Synthesis of Star-Branched Polymers by Means of Anionic Living Polymerization Coupled with Functional Group Transformation

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Received October 26, 1998; Revised Manuscript Received January 29, 1999

ABSTRACT: To synthesize well-defined regular and heteroarmed star-branched polymers, we have developed a new and versatile methodology based on anionic living polymerization coupled with functional group transformation. The synthetic procedure employed in our methodology involves the following three reaction stages: The first stage is to prepare the precursory polymers with a defined number of methoxymethylphenyl groups by reacting polystyryllithium with specially designed reagents. The methoxymethylphenyl groups thus introduced are quantitatively transformed into chloromethylphenyl groups in the second stage reaction. At the third stage, anionic living polymers are reacted to couple with the chlorinated precursory polymers to afford the desired star-branched polymers. In fact, well-controlled three-, four-, and six-armed star polystyrenes were successfully synthesized by using the above-mentioned procedure. More interestingly, well-defined hetero four-armed ABC_2 and five-armed AB_4 star polymers have been readily obtained simply by changing living polymers to be reacted. The resulting star-branched polymers were isolated by SEC fractionation. Their well-defined and controlled structures were demonstrated by SEC, ^{1}H NMR, light scattering, and viscosity measurements.

Introduction

The star-branched polymer is one of the most typical and well-known branched polymers whose physical properties are unique and quite different from those of linear polymers.[1−5] To elucidate fundamental understanding regarding the effect of chain branching on polymer properties, the synthesis of well-defined star-branched polymers with predictable arm lengths and compositions is essential. For this reason, a variety of useful methods for the synthesis of "regular" star polymers have been reported so far. Among them, the most established method to synthesize regular star polymers with a defined number of arms is considered to be based on the end-coupling reactions of anionic living polymers of styrene and 1,3-dienic monomers with multifunctional chlorosilanes.[6−10] Well-defined star poly(1,3-butadiene)s with up to even 128 arms have been successfully synthesized by this end-coupling reaction.[11]

There has recently been growing interest on more complex type star polymers in which arms differ in either molecular weight or composition, the so-called "heteroarmed" star-branched polymers. They are expected to exhibit more unique and interesting properties and morphologies due to their chain branching as well as their heterogenity of structures. Furthermore, the design and synthesis of such star-branched polymers with well-controlled molecular architectures are of special interest from a synthetic point of view.

Pennisi and Fetters first prepared asymmetric three-armed AA'_2 star polystyrenes and polybutadienes by utilizing the method using chlorosilanes established for synthesis of regular star polymers as mentioned above.[12] In these star polymers, one of the three arms differs in molecular weight from the remaining two arms. Their synthetic approach involved the reaction of polystyryllithium (or poly(1,3-butadienyllithium)) with an excess of trichloromethylsilane followed, after removal of the excess trichloromethylsilane, by adding polystyryllithium with a different molecular weight (or poly(1,3-butadienyllithium)). Mays employed a similar approach to synthesize a well-defined A_2B type heteroarmed star polymer where A and B were polyisoprene and polystyrene, respectively.[13] This methodology has been greatly extended by Hadjichristidis and co-workers to synthesize various heteroarmed star polymers such as A_2B_2, ABC, and ABCD star polymers.[14−18] In such heteroarmed star polymer synthesis by the "chlorosilane" method, the addition order of living polymers in the coupling reaction is usually a dominant factor, since differential reactivities of anionic living polymers are utilized.

Recently, a new methodology combining both termination and initiation reactions of anionic living polymerization has been developed independently by Quirk et al., Fujimoto et al., and Abetz et al. Typically, Quirk and co-workers synthesized a hetero A_2B_2 star polymer by reacting exactly 2 equiv of polystyryllithium with 1,3-bis(1-phenylethenyl)benzene followed by crossover polymerization of 1,3-butadiene in a living manner.[19] Similarly, well-controlled $A_2A'_2$ and $AA'A''$ asymmetric star polystyrenes were synthesized by the same reseach group.[20,21] Fujimoto and co-workers reported the synthesis of a hetero three-armed ABC star polymer by reacting polystyryllithium with the 1,1-diphenylethylene end-functionalized poly(dimethylsiloxane) followed by anionic living polymerization of *tert*-butyl methacrylate with the anion generated at the junction between the poly(dimethylsiloxane) and the polystyrene.[22] Starting from the polystyrene end-functionalized with 1,1-diphenylethylene, Abetz and co-workers synthesized a different type hetero three-armed ABC star polymer where A, B, and C were polystyrene, polybutadiene, and poly(methyl methacrylate), respectively.[23] Very recently, Faust and Bae have first demonstrated the successful synthesis of a A_2B_2 heteroarmed star polymer based on living cationic polymerization. Their synthetic approach is similar to that reported by Quirk et al. mentioned above.[19] It involved the living coupling reaction of

10.1021/ma981673t CCC: $18.00

cationic living polymer of isobutylene with 2,2-bis[4-(1-tolylethenyl)phenyl]propane, followed by the cationic living polymerization of methyl vinyl ether with the generated carbocations.[24]

Thus, well-defined heteroarm star polymers with structural variation can be synthesized to a certain extent to date. However, the methods developed so far have their inherent synthetic problems and limitations. Therefore the development of a new methodology for synthesis of heteroarmed star polymers has still been a very important challenge.

In the present study, we report a new and versatile methodology which permits one to synthesize a variety of both regular and heteroarmed star polymers with well-defined structures. The synthetic procedure employed in our methodology basically involves the following three reaction stages: The first stage is to prepare the precursory polymers functionalized with a defined number of anion-stable methoxymethylphenyl (MOM) groups by reacting an anionic living polymer with specially designed reagents. Then, the MOM groups thus introduced in the polymer chain are quantitatively transformed into reactive chloromethylphenyl groups in the second stage reaction. At the third reaction stage, other living polymers are reacted to couple with the resulting chlorinated polymer to afford the desired heteroarmed star polymer. Throughout the synthetic procedure, we can rationally design the structure of heteroarmed star polymers by changing either the reagent or the reaction condition of the reagent with an anionic living polymer, which will be discussed in detail afterward. More importantly, both heteroarmed and regular star polymers can be advantageously synthesized from the same precursory polymer simply by changing the living polymer to be reacted.

To demonstrate the general utility and versatility of our method for the synthesis of regular and heteroarmed star polymers with well-defined structures, we describe here the synthesis of regular star polystyrenes with three, four, and six arms as well as hetero four-armed ABC_2 and five-armed AB_4 star polymers.

