Polyurethane Macroinitiator for Controlled Monomer Insertion of Styrene

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ABSTRACT: Polyurethane containing alkoxyamine units in the main chain were prepared by polyaddition of diisocyanate with TEMPO-based diol. Radical polymerization of styrene was carried out in bulk with TEMPO-based polyurethane as macroinitiator. GPC, NMR, and IR data revealed that the insertion reaction was accurately controlled to afford the segmented copolymers composed of both urethane groups and polystyrene segments. From the results of model polymerization, it is inferred that the well-defined polystyrene chains were inserted into the macroinitiator. The obtained polymers showed quite different solubility in solvents compared with the macroinitiator and styrene homopolymer. The solubility in polar solvents decreases gradually with increasing inserted polystyrene chain length.

Introduction

The desire to control macromolecular structure is a continuing focus in many academic and industrial laboratories. This interest is governed by the belief that control of macromolecular architecture will offer novel mechanical and physicochemical properties.[1] 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 macromolecular structure or the presence of a functional group.[2] The synthesis of well-defined macromolecules by living free-radical polymerization techniques has explosively grown during the past few decades.[3] One of the most widely studied approaches to “living” free-radical polymerizations involves the use of stable nitroxide free radicals such as 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO).[4] The role of the nitroxide in these systems is to mediate the reactivity of the growing polymer chain by forming a dissociative alkoxyamine chain end. Dissociation of the alkoxyamine chain end under the polymerization conditions regenerates the radical chain end, which can then add more monomer units before being capped again by the nitroxide. This thermally reversible capping reaction dramatically reduces the concentration of radical chain ends in the polymerization mixture and leads to a significant degree of “living” character.[5] A number of groups have demonstrated that alkoxyamine-based unimolecular initiators[6] gave accurate control over molecular weight, polydispersity, chain end functional groups,[7] and macromolecular architecture[8] in nitroxide-mediated living free-radical systems. Recent developments have permitted the polymerization of a wide variety of monomer families, with high degree of structural control approaching traditional anionic procedures.[9]

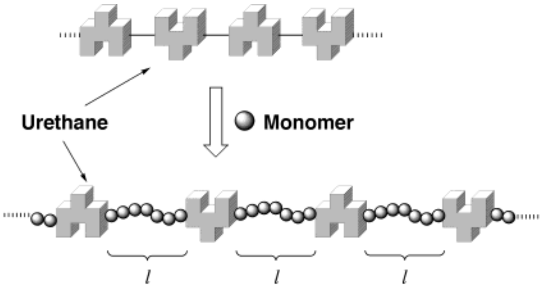

Figure 1. Schematic representation of “controlled monomer insertion method”.

The authors report herein the preparation of segmented copolymers by the use of polyurethane macroinitiator, which contain living radical polymerization initiating units in the main chain. Although the macroinitiators, which contain initiating units such as azo, peroxy, disulfide, and so on in the main, were investigated to prepare block copolymers via free-radical polymerization, the blocks obtained were polydisperse and poorly defined.[10] It is possible to insert well-defined polymer chains into the TEMPO-based polyurethane macroinitiator as illustrated in Figure 1. As a result, polar urethane groups can be dispersed homogeneously in the main chain. This method is expected as a novel synthetic pathway of segmented copolymers containing functional groups, such as urethane, ester, and so on, dispersing homogeneously in the main chain.

Experimental Part

General. 4-Hydroxy-TEMPO was prepared by the method reported previously.[11] Dibutyltin dilaurate (DBTDL), *n*-propyl isocyanate, and benzoyl peroxide (BPO) were used as received (Aldrich). Commercially obtained styrene (Wako, 99%) and hexamethylene diisocyanate (HMDI) (Aldrich, 98%) were distilled under vacuum over CaH_2 immediately prior to use. All other reagents were purchased from Kanto Chemicals or Wako Pure Chemical Industries and were used as received without purification.

Measurements. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic measurements were carried out at 25 °C with a JEOL JNM-EX400 spectrometer and Bruker DPX400 using

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tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$). IR spectra were obtained with a Perkin-Elmer Spectrum One infrared spectrometer as thin films on NaCl or neat. Monomer conversion was determined by ^1H NMR of the crude reaction mixtures (calculated from integral ratio between vinyl protons 5.74 ppm and aliphatic protons 0.8−2.2 ppm of polystyrenes). Number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersity (M_w/M_n) were estimated by gel permeation chromatography (GPC) in THF at 40 °C on a polystyrene gel column [Shodex GPC KF-804L column (300 × 8.0 mm)] 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 six standard polystyrene samples (M_n = 800−152 000; M_w/M_n = 1.03−1.10). Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel (0.25 mm thick).

