Reversible Radical Ring-Crossover Polymerization of an Alkoxyamine-Containing Dynamic Covalent Macrocycle

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ABSTRACT: The synthesis of a macrocycle with alkoxyamine-based dynamic covalent bonds and its dynamic polymerization behavior are described. The macrocyclic alkoxyamine was synthesized by condensation of an alkoxyamine-based diol with adipoyl chloride under high-dilution conditions. Spectroscopic measurements revealed that one of the obtained macrocyclic compounds was a [2 + 2] adduct. The [2 + 2] macrocyclic compound acted as a monomer for "ring-crossover" polymerization to afford the corresponding polymer with M_n = 2000−18 000 due to the intermolecular radical crossover reaction. The polymerization behavior strongly depended on concentration, time, and temperature. Furthermore, under high-dilution conditions, the obtained poly(alkoxyamine) depolymerized to the monomer or oligomers mainly by the intramolecular radical exchange process.

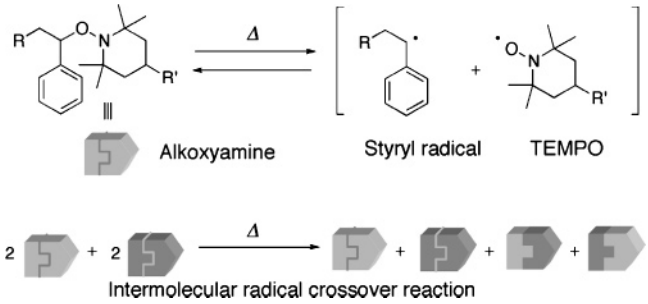
Introduction

Since monomeric units in macromolecules are generally held together by irreversible, strong, and fixed covalent bonds, it is difficult to change the primary structures of polymers after polymerization. If the monomeric units are linked through reversible connections, reversible polymers whose structures and properties are changed and tuned after polymerization can be realized and have potential application to design intelligent materials, chemical recycling, and combinatorial polymer hybridization. Main-chain type supramolecular polymers[1,2] whose main chains are constructed by noncovalent interactions, in particular hydrogen bonding, are typical example of this. However, these polymers are unstable in polar solvents or under high-dilution conditions because the degree of polymerization is determined by the binding constant between monomer units.

Much attention is currently focused on the molecular synthesis utilizing "dynamic covalent bonds"[3,4] such as disulfides,[5] olefins,[6] imines,[7] and hydrazones[8] which can be formed and broken reversibly under thermodynamic control. One of the oldest and most investigated fields in which dynamic covalent chemistry has played an important role is polymer synthesis. Dynamic (equilibrium) polymerizations[9] are observed for a number of cyclic monomers[10] which are capable of ring-opening polymerizations (ROP). Polymerizations of this type usually required the other components such as catalysts and initiators.

We recently reported that the alkoxyamine compounds derived from 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO), which are well-known as initiators for living radical polymerization,[11−13] can be exchanged via radical crossover reaction upon heating (Scheme 1)[14−17] and have developed alkoxyamine-based "dynamic covalent polymers".[14] Compared with supramolecular polymers, the alkoxyamine-based dynamic covalent polymers are as stable under normal conditions as conventional polymers. For instance, one can estimate their molecular weight by conventional gel permeation chromatography due to their structural fixation. Nevertheless, once they are exposed to external stimuli such as heating, they can reorganize to the form reflecting the conditions like supramolecular polymers do. This adaptability potentially offers the development of smart materials that can respond to their environment by the use of dynamic covalent chemistry.[3] If the macrocyclic compound with alkoxyamine units is synthesized, it should polymerize through radical exchange reaction. This dynamic polymerization system should proceed by simple heating without addition of any other components such as initiators. Although free radical ROP has been proposed as a useful route for the synthesis of polymers with various functional groups, such as ester, ether, ketone, amide, and carbamate, in their backbone, their reactivity strongly depends on ring strain, and limited monomers can enjoy the polymerization.[18] This paper reports the synthesis and reversible radical polymerization of a macrocycle with alkoxyamine-based dynamic covalent bonds.

