Macromolecules **2007,** *40,* 1429−1434

Thermal Reorganization and Molecular Weight Control of Dynamic Covalent Polymers Containing Alkoxyamines in Their Main Chains

Hideyuki Otsuka,* Koichiro Aotani, Yuji Higaki, Yoshifumi Amamoto, and Atsushi Takahara*

Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received July 24, 2006; Revised Manuscript Received December 31, 2006

ABSTRACT: Dynamic covalent polymers incorporating thermally reversible alkoxyamine units in the main chain were synthesized, and their thermal structural reorganization behavior was systematically investigated. The model reaction using alkoxyamine derivatives clearly revealed that the exchange reaction between the derivatives occurred upon heating over 60 °C, and the degree of exchange strongly depended on the reaction temperature, time, and concentration. Polycondensation from alkoxyamine-based diol and adipoyl chloride at room temperature successfully afforded the corresponding poly(alkoxyamine ester) without any decomposition of the alkoxyamine units. Their molecular weight can be readily estimated by conventional gel permeation chromatography (GPC). In contrast, their thermal reorganization behavior was completely different from common polymers; for instance, the peak in the GPC profiles of the fractionated polymer with a narrow molecular weight distribution broadened to 1.6−2.0 upon heating. Furthermore, the mixture of poly(alkoxyamine)s with different molecular weights reorganized to form the poly(alkoxyamine) with an average molecular weight that showed as a unimodal peak in the GPC profile. However, NMR spectroscopy measured after heating did not reveal any change in the primary chemical structure of the repeating unit. The thermal reorganization in the presence of excess N−O stable free radical resulted in the scission of the main chain due to the chain transfer reaction.

Introduction

Reorganizable polymers consist of monomer units reversibly connected by covalent and/or noncovalent bonds. Their primary structures and properties can be changed and tuned even after polymerization; therefore, they have the potential to be applied for designing intelligent materials, chemical recycling, polymer hybridization, and so on. However, most of conventional polymers are structurally irreversible because their monomer units are connected by strong and fixed covalent bonds. On the other hand, "supramolecular polymers"[1−3] are representative successful examples of reorganizable polymers. They are constructed by secondary noncovalent interactions such as hydrogen bonds. Lehn et al. reported the first example of supramolecular main-chain polymers;[1] since then, many examples of supramolecular polymers have been reported. For instance, Meijer et al. developed the supramolecular main-chain polymers with a very high molecular weight by using a quadruple hydrogen-bonding system.[3] Supramolecular polymers are not very stable, particularly in solution. Moreover, their superstructures and their molecular weights are strongly dependent on concentration and solvent polarity. Therefore, it is often difficult to characterize and investigate them further.

Rowan et al.[4] introduced the concept of dynamic covalent chemistry, which can offer the possibility of "doing supramolecular chemistry" at the level of covalent bonds. If the main chain of a polymer consists of dynamic covalent bonds[5−7] instead of noncovalent interactions, it can be expected to behave as a reorganizable polymer[8] similar to the behavior of supramolecular polymers. However, in contrast to supramolecular polymers, polymers with dynamic covalent bonds in the main chain are stable under normal conditions and even under high dilution concentration conditions (Figure 1). Nevertheless, once they are exposed to external stimuli such as heating, they can be reorganized to the proper form that reflects the chemical and physical environmental conditions.

Previously, we have preliminarily reported the radical exchange reaction of alkoxyamines derivatives,[9] which have been frequently used as unimolecular initiators for nitroxide-mediated controlled radical polymerization,[10] and also reported the possibility of dynamic covalent polymers by introducing thermally exchangeable covalent bonds into the main chain. We also applied this chemistry to the scrambling process of the different kinds of dynamic covalent polymers,[11] reversible formation of graft copolymer and cross-linked polymer,[12] and radical ring-crossover polymerization of macrocyclic alkoxyamine.[13] In this paper, from the viewpoint of basic mechanism of radical exchange reaction of alkoxyamine-based dynamic covalent polymers, thermal reorganization behavior of alkoxyamine-based dynamic covalent polymers was systematically investigated.

Experimental Section

General. The synthesis of alkoxyamine derivatives **1**[14] and **4**[15] has been reported. Compounds **2** and **3** were synthesized according to the method reported previously.[16] Adipoyl chloride (99%) was purchased from Wako Pure Chemical Industries and distilled over P_2O_5 under vacuum. Dichloromethane (99%), anisole (99+%), and pyridine (98%) were purchased from Wako Pure Chemical Industries and distilled over CaH_2. All the other reagents were purchased from commercial sources and were used without further purification.

Measurements. ^1H and ^{13}C NMR spectroscopic measurements were carried out with a JEOL JNM-EX400 spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$). IR spectra were obtained using a Perkin-Elmer Spectrum One infrared spectrometer on thin films on NaCl or neat. Analytical thin layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel (0.25 mm thick). High-

---

* Corresponding authors: e-mail otsuka@ms.ifoc.kyushu-u.ac.jp, takahara@cstf.kyushu-u.ac.jp; Tel +81-92-642-2318; Fax +81-92-642-2715.

