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Reorganization and Scrambling Behavior of Alkoxyamine-Based Dynamic Covalent Polymers by Macromolecular Radical Crossover Reaction

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Dynamic covalent polymers incorporating thermally dissociable alkoxyamine units in the main chain were synthesized and their reorganization behavior was investigated. 2,2,6,6-Tetramethylpiperidine-1-oxy (TEMPO)-based alkoxyamine derivatives were employed as fundamental units. Poly(alkoxyamine ester) and Poly(alkoxyamine urethane) were synthesized from diol with alkoxyamine moiety. Due to a radical crossover reaction between the alkoxyamine units, an interchange of the main chains in poly(alkoxyamine) was observed upon heating. The macromolecular crossover reaction was successfully monitored by GPC and NMR measurements. Simple heating of the mixture of two polymers with different molecular weights can give one polymer with averaged molecular weight which show unimodal peak in GPC profile. Furthermore, macromolecular radical crossover reaction between different alkoxyamine-based dynamic covalent polymers, "polymer scrambling", was accomplished. This is novel and innovative methodology not only to control the molecular weight of polymers but also to prepare novel polymer hybrid.

Key words: Polymer Reaction, Radical Reaction, Dynamic Covalent Bond, Polyester, Polyurethane

1. INTRODUCTION

Reorganizable polymers are fascinating because their structures and properties can be changed and tuned after polymerization. These polymers can also facilitate a novel polymer synthetic method, in particular, a method that is effective for the preparation of polymeric hybrid materials. "Supramolecular polymers" are representative successful examples of this. Lehn et al reported the first example of supramolecular main-chain polymer.[1] Recently, Meijer et al developed the synthesis of supramolecular polymer with high molecular weight constructed by quadruple hydrogen bonding.[2] These polymers are constructed by secondary non-covalent interactions such as hydrogen bonds, coordination bonds, and so on. However, since supramolecular polymers are under thermodynamic equilibrium in solution, their molecular weights are still strongly dependent on the concentration and solvent polarity.

The chemistry of "dynamic covalent bond" relates to chemical reactions carried out reversibly under conditions of equilibrium control.[3] If the main chain of a polymer consists of reversible dynamic covalent bonds instead of non-covalent interactions, it can be expected to behave as a reversible polymer, like supramolecular polymers do. In contrast to supramolecular polymers, however, polymers with thermally reversible covalent bonds in the main chain are stable under normal conditions, even under high dilution concentration conditions (Fig. 1). Nevertheless, once they are exposed to external stimuli such as heating, they can be reorganized to the proper form reflecting the conditions. In this paper, radical scrambling reaction of alkoxyamine was investigated and the synthesis and macromolecular scrambling reaction alkoxyamine-based dynamic covalent polymers were performed.

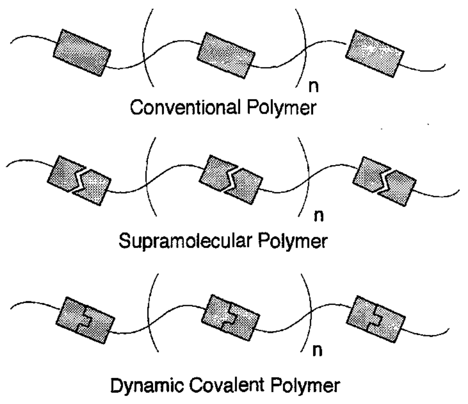


Fig. 1 Schematic representation of conventional polymers, supramolecular polymers, and dynamic covalent polymers.

2. EXPERIMENTAL SECTION

Measurement

^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 with a Perkin Elmer Spectrum One infrared spectrometer as 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 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. 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.

Polymerization

Adipoyl dichloride (255 mL, 1.5 mmol)wasadded to the solution of TEMPO-based diol **1** (418.5 mg, 1.5 mmol) and pyridine (240 mL, 3.0 mmol) in dichloromethane (1.5 mL).Thereactionmixturewas stirred at room temperature under nitrogen for 48 h. After the addition of methanol (1 mL), dicloromethane was added to the reaction mixture and washed with 0.1 mol/L HCl aqueous solution. Then the organic layer was washed with water three times, dried with anhydrous magnesium sulfate, and evaporated to dryness. The residue was purified by reprecipitation with chloroform/hexane and dried in vacuo to give the polymer as a white powder. M_n = 45300, M_w/M_n = 1.73; ^{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 (br, 8H), 2.20 (t, 4H), 4.25 (m, 1H), 4.55 (dd, J = 11 Hz, 5 Hz, 1H), 4.89 (t, J = 6 Hz, 1H), 7.24-7.32(m, aromatic); ^{13}C NMR: δ / ppm 21.08, 24.02, 24.32, 30.31, 33.69, 33.91, 34.11, 44.59, 44.69, 60.29, 60.61, 66.24, 65.81, 66.45, 84.08, 127.73, 127.83, 128.07, 140.07, 172.85, 172.90; FT-IR (KBr, cm^{-1}): 2974, 1735, 1467, 1364, 1175, 1002, 700.