Experimental Section

Materials. Monomers were purified according to the usual procedure. Styrene was finally distilled over dibutylmagnesium (5 mol % was added) on the vacuum line into ampules with break seals that were prewashed with (1,1-diphenylhexyl)lithium in heptane. Similarly, α-methylstyrene and isoprene were distilled over *sec*-butyllithium (*sec*-BuLi) and *n*-butyllithium, respectively, on the vacuum line into ampules with break seals that were prewashed with (1,1-diphenylhexyl)lithium in heptane. Both 1,3-diiodopropane and 1,4-dibromobutane were first distilled over CaH_2 and then distilled over phenylmagnesium chloride on the vacuum line.

1-(4-Bromobutyl)-4-methoxymethylbenzene. This was synthesized by the Li_2CuCl_4-mediated coupling reaction of (4-methoxymethylphenyl)magnesium bromide and 1,4-dibromobutane. To an ice-cooled THF solution (50 mL) containing 1,4-dibromobutane (20.9 g, 96.7 mmol) and Li_2CuCl_4 (0.149 g, 0.68 mmol) was added dropwise (4-methoxymethylphenyl)magnesium bromide in THF (30 mL), prepared from 1-bromo-4-methoxymethylbenzene (6.25 g, 31.1 mmol) and magnesium (1.14 g, 47.4 mmol). The resulting mixture was stirred at 25 °C for 20 h. It was then acidified with 2*N* HCl, extracted with ether, dried over $MgSO_4$. Removal of solvent under reduced pressure followed by fractional distillation yielded 1-(4-bromobutyl)-4-methoxymethylbenzene (5.52 g, 69%) as a colorless liquid: bp 112−113 °C (3.3−3.6 Torr); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 4H, HAr), 4.45 (s, 2H, $-C_6H_4-CH_2-O$), 3.42 (m, 5H, $-OCH_3$, $-CH_2Br$), 2.65 (t, 2H, $-C_6H_4-CH_2-$), 1.78 (m, 4H, $-CH_2CH_2CH_2-CH_2Br$).

1,1-[Bis(3-methoxymethylphenyl)]ethylene (1). 1,1-[Bis(3-methoxymethylphenyl)]ethylene was synthesized by the Grignard reaction of ethyl acetate and (3-methoxymethylphenyl)magnesium bromide, followed by dehydration with *p*-toluenesulfonic acid, according to the usual procedure employed for 1,1-diphenylethylene derivatives. To a stirred solution of the Grignard reagent, prepared from 1-bromo-3-methoxymethylbenzene (4.16 g, 20.7 mmol) and Mg (0.729 g, 30.0 mmol) in THF (30 mL), was added ethyl acetate (1.0 mL, 10.3 mmol) in THF (5 mL) dropwise at 0 °C, and the mixture was stirred for 10 h at 25 °C. Standard workup gave 1,1-[bis(3-methoxymethylphenyl)]ethanol in 78% yield (4.38 g, 16.1 mmol) as a colorless liquid. 1,1-[Bis(3-methoxymethylphenyl)]ethanol thus obtained was then dehydrated with *p*-toluenesulfonic acid (1 mol %) in benzene (30 mL) by refluxing for 2 h. The reaction mixture was basicified with aqueous $NaHCO_3$, extracted with ether, dried over $MgSO_4$, and concentrated. Flash column chromatography on silica gel (hexanes/ethyl acetate, 7/3, v/v) afforded 3.58 g (13.3 mmol, 83%) of **1** as a colorless liquid: 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.29 (m, 8H, $-C_6H_4-$), 5.46 (s, 2H, $C{=}CH_2$), 4.34 (s, 4H, $-CH_2OCCH_3$), 3.38 (s, 6H, $-OCH_3$); 75 MHz ^{13}C NMR ($CDCl_3$) δ 149.9, 141.7, 138.2, 128.3, 127.8, 127.7, 127.2, 114.7, 74.7, 58.2.

Preparation of Anionic Living Polymers of Styrene, α-Methylstyrene, and Isoprene. The polymerizations were carried out under high vacuum condition (10^{-6} Torr) in sealed glass reactors with break seals. The reactors were always prewashed with the initiator solutions after being sealed off from a vacuum line and were used for the polymerizations.

Polystyrylpotassium and polystyryllithium were prepared from the anionic polymerizations of styrene with cumylpotassium and *s*-BuLi in THF at −78 °C for 10 min, respectively. Poly(α-methylstyryl)lithium was prepared from the polymerization of α-methylstyrene with *s*-BuLi in THF at −78 °C for 3 h. Polyisoprenyllithium was prepared from the polymerization of isoprene with *s*-BuLi in heptane at 40 °C for 4 h. In the use of polyisoprenyllithium, the polymerization mixture was cooled to −78 °C after the polymerization, and then an equal volume of THF was added to the mixture at −78 °C prior to the reaction.

These anionic living polymers were used in both first and third reaction stages mentioned as above. In the first reaction stage, living polystyrene was reacted with specially designed reagents to synthesize a variety of precursory polymers functionalized with a defined number of MOM groups. In the third reaction stage, a living polymer of styrene or isoprene was reacted with the chlorinated polymers suitable for the synthesis of regular and heteroarmed star polymers. The conditions of these reactions will be described in the following section.

Preparation of Precursory Polymers. The polystyrene end-functionalized with two MOM groups was prepared by the reaction of polystyryllithium with a 1.2-fold excess of **1** in THF at −78 °C for 1 h. The polystyrene end-functionalized with three MOM groups was prepared by the reaction of polystyryllithium with a 1.2-fold excess of **1** in THF at −78 °C for 1 h, followed by treating with a 1.5-fold excess of 1-(4-bromobutyl)-4-methoxymethylbenzene in THF at −78 °C for 0.5 h. The polystyrene having two MOM groups situated at the middle position of the polymer chain was prepared by the following two reaction steps. First, the polystyrene end-functionalized with two MOM and one iodopropyl groups was prepared by the reaction of polystyryllithium with a 1.2-fold excess of **1** in THF at −78 °C for 1 h, followed by treating with a 10-fold excess of 1,3-diiodopropane in THF at −78 °C for 1 h. This polymer was then reacted with 1.2 equiv of polystyryllithium in THF at −78 °C for 24 h to afford the desired polystyrene with two MOM groups situated at the middle position of the polymer chain. Similarly, the block copolymer of poly(styrene-*b*-α-methylstyrene) with two MOM groups situated at the junction between the blocks was prepared in the above-mentioned reaction in which poly(α-methylstyryl)lithium was used instead of polystyryllithium. The polystyrene end-functionalized with four MOM groups was prepared in the reaction of the end-functionalized polystyrene with two MOM and one iodopropyl groups prepared as mentioned above with the MOM-functionalized 1,1-diphenylalkyllithium, prepared from *s*-BuLi with a 1.2-fold excess of **1** in THF at −78 °C for 1 h. The reaction was carried out with use of a 1.5-fold excess of the organolithium in THF at −78 °C for 24 h. The polystyrene with four MOM groups situated at the middle position of the polymer chain was obtained by the reaction of polystyrylpotassium with a 1.2-fold excess of **1** in THF at −78 °C for 1 h, followed by treatment with 0.5 equiv of 1,3-diiodopropane in THF at −78 °C for 72 h.

