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Synthesis and Chemical Recycling of a Polycarbonate Obtained by Anionic Ring-Opening Polymerization of a Bifunctional Cyclic Carbonate

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ABSTRACT: This article deals with anionic ring-opening polymerization of a bifunctional cyclic carbonate consisting of both five- and six-membered rings (65CCP) and anionic depolymerization of the obtained polymer. Anionic ring-opening polymerization of 65CCP initiated with 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) afforded a polycarbonate remaining a five-membered cyclic carbonate group in the side chain (P(65CCP)) by the selective polymerization of the six-membered cyclic carbonate ring. The equilibrium nature of the polymerization allowed the efficient depolymerization of P(65CCP) by a catalytic amount of DBU to recover 65CCP in high yield, in which the five-membered cyclic carbonate ring also remained unreacted.

Introduction

Polymers bearing carbonate structures in either the main or side chains have been paid much attention because of their applications as biocompatible, optical, high dielectric, and/or adhesive materials.[1] To obtain aliphatic polycarbonates, ring-opening polymerization of cyclic carbonates has been widely investigated.[2,3] However, anionic polymerizations of five-membered cyclic carbonates proceed sluggishly to give polycarbonates containing a considerable amount of ether units in the main chain through competitive elimination of carbon dioxide,[4] despite their reactivity toward nucleophilic reagents including amines.[5] In contrast, six-membered cyclic carbonates are polymerized efficiently via ring-opening to yield the corresponding linear polycarbonates, especially under anionic conditions.[1−3] The anionic ring-opening polymerization of six-membered cyclic carbonates shows equilibrium character[2] as common heterocyclic monomers.[6] The monomers that undergo equilibrium polymerization are useful because they will be applied to chemical recycling of polymeric materials.[7]

The development of excellent methods for recycling of polymeric materials is an issue of great importance in recent polymer science and technology.[8] Chemical recycling is advantageous over other recycling methods for used polymers such as thermal recycling because only chemical recycle can regenerate raw materials from used polymers without wasting petroleum resources. With this in mind, we recently reported a cross-linking−de-cross-linking system based on anionic polymerization−depolymerization of cyclic carbonate moieties in the side chain of polystyrene derivatives.[9] This result revealed that cyclic carbonates are valuable structures in chemical recycling system of polymeric materials. By considering the significantly differing polymerizability of the five- and six-membered cyclic carbonates, a monomer involving both five- and six-membered cyclic carbonate structures may be polymerized via the selective ring-opening of the six-membered carbonate, by which a recyclable polymer carrying carbonate structures in both the main and side chains may be prepared. In this article, we describe selective anionic ring-opening polymerization of a bis(cyclic carbonate) and chemical recycling of the resulting polymers.

Experimental Section

Materials. Allylmalonic acid diethyl ester (Tokyo Kasei Kogyo Co., Inc., >98%) was distilled before use. Chloroformic acid ethyl ester (Tokyo Kasei Kogyo Co., Inc., >98%), *m*-chloroperoxybenzoic acid (MCPBA) (Tokyo Kasei Kogyo Co., Inc., >65%), 1-iodopropane (Kanto Chemical Co., Inc., >98%), lithium aluminum hydride ($LiAlH_4$) (Kanto Chemical Co., Inc., >92%), and anhydrous lithium bromide (Kanto Chemical Co., Inc., >95%) were commercially available and used as received. Triethylamine (TEA) (Kanto Chemical Co., Inc., >99%), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) (Kanto Chemical Co., Inc., >98%), and *N,N*-dimethylformamide (DMF) were distilled over CaH_2 before use. Tetrahydrofuran (THF) was distilled from sodium. Neutral silica gel for column chromatography (particle size 0.063−0.210 mm) was purchased from Kanto Chemical Co., Inc.

Measurements and Instruments. Melting points (mp) were measured on a Yanaco micro-melting point apparatus. ^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Varian INOVA-500 spectrometer in deuterated chloroform ($CDCl_3$) at ambient temperature using tetramethylsilane (TMS) as internal standard. Number-average (M_n) and weight-average (M_w) molecular weights were determined by gel permeation chromatography (GPC) using a Tosoh HLC-8120GPC, UV-8020 instrument equipped with polystyrene−gel tandem columns (Tosoh TSK gels α-2500 (7 μm, $>1 \times 10^4$ g/mol), α-3000 (7 μm, $>1 \times 10^5$ g/mol), α-4000 (10 μm, $>1 \times 10^6$ g/mol), and α-M (13 μm, $>1 \times 10^7$ g/mol)) using DMF (containing 50 mM lithium bromide and 50 mM phosphoric acid, flow rate 1.0 mL/min) as an eluent at 40 °C. Polystyrene standards were used for calibration. Fourier transform infrared (IR) spectra were measured on a Horiba FT-210 spectrometer. High-performance liquid chromatography (HPLC) was performed on a Japan Analytical Industry LC908-C60 recycling preparative HPLC instrument equipped with polystyrene−gel tandem columns (JAIGEL-1H (>1000 g/mol) and JAIGEL-2H (>5000 g/mol)). Elemental analysis was performed on a Perkin-Elmer CHNS/O 2400II analyzer.

