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Syntheses of AB_2 3- and AB_4 5-miktoarm star copolymers by combination of the anionic ring-opening polymerization of hexamethylcyclotrisiloxane and nitroxide-mediated radical polymerization of styrene

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Abstract

AB_2 3- and AB_4 5-miktoarm star copolymers were prepared by combination of the anionic ring-opening polymerization (AROP) of hexamethylcyclotrisiloxane (D_3) and the TEMPO-mediated radical polymerization of styrene (St). Initially, two kinds of dendritic multifunctional initiators were prepared. One has a 4-bromobutoxy group and two TEMPO-based alkoxyamines and the other has a 4-bromobutoxy group and four TEMPO-based alkoxyamines. Treatment of the multifunctional initiators with *tert*-butyllithium gave the corresponding lithiobutoxy derivatives, and AROP of D_3 by the lithiobutoxy derivatives gave poly(D_3) with M_w/M_n of 1.07–1.12. Nitroxide-mediated radical polymerization of St by the poly(D_3)s at 120 °C gave AB_2 3- and AB_4 5-miktoarm star copolymers with M_w/M_n of 1.15–1.28. Their structures were analyzed by means of ^1H NMR and SEC measurements.

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Keywords: Living radical polymerization; Miktoarm star copolymer; Polysiloxanes

1. Introduction

Miktoarm star copolymers have attracted much attention in recent years because they show the interesting unique properties regarding microphase separation in solid state as well as in solution [1–3]. Therefore, those possess potential importance as new functional materials. Although miktoarm star copolymers have been synthesized mainly by the anionic polymerization [1–4], the recent development in the living radical polymerization (LRP) [5–9] has brought about a drastic change in the synthetic methodology for miktoarm star copolymers for the last 5 years [10–34]. The radical polymerization technique is more convenient than the anionic polymerization technique because it does not require strict purification of monomers and solvents and allows the presence of a variety of functional groups. There are two methods for the syntheses of miktoarm star copolymers by the LRP technique: the core-first method and the arm-first method. Although the arm-first method provides a convenient approach to miktoarm star copolymers, it does not afford well-defined miktoarm star copolymers [12,23,24]. On the other hand, the core-first method requires the design and syntheses of appropriate multifunctional initiators, but it provides well-defined structures with the constant arm numbers and constant arm lengths [10–11,13–22,25–34]. In a series of the studies on design and syntheses of well-defined polymeric architectures using the LRP technique [35–41], we synthesized star polymers, miktoarm star copolymers by the core-first method. In the present paper, we report the first successful syntheses of polysiloxane-containing AB_2 3- and AB_4 5-miktoarm star copolymers by combination of the anionic ring-opening polymerization (AROP) of hexamethylcyclotrisiloxane (D_3) and the nitroxide mediated radical polymerization (NMRP) of styrene (St) using dendritic tri- and pentafunctional initiators (Chart 1). It is well known that polysiloxanes are materials that show unique properties such as high chain flexibility, low surface energy, and low solubility parameter, etc. Consequently, the syntheses of polysiloxane-containing polymeric architectures are highly important for designing new materials. Some polysiloxane-containing miktoarm star copolymers were prepared using the anionic polymerization technique. Isono et al. prepared ABC 3-miktoarm star copolymer by the anionic polymerizations of D_3, St, and *t*-butyl acrylate [42], and Hadjichristidis, et al. reported the syntheses of AB_2 and ABC

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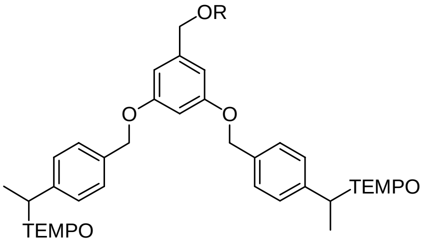
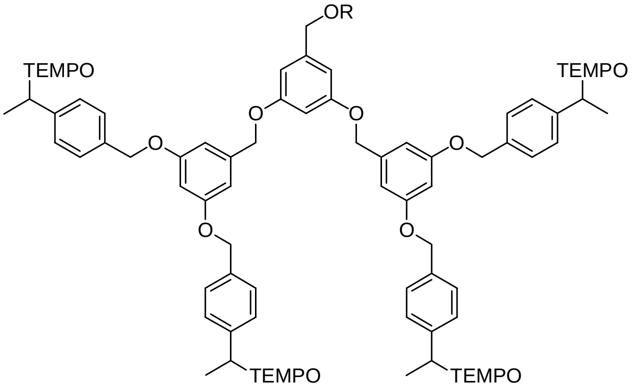


[G-1]-OH: R = H
[G-1]-O(CH$_2$)$_4$Br: R = (CH$_2$)$_4$Br
[G-1]-O(CH$_2$)$_4$Li: R = (CH$_2$)$_4$Li



[G-2]-OH: R = H
[G-2]-O(CH$_2$)$_4$Br: R = (CH$_2$)$_4$Br
[G-2]-O(CH$_2$)$_4$Li: R = (CH$_2$)$_4$Li

TEMPO:

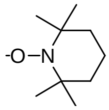


Chart 1.

3-miktoarm star copolymers by the anionic polymerizations of D$_3$ and St, and isoprene [43]. However, the syntheses of polysiloxane-containing miktoarm star copolymers via the LRP technique have never been reported.

2. Experimental section

2.1. General

^{1}H NMR spectra were measured with a JEOL α-400 spectrometer (400 MHz). Chemical shifts (δ) are expressed in ppm downfield from TMS as the internal standard. High resolution (HR) FAB mass spectra were recorded on a JEOL JMS-AX500 spectrometer. Preparative HPLC purification was performed with a Japan Analytical Industry LC-908 preparative recycling HPLC instrument with CHCl$_3$ as the eluant. Size exclusion chromatography (SEC) was carried out with a Tosoh 8020 series using TSKgel G5000H$_{HR}$, MultiporeH$_{XL}$-M, and GMH$_{HR}$-L columns calibrated with polystyrene standards, eluting with THF at 40 °C. Detection was made with a Tosoh refractive index detector RI8020.

2.2. Materials

[**G-1**]-OH and [**G-2**]-OH were prepared by our previously reported method [37,39, 40]. 2,2,6,6-Tetramethylpiperidinyl-*N*-oxyl (TEMPO) was commercially available (Aldrich) and purified by sublimation. *tert*-Butyllithium (*t*-BuLi) was obtained from Kanto Chemical as heptane solution (concentration 1.60 M). Commercially available D$_3$ was refluxed in toluene for 12 h in the presence of CaH$_2$ and, after filtration, the toluene was evaporated and the residue was sublimed prior to use. St was purified prior to use by the usual method. THF and diethyl ether were distilled from benzophenone/Na. Column chromatography was carried out on silica gel (Kanto Chemical N60).