10.1021/ma061667u CCC: $37.00

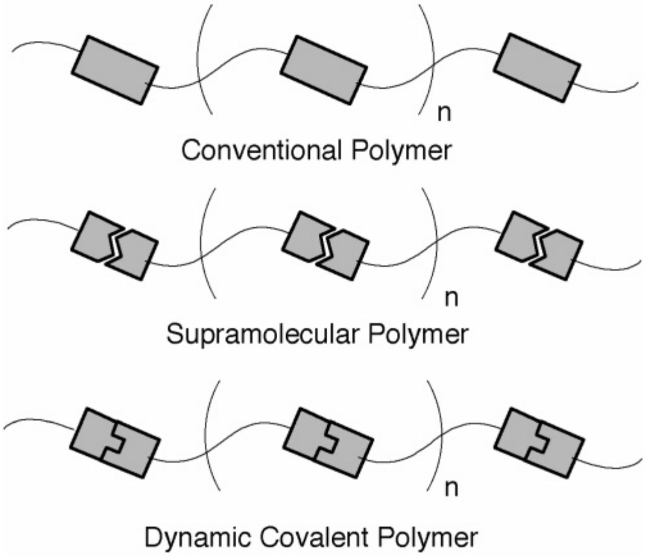


Figure 1. Schematic representations of conventional polymer, supramolecular polymer, and dynamic covalent polymer: connected by usual covalent bonds, noncovalent bonds, and dynamic covalent bonds, respectively.

performance liquid chromatography (HPLC) analyses were performed on a Shimadzu LC-10AT pump equipped with an SPD-10AV variable wavelength detector at a flow rate of 1.0 mL min^{-1} at room temperature and monitored at 254 nm. The number- and weight-average molecular weights (M_n and M_w, respectively) and the molecular weight distribution (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a TOSOH system equipped with a refractive index (RI) detector using THF as eluent at a flow rate of 0.8 mL min^{-1}, calibrated with polystyrene standards.

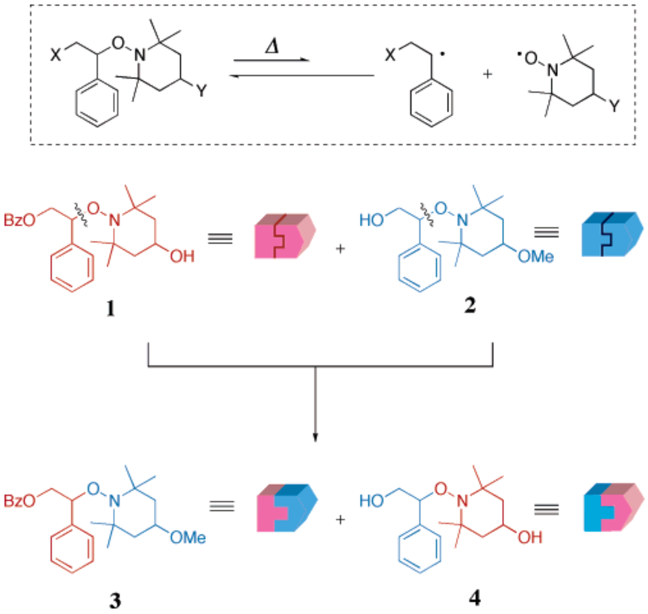
Model Radical Exchange Reaction. Equimolar quantities of alkoxyamine derivatives **1** (79 mg, 0.27 mmol) and **2** (107 mg, 0.27 mmol) were mixed in anisole as a 0.18 mol L^{-1} solution. The solution was charged in a glass tube, sealed under vacuum, and then heated at 100 °C. The reaction was followed by HPLC (eluent: water/acetonitrile = 1/3 v/v).

Poly(alkoxyamine ester). Adipoyl chloride (1.45 mL, 10 mmol) was added to the solution of alkoxyamine-based diol **4** (2.93 g, 10 mmol) and pyridine (1.62 mL, 20 mmol) in anhydrous dichloromethane (10 mL), and the solution was stirred at the room temperature under nitrogen. After 24 h, the reaction was quenched by the addition of methanol, and the solution was stirred at room temperature for 30 min. The solution was then evaporated to dryness, and the residue was partitioned between water and dichloromethane. The organic layer was dried with magnesium sulfate, evaporated to dryness, and dried in vacuo. The crude polymer was diluted with chloroform, and the solution was poured into hexane. The precipitate was collected by vacuum filtration and dried in vacuo to yield polyester **5** as a white powder (4.23 g, 89% yield). M_n = 20 700, M_w/M_n = 1.87. ^{1}H NMR: δ/ppm 0.66 (s, 3H), 1.11 (s, 3H), 1.27 (s, 3H), 1.35 (s, 3H), 1.41−1.85 (m, 8H), 2.1−2.3 (m, 4H), 4.25 (dd, J = 5 Hz, 11 Hz, 1H), 4.89 (t, J = 6 Hz, 1H), 7.24−7.32 (m, aromatic). ^{13}C NMR: δ/ppm 21.8, 24.02, 24.32, 30.31, 33.69, 33.91, 34.11, 44.59, 44.69, 60.29, 60.61, 65.81, 66.45, 84.08, 127.73, 127.83, 128.07, 140.07, 172.85, 172.90. FT-IR (NaCl, cm^{-1}): 2974, 1735, 1467, 1364, 1175, 1002, 700.