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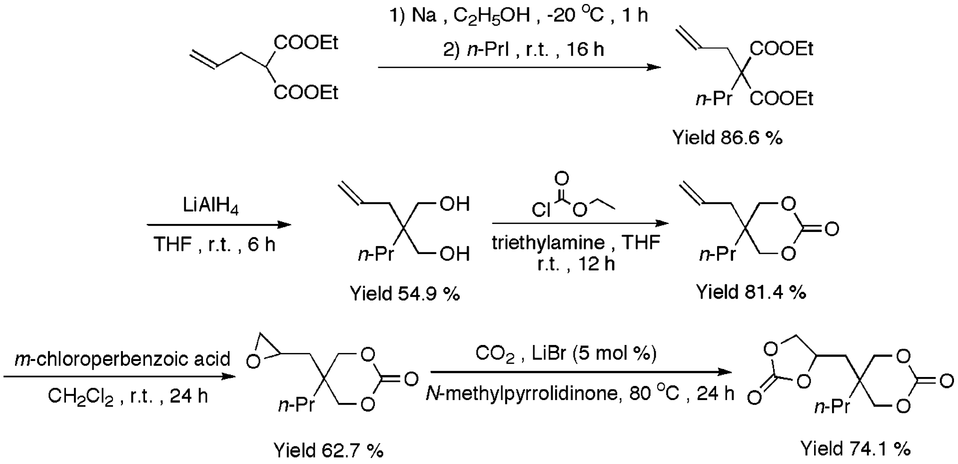
Scheme 1. Synthesis of 65CCP



Semiempirical Calculation of Ring-Opening Reaction of Disubstituted Six-Membered Cyclic Carbonates. All the calculations were performed with Parametrization Method 3 (PM3) using Spartan '04 for Windows (Wavefunction, Irvine, CA) run on a computer equipped with a Mobile Intel Pentium 4 processor (2.80 GHz). The heat of the ring-opening reaction of disubstituted six-membered cyclic carbonates with dimethyl ether was calculated from the heat of formation of each molecule whose conformation was optimized with molecular mechanics calculation.

Synthesis of the Monomer and Its Precursors. The bis(cyclic carbonate), 5-(2-oxo-1,3-dioxolan-4-yl)methyl-5-propyl-1,3-dioxan-2-one (65CCP), was prepared according to Scheme 1.

2-Allyl-2-propylmalonic Acid Diethyl Ester. Allylmalonic acid diethyl ester (24.0 g, 0.120 mol) dissolved in ethanol (35 mL) and 1-iodopropane (20.4 g, 0.120 mol) were added slowly to a solution of sodium (2.76 g, 0.120 mol) in ethanol (65 mL) at −20 °C. After the solution was stirred 15 h at room temperature, the mixture was concentrated under vacuum and then dissolved in ethyl acetate (100 mL). The solution was washed with brine (100 mL) and subsequently with aqueous potassium hydroxide (10 wt %, 50 mL) twice each. After the removal of solvents, the residual product was distilled to obtain 2-allyl-2-methylmalonic acid diethyl ester as colorless liquid in 86.6% yield (25.2 g); bp 94 °C at 4.0×10^2 Pa. ^{1}H NMR: δ 5.52−5.74 (m, 1H, C=C*H*−), 5.06−5.12 (m, 2H, C=C*H*$_2$), 4.16−4.21 (m, 4H, −OC*H*$_2$−), 2.64−2.65 (m, 2H, CH$_2$=CHC*H*$_2$−), 1.83−1.86 (m, 2H, CH$_3$CH$_2$C*H*$_2$−), 1.20−1.28 (m, 2H, CH$_3$C*H*$_2$CH$_2$−), 1.20−1.28 (m, 6H, −OCH$_2$C*H*$_3$), 0.91−0.94 (t, $J = 5.0$ Hz, 3H, −CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR: δ 171.2 (−*C*(=O)O−), 132.5 (C=*C*H−), 118.6 (C=*C*H$_2$), 61.0 (−O*C*H$_2$−), 57.3 (quaternary carbon), 36.8 (CH$_2$=CH*C*H$_2$−), 34.3 (CH$_3$CH$_2$*C*H$_2$−), 17.2 (CH$_3$*C*H$_2$CH$_2$−), 14.3 (−CH$_2$CH$_2$*C*H$_3$), 14.0 (−OCH$_2$*C*H$_3$). IR (NaCl, cm^{-1}): 1735 (−C(=O)O−).

