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Synthesis of well-defined poly(styrene)-*b*-poly(*p*-*tert*-butoxystyrene) multiblock copolymer from poly(alkoxyamine) macroinitiator

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Abstract

The stepwise insertion reaction of styrene (St) and *p*-*tert*-butoxystyrene (BOSt) into poly(alkoxyamine) macroinitiator was carried out to provide well-defined poly(St)-*b*-poly(BOSt) multiblock copolymers. Structural confirmation of the multiblock copolymers was accomplished by NMR and IR measurements. The model reaction also supported that the monomer insertion into the macroinitiator proceeded in accordance with a living fashion.

Keywords: Macroinitiator; Living radical polymerization; Multiblock copolymer

1. Introduction

Interest in the accurate control of macromolecular architecture, a highly important theme in polymer science, is being driven by the desire to prepare advanced materials with new and/or improved properties [1,2]. During the past decades the study on block copolymers has attracted considerable interest with the development of new synthetic strategies and potential industrial uses for these nanostructured materials. Traditionally, such well-defined macromolecules were only available from living procedures, such as anionic polymerization, which are synthetically challenging and not amenable to significant changes in the structure of macromolecule, or the presence of functional group. The desire to develop a simple and versatile method for the preparation of wide variety of polymers stimulate the development of living free radical procedures, such as nitroxide-mediated process [3–8], atom transfer radical polymerization (ATRP) [9–12], reversible addition fragmentation chain transfer (RAFT) [13–15] and organotellurium-mediated living radical polymerization (TERP) [16,17]. The mechanism for these strategies is reversible capping of growing radical chain ends to give dormant species, which significantly reduces the concentration of active species and therefore prevent irreversible termination reactions. These strategies permit the synthesis of a wide variety of materials which are either difficult to prepare or not available via other polymerization processes.

While the synthesis of multiblock copolymer has long been solely performed by condensation procedures, the introduction of the radical polymerization of vinyl monomers with macroazoinitiator greatly extended the scope of synthetic strategy of multiblock copolymer [18–21]. However, the free-radical polymerization has disadvantages over the living radical procedure in structural control. The living radical polymerization has the potential to accomplish the quantitative synthesis and structural control of multiblock copolymers [22].

As was already reported, novel polyurethane macroinitiator containing TEMPO-based initiating units in the main chain has been synthesized by polyaddition of TEMPO-based diol with diisocyanate, and has been applied for preparation of segmented copolymer in which polar urethane groups are dispersed homogeneously in the main chain [23]. The initiating groups in the resulted polymer are assumed to be still active and one can expect the further insertion of other monomers. In this paper, the authors performed stepwise monomer insertion into the poly(alkoxyamine) macroinitiator for living radical polymerization

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to prepare well-defined multiblock copolymer as illustrated in Fig. 1.

2. Experimental section

2.1. Materials

Alkoxyamine initiator **1** and polyurethane macroinitiator **3** were prepared by the method reported previously [23]. Commercially obtained styrene (St) (Wako, 99%) and *p*-*tert*-butoxystyrene (BOSt) (Wako, 99%) were distilled under vacuum over CaH_2 immediately prior to use. Other reagents were purchased from Kanto Chemicals or Wako Pure Chemical Industries and were used as received without purification.

2.2. Measurements

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic measurements were carried out at 25 °C with a JEOL JNM-EX400 spectrometer using tetramethylsilane as an internal standard in chloroform-*d*. IR spectra were obtained with a Perkin Elmer Spectrum One infrared spectrometer as thin films on NaCl or neat. Monomer conversion was determined by ^{1}H NMR of the crude reaction mixtures (Calculated from integral ratio between vinyl protons and aliphatic protons). Number and weight average molecular weights (M_n and M_w, respectively) and polydispersity (M_w/M_n) were estimated by size exclusion chromatography (SEC) in THF at 40 °C on a polystyrene gel column [Shodex GPC KF-804L column (300 × 8.0 mm^2)] that was connected to a TOSOH system equipped with a refractive index (RI) detector at a flow rate of 0.8 ml min^{-1}. The columns were calibrated against 6 standard polystyrene samples (M_n = 800–15 2000; M_w/M_n = 1.03–1.10).