Thermal Reorganization of Fractionated Poly(alkoxyamine). Fractionated poly(alkoxyamine ester) **5** [M_n = 12 000, M_w/M_n = 1.21] was heated in anisole at 100 °C under degassed conditions, and GPC and NMR measurements of the resulting polymers were carried out.

Thermal Reorganization of the Mixture of Poly(alkoxyamine) with Different Molecular Weights. *Typical Example:* Fractionated poly(alkoxyamine ester)s (M_n = 12 000, M_w/M_n = 1.21 as a high molecular weight sample and M_n = 4300, M_w/M_n = 1.17 as a low molecular weight sample) were dissolved in anisole (concentration of each alkoxyamine unit: 0.02 M), sealed, and heated at 100 °C for 12 h. GPC and NMR measurements of the resulting polymers were performed.

Scheme 1



Thermal Reorganization of Poly(alkoxyamine) in the Presence of Stable Radical. Fractionated poly(alkoxyamine ester) **5** [M_n = 11 800, M_w/M_n = 1.21] was heated in the presence of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxy (**6**) free radical in anisole at 30 or 100 °C under degassed conditions, and GPC measurements of the resulting polymers and oligomers were carried out.

Results and Discussion

Model Radical Exchange Reaction. Alkoxyamine derivatives were chosen as candidates for fundamental units. In the case of nitroxide-mediated controlled radical polymerization, the key step in the currently accepted mechanism of this type of polymerization is the reversible capping of the polymer chain end by the stable nitroxide free radical.[17] By using alkoxyamine derivatives as initiators, monomers such as styrene derivatives are polymerized. Interestingly, in the case of the radical polymerization of styrene with unimolecular alkoxyamine initiators, Hawker and co-workers reported that the exchange of the mediating nitroxide moieties occurred at the terminal of growing polymer chains during polymerization.[15] Furthermore, an exchange reaction with an excess of other nitroxide derivatives at the terminal group of the polystyrene prepared by nitroxide-mediated radical polymerization was also reported.[18] Even though there is no styrene in the system and the system is simply heated, the alkoxyamine derivatives can be expected to dissociate and associate reversibly upon heating because the dissociation energy of C−ON bond in the alkoxyamine was reported to be ~30 kcal/mol.[19]

The reversible formation and dissociation of C−ON bond in alkoxyamines can be monitored as an exchange reaction between alkoxyamine derivatives. In order to investigate the degree of exchange between alkoxyamine units, a model exchange reaction was carried out. Alkoxyamine derivatives **1**−**4** were prepared, and the model exchange reaction was performed as illustrated in Scheme 1. Equimolar quantities of **1** and **2** were mixed in anisole as a 0.18 mol L^{-1} solution, and the solution was sealed under vacuum and heated at 100 °C. The reaction was followed by HPLC; Figure 2 shows the HPLC chromato-

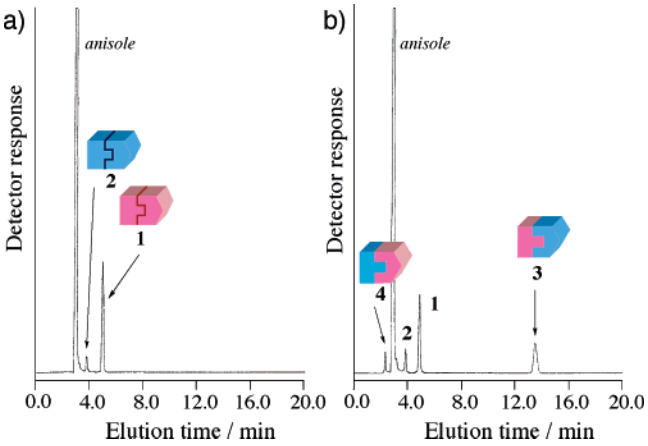


Figure 2. HPLC chromatograms of a mixture (a 1.8 mol L^{-1} anisole solution) of alkoxyamines **1** and **2**: (a) before and (b) after heating (column: JASCO CrestPak C18S; flow rate: 1.0 mL min^{-1}; eluent: H_2O-CH_3CN = 1/3 v/v).

