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# Synthesis of branched polymers by means of living anionic polymerization. 10. Synthesis of well-defined heteroarm star-branched polymers by coupling reaction of chain-functionalized polystyrenes with benzyl halide moieties with living anionic polymers of *tert*-butyl methacrylate

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**Abstract**

The synthesis of well-defined heteroarm star-branched polymers having poly($^t$BMA) arms by the coupling reactions of living anionic polymers of *tert*-butyl methacrylate ($^t$BMA) with chain-functionalized polymers with a definite number of benzyl halide moieties was described. The reaction of living anionic poly($^t$BMA) bearing potassium countercation with benzyl bromide-functionalized polystyrenes proceeded readily and quantitatively in THF at − 40 °C for 1 h and − 78 °C for 5 h, respectively. Similarly heteroarm star-branched polymers of $AB_2$, $AB_3$, $AB_4$, $A_2B_4$, and $ABC_4$ types with well-defined architectures were successfully synthesized. On the other hand, the same living poly($^t$BMA) was sluggish to react with benzyl chloride-functionalized polystyrenes, requiring 168 h to achieve quantitative formation of $AB_4$ star polymer. Moreover, no reaction occurred between living poly($^t$BMA) bearing lithium countercation in the presence of LiCl and benzyl chloride-functionalized polystyrene in THF at − 78 °C for 168 h. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Heteroarm star polymer; Anionic living polymer; Poly(*tert*-butyl methacrylate)

## 1. Introduction

Heteroarm, mixed arm, or miktoarm (mikto comes from Greek word) star-branched polymers are asymmetric star-branched polymers whose arm segments differ in either molecular weight or composition. Recently, much attention has been paid to such heteroarm star-branched polymers, since they are expected to exhibit unique and interesting behaviors and properties in solution, bulk, and melt states due to their chain branching structure as well as multi-component system.

In general, the synthesis of heteroarm star-branched polymers with well-defined architectures is more difficult than that of regular star polymers having same number of arm segment, because all of the arm segments cannot be simultaneously introduced. In addition, a number of high-yielding reactions and fractionations are generally required in reaction steps for the synthesis of heteroarm star-branched polymers. Regardless of synthetic difficulties, successful synthetic examples of several well-defined heteroarm star-branched polymers have so far been reported. They were synthesized mainly by two methodologies based on successive coupling reactions of ω-living anionic polymers (monofunctional living polymers) with multi-functional chlorosilanes [1–9] and linking reactions of non-polymerizable macromonomers with another living polymers, followed by polymerization of additional monomers to prepare new arm segments [10–19]. Hadjichristidis and his coworkers [20,21] have recently reviewed these methodologies and synthetic examples of heteroarm star-branched polymers. In addition, so-called 'in–out' method has been reported for the synthesis of heteroarm star polymers [22–24]. This method involves the coupling reaction of divinylbenzene with ω-living anionic polymers to generate well-defined cores, followed by the addition of second monomers to polymerize with the cores. However, this method lacks the precision and control necessary for the

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synthesis of polymers with well-defined structures. Therefore, variation of architectural parameters such as arm number and chemical composition are still limited.

We have recently developed a general, versatile methodology of using functionalized 1,1-diphenylethylene (DPE) derivatives for the synthesis of various chain-end- and in-chain-functionalized polymers with a definite number of highly reactive benzyl halide moieties [25–28]. By using such benzyl halide-functionalized polymers as prepolymers in the coupling reactions of living anionic polymers of styrene, α-methylstyrene, and isoprene, several well-defined star-branched polymers with same or different arms were successfully synthesized [25,29]. We have also synthesized new star-branched polymers of $AA'_2A''_2$, $AA'_4A''_4$, and $AB_2C_2$ types by the coupling reaction of benzyl halide-functionalized polystyrenes with specially designed polymer anions prepared from DPE-functionalized macromonomers and living anionic polymers [28,30].

Throughout the synthesis of star-branched polymers, the benzyl halide moieties introduced at chain-ends or in-chains reacted efficiently with living anionic polymers of styrene, α-methylstyrene, and isoprene, their modified anions with DPE, and the above-mentioned polymeric 1,1-diphenylalkyl-type anions in THF at −78 °C. Under the similar conditions, however, the benzyl halide moieties were sluggish to react with living anionic polymers of *tert*-butyl methacrylate ($^t$BMA) whose chain-end anions are less reactive enolate anions. It was further observed that the reaction did not occur in a certain case [31].

