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Polymer 47 (2006) 3784–3791

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Facile synthesis of multiblock copolymers composed of poly(tetramethylene oxide) and polystyrene using living free-radical polymerization macroinitiator

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Received 13 February 2006; received in revised form 25 March 2006; accepted 29 March 2006

Abstract

A facile synthetic strategy for well-defined multiblock copolymers utilizing ‘living’ free-radical polymerization macroinitiator has been presented. Polyurethane composed of alkoxyamine initiating units and poly(tetramethylene oxide) (PTMO) segments was prepared by polyaddition of tolylene 2,4-diisocyanate terminated PTMO with an alkoxyamine-based diol. Polymerization of styrene with the polyurethane macroinitiator was carried out under nitroxide-mediated free-radical polymerization (NMRP) condition. GPC, NMR, and IR data revealed that the polymerization was accurately controlled and well-defined polystyrene chains were inserted in the main chain of macroinitiator to give the poly(tetramethylene oxide)-*b*-polystyrene multiblock copolymers. The synthesized multiblock copolymers were characterized by tensile test, differential scanning calorimetry, and dynamic mechanical analysis. Mechanical properties of the multiblock copolymers can be tuned by the sufficient molecular weight control of PS chains. Soft segment of PTMO and hard segment of PS were apparently compatible due to the multiblock structure of low molecular weight segments and polar urethane groups.

Keywords: Macroinitiator; Living radical polymerization; Multiblock copolymers

1. Introduction

The ability to synthesize polymers with complex and controlled architectures has become an important aspect of polymer science [1–3]. Traditional methods for controlling polymeric structure, such as anionic [4] and cationic [5,6] procedures, have suffered from the rigorous synthetic conditions, incompatibility with a wide range of monomers, and inability to form many random copolymers. Conventional free-radical polymerization technique adapts the polymerization of monomers with various functional groups under synthetically robust condition. However, it does not permit the synthesis of block copolymers because of the predominance of termination reactions. Nevertheless, a few methods have been developed to obtain block copolymers by free-radical polymerization, including the use of multifunctional macroinitiators [7–10], iniferters [11,12], and living free-radical polymerizations [13]. Especially, living free-radical polymerization procedures, such as nitroxide-mediated free-radical polymerization (NMRP) [14–18], atom transfer radical polymerization (ATRP) [19,20], and reversible addition fragmentation chain transfer (RAFT) [21–23], have witnessed explosive growth because these techniques permit the polymerization of a wide variety of monomer families, which are either difficult to prepare or not available via other polymerization processes, with high degree of structural control under synthetically robust condition.

On the other hands, free-radical polymerization multifunctional macroinitiators of which contain free-radical polymerization initiating units such as azo, peroxy, disulfide, and so on, in the main or side chain have been applied to the preparation of block and graft copolymers [7–10]. However, the conventional free-radical polymerization multifunctional macroinitiators do not allow the molecular weight control of the block copolymers because the polymerization proceeds through conventional free-radical polymerization process. Recently, novel synthetic strategies for the preparation of well-defined polymers through living free-radical

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doi:10.1016/j.polymer.2006.03.100

polymerization multifunctional macroinitiators have been proposed [24–28]. Polymerization of styrene derivatives with 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO)-based poly(alkoxyamine) multifunctional macroinitiator is fairly controlled under conventional NMRP condition to achieve the insertion of well-defined polymer chains into the macroinitiator. In this report, we describe a synthetic strategy for the multiblock copolymers composed of poly(tetramethylene oxide) (PTMO) and polystyrene (PS) using a TEMPO-based living free-radical polymerization multifunctional macroinitiator. The glass transition temperature (T_g) and tensile properties, and dynamic mechanical property of multiblock copolymers were also analyzed, and these observations were discussed in relation to the polymer structure.

2. Experimental section

2.1. Materials

Alkoxyamine derivative **1** was prepared by the method reported previously [27,29]. Commercially obtained styrene was distilled under vacuum over CaH_2 immediately prior to use. Tolylene 2,4-diisocyanate terminated poly(tetramethylene oxide) (Aldrich) was used as received without further purification. Other reagents were purchased from Wako Pure Chemical Industries and were used as received.

