Living Radical Polymerization of Styrene by a Stable Nitroxyl Radical and Macroazoinitiator

Eri Yoshida* and Sachiko Tanimoto

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Received January 23, 1997; Revised Manuscript Received April 29, 1997[⊗]

ABSTRACT: The radical polymerization of styrene was performed at 130 °C for 72 h using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) and poly(dimethylsiloxane) (PDMS) containing azo moiety (PDMS-AZ) as a macroinitiator. It was found that the block copolymer of DMS with styrene was quantitatively obtained when the ratio of MTEMPO to the azo moiety in PDMS-AZ was 0.6. The structure was expected to be of the A−B type, rather than A−B−A, when the low initiator efficiency and the molecular weight of the PSt segments isolated were taken into account. The polymerization proceeded in accordance with a living mechanism, because the conversion of styrene linearly increased over time, and the molecular weight of the copolymer produced was directly proportional to the conversion. Furthermore, the polymerization of *p*-methoxystyrene was also found to proceed where the PDMS-*block*-polystyrene was used as an initiator, to give the triblock copolymer quantitatively.

Introduction

Remarkable progress has been made in living radical polymerization in recent years. There are a great number of publications on polymerization related to experiments which involve the use of various organic[1−6] or organometallic compounds[7−9] as controlling agents for chain growth. A number of publications have been released on the polymerization of styrene using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) since Georges and his group succeeded in obtaining a polymer with narrow polydispersity (<1.3) by styrene polymerization in the presence of TEMPO.[10] These publications concern kinetics[11−16] and mechanisms of styrene polymerization[17,18] and molecular designs using this polymerization.[19−23] The polymerization using TEMPO has the potential to create the type of polymer envisaged through molecular designs both of the initiator and of TEMPO which acts as a counter radical. This is based on the fact that the initiator and the counter radical exist separately and that it is possible to design the molecules of the initiator and the counter radical independently. Several papers have already been published on syntheses of various polymers through the use of different designs of TEMPO derivatives. Matyjaszewski and co-workers have performed styrene polymerization using TEMPO attached to dendrimers.[24] We have also released a publication on the synthesis of the block copolymrs of THF with styrene, which were obtained using the polymerization of styrene by TEMPO attached to poly(THF) at the chain end.[25] Further, it has already been found that hydroxy-terminated polystyrene was quantitatively obtained by the polymerization of styrene with 4-hydroxy-TEMPO and benzoyl peroxide (BPO).[26] The reason for using TEMPO derivatives in such great variety for the polymerization is not only that it is convenient to prepare these derivatives from TEMPO but also that all the polymers obtained had the aminoxy moiety at their terminals, when the polymerization was carried out with TEMPO.[27] This presence of the aminoxy moiety is important if quantitative synthesis of polymers designed is required. While there are many publications on the synthesis of polymers through such molecular designs of TEMPO, some papers have also been released on the synthesis through designing initiators for the TEMPO-mediated polymerization. A polymer with a fluorescent moiety at the head group[28] and a star polymer[29] have been prepared by using the initiator which contains the fluorescent moiety and the trifunctional initiator, respectively. Hawker and Frechet have obtained a block copolymer of dendrimer and polystyrene by using a dendritic initiator.[30] All these initiators contain TEMPO moieties in their molecules. It is difficult to quantitatively synthesize the required polymers using identity of initiators which do not contain TEMPO moiety in their molecules. This is because not all the components of initiators engage in the polymerization when common initiators are used. For instance, peroxide generally gives two molecular radicals from the one molecule of initiator. However, in the TEMPO-mediated polymerization, the initiator produces the one molecule of radical to initiate the polymerization from the one molecule.[27] This is accounted for by the fact that the initiation of peroxide is likely to be a redox reaction involving the one-electron transfer into the peroxide from TEMPO.[31] In fact, we have recently obtained results in the polymerization of styrene by BPO and 4-methoxy-TEMPO (MTEMPO) which show that not all the polymers produced had benzoyl moiety at their heads and that the molecular weights of the polymers were determined by the initial concentration of MTEMPO rather than that of BPO.[27] This concept is supported by the study on the polymerization by TEMPO and BPO, which was reported by Veregin and co-workers.[32] When these results on the initiation by peroxide are taken into account, it is clear that it is not efficient to quantitatively synthesize polymers through designing initiators of peroxide.

