Synthesis of Six-Arm Star Polymer by Nitroxide-Mediated "Living" Radical Polymerization

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ABSTRACT: A dendritic multifunctional initiator with 6 TEMPO-based alkoxyamine moieties was prepared from 4-bromophenylethylbenzene in 7 steps and 6-arm star polymers were prepared by the radical polymerization of styrene (St) using the dendritic alkoxyamine as an initiator. The St polymerizations were carried out at 120 °C using the dendritic alkoxyamine concentrations of 5.0, 12.8, and 18.8 mmol L^{-1}. When the alkoxyamine concentration was 5.0 mmol L^{-1}, the polydispersity indexes of the resulting star polymers increased with conversion and that of the star polymer at 72% conversion was 1.59. On the other hand, when the alkoxyamine concentrations were 12.8 and 18.8 mmol L^{-1}, the polymerization was well controlled to give star polymers with a low polydispersity index even at high conversion. The side reactions disturbing the "living" fashion were discussed on the basis of the SEC elution curves of the star polymers obtained.

KEY WORDS   Star Polymer / Living Radical Polymerization / Nitroxide / Alkoxyamine / Polydispersity Index /

Since nitroxide-mediated "living" radical polymerization provides well-defined polymers with a low polydispersity index, this technique has attracted much attention from the view of points of both polymer chemistry and polymer industry.[1–4] In this polymerization system the propagating radical chains are capped by nitroxides, giving deactivated (dormant) species, and the resultant dormant species are reactivated *via* the homolytic C–O bond dissociation at high temperature (usually above 110 °C) to give propagating radical chain and nitroxide. Since the equilibrium for the C–O bond dissociation and reformation shifts to the bond formation side, most of the propagating radical chains exist as the dormant species, leading to a very low concentration of the propagating radical compared with the conventional radical polymerization system. This characteristic of the nitroxide-mediated "living" radical polymerization is favorable to syntheses of well-defined star polymers because intermolecular and intramolecular coupling reactions between the propagating radicals must be suppressed. In a previous paper we reported the syntheses of well-defined 3-arm star polymers with a low polydispersity index using 1,3,5-tris(alkoxyamino)benzenes as an initiator.[5] Since the 1,3,5-tris(alkoxyamino)benzenes have no chemically labile bonds, the resultant star polymers are very stable under the strongly acidic or basic conditions. This characteristic makes a wide variety of applications of the resulting star polymers possible. In a continuing synthetic study of star polymers, we synthesized 6-arm star polymers using **Star-6**, a dendritic TEMPO-based alkoxyamine. Herein we wish to report the synthesis of **Star-6** and the TEMPO-mediated "living" radical polymerization of styrene (St) initiated with **Star-6** giving a well defined 6-arm star polymer.

Although many star polymers have so far been prepared by the nitroxide-mediated polymerization,[4] ATRP,[6] and RAFT methods,[7] most were prepared by the ATRP method because the ATRP method has the advantages that a wide variety of monomers are applicable and polyhalogeno compounds as an initiator are readily obtained. However, the ATRP method yields "transition metal contaminated" polymers, different from the nitroxide-mediated or RAFT method. The synthetic approachs to star polymers by the nitroxide-mediated "living" radical method are classified by two methods, as well as the ATRP or RAFT method: the "core-first" method and "arm-first" method. The arm-first method[8] is an easy approach to star polymers compared with the core-first method, but doesn't give structurally regular (arm-number constant) star polymers. On the other hand, the core-first method,[5, 9–11] requires much effort for the syntheses of multifunctional alkoxyamines. Since our aim is in the preparation of structurally well-defined star polymers, the 6-arm star polymer was prepared by the core-first method. Furthermore, since **Star-6** has no chemically labile bonds, as well as the previous 3-functional alkoxyamines,[5] the resulting St-based star polymers are expected to be stable under the acidic or basic conditions.