2-Benzoyl-1-phenylethyl-TEMPO. Briefly, distilled styrene (300 mL, 2.62 mol), benzoyl peroxide (BPO, 4.70 g, 19.4 mmol), and 4-hydroxy-TEMPO (3.00 g, 17.4 mmol) were charged into a round-bottom flask. The mixture was incubated at 90 °C under nitrogen for 30 min. The crude product was purified by flash chromatography eluting with 2:1 hexane/chloroform (v/v) increased to chloroform. The isolated oil was purified by reprecipitation with a chloroform/hexane system and dried in vacuo to give the 2-benzoyl-1-phenylethyl-TEMPO as a white powder (1.31 g, 19% yield). ^1H NMR: δ/ppm 0.74 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.40−2.00 (m, 4H, CH_2), 3.95 (m, 1H, CH), 4.65 (dd, J = 11 Hz, 6 Hz, 2H, CH_2), 5.06 (t, J = 5 Hz, 1H, CH), 7.26−7.93 (m, aromatic 10H). ^{13}C NMR: δ/ppm 21.24, 33.95, 34.06, 34.17, 48.75, 48.80, 60.38, 60.56, 62.99, 66.59, 84.08, 127.60, 127.88, 128.06, 128.24, 129.51, 130.04, 132.83, 140.26, 166.28. FT-IR (neat, cm^{-1}): 3510, 3100−2800, 1694 (C=O), 1450, 1363, 1267, 1138, 1042, 766, 716, 699.

TEMPO-Based Diol (1). Aqueous 2 N sodium hydroxide (3.5 mL of a 2 N solution) was added to the solution of the 2-benzoyl-1-phenylethyl-TEMPO (994 mg, 2.50 mmol) in ethanol (15 mL), and the solution was heated at reflux under nitrogen for 5 h. After cooling, the solution was evaporated to dryness and partitioned between water and dichloromethane. Then the aqueous layer was extracted with dichloromethane, and the combined organic layers were dried with magnesium sulfate and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:3 ethyl acetate/ hexane (v/v). The isolated oil was purified by reprecipitation with a chloroform/hexane system and dried in vacuo to give the TEMPO-based diol **1** as a white powder (623 mg, 85% yield); mp 121−122 °C. ^1H NMR: δ/ppm 1.20 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.40−2.00 (m, 4H, CH_2), 2.08 (br, 1H, OH), 3.72 (m, 1H, CH_2), 3.97-(br, 1H, CH), 4.21 (m, 1H, CH_2), 5.25 (dd, J = 9 Hz, 7 Hz, 1H, CH), 5.43 (br, 1H, OH), 7.26−7.35 (m, aromatic 5H). ^{13}C NMR: δ/ppm 21.17, 21.46, 32.94, 34.65, 48.67, 48.86, 60.74, 61.78, 62.66, 69.06, 83.86, 126.80, 127.97, 128.23, 128.32, 138.58. FT-IR (neat, cm^{-1}): 3350, 3100−2850, 1635, 1452, 1376, 1248, 1183, 1042, 907, 761, 699, 544. Anal. Calcd for $C_{17}H_{27}NO_3$: C, 69.59; H, 9.28; N, 4.77. Found: C, 69.68; H, 9.21; N, 4.67. HRMS exact mass calculated for $[M + 1]^+$ $C_{17}H_{27}NO_3$ 294.2069; found 294.2064.