Azo compounds can be used as initiators for the polymerization with TEMPO. The polymerization with azobisisobutyronitrile (AIBN) and TEMPO has already been performed by both Rizzardo[33] and Hawker.[34] These initiators have the potential to quantitatively give the polymers required, because they initiate radical polymerization *via* simple cleavage of an azo moiety rather than *via* a redox reaction. There have been some publications on the synthesis of block copolymers by free-radical polymerization with macroazoinitiators rather than living polymerization.[35−39] The free-radical

---

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

polymerization has disadvantages over the living radical, in quantitatively synthesizing block copolymers. This is accounted for by the fact that the free-radical polymerization always produces a mixture of a block copolymer and a homopolymer which is generated by chain-transfer reaction. It is also impossible to obtain triblock copolymers by means of further polymerization using the block copolymers as initiators because the growing chain end is dead. The living polymerization has the potential to achieve this quantitative synthesis of block copolymers including triblock copolymers. We found in the radical polymerization of styrene by using MTEMPO and a polymer containing azo groups that the polymerization proceeded in accordance with a living mechanism, giving the block copolymer quantitatively. This paper describes the synthesis of a block copolymer of styrene and dimethylsiloxane by the polymerization of styrene with MTEMPO, using azo-containing poly(dimethylsiloxane) (PDMS-AZ) as a macroinitiator.

Experimental Section

Measurement. Gel permeation chromatography (GPC) was performed with a Tosoh HLC-802A instrument equipped with a Tosoh CP-8000 chromatoprocessor. A combination of two polystyrene gel columns of Tosoh TSK gel G4000H_8 and G2000H_8 was used, with THF as the eluent at 42 °C. The molecular weight was determined by calibrating with polystyrene standards. UV spectra were obtained with a Shimadzu UV-2500PC UV−vis recording spectrophotometer. ^{1}H NMR spectra were also obtained with Bruker ARX-500 and Varian Gemini-200 NMR spectrometers. Gas chromatography (GC) was performed with a Shimadzu GC-6A. DSC spectra were obtained with a Mac Science DSC-3100. Transmission electron micrography (TEM) was performed with JEM 1010.

Materials. PDMS-AZ (azo content: 2.50×10^{-4} mol·g^{-1}), which was prepared by the reaction of diamino-terminated PDMS (M_n: 5000) with 4,4′-azobis(4-cyanopentanoyl) dichloride following a previous method,[39] was supplied from Wako Pure Chemical Industry, Ltd. The pure-grade PDMS-AZ was used without further purification. MTEMPO was prepared by the method described previously.[40] Commercial-grade styrene was washed with an aqueous alkaline solution and water and distilled over calcium hydride. BPO was precipitated from chloroform and then recrystallized in methanol at 0 °C. Benzene as a solvent for the reaction of PDMS-AZ with MTEMPO was washed with concentrated sulfuric acid and water and distilled over sodium. Toluene as an internal standard in GC was also distilled over sodium. THF was refluxed over sodium for several hours and distilled.

Reaction of PDMS-AZ with MTEMPO. A total of 364 mg (azo content: 0.0910 mmol) of PDMS-AZ, 10 mg (0.0538 mmol) of MTEMPO, and 4 mL of benzene were placed in an ampule. After degassing the content, the ampule was sealed *in vacuo*. The reaction was carried out at 80 °C for 14 h. It was terminated by cooling with liquid nitrogen. The resulting solution was subjected to UV analysis to calculate the initiator efficiency, just after the reaction.

Radical Polymerization of Styrene by PDMS-AZ and MTEMPO. A total of 364 mg (azo content: 0.0910 mmol) of PDMS-AZ, 10 mg (0.0538 mmol) of MTEMPO, and 4 mL (34.9 mmol) of styrene were placed in an ampule. After degassing the content, the ampule was sealed *in vacuo*. The polymerization was carried out at 130 °C for 72 h. It was terminated by cooling with liquid nitrogen. The product was dissolved in 10 mL of dichloromethane, purified by repeated precipitations from dichloromethane into methanol, and finally freeze-dried with benzene. A total of 3.11 g of the block copolymer was obtained. After addition of toluene as an internal standard, the dichloromethane solution was subjected to GC to estimate the conversion of styrene.

Hydrolysis of PDMS-*block*-polystyrene (PDMS−PSt). To a solution of PDMS−PSt (300 mg; M_n, 66 000; M_w/M_n, 1.90) in 5 mL of THF was added a solution of KOH (100 mg, 1.79 mmol) in 1 mL of distilled water. After the mixture was refluxed for 48 h, it was poured into 500 mL of methanol. The white precipitates were collected by filtration and then dried *in vacuo* for several hours. A total of 272 mg of PSt segments was obtained. The filtrate was evaporated to remove the methanol, and the residue was dissolved into ether. The ether solution was washed with water to remove KOH. The ether layer was dried with anhydrous magnesium sulfate and then evaporated to remove the ether. However, no product was obtained from the filtrate.