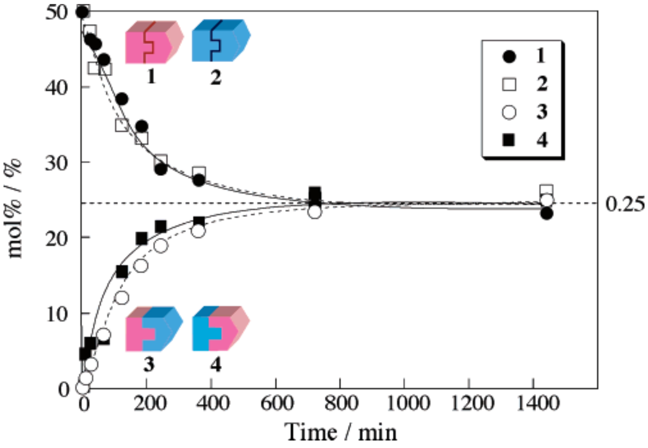


Figure 3. Time-coursed molar percentage of alkoxyamines starting from a 1.8 mol L^{-1} anisole solution of alkoxyamines **1** and **2** at 100 °C.

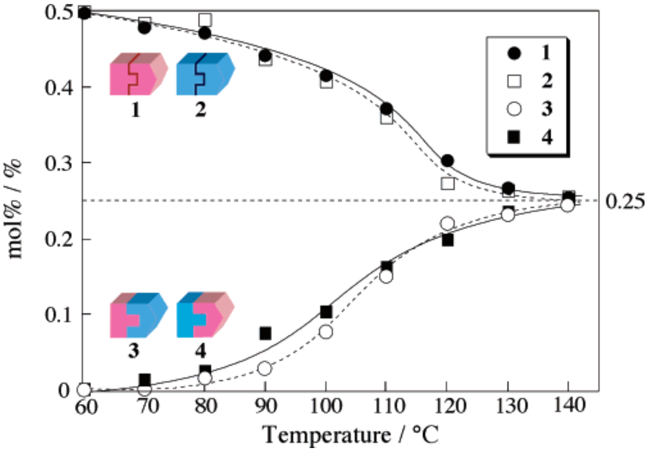
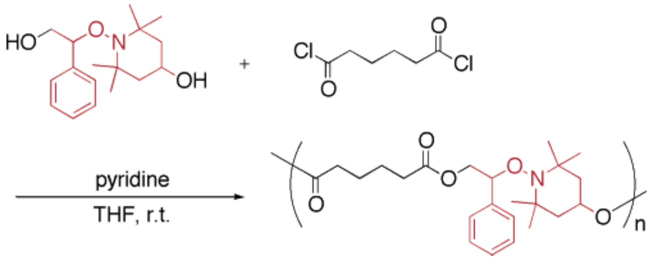


Figure 4. Temperature-dependent molar percentage of alkoxyamines starting from a 1.8 mol L^{-1} anisole solution of alkoxyamines **1** and **2** for 2 h.

Scheme 2



grams of the mixture of alkoxyamines **1** and **2** before and after heating for 2 h at 100 °C. After heating, two additional peaks, which were attributable to **3** and **4**, appeared. Very importantly, apart from alkoxyamines and anisole, no peak corresponding to the coupling reaction of styryl radical derivatives was detected during the crossover reaction. Thin layer chromatographic analysis also supported the HPLC results, thereby implying that the reaction was rather clean despite the occurrence of a thermal radical exchange reaction and was governed by the persistent radical effect.[20]

The proportion of compounds **1**−**4** was estimated from the normalized peak areas in the HPLC analysis. As shown in Figure 3, the molar percentages of compounds **1**−**4** attained equilibrium at 100 °C after 12 h. At equilibrium, the molar percentages are nearly identical in the four different compounds. Furthermore, the reaction rate strongly depended on the reaction temperature, as shown in Figure 4, which revealed that the crossover reaction occurred above 60 °C. The higher the reaction temperature, the faster the molar ratio attained equilibrium. For instance, at 140 °C, the reaction yielded four equimolar alkoxyamine derivatives within 2 h.

Since the exchange reaction proceeds by an intermolecular process, it should be influenced by the reaction concentration and the initiator concentration with respect to one another. In order to investigate the concentration effect, the model reaction was carried out using a 3.6 × 10^{-3} mol L^{-1} solution. The reaction was slower but almost reached equilibrium after 24 h (26.1% and 26.2% for **1** and **2**, respectively, and 23.7% and 23.8% for **3** and **4**, respectively). Few effects were observed in the range 0.18−0.018 mol L^{-1}. From these model experiments, it was inferred that the exchange reaction of alkoxyamine is a promising candidate for the fundamental units in dynamic covalent polymers.

Synthesis and Thermal Reorganization of Poly(alkoxyamine). Poly(alkoxyamine) was synthesized by polycondensation from diol **4** and adipoyl chloride in CH_2Cl_2 in the presence of pyridine at room temperature (Scheme 2). The chemical structure of the obtained poly(alkoxyamine) was confirmed by IR and NMR measurements. In the IR spectrum, the absorption for ester carbonyl group was observed at 1700 cm^{-1}; however, no absorption peak attributable to the OH group was detected. ^1H and ^{13}C NMR spectra revealed that the polymer retained the alkoxyamine units in its skeleton (Figure 5). From all above-mentioned results, it may be inferred that no decomposition of alkoxyamine units occurred during the polycondensation. Since alkoxyamine moieties are stable at room temperature, the GPC measurement of the polymer successfully yielded the number-average molecular weight (M_n) and weight-average molecular weight (M_w). Under the experimental GPC conditions of 40 °C, no peak tailing or concentration effect was observed that would otherwise imply decomposition of the polymer. In reality, the obtained polymer was formed as a white solid and could also be formed as a transparent film by the slow evaporation of chloroform solution. Recently, we also reported the synthesis of poly(alkoxyamine) by ring-crossover polymerization of macrocyclic polyalkoxyamine.[13] Although the basic chemical compositions of the poly(alkoxyamine)s prepared by polycondensation and ring-crossover polymerization are identical, they are structurally different. For example, the signals at 2.1−2.3 ppm for $-COCH_2CH_2CH_2CH_2CO-$ protons show a different splitting pattern. This is probably due to the difference