The precursory polymers thus prepared were purified by repeated precipitation from THF to methanol three times and freeze-drying three times from their absolute benzene solutions for the next chlorination reaction.

Chlorination Reaction. Chlorination of the MOM groups introduced in the polymers was carried out with a 5-fold excess of BCl_3 for each MOM functionality in CH_2Cl_2 at 0 °C for 2 h. The polymers were precipitated in a mixture of MeOH and 2 *N* HCl (8/2, v/v), and purified by repeated precipitation from THF to MeOH. Under the conditions employed, it was observed by ^1H NMR analysis that chlorination reaction for each of the precursory polymers proceeded quantitatively. They were finally freeze-dried three times from their benzene solutions for the synthesis of star polymers.

Synthesis of Star-Branched Polymers by Coupling Reactions of Chlorinated Polymers with Living Polymers. The desired star polymers were synthesized by coupling reactions of the chlorinated prepolymers prepared as described above with the anionic living polymer of either styrene or isoprene. Coupling reactions were carried out under high vacuum condition by using ca. a 1.5-fold excess of living polymers. With the use of poly(styrylpotassium), the reactions were performed in THF at −78 °C for 48−96 h. With the use of poly(isoprenyllithium), the reactions were performed in a mixture of THF and heptane (1/1, v/v) at −78 °C for 72−120 h. The polymers were precipitated in methanol and characterized by SEC to examine what extent the reactions proceeded.

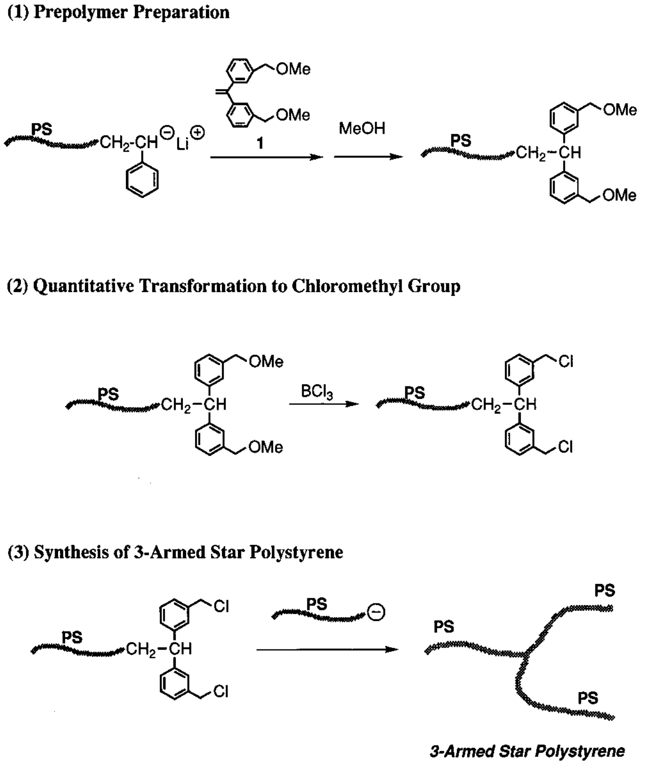
Fractionation of Star Polymers The resulting polymer mixture was fractionated by SEC to remove the homopolymer which was used in excess in the coupling reaction. In the coupling reactions, polymers with higher molecular weights than the desired star-branched polymers and/or lower molecular weight polymers of less branched polymers were often produced. These byproduct polymers were also removed by SEC fractionation.

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX (300 MHz for ^1H and 75 MHz for ^{13}C) in $CDCl_3$. Size-exclusion chromatography (SEC) chromatogram was obtained at 40 °C with a TOSOH HLC 8020 instrument with UV (254 nm) or refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min. Three polystyrene gel columns (TSK_{gel} G4000H_{XL}, G3000H_{XL}, G2000H_{XL} or TSK_{gel} G5000H_{XL}, G4000H_{XL}, G3000H_{XL}) were used. Calibration curves were made to determine $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values with standard polystyrene and polyisoprene samples. Fractionation by SEC was performed at 40 °C using an TOSOH HLC 8020 Type fully automatic instrument equipped with a TSK-G4000H_{HR} colomn (300 mm in length and 7.8 mm in diameter). All runs for fractionation were made with chloroform as an eluent. The concentration of the polymer solution for fractionation was adjusted to 10−20% w/v, depending on the molecular weight of the sample. Laser light scattering measurements were performed with an Ootsuka Electromics DSL-600R instrument in benzene. Intrinsic viscosities of star polymers were measured by Ubbelhode viscometers in toluene at 35 °C.

Results and Discussion

An outline of our methodology using anionic living polymers coupled with functional group transformation from MOM to chloromethyl group has been described in the Introduction. The general utility and versatility of our methodology for the synthesis of well-defined regular star polystyrenes with three, four, and six arms as well as two heteroarmed star polymers is demonstrated in the following sections.

Scheme 1


(1) Prepolymer Preparation

(2) Quantitative Transformation to Chloromethyl Group

(3) Synthesis of 3-Armed Star Polystyrene

Synthesis of three-Armed Star Polymers. For the practical synthesis of star-branched polymers, it is essential to explore the optimal conditions of three reactions employed in the procedure based on our method. We have therefore examined their reaction conditions in detail throughout the synthesis of a three-armed star polystyrene as illustrated in Scheme 1.

The first reaction stage is to prepare the prepolymer suitable to form a three-armed star polystyrene. It was obtained by reacting poly(styryllithium) with a 1.2-fold excess of 1,1-di(3-methoxymethylphenyl)ethylene (**1**) in THF at −78 °C for 1 h. Upon addition of **1** to poly(styryllithium) an immediate color change for orange-red to dark red occurred, indicating rapid generation of the 1,1-diphenylalkyl anion derived from **1**. The color disappeared immediately by quenching with degassed methanol.