2.3. Synthesis of [*G-1*]-O(CH$_2$)$_4$Br

NaH (0.23 g, 9.6 mmol), washed with anhydrous THF, was added to a solution of [**G-1**]-OH (4.49 g, 6.54 mmol) in anhydrous THF (10 mL). After the mixture was stirred for 30 min at room temperature, the THF was removed under reduced pressure. 1,4-Dibromobutane (7.06 g, 32.7 mmol) and dry DMF (3.5 mL) were added and the resultant mixture was stirred at 60 °C for 48 h under N$_2$. After water (50 mL) was added, the mixture was extracted with ether, and the combined ether extracts were dried over anhydrous MgSO$_4$. After filtration, the ether was evaporated under reduced pressure and the residue was chromatographed on silica gel with 1:7 EtOAc–hexane to give [**G-1**]-O(CH$_2$)$_4$Br in 58% yield (3.07 g) as a colorless viscous oil. The oil was further purified with a preparative recycling HPLC instrument using CHCl$_3$. HRFABMS: *m/z* calcd for $C_{47}H_{69}$ $^{79}BrN_2O_5$ $(M+1)^+$ 821.4468. Found: 821.4443. Calcd for $C_{47}H_{69}$ $^{81}BrN_2O_5$ $(M+1)^+$ 823.4468. Found: 823.4459. ^{1}H NMR (CDCl$_3$): δ 0.68, 1.02, 1.16, 1.29 (s, CH$_3$, 24H), 1.37–1.60 (br m, (CH$_2$)$_3$, 12H), 1.47 (d, $J=6.6$ Hz, CHCH_3, 6H), 1.75 (quint, $J=6.4$ Hz, OCH$_2$CH$_2$CH_2CH$_2$Br or OCH$_2$CH_2CH$_2$CH$_2$Br 2H), 1.98 (quint, $J=6.4$ Hz, OCH$_2$CH_2CH$_2$CH$_2$Br or OCH$_2$CH$_2$CH_2-CH$_2$Br, 2H), 3.44 (t, $J=6.4$ Hz, OCH_2CH$_2$CH$_2$CH$_2$Br, 2H), 3.48 (t, $J=6.4$ Hz, OCH$_2$CH$_2$CH$_2$CH_2Br, 2H), 4.44 (s, benzylic, 2H), 4.79 (q, $J=6.6$ Hz, CHCH$_3$, 2H), 5.00 (s, benzylic, 4H), 6.54 (t, $J=2.0$ Hz, aromatic, 1H), 6.59 (d, $J=2.0$ Hz, aromatic, 2H), 7.33 (d, $J=8.4$ Hz, aromatic, 4H), 7.36 (d, $J=8.4$ Hz, aromatic, 4H).

2.4. Synthesis of [*G-2*]-O(CH$_2$)$_4$Br

NaH (60% in oil) (0.050 g, 2.1 mmol), washed with anhydrous THF, was added to a solution of [**G-2**]-OH (2.00 g, 1.35 mmol) in anhydrous THF (5.0 mL). After the mixture was stirred at room temperature for 30 min, THF was removed under reduced pressure. 1,4-Dibromobutane (1.46 g, 6.75 mmol) and dry DMF (3.0 mL) were then added, and the resultant mixture was stirred at 60 °C for 48 h under N$_2$. After water (50 mL) was added, the mixture was extracted with ether and the combined ether extracts were dried over anhydrous MgSO$_4$. After filtration, the ether was evaporated under reduced pressure and the residue was chromatographed on silica gel with 1:4 EtOAc–hexane to give [**G-2**]-O$(CH_2)_4$Br in 69% yield (1.50 g) as a colorless viscous oil. The product was further purified with a recycling preparative HPLC instrument. HRFABMS: *m/z* calcd for $C_{97}H_{135}$ $^{79}BrN_4O_{11}$ M^+ 1610.9311. Found: 1610.9299. ^{1}H NMR ($CDCl_3$): δ 0.67, 1.02, 1.16, 1.29 (s, CH_3, 48H), 1.37–1.60 (br m, $(CH_2)_3$, 24H), 1.47 (d, $J=6.8$ Hz, $CHCH_3$, 12H), 1.74 (quint, $J=6.4$ Hz, $OCH_2CH_2CH_2CH_2Br$ or $OCH_2CH_2CH_2CH_2Br$, 2H), 1.98 (quint, $J=6.4$ Hz, $OCH_2CH_2CH_2CH_2Br$ or $OCH_2CH_2CH_2CH_2Br$, 2H), 3.42 (t, $J=6.8$ Hz, $OCH_2CH_2CH_2CH_2Br$, 2H), 3.47 (t, $J=6.4$ Hz, $OCH_2CH_2CH_2CH_2Br$, 2H), 4.44 (s, benzylic, 2H), 4.79 (q, $J=6.6$ Hz, $CHCH_3$, 4H), 4.97 (s, benzylic, 4H), 5.00 (s, benzylic, 8H), 6.54 (t, $J=2.0$ Hz, aromatic, 1H), 6.56 (t, $J=2.0$ Hz, 2H), 6.58 (d, $J=2.0$ Hz, aromatic, 2H), 6.69 (d, $J=2.0$ Hz, aromatic, 4H), 7.33 (d, $J=8.4$ Hz, aromatic, 8H), 7.36 (d, $J=8.4$ Hz, aromatic, 8H).

2.5. Reaction of [G-1]-O(CH$_2$)$_4$Br with t-BuLi

[**G-1**]-O$(CH_2)_4$Br (0.105 g, 0.128 mmol) and dry ether (1.0 mL) were put into a two-necked flask. After the flask was charged with N_2, the mixture was cooled to −78 °C with a dry-ice MeOH bath and a heptane solution of *t*-BuLi (1.60 M) (0.10 mL, 0.16 mmol) was added through a double septum with a syringe. After being stirred for 2 h at the same temperature, the mixture was gradually warmed to room temperature. Water was added, and the mixture was extracted with ether. The combined ether extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, evaporated under reduced pressure, and dried in vacuum to give 0.102 g of viscous colorless oil. The oil was then subjected to ^{1}H NMR measurements without any purification.

2.6. AROP of D$_3$ with [G-1]-O(CH$_2$)$_4$Li

[**G-1**]-O$(CH_2)_4$Br (0.87 g, 1.05 mmol) and dry ether (2.0 mL) were put into a two-necked flask. After the flask was charged with N_2, the mixture was cooled to −78 °C with a dry-ice MeOH bath and a heptane solution of *t*-BuLi (1.60 M) (0.55 mL, 0.88 mmol) was added through a double septum with a syringe. After being stirred for 2 h at the same temperature, the mixture was gradually warmed to room temperature, and a solution of D_3 (2.50 g, 11.2 mmol) in anhydrous THF (5.0 mL) was added to the ether solution of [**G-1**]-O$(CH_2)_4$Li through the double septum with a syringe. The resultant mixture was stirred at room temperature for 6 h and poured into a large amount of MeOH to give [**G-1**]-O$(CH_2)_4$-poly(D_3) as a viscous colorless oil. After decantation was twice repeated with toluene (ca. 2 mL)/MeOH (ca. 100 mL), the resultant oil was further purified with a preparative recycling HPLC instrument. Yield 1.51 g, (conversion of D_3 55%), $M_{n,NMR}=8000$, $M_{n,SEC}=7200$, $M_w/M_n=1.07$.

2.7. AROP of D$_3$ with [G-2]-O(CH$_2$)$_4$Li

[**G-2**]-O$(CH_2)_4$Br (0.85 g, 0.52 mmol) and dry ether (2.0 mL) were put into a two-necked flask. After the flask was charged with N_2, the mixture was cooled to −78 °C with a dry-ice MeOH bath and a heptane solution of *t*-BuLi (1.56 M) (0.29 mL, 0.45 mmol) was added through a double septum with a syringe. After being stirred for 2 h at the same temperature, the mixture was gradually warmed to room temperature. A solution of D_3 (1.75 g, 7.86 mmol) in anhydrous THF (3.5 mL) was then added to the ether solution of [**G-2**]-O$(CH_2)_4$Li through the double septum with a syringe, and the resultant mixture was stirred at room temperature for 12 h. The mixture was then poured into a large amount of MeOH to give 1.50 g of [**G-2**]-O$(CH_2)_4$-poly(D_3) as a viscous colorless oil. After decantation was twice repeated with toluene (ca. 2 mL)/MeOH (ca. 100 mL), the resultant oil was further purified with a preparative recycling HPLC instrument. Yield 0.71 g (conversion of D_3 34%), $M_{n,NMR}=7300$, $M_{n,SEC}=6700$, $M_w/M_n=1.12$.