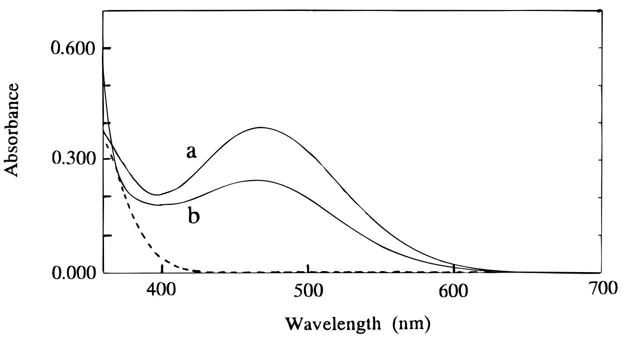


Figure 1. UV spectra of the solution before (a) and after (b) the reaction of PDMS-AZ and MTEMPO, and PDMS-AZ (broken line).

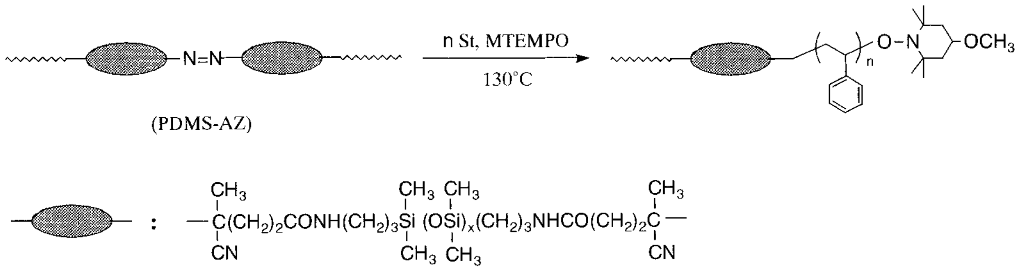
Reaction of *p*-Methoxystyrene by PDMS−PSt. A total of 100 mg of PDMS−PSt (M_n, 66 000; M_w/M_n, 1.90) and 1 mL (7.52 mmol) of *p*-methoxystyrene were placed in an ampule. After degassing the content, the ampule was sealed *in vacuo*. The reaction was carried out at 130 °C for 9 h. It was terminated by cooling with liquid nitrogen. The product was dissolved in 10 mL of dichloromethane, purified by repeated precipitations from dichloromethane into methanol, and finally freeze-dried with benzene. A total of 521 mg of the block copolymer was obtained. After addition of toluene as an internal standard, the dichloromethane solution was subjected to GC to estimate the conversion of *p*-methoxystyrene.

TEM Analysis. The film was prepared on a Cu grid with carbon substrate, by casting from the THF solution of the PDMS−PSt. The film was dried in air for 30 min and dyed for another 30 min in the presence of RuO_4(aq) in a laboratory dish. The film thus obtained was subjected to TEM analysis.

Results and Discussion

The living radical polymerization of styrene with TEMPO has been found to occur not only by the presence of BPO as an initiator but also by thermal initiation.[41,42] The thermal initiation was likely to be induced by an excess of TEMPO, based on our previous study.[27] In the study, we have revealed that the concentration of the growing polymer chain was always equal to the initial concentration of TEMPO, being independent of the initial concentration of BPO. Therefore, the molecular weights of polystyrenes obtained were determined by the ratio of the monomer consumed to the initial concentration of TEMPO rather than that of BPO. Further, it was also found that the molecular weight estimated by GPC was equal to that estimated by ^{1}H NMR, on the basis of the intensity ratio of the aromatic protons of styrene to the protons due to the TEMPO. When these results are taken into consideration, it is expected that TEMPO has the potential to induce the thermal initiation, although the identity of TEMPO does not directly react. When the thermal initiation occurs during the polymerization of styrene by the macroazoinitiator and TEMPO, it is impossible to obtain a block copolymer quantitatively, because homopolystyrene is formed. Therefore, it is necessary to use equivalent numbers of TEMPO to moles of the radical which initiates the polymerization. For the