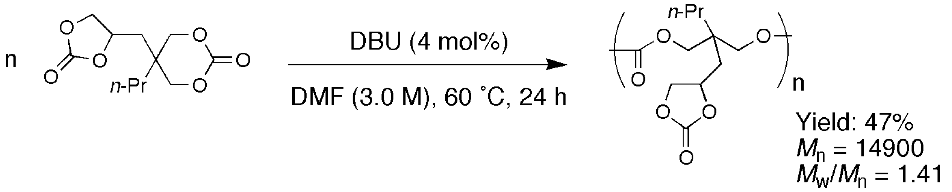
2-Allyl-2-propyl-1,3-propanediol. A solution of 2-allyl-2-propylmalonic acid diethyl ester (31.5 g, 0.130 mol) in THF (10 mL) was added dropwise to a suspension of LiAlH$_4$ (12.0 g, 0.320 mol) in THF (300 mL) at 0 °C. After the addition was completed, the mixture was refluxed for 1 h. The reaction mixture was cooled to 0 °C, and then saturated Na$_2$SO$_4$ aqueous solution was added dropwise to the mixture. The mixture was filtered and the precipitate was washed thoroughly with THF (100 mL). After the removal of solvents, the crude product was distilled to obtain 2-allyl-2-methyl-1,3-propanediol as colorless liquid in 54.9% yield (11.0 g); bp 106 °C at 2.4×10^2 Pa. ^{1}H NMR: δ 5.77−5.82 (m, 1H, C=C*H*−), 5.06−5.11 (m, 2H, C=C*H*$_2$), 3.54−3.57 (m, 4H, −C*H*$_2$OH), 3.40 (s, 2H, −OH), 2.06−2.08 (m, 2H, CH$_2$=CHC*H*$_2$−), 1.19−1.31 (4H, CH$_3$C*H*$_2$CH$_2$−, CH$_3$CH$_2$C*H*$_2$−), 0.90−0.92 (t, $J = 5.0$ Hz, 3H, C*H*$_3$−). ^{13}C NMR: δ 134.0 (C=*C*H−), 117.7 (C=*C*H$_2$), 68.3 (−*C*H$_2$OH), 41.5 (quaternary carbon), 35.5 (CH$_2$=CH*C*H$_2$−), 33.4 (CH$_3$CH$_2$*C*H$_2$−), 16.0 (CH$_3$*C*H$_2$CH$_2$−), 14.9 (*C*H$_3$−). IR (NaCl, cm^{-1}): 3356 (−OH).

5-(2-Propenyl)-5-propyl-1,3-dioxan-2-one. Ethyl chloroformate (30.5 mL, 0.320 mol) and triethylamine (44.4 mL, 0.320 mol) were added dropwise to a solution of 2-allyl-2-propyl-1,3-propanediol (25.3 g, 0.160 mol) in THF (400 mL) at 0 °C. After the solution was stirred for 12 h at room temperature, the reaction mixture was filtered and concentrated by rotary evaporation and then dissolved in ethyl acetate (150 mL). The solution was washed with aqueous hydrochloric acid (1 mol/L, 300 mL) and an adequate amount of water. After the removal of solvents, the residue was purified by silica gel column chromatography (eluent; ethyl acetate/*n*-hexane = 1/1, volume ratio) to obtain 5-(2-propenyl)-5-methyl-1,3-dioxan-2-one as colorless liquid in 81.4% yield (24.0 g). ^{1}H NMR: δ 5.68−5.75 (m, 1H, C=C*H*−), 5.16−5.22 (m, 2H, C=C*H*$_2$), 4.12−4.17 (m, 4H, −OC*H*$_2$−), 2.20−2.22 (m, 2H, CH$_2$=CHC*H*$_2$−), 1.31−1.39 (m, 4H, CH$_3$C*H*$_2$CH$_2$−, CH$_3$CH$_2$C*H*$_2$−), 0.93−0.95 (t, $J = 5.0$ Hz, 3H, C*H*$_3$−). ^{13}C NMR: δ 148.4 (−O*C*(=O)O−), 130.8 (C=*C*H−), 120.2 (C=*C*H$_2$), 74.8 (−O*C*H$_2$−), 35.0 (CH$_2$=CH*C*H$_2$−), 33.7 (CH$_3$CH$_2$*C*H$_2$−), 33.2 (quaternary carbon), 16.0 (CH$_3$*C*H$_2$CH$_2$−), 14.4 (CH$_3$−). IR (NaCl, cm^{-1}): 1751 (〉C=O).