2.3. Synthesis of poly(BOSt) (Scheme 1)

In a typical run, a mixture of alkoxyamine initiator **1** (23.2 mg, 0.05 mmol) and BOSt (1.41 ml, 7.50 mmol) was charged in a polymerization tube, degassed, and sealed off under vacuum. The mixture was heated at 125 °C for 2 h, and after dilution with chloroform the solution was poured into methanol. The resulting polymer precipitated was collected by filtration and dried in vacuum (469 mg, 35% yield). M_n = 10 600, M_w/M_n = 1.28; ^{1}H NMR: (δ, ppm) 0.80–2.20 (br, aliphatic H), 3.05 (br), 3.70–5.00 (br), 6.10–6.90 (br, aromatic H); ^{13}C NMR: (δ, ppm) 28.91 (br), 39.78 (br), 40.00–48.00 (br), 123.49 (br), 127.74 (br), 139.00–142.00 (br), 152.79 (br); FT-IR (NaCl, cm^{-1}): 3100–2850 (C–H), 1725 (C=O), 1607 (C=C), 1505, 1365, 1236, 1163 (C–O), 899, 852.

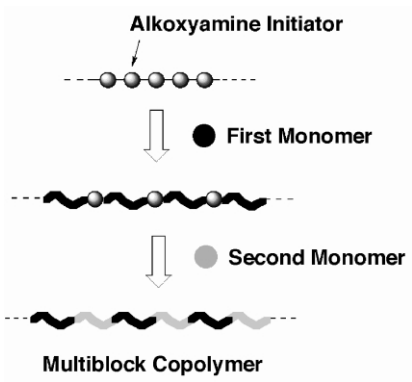
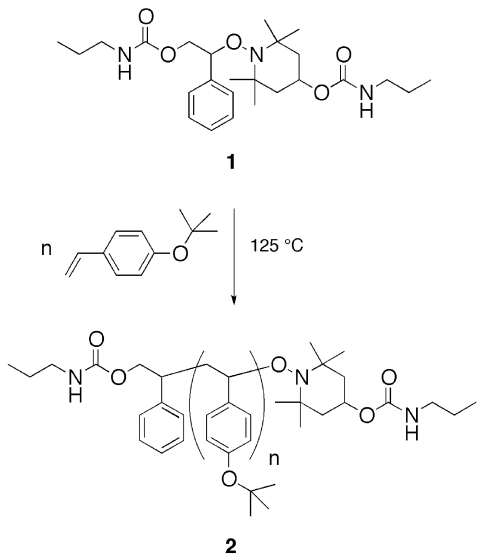


Fig. 1. Schematic representation of multiblock copolymer synthesis by a 'controlled monomer insertion method'.

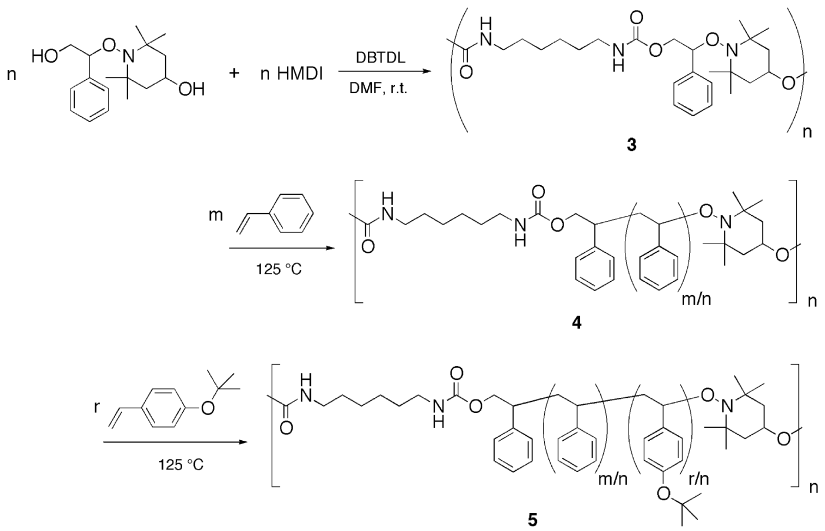


Scheme 1.