Scheme 1



purpose of solving this problem, the initiator efficiency of the macroazoinitiator was investigated before the polymerization was carried out. When the initiator efficiency was assumed to be the efficiency with which MTEMPO captures the radicals generated from the macroinitiator, the initiator efficiency was determined. The initiator efficiency was estimated by the comparison between the UV absorbances at 470 nm, which are based on MTEMPO, before and after the reaction of PDMS-AZ with MTEMPO. Use of this method is based on the fact that PDMS-AZ and the alkoxyamine which is derived from MTEMPO have no UV absorption at this wavelength. The reaction of PDMS-AZ and MTEMPO was carried out at 80 °C under the condition that the ratios of MTEMPO to the azo moiety were 0.6, 1.0, and 2.0. It is possible that the decomposition or homolytic scission of the C−O linkage of the alkoxyamine, which is generated by the combination of MTEMPO with the polymeric radical of PDMS, occurs if the reaction is performed above 100 °C.[3] Figure 1 shows UV spectra before and after the reaction of PDMS-AZ with MTEMPO in benzene at 80 °C for 14 h. It is clear that the absorbance decreased after the reaction. The initiator efficiencies, which were estimated in the cases where the ratios of MTEMPO to the azo moiety were 0.6, 1.0, and 2.0, were 29%, 33%, and 36%, respectively. Each of the efficiencies was lower than that of AIBN. These results differ only slightly from the figure for the efficiency obtained by George and his group.[38]

The bulk polymerization of styrene was carried out for 72 h at 130 °C in the presence of MTEMPO and PDMS-AZ, under the condition that the ratio of MTEMPO to the azo moiety was 0.6, on the basis of the above result for the initiator efficiency, where the ratio was 0.6 (Scheme 1). The red color due to MTEMPO faded out, after the reaction was started. The conversion of styrene was calculated to be 84% by GC. The resulting product was reprecipitated into methanol to remove the styrene and the homopolymer of dimethylsiloxane which was suspected to remain, with the result that the white powder was quantitatively obtained. In addition, no polymer was obtained from the solution of methanol used for the precipitation, after the solution was evaporated to remove methanol. It was suggested that all the chains of PDMS-AZ were engaged in the polymerization. The molecular weight of the product and its polydispersity were estimated to be 66 000 and 1.90, respectively, by GPC, which was calibrated with standard polystyrenes. Figure 2 shows a ^{1}H NMR spectrum of the polymer obtained. A signal was observed at 0.1 ppm originating from DMS, while the signals at 1.2−2.2 and 6.2−7.5 ppm were attributed to styrene. These results show the formation of the block copolymer of dimethylsiloane (DMS) with styrene. PDMS-AZ was expected to contain *ca.* 5 azo groups on average per polymer chain, when it was taken into consideration that PDMS-AZ (M_n, 30 300; M_w/M_n, 2.39) was prepared by polycondensation between the diamino-terminated PDMS with M_n = 5000 and 4,4′-azobis(4-cyanopentanoyl) dichloride. This information, coupled with the initiator efficiency of 29% in the case of 0.6 as the ratio, gave the result that less than 2 azo groups per chain

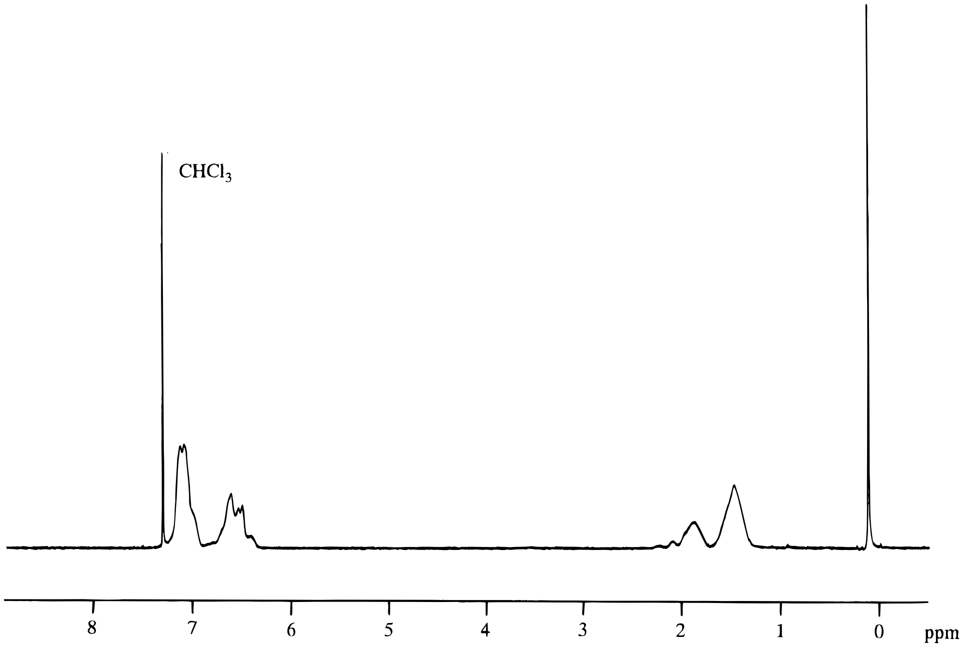


Figure 2. ^{1}H NMR spectrum of the copolymer which was obtained by the radical polymerization of styrene by PDMS-AZ and MTEMPO (solvent: $CDCl_3$).