Scheme 1. Radical Crossover Reaction of Alkoxyamine Derivatives



Experimental Section

Materials. 4-Hydroxy-1-((2′-hydroxy-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (**1**) was prepared by the method reported previously.[12] Adipoyl chloride (99%) was purchased from Wako Pure Chemical Industries and distilled under vacuum over P_2O_5. Dichloromethane (99%), anisole (99+%), and pyridine (98%) were purchased from Wako Pure Chemical Industries and distilled over CaH_2. 4-(Dimethylamino)pyridine

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(DMAP, 99+%) was purchased from Aldrich and used without further purification. All other reagents were purchased from commercial sources and used without further purification.

Measurements. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic measurements were carried out at 25 °C 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 by the KBr method. Number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersities (M_w/M_n) were estimated by gel permeation chromatography (GPC) in THF at 40 °C on a polystyrene gel column [Shodex GPC KF-804L column (300 × 8.0 mm), molecular weight range which is claimed to separate is 400 000−100] that was connected to a TOSOH system equipped with a refractive index (RI) detector at a flow rate of 0.8 mL min^{-1}. The column was calibrated against six standard polystyrene samples (M_n 800−152 000; M_w/M_n 1.03−1.10). Fractionation was conducted on a JAI LC-908 HPLC system equipped with two mixed polystyrene gel columns [JAIGEL-2H, JAIGEL-3H (600 × 20 mm)]. Chloroform was used as an eluent at a flow rate of 3.8 mL min^{-1}. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel (0.25 mm thick). FAB-MS measurements were carried out with a JEOL JMS-HX110A mass spectrometer. Elemental analysis (EA) was performed on a YANAKO CHN CORDER MT-6 instrument.

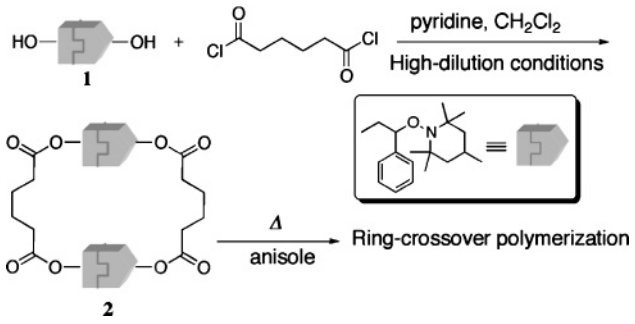
Synthesis of Macrocyclic Alkoxyamine (2). Adipoyl chloride (0.727 mL, 5.0 mmol) was dissolved in dichloromethane (150 mL), and the solution was added to the mixture of diol **1** (1.47 g, 5.0 mmol), dichloromethane (350 mL), DMAP (0.15 g, 1.2 mmol), and pyridine (0.890 mL, 11 mmol). The reaction mixture was stirred for 68 h under a nitrogen atmosphere and washed with 0.1 N HCl and water. The solution was dried with $MgSO_4$, 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 **2** (365 mg, 9.0%) as a white solid. ^{1}H NMR: δ/ppm 0.65 (m, 6H, CH_3), 1.14 (s, 6H, CH_3), 1.28 (m, 6H, CH_3), 1.43 (m, 6H, CH_3), 1.62−1.87 (m, 16H, CH_2), 2.28 (s, 8H, CH_2), 4.27 (m, 2H, CH_2), 4.61 (m, 2H, CH_2), 4.94 (m, 2H, CH), 5.02 (m, 2H, CH), 7.27−7.32 (m, 10H, aromatic). ^{13}C NMR: δ/ppm 21.15, 21.24, 24.39, 33.89, 34.08, 34.23, 44.62, 44.92, 45.00, 60.07, 60.16, 60.29, 60.78, 60.84, 66.23, 66.37, 84.11, 84.25, 127.49, 127.61, 127.71, 127.86, 128.02, 139.84, 139.89, 172.48 (C=O), 172.77 (C=O). FT-IR (KBr, cm^{-1}): 2931, 1734 (C=O), 1459, 1365, 1175, 1003, 701. Anal. Calcd for $C_{46}H_{66}N_2O_{10}$: C, 68.46; H, 8.24; N, 3.47. Found: C, 66.98; H, 8.27; N, 3.38. MS (FAB): 807.5 (M + 1).