2.2. Measurements

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic measurements were carried out at 25 °C with a JEOL JNM-EX400 spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$). Monomer conversion was determined by ^1H NMR measurement of the crude reaction mixtures (calculated from integration ratio between vinyl protons of styrene and aliphatic protons at 0.9–2.4 ppm of polystyrene). Composition of the copolymers was calculated by ^1H NMR spectrum from the integration ratio between the signal for the aliphatic protons of PS units at 0.9–2.4 ppm and the signal for the CH_2–O–CH_2 group of PTMO units at 3.41 ppm. IR spectra of the precipitated polymers were obtained with a Perkin–Elmer spectrum one infrared spectrometer as a thin film on NaCl plate. Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by gel permeation chromatographic (GPC) analysis. GPC was carried out at 40 °C on a JASCO high performance liquid chromatography system equipped with a guard column (TOSOH TSKguardcolumn SuperH-L), three mixed columns (TOSOH TSKgel SuperH6000, 4000, and 2500) and a differential refractometer. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.6 mL/min. Polystyrene standards ($M_n = 800$–152,000; $M_w/M_n = 1.03$–1.10) were used to calibrate the GPC system. Fractionation was conducted on a Japan Analytical Industry LC-908 HPLC system equipped with two mixed polystyrene gel columns (JAIGEL-2H, JAIGEL-3H). Chloroform was used as an eluent at a flow rate of 3.8 mL/min. Differential scanning calorimetry (DSC) was carried out with a Rigaku DSC-8230 instrument. The heating rate was 10 K/min, and the glass transition temperature was reported as the inflection point of the heat capacity jump. Dynamic mechanical analysis (DMA) was carried out with an Orientec Rheovibron DDV-IIFP dynamic mechanical analyzer. The experiments were performed at 11 Hz under nitrogen atmosphere, and the heating rate was 1 K/min. The gauge length was set at 15 mm, and the width of tested specimens was 4 mm in width with ca. 0.5 mm thickness. Tensile test was carried out with a Shimazu EZ-Graph tensile tester. All sample were cut into strips of 4 mm in width with approximate thickness of 0.5 mm. The gauge length was set at 10 mm, and samples were extended at 100 mm/min at room temperature. Strains were measured from the displacement of the crosshead. Reported data are the average of five measurements.

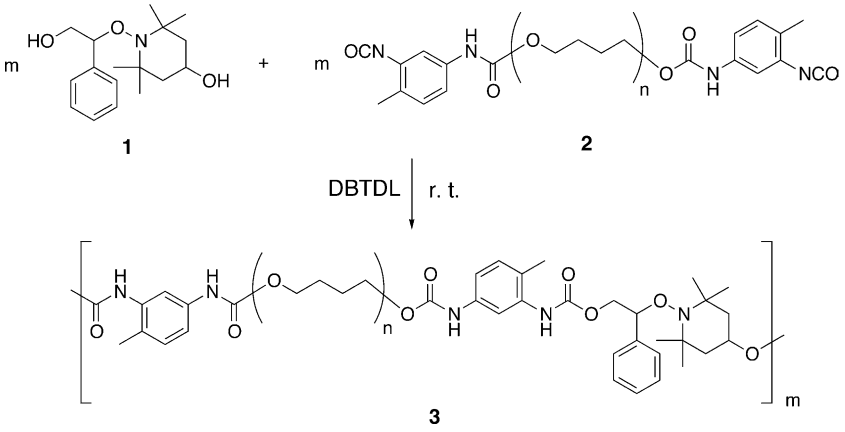
2.3. Synthesis

2.3.1. Polyurethane macroinitiator 3

TEMPO-based diol **1** (1.467 g, 5 mmol) was dissolved in anhydrous DMF (5 mL) and the solution was added to the solution of tolylene 2,4-diisocyanate (TDI) terminated poly (tetramethylene oxide) **2** ($M = 1600$, 8.0 g, 5 mmol) in anhydrous DMF (20 mL) via syringe under nitrogen and stirred at room temperature for 30 min. Then, one drop of dibutyltin dilaurate (DBTDL) was added to the solution as a catalyst and the reaction mixture was stirred at room temperature under nitrogen for 24 h. After the addition of methanol, the reaction mixture was poured into water. The precipitate was dissolved in chloroform and precipitated (twice) into hexane. The gummy precipitate was then collected and dried in vacuum to give the desired polymer **3** as a colorless gum (8.33 g, 88% yield). $M_n = 11,700$, $M_w/M_n = 3.14$; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.6–1.0 (br), 1.11 (br), 1.26 (s), 1.62 (s), 1.8–2.4 (br), 3.41 (s), 3.76 (s), 4.15 (br), 6.8–7.4 (br); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 16.94, 21.20, 25.80, 26.14, 26.45, 33.94, 60.20, 60.50, 64.92, 66.64, 70.06, 70.50, 83.98, 127.64, 127.98, 130.49, 140.08, 153.57; FT-IR (NaCl, cm^{-1}): 2936, 2856, 1731, 1535, 1368, 1111.