TEMPO-Based Model Compound (2). *n*-Propyl isocyanate (187 μL, 2.00 mmol) and 1 drop of DBTDL were added to the solution of the TEMPO-based diol **1** (293 mg, 1.00 mmol) in dry *N*,*N*-dimethylformamide (DMF) (1 mL). The reaction mixture was stirred at room temperature under nitrogen for 15 h. The crude product was purified by flash chromatography, eluting with 3:1 hexane/ethyl acetate (v/v). The crude product was purified by reprecipitation with a chloroform/hexane system and dried in vacuo to give the TEMPO-based model compound **2** as a white powder (460 mg, 99% yield); mp 117−119 °C. ^1H NMR: δ/ppm 0.66 (s, 3H, CH_3), 0.89 (m, 6H, CH_3), 1.12 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.46 (m, 4H, CH_2), 1.40−2.00 (m, 4H, CH_2), 3.08 (m, 4H, CH_2), 4.19 (br, 1H, CH), 4.60−5.0 (br, 5H, CH, CH_2, NH), 7.25−7.32 (m, aromatic 5H). ^{13}C NMR: δ/ppm 11.06, 11.15, 21.01, 23.05, 23.11, 33.88, 42.55, 42.58, 44.99, 45.08, 60.20, 60.55, 66.15, 66.60, 84.29, 127.61, 127.70, 127.94, 140.43, 156.16 (C=O). FT-IR (neat, cm^{-1}): 3336, 3100−2850, 1702 (C=O), 1533, 1461, 1377, 1364, 1264, 1142, 1049, 757, 700. Anal. Calcd for $C_{25}H_{41}N_3O_5$: C, 64.77; H, 8.91; N, 9.06. Found: C, 64.66; H, 8.88; N, 8.98. HRMS exact mass calculated for $[M + 1]^+$ $C_{25}H_{41}N_3O_5$ 464.3124; found 464.3123.

Model Polymerization. In a typical run, a mixture of TEMPO-based initiator **2** (23.2 mg, 0.05 mmol) and styrene (1.15 mL, 10.0 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 precipitate was purified by reprecipitation with a chloroform/methanol system and dried in vacuo to give the polymer **3** as a white powder (236 mg, 22% yield). M_n = 5700, M_w/M_n = 1.22. ^1H 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. Anal. Calcd for $C_{427}H_{443}N_3O_5$: C, 90.07; H, 7.78; N, 0.74. Found: C, 90.28; H, 7.89; N, 0.67.

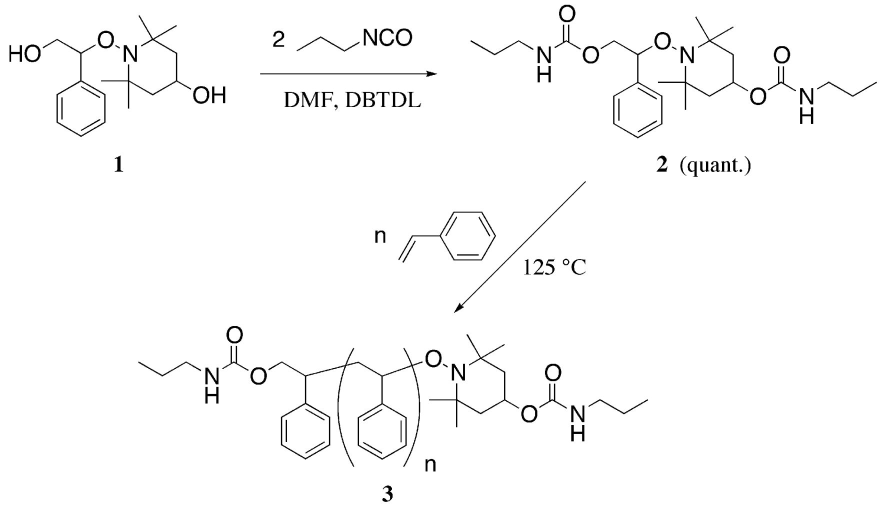
TEMPO-Based Polyurethane (4). HMDI (485 μL, 3.00 mmol) and 1 drop of DBTDL were added to the solution of TEMPO-based diol **1** (880 mg, 3.00 mmol) in dry DMF (3 mL). The reaction mixture was stirred at room temperature under nitrogen for 30 min. After the addition of methanol (1 mL), the reaction mixture was poured into water. The precipitate was purified by reprecipitation with a chloroform/hexane system and dried in vacuo to give the polymer **4** as a white powder (1.28 g, 98% yield). M_n = 2700, M_w/M_n = 1.58. ^1H NMR: δ/ppm 0.66 (br, CH_3), 1.0−2.0 (br, CH_2, CH_3), 3.11 (br, CH_2), 3.65 (s, terminal group (CH_3)), 4.19 (br, CH), 4.62 (br, CH, NH), 4.88 (br, CH_2), 7.30 (s, aromatic H). ^{13}C NMR: δ/ppm 21.10, 26.20, 29.87, 33.96, 40.73, 45.03, 48.81, 51.99, 60.28, 60.60, 63.10, 66.24, 66.74, 84.33, 127.68, 127.75, 128.00, 140.45, 156.19 (C=O), 157.07 (C=O). FT-IR (NaCl, cm^{-1}): 3333, 3100−2850, 1700 (C=O), 1533, 1456, 1377, 1363, 1258, 1143, 1048, 757, 700.