Typical Procedure for Polymerization of Macrocyclic Alkoxyamine (2). Macrocyclic alkoxyamine **2** (16.1 mg, 0.02 mmol) and anisole (111 μL, 0.18 mol·L^{-1}) were charged into a polymerization tube, degassed, and sealed off under vacuum. The solution was incubated at 125 °C for 6 h. The molecular weight and its distribution of the polymer product were determined by GPC without any purification. The polymer part was fractionated by preparative HPLC (GPC column) for NMR characterization. M_n = 13 100, M_w/M_n = 2.0. ^{1}H NMR: δ/ppm 0.66 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.39−1.85 (m, 8H, CH_2), 2.20 (m, 4H, CH_2), 4.26 (m, 1H, CH_2), 4.56 (m, 1H, CH_2), 4.90 (m, 1H, CH), 4.97 (m, 1H, CH), 7.27−7.33 (m, aromatic). ^{13}C NMR: δ/ppm 21.08, 21.18, 24.01, 24.13, 24.22, 24.31, 29.66, 30.30, 30.34, 33.67, 33.72, 33.89, 34.09, 34.19, 44.58, 44.65, 60.23, 60.56, 65.74, 66.37, 84.00, 127.58, 127.68, 127.92, 128.08, 139.91, 172.61 (C=O), 172.66 (C=O). FT-IR (KBr, cm^{-1}): 2974, 1735 (C=O), 1467, 1364, 1175, 1002, 700.

Depolymerization of Poly(alkoxyamine). Poly(alkoxyamine) **3** (M_n = 13 100, M_w/M_n = 2.0, 16.1 mg) was dissolved in anisole (4.0 mL, 0.40 wt % of polymer solution, [alkoxyamine unit] = 0.01 mol L^{-1}), and the solution was charged into a polymerization tube, degassed, and sealed off under vacuum. The solution was incubated at 125 °C for 24 h. The molecular weight of the polymer product and its distribution were determined by GPC without any purification. The yield of macrocyclic alkoxyamine **2** was estimated by GPC chromatogram to be 58%. M_n = 720, M_w/M_n = 1.4. MS (FAB): 807.5 (M + 1).

Depolymerization of poly(alkoxyamine) (M_n = 23 400, M_w/M_n = 2.0) prepared by the polycondensation method[13] was carried out by the same procedure. The yield of macrocyclic alkoxyamine **2** was estimated by the GPC chromatogram to be 54%. M_n = 760, M_w/M_n = 1.4. MS (FAB): 807.5 (M + 1).

Scheme 2. Synthesis and Polymerization of Macrocycle 2



Results and Discussion

Synthesis of Macrocycle. The macrocyclic compound **2** with alkoxyamine units was designed and synthesized by condensation from TEMPO-based diol **1** and adipoyl chloride in CH_2Cl_2 in the presence of pyridine under high-dilution conditions (Scheme 2). The reaction mixture was chromatographed on a silica gel (ethyl acetate/chloroform/hexane = 5/2/15); a compound with an R_f value = 0.35 was obtained in 9.0% yield. In IR measurement, no OH group was detected, but stretching vibration assigned to the ester carbonyl group (1734 cm^{-1}) was clearly observed. As shown in Figure 1A, the product was characterized by NMR spectroscopy as a cyclic compound containing both alkoxyamine and adipate moieties because no peaks attributed to the terminal groups were observed. The FAB-MS measurement clearly revealed that the isolated product is a [2 + 2] macrocycle (**2**).[19]

