Precise synthesis of asymmetric star-shaped polymers by coupling reactions of new specially designed polymer anions with chain-end-functionalized polystyrenes with benzyl bromide moieties

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Abstract

We have developed a novel methodology using polymer anions specially designed to comprise either of the three same or different polymer segments for the synthesis of well-defined regular and asymmetric star-shaped polymers. The polymer anion was prepared by the addition reaction of living anionic polymer to in-chain-functionalized polymer with 1,1-diphenylethylene (DPE) moiety and in situ coupled with chain-end-functionalized polystyrene with two or four benzyl bromide moieties. Although the anions located at the cores of 3-armed star polymers were believed to be highly sterically hindered, the coupling reactions proceeded virtually quantitatively under the conditions in THF at \(-78^\circ\text{C}\) for 24 h. Regular 7-armed A7 and 13-armed A13 star-shaped polystyrenes as well as quite new asymmetric 7-armed A2B2C2D and 13-armed A4B4C4D star-shaped polymers were synthesized in ca. 100% yields. Four polymer segments, A, B, C, and D, were, poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), and polystyrene prepared by sec-BuLi-initiated living anionic polymerization. Thus, three same or different polymer chains could be simultaneously introduced into either two or four benzyl bromide reaction sites only by one-step coupling reaction with the above-prepared polymer anion. The resulting star-shaped polymers all were well-defined in architecture and precisely controlled in-chain length and composition. Accordingly, they have a high molecular weight and structural homogeneity. Among them, asymmetric star-shaped polymers synthesized herein are the first successful examples comprised of four plural different polymer segments. As expected, new morphologies with nanoscopic ordered structures applicable to nanotechnology have been expressed.

Keywords: Asymmetric star-shaped polymer; Regular star-shaped polystyrene; Polymer anion; Living anionic polymerization; Coupling reaction; Precise synthesis; Benzyl bromide functionality

1. Introduction

Star-shaped polymers are defined as branched polymers consisting of more than three linear polymer chains as arm segments linked together at one end by a single junction point. These polymers have attracted much attention from theoretical and practical viewpoints due to physical properties distinct from their linear counterparts in solution, melt, and solid state [1–8]. Among star-shaped polymers, great attention has recently been paid to asymmetric star-shaped polymers in which arm segments differ in either molecular weight or chemical composition, because they are expected to exhibit interesting and specific properties originating from their heterophase structures in addition to chain-branching [9–14]. In particular, heterophase dissimilar structures are manifested by the tendency to phase-separate at molecular level and promote self-assembly, thereby facilitating to fabricate many new nanoscopic ordered suprastructures and characteristic nanomaterials. The possibility to organize megamolecules by further constituting such structures and materials as elementary building blocks is a new challenge on the way of more sophisticated nanodevices. Therefore, the synthesis and development of asymmetric star-shaped polymers have now been strongly associated with the rapid growth of nanotechnology.

In general, well-defined asymmetric star-shaped polymers are much more difficult in synthesis than...
the corresponding regular star-shaped polymers, since several reactions with quantitative nature and isolation of intermediate polymers for their syntheses are required. For such situations, structural variation in the synthesis of asymmetric star-shaped polymers is still quite limited even at the present time [15,16].

In recent years, we have been developing a novel methodology with the use of chain-end- and in-chain-functionalized polymers with a definite number of benzyl bromide moieties as polymeric coupling agents [17–23]. A wide variety of new asymmetric star-shaped polymers were synthesized by the coupling reaction of such benzyl bromide-functionalized polymers with living anionic polymers of styrene, 1,3-butadiene, isoprene, 2-vinylpyridine, methyl methacrylate, tert-butyl methacrylate, and ethylene oxide. The resulting star-shaped polymers are well-defined in architecture and precisely controlled in-chain length. More recently, we have extended the aforesaid methodology by using the newly prepared polymer anions comprised of two polymer chains from living anionic polymers and chain-end-functionalized polymers with 1,1-diphenylethylene (DPE) moiety [24–26]. For example, 5-armed regular and asymmetric star-shaped polymers of the types A$_5$ and AB$_2$C$_2$ could be successfully synthesized by the coupling reaction of such polymer anions with chain-end-functionalized polystyrene with two benzyl bromide moieties as shown in Scheme 1. Thus, we have demonstrated that the same or two different polymer chains can be simultaneously introduced only by one-step coupling reaction with the polymer anion.