Model reaction

Compounds **1** (79 mg, 0.27 mmol) and **2** (107 mg, 0.27 mmol) were dissolved in anisole (3 mL) as standard solution A. The St.A was charged in a glass tube, degassed and sealed under vacuum. The mixture was incubated at 100 °C for 24 h. The reaction mixture was cooled down and after dilution with acetonitrile the solution was analyzed by HPLC.

Polymer reaction

Typical example: A mixtures of poly(alkoxyamine ester)s (M_n=12000, M_w/M_n=1.21 as high molecular weight species and M_n=4300, M_w/M_n=1.17 as low molecular weight species) were dissolved in anisole (total concentration of alkoxyamine unit: 0.04 M), sealed, and heated at 100 °C for 1 h.

3. RESULTS AND DISCUSSION

3.1 Model Reaction

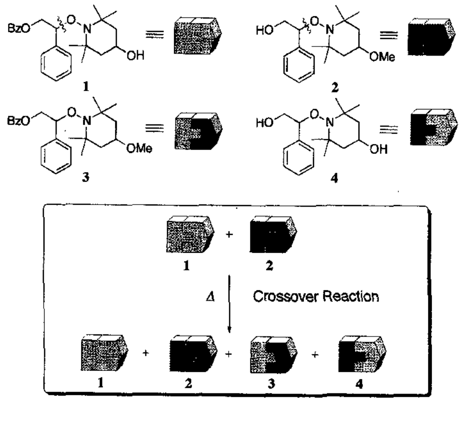


Fig. 2 Model alkoxyamine derivatives used for this study.

2,2,6,6-Tetramethylpiperidine-1-oxy (TEMPO)-containing alkoxyamine derivatives were chosen as candidates for fundamental units. They are frequently used as unimolecular initiators for living radical polymerization in the field of polymer synthesis,[4] and the key step of the currently accepted mechanism of the polymer synthesis is the reversible capping of the polymer chain by the nitroxide radical.[5] Even though there is no monomer in the system, the alkoxyamine unimolecular initiators can be expected to dissociate and associate reversibly by means of heating and exchange.[6,7]

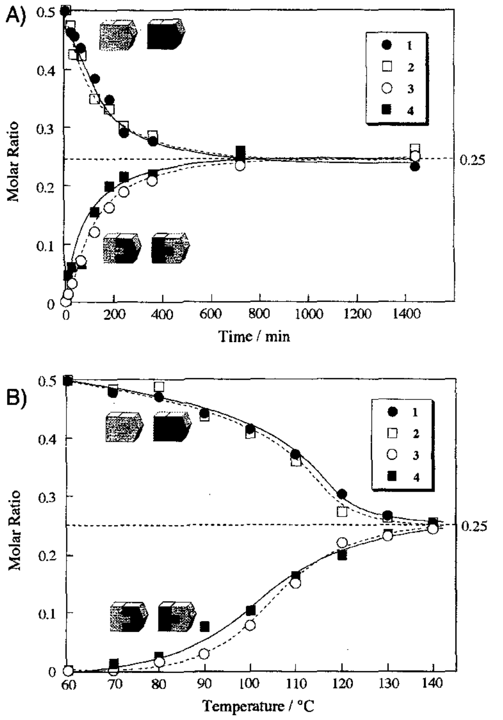
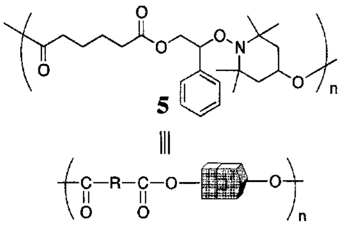


Fig. 3 A) Time-coursed and B) temperature-dependent molar ratios of model alkoxyamine derivatives determined by HPLC measurement.