5-Oxiranylmethyl-5-propyl-1,3-dioxan-2-one. *m*-Chloroperbenzoic acid (34.5 g, 0.200 mol) was added to a solution of 5-(2-propenyl)-5-propyl-1,3-dioxan-2-one (36.8 g, 0.200 mol) in dichloromethane (400 mL) at room temperature. After the solution was stirred 24 h, the reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent; ethyl acetate/*n*-hexane = 1/1, volume ratio) to obtain 5-methyl-5-oxiranylmethyl-1,3-dioxan-2-one as colorless liquid in 62.7% yield (25.1 g). ^{1}H NMR: δ 4.20−4.31 (m, 4H, −OC*H*$_2$−), 2.96−2.99 (m, 1H, −OC*H*〈), 2.47−2.81 (m, 2H, −OC*H*$_2$CH〈), 1.50−1.59 (m, 2H, CH$_3$CH$_2$C*H*$_2$−), 1.39−1.92 (m, 2H, −C*H*$_2$CH〈), 1.33−1.43 (m, 2H, CH$_3$C*H*$_2$CH$_2$−), 0.97−0.99 (t, $J = 5.0$ Hz, 3H, C*H*$_3$−). ^{13}C NMR: δ 148.0 (−OC(=O)O−), 75.3, 74.2 (−O*C*H$_2$−), 47.4 (−O*C*H〈), 46.2 (−O*C*H$_2$CH−), 33.9 (quaternary carbon), 33.8 (−*C*H$_2$CH〈), 33.5 (CH$_3$CH$_2$*C*H$_2$−), 16.1 (CH$_3$*C*H$_2$CH$_2$−), 16.3 (*C*H$_3$−). IR (NaCl, cm^{-1}): 1751 (〉C=O).

5-(2-Oxo-1,3-dioxolan-4-yl)methyl-5-propyl-1,3-dioxan-2-one (65CCP). A solution of 5-propyl-5-oxiranylmethyl-1,3-dioxan-2-one (4.00 g, 20.0 mmol) and lithium bromide (86.9 mg, 1.00 mmol) in *N*-methylpyrrolidinone (20 mL) was stirred for 24 h under atmospheric pressure of CO$_2$ at 80 °C. The reaction mixture was dissolved in ethyl acetate (150 mL), and the solution was washed with brine (150 mL). After the removal of solvents, the residue was purified by recrystallization from nitromethane to obtain 65CCP as colorless solid in 71.4% yield (3.49 g); mp 122 °C. ^{1}H NMR: δ 4.84−4.90 (m, 1H, −OC*H*〈), 4.05−4.64 (m, 2H, −OC*H*$_2$CH〈), 4.17−4.30 (m, 4H, −OC*H*$_2$−), 1.80−2.00 (m, 2H, −C*H*$_2$CH〈), 1.36−1.67 (m, 2H, CH$_3$CH$_2$C*H*$_2$−), 1.22−1.27 (m, 2H, CH$_3$C*H*$_2$CH$_2$−), 0.98−1.00 (t, $J = 5.0$ Hz, 3H, C*H*$_3$−). ^{13}C NMR: δ 154.0 (−O*C*(=O)O−), 147.7 (−O*C*(=O)O−), 75.9, 73.7 (−O*C*H$_2$−), 72.9 (−O*C*H〈), 69.6 (−O*C*H$_2$CH〈), 35.1 (−*C*H$_2$CH〈), 33.6 (CH$_3$-

Scheme 2. Anionic Polymerization of 65CCP (DBU = 1,8-Diazabicyclo[5.4.0]-7-undecene and DMF = *N,N*-Dimethylformamide)



CH_2CH_2-), 33.4 (quaternary carbon), 16.3 ($CH_3CH_2CH_2-$), 14.4 (CH_3-). IR (KBr, cm^{-1}): 1797 ($\rangle C{=}O$), 1743 ($\rangle C{=}O$). Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 53.90; H, 6.76.