Herein, we will study in more detail the coupling reaction of benzyl halide-functionalized polymers with living anionic polymers of $^t$BMA. The objective of this work is to establish the synthetic procedure by the coupling reaction as a general method for the synthesis of well-defined heteroarm star-branched polymers having poly($^t$BMA) arms. One more advantage of the introduction of poly($^t$BMA) segment into star polymer is that poly($^t$BMA) can be quantitatively transformed into poly(methacrylic acid) with a variety of attractive applications.

## 2. Experimental

### 2.1. Materials

Styrene (Aldrich), α-methylstyrene (Aldrich), DPE (Aldrich), and $^t$BMA (Aldrich), after usual purification work-up, were distilled over $CaH_2$ twice under a nitrogen atmosphere. Styrene, α-methylstyrene, and DPE were finally distilled over dibutylmagnesium (3 mol%) on the vacuum line into ampoules equipped with break seals that were prewashed with (1,1-diphenylhexyl)lithium in heptane. $^t$BMA was finally distilled over trioctylaluminium (2 mol%) on the vacuum line into ampoules equipped with break seals that were prewashed with potassium naphthalenide in THF. THF (Tokyo Kasei, Japan) was distilled successively from Na wire and $LiAlH_4$ under a nitrogen atmosphere. It was finally distilled from its sodium naphthalenide solution on the vacuum line. *sec*-Butyllithium (*sec*-BuLi) (Kanto Chemicals, Japan) was used without purification. The concentration was determined by colorimetric titration from dark red color to colorless end-point after transformation of *sec*-BuLi into 3-methyl-1,1-diphenylpentyllithium in THF at −78 °C by treatment with a 1.2-fold excess of DPE. Diphenylmethylpotassium was prepared by the reaction of potassium naphthalenide with a 1.1-fold excess of diphenylmethane according to the procedure previously reported [32]. Boron trichloride in $CH_2Cl_2$ (1.0 M) was used as received from Aldrich. Both 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) and 1-(4-bromobutyl)-4-(*tert*-butyldimethylsilyloxymethyl)benzene (**2**) was synthesized according to the procedures reported in our previous papers [26].

### 2.2. Preparation of living anionic polymers of styrene, α-methylstyrene, and $^t$BMA

Polymerizations were carried out under high vacuum condition ($10^{-6}$ Torr) in sealed glass reactors equipped with break seals. The reactors were always prewashed with initiator solutions after being sealed off from a vacuum line and were used for the polymerizations. Both styrene and α-methylstyrene were polymerized with *sec*-BuLi in THF at −78 °C for 15 min and 3 h, respectively. $^t$BMA was polymerized with 3-methyl-1,1-diphenylpentyllithium in the presence of LiCl or diphenylmethylpotassium in THF at −78 °C for 4 h. 3-Methyl-1,1-diphenylhexyllithium was prepared by the reaction of *sec*-BuLi and a 1.2-fold excess of DPE in THF at −78 °C for 0.5 h. A 5-fold excess of LiCl to the initiator was used. Concentrations of the monomers and the initiators were in the ranges of ca. 0.5–1.0 and $3–20 \times 10^{-3}$ M, respectively.

### 2.3. Preparation of chain-functionalized polymers with benzyl halide moieties

Both chain-end- and in-chain-functionalized polymers were synthesized by the procedures reported by our previous paper [26].

### 2.4. Synthesis of heteroarm star-branched polymers by coupling reactions of living anionic polymers of $^t$BMA with chain-functionalized polymers with benzyl halide moieties

The coupling reactions were usually carried out in THF at −78 or −40 °C for 1–168 h under high vacuum conditions using break-seal technique. Since living anionic polymer of $^t$BMA is less reactive than those of styrene and 1,3-diene monomers, a 2-fold excess of living anionic polymer of $^t$BMA was usually used to force the reaction to completion in each coupling reaction. We previously reported that living anionic polymer of $^t$BMA is stable at

− 40 °C for a longer reaction time of 168 h [31]. A typical reaction was as follows: chain-end-functionalized polystyrene with four benzyl bromide moieties (0.220 g, 0.154 mmol for benzyl bromide function, $M_n = 5710$) dissolved in THF (4 ml) was added to the living polymer of ${}^t$BMA (2.00 g, 14.1 mmol, $M_n = 4100$) initiated with diphenylmethylpotassium (0.452 mmol) in THF (22 ml) at − 78 °C and the reaction mixture was allowed to stand at − 78 °C for 5 h. The reaction was terminated with degassed methanol. The polymer was precipitated by adding large amount of methanol and purified by reprecipitation three times from THF to methanol and freeze-dried from its benzene solution for 24 h. The poly(${}^t$BMA) used in excess in the reaction was nearly quantitatively recovered from the methanol solutions.