Herein, we report on a further development of the extended methodology by using specially designed polymer anions comprised of three polymer chains. The objective of the present study is to examine the synthetic potential of the methodology using polymer anions and establish it as a more general synthetic procedure, which allows to readily access asymmetric star-shaped polymers with many potential applications to nanotechnology.

Scheme 1. Synthesis of A$_5$ and A$_2$B$_2$C star-shaped polymers.
2. Experimental section

2.1. Materials

The reagents were purchased from Aldrich, Japan and purified by usual procedures reported elsewhere [22,26,27]. Styrenic monomers were finally distilled over dibutylmagnesium (ca.3 mol%) on the vacuum line into ampoules equipped with break seals. Tetrahydrofuran (THF) was refluxed over Na wire for overnight and distilled over LiAlH₄ under nitrogen. It was finally distilled from its sodium naphthalenide solution on the vacuum line. 1-[4-(4-LiAlH₄ under nitrogen. It was finally distilled from its refluxed over Na wire for overnight and distilled over LiAlH₄ under nitrogen. It was finally distilled from its sodium naphthalenide solution on the vacuum line. 1-[4-(4-

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2.2. Measurements

Both ¹H and ¹³C NMR spectra were measured on a Bruker DPX300 (300 MHz for ¹H and 75 MHz for ¹³C) in CDCl₃. Size-exclusion chromatograms (SEC) were measured with a TOSOH HLC-8020 at 40 °C with UV (254 nm) or refractive index detection. Fractionation by HPLC was performed at 40 °C using TOSOH HLC-8020 type fully automatic instrument equipped with a TSK-G4000HHR column (600 mm in length and 21.5 mm in diameter). Static light scattering (SLS) equipped with a He–Ne laser (λ = 632.8 nm) was performed with Ohotuka Electronics SLS-600R instrument in THF at 25 °C. The refractive index increment (dn/dc) was determined with an Ohtsuka Electronics DRM-1020 refractometer operating at 632.8 nm. Vapor pressure osmometry measurements were made with a Corona 117 instruments in benzene at 40 °C with a highly sensitive thermoelectric couple (TM-32K: sensitivity 35,000 µV ± 10%/1 M) and with equipment of very exact temperature control.

2.3. Preparation of polymer anions

All polymerizations and reactions were carried out under high vacuum conditions (10⁻⁶ Torr) in sealed glass reactors equipped with break seals. All reactors were pre-washed with initiator solutions after being sealed off from a vacuum line. The polymer anion comprised of three polymer chains was prepared as follows: in-chain-functionalized polystyrene with DPE moiety was first prepared by the addition reaction of polystyryllithium (PSLi) to DPE-chain-end-functionalized polystyrene, followed by treating with 1 to introduce the DPE moiety. The reactions completely proceeded in THF at −78 °C for 2 h. The resulting in-chain-functionalized polystyrene with DPE moiety was then isolated by fractional precipitation and purified by reprecipitation twice and freeze-dried. The polymer anion comprised of three polymer chains was prepared by reacting PSLi with the in-chain-functionalized polystyrene with DPE moiety in THF at −78 °C for 1 h and in situ used in the next coupling reaction. The polymer anion comprised of three different polymer chains were prepared in the similar manner by reacting poly(4-methylstyryl)lithium with in-chain-end-functionalized block copolymer of 4-trimethylsilylstyrene and 4-methoxystyrene with DPE moiety.