2.3.2. PTMO-b-PS multiblock copolymer 4

In a typical run, a mixture of the fractionated polyurethane **3** ($M_n = 12,300$, $M_w/M_n = 1.10$, 213 mg) and styrene (1.15 mL, 10 mmol) was degassed by three freeze/thaw cycles and heated under argon at 125 °C for 1 h. The viscous reaction mixture was then dissolved in chloroform and precipitated into methanol. The precipitate was collected by vacuum filtration and dried in vacuum to give the purified polymer **4** as a white powder (412 mg, 33% yield). $M_n = 21,600$, $M_w/M_n = 1.82$; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.22 (br), 0.40 (br), 0.90–2.40 (br, aliphatic H), 1.75 (s), 3.41 (br), 3.77 (s), 4.15 (br), 6.10–7.60 (br, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.71, 40.57 (br), 70.83, 125.85, 127.85, 145.70; FT-IR (NaCl, cm^{-1}): 3026, 2925, 2853, 1732, 1601, 1535, 1493, 1452, 1223, 1111, 757, 698.



Scheme 1. Preparation of polyurethane macroinitiator.

2.4. Film preparation

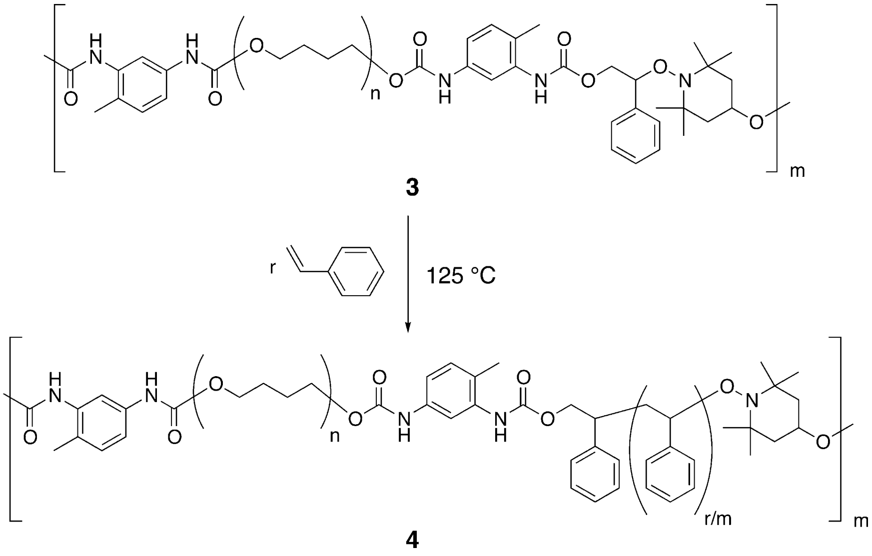
As-cast specimens were prepared by slow evaporation of 5 wt% polymer chloroform solution at room temperature. Specimens were then dried in a vacuum oven at 40 °C for 1 or 2 days and annealed at 110 °C for 2 h prior to the analysis. DSC, DMA and tensile test were carried out with annealed samples of thermodynamic equilibrium morphology to appreciate correct aggregation structure and mechanical properties reflecting PS content.

3. Results and discussion

3.1. Synthesis of PTMO-b-PS multiblock copolymers

Polyurethane macroinitiator **3** composed of TEMPO-based initiating units and poly(tetramethylene oxide) (PTMO) segments was prepared by polyaddition of TEMPO-based diol **1** with tolylene 2,4-diisocyanate terminated PTMO **2** at room temperature in the presence of DBTDL as a catalyst (Scheme 1). The polyaddition proceeded at room temperature to afford the corresponding polyurethane without dissociation or decomposition of alkoxyamine units. The structure of synthesized polymer **3** was confirmed by ^{1}H and ^{13}C NMR and IR measurements. In ^{1}H NMR spectrum, the signals assigned to alkoxyamine unit were observed at 0.5–2.5 and 4.0–5.2 ppm. The resonance assigned to methylene protons of PTMO segments appeared at 1.61 and 3.41 ppm. The IR spectrum had an absorption band at 1731 cm^{-1}, which is assignable to the stretching vibration of urethane carbonyl groups. To follow the polymerization behavior, the polyurethane macroinitiator was fractionated by preparative HPLC connected with SEC columns. By careful fractionation, polymers with narrow polydispersity were successfully obtained.