Controlled Monomer Insertion of Styrene. In a typical run, a mixture of the prepared polyurethane **4** (M_n = 2700, M_w/M_n = 1.58, 20 mg, 0.04 mmol initiating sites) and styrene (1.15 mL, 10.0 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 precipitate was purified by reprecipitation with a chloroform/methanol system and dried in vacuo to give the polymer **5** as a white powder (253 mg, 23.8% yield). M_n = 28 900, M_w/M_n = 1.84. ^1H NMR: δ/ppm 0.21 (br, CH_3), 0.38 (br, CH_3), 0.66 (br, CH_3), 0.90−2.40 (br, aliphatic H), 3.08 (br, CH_2), 3.64 (s, terminal group (CH_3)), 3.80−5.00 (br, CH, CH_2), 6.20−7.40 (br, aromatic H). ^{13}C NMR: δ/ppm 20.97, 26.18, 29.82, 33.91, 40.31, 41.0−47.0 (br), 59.22, 60.32, 125.0−130.0 (br), 144.5−146.0 (br), 156.17 (C=O), 156.36 (C=O). FT-IR (NaCl, cm^{-1}): 3100−2850, 1724 (C=O), 1601 (C=C), 1493, 1453, 1219, 1028, 907, 757, 698, 540. Anal. Calcd for $C_{2158}H_{2239}N_{17}O_{29}$: C, 89.80; H, 7.76; N, 0.83. Found: C, 90.61; H, 7.84; N, 0.51.

Results and Discussion

The model reaction of controlled monomer insertion into polyurethane was carried out according to Scheme 1. Diol **1** was treated with *n*-propyl isocyanate catalyzed by DBTDL to afford the model compound **2** quantitatively. Styrene was polymerized in bulk with **2** as an initiator. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the resulting polymers were determined by GPC with polystyrene standards. M_n and M_w/M_n are plotted as a function of conversion in Figure 2. The dashed line in Figure 2 reveals the theoretical M_n. The M_n increases with conversion, and

Scheme 1



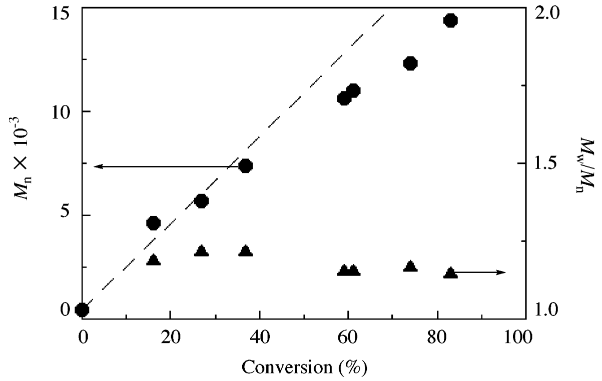


Figure 2. Dependence of molecular weights and polydispersities on conversion of the polymerization of styrene (1.15 mL, 10 mmol) with **2** (23.2 mg, 0.05 mmol) as an initiator: in bulk at 125 °C. The dashed line in the figure represents the theoretical prediction.