The resulting polymers were characterized by various analytical methods including ${}^1$H NMR, size-exclusion chromatography (SEC), and static light scattering, respectively. The results are summarized in Table 3 (see AM07). It should be mentioned herein that several attempts to determine $M_n$ values of the synthesized star-branched polymers were not successful by vapor pressure osmometry, although the reason was not clear at present. We are tentatively considering that the *tert*-butyl ester of P(${}^t$BMA) is hydrolyzed to small extent during work-up and the resulting polymers may aggregate to form reversed micelles.

### 2.5. Measurements

Both ${}^1$H and ${}^{13}$C NMR spectra were recorded on a BRUKER DPX (300 MHz for ${}^1$H and 75 MHz for ${}^{13}$C) in $CDCl_3$. SEC 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 $G5000H_{XL} + G4000H_{XL} + G3000H_{XL}$) ($G2000H_{XL}$ (20 Å), $G3000H_{XL}$ (75 Å), $G4000H_{XL}$ (200 Å), and $G5000H_{XL}$ (650 Å)) were used. Measurable molecular weight ranges in these columns are from $10^3$ to $4 \times 10^6$ g/mol. Calibration curves were made to determine $M_n$ and $M_w/M_n$ values with standard polystyrene samples. Laser light scattering measurements (633 nm) were performed with an Ootsuka Electronics DSL-600R instrument in chloroform.

## 3. Results and discussion

Hadjichristidis and his coworkers have recently reported the successful synthesis of regular star poly(alkyl methacrylate)s by the coupling reaction of living anionic polymers of alkyl methacrylates with 1,2,4,5-tetra(bromomethyl)benzene [33]. By using living anionic polymer of methyl methacrylate (MMA) initiated with 1,1-diphenylhexyllithium, the reaction quantitatively proceeded in THF at − 78 °C for 48 h to afford the expected four-arm star PMMA. Under the same conditions, however, living anionic polymer of ${}^t$BMA in the presence of LiCl was very sluggish to react with 1,2,4,5-tetra(bromomethyl)benzene even in THF at − 20 °C, requiring three weeks to achieve quantitative conversion.

It was observed in our preliminary experiments that under the conditions in THF at − 78 °C for one week (168 h), no reaction occurred between chain-end-functionalized polystyrene with two benzyl chloride moieties and the living anionic polymer of ${}^t$BMA initiated with 3-methyl-1,1-diphenylpentyllithium in the presence of LiCl [31]. In contrast, the reaction of the same benzyl chloride-functionalized polystyrene with the living anionic polymer of ${}^t$BMA initiated with diphenylmethylpotassium quantitatively proceeded to afford the corresponding $AB_2$ heteroarm star-branched polymer where A and B were polystyrene and poly(${}^t$BMA), respectively.