Polymerization of Macrocyclic Alkoxyamine. The alkoxyamine macrocycle should polymerize by intermolecular radical exchange reaction due to its dynamic covalent bonds. The polymerization of macrocycle **2** was carried out in 0.18 mol L^{-1} anisole solution at 125 °C for 6 h. Figure 2 shows the GPC profiles before and after polymerization of **2**. The profiles clearly show that macrocycle **2** thermally polymerized, and the molecular weight and molecular weight distribution of the polymer part (after heating) in GPC profile were M_n = 13 100 and M_w/M_n = 2.0, respectively. The polymer part (**3**) was fractionated by preparative HPLC (GPC column) to determine the structure. Polymer **3** was isolated as white solid, and no detectable decomposition of alkoxyamine moieties occurred during the polymerization. Figure 1B shows the ^{1}H NMR spectrum of **3**. Although some chemical shift values and splitting patterns slightly changed after polymerization, all signals could be assigned to the corresponding poly(alkoxyamine) structure. These findings indicate that macrocycle **2** can thermally polymerize by intermolecular radical crossover reaction.

Effect of Concentration, Time, and Temperature on Polymerization. The effect of the initial concentration of **2** on the molecular weight of the polymer part was examined. The polymerization of **2** was carried out in 0.02, 0.06, and 0.18 mol L^{-1} anisole solutions at

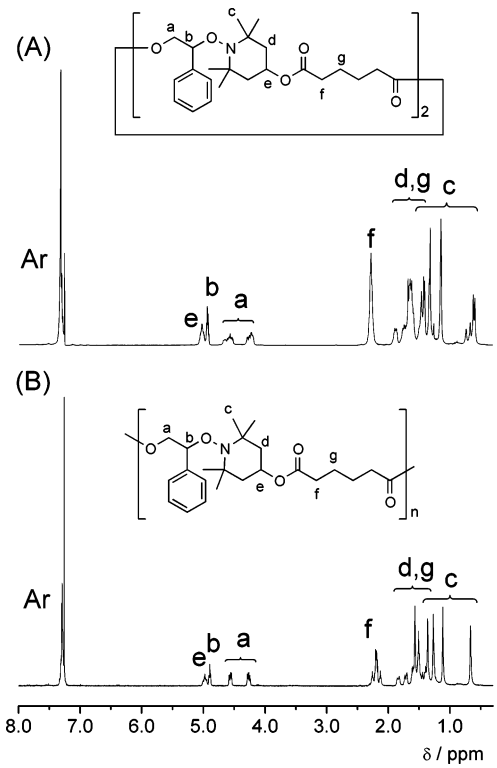


Figure 1. ^{1}H nuclear magnetic resonance (NMR) spectra of (A) alkoxyamine-based macrocycle **2** and (B) the polymer part (M_n = 13 100, M_w/M_n = 2.0) fractionated after polymerization of macrocycle **2**.

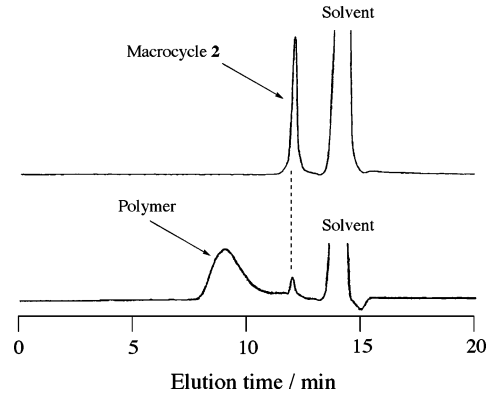


Figure 2. Gel permeation chromatography profiles of macrocycle **2** (upper) and the obtained polymer by heating (lower). The polymerization of macrocycle **2** was carried out in 0.18 mol L^{-1} anisole solution at 125 °C for 6 h.

125 °C for 6 h. The M_n (M_w/M_n) values of polymer part after heating at 0.02, 0.05, and 0.18 mol L^{-1} were 2700 (1.8), 10 400 (1.8), and 13 100 (2.0), respectively. The higher the initial concentration of **2** was, the higher the molecular weight of the resulted polymer was. This is due to the increase of possibility for intermolecular exchange reaction under high-concentration conditions.