2.4. Synthesis of poly(St)-b-poly(BOSt) multiblock copolymer (Scheme 2)

2.4.1. Controlled monomer insertion of St into polyurethane macroinitiator

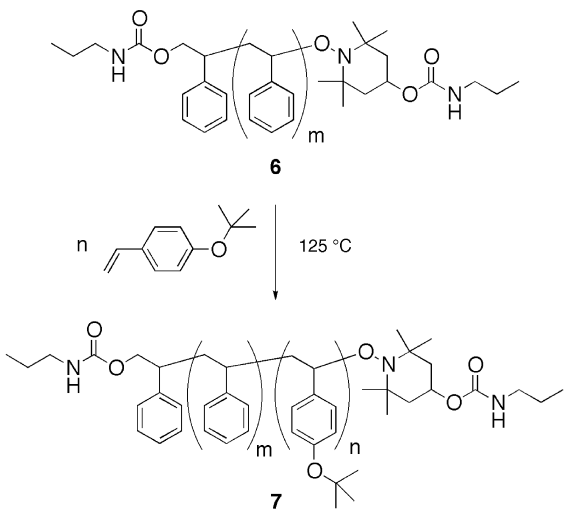
In a typical run, a mixture of polyurethane macroinitiator **3** (M_n = 2650, M_w/M_n = 1.58, 80 mg, 173 μmol initiating sites) and St (1.15 ml, 10 mmol) was charged in a polymerization tube, degassed, and sealed off under vacuum. The mixture was incubated at 125 °C for 2 h, and after dilution with chloroform the solution was poured into methanol. The resulting polymer precipitated was collected by filtration and dried in vacuum (376 mg, 34% yield). M_n = 11 800, M_w/M_n = 1.77; ^{1}H NMR: (δ, ppm) 0.21 (br), 0.90–2.40 (br, aliphatic H), 3.02 (br), 3.64 (s), 3.70–5.00 (br), 6.20–7.40 (br, aromatic H); ^{13}C NMR: (δ, ppm) 20.97, 26.18, 29.82, 33.91, 40.31 (br), 39.00–49.00 (br), 59.22, 60.32, 125.62 (br), 127.61 (br), 145.25 (br), 156.17, 156.36; FT-IR (NaCl, cm^{-1}): 3100–2850 (C–H), 1724 (C=O), 1601 (C=C), 1493, 1453, 757, 698.



Scheme 2.

2.4.2. Controlled monomer insertion of BOSt into poly(St) macroinitiator

In a typical run, a mixture of poly(St) macroinitiator **4** ($M_n = 11\,800$, $M_w/M_n = 1.77$, 55 mg) and BOSt (942 μl, 5 mmol) was charged in a polymerization tube, degassed, and sealed off under vacuum. The mixture was incubated at 125 °C for 2 h, and after dilution with chloroform the solution was poured into methanol. The resulting polymer precipitated was collected by filtration and dried in vacuum (244 mg, 26% yield). $M_n = 49\,200$, $M_w/M_n = 1.77$; ^{1}H NMR: (δ, ppm) 0.80–2.20 (br, aliphatic H), 3.02 (br), 3.64 (s), 3.70–5.00 (br), 6.10–7.40 (br, aromatic H); ^{13}C NMR: (δ, ppm) 28.90 (br), 39.00–47.00 (br), 123.50 (br), 125.50 (br), 127.85 (br), 139.00–142.00 (br), 152.78 (br); FT-IR (NaCl, cm^{-1}): 3100–2850 (C–H), 1725 (C=O), 1606 (C=C), 1505, 1365, 1236, 1163 (C–O), 899, 852, 758, 699.



Scheme 3.

2.5. Synthesis of poly(St)-b-poly(BOSt) diblock copolymer (Scheme 3)

2.5.1. Radical polymerization of St initiated with alkoxyamine *1*

A mixture of alkoxyamine initiator **1** (80.2 mg, 173 μmol) and styrene (1.15 ml, 10.0 mmol) were charged in a polymerization tube, degassed, and sealed off under vacuum. The mixture was incubated at 125 °C for 2 h, and after dilution with chloroform the solution was poured into methanol. The resulting polymer precipitated was collected by filtration and dried in vacuum (239 mg, 21% yield). $M_n = 3300$, $M_w/M_n = 1.10$; ^{1}H NMR: (δ, ppm) 0.22 (br), 0.80–2.40 (br, aliphatic H), 3.07 (br, CH_2), 3.80–5.00 (br, CH, CH_2), 6.20–7.40 (br, aromatic H); ^{13}C NMR: (δ, ppm) 11.18, 20.96, 23.13, 40.31, 41.0–47.0 (br), 59.22, 94.07, 125.0–130.0 (br), 144.5–146.0 (br), 156.20 (C=O), 156.35 (C=O); FT-IR (NaCl, cm^{-1}): 3100–2850, 1724 (C=O), 1601 (C=C), 1493, 1453, 1219, 1028, 907, 757, 698. 539