The synthetic procedure of poly(tetramethylene oxide)-*b*-polystyrene multiblock copolymers (PTMO-*b*-PS) is shown in Scheme 2. We have already found that an alkoxyamine initiator modified with urethane group permits polymerization control of styrene [27]. Radical polymerization of styrene was carried out in bulk with fractionated **3** ($M_n = 12{,}300$, $M_w/M_n = 1.10$) as a macroinitiator. The average number of alkoxyamine initiating sites was roughly calculated from the molecular



Scheme 2. Polymerization of styrene by the use of living free-radical polymerization macroinitiator **3**.

weight of TEMPO-based diol **1** and the average molecular weight of tolylene 2,4-diisocyanate terminated PTMO **2** to be 6.5 (12,300/1600+293). Since, an alkoxyamine initiating site is included in repeating unit of the polyurethane main chain, the average block number of the multiblock copolymer nearly corresponds to the twice average number of alkoxyamine initiating sites. Thus, the multiblock copolymers synthesized by the use of the macroinitiator were composed of 13 average block number. It is assumed that the average block number is approximately constant throughout the polymerization because alkoxyamine units hardly get inactive and/or decomposed. GPC profiles of the macroinitiator and postpolymers are shown in Fig. 1. A unimodal peak of the postpolymer shifted from that of the macroinitiator toward the higher molecular weight region. Additionally, corresponding shoulder peaks due to the macroinitiator were not observed. The $\ln([M]_0/[M]_t)$ vs. time plots are shown in Fig. 2(A). A first-order relationship between $\ln([M]_0/[M]_t)$ and time indicates the constant concentration of active radicals. Fig. 2(B) shows the dependence of M_n and M_w/M_n on monomer conversion. Molecular weight and M_w/M_n were evaluated without precipitation. M_ns increased linearly with conversion, which is fully consistent with controlled free-radical polymerizations. However, the M_w/M_n immediately increased to 1.70–1.80, and low molecular weight species that shows up at high elution time was observed. This strange feature would be caused by the migration of nitroxide radicals during polymerization. Hawker et al. have reported that radical exchange of nitroxide radicals during nitroxide-mediated free-radical polymerization is a facile process [29]. We have recently demonstrated that radical exchange of nitroxide radicals occurs among the main chain of poly(alkoxyamine)s even without monomers in the system [30,31]. The exchange property of nitroxide radicals has been utilized to the functionalization of polymer chain-end [32] and to the reversible transformation of polymer architecture [33,34]. To confirm the degree of radical migration, an anisole solution of narrow polydispersity macroinitiator **3** ($M_n=17{,}200$, $M_w/M_n=1.09$) was degassed and incubated at 125 °C under argon in the absence of monomer. The broadening of the GPC profile was clearly observed, and M_w/M_n increased immediately after incubation to approach 1.70–1.80 (Fig. 3). Significantly, time dependence of M_w/M_n resulted in a similar behavior with that on the polymerization of styrene. Thus, it can be surely mentioned that the radical exchange among main chain of the macroinitiator cause the significant increase of M_w/M_n at the initial stage of the polymerization and the formation of lower molecular weight species at elution time that is greater than the macroinitiator.

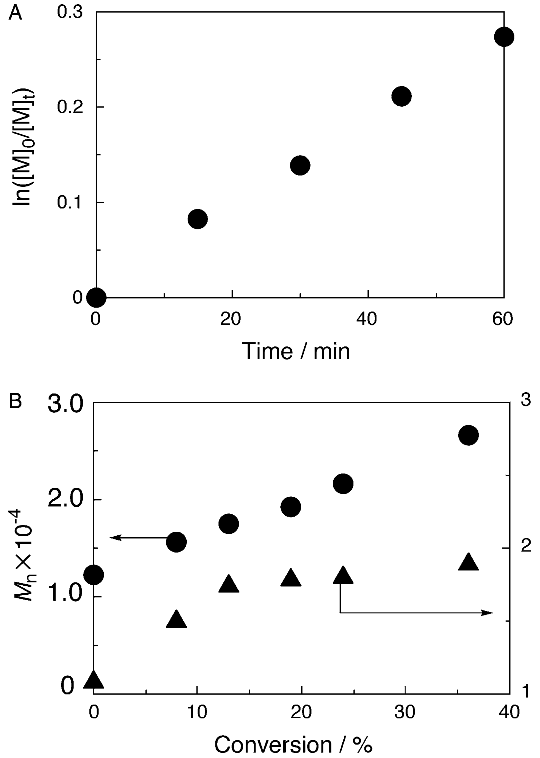


Fig. 2. (A) Semilogarithmic kinetic plots for the polymerization of styrene (10 mmol) with polyurethane macroinitiator **3** ($M_n=12{,}300$, $M_w/M_n=1.10$, 213 mg); in bulk at 125 °C. (B) Dependence of molecular weights and polydispersities with conversion for the polymerization of syrene (10 mmol) with polyurethane macroinitiator **3** ($M_n=12{,}300$, $M_w/M_n=1.10$, 213 mg); in bulk at 125 °C.