The ^1H NMR spectrum of the resulting polymer showed clearly two characteristic resonances at 3.2 and 4.3 ppm assigned to methyl and methylene protons of the MOM group. These resonances appeared as multiplets. It was observed by integration ratio of these peaks at 3.2 and 4.3 ppm with that at 0.7 ppm for methyl protons of the initiator (*s*-BuLi) residue in this spectrum that two MOM groups were quantitatively introduced into polystyrene. The $\bar{M}_n$s of the precursory polystyrenes end-functionalized with two MOM groups prepared here ranged from 2400 to 6000. The results are summarized in Table 1. As described later, this reaction always provides access to various precursory polystyrenes that allow synthesis of all the star polymers synthesized in this study.

Table 1. Synthesis of Polystyrenes End-functionalized with Two Methoxymethyl Groups by Reaction of Polystyryllithium with 1,1-[Bis(3-methoxymethyl)phenyl]ethylene (1) in THF at −78 °C for 1 h[a]

amount of *s*-BuLi, mmol	amount of styrene, mmol	amount of **1**, mmol	polymers[b] $\bar{M}_n$ (calcd)	$\bar{M}_n$ (obsd)	$\bar{M}_w/\bar{M}_n$
0.460	11.0	0.660	2700	2400	1.10
0.440	11.0	0.590	2800	2600	1.09
0.258	12.0	0.362	5200	5100	1.04
0.362	18.3	0.419	5600	6000	1.07

[a] Yields of polymers: 100 % in all cases. [b] Functionality of each polymer sample is 2.00 ± 0.05.

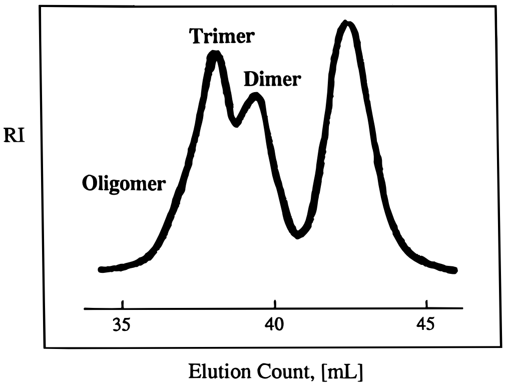


Figure 1. SEC curve of the reaction products obtained by the reaction of polystyryllithium with **1** in benzene at 30 °C.

Similar to the reactions of 1,1-diphenylethylene derivatives with organolithium compounds previously reported, **1** reacted quantitatively with polystyryllithium only in a monoaddition manner. No oligomerization of **1** was observed to occur in THF at −78 °C up to 12 h. When the mixture was allowed to stand for 24 h, however, a small but detectable amount (ca. 8%) of high molecular weight shoulder, which seemed double the molecular weight of the parent polymer, was observed in the SEC curve of the resulting polymer. A more serious problem was caused in the reaction of **1** with polystyryllithium in benzene at 30 °C for 1 h. The benzene solution immediately turned dark red upon adding **1**, similar to the case in THF. It was however observed from the SEC of the resulting polymer terminated after 1 h that rather large quantities of the dimeric, trimeric, and even higher oligomeric products of the starting living polystyrene were formed as shown in Figure 1. The degree of functionalization in these product mixtures was determined to be 60% by ^{1}H NMR analysis. Accordingly, the MOM groups of **1** were not stable in benzene at 30 °C and undesired coupling reactions among the polymers apparently occurred. We are now considering the anion attack on the benzyl carbon of **1** as a side reaction candidate, although direct evidence is not available at the present time.

In the second reaction the MOM groups are quantitatively transformed into highly reactive chloromethyl (CM) groups. The chlorination reaction of the two MOM groups at the polymer chain end was carried out with BCl_3 in CH_2Cl_2 at 0 °C for 2 h. ^{1}H NMR of the product showed that multiplets at 3.2 and 4.3 ppm were completely replaced by a new resonance at 4.45 ppm corresponding to chloromethyl protons. The SEC traces exhibited the same narrow molecular weight distribution as the precursory polystyrene; therefore, it is assumed that there is almost no change in the polymers before and after the chlorination reaction. Thus, the use of BCl_3 proved to be satisfactory.

The chlorination reaction with BCl_3 appears to be sensitive to the reaction conditions. In particular, the choice of reaction temperature is critical. For example, keeping the reaction temperature at 10 °C or above led to formation of undesired high molecular weight products (ca. 10% or more in some cases) possibly resulting from a Friedel−Crafts reaction among the polymer chains, which were essentially troublesome for further reaction. Meanwhile, the reaction proceeded sluggishly at −20 °C and was incomplete after 2 h. Also, high molecular weight byproducts were produced for longer reaction times.

For the next coupling reaction with anionic living polymers, the chlorinated polymer was purified carefully by repeated precipitation and freeze-drying from the absolute benzene solution.

In the third reaction, living polystyrene with two CM groups was reacted to form a three-armed star polystyrene. Similar coupling reactions of anionic living polymers with 1,2,4,5-tetrakis(chloromethyl)benzene and hexakis[*p*-(chloromethyl)phenyl]benzene have been previously reported,[25−27] and star-branched polymers with more and less arms than the theoretical ones were produced. This may be caused by competitive side reactions such as a metal−halogen exchange reaction and/or a single-electron-transfer reaction followed by coupling reactions between the generated intermediates. Several attempts were made by changing reaction variables to suppress or minimize these competitive side reactions. For example, it was reported that, for the lithium countercation, a solvent mixture of benzene and THF (ca. 1/1, v/v) and elevated temperature are favored. The use of potassium countercation also resulted in the same effect in these reactions.

We have examined the reaction of living polystyrene with two CM terminal functionalities of the polystyrene under various conditions. In all the coupling reactions, about 1.2−1.5 equiv of living polymer to the CM group were used. The $\bar{M}_n$s of both living polystyrene and the polystyrene end-functionalized with two CM groups were adjusted to be 5000 as much as possible.

At first, poly(styrylpotassium) was used in the coupling reaction, and the reaction mixture was allowed to stand in THF at −78 °C for 48 h. An SEC trace of the reaction mixture shows it to consist mainly of two sharp peaks which correspond to polystyrenes with $\bar{M}_n$s of 15000 and 5000, respectively, as can be seen in Figure 2. Obviously, the coupling reaction proceeded smoothly in a desired manner to produce a three-armed star polystyrene in a near quantitative yield. However, a small low molecular weight tail was also observed between the peaks of the three-armed star polystyrene and unreacted and excess polystyrene, the amount being less than 5% based upon peak areas. It is probably ascribed to the presence of dimeric product. Such a small peak was still observed even by either employing a longer reaction time to 168 h or using polystyrylpotassium in a 3-fold excess. Therefore, the type of the intermediate dimer leading to the three-armed star polymer seems to be unlikely. This is also supported by the fact that ^{1}H NMR of the polymer mixtures showed no chloromethyl groups at all within the analytical limit. The dimer may possibly be byproduct dimers produced by the above-mentioned side reactions such as K−Cl

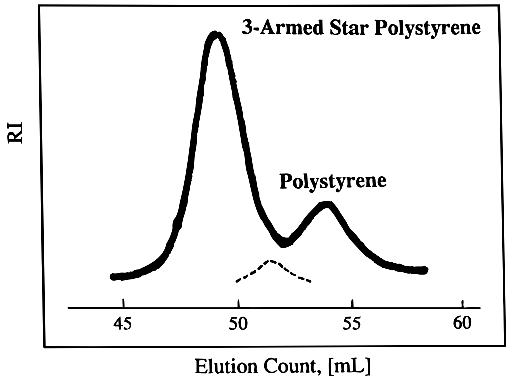


Figure 2. SEC curve of the resulting polymer mixture obtained by the coupling reaction for the synthesis of three-armed star-branched polystyrene in THF at −78 °C.