Table 1. Radical Polymerization of Styrene with MTEMPO Using PDMS-AZ[a]

MTEMPO/AZ[b]	conversion,[c] %	M_n[d]	M_w/M_n[d]
0.6	84	66 000	1.90
0.8	85	55 500	1.88
1.0	67	31 800	2.02
1.3	75	30 000	2.26
1.5	72	25 800	1.88
2.0	70	13 200	1.98
4.0	83	7 230	1.91

[a] Polymerized at 130 °C for 72 h. [styrene]$_0$: 34.9 mmol, [azo group]$_0$: 0.0910 mmol. [b] Ratio of MTEMPO to the azo group. [c] Calculated by GC. [d] Estimated by GPC based on standard polystyrenes.

on average initiated the polymerization. The other azo groups, which were not engaged in the initiation, were probably deactivated by coupling between their radicals. It is expected that the coupling occurred between the radicals which were bonded to the same azo group, rather than to the different azo groups. This can be accounted for by the fact that each azo group is isolated from the others by the polymer chains of PDMS in the macroinitiator and that the radical generated is difficult to diffuse into the reaction system, due to the high viscosity of the solution of the macroinitiator with a high molecular weight. In fact, no homopolymer of PDMS was obtained after the polymerization. In order to determine the structure of the copolymer obtained, hydrolysis of the amide group in the copolymer was performed. The reaction of copolymer (M_n, 66 000; M_w/M_n, 1.90) was refluxed in a mixed solvent of THF and water for 2 days using KOH as a catalyst. The reaction proceeded homogeneously to obtain the polystyrene segments with the molecular weight of 34 400 and the dispersity of 1.53. It was confirmed that the segments hardly contained PDMS units by ^{1}H NMR. The PDMS segments could not be collected because they were also hydrolyzed by KOH into water-soluble low molecular weight compounds. When less than 2 azo groups per chain of the macroinitiator and this molecular weight of the PSt segment are taken into account, we concluded that the structure of the block copolymer obtained through this polymerization was of the A–B type rather than A–B–A. Synthesis of the A–B–A type of block copolymer of DMS with styrene using the living radical polymerization catalyzed by the Cu(I)/bipyridyl system with a macroinitiator of PDMS, has recently been reported by Matyjaszewski.[43]

When the ratio of MTEMPO to the azo moiety was greater than 0.6, the polymers were also obtained quantitatively. However, the molecular weight of the resulting polymer decreased with an increase of the ratio, and the polydispersities were slightly broadened, as listed in Table 1. Further, all the polymers obtained did not show unimodal GPC curves, except for the polymer which was obtained from the ratio 0.6. These GPC curves are illustrated in Figure 3. Some shoulders were discerned in the GPCs, except for that in the case of 0.6. It is suggested that the homopolymerization occurred by thermal initiation caused by an excess of MTEMPO. These results support the former results on the initiator efficiency.

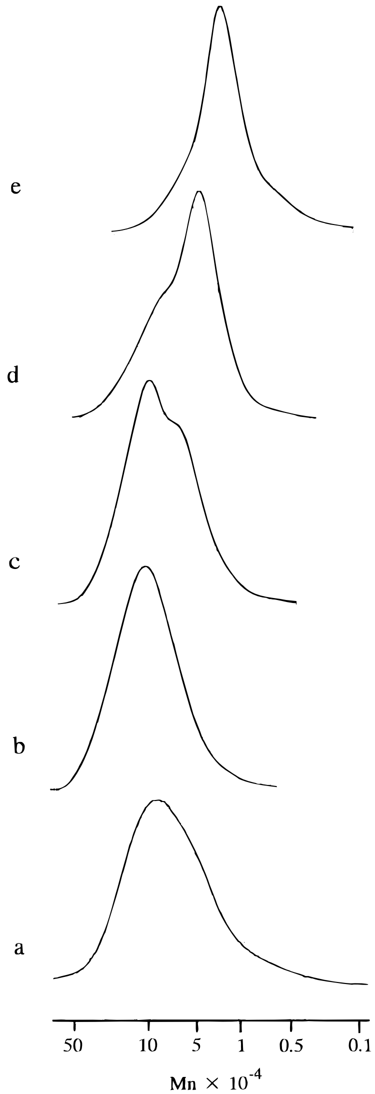


Figure 3. GPC profiles of PDMS-AZ (a) and the block copolymers obtained from the polymerization of styrene by PDMS-AZ and MTEMPO where the ratios of MTEMPO to the azo moiety were 0.6 (b), 0.8 (c), 1.0 (d), and 2.0 (e).

