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Monomer-Isomerization Polymerization of 3-Methyl-3-(phthalimidomethyl)oxetane with Two Different Ring-Opening Courses

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ABSTRACT: The cationic polymerization of 3-methyl-3-(phthalimidomethyl)oxetane (**1**) afforded two kinds of polymers. One was a polyacetal, i.e., poly{oxy(8,9-benzo-4-methyl-7-oxo-2,6-oxazabicyclo[4.3]nona-8-ene-1,4-diyl)methylene} (**3**), produced at 50 °C and below, and the other was a polyether, i.e., poly[oxy-(2-methyl-2-phthalimidomethyltrimethylene)] (**4**), produced at 80 °C and above. This new polymerization with the two ring-opening courses was accompanied by the monomer-isomerization process of **1** to give 5,6-benzo-1-methyl-8,11,3-dioxazatricyclo[5.2.2.0^{3,7}]undeca-5-en-4-one (**2**). The cyclic acetal **2**, therefore, functioned as the real monomer, and either single or double ring-opening polymerization took place to give **3** or **4**, respectively, depending on the reaction temperature. The strain of **2** for ring-opening is discussed on the basis of the result of X-ray structure analysis. The single ring-opening process of **2** was an equilibrium polymerization having the standard enthalpy and entropy changes in dichloromethane equal to -15.8 kJ mol^{-1} and -46.0 J mol^{-1} K^{-1}, respectively, and the ceiling temperature (T_c) equal to 70.1 °C for 1 mol L^{-1} solution. The critical temperature, where the structure of the product polymer changed, was related to a T_c calculated for the conditions employed (59.1 °C for polymerization in 0.83 mol L^{-1} dichloromethane solution). Therefore, **3** was successfully transformed to **4** with a thermal latent catalyst at a higher temperature than the T_c through the ring-closure depolymerization of **3** to **2** followed by the repolymerization of **2** in the double ring-opening manner. When **1** was polymerized in a temperature step-down mode, a block copolymer with the **3**-**4** sequence was prepared from the single monomer. Moreover, **1** was copolymerized with a nonisomerizable oxetane, accompanying the monomer isomerization of **1**.

Introduction

Oxetane is still considered one of the typical monomers for cationic ring-opening polymerization,[1] although Aida et al. recently have revealed that it can be smoothly polymerized in an anionic mode.[2] Many polyethers having various pendant groups have been so far synthesized by the cationic ring-opening polymerization of the corresponding functionalized oxetanes. Because of the high nucleophilicity of the cyclic ether, the propagation of electrophilic growing species can proceed even in the presence of other functional groups such as olefin, ether, ester, ketone, nitrile, amide, imide, azo, sulfonate, as already exemplified in our work.[3,4] However, a few exceptions have been reported in the Lewis acid-catalyzed reactions of oxetanes carrying a γ-carbonyl-containing functional group at the 3-position.[5−7] Corey et al. observed the first example of ortho ester synthesis from ester-substituted oxetanes.[5a] Recently, we have found the intramolecular acetalization of cyclic imide-substituted oxetanes[6] and the chemoselective isomerization of amide-substituted oxetanes.[7] In these isomerizations, accessibility between the oxonium α-carbon atoms and the carbonyl oxygen atoms (relatively 1,6-positioned) renders the intramolecular nucleophilic attack preferable.[6] Consequently, the oxetanyl group functions as a propanediol equivalent.

As an extension of the carbonyl-assisted isomerization of oxetane, we intended to design a novel type of cationic ring-opening polymerization involving the above-mentioned neighboring group participation. As a monomer, 3-methyl-3-(phthalimidomethyl)oxetane (**1**) has been chosen. The polymerization of **1** with a Lewis acid gave two different polymers by changing the polymerization temperature. This polymerization is a noticeable example showing that geometrically isomeric polymers are selectively produced from a single monomer.[8−10] One is a polyacetal containing tetrahydro-1,3-oxazine rings in the main chain, i.e., poly{oxy(8,9-benzo-4-methyl-7-oxo-2,6-oxazabicyclo[4.3]nona-8-ene-1,4-diyl)methylene} (**3**). Thus, the main chain of **3** formally takes an alternate arrangement of the oxetanyl group and one of the carbonyl groups, although the phthalimide groups are generally regarded as nonpolymerizable groups. The other is a polyether having phthalimide pendants, i.e., poly[oxy(2-methyl-2-phthalimidomethyltrimethylene)] (**4**). Although it might be suspected that the latter polymer was produced by the usual ring-opening polymerization of **1**, this is not the case. In the present paper, we report