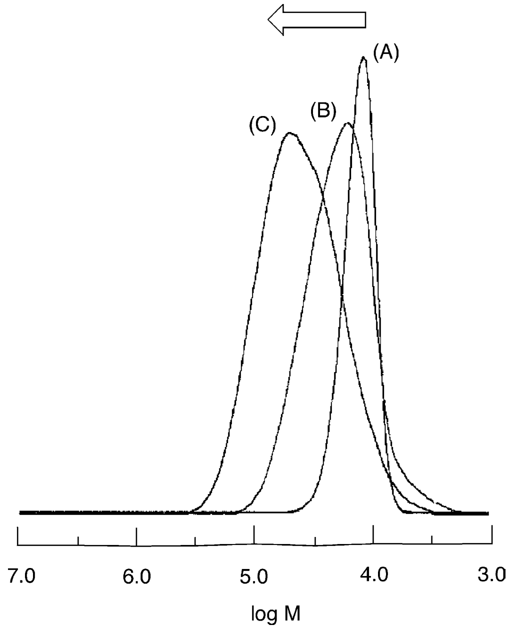


Fig. 1. Comparison of GPC profiles for (A) polyurethane macroinitiator **3** ($M_n=12{,}300$, $M_w/M_n=1.10$); (B) postpolymer **4** prepared through the polymerization of styrene (10 mmol) with **3** ($M_n=12{,}300$, $M_w/M_n=1.10$, 213 mg) at 125 °C for 15 min ($M_n=15{,}600$, $M_w/M_n=1.52$); and (C) for 2 h ($M_n=26{,}600$, $M_w/M_n=1.91$).

A comparison of ^{1}H NMR spectra of macroinitiator **3** and precipitated postpolymer **4** of 8 and 38% conversion are shown in Fig. 4. The broad peaks assigned to aromatic protons of PS units were observed in 6.3–7.2 ppm as well as the two peaks assigned to methylene protons of PTMO units at 1.62 and 3.41 ppm. The integration value of the signals assigned to PS units increased with increasing conversion. From a comparison

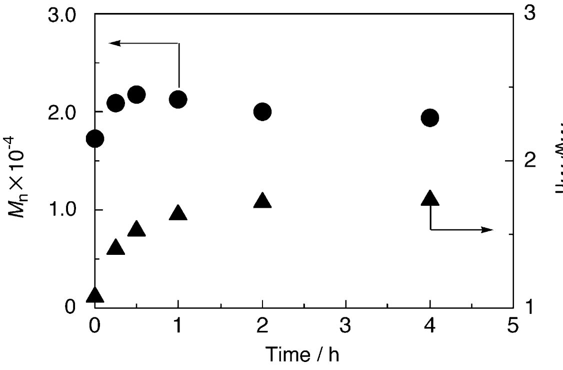


Fig. 3. Dependence of molecular weights and polydispersities with reaction time for the radical exchange reaction of polyurethane macroinitiator **3** (M_n = 17,200, M_w/M_n = 1.09, 213 mg) in anisole (10 mmol) at 125 °C.

of integration values for the aliphatic and aromatic protons of the ^{1}H NMR spectra, molar content of PS units on multiblock copolymers was calculated. As is expected in controlled polymerization, relative ratio of PS to PTMO shows a regular increase with increasing conversion.

The IR spectra of macroinitiator **3** and precipitated postpolymer **4** of 13 and 38% conversion in Fig. 5 exhibit an absorption at around 1732 cm^{-1} corresponding to the stretching vibration mode of urethane carbonyl groups (C=O) associated with the ether groups [35,36] and a strong absorption at 1111 cm^{-1} assigned to the stretching vibration mode of ether (C–O–C) groups in PTMO. After the insertion of PS chains, absorptions corresponding to the stretching vibration mode of aromatic groups (C=C, 1601 cm^{-1}) and the deformation vibration mode of aromatic groups (C–H, 699 and 758 cm^{-1}) were observed as well as absorptions corresponding to C=O and C–O–C, which are derived from the macroinitiator. Absorbance integral ratio of A(C=C)/A(C=O) increased with increasing the molecular weight of inserted PS chains.