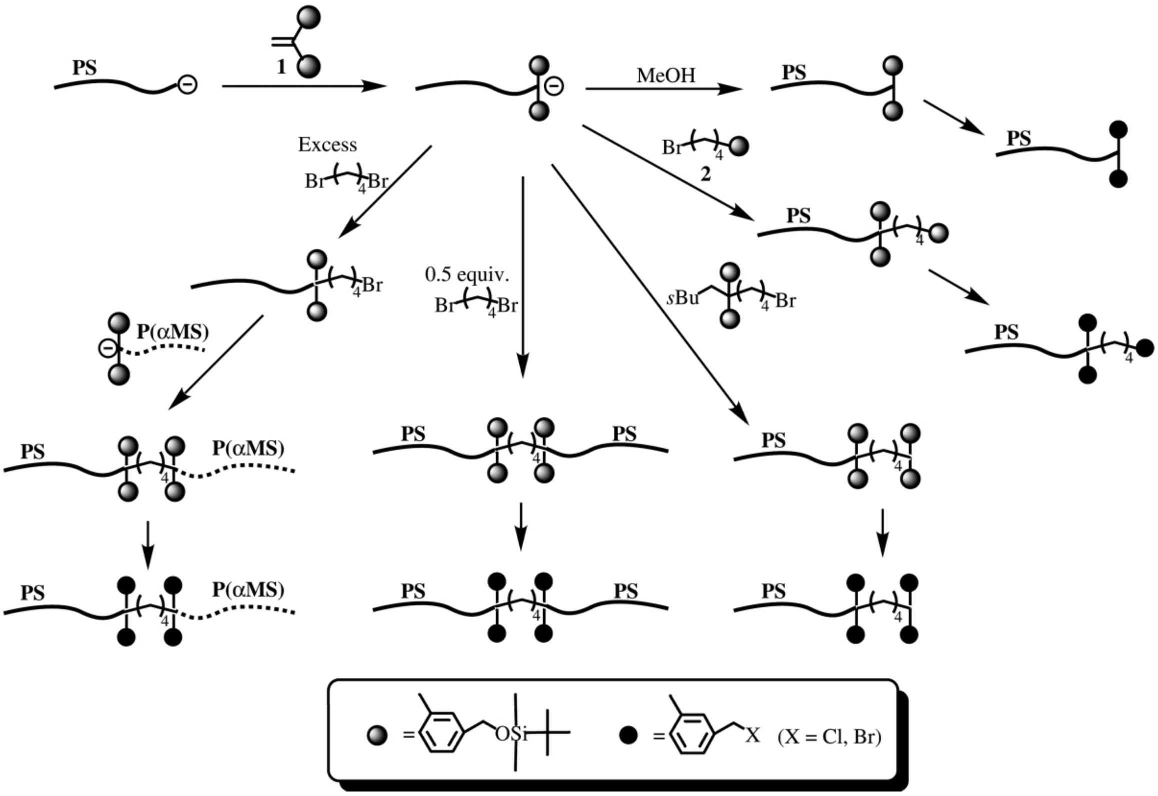
Very recently, we have successfully synthesized a series of graft copolymers of polystyrene-*graft*-poly(${}^t$BMA) by the coupling reaction of poly(*m*-bromomethylstyrene) with the living anionic polymer of ${}^t$BMA initiated with diphenylmethylpotassium [34]. The reaction was complete in THF at − 40 °C for four weeks to afford a highly dense graft copolymer having one poly(${}^t$BMA) segment in each repeating unit. Under the same conditions, however, the reaction of poly(*m*-chloromethylstyrene) with the same living anionic polymer of ${}^t$BMA proceeded relatively slow and yielded 75%.

These previous studies indicate that the coupling reactions of benzyl bromide derivatives with living polymers of ${}^t$BMA quantitatively proceed under appropriate conditions. Caution should be, however, paid to use of the benzyl chloride derivatives in the reaction. Furthermore, the countercation of living poly(${}^t$BMA) may also be very a important factor in the coupling reaction, the living polymer bearing potassium countercation being more effective than that with lithium countercation. Taking these results into consideration, we will examine the coupling reactions of benzyl halide-functionalized polymers with living anionic polymers of ${}^t$BMA in order to synthesize heteroarm star polymers.

### 3.1. Synthesis of chain-functionalized polymers with benzyl halide moieties

First of all, we synthesized chain-end-functionalized polystyrenes with two, four benzyl chloride and three, four benzyl bromide moieties as prepolymers. In addition, in-chain-functionalized polystyrene with four benzyl bromide moieties and a new functionalized block copolymer, polystyrene-*block*-poly(α-methylstyrene), with four benzyl bromide moieties between both blocks were also synthesized. Synthetic schemes for such functionalized polymers are illustrated in Scheme 1.

Chain-end-functionalized polystyrene with two benzyl



Scheme 1. Synthetic scheme of chain-end and in-chain functionalized polymers with benzyl halide moieties.

chloride moieties was synthesized by the addition reaction of polystyryllithium to **1** in THF at −78 °C for 0.5 h, followed by treatment with $BCl_3$. For the synthesis of chain-end-functionalized polystyrene with three benzyl bromide moieties, polystyryllithium was reacted with **1**, followed by treatment in situ with **2**. Three *tert*-butyldimethylsilyloxy groups thus introduced were quantitatively transformed into the bromides by treatment with LiBr–$(CH_3)_3SiCl$.