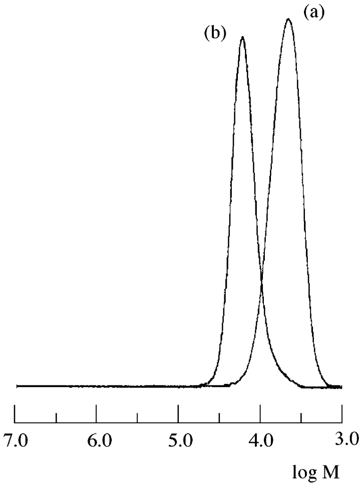


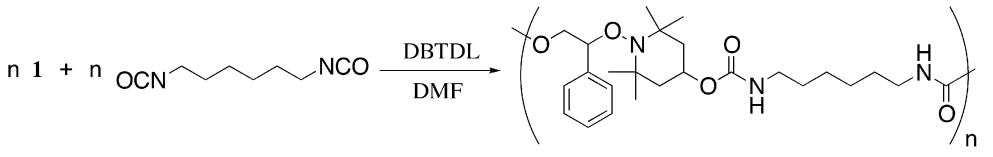
Figure 3. GPC profiles of polystyrenes obtained by the polymerization of styrene (1.15 mL, 10 mmol) with **2** (23.2 mg, 0.05 mmol) as an initiator after (a) 16% and (b) 84% conversion; in bulk at 125 °C.

the M_w/M_n value decreases slightly with conversion to about 1.15. Figure 3 shows the GPC profiles of the resulting polymers **3** obtained after 16% and 84% conversion. The polymers gave a fairly sharp unimodal GPC curve, and the molecular weight increases with increasing conversion. In the ^{1}H NMR spectrum of **3**, the resonances of the terminal groups derived from the initiator are observed at 3.0−5.0 ppm (Figure 4A,B). Integration of the terminal groups proved that the urethane groups remain quantitatively at the chain ends. The polymerization rate is faster than the reported nitroxide-mediated free-radical polymerization of styrene. The use of a TEMPO derivative, which substituted in the 4-position with a phosphonic acid group, was reported to be significantly enhanced the polymerization rate.[12] Presumably, the ability to form an intramolecular hydrogen bond in TEMPO derivative leads to a change in mediating ability. Similarly, an intramolecular hydrogen bond between the urethane bond and oxygen in this system is presumed to contribute to the rate enhancement effect.

Polyurethane **4** containing TEMPO-based initiating units in the main chain was prepared by polyaddition of the TEMPO-based diol **1** with hexamethylene diisocyanate in the presence of DBTDL as a catalyst (Scheme 2). The polyaddition proceeded after mixing the monomers at room temperature to afford the corresponding polyurethane. Although the yield of the polyurethane is indeed quantitative, the orientation of adjacent alkoxyamines is unknown. The structure of the resulting polymer **4** was confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectra. Comparison of the ^{1}H and ^{13}C NMR spectra of the polyurethane **4** with the model compound **2** revealed a number of corresponding features (Figure 4A,C). In the ^{1}H NMR spectra, the signals assigned to the diol units are observed at 0.5−2.0 and 4.0−5.0 ppm. The resonances assigned to the methylene and methyl groups of **2** appear at 0.88, 1.46, and 3.06 ppm. The corresponding methylene signals of **4** are observed as broad peaks at 1.0−1.6 and 3.12 ppm. The signals of the terminal group of **4** at 3.65 ppm are not visible in the spectrum of higher molecular weight polymer prepared after longer reaction times. In the ^{13}C NMR spectra, the signals for the generated carbonyl carbon were observed at 156 and 157 ppm. The IR spectra of **2** and **4** have absorption bands at 1702 and 1700 cm^{-1}, respectively, which are both assignable to hydrogen-bonded urethane carbonyl stretching.

Styrene was polymerized in bulk with **4** as a macroinitiator (Scheme 3, Table 1). The resulting product was precipitated into methanol to remove unreacted styrene. No polymer was recovered from the solution of methanol used for precipitation, after the solution was evaporated. Since the macroinitiator is soluble in methanol, this was