In order to investigate the degree of exchange between alkoxyamine units, a model exchange reaction was carried out. Four TEMPO-based alkoxyamine derivatives **1-4** were synthesized, and the model exchange reaction was carried out as shown in Fig. 2. Equimolar amounts of **1** and **2** were mixed in anisole as standard solution A (St.A, 0.18 M), which was sealed under vacuum and heated at a fixed temperature. The proportion of compounds **1-4** was estimated from normalized peak area ratios in an HPLC analysis. As shown in Fig. 3A, the molar ratios of the compounds **1-4** attained equilibrium at 100 °C after 12 h. The molar ratios are almost the same. No significant peak was detected during the crossover reaction except for alkoxyamines and anisole. The reaction rate strongly depended on the reaction temperature, as shown in Figure 3B, which reveals that the crossover reaction occurred above 60 °C. The higher the reaction temperature became, the faster the molar ratio reached equilibrium.

3.2 Syntheses and Reaction of Dynamic Covalent Polymers[8]

TEMPO-containing poly(alkoxyamine ester)s were synthesized by polycondensation from diol **4** and adipoyl chloride in CH_2Cl_2 in the presence of pyridine at room temperature. By fractionation of the obtained polyester **5** using preparative HPLC, two polymers, **5a** (M_n = 4300, M_w/M_n = 1.17) and **5b** (M_n = 12000, M_w/M_n = 1.21), were successfully isolated. The mixture of polymers **5a** and **5b** showed two apparent peaks in the gel permeation chromatography (GPC) profile as shown in Fig. 4A. Equal amounts of **5a** and **5b** were mixed in anisole (total concentration of alkoxyamine: 0.04 M), sealed, and heated at 100°C for 1 h. As the reaction proceeded, the peaks derived from **5a** and **5b** clearly fused into a unimodal peak. Fig. 4B indicates the GPC profiles of polymer **5c** (M_n = 5600, M_w/M_n = 1.86) after the exchange reaction. Since transesterification is not expected to occur under these conditions, the phenomenon could undoubtedly be attributed to the crossover reaction of alkoxyamine units between the main chains. These findings showed strongly that the obtained TEMPO-containing poly(alkoxyamine ester)s are reorganizable polymers that can dissociate and associate reversibly in the main chain like supramolecular polymers when triggered by external stimulation such as heating.



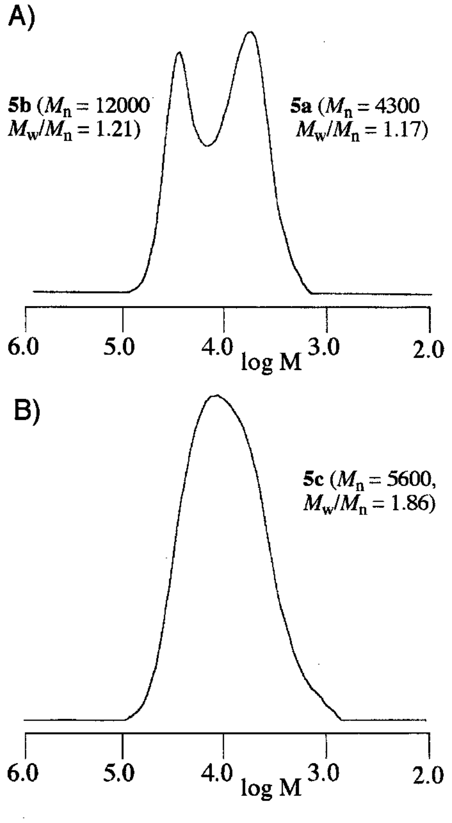


Fig. 4 GPC profiles of the mixture of **5a** and **5b** A) before heating and B) after heating.

3.3 "Radicalolysis" of dynamic covalent polymer.

Alkoxyamine-baesd dynamic covalent polymers are thermally reorganizable due to the radical crossover between the main chains. The addition of nitroxyl stable free radical in reorganization process can be expected to cause the scission of the polymer main chain because of the competitive addition to styryl radical. Stable free radical 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxy (**6**) is employed for this experiment.

Polymer **5d** (M_n = 11800, M_w/M_n= 1.21) was heated in the presence of stable free radical **6** in anisole at 100 °C. In the absence of stable radical, the M_n of polymer **5d** did not change. In contrast, in the presence of excess amount of stable free radical **6**, the M_n of **5d** drastically decreased as shown in Fig.5. Furthermore, even in the presence of 1 equivalent of **6**, the M_n of **5d** decreased to 1200 after 6 hours.