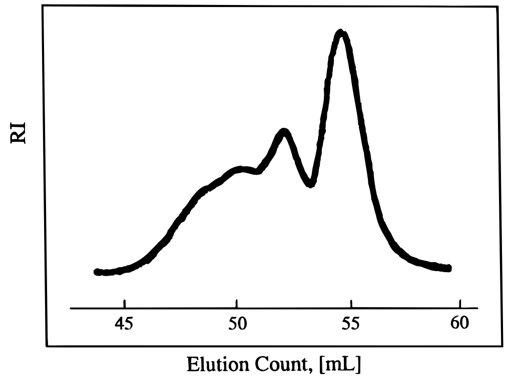


Figure 3. SEC curve of the resulting polymer mixture obtained by the coupling reaction in benzene at 30 °C.

exchange and/or single electron-transfer reactions, followed by coupling among the generated intermediates.

A very similar result was obtained by use of poly(styryllithium) instead of poly(styrylpotassium) in THF at −78 °C for 48 h. At the present time, we have not been successful in suppressing the side reactions completely. Estimated from SEC traces, dimers of ca. 5% or less were usually formed, although apparently this was not a serious problem as previously reported. On the other hand, higher molecular weight polymers with more than three arms were not observed under the conditions employed here.

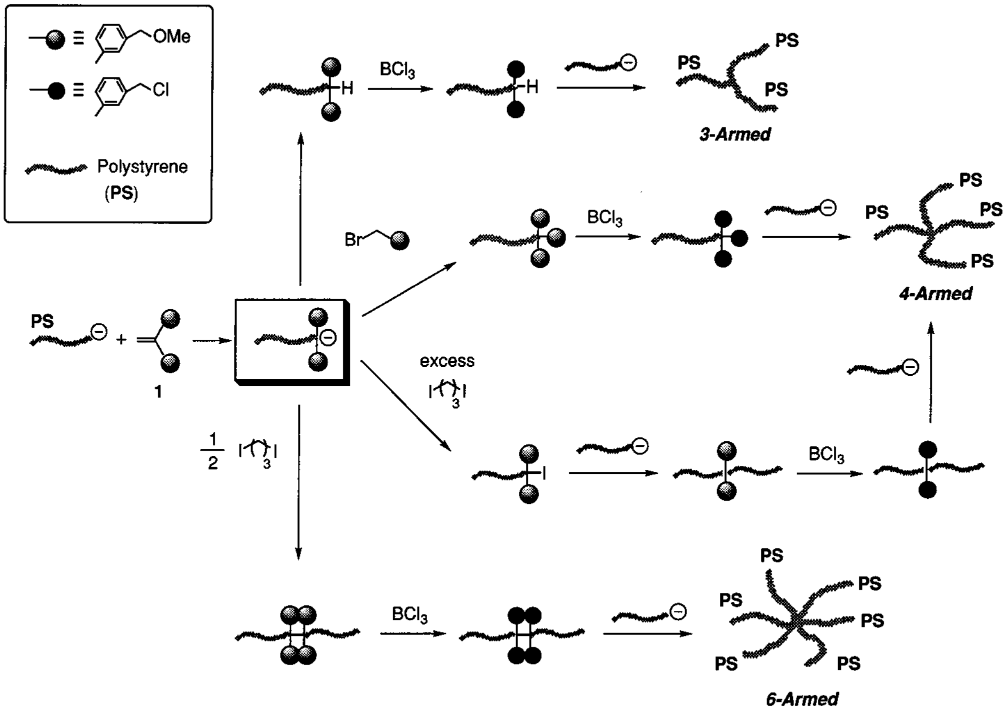
Interestingly, poly(isoprenyllithium) was found to couple efficiently with the polystyrene with two terminal CM groups in a THF−heptane mixture (1/1, v/v) at −78 °C for 72 h. In this case, the product is a hetero three-arm AB_2 star polymer. It was observed from the SEC trace that a small amount of dimer (ca. 5%) was also produced.

In contrast, when the reaction was conducted in benzene at 30 °C in the presence of TMEDA as an additive, polymers with more and less arms were produced in considerably greater amounts as can be seen in Figure 3. On the basis of the results, the coupling reactions of anionic living polymers with the chlorinated precursory polymers for the synthesis of other star polymers will be carried out in THF (or THF−heptane mixture) at −78 °C.

Synthesis of four-Armed Star Polystyrenes. The reaction sequence for the synthesis of a four-armed star polystyrene is illustrated in Scheme 2. At first, a prepolymer having three MOM groups at the chain end was prepared by reacting poly(styryllithium) with **1** in THF at −78 °C for 1 h, followed by treating with 1-(4-bromobutyl)-4-methoxymethylbenzene in THF at −78 °C for 0.5 h. The product had a symmetrical SEC distribution composed of a single sharp peak ($\bar{M}_n$ = 5500, $\bar{M}_w/\bar{M}_n$ = 1.05). The degree of end-functionalization was 3.10 ± 0.10 based on the ^{1}H NMR spectrum, indicating that the reaction was quantitative. Chlorination of the MOM groups with BCl_3 proceeded also quantitatively in CH_2Cl_2 at 0 °C for 2 h.

With the polystyrene with three CM groups in hand, a four-armed star polystyrene was synthesized by treating with a 1.5-fold excess of polystyrylpotassium in THF at −78 °C for 48 h. As can be seen in Figure 4,

Scheme 2



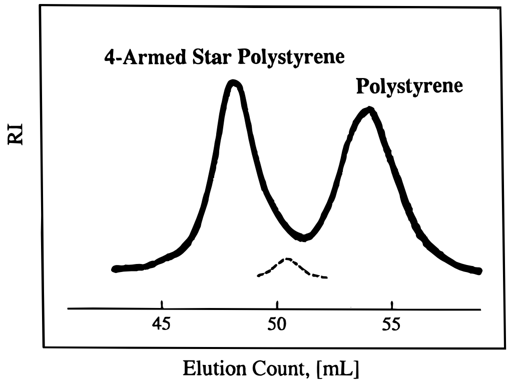


Figure 4. SEC curve of the resulting polymer mixture obtained by the coupling reaction for the synthesis of four-armed star-branched polystyrene in THF at −78 °C.