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EXPERIMENTAL

Measurements

^{1}H NMR spectra were recorded on a JEOL α 400 NMR spectrometer (400 MHz) using TMS as the internal standard. High resolution HAB mass spectra (HRHABMS) were obtained with a JEOL JMS-AX500 spectrometer with a direct method. Size exclusion chromatography (SEC) measurements were carried out with a Tosoh GPC 8020 series using TSK$_{gel}$ G5000 H$_{HR}$, Multiporeh$_{XL}$-M, and GMH$_{HR}$-L columns calibrated with the polystyrene standards, eluting with THF at 40 °C. Detection was made with a Tosoh refractive index detector RI8020. Preparative high performance liquid chromatography (HPLC) was carried out with a Japan Analytical Industry LC-908 recycling HPLC instrument, using CHCl$_3$ as the eluant. The light scattering measurements were carried out in THF at 30 °C with an Otsuka Electronics DLS-700 dynamic light scattering spectrophotometer over the angular range between 30–150 °C, using unpolarized light of wavelength 632.8 nm.

Materials

2,2,6,6-Tetramethylpiperidinyl-N-oxyl (TEMPO) was commercially available. Di-tert-butyl diperoxyoxalate (DBDP) was obtained by the reported method.[12] 1-(4-Hydroxymethylphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxyl) ethane (**3**) was prepared by our previous procedure.[13] Column chromatographic purification was carried out on silica gel 60 N (Kanto Chemical Co., Inc.).

1-(4-Bromomethylphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (4). A solution of **3** (2.16 g, 7.41 mmol) in dry ether (150 mL) was cooled to −70 °C, and PBr$_3$ (0.48 mL, 5.2 mmol) was added dropwise with stirring. After the addition, the solution was raised to room temperature and stirring was continued for 2 h. The mixture was again cooled to −70 °C, and water was added to decompose the unreacted PBr$_3$. The mixture was then extracted with ether, dried over anhydrous MgSO$_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene, and recrystallization from methanol gave colorless needles in 67% yield (1.76 g). Mp 51–52 °C, ^{1}H NMR (400 MHz, in CDCl$_3$): δ 0.66, 1.02, 1.16, 1.26 (each s, CH$_3$, 12 H), 1.26–1.37 (br m, (CH$_2$)$_3$, 6 H), 1.46 (d, J = 6.8 Hz, CHC**H**$_3$, 3 H), 4.50 (s, benzylic, 2 H), 4.78 (q, J = 6.8 Hz, C**H**CH$_3$, 1 H), 7.29 (d, J = 8.3 Hz, aromatic, 2 H), 7.33 (d, J = 8.3 Hz, aromatic, 2 H).

[G-1]-OH. A mixture of **4** (1.00 g, 2.82 mmol),

3,5-dihydroxybenzyl alcohol (0.190 g, 1.36 mmol), 18-crown-6 (35 mg, 0.13 mmol), and K$_2$CO$_3$ (0.57 g) in acetone (15 mL) was gently refluxed for 24 h under nitrogen. After filtration, the filtrate was evaporated under reduced pressure, and the residue was chromatographed on silica gel with 1 : 2 ethyl acetate–hexane to give **[G-1]-OH** as a colorless oil in 67% yield (0.683 g). ^{1}H NMR (400 MHz, in CDCl$_3$): δ 0.68, 1.03, 1.16, and 1.29 (each s, CH$_3$, 24 H), 1.26–1.37 (br m, (CH$_2$)$_3$, 12 H), 1.47 (d, J = 6.8 Hz, CHC**H**$_3$, 6 H), 1.81 (s, OH, 1 H), 4.61 (s, C**H**$_2$OH, 2 H), 4.79 (q, J = 6.8 Hz, C**H**CH$_3$, 2 H), 5.00 (s, benzylic, 4 H), 6.54 (t, J = 2.4 Hz, aromatic, 1 H), 6.62 (d, J = 2.4 Hz, aromatic, 2 H), 7.32 and 7.35 (each d, J = 8.5 Hz, aromatic, 8 H). HRHABMS: calcd for C$_{43}$H$_{63}$N$_2$O$_5$ [M + H]$^+$ 687.4737, found 687.4738. Anal. Calcd for C$_{43}$H$_{62}$N$_2$O$_5$: C, 75.18%; H, 9.10%; N, 4.08%. Found: C, 76.05%; H, 9.51%; N, 4.07%.