Anionic Polymerization. Typical Procedure. All glass vessels were heated in vacuo before use, filled with dry nitrogen, and handled in a dry nitrogen stream. DBU (6.0 μL, 4.0 mol %) was added to a solution of 65CCP (0.24 g, 1.0 mmol) in DMF (3.0 M). Then, the tube was evacuated and sealed off. After the reaction mixture was stirred at 60 °C for 12 h, a few drops of acetic acid were added to the reaction mixture to quench the polymerization. The obtained polymer P(65CCP) was purified by preparative HPLC with chloroform eluent. Yield: 47%. M_n = 14 900, M_w/M_n = 1.41. ^{1}H NMR: δ 4.93–4.94 (1H, $-OCH\langle$), 4.03–4.62 (2H, $-OCH_2CH\langle$), 3.99–4.18 (m, 4H, $-OCH_2-$), 1.69–2.02 (m, 2H, $-CH_2CH\langle$), 1.37–1.50 (m, 2H, $CH_3CH_2CH_2-$), 1.26–1.35 (m, 2H, $CH_3CH_2CH_2-$), 0.93–0.96 (m, 3H, CH_3-). ^{13}C NMR: δ 154.8 ($-OC({=}O)O-$), 154.6 ($-OC({=}O)O-$), 73.8 ($-OCH\langle$), 70.2 ($-OCH_2CH\langle$), 69.6 ($-OCH_2-$), 69.3 ($-OCH_2-$), 39.8 (quaternary carbon), 36.6 ($-CH_2CH\langle$), 34.4 ($CH_3CH_2CH_2-$), 16.1 ($CH_3CH_2CH_2-$), 14.6 (CH_3-). IR (KBr, cm^{-1}): 1797 ($\rangle C{=}O$), 1743 ($\rangle C{=}O$). Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 53.82; H, 6.70.

Depolymerization of P(65CCP). A typical procedure is shown as follows. All glass vessels were heated under reduced pressure before use, filled with dry nitrogen, and handled in a dry nitrogen stream. DBU (5.97 μL, 4.0 mol %) was added to a solution of P(65CCP) (0.24 g, 1.0 mmol) in DMF (0.5 M relative to the monomer unit). Then, the tube was evacuated and sealed off. After the reaction mixture was stirred at 60 °C for 24 h, a few drops of acetic acid were added to the reaction mixture to quench the depolymerization. The monomer 65CCP was obtained by preparative HPLC using chloroform as an eluent. Conversion: 89%; yield: 86%. ^{1}H NMR (recovered 65CCP): δ 4.84–4.90 (m, 1H, $-OCH\langle$), 4.05–4.64 (m, 2H, $-OCH_2CH\langle$), 4.17–4.30 (m, 4H, $-OCH_2-$), 1.80–2.00 (m, 2H, $-CH_2CH\langle$), 1.36–1.67 (m, 2H, $CH_3CH_2CH_2-$), 1.22–1.27 (m, 2H, $CH_3CH_2CH_2-$), 0.98–1.00 (t, J = 5.0 Hz, 3H, CH_3-).

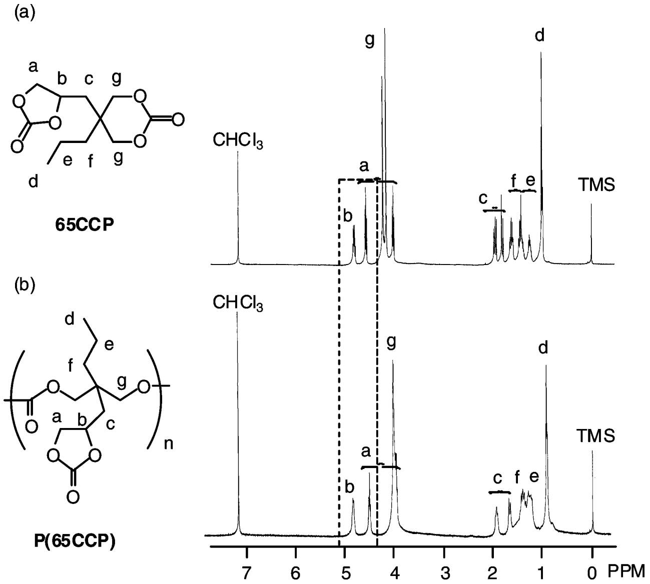


Figure 1. ^{1}H NMR spectra of 65CCP (a) and P(65CCP) (b) obtained in the anionic ring-opening polymerization (60 °C, 12 h, 3.0 M in DMF using 4 mol % of DBU).

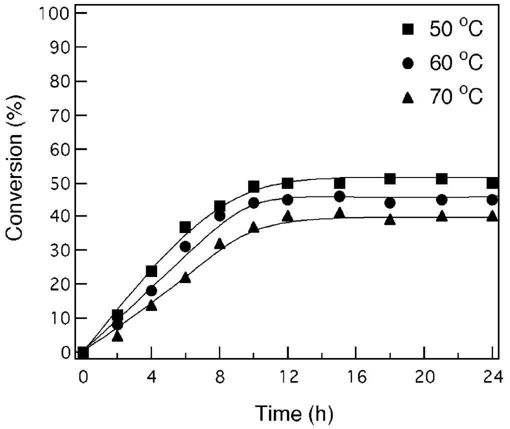


Figure 2. Relationship between time and conversion in anionic ring-opening polymerization of 65CCP initiated by 1,8-diazabicyclo[5.4.0]-7-undecene in *N,N*-dimethylformamide (3.0 M) at 50, 60, and 70 °C.