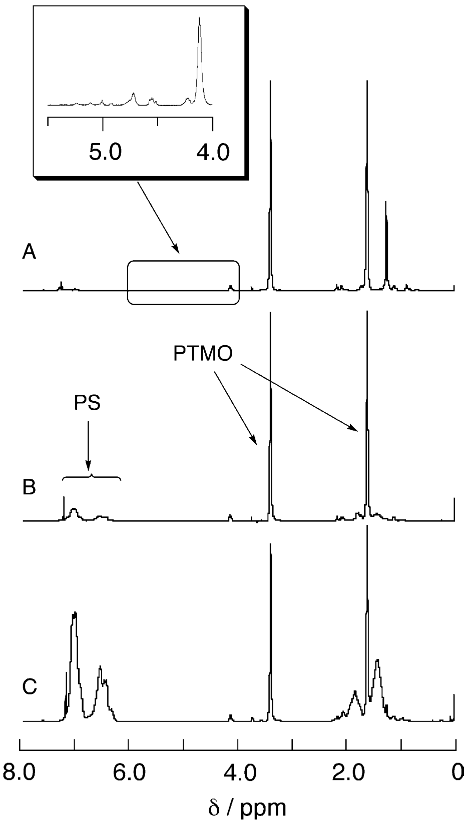


Fig. 4. ^{1}H NMR spectra of (A) polyurethane macroinitiator **3** (M_n = 12,300, M_w/M_n = 1.10); (B) precipitated PTMO-*b*-PS multiblock copolymer **4** at 8% conversion (M_n = 15,600, M_w/M_n = 1.52); and (C) precipitated PTMO-*b*-PS multiblock copolymer **4** at 36% conversion (M_n = 26,600, M_w/M_n = 1.91).

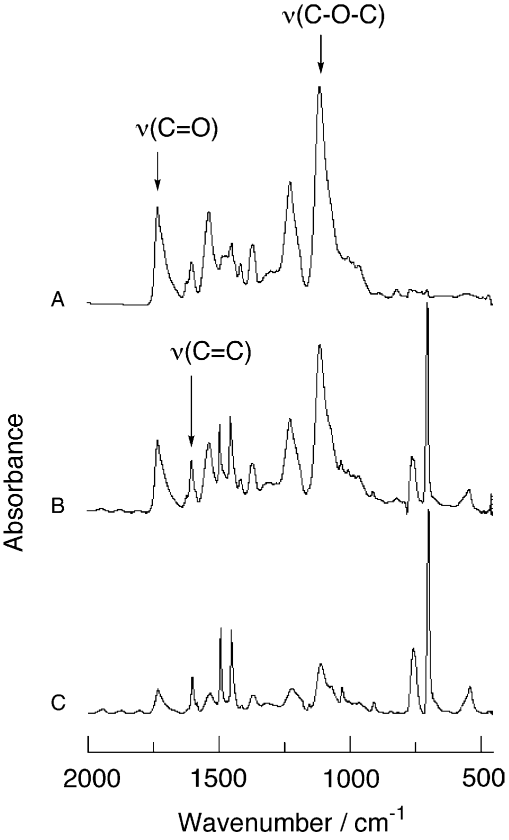


Fig. 5. Partial IR spectra of (A) polyurethane macroinitiator **3** (M_n = 12,300, M_w/M_n = 1.10); (B) precipitated PTMO-*b*-PS multiblock copolymer **4** at 13% conversion (M_n = 17,500, M_w/M_n = 1.76); (C) precipitated PTMO-*b*-PS multiblock copolymer **4** at 36% conversion (M_n = 26,600, M_w/M_n = 1.91).

3.2. Molecular aggregation states and mechanical properties of PTMO-b-PS multiblock copolymers

The mechanical property of block copolymers depends on the molecular weight and volume fraction of the blocks, and the number of blocks [3,37]. By utilizing the living free-radical polymerization multifunctional macroinitiator technique, molar content of PS chains can be controlled and a series of the multiblock copolymers is easily obtained under synthetically robust condition. Thus, this facile synthetic strategy can be applied to the systematic evaluation of the relationship between physical properties and polymer structure. Table 1 represents preparation conditions and characterizations of

Table 1
Preparation conditions[a] and characteristics of PTMO-*b*-PS multiblock copolymers

Sample	Time[b]	Conv. (%)[c]	Molar content of PS (%)[d]	M_n[e]	M_w/M_n[e]
A	0.25	5	12.2	24,100	4.83
B	0.75	11	21.3	25,900	4.23
C	1.00	16	29.3	26,400	3.47
D	1.50	23	35.8	27,500	3.82
E	2.50	32	41.6	29,300	3.66

[a] Polyurethane **3** (M_n=20,200, M_w/M_n=5.15) was used as a macroinitiator. Polymerization was carried out by heating the mixture of the polyurethane macroinitiator (2.0 g) and styrene (11.5 mL, 0.1 mol) at 125 °C under argon.

[b] Polymerization time in hours.

[c] Monomer conversion was determined by ^{1}H NMR.

[d] Molar content of PS was calculated by comparing integration values of the peaks derived from PTMO and PS on ^{1}H NMR spectra.

[e] Molecular weight of the polymers after precipitation was estimated by GPC, using linear polystyrene standards.

PTMO-*b*-PS multiblock copolymers. Molar content of PS was calculated by comparing integration values of the peaks derived from PTMO and PS on ^{1}H NMR spectrum. The content of PS is controlled to give a variety of PTMO-*b*-PS multiblock copolymers. Films were prepared by casting a chloroform solution (5.0 wt%) of the copolymers and annealed to appreciate correct aggregation structure and mechanical properties reflecting PS content. Sample A is too sticky and sample E is too fragile to get the self-supporting film. Other samples (samples B–D) give the colorless, transparent, and elastomeric films with a smooth surface.