[G-1]-Br. **[G-1]-OH** (1.34 g, 1.95 mmol) was dissolved in anhydrous THF (15 mL) and heated to 60 °C with stirring under nitrogen. After CBr$_4$ (1.29 g, 3.90 mmol) was added, PPh$_3$ (1.00 g, 3.81 mmol) was added in four portions over 2 h, and the resulting mixture was stirred at the same temperature for 12 h. After cooling, water was added and the reaction mixture was extracted with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ layer was dried over anhydrous MgSO$_4$ and evaporated under reduced pressure. The residue was then chromatographed on silica gel with benzene, giving a colorless oil of **[G-1]-Br** in 57% yield (0.83 g). ^{1}H NMR (400 MHz, in CDCl$_3$): δ 0.68, 1.02, 1.16, 1.29 (each s, CH$_3$, 24 H), 1.26–1.37 (br m, (CH$_2$)$_3$, 12 H), 1.47 (d, J = 6.8 Hz, CHC**H**$_3$, 6 H), 4.40 (s, CH$_2$Br, 2 H), 4.79 (q, J = 6.8 Hz, C**H**CH$_3$, 2 H), 4.99 (s, benzylic, 4 H), 6.56 (t, J = 2.0 Hz, aromatic, 1 H), 6.63 (d, J = 2.0 Hz, aromatic, 2 H), 7.33 and 7.35 (each d, J = 8.5 Hz, aromatic, 8 H).

Star-6. A mixture of **[G-1]-Br** (1.00 g, 1.33 mmol), 1,3,5-benzenetriol (42 mg, 0.33 mmol), K$_2$CO$_3$ (0.32 g), and 18-crown-6 (70 mg, 0.26 mmol) in acetone (30 mL) was heated at 40 °C for 48 h with stirring under nitrogen. After filtration, the filtrate was evaporated under reduced pressure, and the residue was chromatographed on silica gel with 1 : 4 ethyl acetate–hexane. Further purification on a preparative recycling HPLC gave **star-6** as a colorless oil in 16% yield (111 mg). ^{1}H NMR (400 MHz, in CDCl$_3$): δ 0.67, 1.02, 1.16, 1.29 (each s, CH$_3$, 72 H), 1.25–1.36 (br m, (CH$_2$)$_3$, 36 H), 1.47 (d, J = 6.8 Hz, CHC**H**$_3$, 18 H), 4.79 (q, J = 6.8 Hz, C**H**CH$_3$, 6 H), 4.93 (s, benzylic, 6 H), 5.00 (s, benzylic, 12 H), 6.26 (s, aromatic, 3 H), 6.56 (t, J = 2.0 Hz, aromatic, 3 H), 6.68 (d, J = 2.0 Hz, aromatic, 6 H), 7.32 and 7.35 (each d, J = 7.8 Hz, aromatic, 24 H). HRHABMS: calcd for C$_{135}$H$_{187}$N$_6$O$_{15}$
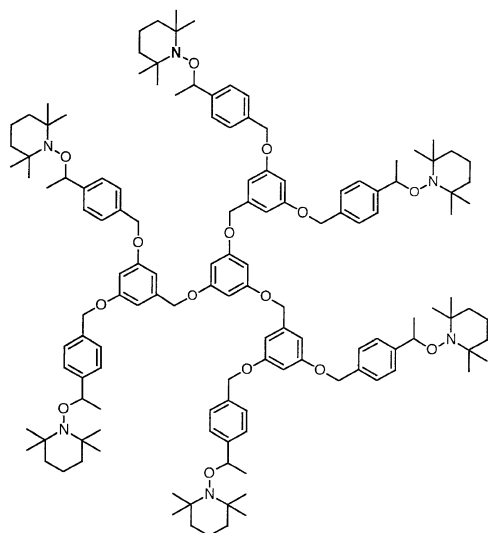
Star-6