Table 2. Synthesis of four, four-, and six-Armed Star Polymers

	star polymer			
type (arms)[a]	$\bar{M}_n$(calcd)	$\bar{M}_n$(SEC)	$\bar{M}_n$(SLS + SEC)[b]	$\bar{M}_w/\bar{M}_n$
AA'_3 (4)	22 000	19 000	24 000	1.04
$AA'A''_2$ (4)	20 000	16 000	22 000	1.05
$A_2A'_4$ (6)	32 000	26 000	33 000	1.04

[a] The $\bar{M}_n$s of all precursory polystyrenes and polystyrylpotassium used as arm segments ranged from 4800 to 5400. $\bar{M}_w/\bar{M}_n < 1.05$. [b] The $\bar{M}_n$s were determined from the values of $\bar{M}_w$ by SLS and $\bar{M}_w/\bar{M}_n$ by SEC.

the coupling reaction proceeded well, although a small amount (ca. 3%) of the formation of byproducts with less than four arms is observed in the SEC curve of the resulting polymer mixture. The $\bar{M}_n$ of the resulting four-armed star polystyrene estimated by SEC using standard polystyrene calibration was somewhat lower than the calculated value (19 000 vs 22 000). This suggests the branched structure of the resulting polymer. The four-armed star polymer can be isolated by SEC fractionation and characterized later (see Tables 2 −4).

A four-armed star polystyrene could also be synthesized by an alternative procedure as illustrated in Scheme 2. In this procedure, we have prepared a different type prepolymer. The living end-functionalized polystyrene with two MOM groups was prepared from poly(styryllithium) and **1**, and then the product was reacted with a 10-fold excess of 1,3-diiodopropane to prepare the polystyrene with two MOM groups and one iodopropyl group. The degrees of both end-functionalizations for MOM and iodopropyl groups were nearly quantitative as quantified from the ^{1}H NMR spectrum. A precursory polymer was obtained by reacting this polymer with a 1.2-fold excess of poly(styryllithium) separately prepared. It was, without fractionation, treated with BCl_3 to make the polystyrene having two CM groups situated at the middle of the polymer chain.

Finally, two polystyrene arms were introduced by reacting the polystyrene having two CM groups with a 2.5-fold excess of poly(styrylpotassium). The coupling reaction proved to proceed slowly and was incomplete under our usual conditions in THF at −78 °C for 48 h. It was observed from the SEC trace that greater than 20% amounts of polystyrenes with two and probably three arms still remained in the resulting polymer mixture. The SEC chromatogram was shown in Figure 5. This is presumably a consequence of steric hindrance at the vicinity of the CM groups situated at the middle position of the polymer chain.

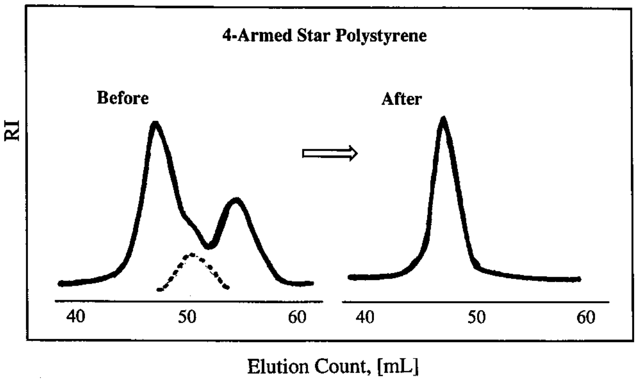


Figure 5. SEc curves of four-armed polystyrenes before and after fractionation.

Both four-armed star polystyrenes synthesized according to Schemes 2 and 3 were isolated by SEC fractionation. They were characterized by SEC and static light scattering (SLS) measurements. These data are listed in Table 2. The fractionated polymers possessed quite narrow molecular weight distributions, 1.04 and 1.05, respectively. Although their $\bar{M}_n$s estimated by SEC are lower than those calculated as expected, the $\bar{M}_n$s determined from both $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ values by SLS and SEC agreed well with those calculated. These results clearly indicate well-controlled structures of the product four-armed star polystyrenes. Further evidence for the branched structure by their viscosity measurements will be discussed later.

Synthesis of six-Armed Star Polystyrene. The synthetic procedure for a six-armed star polystyrene was also illustrated in Scheme 2. In this approach, a polystyrene having four MOM groups at the middle of the polymer chain is required as a precursory polymer. It was prepared by the reaction of 1,3-diiodopropane with 2 equiv of living functionalized polystyrene with two MOM groups, prepared from polystyryllithium and **1**, in THF at −78 °C for 72 h. In this reaction, however, a small quantity of unreacted starting polystyrene was a contaminant in the product, from the SEC trace, since perfect stoichiometry of the reagents was not applied in the reaction.

The resulting prepolymer was used in chlorination reaction with BCl_3, without fractionation, followed by coupling with a 1.8-fold excess of polystyrylpotassium in THF at −78 °C for 96 h. The SEC trace of the six-armed star polymer showed that the product quality was satisfactory. It was, however, observed that there was a small amount of (ca. 10%) high molecular weight shoulder corresponding to the polystyrenes with more than six arms. Furthermore, a small quantity (ca. 8%) of the polymers with less than six arms was also observed. A six-armed star polystyrene was isolated by SEC fractionation and characterized by SEC and SLS, respectively. The results are also summarized in Table 2.

The fractionated six-armed star polystyrene exhibited a quite narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.04) and a $\bar{M}_n$ value of 26 000 by SEC measurement. The $\bar{M}_n$ value was lower than calculated value (32 000). The absolute $\bar{M}_w$ was obtained by SLS to be 34 000. The $\bar{M}_n$ determined by using the $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ was 33 000 and agreed very well with calculated value of 32 000. These results are consistent with essentially the successful synthesis of the six-armed star polystyrene with a well-controlled structure.

