

Polymer Scrambling: Macromolecular Radical Crossover Reaction between the Main Chains of Alkoxyamine-Based Dynamic Covalent Polymers

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Blending different polymers is an extremely attractive and inexpensive way of obtaining new structural materials from a limited palette. A route to achieve this has been studied so far; one effective approach is to add a block copolymer as a compatibilizer, and the other way is to use block copolymers themselves as materials.¹ However, in conjunction with the recent advancement of nanotechnology, a new hybridization method at the nanometer scale for polymers with various functional groups has been required.

Very recently, the authors developed “dynamic covalent polymers” whose structures and properties were changeable and tunable after polymerization.^{2,3} Because the reorganizability of the dynamic covalent polymers is attributed to the exchange of covalent bonds⁴ in the main chain triggered by external stimulation, the process can be useful as a novel synthetic method of new polymers. The exchange in the alkoxyamine-based dynamic covalent polymer occurs in a radical process that is tolerant to many functional groups and does not require very high temperature.⁵ 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. In this communication, the authors preliminarily report a novel and innovative method for the hybridization of different dynamic covalent polymers by “polymer scrambling” at the main chain level (Figure 1).

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)-based alkoxyamine derivatives were employed as fundamental units (Chart 1). They have been frequently used as unimolecular initiators for living radical polymerization in the field of polymer synthesis,⁶ and the key step of the currently accepted mechanism is the reversible capping of the polymer chain by the nitroxide radical.⁷ According to the results of the model reaction, even though there is no monomer in the system, the alkoxyamine unimolecular initiator can dissociate and associate reversibly by heating.^{3,8,9}

Dynamic covalent polymers, TEMPO-containing polyester **2** and polyurethane **3**, were synthesized by polycondensation or polyaddition from diol **1** with adipoyl chloride or hexamethylene diisocyanate, respectively. By careful fractionation of the obtained polyester **2** and polyurethane **3** using preparative HPLC, two prepolymers, polyester **2** ($M_n = 93\,000$, $M_w/M_n = 1.25$) and polyurethane **3** ($M_n = 5800$, $M_w/M_n = 1.10$), were successfully isolated. The mixture of polymers **2** and **3** showed two apparent peaks in the GPC profile. The scrambling reaction was carried out in anisole by using a mixture of **2** and **3** as the starting material. The mixture ([alkoxyamine unit] = 0.02 M, each) of **2** and **3** was dissolved in anisole, sealed, and heated at 100 °C for 24 h. After the radical crossover reaction, the peaks derived from **2** and **3** clearly

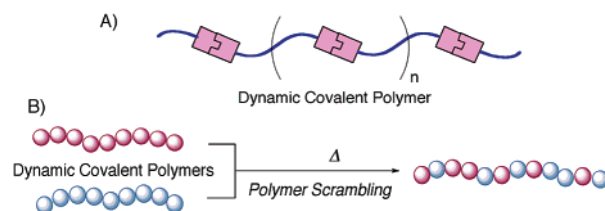


Figure 1. Schematic representation of the (A) “dynamic covalent polymer” and (B) “polymer scrambling” reaction of dynamic covalent polymers.

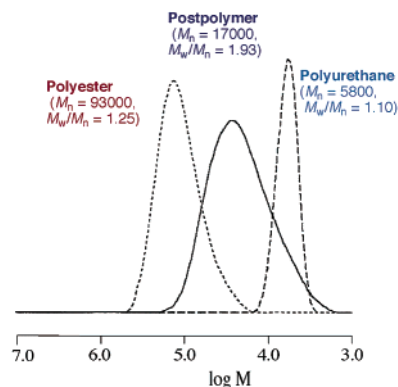
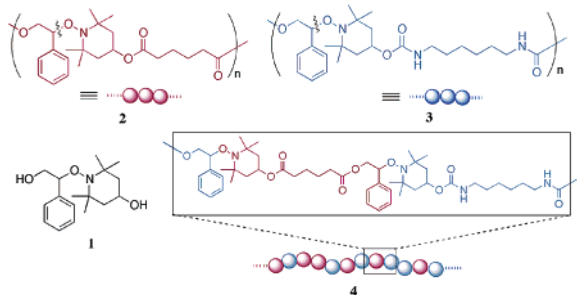


Figure 2. GPC profiles of the polyester ($M_n = 93\,000$, $M_w/M_n = 1.25$) and polyurethane ($M_n = 5800$, $M_w/M_n = 1.10$) containing TEMPO-based alkoxyamine units and the postpolymer ($M_n = 17\,000$, $M_w/M_n = 1.93$) which resulted from the “polymer scrambling” reaction in anisole heated at 100 °C.