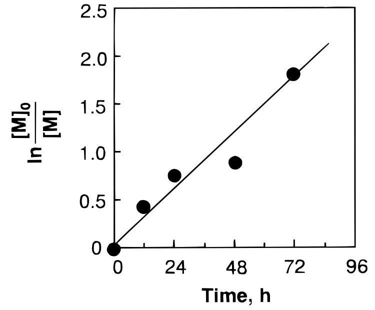


Figure 4. First-order time–conversion plots in the polymerization of styrene by PDMS-AZ and MTEMPO where the ratio of MTEMPO to the azo moiety was 0.6.

To confirm whether this radical polymerization proceeds in accordance with a living mechanism, the relation between the molecular weight of the polymer produced and the conversion of styrene was investigated. The polymerization was performed under the condition that the ratio was 0.6 in all cases. Figure 4 shows the first-order time–conversion plots in the polymerization. It was found that ln $[M]_0/[M]$ linearly increased over time, indicating that the number of the growing polymer chains was almost constant during the polymerization. The product polymers show unimodal GPCs, while the molecular weight of the polymer increased with an increase of the conversion, as shown in Figure 5. The molecular weights of copolymers obtained were not real because they were estimated by GPC based on standard polystyrenes. The molar ratios

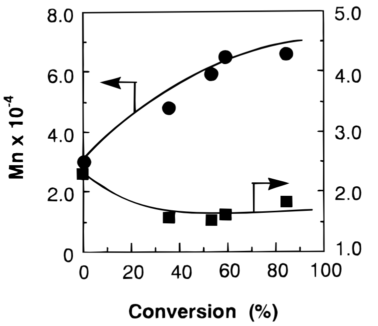


Figure 5. Conversion−molecular weight and polydispersity index plots in the polymerization of styrene by PDMS-AZ and MTEMPO where the ratio of MTEMPO to the azo moiety was 0.6.

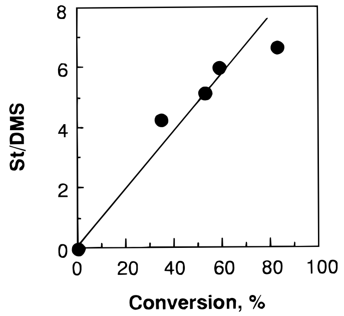


Figure 6. Plots of the molar ratio of styrene to DMS units in the copolymer versus conversion.

of styrene to DMS units (St/DMS) in the copolymers could be estimated by ^{1}H NMR analysis. Figure 6 shows the conversion−St/DMS plots thus calculated. It is obvious that St/DMS linearly increased as a result of increasing the conversion. These results indicate that this polymerization proceeded in accordance with a living mechanism by MTEMPO and the macroazoinitiator.

These polymers produced had two peaks of glass transition in their DSC spectra. Figure 7 shows the DSC curves of the three types of polymers. PDMS-AZ (a) showed that the peak of glass transition was observed at −18 °C, while a polystyrene (b) had the glass transition at 93 °C. The product polymer (c) showed both the peaks of glass transition based on the PDMS at −21 °C and on the polystyrene at 101 °C. It is clear that the polymerization of styrene occurred because of the presence of MTEMPO and PDMS-AZ, giving the block copolymers of DMS with styrene.

The copolymers obtained are expected to show microphase segregation, because they exhibited two peaks of glass transition due to the respective segments. The films prepared by casting from THF solutions of the copolymers were subjected to TEM analysis, after the films were dyed with ruthenium tetraoxide. Figure 8 shows the TEM picture of the copolymer. As expected, the copolymers were found to show microphase segregation on their surface. The film of the block copolymer with a molecular weight of 66 000 had good optical qualities; it was colorless and had a high transparency and flexibility. However, those of the copolymers with molecular weights below 60 000 were somewhat brittle. These copolymers are expected to be elastomers with excellent optical qualities.