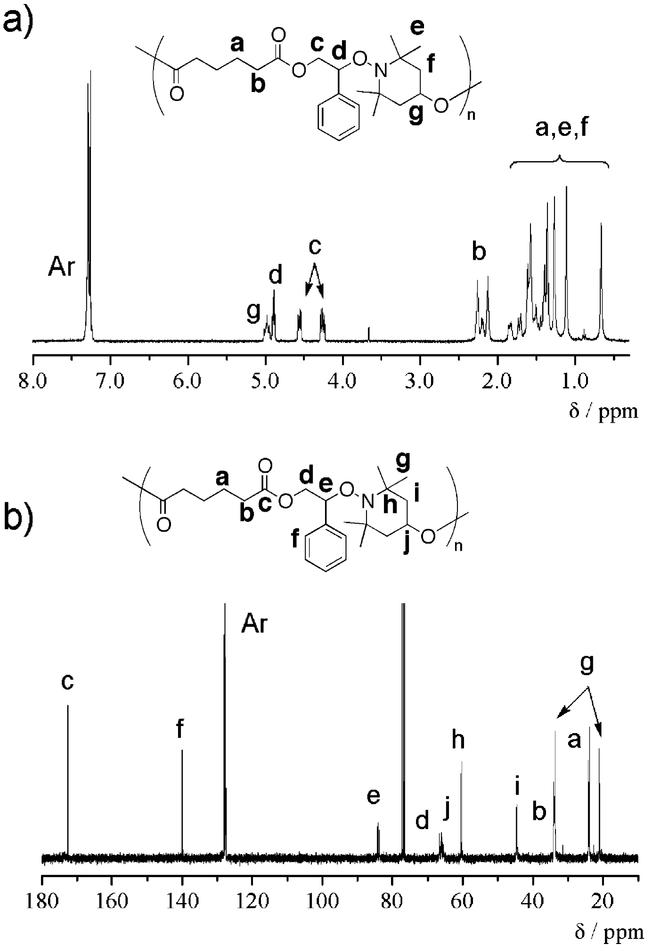


Figure 5. ^{1}H and ^{13}C NMR spectra of poly(alkoxyamine) **5** prepared by condensation from **4** and adipoyl chloride.

of the degree of ordered structure (head to head/head to tail) for the alkoxyamine units in polymer skeletons.

The treatment of the poly(alkoxyamine) with ester groups at room temperature is unremarkable; a type of polyester is formed by this treatment. However, the thermal reaction behavior is completely different from common polymers. In order to investigate the thermal reaction behavior of the poly(alkoxyamine), the polymer was fractionated by a preparative HPLC. The fractionated poly(alkoxyamine) [$M_n = 12\,000$, $M_w/M_n = 1.21$] was heated in anisole at 100 °C under degassed conditions, and GPC and NMR measurements of the reacted polymer were carried out. Although the NMR spectrum did not change after heating for 24 h, the GPC profiles drastically changed upon heating. Figure 6a shows the GPC profiles of the poly(alkoxyamine) before and after heating (0.5 and 6 h). The molecular weight distribution broadened with no significant change in the peak tops as the reaction proceeded. Since the generated polymer was observed in both the higher and lower molecular weight regions as compared with the parent peak, the occurrence of some crossover reaction between the main chains of the poly(alkoxyamine) can be expected. Under the present condition, no transesterification is expected to occur; therefore, the phenomenon could undoubtedly be attributed to the radical crossover reaction of the alkoxyamine units between the main chains (Scheme 3). Figure 6b shows the M_n vs time and the M_w/M_n vs time plots for the thermal reaction behavior of the poly(alkoxyamine) in anisole at 100 °C. The reorganization appeared to attain equilibrium after 6−12 h, and no further change in M_n and M_w/M_n was observed.