In order to synthesize chain-end-functionalized polystyrenes with four benzyl chloride and bromide moieties, a prepolymer was prepared by the reaction of polystyryllithium with **1**, followed by treatment with a 10-fold excess of 1,4-dibromobutane. The prepolymer was then reacted with the functionalized anion prepared from **1** and *sec*-BuLi in THF at −78 °C for 24 h. The objective functionalized polymers with four benzyl chloride and bromide moieties were obtained by treatment with $BCl_3$ and LiBr–$(CH_3)_3SiCl$, respectively.

In-chain-functionalized polystyrene with four benzyl bromide moieties was synthesized by the reaction of the prepolymer with polystyryllithium end-capped with **1**, followed by treatment with LiBr–$(CH_3)_3SiCl$. Similarly, the functionalized block copolymer was obtained by the reaction of the prepolymer with the end-capped poly(α-methylstyryl)lithium with **1**, followed by treatment with LiBr–$(CH_3)_3SiCl$. In each of both reactions, a 1.1-fold excess of the living polymer was used to force the reaction to completion. Therefore, the objective polymers were isolated by fractionation with SEC prior to the transformation reactions.

All of the polymers synthesized here showed sharp symmetrical monomodal SEC peaks without any shoulders and tailings. The molecular weight distributions were narrow, the $M_w/M_n$ values ranging from 1.03 to 1.07. The observed molecular weights by SEC using standard polystyrene calibration were in good agreement with those calculated from [monomer] to [initiator] ratios in all samples. The $M_n$ values could also be determined by $^1H$ NMR by using two resonances at 6.2–7.2 ppm (aromatic protons) and 0.7 ppm (methyl protons of the initiator fragment). They also agreed quite well with those calculated. The degrees of benzyl halide-functionalization were determined by $^1H$ NMR by using two resonances at 4.2–4.5 ppm (halomethylene protons of the benzyl halides) and 0.7 ppm (methyl protons of the initiator fragment). The values thus determined were very close to those expected. These results are summarized in Table 1.

### 3.2. Synthesis of heteroarm star-branched polymers by coupling reaction of benzyl chloride-functionalized polystyrenes with living anionic polymers of tert-butyl methacrylate

In our previous paper [31], it was observed that under the conditions in THF at −78 °C for 168 h, no reaction occurred between chain-end-functionalized polystyrene with two benzyl chloride moieties and living anionic

Table 1
Synthesis of chain-functionalized polystyrenes with benzyl halide moieties

| Halide | Position | $M_n$ ( × $10^{-3}$) | | | $M_w/M_n$ | Functionality | |
|---|---|---|---|---|---|---|---|
| | | Calcd | SEC | NMR | | Calcd | $^1$H NMR |
| Cl | End | 5.28 | 4.87 | 4.91 | 1.06 | 2 | $2.0_0$ |
| Cl | End | 5.89 | 5.92 | 5.62 | 1.04 | 4 | $4.2_4$ |
| Br | End | 13.8 | 12.9 | 13.3 | 1.03 | 3 | $2.9_0$ |
| Br | End | 5.63 | 5.71 | 5.61 | 1.04 | 4 | $4.0_8$ |
| Br | End | 14.0 | 16.3 | 16.0 | 1.04 | 4 | $4.0_5$ |
| Br | Middle | 10.0 | 9.27 | 10.0 | 1.05 | 4 | $4.0_8$ |
| Br[a] | Middle | 13.4 | 13.5 | 12.9 | 1.02 | 4 | $3.9_2$ |

[a] Polystyrene-*block*-poly(α-methylstyrene).

polymer of either MMA or $^t$BMA initiated with 3-methyl-1,1-diphenylpentyllithium in the presence of LiCl. Although the same reactions were repeated again in this study, no reactions occurred at all. On the other hand, the coupling reaction of the same functionalized polystyrene with the living anionic poly($^t$BMA) initiated with diphenylmethylpotassium proceeded quantitatively under the same conditions. The yield of the expected $AB_2$ star-branched polymer was 100% after fractionation with methanol. Thus, the effect of countercation of living anionic poly($^t$BMA) was very critical in the coupling reaction. In this study, it was further observed that the reaction was complete within 24 h at −78 °C. The results are summarized in Table 2.