Results and Discussion

Anionic Ring-Opening Polymerization of 65CCP. Anionic ring-opening polymerization of a bifunctional carbonates (65CCP) was conducted using 4 mol % of DBU as an initiator in DMF with the initial monomer concentration ([65CCP]$_0$) of 3.0 M at 60 °C for 12 h (Scheme 2). The resulting polymer (P(65CCP)) was characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum of P(65CCP) showed that the signals assignable to the five-membered cyclic carbonate moiety remained (Figure 1). It has been reported that five-membered cyclic carbonates such as ethylene carbonate may not be polymerized below 100 °C using typical initiators.[4] The IR spectrum also showed the presence of the carbonate moieties in both the main (1743 cm^{-1}) and the side chains (1797 cm^{-1}). Since the result of elemental analysis agrees well with the theoretical value, it turned out that side reactions, such as decarboxylation which takes place in the polymerization of five-membered cyclic carbonates, have not occurred. These observations indicate that 65CCP was selectively polymerized via the anionic ring-opening of the six-membered cyclic carbonate moiety without the polymerization of the five-membered cyclic carbonate moiety.

We evaluated the equilibrium nature of the anionic polymerization of 65CCP. Figure 2 shows the time–conversion relationships in the anionic ring-opening polymerization of 65CCP with [65CCP]$_0$ of 3.0 M at 50, 60, and 70 °C. The conversions of 65CCP became constant after 10 h in every case. It was confirmed that the monomer conversion decreases with raising the polymerization temperature, as typically observed in equilibrium polymerization. The equilibrium monomer concentrations ([65CCP]$_e$) were estimated as 1.58 M (50

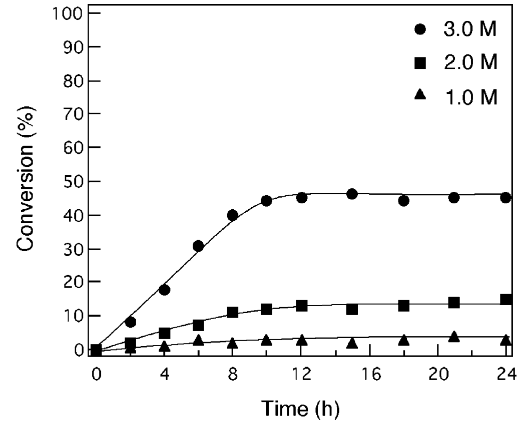


Figure 3. Relationship between time and conversion in anionic ring-opening polymerization of 65CCP initiated by 1,8-diazabicyclo[5.4.0]-7-undecene (4 mol %) at 60 °C under 1.0, 2.0, and 3.0 M of 65CCP in *N,N*-dimethylformamide.

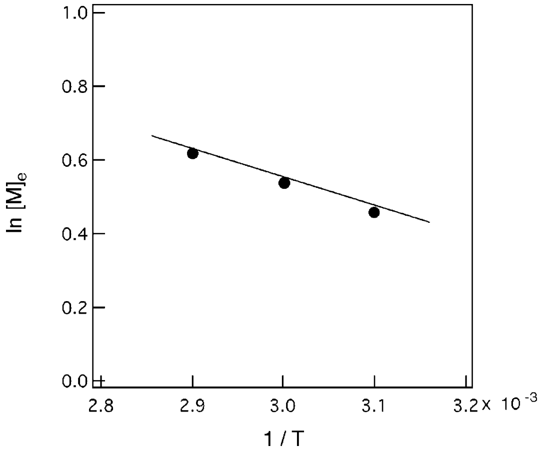


Figure 4. Relationship between ln $[M]_e$ and $1/T$ in the anionic ring-opening polymerization of 65CCP in DMF (3.0 M) with DBU (4 mol %).

°C), 1.71 M (60 °C), and 1.86 M (70 °C). In the polymerizations at 60 °C under various $[65CCP]_0$ (1.0, 2.0, and 3.0 M), it was confirmed that the conversion of 65CCP also became constant after 10 h, and $[65CCP]_e$ was estimated as 0.98 and 1.74 M for polymerizations with $[65CCP]_0$ of 1.0 and 2.0 M, respectively (Figure 3).