2.4. Synthesis of star-shaped polymers

Both regular and asymmetric star-shaped polymers were synthesized by in situ coupling with the polymer anions with chain-end-functionalized polystyrenes with two and four benzyl bromide moieties in THF at −78 °C for 24 h. A 1.5-fold excess of the polymer anion towards the benzyl bromide moiety was always used to complete the reaction. The requisite star-shaped polymers were isolated in 80–90% yields by fractional precipitation and purified by reprecipitation twice and freeze-dried.

3. Results and discussion

We previously demonstrated that the polymer anions of two same or different polymer chains reacted quantitatively with chain-end-functionalized polystyrenes with two, four, eight, and even sixteen benzyl bromide moieties to afford five, nine, seventeen, and thirty-three armed regular and asymmetric star-shaped polymers. Accordingly, the steric limitation as predicted from the structure of the polymer anion is not practically present in the coupling system with the polymer anion. These successful results led us to further develop the methodology by using specially designed star-shaped polymer anions comprised of three polymer chains.

3.1. Preparation of polymer anions comprised of three polymer chains

The polymer anions specially designed to comprise of three either same or different polymer chains are prepared as illustrated in Scheme 2. For this preparation, at first in-chain-functionalized polystyrene with DPE moiety was prepared by reacting PSLi with chain-end-functionalized polystyrene with DPE moiety, followed by in situ treatment with 1 to introduce a DPE moiety at the linking point via the anion. Then, PSLi was treated with the resulting in-chain-functionalized polystyrene with DPE moiety to afford the objective polymer anion comprised of three polystyrene chains. As can be seen in Scheme 2, the polymer anion thus prepared can be regarded as a 3-armed star-shaped polystyrene carrying an anion at the core.

By using in-chain-functionalized block copolymer of 4-trimethylsilylstyrene and 4-methoxystyrene with DPE moiety and poly(4-methylstyryl)lithium in the final reaction
stage, we also obtained a 3-armed star-shaped polymer anion comprised of poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), and poly(4-methylstyrene) segments. Prior to the coupling reaction, these star-shaped polymer anions were partly sampled and characterized by SEC, $^1$H NMR, and SLS, respectively. The results are summarized in Table 1. SEC profiles of the polymer anions deactivated showed sharp monomodal distributions. Their molecular weights predicted were in good agreement with those determined by SLS. Agreement of the composition between calculated and observed by $^1$H NMR was also quite satisfactory. These results clearly indicate the expected and well-controlled structures of the star-shaped polymer anions.
3.2. Synthesis of regular star-shaped polystyrenes

In order to examine the possible use of the newly prepared polymer anion comprised of three polymer chains in this study, we first tried to synthesize a 7-armed star-shaped polystyrene by coupling the polymer anion comprised of three polystyrene chains with chain-end-functionalized polystyrene with two benzyl bromide moieties as illustrated in Scheme 3. This is because the anion is located at the core of 3-armed star-shaped polystyrene and thereby seems to be highly sterically hindered. The coupling reaction was carried out in THF at \(-78^\circ C\) for 24 h. Fig. 1(A) shows the SEC profile of the reaction mixture. There are a high molecular weight main peak corresponding to the objective star-shaped polymer and two small low molecular weight peaks for the deactivated star-shaped polymer anion and DPE-in-chain-functionalized polystyrene used in excess in the reactions.

![Scheme 3. Synthesis of 7- and 13-armed regular star-shaped polystyrenes by the coupling reaction of star-shaped polymer anion with chain-end-functionalized polystyrene with either two or four benzyl bromide moieties.](image)

### Table 1

| Type   | $M_n$ (kg/mol) | $M_w$ (kg/mol) | $M_w/M_n$, SEC |
|--------|----------------|----------------|----------------|
| Calculated | Calculated$^a$ | SEC | $^1$H NMR | SLS$^b$ | dn/dc$^b$ |
| A$^c$ | 33.7 | 29.7 | 34.0 | 34.7 | 35.1 | 0.191 | 1.03 |
| ABC$^d$ | 30.5 | 26.2 | 31.0 | 30.8 | 31.4 | 0.169 | 1.01 |

$^a$ Calculated from $M_n$ (calcd) and $M_w/M_n$ (SEC).