[M + H]+ 2133.4088, found 2133.3984. Anal. Calcd for $C_{135}H_{186}N_6O_{15}$: C, 76.02%; H, 8.79%; N, 3.94%. Found: C, 74.72%; H, 8.28%; N, 3.92%.
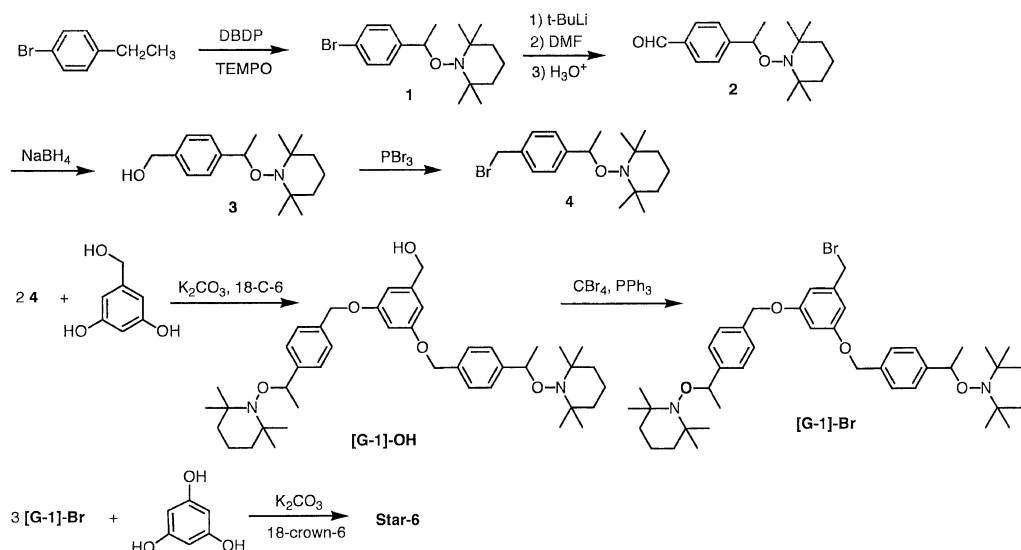
Polymerization

A styrene solution (0.50 mL, 4.4 mmol) of **Star-6** (5.0 mmol L^{-1}) was put onto a Pyrex glass tube and, after the mixture was degassed by three freeze-pump-thaw cycles, the tube was sealed off. The glass tube was then heated at 120 °C for the prescribed time, and the polymerization mixture was dissolved in benzene (5 mL) and poured into a large excess of methanol. The polystyrene collected was purified by reprecipitation (benzene/MeOH). Conversions were determined by the weights of polystyrenes obtained, and the number average molecular weights (M_n) and polydispersity indexes (M_w/M_n) were determined by SEC.

RESULTS AND DISCUSSION

Preparation of Star-6

Star-6 was prepared according to Scheme 1. (4-Bromophenyl)alkoxyamine **1** was obtained in 88% yield by the reaction of 4-bromoethylbenzene with di-*tert*-butyl diperoxyoxalate in the presence of tetramethylpiperidinyl-*N*-oxyl (TEMPO). Lithiation of **1** with *tert*-butyllithium and subsequent reaction with DMF gave (4-formylphenyl)alkoxyamine **2** in 95% yield. Reduction of **2** with NaBH$_4$ in methanol gave **3** in 89% yield. Bromination of **3** with PBr$_3$ gave **4** in 67% yield as colorless needles. Reaction of 2 equiv of **4** with 3,5-dihydroxybenzyl alcohol in acetone in the presence of K$_2$CO$_3$ and 18-crown-6 gave **[G-1]-OH** in 67% yield as a pure colorless oil. Bromination of **[G-1]-OH** was carried out by treating **[G-1]-OH** with CBr$_4$ and PPh$_3$ in THF at 60 °C, and **[G-1]-Br** was obtained in 57% yield as a colorless oil. Reaction of 3 equiv of **[G-1]-Br** with 1,3,5-benzenetriol was carried out at 40 °C in acetone in the presence of K$_2$CO$_3$ and 18-crown-6. Column chromatographic purification of the reaction mixture gave a semi-solid sample of **Star-6** containing small amounts of impurities. Since further purification by recrystallization gave only a viscus oil, the final purification of **Star-6** was performed on a preparative HPLC chromatograph. The solvent-free sample of **Star-6** was obtained by freeze-drying of a benzene solution of the **Star-6** (the yield for the final step 16%).