2.5.2. Radical polymerization of BOSt initiated with alkoxyamine terminated poly(St) *6*

A mixture of alkoxyamine terminated poly(St) **6** ($M_n = 3300$, $M_w/M_n = 1.10$, 110 mg) and BOSt (1.88 ml, 10 mmol) was degassed and sealed off under vacuum. The mixture was heated at 125 °C for 30 min, and after dilution with chloroform the solution was poured into methanol. The resulting polymer precipitated was collected by filtration and dried in vacuum (542 mg, 35% yield). $M_n = 8800$, $M_w/M_n = 1.37$; ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm) 0.80–2.20 (br, aliphatic H), 3.06 (br), 3.70–5.00 (br), 6.10–7.30 (br, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$): (δ, ppm) 28.90 (br), 39.75 (br), 40.00–48.00 (br), 123.47 (br), 127.69 (br), 139.00–142.00 (br), 152.76 (C=O); FT-IR (NaCl, cm^{-1}): 3100–2850, 1725 (C=O), 1606 (C=C), 1505, 1365, 1236, 1162, 898, 852, 699

3. Results and discussion

3.1. Synthesis of poly(BOSt) homopolymer

Previously the authors have demonstrated that polyurethane **3** containing TEMPO-based alkoxyamine initiating units in the main chain can be used as the macroinitiator for the living radical polymerization of styrene to accomplish the insertion of well-defined polystyrene chain [23]. The alkoxyamine initiators are suitable for the polymerization of various styrene derivatives and are applied for the preparation of block copolymers [24,25]. BOSt is one of the functional monomers because poly (BOSt) can readily be converted into poly(*p*-vinyl phenol), which has a wide variety of applications [26–28]. To investigate whether the structural control is accomplished in the polymerization of BOSt with the polyurethane macroinitiator **3**, the effectiveness of alkoxyamine unimolecular initiator **1** with urethane moieties for the living free radical polymerization of BOSt was investigated under bulk conditions at 125 °C with special attention being paid to molecular weight and polydispersity control (Scheme 1).

The M_n vs. conversion and the M_w/M_n vs. conversion plots are shown in Fig. 2. In agreement with the results of Fukuda et al. [27], M_n was observed to evolve in a linear fashion with conversion, which is indicative of a living process. The polydispersities of polymers decrease with conversion to 1.24 at the highest studied conversion. Significantly, the ^{1}H NMR spectra of **2** showed the expected signals for both the aliphatic and aromatic protons of poly(BOSt) backbone as well as the resonances for the chain ends resulting from initiator **1**.

Interestingly, the polymerization rate is faster than the reported nitroxide mediated free radical polymerization of BOSt. The use of a TEMPO derivative substituted in the 4-position with a phosphonic acid group was reported to be significantly enhanced the polymerization rate [24,25]. Presumably the ability to form an intramolecular hydrogen bond in TEMPO derivative leads to a change in mediating ability. Similarly, intramolecular hydrogen bond between urethane bond and oxygen in this system is presumed to contribute to the rate enhancement effect. These results indicate that the alkoxyamine **1** is an efficient initiator for the nitroxide mediated controlled radical polymerization of not only styrene but also BOSt to afford well-defined polymer.

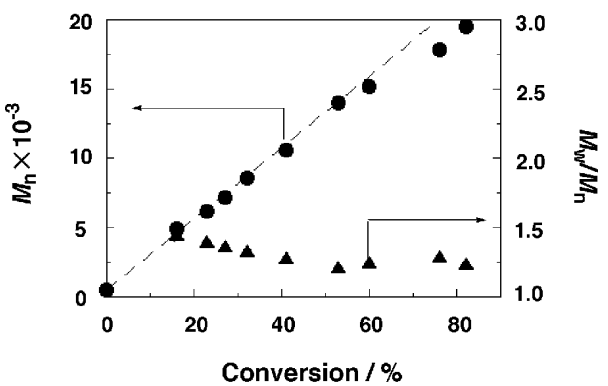


Fig. 2. The M_n vs. conversion and the M_w/M_n vs. conversion plots for the polymerization of BOSt (7.50 mmol) with **1** (0.05 mmol) as an initiator in bulk at 125 °C. The calculated molecular weights are shown in a broken line.