Next, the reaction of chain-end-functionalized polystyrene with four benzyl chloride moieties with the living poly($^t$BMA) bearing $K^+$ was carried out in THF at −78 °C for 24 h. The resulting polymer was isolated by fractionation with methanol (see AM02 in Table 2). The isolated polymer showed a sharp monomodal SEC peak ($M_w/M_n$ = 1.06). Neither shoulder nor tailing was present. The observed molecular weights determined by $^1$H NMR as well as SLS were 18.1 and 20.8 kg/mol ($M_w$ value in this case), respectively. These values were, however, smaller than those calculated (22.9 and 24.3 kg/mol) based on the formation of $AB_4$ star polymer. The number of the introduced poly($^t$BMA) segment determined by $^1$H NMR and SLS were $2.9_3$ and $3.2_6$, respectively. Accordingly, the resulting polymer may be mainly an $AB_3$, but not the expected $AB_4$ heteroarm star-branched polymer. The evidence for the incomplete coupling reaction is also provided by $^1$H NMR spectrum of the resulting polymer showing that the resonance at 4.2 ppm characteristic to chloromethylene protons of the benzyl chloride moiety remained as a small resonance peak. Unfortunately, the peak area was too broad to be measured accurately.

The reaction was therefore allowed to stand at −78 °C for 168 h. The resulting polymer was then isolated by fractionation with methanol. The polymer weight was very close to that based on the formation of $AB_4$ star polymer. The SEC trace showed a sharp monomodal distribution ($M_w/M_n = 1.05$). The observed $M_n$ and $M_w$ values by $^1$H NMR and SLS were 28.8 and 30.5 kg/mol and agreed with those calculated (29.0 and 30.5 kg/mol). The numbers of the arm segment were $3.9_7$ and $4.0_0$, respectively. No resonance at 4.2 ppm was detected in the $^1$H NMR spectrum. Thus, the expected $AB_4$ star polymer was successfully obtained under the conditions. Therefore, the reaction time was not sufficient in 24 h, but 168 h in case of the $AB_4$ heteroarm star-branched polymer synthesis. The same results were obtained when the reaction was carried out in THF at −40 °C for 168 h. Molecular characterization results by $^1$H NMR, SEC, and SLS revealed that a well-defined $AB_4$ heteroarm star-branched polymer was also obtained (Table 2).

In summary, both $AB_2$ and $AB_4$ heteroarm star-branched polymers with well-defined architectures were quantitatively obtained in THF at −78 °C for 24 and 168 h, respectively, by the coupling reaction of benzyl chloride-functionalized polystyrenes with living anionic poly($^t$BMA) bearing $K^+$. In the reaction, however, the effect of countercation was very critical. Living anionic polymers of both MMA and $^t$BMA bearing $Li^+$ could not react at all with benzyl chloride-functionalized polystyrenes in THF at −78 °C for 168 h. In addition to the difference of countercation in these cases, the effect of LiCl may also be considered because LiCl is known to considerably reduce the reactivities of chain-end enolate anions by μ-type complex formation.

Table 2
Synthesis of heteroarm star polymers by coupling reaction of chain-end-functionalized polystyrenes with benzyl chloride moieties with living anionic polymers of $^t$BMA

| No. | Type | $M^+$ in P($^t$BMA)$^-M^+$ | Temp. (°C) | Time (h) | Star polymer | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $M_n$ ( × $10^{-3}$) | | | $M_w/M_n$ | Arm number of P($^t$BMA) segment | | |
| | | | | | Calcd | $^1$H NMR | SLS ($M_w$) | | Calcd | $^1$H NMR | SLS |
| AM01 | $AB_2$ | $Li^+$ | −78 | 168 | No reaction | | | | | | |
| MH01 | $AB_2$ | $K^+$ | −78 | 168 | 14.9 | 14.3 | 15.6 | 1.05 | 2 | $1.8_7$ | $2.0_0$ |
| AM02 | $AB_4$ | $K^+$ | −78 | 24 | 22.9 | 18.1 | 20.8 | 1.06 | 4 | $2.9_3$ | $3.2_6$ |
| AM03 | $AB_4$ | $K^+$ | −78 | 168 | 29.0 | 28.8 | 30.5 | 1.05 | 4 | $3.9_7$ | $4.0_0$ |
| AM04 | $AB_4$ | $K^+$ | −40 | 168 | 29.6 | 28.9 | 29.7 | 1.06 | 4 | $3.8_8$ | $4.0_2$ |