Scheme 2



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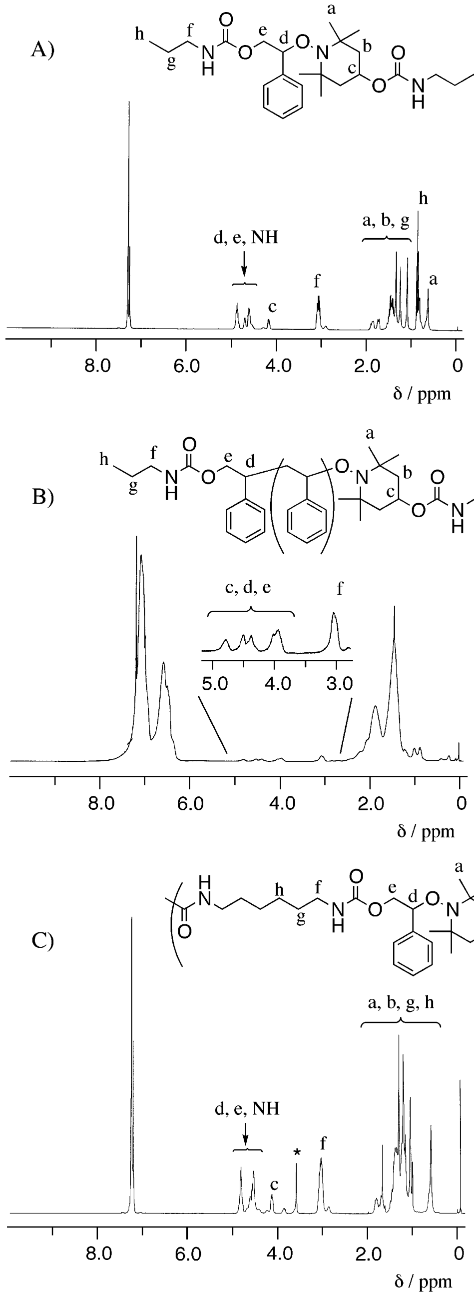

Figure 4. ^{1}H NMR spectra of (A) TEMPO-based model compound **2,** (B) polystyrene **3** (M_n = 5700, M_w/M_n = 1.22), and (C) polyurethane **4** (M_n = 2700, M_w/M_n = 1.58). Asterisks (*) mark bands of end groups.

Scheme 3

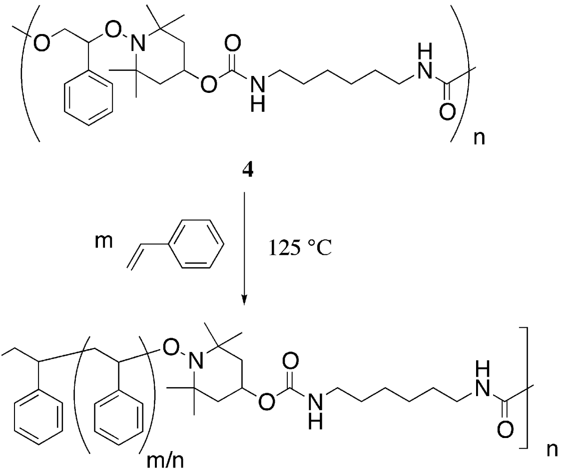

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Table 1. Experimental Conditions[a] and Polymers Synthesized by Controlled Monomer Insertion Method.

sample	$[M_0]/[I_0]$ [b]	time[c]	conv (%)[d]	theor M_n[e]	exptl M_n[f]	M_n/M_n
5a	231	0.5	9	15 300	13 200	1.70
5b	231	1.0	16	25 200	19 600	1.79
5c	231	1.5	23	35 000	27 300	1.85
5d	231	2.5	31	46 200	33 600	1.87
5e	231	3.0	40	58 800	43 100	1.73
5f	923	2.0	31	176 800	84 700	1.70
5g	462	2.0	28	81 300	46 000	1.80
5h	231	2.0	28	42 000	28 900	1.84
5i	115	2.0	31	24 500	18 400	1.80
5j	58	2.0	36	15 300	11 800	1.77

[a] Polymerization temperature is 125 °C. Polyurethane (M_n = 2700, M_w/M_n = 1.58) was used as prepolymer. [b] Feed molar ratio of the monomer $[M_0]$ to initiator $[I_0]$. [c] Polymerization time in hours. [d] Conversion determined by ^{1}H NMR. [e] M_n calculated according to theoretical $M_n = 2700 + [M_0]/[I_0] \times \text{conv} \times 104 \times 2700/462$, where 2700 and 104 are the molecular weights of macroinitiator and monomer, respectively. [f] Estimated by GPC, using linear polystyrene standards.