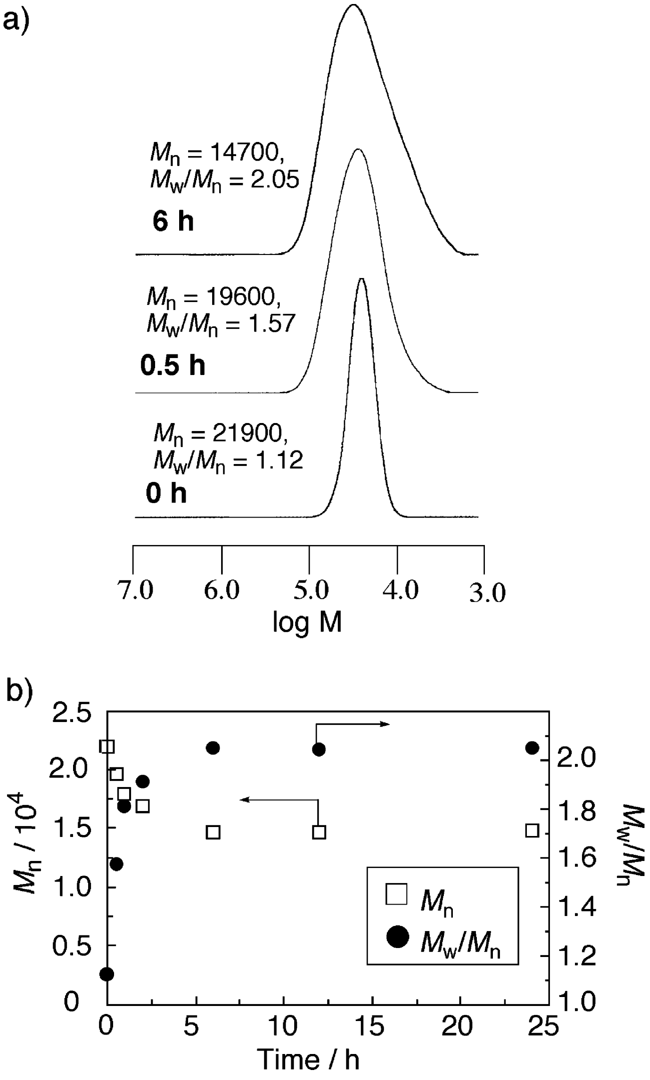
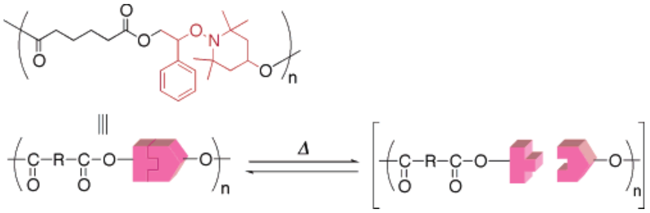


Figure 6. (a) GPC profiles of poly(alkoxyamine) **5** [$M_n = 12\,000$, $M_w/M_n = 1.21$] before and after heating in anisole at 100 °C (0.5 and 6 h). (b) M_n vs time and M_w/M_n vs time plots for the thermal reaction behavior of the poly(alkoxyamine) in anisole at 100 °C.

Scheme 3



Molecular Weight Control of Poly(alkoxyamine) by Reorganization. By the fractionation of polyester **5** using preparative HPLC, two polymers—**5a** ($M_n = 4300$, $M_w/M_n = 1.17$) and **5b** ($M_n = 12\,000$, $M_w/M_n = 1.21$)—were successfully isolated. The mixture of polymers **5a** and **5b** showed two apparent peaks in the GPC profile, as shown in Figure 7a. Equal quantities of **5a** and **5b** were mixed in anisole (total concentration of alkoxyamine: 0.04 M), sealed, and heated at 100 °C for 12 h. As the reaction proceeded, the peaks derived from **5a** and **5b** clearly fused into a unimodal peak. Figure 7b indicates the GPC profiles of the polymer **5c** ($M_n = 5600$, $M_w/M_n = 1.86$) after the exchange reaction.

Table 1 shows the change in molecular weight during the radical crossover reaction between fractionated narrowly dispersed poly(alkoxyamines)s with various molecular weights. In

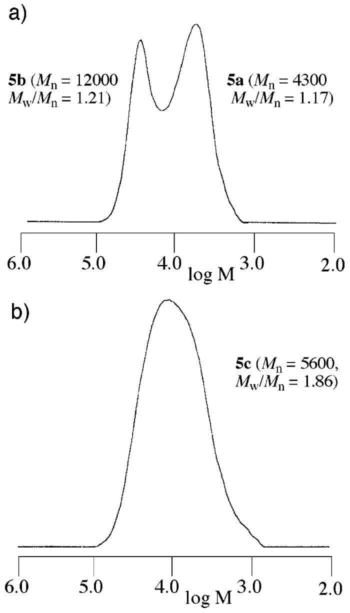


Figure 7. (a) GPC profiles (THF, polystyrene standard) of the mixture of polymers **5a** (M_n = 4300, M_w/M_n = 1.17) and **5b** (M_n = 12 000, M_w/M_n = 1.21) before heating and (b) the resultant polymer **5c** (M_n = 5600, M_w/M_n = 1.86) after heating in anisole (total concentration of alkoxyamine unit: 0.04 M) at 100 °C.