Table 3
Synthesis of heteroarm star polymers by coupling reaction of chain-functionalized polystyrenes with benzyl bromide moieties with living anionic polymer of $^{t}$BMA

| No. | Type | Temp. (°C) | Time (h) | Star polymer | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $M_n$ ($\times 10^{-3}$) | | | $M_w/M_n$ | Arm number of B segment | | |
| | | | | Calcd | $^1$H NMR | SLS ($M_w$) | | Calcd | $^1$H NMR | SLS |
| AM05 | $AB_4$ | −78 | 168 | 30.3 | 31.8 | 31.4 | 1.03 | 4 | 4.24 | 4.01 |
| AM06 | $AB_4$ | −78 | 168 | 69.1 | 69.5 | 74.0 | 1.05 | 4 | 4.03 | 4.11 |
| AM07 | $AB_4$ | −78 | 5 | 22.1 | 21.6 | 23.9 | 1.04 | 4 | 3.88 | 4.21 |
| AM08 | $AB_4$ | −40 | 1 | 30.8 | 30.5 | 33.6 | 1.04 | 4 | 3.95 | 4.24 |
| AM09 | $AB_3$ | −78 | 168 | 46.2 | 47.2 | 47.0 | 1.04 | 3 | 3.09 | 2.76 |
| AM10 | $A_2B_4$ | −78 | 168 | 27.8 | 28.3 | 29.8 | 1.06 | 4 | 4.11 | 4.07 |
| AM11 | $ABC_4$[a] | −78 | 168 | 31.4 | 32.0 | 33.4 | 1.03 | 4 | 4.14 | 4.23 |

[a] A, B, and C are polystyrene, poly(α-methylstyrene), and poly(*t*-butyl methacrylate), respectively.

### *3.3. Synthesis of heteroarm star-branched polymers by coupling reaction of benzyl bromide-functionalized polystyrenes with living anionic polymers of tert-butyl methacrylate*

It is generally known that benzyl bromide is more reactive than benzyl chloride in $S_N2$ reactions like the coupling reaction herein studied. Therefore, the use of benzyl bromide-functionalized polystyrenes is expected to greatly accelerate the coupling reaction with living poly($^{t}$BMA). However, we have recently observed that the reaction of poly(*m*-bromomethylstyrene) with polystyryllithium proceeds along with serious side reactions, whereas the same reaction with use of poly(*m*-chloromethylstyrene) undergoes cleanly and quantitatively under exactly identical conditions [34]. For this reason, the reaction of chain-end-functionalized polystyrene with four benzyl bromide moieties with living anionic poly($^{t}$BMA) initiated with diphenylmethylpotassium was first carried out in THF at −78 °C for 168 h. Under the conditions, we attempted to synthesize two $AB_4$ star polymers whose arm segments were designed to be ca. 6 and 15 kg/mol in molecular weight. The results are summarized in Table 3.

Yields of both polymers were quantitative based on the assumption that $AB_4$ star polymers were formed in 100% yield. The resulting polymers showed sharp monomodal SEC peaks, the $M_w/M_n$ values being 1.03 and 1.05, respectively. The observed molecular weights by $^1$H NMR and SLS were agreed with those calculated. The agreement between the compositions observed by $^1$H NMR and calculated is quite satisfactory in each sample. These results clearly indicate that the coupling reactions proceed quantitatively as desired to afford well-defined $AB_4$ heteroarm star-branched polymers.

Identical reactions were carried out for various reaction times of 48, 24, and 5 h in order to examine the acceleration extent of the reaction. It was finally observed that the coupling reaction was virtually complete within even 5 h at −78 °C (see AM07). The higher reactivity of benzyl bromide-functionalized polystyrene than the corresponding benzyl chloride-functionalized polystyrene in the coupling reaction is thus obvious as expected. Furthermore, raising the reaction temperature to −40 °C, the reaction became faster and indeed complete within 1 h without problem (see AM08). Fig. 1 shows typical SEC traces of the polymers before and after fractionation with methanol.