Figure 3 shows the time-coursed polymer percentage of the reaction mixture during polymerization of macrocycle **2** at 0.02, 0.06, and 0.18 mol L^{-1}. The polymer percentage, which was determined from the peak areas in GPC profiles, changed during the polymerization at 125 °C. The polymer percentage did not attain 100%, and each polymerization reached equilibrium. The final polymer percentage depended on the initial concentration of **2**.

The effect of temperature on the polymer percentage was also examined. The polymerization of **2** was carried

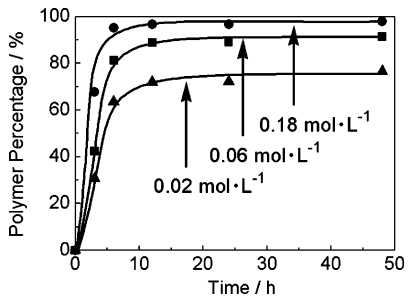


Figure 3. Evolution of polymer percentage of the reaction mixture during polymerization of macrocycle **2** as a function of reaction time at 0.02, 0.06, and 0.18 mol L^{-1}. The polymerization was carried out in anisole solutions at 125 °C.

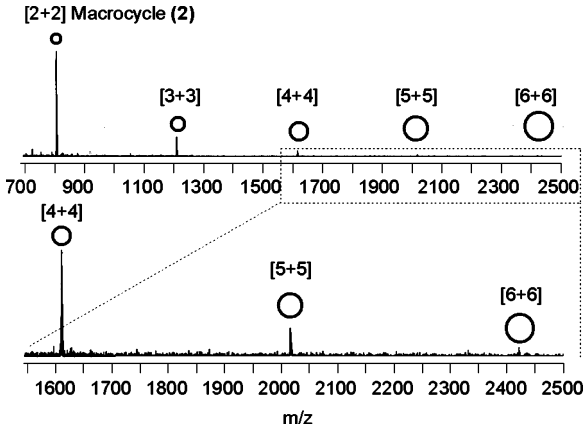


Figure 4. Fast atom bombardment (FAB) mass spectrum of the obtained oligomers (M_n < 2500). The sample was obtained by polymerization of macrocycle **2** in 0.02 mol L^{-1} anisole solution at 125 °C for 24 h.

out in 0.06 mol L^{-1} anisole solutions at 75, 100, and 125 °C for 48 h. The polymer percentage was 31% at 100 °C, and it became 98% at 125 °C. Below 75 °C, no significant polymerization was observed even after 48 h. In our previous report,[13] the model reaction revealed that the degree of exchange between alkoxyamine derivatives strongly depends on the reaction temperature. The result of polymerization in this experiment agrees with the model reaction.

Structure of Poly(alkoxyamine). The FAB mass spectrum of the obtained oligomers (M_n < 2500) after the reaction was measured to determine the structures in equilibrium. The sample was obtained by polymerization of macrocycle **2** in 0.02 mol L^{-1} anisole solution at 125 °C for 24 h. As shown in Figure 4, the periodic peaks were observed indicating the presence of a mixture of macrocyclic alkoxyamine oligomers. No significant peak derived from linear polymer was observed. The detected macrocycles were up to hexamers under the present conditions. Previously, we carried out the model reaction to confirm the detail of radical crossover reaction between alkoxyamine derivatives, and no significant TEMPO−TEMPO and/or styryl−styryl coupling products were observed.[14] In the present polymerization system, no product derived from bimolecular termination of styryl radicals was also observed in the NMR spectrum of the resulting products, and no color change occurred through the reaction, which provides further support for the absence of significant generation of nitroxide end in polymerization of the macrocyclic alkoxyamine. Thus, it is assumed that bimolecular termination of styryl radicals is apparently negligible in the present polymerization system, sug-