3.2. Synthesis of poly(St)-b-poly(BOSt) multiblock copolymer

The procedure for the preparation of poly(St)-*b*-poly (BOSt) multiblock copolymer is described in Scheme 2. Polyurethane macroinitiator **3** was prepared by polyaddition of the TEMPO-based diol with HMDI at room temperature for 30 min under N_2 in the presence of dibutyltin dilaurate as a catalyst. After the addition of methanol, the mixture was purified by reprecipitation from chloroform into hexane to afford **3** ($M_n = 2650$, $M_w/M_n = 1.58$) as a white powder without detectable amounts of crosslinked or insoluble materials. Bulk polymerization of St initiated with polyurethane macroinitiator **3** was carried out at 125 °C for 2 h. The crude product was poured into methanol to give poly(St) macroinitiator **4** ($M_n = 11\,800$, $M_w/M_n = 1.77$) as white powder. Subsequent insertion reaction of BOSt into macroinitiator **4** was conducted in bulk at 125 °C.

The $\ln([M]_0/[M]_t)$ vs. time plots are shown in Fig. 3. A linear relationship between $\ln([M]_0/[M]_t)$ vs. time is established throughout polymerization, indicating that the number of the propagating chains is constant. The M_n vs. conversion and the M_w/M_n vs. conversion plots are shown in Fig. 4. Fig. 4 exhibits that M_ns increase in linear fashion, which is fully consistent with a controlled or living free radical polymerization. Thus, it is assumed that the monomer insertion reaction proceeds with controlled nature. However, the polydispersities of the obtained polymers were maintained in 1.7–1.8 throughout polymerization without significant increase. The large polydispersities of the obtained polymers are considered to be due to the large polydispersity of macroinitiator. In addition, the

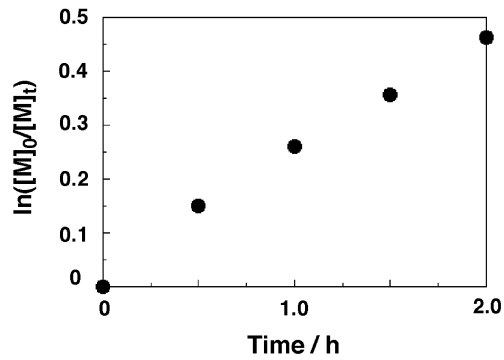


Fig. 3. The $\ln([M]_0/[M]_t)$ vs. time plots for the polymerization of BOSt (5 mmol) in the presence of **4** ($M_n = 11\,800$, $M_w/M_n = 1.77$, 55 mg) as macroinitiator in bulk at 125 °C.

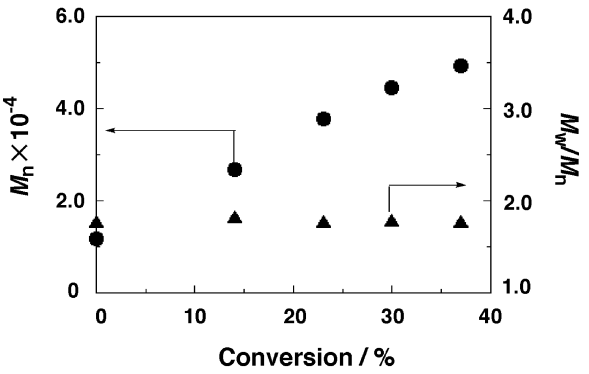


Fig. 4. The M_n vs. conversion and the M_w/M_n vs. conversion plots for the polymerization of BOSt (5 mmol) in the presence of **4** ($M_n = 11\,800$, $M_w/M_n = 1.77$, 55 mg) as macroinitiator in bulk at 125 °C.

feature is caused by the migration of the nitroxide radicals during polymerization. We demonstrated previously that radical crossover reaction of nitroxide proceeds among main chain to give the hybrid polymer [29,30]. Thus, although the radical crossover reaction among main chain caused during polymerization, on account of the large polydispersity of macroinitiator, polydispersities are apparently constant.