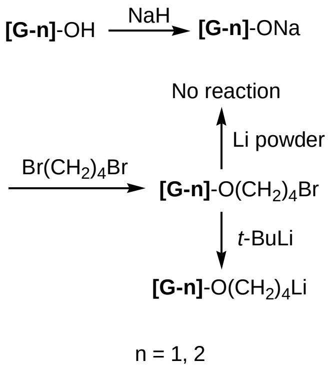
2.8. NMRP of St from [G-n]-O(CH$_2$)$_4$-poly(D$_3$) (n=1, 2)

St (1.00 mL, 8.7 mmol) and [**G-n**]-O$(CH_2)_4$-poly(D_3) (0.010 mmol) were put into a Pyrex glass tube, and the tube was then degassed by three freeze-pump-thaw cycles using a high-vacuum system and sealed off. The mixture was then heated at 120 °C for a given time and poured into a large amount of MeOH. The resultant powder was collected by filtration and dried in vacuum. Yields were determined by gravimetric method. After decantation with toluene/MeOH, ^{1}H NMR and SEC measurements were conducted.

3. Results and discussion

3.1. Synthesis of [G-n]-O(CH$_2$)$_4$Br (n=1, 2)

Dendritic multifunctional initiators, [**G-n**]-OH, were prepared according to a previous method reported by our group [37,39,40]. [**G-n**]-OH was then treated with NaH in anhydrous THF and the resultant [**G-n**]-ONa was allowed to react with a large excess of 1,4-dibromobutane in dry DMF at 60 °C (Scheme 1). After column chromatography and subsequent



Scheme 1.

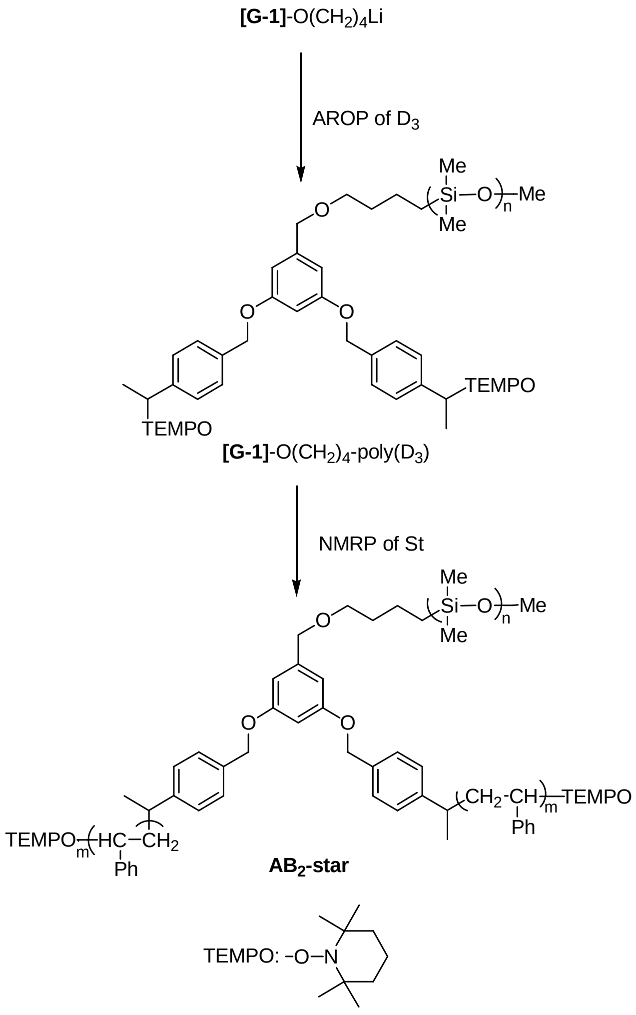
preparative HPLC purification, [**G-n**]-O(CH_2)$_4$Br was obtained as a colorless viscous oil in 58% ($n=1$) and 69% yields ($n=2$), respectively. Their structures were confirmed by ^{1}H NMR spectra and HRFAB mass spectra.

*3.2. Lithiation of [G-**n**]-O(CH_2)$_4$Br (n = 1, 2)*

For the lithiation of [**G-n**]-O(CH_2)$_4$Br the first attempt was treating [**G-n**]-O(CH_2)$_4$Br with Li powder in dry ether. After a mixture of [**G-n**]-O(CH_2)$_4$Br and Li powder in dry ether was stirred at room temperature for 5 h under N_2, the resultant mixture was quenched with MeOH and a large amount of water was added. After the mixture was extracted with ether, the combined ether extracts were dried and evaporated, and the residue was subjected to ^{1}H NMR measurements without any purification. The obtained ^{1}H NMR spectra completely agreed with those of [**G-n**]-O(CH_2)$_4$Br, indicating that lithiation of [**G-n**]-O(CH_2)$_4$Br with Li powder was unsuccessful. The steric congestion around the bromides might make the lithiation of [**G-n**]-O(CH_2)$_4$Br difficult. The second method was treating [**G-n**]-O(CH_2)$_4$Br with *t*-BuLi. A solution of [**G-1**]-O(CH_2)$_4$Br in ether was cooled to −78 °C and 1.3 equivalent of *t*-BuLi (in heptane solution) was added. After being stirred for 2 h at the same temperature, the mixture was raised to 0 °C and quenched with water. The mixture was then extracted with ether and the combined ether extracts were dried and evaporated, and the residue was subjected to ^{1}H NMR measurements without purification. Although the ^{1}H NMR spectrum was complex due to the presence of impurities, it was clearly different from that of [**G-1**]-O(CH_2)$_4$Br. A new triplet peak due to $CH_3CH_2CH_2CH_2O$ ($J=6.3$ Hz) was observed at 0.86 ppm and the triplet peak due to $BrCH_2CH_2CH_2CH_2O$ at 3.48 ppm was significantly weakened. On the basis of the above NMR results it was concluded that that [**G-1**]-O(CH_2)$_3$Br was converted to the corresponding [**G-1**]-O(CH_2)$_3$Li by treating [**G-1**]-O(CH_2)$_3$Br with *t*-BuLi. Therefore, lithiation of [**G-n**]-O(CH_2)$_4$Br was decided to carry out by treating with *t*-BuLi.