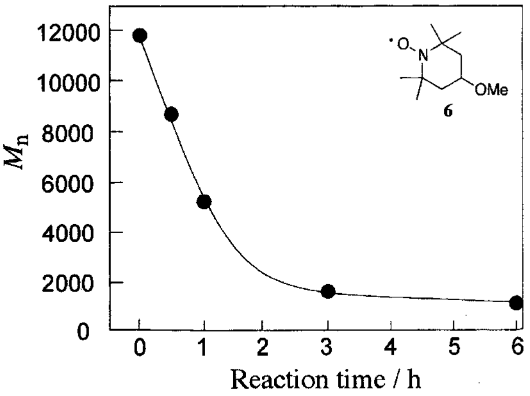
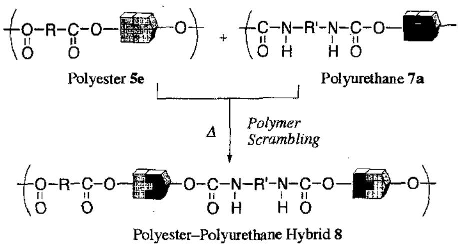


Fig. 5 "Radicalolysis" reaction of polyester **5d** by heating in the presence of free radical **6** at 100 °C.

3.4 Polymer Scrambling Reaction[9]

The exchange in alkoxyamine–based dynamic covalent polymer occurs in radical process that is tolerant to many functional groups and does not require very high temperature. Consequently, the exchange process can be applicable to polymers with many functional groups. If the two different dynamic covalent polymers are mixed and the system is reorganized, it can be expected that they afford one hybridized polymer. These reorganizable polymers can facilitate a novel polymer synthetic method, in particular, a method that is effective for the preparation of polymeric hybrid materials at the nanometer level. TEMPO-containing polyurethane **7** was synthesized by polyaddition of diol **1** with hexamethylene diisocyanate. By careful fractionation of polyester **5** and polyurethane **7** using preparative HPLC, two prepolymers, polyester **5e** (M_n = 93000, M_w/M_n = 1.25) and polyurethane **7a** (M_n = 5800, M_w/M_n = 1.10), were successfully isolated. The mixture of polymers **5e** and **7a** showed apparent two peaks in GPC profile. The scrambling reaction was carried out in anisole by using a mixture of **5e** and **7a** as starting materials. The mixture ([alkoxyamine unit] = 0.02 M, each) of **5e** and **7a** was dissolved in anisole, sealed, and heated at 100 °C for 24 h. After the radical crossover reaction, the peaks derived from **5e** and **7a** clearly fused into unimodal peak of polymer **8** with M_n = 17000,



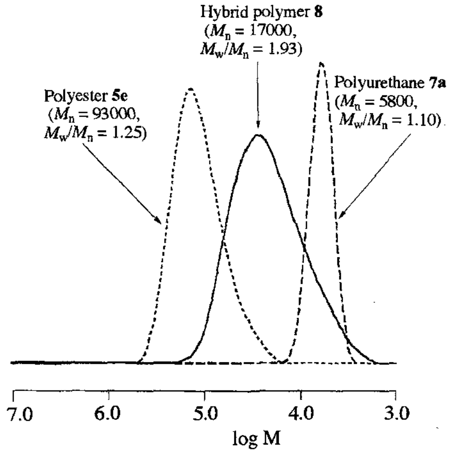


Fig. 6 GPC profiles of polyeste **5e**, polyurethane **7a**, and hybrid polymer **8** resulted by polymer scrambling reaction.

M_w/M_n = 1.93 (Fig. 6). No color change was observed after the scrambling reaction, although nitroxide radical has red color. The phenomenon is undoubtedly attributed to the macromolecular crossover reaction of alkoxyamine units in the main chain between polyester **5e** and polyurethane **7a**.

4. CONCLUSION

In conclusion, the present study demonstrated the possibility of synthesizing thermally reversible covalent polymers by incorporating a reversible alkoxyamine unit into the main chain. The methodology described here is not only novel and innovative to control the molecular weight of polymers, but it can also be applied to the preparation of novel polymer hybrids at the nanometer level by reorganizing some kinds of different polymers.

5. ACKNOWLEDGEMENT

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