The SEC elution curves are depicted in Fig. 5. All of the SEC elution curves for **3**–**5** show the unimodal peak, and more importantly, leaving no significant shoulder peak at the elution position of the prepolymers, indicating that all the macroinitiators initiated the polymerization. In the case of the insertion of BOSt [Fig. 5(c) and (d)], the peaks shift to a higher molecular weight region with conversion.

Structural characterization of the multiblock copolymer was accomplished by a number of techniques. ^{1}H and ^{13}C NMR and infrared spectra of the multiblock copolymers showed signals corresponding to both the poly(St) and

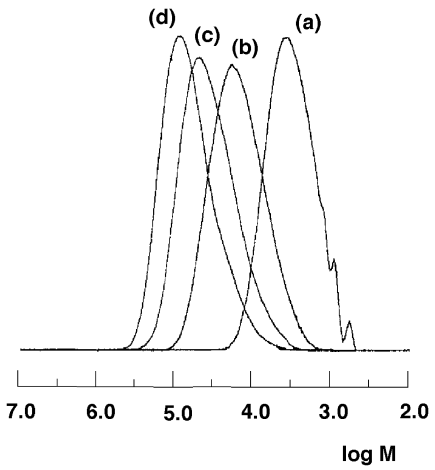


Fig. 5. Comparison of SEC curves for (a) the polyurethane macroinitiator, **3**, $M_n = 2700$, $M_w/M_n = 1.58$; (b) the poly(St) macroinitiator, **4**, $M_n = 11\,800$, $M_w/M_n = 1.77$; (c) the poly(St)-*b*-poly(BOSt) multiblock copolymer, **5**, at 14% conversion, $M_n = 26\,700$, $M_w/M_n = 1.82$; (d) the poly(St)-*b*-poly(BOSt) multiblock copolymer, **5**, at 37% conversion, $M_n = 49\,200$, $M_w/M_n = 1.77$.

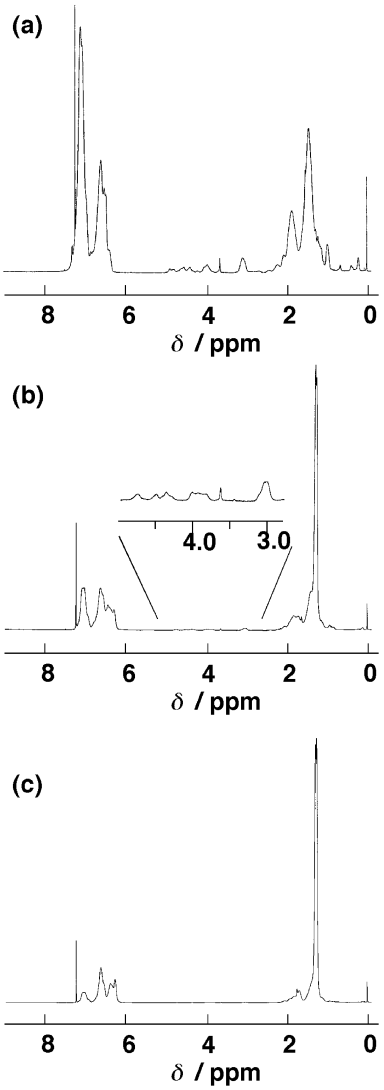


Fig. 6. ^{1}H NMR spectra of (a) the poly(St) macroinitiator, **4**, $M_n = 11\,800$, $M_w/M_n = 1.77$; (b) the poly(St)-*b*-poly(BOSt) multiblock copolymer, **5**, at 14% conversion, $M_n = 26\,700$, $M_w/M_n = 1.82$; (c) the poly(St)-*b*-poly (BOSt) multiblock copolymer, **5**, at 37% conversion, $M_n = 49\,200$, $M_w/M_n = 1.77$.

poly(BOSt) segments. Comparison of the ^{1}H NMR spectra of poly(St) macroinitiator **4** and poly(St)-*b*-poly(BOSt) multiblock copolymer **5** is shown in Fig. 6. It is obvious that the significant peak of *tert*-butoxy protons appeared at 1.2 ppm after the insertion of BOSt. Both spectra showed minor resonances at 3–5 ppm, which have previously been assigned to the methylene and methine protons of alkoxyamine moiety in the main chain of polyurethane macroinitiator. Further evidence for the designed structure was obtained by comparing the IR spectrum of the initial polyurethane macroinitiator **3** with those of **4** and **5**. Fig. 7 shows partial IR spectra of **3**–**5** of 14 and 37% conversion. The stretching vibration mode of the urethane carbonyl groups (C=O) was observed in each polymer. The stretching vibration mode of the aromatic groups (C=C) was observed