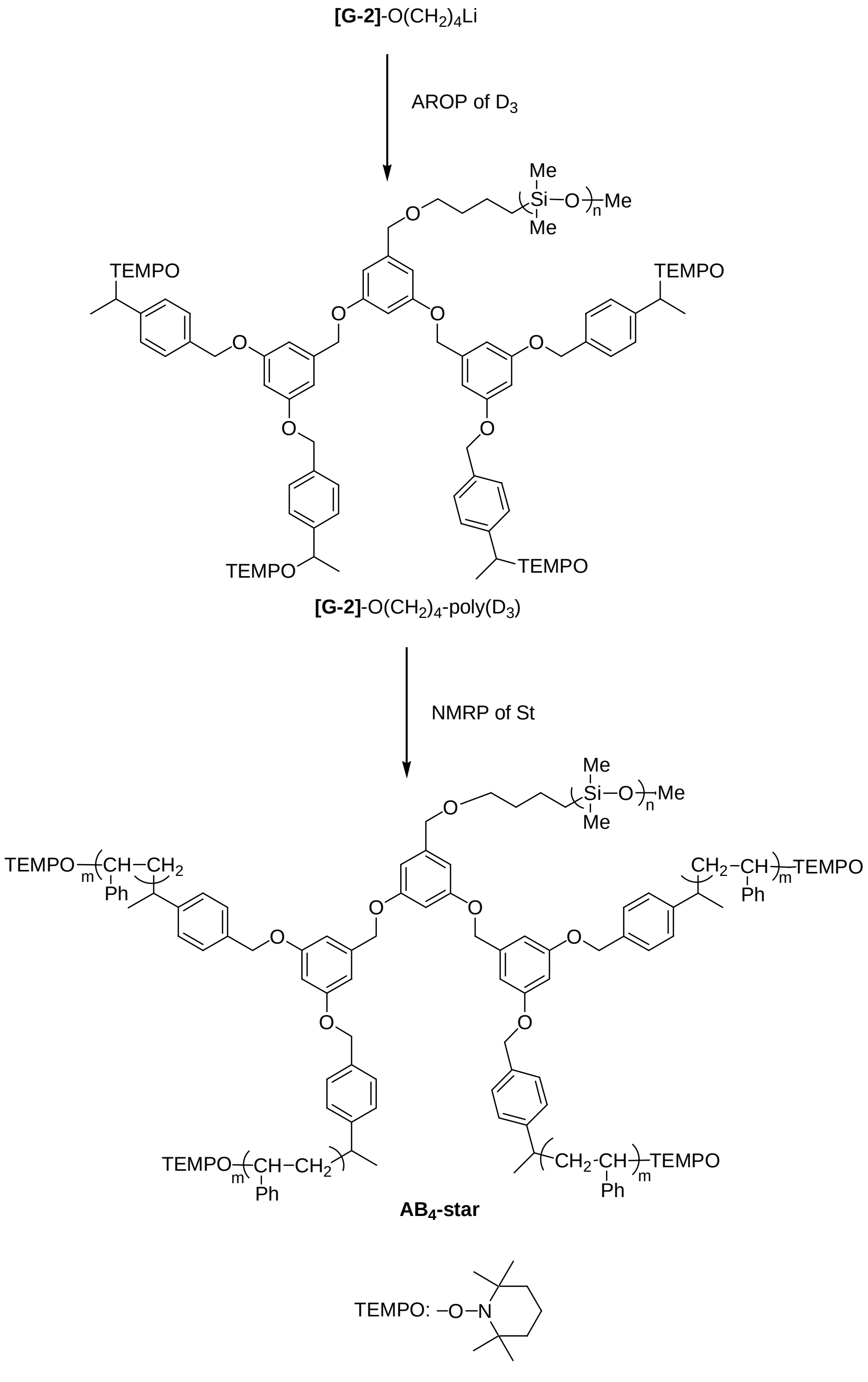
*3.3. AROP of D_3 with [G-**n**]-O(CH_2)$_4$Li (n = 1, 2)*

A ether solution of [**G-n**]-O(CH_2)$_4$Br was cooled to −78 °C and ∼0.9 equivalent of *t*-BuLi was added. After being stirred for 2 h at the same temperature, the mixture was gradually raised to room temperature and a THF solution of D_3 was added. After being stirred for 6–12 h at room temperature, the mixture was poured into a large amount of MeOH to give [**G-n**]-O(CH_2)$_4$-poly(D_3) ($n=1$, 2) as a colorless viscous oil (Schemes 2 and 3). To avoid AROP of D_3 by *t*-BuLi the amount of *t*-BuLi added was smaller than [**G-n**]-O(CH_2)Br (0.9 equivalent for [**G-n**]-O(CH_2)Br). Therefore, [**G-n**]-O(CH_2)$_4$-poly(D_3) contained the unreacted [**G-n**]-O(CH_2)$_4$Br. This was shown by their SEC measurements. The SEC traces showed that the of [**G-1**]-O(CH_2)$_4$-poly(D_3) contained a large amount of the unreacted [**G-1**]-O(CH_2)$_4$Br, together with small amounts of high molecular weight compounds. Fortunately, the unreacted [**G-1**]-O(CH_2)$_4$Br and high molecular weight compounds could be removed by repeated decantation (usually two times) with toluene/MeOH. When they could not be completely removed by decantation, it was further purified with a preparative recycling HPLC. Similar to [**G-1**]-O(CH_2)$_4$-poly(D_3), [**G-2**]-O(CH_2)$_4$-poly(D_3) contained a large amount of the unreacted [**G-n**]-O(CH_2)$_4$Br and small amounts of high molecular weight compounds. Unfortunately, the unreacted [**G-2**]-O(CH_2)$_4$Br could not be completely removed only by decantation with toluene/MeOH, different from the case of [**G-1**]-O(CH_2)$_4$-poly(D_3). Accordingly, the [**G-2**]-O(CH_2)$_4$-poly(D_3) sample was further purified with a preparative recycling HPLC, and the HPLC purification gave [**G-2**]-O(CH_2)$_4$Br-free sample. In the following NMRP of St [**G-n**]-O(CH_2)$_4$Br-free [**G-n**]-O(CH_2)$_4$-poly(D_3) samples were used as the macroinitiator.



Scheme 2.

A typical ^{1}H NMR spectrum of [**G-1**]-O(CH_2)$_4$-poly(D_3) is depicted in Fig. 1. A singlet peak due to $-OSi(CH_3)_2-$ is observed at 0.07 ppm and a singlet peak due to the $-OSi(Me_2)OCH_3$ is observed at 3.48 ppm. Upon recording at high gain, the peaks due to the protons in the dendritic moiety are clearly observed. Four singlets at 0.68, 1.02, 1.16 and 1.29 ppm are assigned to H_a (24H) and a doublet at 1.47 ppm is assigned to H_c(6H). A quartet at 4.79 ppm is assigned to H_d (2H), and two



Scheme 3.

singlets at 4.44 and 5.00 ppm are assigned to H_i (2H) and H_f (4H), respectively. On the other hand, two doublets at 7.33 and 7.36 ppm are assigned to H_e (8H), and a triplet at 6.54 ppm and a doublet at 6.59 ppm are assigned to H_g (1H) and H_h (2H), respectively. The observed integrated ratios, H_a:H_d:H_e:H_f:($H_g + H_h$):H_i = 23.72:2.12:7.92:4.00:3.11:1:93, well agree with the theoretical ratios (24:2:8:4:3:2), indicating no or negligible decomposition of the [**G-1**] part.