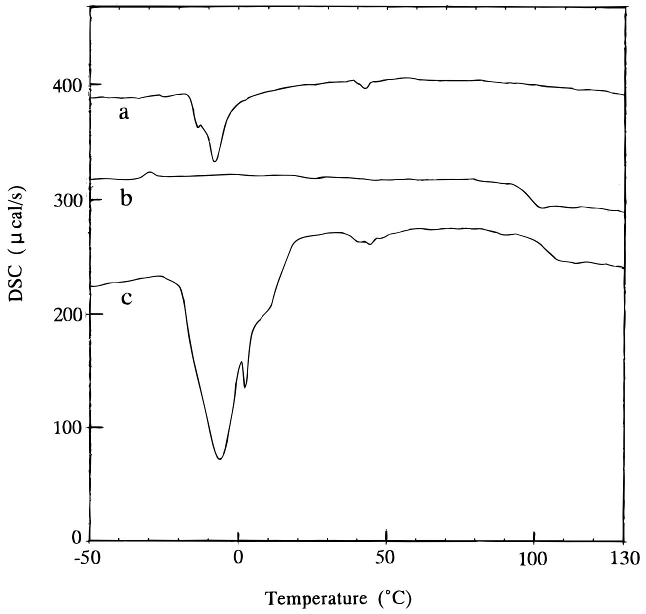


Figure 7. DSC spectra of PDMS-AZ (a), polystyrene (b; M_n = 13 600, M_w/M_n = 1.53), and the copolymer (c; M_n = 66 000, M_w/M_n = 1.90) obtained from the polymerization of styrene by PDMS-AZ and MTEMPO where the ratio of MTEMPO to the azo moiety was 0.6.

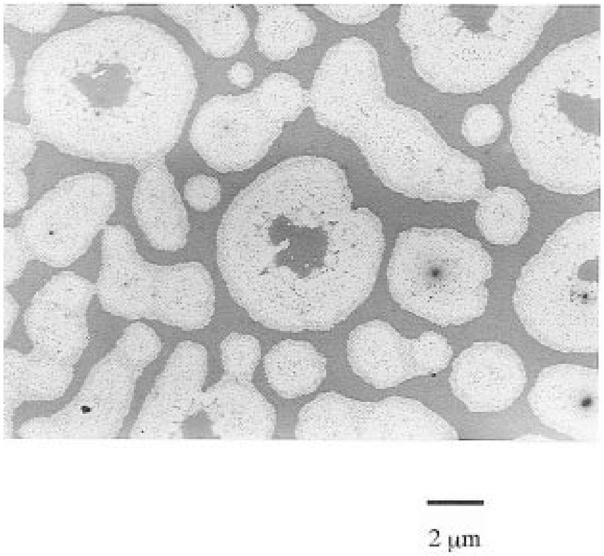
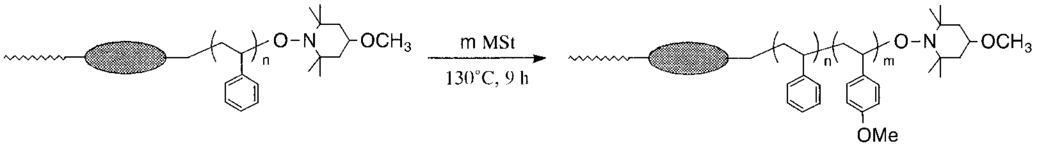


Figure 8. TEM picture of the copolymer (M_n, 66 000; M_w/M_n, 1.90) obtained from the polymerization of styrene by PDMS-AZ and MTEMPO where the ratio of MTEMPO to the azo moiety was 0.6. The film was prepared by casting from the THF solution of the copolymer and dyed with RuO_4.

To demonstrate further polymerization, the reaction of the PDMS-*block*-polystyrene with *p*-methoxystyrene (MSt) was examined at 130 °C for 9 h (Scheme 2). The conversion of MSt was calculated to be 96% by GC. After the purification, the polymer obtained was shown by ^{1}H

Scheme 2



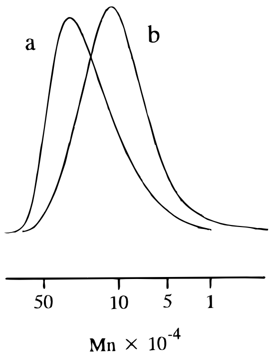


Figure 9. GPC profiles of the triblock copolymer (a) and PDMS-*block*-polystyrene (b; $M_n = 66\,000$, $M_w/M_n = 1.90$) which were obtained from the polymerization of styrene by PDMS-AZ and MTEMPO where the ratio of MTEMPO to the azo moiety was 0.6.

NMR to have the molar ratio DMS:St:MSt = 1:6.67:44.5. As illustrated in Figure 9, the GPC curve shifted to the higher molecular weight side after the reaction, and the molecular weight increased from $M_n = 66\,000$ (M_w/M_n: 1.90) to 135 000 (M_w/M_n: 1.43). These results indicate that quantitative formation of the triblock copolymer could be achieved using PDMS-*block*-polystyrene.