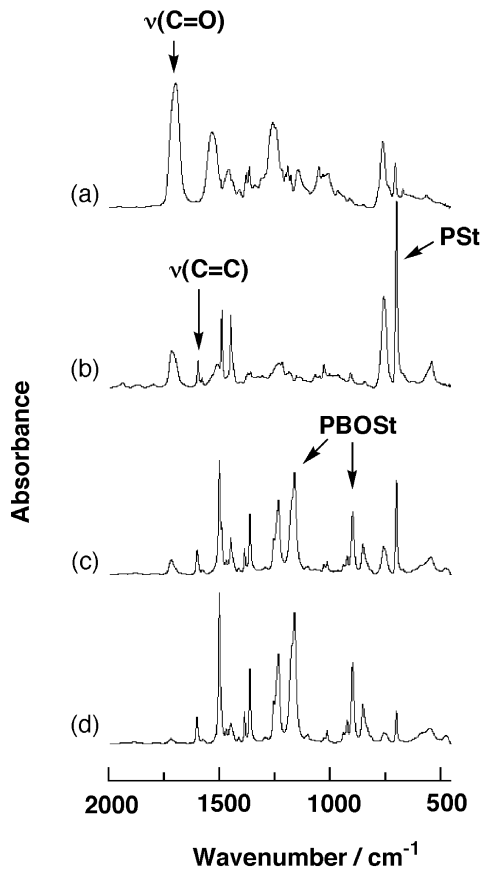


Fig. 7. Partial IR spectra of (a) the polyurethane macroinitiator, **3**, M_n = 2700, M_w/M_n = 1.58; (b) the poly(St) macroinitiator, **4**, M_n = 11 800, M_w/M_n = 1.77; (c) the poly(St)-*b*-poly(BOSt) multiblock copolymer, **5**, at 14% conversion, M_n = 26 700, M_w/M_n = 1.82; (d) the poly(St)-poly (BOSt) multiblock copolymer, **5**, at 37% conversion, M_n = 49 200, M_w/M_n = 1.77.

at 1600 cm^{-1} after insertion of St and BOSt. After the insertion of St, the absorption bands at 698 and 757 cm^{-1} corresponding to poly(St) units appeared. During the insertion of BOSt, the absorption bands at 852, 899, 1163 and 1236 cm^{-1}, which correspond to BOSt units, increased with increasing conversion. Fig. 8 shows the dependence of absorbance integral ratio between stretching vibration of urethane carbonyl groups (1650–1780 cm^{-1}) and stretching vibration of aromatic rings (1560–1630 cm^{-1}) (A(C=C)/A(C=O)) on conversion. A(C=C)/A(C=O) increased linearly with increasing conversion. A(C=C)/A(C=O) is considered to correspond to the molecular weight of inserted block copolymers into macroinitiators. It can be confirmed from a linear relationship between A(C=C)/A(C=O) vs. conversion that the molecular weight of inserted block copolymers is controlled.

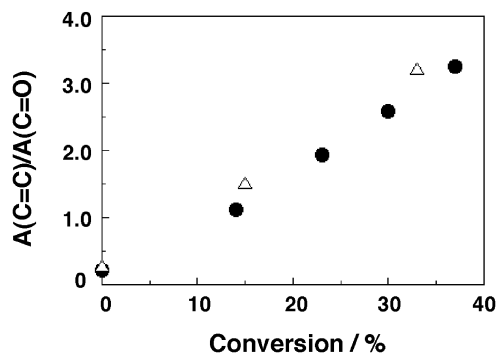


Fig. 8. Evolution of relative IR absorbance integral ratio between stretching vibration of urethane carbonyl groups (1650–1780 cm^{-1}) and stretching vibration of aromatic rings (1560–1630 cm^{-1}) (A(C=C)/A(C=O)) on conversion for (circle) the polymerization of BOSt (5 mmol) with **4** (M_n = 11 800, M_w/M_n = 1.77, 55 mg) as macroinitiator, in bulk at 125 °C; (triangle) the polymerization of BOSt (10 mmol) in the presence of **6** (M_n = 3300, M_w/M_n = 1.10, 110 mg) as macroinitiator in bulk at 125 °C.

