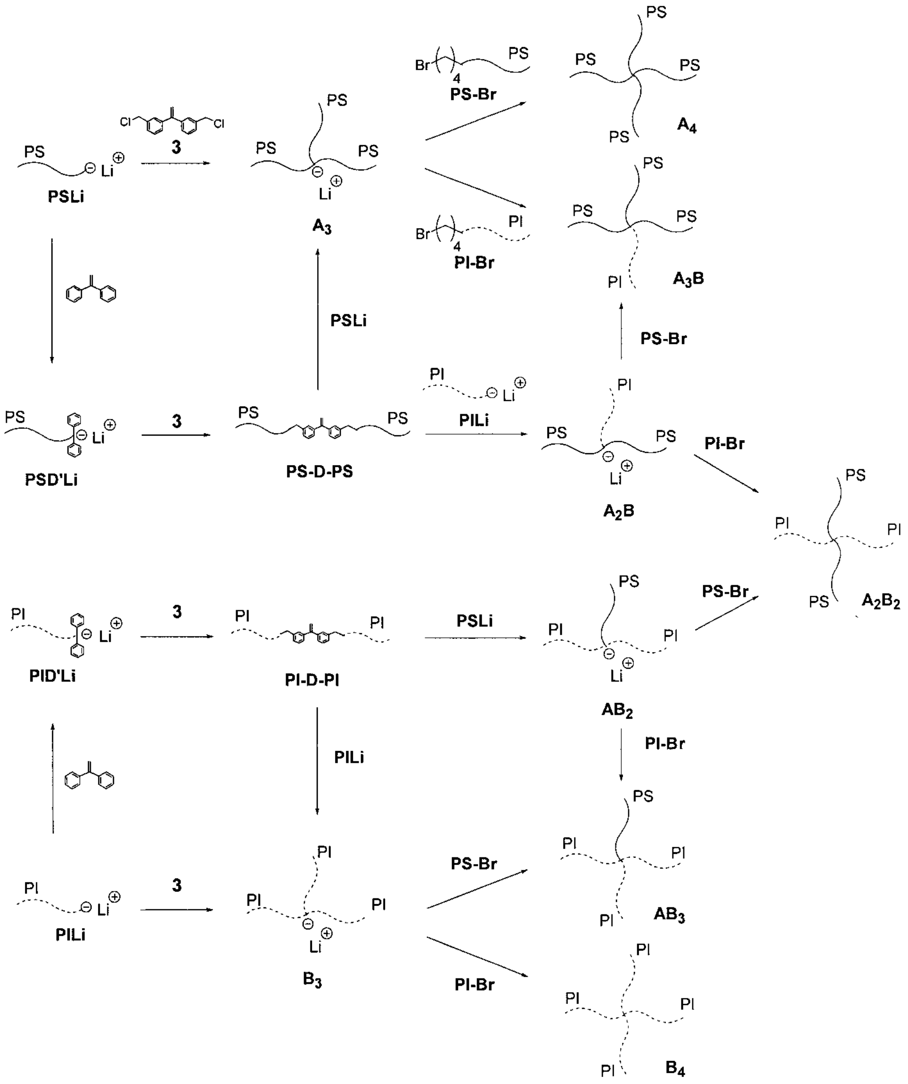
Materials. 1,1-Bis(3-chloromethylphenyl)ethylene (**3**) was synthesized according to the procedure previously reported by us.[13] All chemicals and solvents (> 98% from Aldrich, Japan) were purified as described elsewhere or used as received. ω-4-Bromobutyl-functionalized polystyrene and polyisoprene (designated as PS-Br and PI-Br) were synthesized by the procedure previously reported by us.[14]

Measurements. Both ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Size-exclusion chromatograms (SEC) were generated in THF with a TOSOH HLC-8020 at 40 °C with UV (254 nm) or refractive index detection. Fractionation by SEC was performed at 40 °C using a TOSOH HLC-8020 type fully automatic instrument. The measurements for static light scattering (SLS) were performed with an Ohtsuka Electronics SLS-600R instrument equipped with a He-Ne laser (633 nm) in THF at 25 °C. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instruments in benzene at 40 °C with a highly sensitive thermoelectric couple and with equipment of very exact temperature control.