Although the elemental analyses for **[G-1]-OH** and **Star-6** didn't give satisfactory agreements with the calculations (see Experimental Section), ^{1}H NMR and
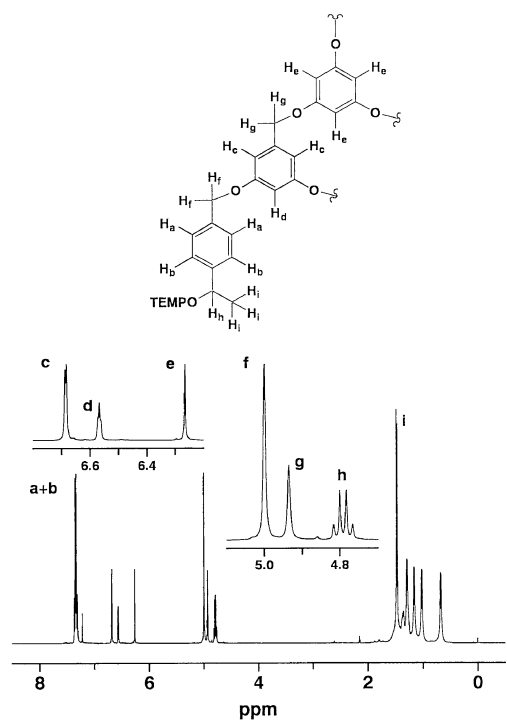

Scheme 1.

Figure 1. ^{1}H NMR spectrum (400 MHz) of **Star-6** in CDCl$_3$.

Figure 2. $\ln([M]_0/[M]_t)$ vs. time plots for the bulk polymerization of St at 120 °C initiated with **Star-6**; St 4.37 mmol (0.50 mL), [**Star-6**] 5.0 mmol L^{-1}.

Figure 3. M_n vs. conversion (a) and M_w/M_n vs. conversion plots (b) for the bulk polymerization of St at 120 °C initiated with **Star-6**. ( ) Determined by SEC; ($\bigcirc$) determined by ^{1}H NMR spectroscopy. The dotted line shows the M_n calculated by eq 1. St 4.37 mmol (0.50 mL), **Star-6** 5.0 mmol L^{-1}.

high resolution mass spectra confirmed their structures. A ^{1}H NMR spectrum of **Star-6** is depicted in Figure 1. The 72 H for the 24 methyl groups at the 2 and 6 positions of the piperidine ring are observed as 4 singlets at 0.67, 1.02, 1.16, and 1.29 ppm. The four singlet pattern is characteristic of TEMPO-based alkoxyamines. The doublet and quintet peaks due to –CH(TEMPO)CH$_3$ are observed at 1.47 (H$_i$) and 4.79 ppm (H$_h$) with a coupling constant of 6.8 Hz, respectively. The integration ratios for H$_i$ and H$_h$ revealed to correspond to 6 H and 18 H, respectively. A singlet due to H$_e$ is observed at 6.26 ppm with an integration ratio corresponding to 3 H. A doublet and triplet peaks due to H$_c$ and H$_d$ are observed at 6.68 and 6.56 ppm with a coupling constant of 2.0 Hz, and their integration ratios indicated to correspond to 6 H and 3 H, respectively. Two singlets due to two kinds of benzylic protons, H$_g$ and H$_f$, are observed at 4.93 and 5.00 ppm with integration ratios corresponding to 6 H and 12 H, respectively. Accordingly, the ^{1}H NMR spectrum for **Stir-6** was completely assigned. Similarly, those of **[G-1]-OH** and **[G-1]-Br** were also satisfactorily assigned.