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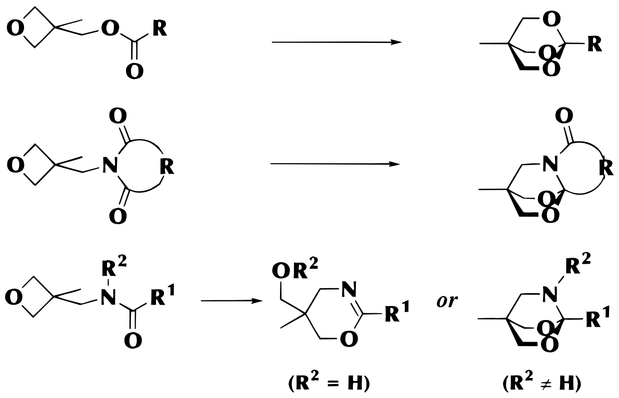
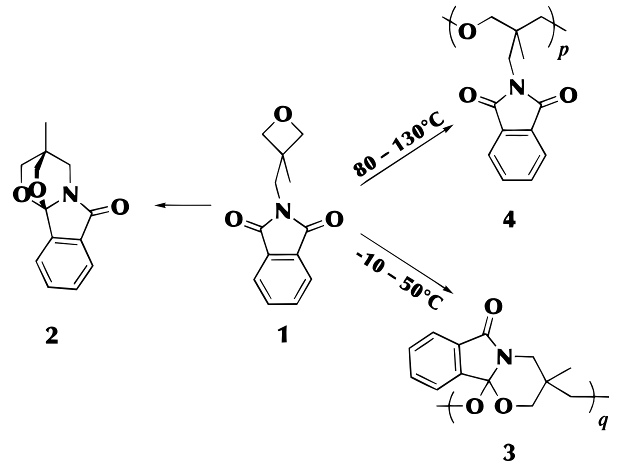
Scheme 1



Scheme 2



a detailed investigation on the synthetic and mechanistic aspects of the cationic polymerization of **1** with two different ring-opening courses.

Experimental Section

Materials. Boron trifluoride etherate ($BF_3 \cdot OEt_2$), trimethylsilyl trifluoromethanesulfonate (TMSOTf), tin(IV) chloride, and titanium(IV) chloride were purified by fractional distillation under reduced pressure in a nitrogen atmosphere. Benzylthiolanium hexafluoroantimonate (BnTA) was prepared by Endo's method:[11] 60% yield, mp 112−113 °C (lit.[11] mp 121.5−122 °C). Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) was prepared by Aida's method[12] and recrystallized from hexane under a nitrogen atmosphere: 60% yield. Trimethylaluminum (Me_3Al) in hexane, triethyloxonium tetrafluoroborate (Et_3OBF_4) in dichloromethane, and triphenylboron (BPh_3) were used as received. Anhydrous triethylamine (Et_3N) and anhydrous solvents, such as dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), deuterated chloroform ($CDCl_3$), chlorobenzene (PhCl), and toluene, were purified by the conventional methods and distilled under dry nitrogen before use.

Preparation of Oxetanes. 3-Methyl-3-(phthalimidomethyl)oxetane (1). According to our previously reported method,[4,6] **1** was prepared from 2-hydroxymethyl-2-methylpropane-1,3-diol. The overall yield after recrystallization from acetone−diethyl ether was 64% based on the starting alcohol. The crystals obtained were dried over phosphorus pentoxide (P_2O_5) under reduced pressure at 80 °C and used for polymerization. **1**: colorless needles; mp 107−109 °C; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 1.36 (s, 3H, CH_3), 3.87 (s, 2H, NCH_2), 4.35, 4.72 (each d, J 6.4 Hz, each 2H, cis and trans OCH_2 to CH_3), 7.74, 7.86 (each dd, J_1 5.4 Hz, J_2 2.9 Hz, each 2H, carbonyl *m*- and *o*-H_{Ar}); ^{13}C NMR (100.54 MHz, $CDCl_3$) δ 22.2 (CH_3), 41.6 (C-CH_3), 44.3 (NCH_2), 80.5 (t, $^1J_{CH}$ 150.7 Hz, OCH_2), 123.3 (carbonyl *o*-C_{Ar}), 131.8 (carbonyl *ipso*-C_{Ar}), 134.1 (carbonyl *m*-C_{Ar}), 168.7 (C=O); FT-IR (KBr) 1769, 1763, 1720, 1707 ($\nu_{\text{imide C=O}}$), 975, 830 cm^{-1} ($\nu_{\text{C−O}}$); HRMS found, *m/e* 231.0893 (calcd for $C_{13}H_{13}NO_3$, *m/e* 231.0896). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.60; H, 5.59; N, 5.87.