Dainton's equation[10] can be applied to this type of equilibrium polymerization, where T, $[M]_e$, $\Delta H_p°$, and $\Delta S_p°$ denote the polymerization temperature, monomer concentration at equilibrium, standard enthalpy, and standard entropy change for the polymerization of 65CCP in a solution, respectively (eq 1).

$$\ln [M]_e = \Delta H_p°/RT - \Delta S_p°/R \qquad (1)$$

Figure 4 indicates the relationship between the logarithms of $[M]_e$ vs reciprocal of the polymerization temperature ($1/T$). The linear relationships clearly indicate that the polymerization of 65CCP obeys Dainton's equation, supporting the equilibrium character of the polymerization. The thermodynamic parameters calculated from the plots are $\Delta H_p° = -1.80$ kcal/mol, $\Delta S_p° = -6.46$ cal/(K mol), and $\Delta G_p° = 357$ cal/mol (at 60 °C). The low $\Delta H_p°$ value may be ascribed to the relatively larger steric hindrance of the substituents whose repulsion decreases the thermodynamic stability of the poly(carbonate) chain.[11] Both $\Delta H_p°$ and $\Delta S_p°$ values for 65CCP are comparable to those for disubstituted six-membered cyclic carbonates.[11] To validate the $\Delta H_p°$ value, the heats of the ring-opening reactions (ΔH_r) of disubstituted six-membered cyclic carbonates with dimethyl ether were evaluated by semiempirical calculation at the PM3 level (Figure 5). Disubstituted six-membered cyclic carbonates are 5-methyl-5-phenyl-1,3-dioxane-2-one (MP6C) and 5-ethyl-5-phenyl-1,3-dioxane-2-one (EP6C), whose $\Delta H_p°$ values are −4.0 and −1.2 kcal/mol, respectively.[11] The orders of both the calculated ring-opening reaction and the $\Delta H_p°$ values agreed well, supporting the validity of the $\Delta H_p°$ value of 65CCP. The order of the ring-opening tendencies is postulated to depend on the order of the steric hindrance of the substituents.

The positive $\Delta G_p°$ value, indicating the ΔG_p value in the polymerization at $[65CCP]_0 = 1.0$ M at 60 °C, agrees well with the very low conversion of 65CCP (i.e., 2.4%). The ΔG_p values at other concentrations were also calculated on the basis of the following approximation (eq 2).[13]

$$\Delta G_p = \Delta H_p° - T(\Delta S_p° + R \ln[M]) \qquad (2)$$

The ΔG_p values at 2.0 and 3.0 M were calculated to be −102 and −370 cal/mol (60 °C), respectively. The negative but low ΔG_p values are responsible for the relatively lower conversions.

Depolymerization of P(65CCP). On the basis of the equilibrium nature of the polymerization, we examined the depolymerization of P(65CCP) (M_n = 20 800) with DBU (4 mol % relative to repeating unit) as a catalyst in DMF (0.50 M) at 60 °C for 24 h. The original polymers were completely transformed to oligomers and 65CCP by the nucleophilic attack of the imine nitrogen in