To estimate the molecular weight and polydispersities of the inserted chains, poly(St)-*b*-poly(BOSt) diblock copolymers were synthesized with alkoxyamine terminated poly(St) **6** as control experiment under the similar conditions to the synthesis of multiblock copolymers (Scheme 3). The M_n vs. conversion and the M_w/M_n vs. conversion plots are shown in Fig. 9. As can be seen in Fig. 9, M_ns increase linearly with conversion and are in good agreement with those calculated. Although the M_w/M_n is high (1.37) at the initial stage of polymerization, the one decreases slightly with conversion to 1.22. In ^{1}H NMR spectra of the products, the signals assigned to initiator unit are clearly observed at 3–5 ppm as well as the major signals of poly(St) and poly(BOSt) segments. From the integration values for the aliphatic and aromatic protons of the ^{1}H NMR spectra, the block components of multiblock copolymers and diblock copolymers were estimated (Fig. 10). Relative ratio of poly(BOSt) to poly(St) increase linearly with conversion in both systems, and more importantly, the plots of control experiment agreed very closely with the result of macroinitiator system. In addition, the IR absorbance integration ratios of A(C=C)/A(C=O) are fair agreement with the results of macromolecular system (Fig. 8). Accordingly, it is concluded from the results obtained both NMR and IR spectra that the prepared diblock copolymers correspond to the inserted chain into the macroinitiator, in other words, well-defined diblock polymers were inserted to the macroinitiator.

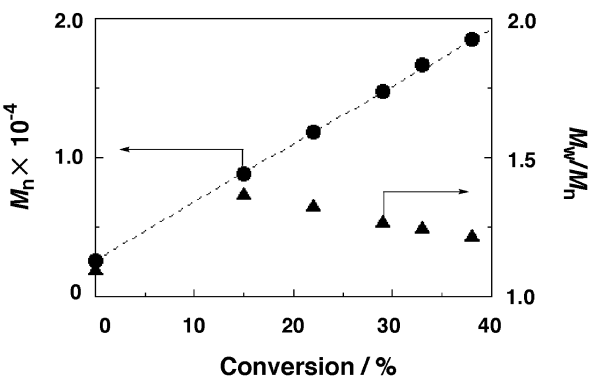


Fig. 9. The M_n vs. conversion and the M_w/M_n vs. conversion plots for the polymerization of BOSt (10 mmol) in the presence of **6** (M_n = 3300, M_w/M_n = 1.10, 110 mg) as macroinitiator in bulk at 125 °C.

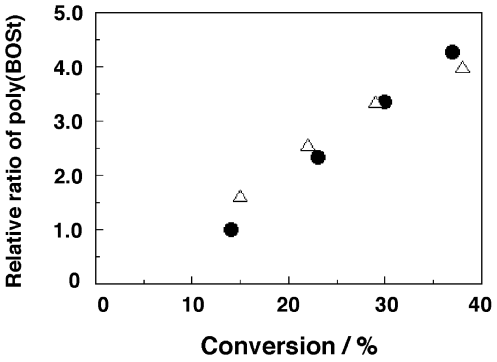


Fig. 10. Evolution of relative ratio of poly(BOSt) block, which was calculated from the integration value of ^{1}H NMR spectra, with percent conversion for (circle) the polymerization of BOSt (5 mmol) with **4** ($M_n = 11\,800$, $M_w/M_n = 1.77$, 55 mg) as macroinitiator, in bulk at 125 °C; (triangle) the polymerization of BOSt (10 mmol) in the presence of **6** ($M_n = 3300$, $M_w/M_n = 1.10$, 110 mg) as macroinitiator in bulk at 125 °C.

4. Conclusion

The poly(St)-*b*-poly(BOSt) multiblock copolymers were prepared by nitroxide mediated living free radical polymerization with poly(alkoxyamine) macroinitiator. The use of the poly(alkoxyamine) macroinitiator permits the molecular weight and polydispersity of the inserted polymer chains to be controlled while also allowing the formation of multiblock structure by the stepwise insertion of monomers. In comparison with traditional free radical macroinitiator systems, accurate control of macromolecular architecture was accomplished. The proposed synthetic strategy permits the design of novel well-defined multiblock copolymers via versatile radical polymerization.

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