Table 1. Change in Molecular Weight and Molecular Weight Distribution in Radical Crossover Reaction between Poly(alkoxyamine)s[a]

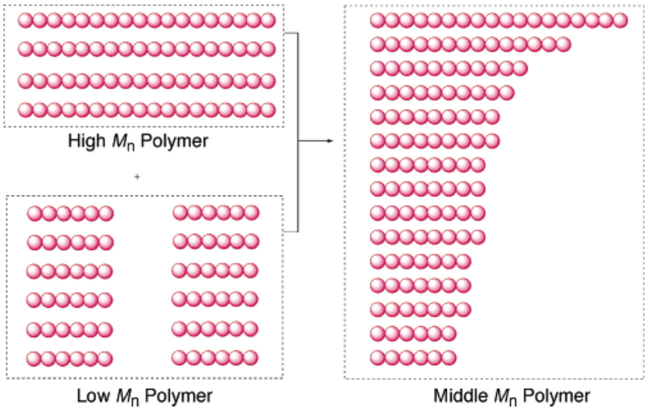
	prepolymer (high M_n)		prepolymer (low M_n)		postpolymer	
entry	M_n	M_w/M_n	M_n	M_w/M_n	M_n	M_w/M_n
1	17 400	1.37	8200	1.18	9800	1.88
2	17 400	1.37	6300	1.31	8400	1.77
3	17 400	1.37	4300	1.17	6000	1.82
4	12 000	1.21	6300	1.31	6900	1.71
5	12 000	1.21	4300	1.17	5600	1.86

[a] Equal quantities of polymers with different molecular weights were mixed, and the total concentration of alkoxyamine units was 0.04 mol L^{-1}. Macromolecular crossover reaction was carried out at 100 °C for 12 h.

all cases, the M_n values of postpolymers were midway between the high and low M_n values of prepolymers. The M_w/M_n values of the postpolymers were 1.7−1.9, whereas those for each prepolymer were 1.1−1.4. Although there exists a possibility of forming ring compounds, the end-group analyses by NMR measurements of the prepolymers and the obtained polymer under this concentration condition yielded no significant information on whether or not any cyclic compounds were formed.[13,21] These findings strongly suggested that the obtained poly(alkoxyamine) is a thermally reorganizable polymer and, further, that it can dissociate and associate reversibly in the main-chain-like supramolecular polymers when triggered by an external stimuli such as heating. The polymers with various molecular weights were combinatorially produced by reorganization between high- and low-M_n polymers (Scheme 4).

Chain Transfer Reaction of Dynamic Covalent Polymer. As described above, alkoxyamine-based dynamic covalent polymers are thermally reorganizable due to the radical crossover between the main chains. Here, the addition of nitroxide stable free radical in the reorganization process can be expected to cause the scission of the polymer main chain because of the competitive chain transfer reaction of added radical to the generated styryl radicals. Stable free radical 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxy (**6**) was employed for this experiment.

Scheme 4



Scheme 5

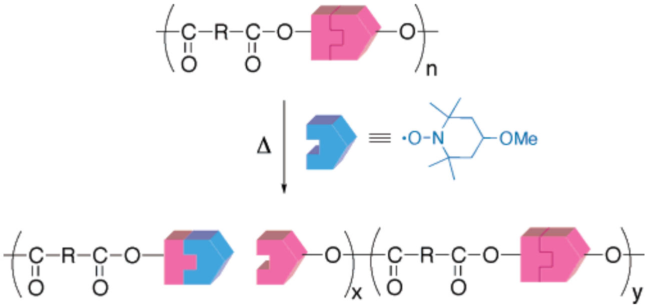


Table 2. Chain Transfer Reaction of Dynamic Covalent Polymer 5d (M_n = 11 800, M_w/M_n = 1.21) by 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl Free Radical (6)[a]

entry	added **6** (equiv/unit)	time/h	temp/°C	M_n	M_w/M_n
1	1.0	1.0	30	11800	1.21
2	1.0	0.5	100	8800	1.49
3	1.0	1.0	100	5100	1.45
4	2.0	1.0	100	4500	1.38
5	5.0	1.0	100	4000	1.34
6	1.0	3.0	100	1700	1.88
7	1.0	6.0	100	1200	1.71

[a] Concentration of alkoxyamine units was 0.04 mol L^{-1}.

Polymer **5d** (M_n = 11 800, M_w/M_n = 1.21) was heated in the presence of the stable free radical **6** in anisole at 100 °C, as shown in Scheme 5. Table 2 summarizes the results of the chain transfer reaction of dynamic covalent polymer **5d** by free radical **6**. As shown in Table 2, M_n of polymer **5d** did not change at 30 °C. In contrast, at 100 °C and in the presence of stable free radical **6**, M_n of **5d** decreased drastically. Moreover, even in the presence of 1 equiv of **6**, M_n of **5d** decreased to 1200 after 6 h. These results strongly suggest that the macromolecular exchange reaction in poly(alkoxyamine)s proceeded by a radical process and occurred only at a high temperature.