To further confirm the structure of **Star-6** and **[G-1]-OH**, high resolution HAB mass spectra (HRHABMS) were measured. In the HRHABMS of **Star-6** a peak due to [M + 1]$^+$ was observed at 2133.3984, which agreed with the calculation (2133.4088). Similarly, **[G-1]-OH** gave a peak due to [M + 1]$^+$ at 687.4738, which agreed with the calculation (687.4737). On the basis of the above ^{1}H NMR and HRFABMS results, it is
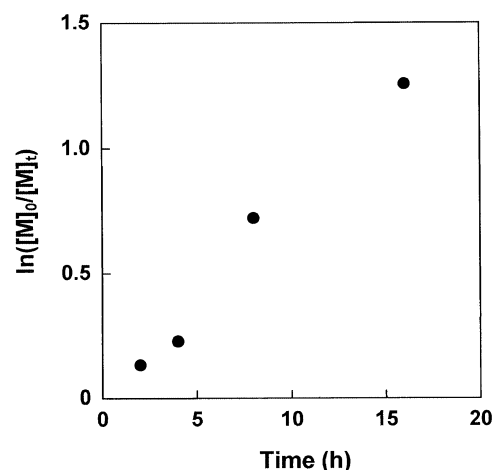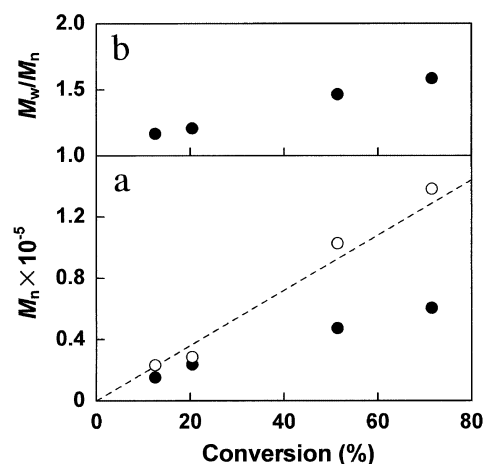
concluded that **Star-6** and **[G-1]-OH** have the desired structure.

Bulk Polymerization of Styrene Initiated with *Star-6*

Bulk polymerization of styrene (St) initiated with **Star-6** was carried out at 120 °C in degassed Pyrex tubes. After heating for the prescribed times, the reaction mixtures were poured into a large amount of MeOH, and the resulting poly(St)s were collected by filtration. The polymers were purified by reprecipitation (benzene/MeOH).

In Figure 2, $\ln([M]_0/[M]_t)$s are plotted against time. A linear relationship between $\ln([M]_0/[M]_t)$ and time is found up to a high conversion. This indicates that the number of propagating radical chains is constant during the polymerization. The M_n vs. conversion and M_w/M_n vs. conversion plots are depicted in Figures 3a and 3b,

respectively. The M_n's increase linearly with conversion up to a high conversion. However, there is a large discrepancy between the experiments and the calculations. The calculated M_n's are derived using eq 1.

$$M_n = \frac{[St]_0}{[\textbf{Star-6}]} \bullet M_{W(St)} \bullet \text{conversion} + M_{W(\textbf{Star-6})}$$

(1)

Since star polymers have hydrodynamic volumes smaller than those of linear polymers of comparable molecular weights, this discrepancy in M_n can be explained in terms of the smaller hydrodynamic volumes. To confirm the above explanation, the M_n's were determined by the ^{1}H NMR measurements of the star polymers obtained. A ^{1}H NMR spectrum of the star polymer at 72% conversion is depicted in Figure 4. The aromatic protons and main chain protons are observed at 1.2–2.3 and 6.3–7.3 ppm, respectively. Upon recording at high gain, a singlet peak due to the benzylic protons (12 H + 6 H) in the **Star-6** core was clearly observed at 4.91 ppm. The M_n's of the star polymers were determined by the integration ratio of the aromatic protons to the benzylic protons. Since the **Star-6** core has 36 aromatic protons corresponding to 7.2 styrene units, those protons were taken into account for the calculations of M_n by ^{1}H NMR. As found in Figure 3, the M_n's determined by the ^{1}H NMR method are in excellent agreement with the calculations. Accordingly, it can be concluded that the low M_n's determined by SEC can be ascribed to the smaller hydrodynamic volume of the star polymers. We furthermore determined M_w by the light scattering method. The samples measured were the star polymers at 51 and 72% conversions, and the light scattering measurements showed 93600 and 125000 as M_w for the star polymers, respectively. Since the M_n's of the star polymers determined by the ^{1}H NMR method are 103000 and 138000 and their polydispersity indexes are 1.47 or 1.59, the values determined by the light scattering method are much lower than the expected ones. This discrepancy in M_w may be explained in terms of the unique shape of star polymers. Further experiments will be required to clarify this point.