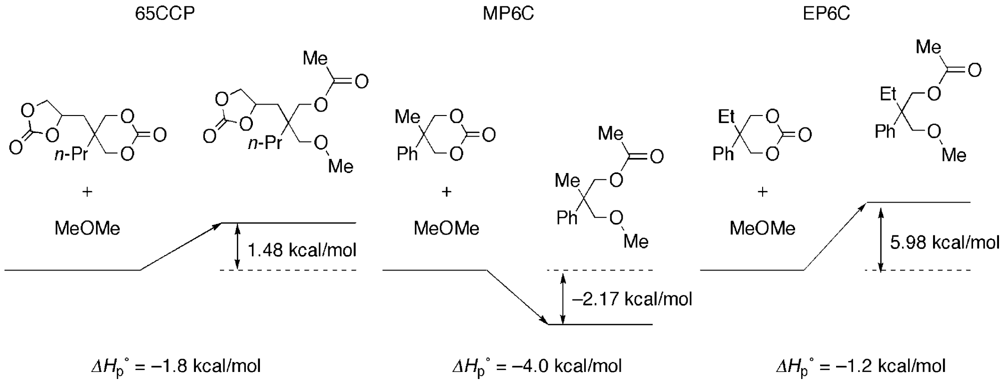
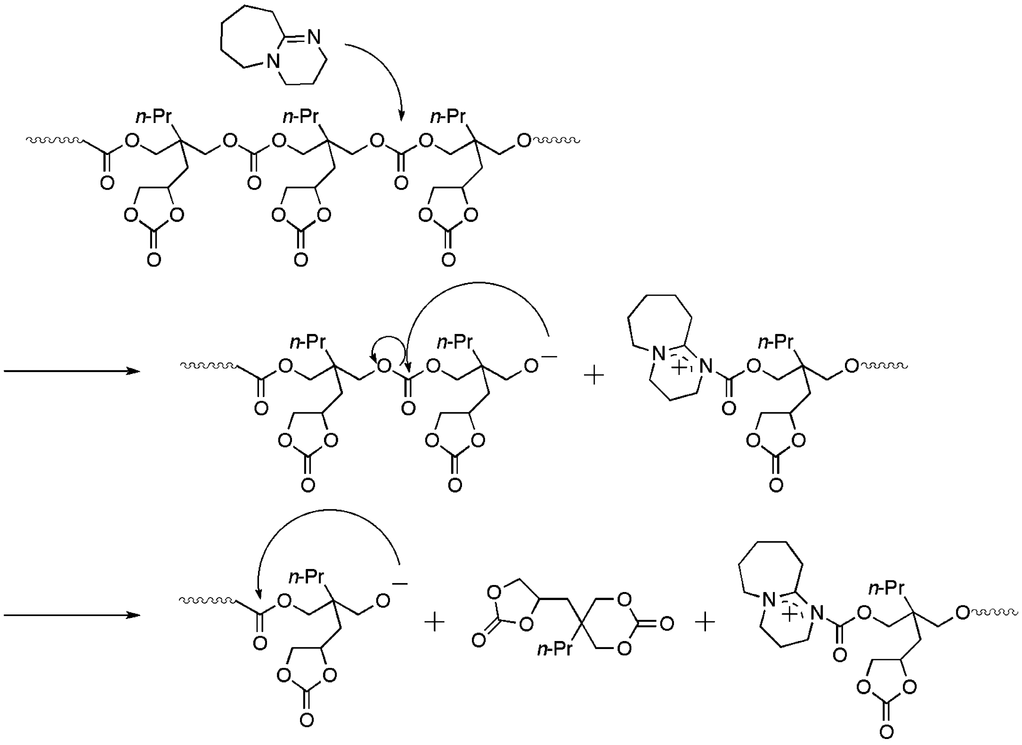


Figure 5. Heat of ring-opening reactions of disubstituted six-membered cyclic carbonates with dimethyl ether calculated by semiempirical calculation (Parametrization Method 3). The $\Delta H_p°$ values for MP6C and EP6C are cited from ref 11.

Scheme 3. Plausible Mechanism of Anionic Depolymerization of P(65CCP)



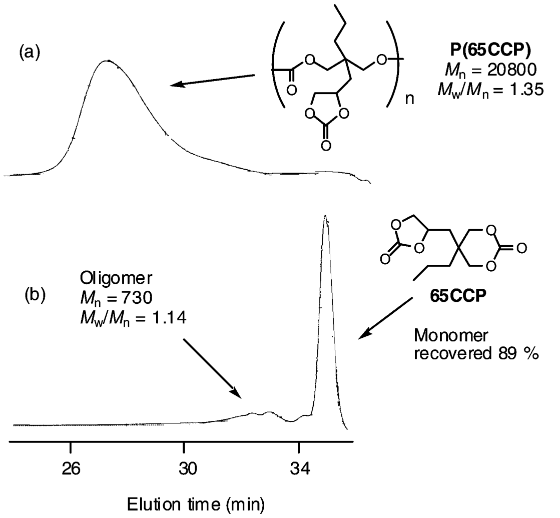


Figure 6. Gel permeation chromatography profiles of (a) P(65CCP) and (b) the reaction mixture obtained by the depolymerization of P(65CCP) at 60 °C for 24 h in DMF (0.50 M).

DBU[14] to the carbonyl group in the main chain to produce alkoxide, as shown in the GPC profiles before and after depolymerization (Scheme 3 and Figure 6). The amount of regenerated 65CCP and M_n of the resulting product reached a constant value after 15 h, and 65CCP was recovered in 86% yield. The high recovery ratio suggests that P(65CCP) depolymerizes in an unzipping manner, which is similar to common depolymerization of vinyl-type polymers. The saturation of the depolymerization ratio is ascribable to the equilibrium nature of this polymerization–depolymerization system.

Summary

In conclusion, a bifunctional cyclic carbonate 65CCP was synthesized, and its anionic ring-opening polymerization/depolymerization behavior was investigated. The anionic ring-opening polymerization of 65CCP initiated by DBU proceeds through a selective polymerization of the six-membered cyclic carbonate groups to afford a polycarbonate remaining the five-membered cyclic carbonate groups quantitatively in the side chain. The equilibrium nature enabled the effective anionic depolymerization of P(65CCP) that recovers 65CCP in high yield. Our further research is directed to application of the chemoselective depolymerization system to de-cross-linking of networked polymers obtained by reactions of the cyclic carbonate moiety in the side chain.

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