Conclusions

In conclusion, the present study has demonstrated the possibility of synthesizing thermally reversible dynamic covalent polymers by incorporating alkoxyamine units as reversible covalent bonds into the main chain. Although poly(alkoxyamine)s behave as common polymers at room temperature, their primary structures can be reorganized by simple heating. This is an innovative methodology for tuning the molecular weight of polymers by a combinatorial approach.

Acknowledgment. This research was supported by the Industrial Technology Research Grant Program in ’05 of the

New Energy and Industrial Technology Development Organization (NEDO) of Japan. Financial supports from Mazda Foundation and Sekisui Chemical Grant Program for Research Projects are also acknowledged.

References and Notes

(1) (a) Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990**, *2*, 254−257. (b) Lehn, J.-M. *Macromol. Chem., Macromol. Symp.* **1993**, *6*, 1−17.

(2) (a) Bladon, P.; Griffin, A. C. *Macromolecules* **1993**, *26*, 6604−6610. (b) Ciferri, A. *Supramolecular Polymers*; Marcel Dekker: New York, 2000. (c) For a recent review see: Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097.

(3) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601−1604.

(4) Rowan, S. J.; Cantrill, S. J.; Cousin, G. R. L.; Sanders, J. K. M; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898−952.

(5) (a) Furusho, Y.; Oku, T.; Hasegawa, T.; Tsuboi, A.; Kihara, N.; Takata, T. *Chem.—Eur. J.* **2003**, *9*, 2895−2903. (b) Oku, T.; Furusho, Y.; Takata, T. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 119−123. (c) Oku, T.; Furusho, Y.; Takata, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 966−969. (d) Otto, S.; Furlan, R. L. E.; Sanders, J. K. M. *J. Am. Chem. Soc.* **2000**, *122*, 12063−12064. (e) Otto, S.; Furlan, R. L. E.; Sanders, J. K. M. *Science* **2002**, *297*, 590−593.

(6) (a) Nishinaga, T.; Tanatani, A.; Oh, K.; Moore, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 5934−5935. (b) Oh, K.; Jeong, K.-S.; Moore, J. S. *J. Org. Chem.* **2003**, *68*, 8397−8403. (c) Glink, P. T.; Oliva, A. I.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1870−1875.

(7) (a) Furlan, R. L. E.; Cousins, G. R. L.; Sanders, J. K. M. *Chem. Commun.* **2000**, 1761−1762. (b) Skene, W. G.; Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 8270−8275. (c) Kolomiets, E.; Lehn, J.-M. *Chem. Commun.* **2005**, 1519−1521. (d) Ono, T.; Nobori, T.; Lehn, J.-M. *Chem. Commun.* **2005**, 1522−1524. (e) Kamplain, J. W.; Bielawski; C. W. *Chem. Commun.* **2006**, 1727−1729.

(8) There have been some examples of thermally reversible polymers, but most of them showed reversibility between polymers and monomers or linear polymers and cross-linked polymers: (a) Salamone, J. C.; Chung, Y.; Clough, S. B.; Watterson, A. C. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2923−2939. (b) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1990**, *23*, 2636−2641. (c) Ilhan, F.; Rotello, V. M. *J. Org. Chem.* **1999**, *64*, 1455−1458. (d) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698−1702.

(9) (a) Otsuka, H.; Aotani, K.; Higaki, Y.; Takahara, A. *Chem. Commun.* **2002**, 2838−2839.

(10) (a) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185−11186. (b) For reviews see: Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(11) Otsuka, H.; Aotani, K.; Higaki, Y.; Takahara, A. *J. Am. Chem. Soc.* **2003**, *125*, 4064−4065.

(12) (a) Higaki, Y.; Otsuka, H.; Takahara, A. *Macromolecules* **2004**, *37*, 1696−1701. (b) Higaki, Y.; Otsuka, H.; Takahara, A. *Macromolecules* **2006**, *39*, 2121−2125.

(13) Yamaguchi, G.; Higaki, Y.; Otsuka, H.; Takahara, A. *Macromolecules* **2005**, *38*, 6316−6320.

(14) Higaki, Y.; Otsuka, H.; Endo, T.; Takahara, A. *Macromolecules* **2002**, *36*, 1494−1499.

(15) Hawker, C. J.; Barclay, G. G.; Dao, J. *J. Am. Chem. Soc.* **1996**, *118*, 11467−11471.

(16) (a) Matsuno, R.; Yamamoto, K.; Otsuka, H.; Takahara, A. *Chem. Mater.* **2003**, *15*, 3−5. (b) Matsuno, R.; Yamamoto, K.; Otsuka, H.; Takahara, A. *Macromolecules* **2004**, *37*, 2203−2209.

(17) Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1997**, *30*, 2503−2506.

(18) Turro, N. J.; Lem, G.; Zavarine, I. S. *Macromolecules* **2000**, *33*, 9782−9785.

(19) Skene, W. G.; Belt, S. T.; Connolly, T. J.; Hahn, P.; Scaiano, J. C. *Macromolecules* **1998**, *31*, 9103−9105.

(20) Fischer, H. *Chem. Rev.* **2001**, *101*, 3851−3610.

(21) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600−1606.

MA061667U