The polydispersity indexes (M_w/M_n) determined by SEC at 13 and 20% conversions are 1.17 and 1.21, respectively, indicating that the polymerization is well controlled at low conversion. However, the polydispersity index gradually increases with conversion, and at 51 and 72% conversions they were 1.47 and 1.59, respectively. The magnitude of 1.59 is beyond the theoretical limit of 1.5 for the living polymerization. This means that the influences of side reactions disturbing the "living" fashion are no longer ignored at high conversion.
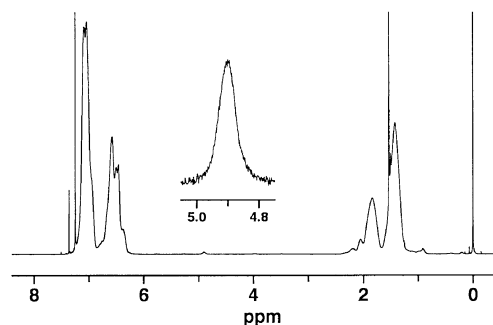

Figure 4. ^{1}H NMR spectrum (400 MHz) of the polyer obtained by "living" radical polymerization of St at 120 °C initiated with **Star-6**. Conversion 72% (M_n 60600, M_w/M_n 1.59), solvent CDCl$_3$.
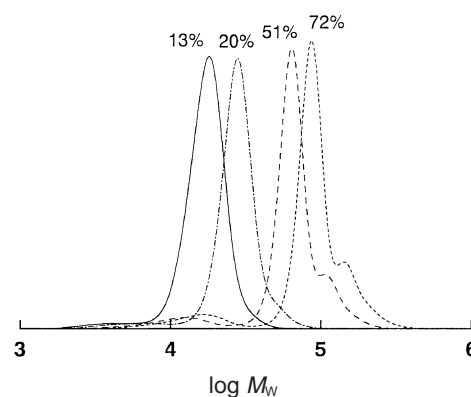

Figure 5. SEC elution curves of the star polymers at 13% (M_n 15300, M_w/M_n 1.17), 20% (M_n 23700, M_w/M_n 1.21), 51% (M_n 47400, M_w/M_n 1.47), and 72% conversions (M_n 60600, M_w/M_n 1.59) in the polymerization of St initiated with **Star-6** in the concentration of 5.0 mmol L^{-1}.

To elucidate the side reactions, the SEC elution curves were inspected. In Figure 5 the SEC elution curves are drawn. Below 20% conversion the elution curves show an unimodal molecular weight distribution, in agreement with the low polydispersity indexes of the corresponding polymers. However, the SEC elution curves at 51 and 72% conversions are no longer an unimodal molecular weight distribution. A small peak is observed in the low molecular weight region, and a shoulder is observed at the high molecular weight region, respectively. The M_n's for the lower molecular weight peaks at 51% and 72% conversions are 11000 and 14000, respectively, which seem to correspond to those of linear poly(St) formed by the thermal initiation of St. On the other hand, the peak top values for the shoulders are 106000 at 51% conversion and 142000 at 72% conversion, which are approximately twice M_n's of the main peaks (62000 at 51% conversion and 84000 at 72% conversion). Accordingly, it is suggested that the shoulder corresponds to the 10 arm-star polymer yielded by the star–star coupling reaction.[14] Since the propagating radicals have 6 active sites per molecule, the star–star coupling reaction must occur considerably.