Conclusions

The radical polymerization of styrene was performed by the macroazoinitiator of PDMS and MTEMPO to give the block copolymer quantitatively. The structure was expected to be of the A−B type, rather than A−B−A, when the low initiator efficiency and the molecular weight of the PSt segments isolated were taken into account. It was found that the polymerization proceeded in accordance with a living mechanism, because the conversion of styrene linearly increased over time, and the molecular weight of the copolymer was directly proportional to the conversion. PDMD-*block*-polystyrene had two glass transitions due to PDMS and polystyrene and exhibited microphase segregation on the surface. The films of these copolymers are expected to be elastomers with the good optical qualities of colorlessness, high transparency, and flexibility. Furthermore, the polymerization of *p*-methoxystyrene was also initiated by the block copolymer, to give the triblock copolymer quantitatively. Macroazoinitiators of polyisobutylene,[35] poly(ethylene glycol),[36] polyester,[37] polycarbonate,[44] and polyamide,[38] in addition to PDMS have been prepared.[39] They have the potential to initiate the living radical polymerization in the presence of TEMPO, giving their block copolymers. Therefore, this polymerization is expected to be a convenient method to prepare the block copolymers quantitatively through radical polymerization.

References and Notes

(1) Chung, T. C.; Janvikul, W.; Lu, H. L. *J. Am. Chem. Soc.* **1996**, *118*, 705.
(2) Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32.
(3) Solomon, D. H.; Waverley, G.; Rizzardo, E.; Hill, W.; Cacioli, P. U.S. Patent 4,581,429, 1986.
(4) Druliner, J. D. *Macromolecules* **1991**, *24*, 6079.
(5) Otsu, T.; Matsunaga, T.; Kuriyama, A.; Yoshida, M. *Eur. Polym. J.* **1989**, *25*, 643.
(6) Bledzki, A.; Braun, D.; Titzschkau, K. *Makromol. Chem.* **1983**, *184*, 745.
(7) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.
(8) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(9) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.
(10) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(11) Greszta, D.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 5239.
(12) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 3346.
(13) Catala, J. M.; Bubel, F.; Hammouch, S. O. *Macromolecules* **1995**, *28*, 8441.
(14) Saban, M. D.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 7032.
(15) Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 4391.
(16) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Polym. Mater. Sci. Eng.* **1993**, *68*, 8.
(17) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T. *Macromolecules* **1996**, *29*, 6393.
(18) Li, I.; Howell, B. A.; Matyjaszewski, K.; Shigemoto, T.; Smith, P. B.; Priddy, D. B. *Macromolecules* **1995**, *28*, 6692.
(19) Yoshida, E. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 2937.
(20) Yoshida, E.; Fujii, T. *J. Polym. Sci., Chem.*, in press.
(21) Frank, B.; Gast, A. P.; Russell, T. P.; Brown, H. R.; Hawker, C. *Macromlecules* **1996**, *29*, 6531.
(22) Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993.
(23) Keoshkerian, B.; Georges, M. K.; Boissier, D. B. *Macromolecules* **1995**, *28*, 6381.
(24) Matyjaszewski, K.; Shigemoto, T.; Frechet, J. M. J.; Leduc, M. *Macromolecules* **1996**, *29*, 4167.
(25) Yoshida, E.; Sugita, A. *Macromolecules* **1996**, *29*, 6422.
(26) Yoshida, E.; Okada, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 275.
(27) Yoshida, E.; Okada, Y. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 3631.
(28) Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686.
(29) Hawker, C. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1456.
(30) Leduc, M. R.; Hawker, C. J.; Dao, J.; Frechet, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 11111.
(31) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316.
(32) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 2746.
(33) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722.
(34) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* **1996**, *29*, 5245.
(35) Mishra, M. K. *Macromolecules* **1996**, *29*, 5228.
(36) Ueda, A.; Nagai, S. *J. Polym. Sci., Polym. Chem.* **1986**, *24*, 405.
(37) George, M. K.; Ward, J. R. *J. Polym. Sci., Polym. Chem.* **1973**, *11*, 2909.
(38) Ueda, A.; Nagai, S. *J. Polym. Sci., Polym. Chem.* **1984**, *22*, 1611.
(39) Inoue, H.; Ueda, A.; Nagai, S. *J. Polym. Sci., Polym. Chem.* **1988**, *26*, 1077.
(40) Miyazawa, T.; Endo, T.; Shiihashi, S.; Okawara, M. *J. Org. Chem.* **1985**, *50*, 1332.
(41) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 870.
(42) Gaynor, S.; Greszta, D.; Mardare, D.; Teodorescu, M.; Matyjaszewski, K. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1561.
(43) Nakagawa, Y.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (2), 270.
(44) Shimada, M.; Uetoshi, Y.; Makimura, Y. *Polym. Prepr. Jpn.* **1996**, *8*, 1958.

MA9700892