Scheme 3

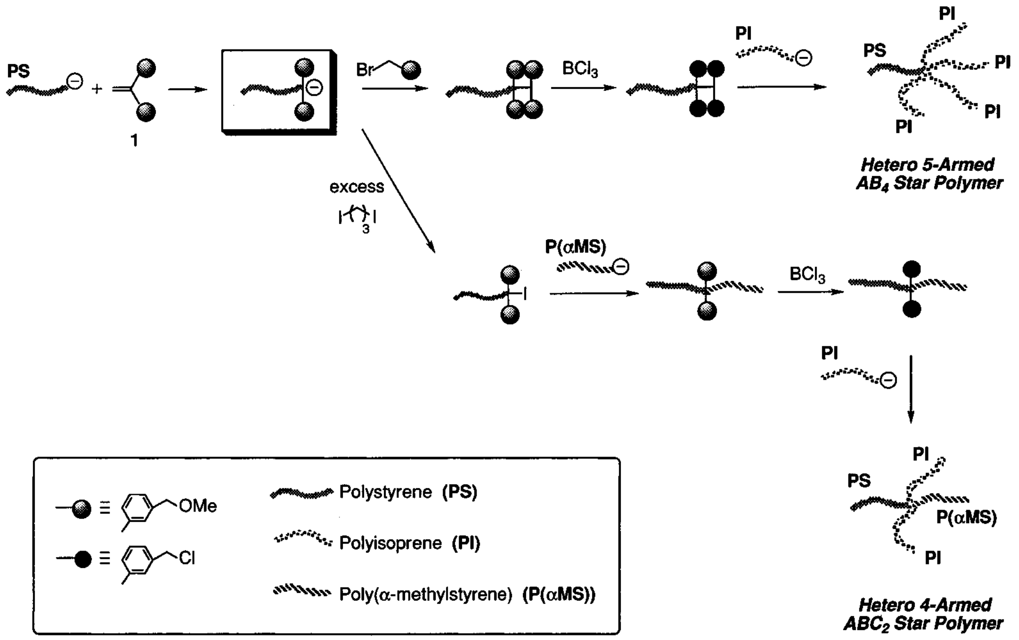


Table 3. Experimental and Theoretical g' for four-, four-, and six-Armed Star Polystyrenes

type (arms)	experimental g' [a]	theoretical g' [b]
AA'_3 (4)	0.67	0.73
$AA'A''_2$ (4)	0.66	0.73
$A_2A'_4$ (6)	0.52	0.57

[a] Obtained in toluene at 35 °C. [b] Calculated from the appropriate equation: $g' = [(3f - 2)/f^2]^{0.58}[0.724 - 0.015(f - 1)/0.724]$.

Table 4. Data for All Molecular Weights of four-, four-, and six-Armed Star Polystyrenes

type (arms)	$\bar{M}_n$ (calcd)	$\bar{M}_n$ (SEC)	$\bar{M}_w$ (SLS)	$\bar{M}_n$ (SLS + SEC)[a]	molecular weight from equations[b]
AA'_3 (4)	22 000	19 000	25 000	24 000	22 000
$AA'A''_2$ (4)	20 000	16 000	24 000	23 000	22 000
$A_2A'_4$ (6)	32 000	26 000	34 000	33 000	35 000

[a] Determined from $\bar{M}_w$(SLS) and $\bar{M}_w/\bar{M}_n$(SEC). [b] Obtained by the Mark–Houwink relationships. K and a for four- and six-armed star polystyrenes were 7.4×10^{-3} and 0.73 and were 5.8×10^{-3} and 0.726, respectively.

Characterization of four- and six-Armed Star Polystyrenes by Viscosity Measurements. It is well-known that one of the most useful method to characterize branching architecture is the measurement of the intrinsic viscosity. Therefore, the intrinsic viscosities of the two kinds of four-armed and six-armed star polystyrenes synthesized here were measured in toluene at 35 °C. Consequently, the g' value defined by the intrinsic viscosity ratio of the star branched to the corresponding linear polymer was determined for each polymer. These experimental g' values as well as theoretically calculated ones by Roovers, Douglas, and Freed[28–30] are listed in Table 3.

Strictly speaking, our samples are not regular A_4 and A_6 type star-branched polymers. They are asymmetric AA'_3, $AA'A''_2$, and $A_2A'_4$ star-branched polymers, although each of their arm molecular weights is very close to 5000. Therefore, experimental g' values of our samples contains some deviation from the real definition. Nonetheless, the results has provided valuable insight into the branching structures of our polymer samples. As can be seen in Table 3, the experimental g′ values for four-, four-, and six-armed star polymers are in fair agreement with those theoretically calculated. It is indicated from the results that our polymer samples have expectedly four-, four-, and 6-branched structures, respectively.

Molecular weights of our four-, four-, and six-armed star polystyrenes can also be estimated by introducing their viscosity values into the Mark–Houwink relationships for well-defined four- and six-armed star polystyrenes reported previously.[31,32] The results are summarized in Table 4. The values of $\bar{M}_n$ calculated, $\bar{M}_n$ by SEC, $\bar{M}_w$ by SLS, and $\bar{M}_n$ determined from the $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ values by SLS and SEC are also listed in this table as references. The molecular weights estimated by the Mark–Houwink relationships are agreed well with those values except for $\bar{M}_n$s by SEC. Again, these results indicate strongly that our samples are four-, four-, and six-armed star-branched polymers.

Synthesis of Heteroarmed Star Polymers. In the preceding sections, we successfully synthesized well-controlled three-, four-, and six-armed star polystyrenes. We have next focused our attention on the synthesis of a heteroarmed star polymer by utilizing the methodology described above. As mentioned in the Introduction, in principle, heteroarmed star polymers can possibly be synthesized simply by changing living polymers to be reacted. Here, we have attempted to synthesize two heteroarmed star polymers of four-arm ABC_2 and five-arm AB_4 types.

For the synthesis of an ABC_2 type heteroarmed star polymer where A, B, and C are polystyrene, poly(α-methylstyrene), and polyisoprene segments, respectively, we have employed a synthetic procedure very similar to that used for the synthesis of four-armed $AA'A''_2$ type star polystyrene. The procedure is illustrated in Scheme 3.

The polystyrene end-functionalized with two MOM groups and an iodopropyl group was also used as a prepolymer for this synthesis. It was reacted with 1.2 equiv of poly(α-methylstyryl)lithium in THF at −78 °C for 48 h. The reaction proceeded efficiently to afford a

Table 5. Molecular Weights and Molecular Weight Distributions of Hetero four-Armed ABC_2 and five-Armed AB_4 Star Polymers[a]

	compositions (A:B:C or A:B)		$\bar{M}_n$				
type (arms)	calcd	NMR	calcd	SLS + SEC[b]	NMR + SEC[c]	$\bar{M}_w$[d]	$\bar{M}_w/\bar{M}_n$
ABC_2 (4)	22:18:60	21:21:58	22000	22000	23000	23000	1.04
AB_4 (5)	13:87	17:83	27000	26000	27000	27000	1.03

[a] ABC_2: A, B, and C are polystyrene, poly(α-methylstyrene), and polyisoprene, respectively. AB_4: A and B are polystyrene and polyisoprene, respectively. [b] Determined from $\bar{M}_w$(SLS) and $\bar{M}_w/\bar{M}_n$(SEC). [c] Determined from $\bar{M}_n$s(SEC) of precursory polystyrenes and compositions by NMR. [d] Obtained by SLS in benzene.

