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A dynamic (reversible) covalent polymer: radical crossover behaviour of TEMPO–containing poly(alkoxyamine ester)s

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A dynamic covalent polymer incorporating thermally alkoxyamine units in the main chain was synthesized. Due to a radical crossover reaction between the alkoxyamine units, an interchange of the main chains in poly(alkoxyamine ester) was observed on heating.

Reversible polymers are fascinating because the polymer structures and properties can be changed and tuned after polymerisation. 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'[1,2] are a representative successful example of this. 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.[1]

If the main chain of a polymer consists of reversible dynamic covalent bonds[3] 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 that reflects the conditions. In this communication, our preliminary results on reorganizable polymers[4] with thermally reversible covalent bonds are described.

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,[5] 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.[6] 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.[7,8]

In order to investigate the degree of exchange between alkoxyamine units, a model exchange reaction was carried out.

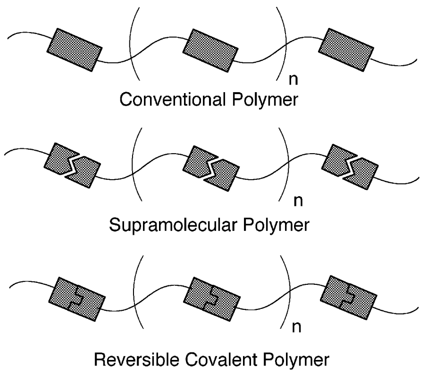
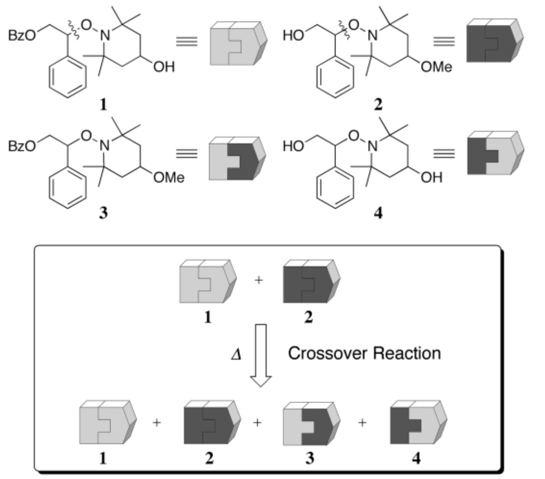


Fig. 1 Schematic representation of conventional polymer, supramolecular polymer, and reversible covalent polymer.

Four TEMPO–based alkoxyamine derivatives **1**–**4** were synthesized, and the model exchange reaction was carried out as shown in Scheme 1. 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 (Fig. 2). 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 Fig. 3B, which reveals that the crossover reaction occurred above 60 °C. The higher the reaction temperature became, the faster the molar ratio reached equilibrium. Focusing on the concentration effect, fewer effects were observed in the range of concentration from 0.18–0.018 M, although in the case of a 3.6×10^{-3} M solution the reaction became slower.

TEMPO–containing poly(alkoxyamine ester)s were synthesized by polycondensation from diol **4** and adipoyl chloride in



Scheme 1

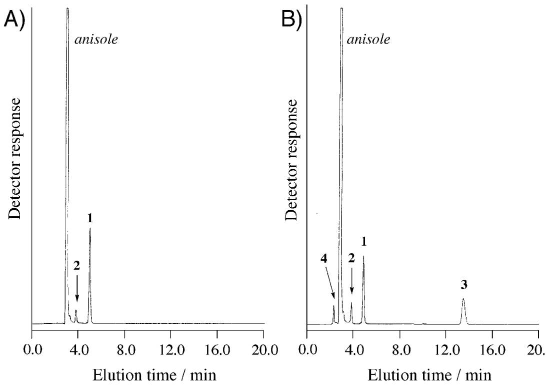


Fig. 2 HPLC chromatograms of St.A solution (A) before and (B) after heating (Column: JASCO CrestPak C18S, flow rate: 1.0 mL min^{-1}, eluent: H_2O–CH_3CN = 1/3 v/v).

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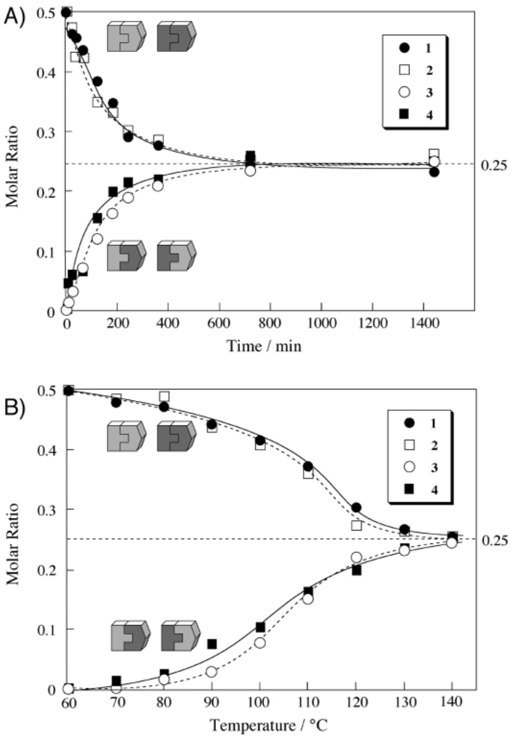

Fig. 3 (A) Time–coursed molar ratios of alkoxyamines started from St.A at 100 °C and (B) Temperature–dependent molar ratios of alkoxyamines started from St.A for 2 h.

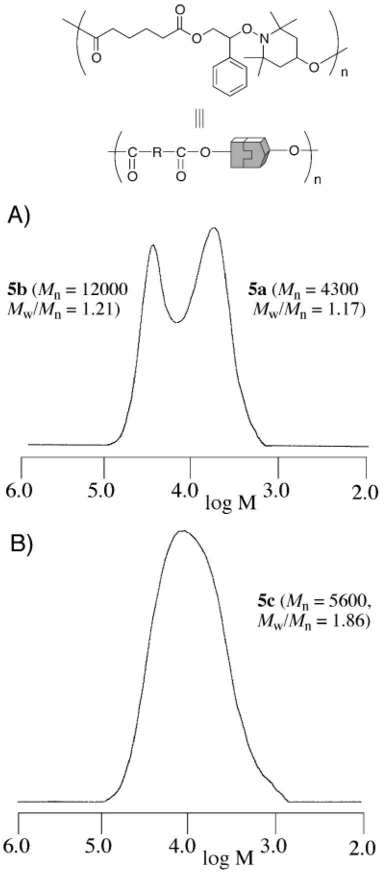

Fig. 4 GPC profiles (THF, polystyrene standard) of (A) the mixture of polymers **5a** (M_n = 4300, M_w/M_n = 1.17) and **5b** (M_n = 12000, M_w/M_n = 1.21) before heating and (B) the resultant polymer **5c** (M_n = 5600, M_w/M_n = 1.86) after heating in anisole (total concentration of alkoxyamine unit: 0.04 M) at 100 °C.

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. Although the possibility of the formation of ring compounds, by NMR measurements the end group analyses of the prepolymers and the obtained polymer under this concentration condition gave no significant information whether any cyclic compounds were formed or not.[9] 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.

In summary, 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.

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