In contrast to the above results, the coupling reaction of chain-end-functionalized polystyrene with living poly($^{t}$BMA) initiated with 3-methyl-1,1-diphenylpentyllithium in the presence of LiCl slowly proceeded in THF at −78 °C for 24 h. The SEC trace of the reaction mixture exhibited a multi-modal distribution, showing that both AB block (28%) and $AB_2$ star (60%) were formed in addition to unreacted polystyrene prepolymer (12%) estimated from peak area. No stars with more than three arms were produced under the conditions. More reaction time is therefore required in the coupling reaction by this combination as previously reported by Hadjichristidis et al. [33].

Both $AB_3$ and $A_2B_4$ star-branched polymer with well-defined architectures were similarly synthesized by the reactions of living poly($^{t}$BMA) bearing $K^+$ with chain-end-functionalized polystyrene with three benzyl bromide moieties and in-chain-functionalized polystyrene with four

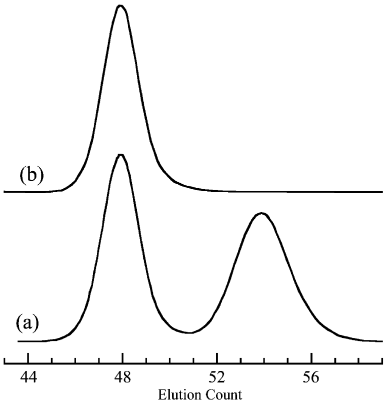


Fig. 1. SEC traces of $AB_4$ heteroarm star-branched polymers: (a) before and (b) after fractionation with methanol.

benzyl bromide moieties, respectively (see AM09 and 10). Interestingly, an ABC$_4$ heteroarm star-branched polymer could be synthesized by using a new well-defined block copolymer, polystyrene-*block*-poly(α-methylstyrene) functionalized with four benzyl bromide moieties between both blocks. In this star polymer, A, B, and C segments were polystyrene, poly(α-methylstyrene), and poly($^t$BMA), respectively. The well-defined architecture of this polymer is clearly demonstrated (see AM11 in Table 3). Thus, the reaction of benzyl bromide-functionalized polymers with living anionic polymers of $^t$BMA bearing K$^+$ becomes an efficient, general procedure for the synthesis of well-defined heteroarm star-branched polymers having poly($^t$BMA) arm segments. The availability of various both chain-end- and in-chain-functionalized polymers with benzyl bromide moieties is an additional advantage of this procedure [25–28,35].

Previously, Fujimoto et al. [10], Abetz et al. [11,18], Hadjichristidis et al. [36] and Young et al. [17] reported the successful synthesis of ABC and A$_2$B$_2$ heteroarm star-branched polymers having poly(alkyl methacrylate) segments. All of these polymers were synthesized by in situ formation of polymer anions consisting of two different polymer segments, followed by initiating the living anionic polymerization of alkyl methacrylates to make poly(alkyl methacrylate) segments. The arm number was, however, limited to either one or two in these cases. Therefore, the star polymers having more than three poly($^t$BMA) arms synthesized herein are new heteroarm star-branched polymers. The synthesis of various star-branched polymers having a large number of poly($^t$BMA) arms up to ten or more numbers by extending the developed procedure is now under investigation.

## 4. Conclusions

Several new heteroarm star-branched polymers having poly($^t$BMA) arm segments with well-defined architectures were synthesized by the coupling reaction of benzyl bromide (or chloride)-functionalized polystyrenes with living anionic polymers of $^t$BMA bearing K$^+$. The heteroarm star-branched polymers synthesized were those of AB$_2$, AB$_3$, AB$_4$, A$_2$B$_4$, and ABC$_4$ types where A and B were polystyrene and poly($^t$BMA) in the AB series and A, B, and C were polystyrene, poly(α-methylstyrene), and poly($^t$BMA) in the ABC$_4$ type.

In the coupling reaction, the countercation of living poly($^t$BMA) is essentially critical. The living anionic polymers of $^t$BMA bearing K$^+$ reacted readily and quantitatively with the benzyl bromide moieties in the polymer chains in THF at −40 °C for 1 h and at −78 °C for 5 h, respectively. On the other hand, the living polymer bearing Li$^+$ in the presence of LiCl was relatively slow to react with the same functionalized polymer, requiring 168 h to achieve quantitative formation of AB$_4$ star polymer. Moreover, both the living polymers of MMA and $^t$BMA bearing Li$^+$ in the presence of LiCl could not react with the benzyl chloride moieties in THF at −78 °C even for a longer reaction time of 168 h.

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