Chart 1. Alkoxyamine Derivatives



fused into the unimodal peak of polymer **4** with $M_n = 17\,000$, $M_w/M_n = 1.93$ (Figure 2). No color change was observed after the scrambling reaction, although the nitroxide radical has a red color. The phenomenon is undoubtedly attributed to the macromolecular crossover reaction of alkoxyamine units in the main chain between polyester **2** and polyurethane **3**.

To obtain further insight into the scrambling reaction, the scrambling reactions were stopped after a certain time, and each reaction mixture was fractionated into six fractions by elution time

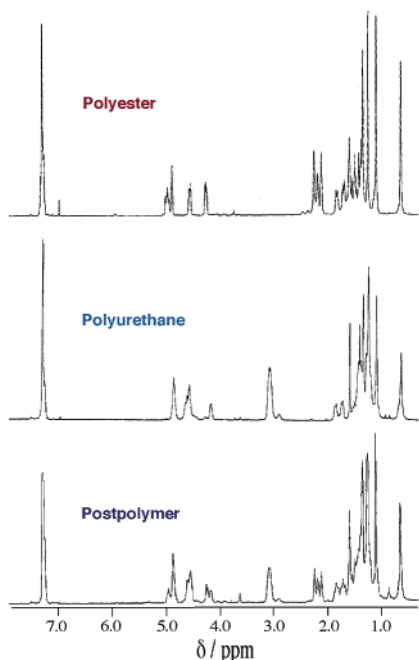


Figure 3. ^1H NMR spectra of polyester **2**, polyurethane **3**, and the first fraction (of six fractions) of fractionated postpolymer **4** which resulted from the “polymer scrambling” reaction (400 MHz, in CDCl_3).

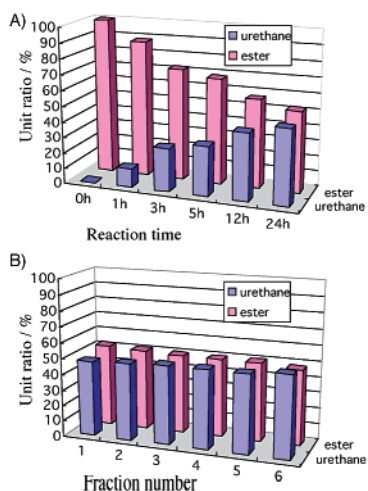


Figure 4. Unit molar ratios of the ester and urethane moieties after the scrambling reaction of polyester **2** ($M_n = 23\,000$, $M_w/M_n = 1.86$) and polyurethane **3** ($M_n = 5800$, $M_w/M_n = 1.10$), heated in anisole at $100\text{ }^\circ\text{C}$. (A) Unit molar ratio of first fractions on reaction time; (B) after 24 h: fraction 1, $M_n = 32\,800$ ($M_w/M_n = 1.09$); fraction 2, $19\,000$ (1.09); fraction 3, $11\,200$ (1.10); fraction 4, 7600 (1.12); fraction 5, 4800 (1.05); and fraction 6, 2500 (1.12).

using preparative HPLC (GPC column), and ^1H NMR analyses of all fractions were carried out. Figure 3 shows ^1H NMR spectra of polyester **2** ($M_n = 23\,000$, $M_w/M_n = 1.86$), polyurethane **3** ($M_n =$

5800 , $M_w/M_n = 1.10$), and the first fraction (the highest molecular weight region) of polymer **4**. The ^1H NMR spectrum of the first fraction of **4** was assignable to the mixture of the polyester and the polyurethane without any decomposition. The ester/urethane ratios can be estimated by integral intensities of the ^1H NMR spectra. Figure 4A shows the time-coursed ester/urethane ratios of the first fractions during the scrambling reaction. Before the scrambling reaction, there was no urethane component in the molecular weight region of the first fraction. As the scrambling reaction proceeded, the urethane ratio of the first fraction increased. There were no significant changes observed in the molecular weights and their distributions, and the peaks of the polymers in GPC profiles remained unimodal from after 1 h. Finally, the ester/urethane ratio reached 50%/50% in all fractions (Figure 4B), indicating that two polymers were fully scrambled at the main chain level.

In summary, the present study demonstrated a polymer scrambling reaction between reorganizable polymers by incorporation of dynamic covalent bonds into the main chain. The methodology shown here may enable a novel combinatorial approach to polymer hybrids and is generally applicable to other dynamic covalent polymer systems. Further studies are currently in progress.

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