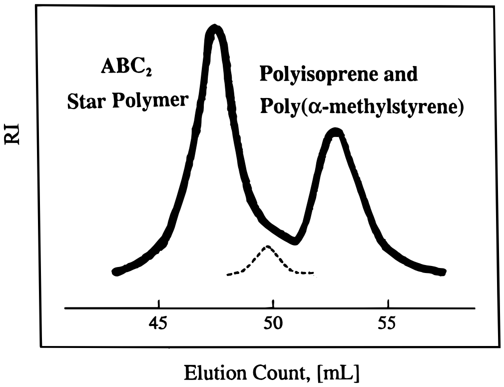


Figure 6. SEC curve of the resulting polymer mixture obtained by the coupling reaction for the synthesis of four-armed ABC_2 polymer.

block copolymer of poly(styrene-*b*-α-methylstyrene) functionalized with two MOM groups at the junction of two segments. The resulting copolymer, although it was contaminated with the poly(α-methylstyrene), used in excess, was used in the next reaction without fractionation. Chlorination of the two MOM groups proceeded quantitatively with BCl_3 in CH_2Cl_2 at 0 °C for 2 h. Finally, a 2-fold excess of polyisoprenyllithium was reacted with the chlorinated polymer in THF−heptane (1/1, v/v) at −78 °C for 72 h to introduce the C segment.

Figure 6 shows the SEC trace of the resulting polymer mixture. As can be seen, a sharp high molecular weight peak possibly for the desired hetero four-arm ABC_2 star polymer is clearly observed, while low molecular weight peaks may be ascribed to both unreacted poly(α-methylstyrene) and polyisoprene used in excess at the second and final reactions. A small peak is also observed among the high and low molecular weight peaks and assigned to unreacted intermediate polymers and/or byproducts probably resulting from well-known side reactions such as Li−Cl exchange and/or single-electron transfer followed by coupling. The ABC_2 heteroarmed star polymer thus synthesized was readily isolated by SEC fractionation and characterized by SEC, ^{1}H NMR, and SLS measurements. The results are summarized in Table 5.

The polymer possessed a narrow molecular weight distribution, namely 1.04. The $\bar{M}_w$ value of 23 000 was obtained by SLS. The $\bar{M}_n$ value was determined to be 22 000 from both the $\bar{M}_w$ by SLS and the $\bar{M}_w/\bar{M}_n$ by SEC. This is in a complete agreement with 22 000 for the calculated value. The observed $\bar{M}_n$ of 23 000 was also obtained from the $\bar{M}_n$ of the starting polystyrene and each composition of the resulting copolymer and was close to the calculated value. Furthermore, it is calculated from ^{1}H NMR spectrum that the compositional ratio of three-arm segments is consistent with the actual feed ratio. All of the analytical results strongly support that the fractionated polymer is a well-defined hetero four-arm ABC_2 star polymer.

Next, the synthesis of a hetero five-arm AB_4 star polymer where A and B are polystyrene and polyisoprene, respectively, has been attempted. The procedure is also illustrated in Scheme 3. For this synthesis, a precursor polymer functionalized with four MOM termini is required. The functional 1,1-diphenylalkyl anion with two MOM groups was prepared by reacting a 1.2-fold excess of **1** with s-BuLi in THF at −78 °C for 1 h which was then reacted with the terminal iodopropyl group of the styrene with two MOM groups (see Scheme 2) in THF at −78 °C for 15 h. The degree of MOM end-functionalization of the prepolymer prepared was found to be 3.99 by the ^{1}H NMR spectrum. Chlorination of the polymer with BCl_3 followed by coupling with a 2-fold excess of polyisoprenyllithium in THF at −78 °C for 72 h.

The SEC trace of the resulting polymer mixture showed a sharp main peak for the desired star polymer and small amounts (ca. 8%) of polymers with arms less than 5. Then the polymer mixture was then fractionated by SEC and characterized by SEC, ^{1}H NMR, and SLS measurements. The results are also summarized in Table 5. As can be seen in the table, the polymer possesses a narrow molecular weight distribution. The calculated and observed molecular weights are almost identical. The compositional ratio determined by ^{1}H NMR is in good agreement with the feed ratio. Accordingly, these results indicate strongly that the fractionated polymer is a well-defined hetero five-arm AB_4 star polymer. We were thus successful in synthesizing ABC_2 and AB_4 heteroarm star-branched polymers on the basis of our methodology.

Conclusion

We have developed here a new, versatile methodology for the synthesis of well-controlled regular and heteroarmed star polymers with defined number of arms. Particularly, synthetic versatility of our methodology is demonstrated through the successful synthesis of regular star polystyrenes with three, four, and six arms and heteroarmed star polymers of ABC_2 and AB_4 types.

There are several advantages to our methodology. For example, prepolymers are always prepared by reacting living polymers with electrophiles containing anion-stable MOM groups. Therefore, the structure of a star-branched polymer can be rationally designed in this reaction by changing the electrophile and the number of MOM groups as well as the reaction mode of living polymer with electrophiles including α,ω-dihalides. The methodology involves one or more reaction steps in which living polymers are used. By changing the molecular weight and/or kind of living polymers at each stage, not only regular polymers but also a wide variety of asymmetric and heteroarmed star polymers can be advantageously synthesized. In other words, regular and heteroarmed star polymers can be synthesized from the same prepolymer simply by changing the living polymer to be reacted. Moreover, during the course of our investigations we have prepared a number of synthetically useful new functionalized polystyrenes with a defined number of chloromethyl groups which should be of great interest as another precursory polymers in the preparation of novel functionalized polymers.

Unfortunately, small amounts (10% or less) of byproduct polymers are usually contaminated in the final products. The formation of these byproduct polymers may possibly be the result from the side reactions occurred competitively with the desired coupling reactions. Although they are not serious under our conditions in THF at −78 °C, more optimization to the reaction variables could be needed. Hopefully, the information gained from these results in this study will enable us to create more complex star-branched polymers.

Acknowledgment. This research was supported by a Grant-in-aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan. M.H. gratefully acknowledges the Japan Society for the Promotion of Science Research Fellowships for Young Scientists for providing financial support.

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MA981673T