Procedures. Anionic polymerizations and reactions were carried out under high vacuum conditions (10^{-6} torr) using the usual break-seal technique. Polystyryllithium (PSLi) and polyisoprenyllithium (PILi) were prepared by the living anionic polymerization of styrene with *sec*-BuLi in THF at –78 °C for 0.5 h or isoprene with *sec*-BuLi in heptane at 40 °C for 2 h. In certain cases, PSLi and PILi were end-capped with a 1.5-fold excess of DPE in THF at –78 °C for 0.5 h and 12 h, respectively. They have been designated as PSD'Li and PID'Li. The reaction of living polymer with **3** was usually carried out in THF at –78 °C for 1 ~ 24 h. The resulting intermediate polymer anion was *in-situ* linked with ω-4-bromobutyl-functionalized polymer in THF at –78 °C for 12 h. Prior to the linking reaction, dibutylmagnesium (*ca.* 2 mol-%) was added to kill impurities in the ω-functionalized polymer. A 1.2 -fold excess of PSLi toward each reaction site of **3** was used in the reaction. A 1.2-fold excess of PS-Br or PI-Br was used toward total PSLi in the linking reaction. Each arm segment of star-branched polymers was designed to be *ca.*10 kg/mol in molecular weight. The resulting star-branched polymers were precipitated in methanol and isolated in more than 90% yields by fractional precipitation using cyclohexane-hexanes or fractionation with SEC. They were purified by twice reprecipitating and freeze-drying from their dry benzene solutions for 24 h.

Results and Discussion

Synthesis of Four-Arm Star-Branched Polymers. As illustrated in Scheme 2, we have developed a new convenient methodology using **3** for the synthesis of four-arm star-branched



Scheme 2. Convenient synthesis of star-branched polymers by using **3**.

polymers comprised of polystyrene (PS) and polyisoprene (PI) segments. Either PSLi or PSD'Li was reacted with **3** in THF at –78 °C in order to examine the reactivity of **3**. PSLi underwent reactions with both the chloromethyl and vinylene groups of **3** to afford an intermediate three-armed star-branched polymer anion, while PSD'Li reacted only with the chloromethyl group of **3** as expected. In-chain-functionalized PS with a DPE moiety, PS-D-PS, was quantitatively obtained in the latter reaction. Thus, the differentiation between these two reaction sites of **3** is possible by using PSLi and PSD'Li.

A four-arm A_4 regular star-branched polystyrene was synthesized by a one-pot reaction involving the reaction of three equivalents of PSLi with **3** followed by the *in-situ* linking with PS-Br. Similarly, an asymmetric A_3B star was obtained by the use of PI-Br instead of PS-Br in the *in-situ* linking reaction. The SEC trace of the reaction mixture in the A_4 star synthesis shown in Figure 1(A) consisted of three peaks. They appear to correspond the objective A_4 star-branched polymer, a coupled product from PS-Br and the unreacted PSLi, and the unreacted PS-Br used in excess.

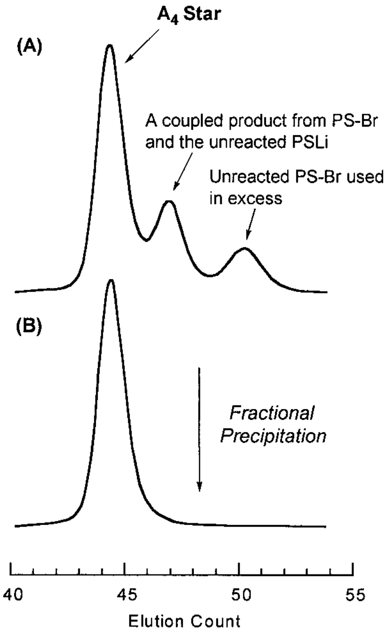


Figure 1. SEC RI traces of the polymers obtained by the addition reaction of three equivalents of PSLi with **3** followed by the in-situ linking with PS-Br. (A): before fractionation, (B): after fractionation.

A very similar SEC profile was also observed in the synthesis of an A_3B star. Overall yields of the star-branched polymers were estimated to be *ca.* 95% by comparing SEC peak areas (UV detector). These stars were isolated in *ca.* 90% yields using fractionation (see Figure 1(B)) and characterized by ^1H and ^{13}C NMR, FT-IR, SEC, and SLS. The results are summarized in Table 1.