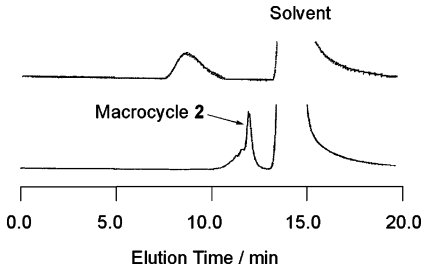


Figure 5. Gel permeation chromatography profiles of poly(alkoxyamine) **3** (M_n = 13 100, M_w/M_n = 2.0) (upper) and the depolymerized products by heating (lower). The depolymerization was carried out in 0.40 wt % anisole solution ([alkoxyamine unit] = 0.01 mol L^{-1}) at 125 °C for 24 h.

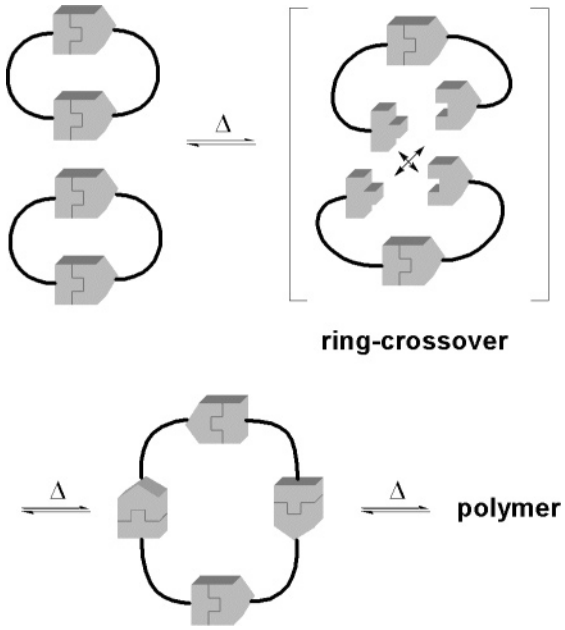


Figure 6. Schematic representation of reversible radical ring-crossover polymerization system.

gesting that most of the obtained polymers and oligomers are cyclics. These results suggested that macrocycle **2** polymerized via a radical "ring-crossover" process.

Depolymerization of Poly(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 polymer **3** (M_n = 13 100, M_w/M_n = 2.0) was conducted in 0.40 wt % anisole solution ([alkoxyamine unit] = 0.01 mol L^{-1}) at 125 °C for 24 h. After heating, the molecular weight (M_n) of **3** drastically decreased as shown in Figure 5. GPC profiles, TLC analysis, and FAB-MS measurement of the reaction mixture confirmed that the generated major product is monomer **2**. From the results obtained above, poly(alkoxyamine) **3** depolymerized to the monomers principally by the intramolecular radical exchange process under high-dilution conditions.

As illustrated in Figure 6, the present ring-crossover polymerization and depolymerization system is reversible and is heavily dependent on temperature and concentration. Moreover, the poly(alkoxyamine)[14] prepared by polycondensation from diol **1** and adipoyl chloride also depolymerized to the monomers under high-dilution conditions as well as poly(alkoxyamine) **3** obtained by radical ring-crossover polymerization.

Conclusions

The present study has demonstrated the synthesis of the macrocycle with alkoxyamine-based dynamic covalent bonds and its dynamic polymerization behavior. The macrocyclic alkoxyamine **2** was synthesized by condensation reaction of alkoxyamine-based diol **1** and adipoyl chloride under high-dilution conditions. Simple heating of the macrocyclic compound **2** in anisole solution afforded the corresponding polymer due to the intermolecular radical crossover reaction. The obtained poly(alkoxyamine) depolymerized to the monomers mainly by the intramolecular radical exchange process under high-dilution conditions. 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.

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(19) The [2 + 2] product was identified as a mixture of cis and trans isomers. The other isolated product with an R_f value = 0.25 was also assigned to be a [3 + 3] macrocycle by NMR and FAB-MS measurements. A [1 + 1] product was not detected in this experiment.

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