Other oxetanes, such as 3-methyl-3-(6-phthalimido-2-oxahexyl)oxetane (**6**)[4] and 3-(6-bromo-2-oxahexyl)-3-methyloxetane (**7**),[13] were prepared according to our reported methods.

6: yield 90%; colorless liquid; ^{1}H NMR ($CDCl_3$, 99.55 MHz) δ 1.30 (s, 3H, CH_3), 1.44−1.97 (m, 4H, $OCH_2(CH_2)_2CH_2N$), 3.47 (s, 2H, C−CH_2O), 3.50 (t, J 6.1 Hz, 2H, OCH_2CH_2), 3.72 (t, J 7.0 Hz, 2H, NCH_2), 4.33, 4.50 (each d, J 5.6 Hz, each 2H, cis and trans ring-OCH_2 to CH_3), 7.65−7.90 (symmetrical m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.3 (CH_3), 25.3, 26.8 ($OCH_2(CH_2)_2CH_2N$), 37.7 (NCH_2), 39.8 (C-CH_3), 70.7 (OCH_2CH_2), 76.1 (C-CH_2O), 80.1 (ring-OCH_2), 123.1 (carbonyl *o*-C_{Ar}), 132.1 (carbonyl *ipso*-C_{Ar}), 133.8 (carbonyl *m*-C_{Ar}), 168.2 (C=O); IR (neat) 1775, 1710 ($\nu_{\text{imide C=O}}$), 1115 ($\nu_{\text{acyclic COC}}$), 980, 835 cm^{-1} ($\nu_{\text{cyclic COC}}$). Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.27; H, 6.92; N, 4.62. Found: C, 67.06; H, 6.90; N, 4.59.

Poly(6). The polymer was prepared by the usual cationic ring-opening polymerization of **6** using $BF_3 \cdot OEt_2$ (5 mol %) in toluene (1.80 mol L^{-1}, 3.5 mL, 6.3 mmol) at 25 °C for 20 h: yield 85%; ^{1}H NMR ($CDCl_3$, 99.55 MHz) δ 0.86 (s, 3H, CH_3), 1.30−1.85 (br s, 4H, $OCH_2(CH_2)_2CH_2N$), 3.15 (br s, 6H, three C−CH_2O), 3.36 (br t, 2H, OCH_2CH_2), 3.67 (br t, 2H, NCH_2), 7.65−7.90 (symmetrical m, 4H, H_{Ar}); IR (neat) 1770, 1720 ($\nu_{\text{imide C=O}}$), 1100 cm^{-1} (ν_{COC}); M_n^{GPC} (PSt standards) 24500.

7: yield 62%; colorless liquid; bp 71−74 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$, 99.55 MHz) δ 1.31 (s, 3H, CH_3), 1.7−2.1 (m, 4H, $OCH_2(CH_2)_2CH_2Br$), 3.45, 3.51 (each t, J 6.6 and 5.9 Hz, each 2H, $BrCH_2$ and OCH_2CH_2), 3.47 (s, 2H, C−CH_2O), 4.35, 4.51 (each d, J 5.6 Hz, each 2H, cis and trans ring-OCH_2 to CH_3); IR (neat) 1120 ($\nu_{\text{acyclic COC}}$), 980, 835 cm^{-1} ($\nu_{\text{cyclic COC}}$). Anal. Calcd for $C_9H_{17}BrO_2$: C, 45.58; H, 7.24; Br, 33.69. Found: C, 45.77; H, 7.45; Br, 33.69.