Table 1. Synthesis of A_4, A_3B, A_2B_2, AB_3, and B_4 Star-Branched Polymers.

	M_n (kg/mol)				M_w (kg/mol)			M_w/M_n	Composition (wt-%) PS/PI	
type	calcd	SEC[a]	^1H NMR	VPO	Calcd[b]	SLS[c]	d*n*/d*c*[c] (mL/g)	SEC[a]	calcd	^1H NMR
A_4	43.3	35.4	42.5	41.3	44.6	46.8	0.188	1.03	-	-
A_3B	43.5	37.9	43.0	43.3	45.7	44.2	0.170	1.05	79/21	81/19
A_2B_2	40.8	42.8	40.0	41.2	41.6	42.8	0.162	1.02	50/50	51/49
AB_3	40.8	44.1	41.0	40.0	42.4	42.3	0.144	1.04	24/76	26/74
B_4	42.1	38.5[d]	42.7	41.9	43.4	44.0	0.137	1.03	-	-

[a] Estimated from the caribration using polystyrene standards.
[b] Calculated from M_n (calcd) and M_w/M_n (SEC).
[c] Measured in THF at 25 °C.
[d] Estimated from the caribration using polyisoprene standards.

Both A_4 and A_3B stars exhibited sharp monomodal SEC distributions, the M_w/M_n values being 1.03 and 1.05, respectively. Their molecular weights determined by VPO (M_n) and SLS (M_w) were in good agreement with those predicted. The expected structure of the A_3B star was also confirmed by agreement of the [A]/[B] ratio measured by ^1H NMR with that calculated. Thus, two architecturally different stars could be synthesized from the same intermediate A_3 star-branched polymer anion. These stars were also obtained in more than 95% yields by the reaction of PSLi with PS-D-PS, followed by *in-situ* linking with PS-Br and PI-Br, respectively.

In order to synthesize A_2B_2 asymmetric star-branched polymer, PILi was reacted with PS-D-PS, followed by *in-situ* linking with PI-Br. The yield of the objective A_2B_2 star was however only 25% yield even after 168 h because the reaction of PILi with the DPE moiety of PS-D-PS proceeded very sluggishly in THF at –78 °C. On the other hand, PSLi reacted virtually quantitatively with PS-D-PS after 24 h under the same conditions as mentioned above. Thus, the reactivity difference between PSLi and PILi toward the DPE moiety of PS-D-PS is evident.

We have succeeded in synthesizing A_2B_2 star-branched polymer by changing the reaction route. At first, an in-chain-functionalized polyisoprene with DPE moiety, PI-D-PI, was prepared by the reaction of **3** with PID'Li. PSLi efficiently reacted with the PI-D-PI to afford an intermediate AB_2 star-branched polymer anion. By *in-situ* linking of the intermediate polymer anion with PS-Br, an A_2B_2 asymmetric star-branched polymer was successfully obtained in 97% yield. With use of PI-Br instead of PS-Br in the *in-situ* reaction, an AB_3 star could be obtained in 99% yield. As was seen in Table 1, they were well defined in architecture and precisely controlled in chain length.

Again, difficulty arose in the synthesis of B_4 regular star-branched polyisoprene due to the extremely low reactivity of PILi toward PI-D-PI. The reaction was therefore examined in more detail to increase the yield under various conditions: in THF at –78 °C for 14 days and in either heptane or *tert*-butylbenzene in the absence and presence of a small amount of THF at 30 °C for 24 ~ 48 h. Unfortunately, the yields were always low (< 25%). There was no further increase in reaction yield by raising the reaction temperature from –78 °C to –40 °C followed by –20 °C in THF. Instead, undesirable high molecular weight polymers were significantly produced presumably by the attack of PILi on the vinyl side chain of PI. Thus, all attempts were not successful to improve the yield in the reaction of PILi with PI-D-PI.

Surprisingly, PILi reacted efficiently with **3** to afford an intermediate B_3 star-branched polymer anion in *ca.* 85% yield in THF at –78 °C for 24 h. This suggests that PILi reacts predominately with the vinylene group of **3** prior to the reaction of PILi with the two chloromethyl groups that yields less reactive PI-D-PI. A regular B_4 star-branched polyisoprene was obtained by the reaction of PILi with **3** followed by the *in-situ* reaction with PI-Br.[15] Thus, all combinations of well-defined four-arm stars comprising of PS (A) and PI (B) segments could be successfully synthesized by developing the methodology using **3**.