confirms that the polyurethane macroinitiator converted completely to initiate polymerization. Figure 5 shows the GPC profiles of the polyurethane macroinitiator **4** and postpolymers (**5a** and **5e**). GPC profiles revealed that the unimodal peak of the postpolymers shifted from that of macroinitiator toward the higher molecular weight region. On the other hand, the polydispersities of the postpolymers were 1.70−1.80, which are usually regarded as uncontrolled. The macroinitiator **4** already possesses a less than narrow polydispersity and therefore is less than ideal for giving narrow polydispersity. From the data presented, the polydispersities obtained are not much worse, i.e., 1.6 vs 1.8, than the macroinitiator. Further, it can be assumed that the migration of the nitroxide radicals during polymerization contributes to the large polydispersities. Hawker et al.[13] have reported that radical crossover reaction of nitroxide during "living" radical polymerization is a facile process. The radical migration among the main chain should cause the large polydispersities. In this case the polydispersities are apparently constant due to the large polydispersity of macroinitiator. Although the polydispersities of postpolymers were not controlled in this system, the results of averaged molecular weights still suggested that well-defined polystyrene chains were inserted into the macroinitiator. This feature can be

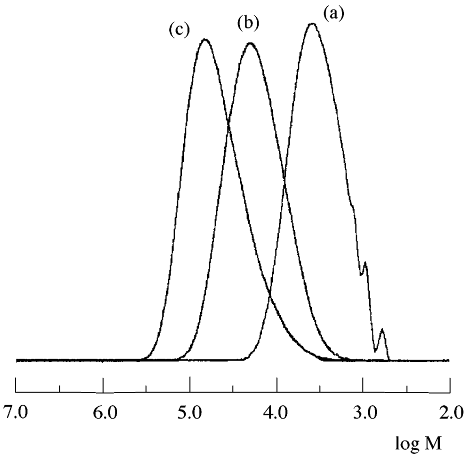

Figure 5. Comparison of the GPC profiles for (a) TEMPO-based polyurethane **4** (M_n = 2700, M_w/M_n = 1.58), (b) postpolymer **5a** (M_n = 13 200, M_w/M_n = 1.70), and (c) postpolymer **5e** (M_n = 43 100, M_w/M_n = 1.73).

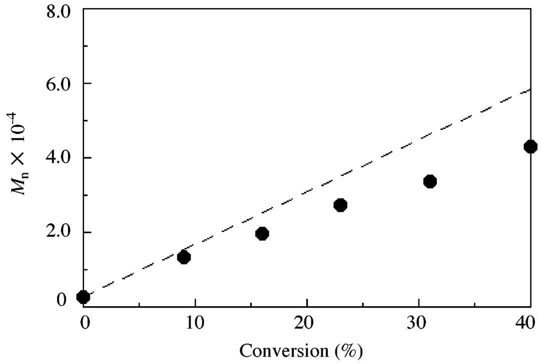

Figure 6. Evolutionof molecular weight, M_n, with conversion for the polymerization of styrene (10 mmol) in the presence of TEMPO-based polyurethane **4** (M_n = 2700, M_w/M_n = 1.58, 20 mg) as an macroinitiator; in bulk at 125 °C. The dashed line in the figure represents the theoretical prediction.

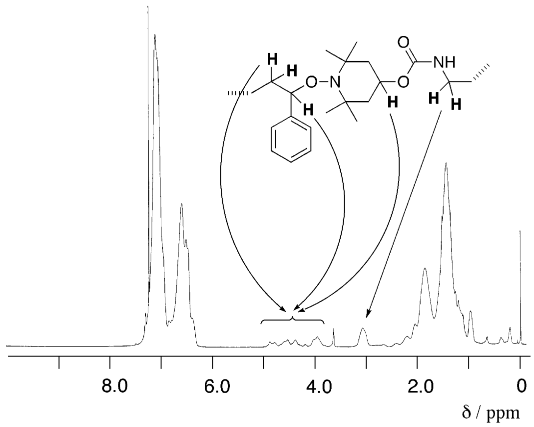

Figure 7. ^{1}H NMR spectrum of postpolymer **5a** (M_n = 13 200, M_w/M_n = 1.70).

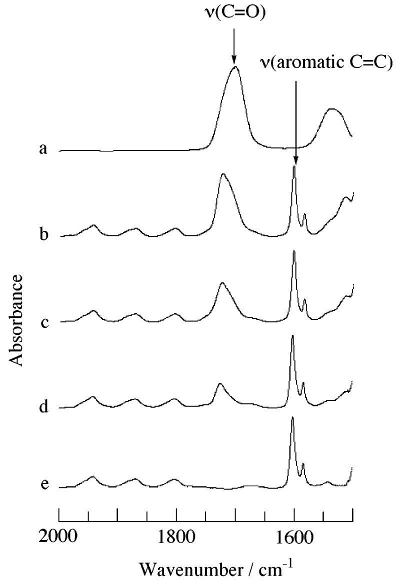

Figure 8. IR spectra of (a) TEMPO-based polyurethane **4** (M_n = 2700, M_w/M_n = 1.58), (b) postpolymer **5b** (M_n = 19 600, M_w/M_n = 1.79), (c) postpolymer **5h** (M_n = 28 900, M_w/M_n = 1.84), (d) postpolymer **5e** (M_n = 43 100, M_w/M_n = 1.73), and (e) polystyrene (M_n = 6900, M_w/M_n = 1.20) obtained from the polymerization of styrene in the presence of **1** as an initiator; in bulk at 125 °C.