In order to confirm the end structure of polysiloxane part, the integrated intensity of the peak due to $–OSi(Me_2)OCH_3$ was determined by comparing with that of the peak due to H_i, and it was determined to be 2.73H. The magnitude, 2.77, indicates that the end structure of the polysiloxane chain is $–OSi(Me_2)OCH_3$. Furthermore, the degree of polymerization (DP) for the poly(D_3) arm was estimated by comparison of the integrated intensity of the peak due to $Si(CH_3)_2$ with that of H_i, and it was determined to be 32.6. Based on the value the $M_{n,NMR}$ was calculated to be 8000, which agreed with the M_n value of 7200 determined by SEC (the polydispersity index (M_w/M_n), 1.07). Based on the yield (1.51 g) of [**G-1**]-O(CH_2)$_4$-poly(D_3) the conversion of D_3 was calculated to be 55%, and the yield based on [**G-1**]-

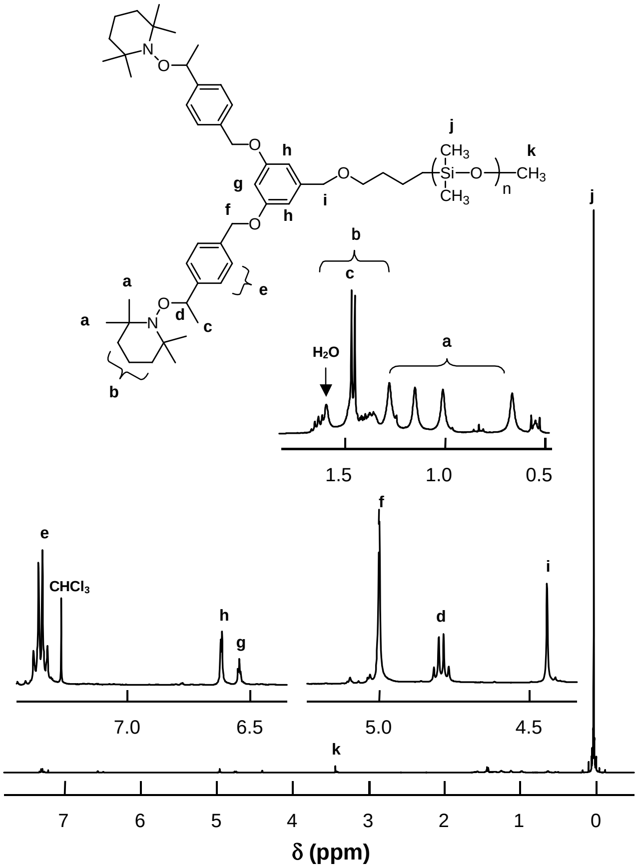


Fig. 1. ^{1}H NMR spectrum of [**G-1**]-O(CH_2)$_4$-poly(D_3) in $CDCl_3$.

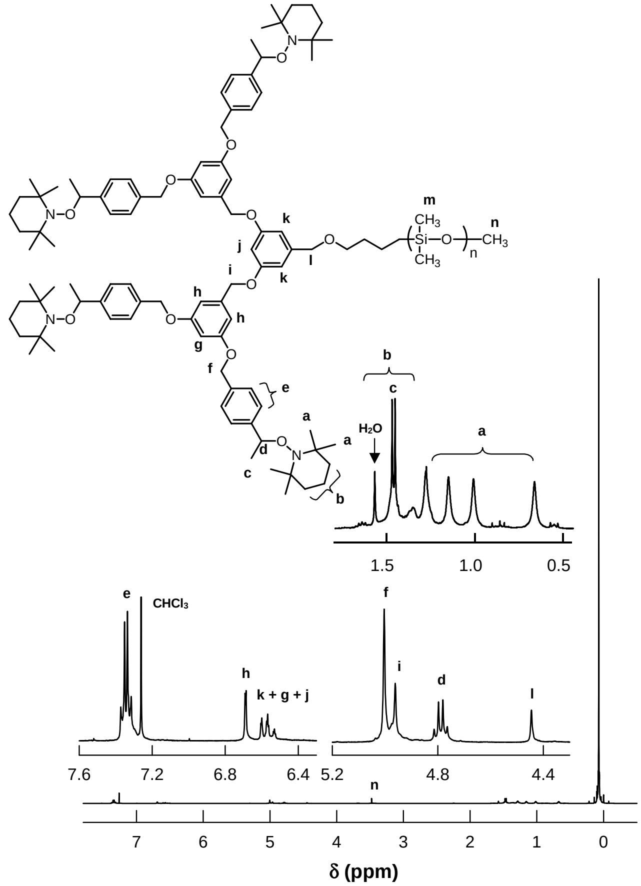


Fig. 2. ^{1}H NMR spectrum of [**G-2**]-O(CH_2)$_4$-poly(D_3) in $CDCl_3$.

O(CH_2)$_4$Br was derived to be 18%. The low yield of [**G-1**]-O(CH_2)$_4$-poly(D_3) based on [**G-1**]-O(CH_2)$_4$Br is indicative of the insufficient lithiation of [**G-1**]-O(CH_2)$_4$Br.

A typical ^{1}H NMR spectrum of [**G-2**]-O(CH_2)$_4$-poly(D_3) is depicted in Fig. 2. Similar to Fig. 1, a sharp singlet peak is observed at 0.07 ppm and a weak singlet peak due to the –OSi(Me_2) OCH_3 is observed at 3.48 ppm. Upon recording at high gain, many signals due to the protons in the dendritic part could be observed. Four singlets at 0.68, 1.02, 1.16 and 1.29 ppm are assigned to H_a (48H) and a doublet at 1.47 ppm is assigned to H_c (12H). A quartet peak assigned to the mechine protons H_d (4H) is observed at 4.79 ppm, and singlet peaks assigned to H_l (2H), H_i (4H), and H_f (8H) are observed at 4.44, 4.97, and 5.00 ppm, respectively. As for the aromatic protons, two doublets at 7.33 and 7.36 ppm are assigned to H_b (16H), two doublets at 6.58 and 6.69 ppm to H_k (2H) and H_h (4H), respectively, and two triplets at 6.54 and 6.56 ppm to H_j (1H) and H_g (2H), respectively. The observed integrated ratios, H_a:H_d:H_e:(H_f+H_i):($H_g+H_h+H_j+H_k$):H_l= 47.47:4.15:16.16:12.00:9.17:1.96, are in good agreement with the theoretical ratios (48:4:16:12:9:2), indicating no or negligible decomposition of the [**G-2**] part.

In order to confirm the end structure of polysiloxane part, the integrated intensity of the peak due to –OSi(Me_2)OCH_3 was measured by comparing with that of the peak due to H_l, and it was determined to be 3.34H. Although the value is somewhat larger than 3H, it indicates that the end structure of the polysiloxane chain is –OSi(Me_2)OCH_3. The DP for the poly(D_3) arm was estimated by comparing the integrated intensity of the peak due to Si$(CH_3)_2$ with that of H_l, and it was determined to be be 25.9. Based on the value the $M_{n,NMR}$ was calculated to be 7300, which agreed with the $M_{n,SEC}$ value of 6700 determined by SEC measurements (M_w/M_n 1.12). Based on the yield of 0.71 g of [**G-2**]-O(CH_2)$_4$-poly(D_3) the conversion of D_3 was calculated to be 34% and the yield based on [**G-2**]-O(CH_2)$_4$Br was 18%. Again, the low yield of [**G-2**]-O(CH_2)$_4$-poly(D_3) is indicative of the insufficient lithiation of [**G-2**]-O(CH_2)$_4$Br. In addition, the product is in part discarded in decantation and HPLC purification. This results in a reduction in the yield.

*3.4. NMRP of St from [**G-n**]-O(CH_2)$_4$-poly(D_3) (n=1, 2)*

The NMRPs of St from [**G-1**]-O(CH_2)$_4$-poly(D_3) and [**G-2**]-O(CH_2)$_4$-poly(D_3) were carried out at 120 °C using 1.0 mL (8.7 mmol) of St and 0.010 mmol of the macroinitiator. After the mixtures were heated for a given time at 120 °C, they were poured into a large amount of MeOH, and the resultant precipitates were collected by filtration and dried in vacuum. The yields were determined by gravimetric method.