Fig. 6 compares the stress–strain curves for the samples B–D (Table 1) at room temperature. The stress–strain curves clearly depended on PS content of the multiblock copolymers. The elongation at break systematically decreased with increasing PS content, whereas the decrease of ultimate tensile strength was hardly observed. The yield stress increased with increasing PS content, and a yielding point was clearly observed in samples C and D indicating a continuous or semicontinuous PS phase in the PTMO phase. As expected, the initial modulus and unrecovered deformation also increased with increasing PS content.

DSC measurement is a very useful technique to detect the state of phase separation in binary blends and block

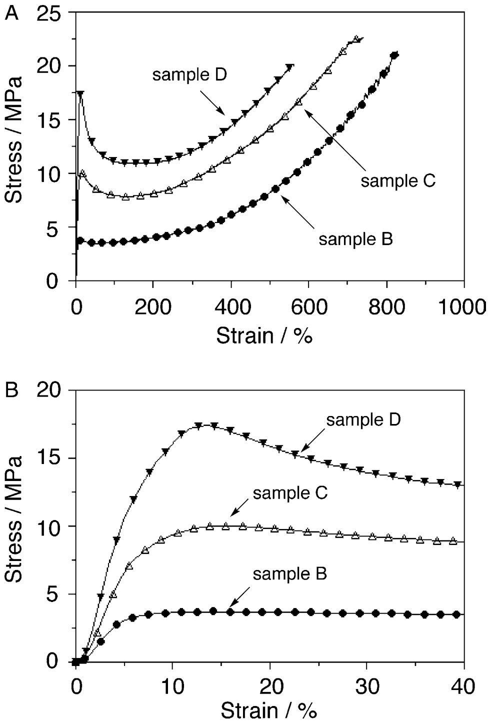


Fig. 6. Stress–strain curves for PTMO-*b*-PS multiblock copolymers: (A) full curves and (B) curves in the small strain region: samples B (M_n=25,900, M_w/M_n=4.23, PS content=21.3%), C (M_n=26,400, M_w/M_n=3.47, PS content=29.3%) and D (M_n=27,500, M_w/M_n=3.82, PS content=35.8%).

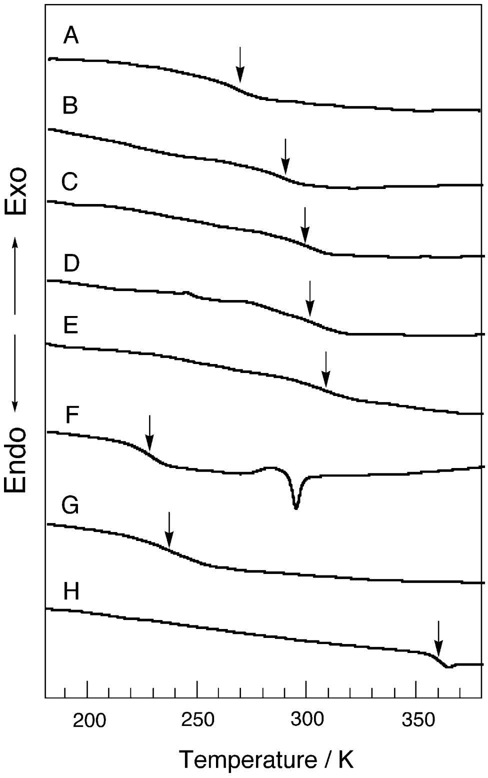


Fig. 7. DSC traces of PTMO-*b*-PS multiblock copolymers: samples A–E, (F) TDI-terminated PTMO **2** capped with methanol, (G) macroinitiator **3** (M_n= 20,200, M_w/M_n=5.15), and (H) polystyrene synthesized through NMRP with an urethane functionalized alkoxyamine initiator (M_n=2200, M_w/M_n=1.25). Heating rate: 10 K/min. The arrows indicate glass transition temperature.

copolymers. DSC curves for samples A–E (Table 1) are shown in Fig. 7 with that for TDI-terminated PTMO **2**, macroinitiator **3** ($M_n=20{,}200$, $M_w/M_n=5.15$), and polystyrene ($M_n=2200$, $M_w/M_n=1.25$) synthesized through NMRP with an urethane functionalized alkoxyamine initiator [27]. Although T_m of PTMO crystal was observed on **2** at 294.6 K, the peak disappeared on macroinitiator and multiblock copolymers. Consequently, PTMO chains behave as a flexible soft segment on multiblock copolymers without crystallization. A transition assigned to glass transition (T_g) was clearly observed for all samples; however, T_gs corresponding to PS and PTMO domain were not observed. Observation of single glass transition in block copolymers indicates that the materials are not phase-separated. Indeed, T_g of the multiblock copolymers increased with increasing the PS content as would be expected in compatible system. On the other hand, it is well known that the T_g of PS increase with increasing the molecular weight [38,39]. Consequently, it is assumed that the increase of the compatible multiblock copolymer T_g was derived from both increase of PS molecular weight and increase of PS content.