$^b$ Measured in THF at 25 °C.

$^c$ 3-Armed regular star-shaped polystyrene.

$^d$ ABC star-shaped polymer where A, B, and C are poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstylene), respectively. A/B/C (wt%) = 33/35/32 (calcd), 32/35/33 ($^1$H NMR).
The yield of the star-shaped polymer was virtually quantitative based on these peak areas. The star-shaped polymer was isolated by fractional precipitation and characterized by SEC, SLS, and viscosity measurements, respectively. The results are summarized in Table 2.

The isolated polymer, shown in Fig. 1(B), exhibits a sharp monomodal SEC distribution, the $M_w = M_n$ value being 1.04. Importantly, neither shoulder nor tailing was observed at all. The $M_n$ value estimated by SEC relative to polystyrene was smaller than that predicted as expected from its branched structure. On the other hand, the absolute $M_w$ of 83.0 kg/mol determined by SLS agreed quite well with the expected value of 81.3 kg/mol assuming that the polymer anion was completely reacted with the terminal two benzyl bromide functionalities. Moreover, the experimentally observed $g'$ value defined as $[\eta]_{\text{star}}/[\eta]_{\text{linear}}$ was consistent with that calculated by the established equation. These analytical results clearly indicate that the expected 7-armed regular star-shaped polystyrene is successfully synthesized by the coupling reaction with the polymer anion.

We have further performed the coupling reaction of the same polymer anion with chain-end-functionalized polystyrene with four benzyl bromide moieties again as illustrated in Scheme 3. Under the identical conditions, the reaction was observed to proceed quantitatively. The star-shaped polymer was carefully isolated by fractional precipitation. The characterization results are summarized in Table 2.

The isolated polymer showed a sharp monomodal SEC distribution ($M_w/M_n = 1.03$). The $M_n$ value estimated by SEC is much smaller than that calculated as expected. Agreement of $M_w$ values between calculated and determined by SLS is satisfactory within an experimental error. The $g'$ value experimentally determined is very close to that calculated from the equation regarded as 13-armed star-shaped polymer. Thus, the star-shaped polymer anion could also react efficiently and quantitatively even with the four terminal benzyl bromide functionalities to afford a 13-armed star-shaped polystyrene. The possible use of the polymer anion for the star-shaped polymer synthesis is thus evident.

3.3. Synthesis of asymmetric star-shaped polymer

Based on the successful results described in the preceding section, we have synthesized asymmetric star-shaped polymers by the coupling reaction of the polymer anion comprised of three different polymer chains, namely, poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), and poly(4-methylstyrene) segments, with chain-end-functionalized polystyrene with either two or four benzyl bromide moieties. If these coupling reactions occurred as desired, 7-armed $A_2B_2C_2D$ and 13-armed $A_4B_4C_4D$ asymmetric star-shaped polystyrenes after fractionation were more than 85% in both cases.

### Table 2

| Type   | $M_n$ (kg/mol) | $M_w$ (kg/mol) | $M_w/M_n$, SEC | $g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}}$ | Calculated | Experimental |
|--------|----------------|----------------|----------------|-------------------------------------------------|------------|--------------|
| 7-Arm  | 78.2           | 62.3           | 81.3           | 0.190                                            | 1.04       | 0.51         |
| 13-Arm | 134            | 73.8           | 138            | 0.191                                            | 1.03       | 0.31         |

Yields of star-shaped polystyrenes after fractionation were more than 85% in both cases.

1. Intrinsic viscosity of star-shaped polystyrene ($[\eta]_{\text{star}}$) was measured in toluene at 35 °C. Intrinsic viscosity of polystyrene with the same molecular weight to that of corresponding star-shaped polystyrene ($[\eta]_{\text{linear}}$) was calculated from the equation $[\eta] = 1.26 \times 10^{-4} \times M_w$ (SLS) [29].