A typical ^{1}H NMR spectrum of AB_4 5-miktoarm star polymers (AB_4-star) is shown in Fig. 3. A similar ^{1}H NMR spectrum was observed for AB_2 3- (AB_2-star). In the spectrum the characteristic peaks due to the St unit are observed at 1.3–

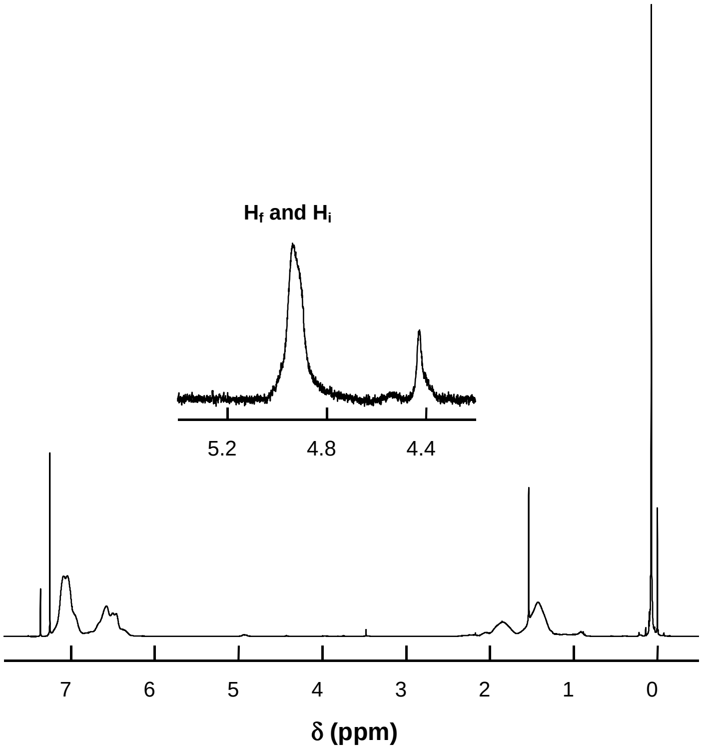


Fig. 3. ^{1}H NMR spectrum of AB_5 5-miktoarm star copolymer in $CDCl_3$.

2.2 and 6.3–7.3 ppm, along with a singlet peak due to $Si(CH_3)_2$ of the poly(D_3) unit at 0.07 ppm. The $M_{n,NMR}$s for AB_2-star and AB_4-star were determined by comparing the integrated intensity of the signals due to the aromatic protons of the poly(St) unit with that of the singlet due to the benzylic protons (for AB_2-star H_f and for AB_4-star H_f and H_i). The $M_{n,NMR}$s were also determined by comparing the integrated intensity of the signals due to the aromatic protons of the poly(St) unit with that of the signal due to $Si(CH_3)_2$, and they were in excellent agreement with each other. For example, the $M_{n,NMR}$ for AB_2-star at 47% conversion determined using $Si(CH_3)_2$ as the reference is 62,400, and that determined using the benzylic protons is 61,800.

The first-order plots for the NMRP of St using [**G-1**]-$O(CH_2)_4$-poly(D_3) are depicted in Fig. 4. A linear relationship between $\ln([M]_0/[M]_t)$ and time is found up to high conversion. This result indicates that the number of the propagating chains is constant throughout the polymerization. Fig. 5(a) and (b) show M_n vs conversion and M_w/M_n vs conversion plots. Both $M_{n,SEC}$ and $M_{n,NMR}$ increase linearly with conversion

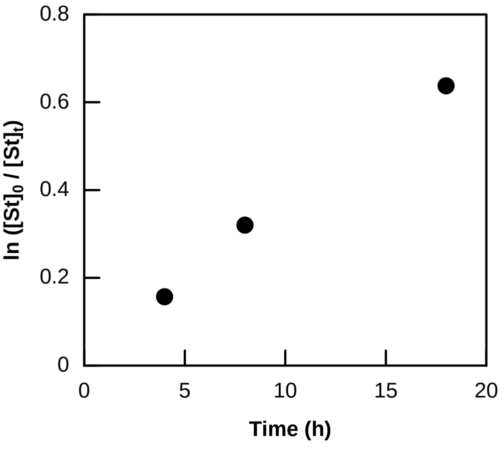


Fig. 4. $\ln([M]_0/[M]_t)$ vs time plots for the NMRP of St initiated with [**G-1**]-$O(CH_2)_4$-poly(D_3) at 120 °C. St 1.0 mL (8.7 mmol), [**G-1**]-$O(CH_2)_4$-poly(D_3) 0.010 mmol.

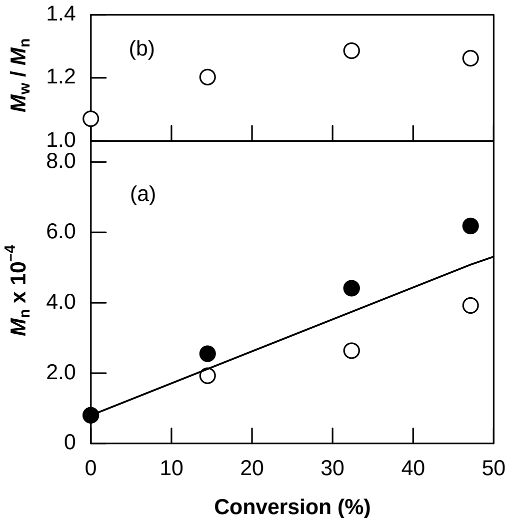


Fig. 5. M_n vs conversion (a) and M_w/M_n vs conversion plots (b) for the NMRP of St initiated with [**G-1**]-$O(CH_2)_4$-poly(D_3) at 120 °C. (●) M_n determined by ^{1}H NMR ($M_{n,NMR}$), (○) M_n determined by SEC ($M_{n,SEC}$). The solid line shows the theoretical M_n. St 1.0 mL (8.7 mmol), [**G-1**]-$O(CH_2)_4$-poly(D_3) 0.010 mmol.

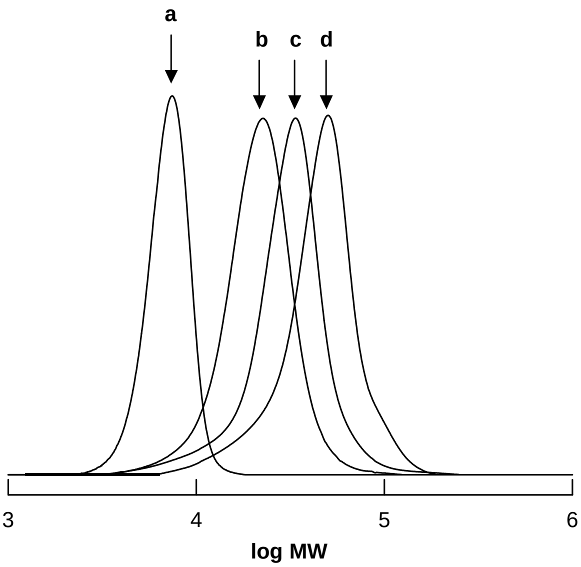


Fig. 6. SEC traces of [**G-1**]-O$(CH_2)_4$-poly(D_3) and AB_2 3-miktoarm stars. (a) [**G-1**]-O$(CH_2)_4$-poly(D_3) ($M_{n,SEC}=7200$, $M_{n,NMR}=8000$, $M_w/M_n=1.07$), (b) star at 14% conversion ($M_{n,SEC}=19{,}200$, $M_{n,NMR}=25{,}500$, $M_w/M_n=1.20$), (c) star at 32% conversion ($M_{n,SEC}=26{,}500$, $M_{n,NMR}=44{,}100$, $M_w/M_n=1.28$), star at 47% conversion ($M_{n,SEC}=39{,}200$, $M_{n,NMR}=61{,}800$, $M_w/M_n=1.26$).

throughout the polymerization and agree with the theoretical values ($M_{n,theor}$) calculated using Eq. (1). As shown in the figure, the $M_{n,SEC}$s are always somewhat lower than $M_{n,theor}$ and the $M_{n,NMR}$s are always somewhat higher. It is known that the molecular weights of star polymers determined by SEC tend to show lower values than the theoretical ones because small hydrodynamic volumes are smaller that those of the corresponding linear polymers. Therefore, the observed lower $M_{n,SEC}$ values can be explained by the lower hydrodynamic volume of AB_2-star. On the other hand, the observed higher $M_{n,NMR}$s can be ascribed to the contamination of poly(St) homopolymer originated from the thermal initiation of St. As discussed later, the SEC traces for AB_2-star suggest that it contains poly(St) homopolymer, though it is very small.