Fig. 8 shows the temperature dependence of dynamic modulus (E') and loss tan δ ($=E''/E'$) from 240 to 340 K for samples B–D (Table 1). The rubbery plateau and the individual α_a-absorption of PS and PTMO phases derived from the phase separation were not observed for all the multiblock copolymers. An α_a-absorption was clearly observed for all samples and shifted to higher temperature with increasing PS content. This result indicates that PS segments and PTMO segments are compatible, in agreement with the result of DSC analysis. The multiblock structure of low molecular weight segments and polar urethane groups would lead the high compatibility between PTMO segments and PS segments. In the case of block copolymers with immiscible polymer segments, the degree of mutual compatibility of the segments increases with decreasing the molecular weight [40]. In addition, as the number of blocks in block copolymer samples increases, the entropy change on microphase separation becomes more and more negative due to the immobilization of linking points at the interface between two phases. In other words, entropy contribution make microphase separation more difficult as the number of blocks per molecule increases [41]. The existence of polar urethane groups associated with ether groups of PTMO would also lead PTMO segments and PS segments to be compatible.

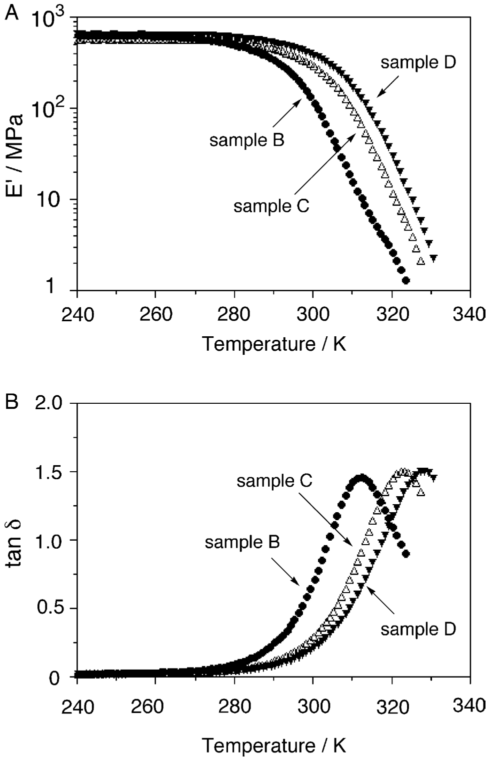


Fig. 8. (A) Storage modulus (E') and (B) mechanical loss tan δ ($=E''/E'$) at 11 Hz for PTMO-*b*-PS multiblock copolymers in the glass transition regime: samples B ($M_n=25{,}900$, $M_w/M_n=4.23$, PS content=21.3%), C ($M_n=26{,}400$, $M_w/M_n=3.47$, PS content=29.3%) and D ($M_n=27{,}500$, $M_w/M_n=3.82$, PS content=35.8%).

4. Conclusion

Poly(alkoxyamine) including PTMO segments can be used as a macroinitiator for NMRP of styrene. The linear relationship between number average molecular weight and monomer conversion as well as the regular increase of PS content on the polymerization reveal the controlled polymerization of styrene and the insertion of well-defined molecular weight PS chains. PTMO segments and PS segments of the multiblock copolymers were apparently compatible due to the multiblock structure of low molecular weight segments and polar urethane groups. Mechanical properties of the multiblock copolymers can be tuned by the sufficient molecular weight control of PS chains. The strategy described here is available for the preparation of a wide variety of well-defined multiblock copolymer libraries to be readily prepared in the minimum number of steps under synthetically robust conditions, and is expected as a powerful systematic screening tool for the preparation of the excellent polymeric materials.

Acknowledgements

The authors gratefully acknowledge the financial support of Nissan Science Foundation, Shiseido Fund for Science and Technology, Research Foundation Materials Science, and a Grant-in-Aid for Scientific Research (14750699) from the Ministry of Education, Culture, Science, Sports and Technology of Japan. The present work is also supported by a Grant-in-Aid for the 21st Century COE Program, 'Functional Innovation of Molecular Informatics' from the Ministry of Education, Culture, Science, Sports and Technology of Japan. Y.H. acknowledges the financial support of Grant-in-Aid for JSPS Fellows.

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