appreciated by the fact that evolution of molecular weight with conversion is linear, which is fully consistent with a controlled or living free-radical polymerization (Figure 6). The dashed line in Figure 6 reveals the theoretical M_n. Because of the use of macroinitiator containing plural initiating sites, the theoretical molecular weight would not be clear. In addition, the large polydispersities also make the evaluation of the theoretical M_n difficult. Although the slight difference was observed between the theoretical and experimental molecular weight, the control of molecular weight of inserted polystyrene chains was accomplished in this system. The polymerization rate and polydispersity were independent of the "initiator" (macroinitiator) concentration (**5f**–**5j**), which agrees with previous works of nitroxide-mediated free-radical polymerization.[14] As shown in Figure 7, the ^{1}H NMR spectrum of the postpolymer **5a** indicates the resonance for the macroinitiator at 3.0–5.0 ppm. The ^{13}C NMR and IR spectra show signals corresponding to the macroinitiator. Comparison of elemental analysis between postpolymers and polystyrenes, which prepared with model compound as initiator, indicates that the postpolymers contain the plural urethane groups in the main chain.

The IR spectra of the polymers in Figure 8 exhibit an absorption corresponding to the stretching vibration of carbonyl groups (C=O). The carbonyl region in the IR spectra is most applicable to the analysis of the state of hydrogen-bonding properties.[15] For the prepolymer, the absorption associated with the hydrogen-bonded urethane carbonyl groups is observed at 1700 cm^{-1}. After the insertion of polystyrene chains, the absorption corresponding to the carbonyl groups shifted to higher wavenumber region than that of prepolymer. This suggests that the dispersion of urethane groups was achieved as a result of the insertion of polystyrene chains to be observed as the free carbonyl stretching. The absorbance ratio of ν(aromatic C=C)/ν(C=O) increased with increasing inserted chain length. These spectral changes were apparently due to the insertion of polystyrene chain.

The prepared polymers should have quite different solubilities in different solvents compared to the prepolymer and conventional styrene homopolymer. Table 2 shows the solubilities of polymers in various solvents. The prepolymer was soluble in poor solvents for polystyrene, such as methanol, acetone, and dimethyl sulfoxide (DMSO). The hydrophobicity of the polymer increased with insertion of polystyrene chain. Particularly, the solubility of the prepared polymers in acetone

Table 2. Qualitative and Quantitative Solubilities of Polymers Synthesized by Controlled Monomer Insertion Method[a]

sample[b]	methanol	toluene	acetone	DMSO
4	+++	−	+++	+++
5b	−	+++	++	+
5c	−	+++	+	−
5e	−	+++	+	−
polystyrene[c]	−	+++	−	−

[a] The experiment was carried out at room temperature. The amounts of polymer and solvent were 10 mg and 1.0 mL, respectively. Symbols: +++ = soluble, ++ = slightly soluble, + = cloudy, and − = insoluble. [b] See Table 1. [c] M_n = 16 300, M_w/M_n = 1.17, prepared by polymerization of styrene in the presence of **2** as an initiator: in bulk at 125 °C.

and DMSO decreased gradually with increasing polystyrene chain length. Further, despite the molecular weight being higher than that of polystyrene, **5b** is soluble in DMSO compared to polystyrene.

Conclusion

From the results obtained above, it is apparent that the controlled insertion of styrene into the TEMPO-based polyurethane backbone proceeded with a living mechanism to give segmented copolymers dispersing urethane groups homogeneously in the main chain. The use of living free-radical polymerization macroinitiator makes possible to control molecular weight of inserted polymer chain. The present polymerization method permits novel segmented copolymers to be readily prepared in the minimum number of steps under synthetically nondemanding conditions.

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