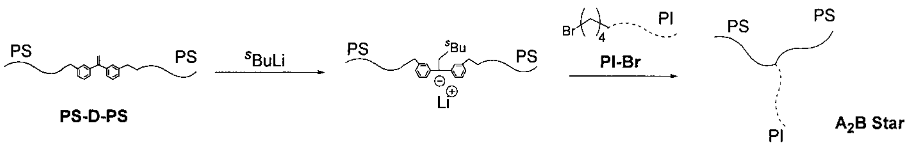
Synthesis of Three-Arm Star-Branched Polymers. Three-arm star-branched polymers were synthesized only by reacting properly living anionic polymers or the DPE-end-capped polymer anion with **3**. For example, a regular A_3 or B_3 star-branched polymer was readily synthesized by the reaction of PSLi or PILi with **3**. The same A_3 star could also be obtained by the reaction of two equivalents of PSD'Li with **3**, followed by reacting with PSLi. Similarly, an AB_2 star was synthesized by reacting successively two equivalents of PID'Li and PSLi with **3**. These results are listed in Table 2.

Table 2. Synthesis of A_3, A_2B, and B_3 Star-Branched Polymers.

	M_n (kg/mol)				M_w (kg/mol)			M_w/M_n	Composition (wt-%) PS/PI	
type	calcd	SEC[a]	^{1}H NMR	VPO	Calcd[b]	SLS[c]	dn/dc[c] (mL/g)	SEC	calcd	^{1}H NMR
A_3	32.6	31.1	32.0	31.5	33.6	34.1	0.187	1.03	-	-
A_2B	30.5	29.7	31.2	30.0	31.4	31.7	0.170	1.03	67/33	69/31
B_3	31.1	28.4[d]	31.7	30.9	31.7	32.5	0.138	1.02	-	-

[a] Estimated from the caribration using polystyrene standards.
[b] Calculated from M_n (calcd) and M_w/M_n (SEC).
[c] Measured in THF at 25 °C.
[d] Estimated from the caribration using polyisoprene standards.

Unfortunately, an A_2B star was synthesized only in 25% yield due to the low reactivity of PILi toward PS-D-PS prepared from PSD'Li and **3**. We have therefore proposed an alternative procedure for the synthesis of A_2B star-branched polymer as illustrated in Scheme 3. An A_2B star could be synthesized in 90% yield by this procedure involving the addition reaction of *sec*-BuLi with PS-D-PS, followed by *in-situ* linking with PI-Br.



Scheme 3. Synthesis of A_2B star-branched polymer.

Conclusions

A simple and convenient methodology for the synthesis of well-defined three- and four-arm star-branched polymers comprising of PS and PI segments has been developed by using living anionic polymers and a new functional DPE derivative, **3**, as a core compound. All possible star-branched polymers, A_4, A_3B, A_2B_2, AB_3, B_4, A_3, A_2B, AB_2, and B_3 could be successfully synthesized. However, one limitation of this methodology is the relative lack of reactivity of PILi toward both PS-D-PS and PI-D-PI. Reaction routes and yields of certain star-branched polymers were indeed influenced by the limitation. Therefore, in order to establish the present methodology using **3** as a general procedure, further experiments should be needed by changing B segment from PILi to another living anionic polymer.

In this study, arm segments of all star-branched polymers synthesized herein were *ca.* 10 kg/mol in molecular weight. If molecular weight of the arm segment is different, a series of asymmetric star-branched polymers whose arms differ in molecular weight such as A_3A', $A_2A'_2$, and even $A_2A'A''$ may possibly be synthesized. In the same sense, the synthesis of four-arm star-branched polymers comprised of three kinds (A, B, and C) of polymer segments is now under investigation.

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[15] In addition to a B_3 star-branched polymer anion, PI-D-PI (~ 10%) and high molecular weight polymers (~ 5%) were also produced in the reaction of PILi with **3**. Therefore, the resulting regular B_4 star-branched polyisoprene was carefully isolated in *ca.* 60% yield by SEC fractionation.