

## Radical Ring-Crossover Polymerization of Macrocycles with Radically Exchangeable Dynamic Covalent Bonds

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### Introduction

Reorganizable polymers are fascinating because their structures and properties can be changed and tuned after polymerization. If the main chain of a polymer consists of reversible “dynamic covalent bonds”[1], it can be expected to behave as reorganizable polymers. Very recently, the authors developed alkoxyamine-based “dynamic covalent polymers” whose structures and properties were changeable and tunable even after polymerization[2,3]. 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[4,5]. Hence, the exchange process can be applicable to polymers with many functional groups. Because the reorganizability of the dynamic covalent polymers is attributed to the exchange of covalent bonds in the main chain triggered by external stimulation, the process can be useful as a novel synthetic method of polymers themselves. Here, the authors report the synthesis and radical ring-crossover polymerization of macrocycles with radically exchangeable dynamic covalent bonds (Figure 1).

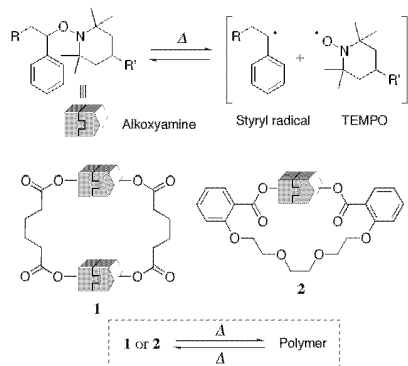


Figure 1 Ring-crossover polymerization of macrocyclic alkoxyamines.

### Experimental

**Synthesis of Macrocyclic Alkoxyamine(1).** *Typical example:* Adipoyl chloride (0.727 mL, 5.0 mmol) was dissolved into dichloromethane (125 mL) and the solution was added to the mixture of diol (1.47 g, 5.0 mmol), dichloromethane (375 mL), and pyridine (0.809 mL, 10 mmol). The reaction mixture was stirred for 58 h under nitrogen atmosphere and washed with 0.1 N HCl and water. The solution was dried with MgSO<sub>4</sub> and the solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel, ethyl acetate/chloroform/hexane = 5/2/15) to give **1** (250 mg, 6.2%) as a white solid.

**Polymerization of Macrocyclic Alkoxyamine(1).** *Typical example:* To a polymerization tube was added 0.18 M anisole solution of macrocyclic alkoxyamine **1** (16.1 mg, 0.02 mmol). The tube was then purged with dry nitrogen gas, sealed, and placed in a 125 °C constant temperature oil bath. The polymerization was carried out for 6 h with continuous stirring, and then quenched by immersing the tube in an ice-water bath. The molecular weight and its distribution of the polymer product were determined by GPC without purification. The polymer part was fractionated by preparative HPLC (GPC column) for NMR characterization.  $M_n = 13100$ ,  $M_w/M_n = 2.0$ .

### Results and discussion

Alkoxyamine compounds[6] derived from 2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO, can be exchanged in a radical process upon heating[2,5]. The macrocyclic compounds (**1** and **2**) with alkoxyamine units were designed and synthesized by

condensation from alkoxyamine-based diol and the corresponding acid chloride in CH<sub>2</sub>Cl<sub>2</sub> in the presence of pyridine under high-dilution condition. After working up the reaction mixture, compound **1** was isolated by column chromatography in 6.2%. In IR measurement, no OH group was detected but stretching vibration of ester carbonyl group (1734 cm<sup>-1</sup>) was observed. The product was characterized by NMR spectroscopies as cyclic compound containing both alkoxyamine and adipic acid moieties. The FAB-MS measurement clearly revealed that the product is [2+2] macrocycle (**1**). The synthesis and characterization of [1+1] macrocycle (**2**) were carried out in a similar method.

The alkoxyamine macrocycles can be expected to polymerize by intermolecular radical exchange reaction. The polymerization of macrocycle **1** and **2** was carried out for 6 h in anisole at 125 °C. GPC profiles before and after polymerization of **1** clearly show that macrocycle **1** thermally polymerized and the polymer part (after heating) in GPC profile has  $M_n = 13100$ ,  $M_w/M_n = 2.0$ . The polymer part was fractionated by preparative HPLC (GPC column) to determine the structure. The polymer part was isolated as a white solid, and no detectable decomposition of alkoxyamine moieties occurred during the polymerization. Although some chemical shift values and splitting patterns changed after polymerization in <sup>1</sup>H NMR spectra, all signals could be assigned to the corresponding poly(alkoxyamine) structure. These findings revealed that macrocycle **1** can be thermally polymerized by intermolecular radical crossover reaction.

The polymerization behavior of **1** strongly depended on concentration, time, and temperature. Below 80 °C, no significant polymerization was observed even after 48 h. The higher the concentration of macrocycle was, the higher the molecular weight of the resulted polymer was. Furthermore, the FAB mass spectrum of the obtained oligomers ( $M_n < 2500$ ) after the reaction was measured to determine the structures in equilibrium. The periodic peaks of macrocyclic alkoxyamine oligomers were clearly observed. Macrocyclic compound **2** also acted as a monomer for polymerization to afford the structurally-ordered polymer due to the dissymmetric dynamic covalent bond of alkoxyamine.

The obtained polymer containing alkoxyamine units in the main chain is also expected to depolymerize to the monomers via intramolecular radical exchange reaction. The depolymerization of the fractionated polymers was conducted in 0.40wt% anisole solution ([alkoxyamine unit] = 0.01 mol·L<sup>-1</sup>) at 125 °C for 24 h. After heating, the molecular weight ( $M_n$ ) drastically decreased. GPC profiles, TLC analysis, and FAB-MS measurement of the reaction mixture confirmed that the generated major products are monomers **1** and **2**. From the results obtained above, poly(alkoxyamine)s depolymerized to the monomers principally by the intramolecular radical exchange process under high-dilution conditions.

### Conclusions

The present study has demonstrated the synthesis of the macrocycles with radically exchangeable dynamic covalent bonds and their dynamic polymerization behavior. Since the novel dynamic polymerization system proceeded in a radical process that is tolerant to many functional groups and does not require very high temperature, the methodology is applicable to monomers with a variety of functional groups.

### References

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