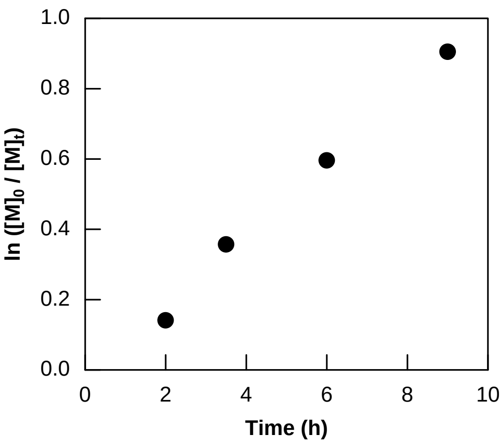


Fig. 7. $\ln([M]_0/[M]_t)$ vs time plots for the NMRP of St initiated with [**G-2**]-O$(CH_2)_4$-poly(D_3) at 120 °C. St 1.0 mL (8.7 mmol), [**G-2**]-O$(CH_2)_4$-poly(D_3) 0.010 mmol.

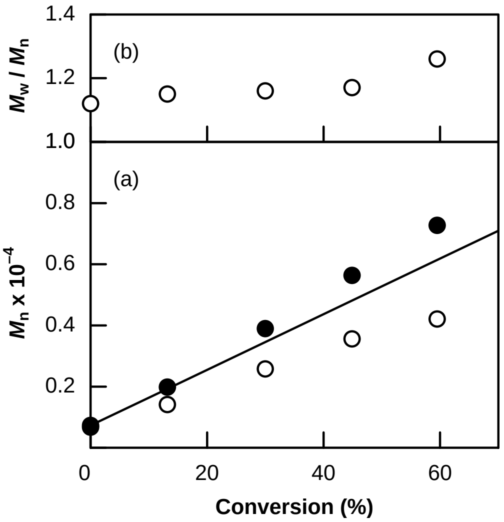


Fig. 8. M_n vs conversion (a) and M_w/M_n vs conversion plots (b) for the NMRP of St initiated with [**G-2**]-O$(CH_2)_4$-poly(D_3) at 120 °C. (●) M_n determined by ^{1}H NMR ($M_{n,NMR}$), (○) M_n determined by SEC ($M_{n,SEC}$). The solid line shows the theoretical M_n. St 1.0 mL (8.7 mmol), [**G-2**]-O$(CH_2)_4$-poly(D_3) 0.010 mmol.

$$M_n(\text{theor}) = ([\text{St}]/[[\mathbf{G-n}]-\text{O}(\text{CH}_2)_4 - \text{poly}(\text{D}_3)]) \cdot \text{conversion} \cdot \text{MW}_{\text{St}} + \text{MW}_{[\mathbf{G-n}]-\text{O}(\text{CH}_2)_4-\text{poly}(\text{D}_3)} \qquad (1)$$

In Fig. 6, the SEC traces for AB_2-star are depicted, together with that of [**G-1**]-O$(CH_2)_4$-poly(D_3). Obviously, the SEC traces shift to a higher molecular weight region with conversion, demonstrating that the polymerization of St was initiated by [**G-1**]-O$(CH_2)_4$-poly(D_3). Although the SEC traces are essentially unimodal, a tailing towards low molecular weight is observed on the low molecular weight side. This tailing is ascribed to the contamination with poly(St) homopolymer originated from the thermal initiation of St. In addition, a small shoulder is observed on the SEC trace at 47% conversion. The shoulder is assigned to star dimer, which is probably generated by the coupling reaction between the growing chains of the star polymers. Therefore, the formation of star dimer will increase with an increase in the arm numbers of star polymers. As is shown below, the shoulder is more clearly observed for AB_4-star.

Fig. 7 shows the first-order plots for NMRP of St initiated with [**G-2**]-O$(CH_2)_4$-poly(D_3). The $\ln([M]_0/[M]_t)$ vs time plots show a linear relationship up to high conversion, demonstrating the number of the propagating chains is constant throughout the polymerization. The M_n vs conversion and M_w/M_n vs conversion plots are depicted in Fig. 8(a) and (b), respectively. Both $M_{n,SEC}$s and $M_{n,NMR}$s increase linearly with conversion and agree with $M_{n,theor}$. Similar to AB_2-star, the $M_{n,SEC}$s are always somewhat lower than $M_{n,theor}$, and the $M_{n,NMR}$s are always somewhat higher than $M_{n,theor}$, except for that at 13% conversion. Again, the observed lower $M_{n,SEC}$ values can be accounted for in terms of the smaller hydrodynamic volume of AB_4-star relative to

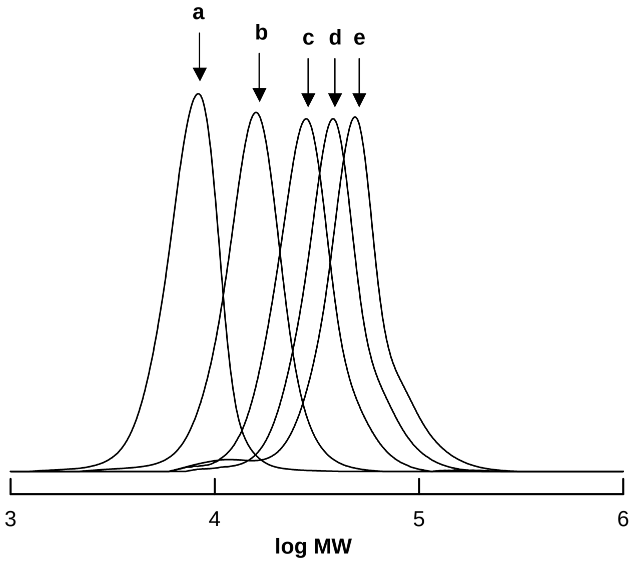


Fig. 9. SEC profiles of [**G-2**]-O(CH_2)$_4$-poly(D_3) and AB_4 5-miktoarm stars. (a) [**G-2**]-O(CH_2)$_4$-poly(D_3) ($M_{n,SEC}=6700$, $M_{n,NMR}=7300$, $M_w/M_n=1.12$), (b) star at 13% conversion ($M_{n,SEC}=14{,}100$, $M_{n,NMR}=18{,}800$, $M_w/M_n=1.15$), (c) star at 30% conversion ($M_{n,SEC}=25{,}800$, $M_{n,NMR}=37{,}000$, $M_w/M_n=1.16$), (d) star at 45% conversion ($M_{n,SEC}=35{,}600$, $M_{n,NMR}=56{,}300$, $M_w/M_n=1.17$), (e) star at 60% conversion ($M_{n,SEC}=42{,}100$, $M_{n,NMR}=72{,}700$, $M_w/M_n=1.26$).

the corresponding liner polymer and the observed higher $M_{n,NMR}$s values can be explained in terms of the contamination with poly(St) homopolyer. Although the M_w/M_n is gradually increased with conversion, it maintains the low values below 1.17 until the conversion exceeds 50%. However, at 60% conversion it is 1.26, which suggests accumulations of the star dimer and poly(St) homopolymer.