Table I. Dependence of the polydispersity indexes (M_w/M_n) on the concentrations of **Star-6** in the radical polymerization of St initiated with **Star-6**[a]

Run	[**Star-6**]/mol L^{-1}	Conversion/%	$M_{n,SEC}$[b]	M_w/M_n[b]	$M_{n,NMR}$[c]	$M_{n,calc}$[d]
1	5.0×10^{-3}	72	60600	1.59	138000	132000
2	12.8×10^{-3}	64	28800	1.35	50800	47300
3	18.8×10^{-3}	70	20700	1.29	34000	36000

[a]St 4.37 mmol (0.50 mL), temperature 120 °C, time 16 h. [b]Determined by SEC. [c]Determined by ^{1}H NMR spectroscopy. [d]Calculated by eq 1.

It was reported that in the nitroxide-mediated living radical polymerization of St, the polydispersity indexes of the resulting polymers decrease with an increase in the concentration of the alkoxyamine used.[15] This observation suggests that the side reactions disturbing the "living" fashion are suppressed with an increase in the concentration of the alkoxyamine. We conducted the polymerizations of St using higher concentrations of **Star-6** (12.8 and 18.8 mmol L^{-1}). The concentrations of 12.8 and 18.8 mmol L^{-1} are 2.56 and 3.76 times higher than that in the polymerization described above. The results are summarized in Table I. Interestingly, when the initial concentrations of **Star-6** were 12.8 mmol L^{-1}, the polydispersity index of the resulting star polymer was 1.35 at 64% conversion, and when the initial concentration was 18.8 mmol L^{-1}, it was 1.29 at 70% conversion. On the basis of the results we can say that, when the concentration of alkoxyamine is high enough, well-controlled star polymers can be obtained in the TEMPO-mediated "living" radical polymerization.

In Figure 6, their SEC elution curves are shown, together with that for the above star polymer. Although both the SEC elution curves still show side peaks in the lower molecular weight and higher molecular weight regions, as well as the above star polymer, such side peaks are obviously smaller than for the above star polymer. Accordingly, the undesired side reactions disturbing the "living" fashion are not completely, but considerably suppressed, well-controlled 6-arm star polymer with a low polydispersity being afforded.

CONCLUSION

A 6-arm star polymer was prepared by the nitroxide-mediated "living" radical polymerization of St initiated with an dendritic TEMPO-based alkoxyamine with 6 active sites. When the polymerization of St was carried out using **Star-6** of the concentration of 5.0 mmol L^{-1}, well-defined star polymer was obtained with a low polydispersity index below 1.3 at low conversion. At high conversions, however, the polydispersity index of the resultant star polymer was beyond 1.5, indicating that the control of polymerization was insufficient.
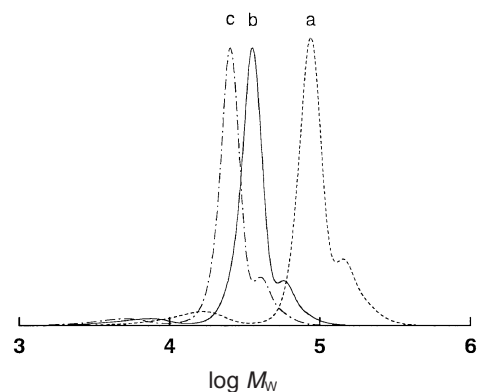

Figure 6. SEC elution curves of the star polymers:(a) **Star-6** 5.0 mmol L^{-1}, 72% conversion (M_n 60600, M_w/M_n 1.59); (b) **Star-6** 12.8 mmol L^{-1}, 64% conversion (M_n 28800, M_w/M_n 1.35); (c) **Star-6** 18.8 mmol L^{-1}, 70% conversion (M_n 20700, M_w/M_n 1.29).

On the other hand, when the polymerization was conducted using **Star-6** of the concentration of 12.8 and 18.8 mmol L^{-1}, the polymerization was well controlled and well-defined star polymer with a low polydispersity index was obtained. This result indicates that for the preparation of well-defined star polymers, particularly, in the case of high arm-numbers star polymers, the concentrations of alkoxyamines are important.

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