2. Calculated from $M_n$ (calcld) and $M_w/M_n$ (SEC).

3. Measured in THF at 25 °C.

4. Calculated from the equation $g' = ([3f - 2]f^2)^{0.58} \times 0.724 - 0.015(f - 1)/0.724 : f = \text{arm number (3 ≤ f ≤ 18)}$ [30].
star-shaped polymers would result as illustrated in Scheme 4.

The SEC profiles of the both reaction mixtures were very similar to Fig. 1(A). Based on the peak areas, the coupling reactions were complete under the conditions. The isolated polymer in either case showed sharp monomodal SEC distributions without any shoulders and tailings. Their $M_w/M_n$ values were 1.03 and 1.02, respectively. The results are summarized in Table 3. The compositions of four polymer segments observed by $^1$H NMR agreed well with those calculated from the feed ratios. The $M_n$ values calculated from these observed composition ratios and the molecular weights of polymer anions were in good agreement with those calculated. Furthermore, the absolute $M_w$ values determined by SLS were also very close to those calculated in both samples. All of the analytical results

Scheme 4. Synthesis of 7-armed $A_2B_2C_2D$ and 13-armed $A_4B_4C_4D$ star-shaped polymers.

Yields of asymmetric star-shaped polymers after fractionation were more than 80% in both cases.

Table 3
Synthesis of 7-armed $A_2B_2C_2D$ and 13-armed $A_4B_4C_4D$ star-branched polymers

| Type      | $M_n$ (kg/mol) | $M_w$ (kg/mol) | $M_w/M_n$, SEC | Composition (A/B/C/D wt%) |
|-----------|----------------|----------------|----------------|---------------------------|
| A$_2$B$_2$C$_2$D | 71.5            | 51.0           | 72.0           | 73.6                      | 77.9 | 1.71 | 1.03 | 27/30/28/15 | 26/28/31/15 |
| A$_4$B$_4$C$_4$D | 131             | 64.5           | 129            | 135                       | 133  | 0.70 | 1.02 | 30/33/29/8  | 28/31/32/9  |

a. $A$, $B$, $C$ and $D$ are poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), and polystyrene, respectively.
b. Calculated from $M_n$ (calcd) and $M_w/M_n$ (SEC).
c. Measured in THF at 25 °C.

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indicate the formation of the expected 7-armed A2B2C2D and 13-armed AB3C3D symmetric star-shaped polymers consisting of poly(4-trimethylsilylstyrene), poly(4-methoxy-styrene), poly(4-methylstyrrene), and polystyrene segments. Thus, we have again demonstrated that it is also possible to simultaneously introduce three different polymer chains in the coupling reaction with use of the polymer anion. The possible introduction of different three polymer segments by one-step coupling reaction via one benzyl bromide functionality is particularly attractive from a viewpoint of asymmetric star-shaped polymer synthesis.

The two stars synthesized herein are the first successful examples of asymmetric star-shaped polymers consisting of four different plural polymer segments. It was observed by transmission electron microscopy that new morphologies with nanoscopic ordered structures were suggested to form in both samples. These studies are now under investigation.  

4. Concluding remarks

We have demonstrated that the coupling reactions of benzyl bromide-functionalized polystyrenes with the polymer anions comprised of three same or different polymer chains is an efficient and versatile methodology for the synthesis of well-defined regular and asymmetric star-shaped polymers. In particular, the use of the polymer anion comprised of different three polymer anions may allow a versatile and promising procedure for asymmetric star-shaped polymers that cannot be synthesized by any other methods so far reported. The availability of a variety of chain-end- and in-chain-functionalized polymers with benzyl bromide moieties is an additional advantage of the present methodology [22,27,31,32]. In forthcoming research, the synthesis of functional asymmetric star-shaped polymers consisting of amphiphilic segments and conducting polymer segments by this methodology as well as their morphologies at molecular level leading to nanoscale ordered suprastructures and nanomaterial formation will be reported.

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