The SEC traces for AB_4-stars are shown in Fig. 9, together with that of [**G-2**]-O(CH_2)$_4$-poly(D_3). The peaks are shifted to higher molecular weight region with conversion, demonstrating that the polymerization of St is initiated by [**G-2**]-O(CH_2)$_4$-poly(D_3). In 13–45% conversion the SEC traces are unimodal and no tailing is observed. However, that at 60% conversion is not unimodal. This is in agreement with a high polydispersity index of 1.26. A small shoulder is clearly observed on the high molecular weight side and a small peak is found on the low molecular weight side. The peak-top value of the shoulder is ca. 90,000, which is approximately half the peak top value of the main peak, 48,100. Accordingly, it can be assigned to star dimer [39,40,44–46]. On the other hand, the small peak observed on the low molecular weight side is assigned to poly(St) homopolymer. Formation of poly(St) homopolymer has often been observed in the preparation of star polymers by NMRP of St using the core-first method [39,40,44–46].

4. Conclusion

AB_2 3- and AB_4 5-miktoarm star copolymers were prepared by combination of the AROP of D_3 and the NMRP of St. Initially, [**G-n**]-O(CH_2)$_4$Br ($n=1$, 2) was prepared by the reaction of [**G-n**]-ONa with Br(CH_2)$_4$Br. Lithiation of them was successfully performed by treating the bromides with *t*-BuLi. The AROP of D_3 with [**G-n**]-O(CH_2)$_4$Li yielded [**G-n**]-O(CH_2)$_4$-poly(D_3) with narrow polydispersities of 1.07–1.12. The NMRP of St from [**G-1**]-O(CH_2)$_4$-poly(D_3) at 120 °C gave AB_2 3-miktoarm star copolymers with $M_w/M_n=1.20$–1.28 at 14–47% conversions, and the NMRP of St from [**G-2**]-O(CH_2)$_4$-poly(D_3) at 120 °C gave AB_4 5-miktoarm star copolymers with $M_w/M_n=1.12$–1.26 at 13–60% conversions. A gradual increase in M_w/M_n with conversion was observed in both cases, which was explained in terms of the accumulations of poly(St) homopolymer and star dimer.

References

[1] Pitsikalis M, Pispas S, Maysi JW, Hadjichristidis N. Adv Polym Sci 1998;135:1.
[2] Hadjichristidis N. J Polym Sci, Part A: Polym Chem 1999;37:857.
[3] Hadjichristidis N, Pitsikalis M, Pispas S, Iatrou H. Chem Rev 2001;101:3747.
[4] Hirao A, Hayashi M, Surapich L, Sugiyama K, Ryu SW, Haraguchi N, et al. Prog Polym Sci 2005;30:111.
[5] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661.
[6] Matyjaszewski K, Xia J. Chem Rev 2001;101:2921.
[7] Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689.
[8] Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, et al. Macromolecules 1998;31:5559.
[9] Chong YK, Le TPT, Moad G, Rizzardo E, Thang SH. Macromolecules 1999;32:2071.
[10] Guo Y-M, Pan C-Y. Polymer 2001;24:2863.
[11] Guo Y-M, Xu J, Pan C-Y. J Polym Sci, Part A: Polym Chem 2001;39:437.
[12] Tsoukatos T, Pispas S, Hadjichristidis N. J Polym Sci, Part A: Polym Chem 2001;39:320.
[13] Heise A, Trollsås M, Magbitang T, Hedrick JL, Frank CW, Miller RD. Macromolecules 2001;34:2798.
[14] Feng X-S, Pan C-Y. Macromolecules 2002;35:2084.
[15] Feng X-S, Pan C-Y. Macromolecules 2002;35:4888.
[16] Glauser T, Stancik CM, Möller M, Voytek S, Gast AP, Hedrick JL. Macromolecules 2002;35:5774.
[17] Francis R, Lepoittevin B, Taton D, Gnanou Y. Macromolecules 2002;35:9001.
[18] Li Y-G, Wang Y-M, Pan C-Y. J Polym Sci, Part A: Polym Chem 2003;41:1243.
[19] Celik C, Hizal G, Tunca U. J Polym Sci, Part A: Polym Chem 2003;41:2542.
[20] Erdogan T, Ozyurek Z, Hizal G, Tunca U. J Polym Sci, Part A: Polym Chem 2004;42:2313.
[21] Cai Y, Burguiere C, Armes SP. Chem Commun 2004;802.
[22] He T, Li D, Sheng X, Zhao B. Macromolecules 2004;37:3128.
[23] Du J, Chen Y. Macromolecules 2004;37:3588.
[24] Du J, Chen Y. J Polym Sci, Part A: Polym Chem 2004;42:2263.
[25] Cai Y, Tang Y, Armes SP. Macromolecules 2004;37:9728.
[26] Tunca U, Ozyurek Z, Erdogan T, Hizal G. J Polym Chem, Part A: Polym Chem 2004;42:4228.
[27] Shi P-J, Li Y-G, Pan C-Y. Eur Polym J 2004;40:1283.
[28] Birshtein TM, Polotsky AA, Abetz V. Macromol Theory Simul 2004;13:512.
[29] Li Z, Kesselman E, Talmon Y, Hillmyer MA, Lodge TP. Science 2004;306:98.
[30] Lutz J-F, Laschewsky A. Macromol Chem Phys 2005;206:813.
[31] Jiang G, Wang L, Chen T, Yu H. Polymer 2005;46:81.
[32] Chen J, Zhang H, Wang X, Wang X. Polym Bull 2005;53:223.

[33] Cai Y, Armes SP. Macromolecules 2005;38:271.
[34] Babin J, Leroy CL, Lecommandoux S, Borsali R, Gnanou Y, Taton D. Chem Commun 2005;1993.
[35] Miura Y, Hirota K, Moto H, Yamada B. Macromolecules 1999;32:8356.
[36] Miura Y, Yoshida Y. Macromol Chem Phys 2002;203:879.
[37] Miura Y, Yoshida Y. Polym J 2002;34:748.
[38] Miura Y, Okada M. Polymer 2004;45:6539.
[39] Miura Y, Sakai Y, Yamaoka K. Macromol Chem Phys 2005;206:504.
[40] Miura Y, Dote H. J Polym Sci, Part A: Polym Chem 2005;43:3689.
[41] Miura Y, Miyake K. J Polym Sci, Part A: Polym Chem 2005;43:6153.
[42] Fujimoto T, Zhang H, Kazama T, Isono Y, Hasegawa H, Hashimoto T. Polymer 1992;33:2208.
[43] Bellas V, Iatrou H, Hadjichristidis N. Macromolecules 2000;33:6993.
[44] Robin S, Guerret O, Couturies J-L, Gnanou Y. Macromolecules 2002;35:2481.
[45] Kakuchi T, Narumi A, Matsuda T, Miura Y, Sugimoto N, Satoh T, et al. Macromolecules 2003;36:3914.
[46] Pyun J, Rees I, Fréchet JMJ, Hawker CJ, Aust J. Chem 2003;56:775.