Preparation of 5,6-Benzo-1-methyl-8,11,3-dioxazatricyclo[5.2.2.0^{3,7}]undeca-5-en-4-one (2). To a solution of **1** (8.0 g, 34.6 mmol) in anhydrous PhCl (32 mL) was added a hexane solution of Me_3Al (1.0 M, 1.7 mL) under dry nitrogen. The resulting solution was allowed to stand at 120 °C for 12 h and the reaction was quenched by adding anhydrous Et_3N (1.6 mL). The mixture was diluted with CH_2Cl_2 (50 mL) to deposit insoluble materials, which were removed by filtration. After decolorization of the filtrate with charcoal followed by evaporation, the residue was recrystallized from CH_2Cl_2−hexane to give **2**: 91% yield (7.28 g). The crystals were dried over P_2O_5 under reduced pressure at 80 °C and used for polymerization. **2**: colorless needles; mp 172−174 °C; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 0.95 (s, 3H, CH_3), 3.63 (s, 2H, NCH_2), 3.94, 4.07 (each d, J 8.3 Hz, each 2H, equatorial and axial OCH_2 with respect to a boat-type 1,3-dioxane ring), 7.44−7.53 (m, 3H, carbonyl *m*- and *p*-H_{Ar}), 7.72 (d, J 7.3 Hz, 1H, carbonyl *o*-H_{Ar}); ^{13}C NMR (100.54 MHz, $CDCl_3$) δ 15.6 (CH_3), 31.2 (C-CH_3), 49.3 (NCH_2), 74.0 (t, $^1J_{CH}$ 150.8 Hz, OCH_2), 101.2 (acetal-C), 121.8 (acetal *p*-C_{Ar}), 123.2 (carbonyl *o*-C_{Ar}), 130.5 (acetal *o*-C_{Ar}), 132.0 (carbonyl *p*-C_{Ar}), 132.9 (acetal *ipso*-C_{Ar}), 139.6 (carbonyl *ipso*-C_{Ar}), 163.9 (C=O); FT-IR (KBr) 1721, 1711 ($\nu_{\text{lactam C=O}}$), 1132, 1055−968 cm^{-1} (ν_{acetal}); HRMS found, *m/e* 231.0885 (calcd for $C_{13}H_{13}NO_3$, *m/e* 231.0896). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.29; H, 5.73; N, 5.98.

Polymerization of 1 or 2 by Lewis Acid. Typically, a 25-mL tube equipped with a three-way stopcock, containing **1** or **2** (0.5 g, 2.2 mmol) as a monomer, was repeatedly evacuated and filled with dry nitrogen. To the tube were charged an anhydrous solvent and a solution of a catalyst (0.11 mmol) by syringes in a nitrogen stream, and the resulting solution was allowed to stand at an appropriate temperature. After the reaction was quenched by adding anhydrous Et_3N (0.1 mL), the mixture was diluted with CH_2Cl_2 (10 mL). When insoluble materials separated, they were removed by filtration and then the solvent(s) was evaporated to dryness. A small amount of the residue was subjected to ^{1}H NMR and gel permeation chromatography (GPC) analyses to determine the product ratio and average molecular weights (M_n and M_w) of the produced polymer, respectively. Usually, the polymer was separated by short column chromatography on EM Aluminiumoxid 90 (70−230 mesh ASTM) using ethyl acetate as an eluent and dried over P_2O_5 under reduced pressure at 80 °C. The isolated polymers, if necessary, were further purified by reprecipitation from concentrated $CHCl_3$ solutions with diethyl ether to give white powders, but low molecular weight parts were lost to a substantial extent. The polymers having M_ns more than ca. 3000 were chosen as analytical samples.

Poly{oxy(8,9-benzo-4-methyl-7-oxo-2,6-oxazabicyclo[4.3]nona-8-ene-1,4-diyl)methylene} (3): ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 0.7−1.1 (br s with fine splitting, 3H, CH_3), 2.6−3.8 (m, 4H, OCH_2), 3.9−4.5 (m, 2H, NCH_2), 7.3−7.9 (m, 4H, H_{Ar}); ^{13}C NMR (100.54 MHz, $CDCl_3$) δ 18.1 (CH_3), 33.6 (C-CH_3), 41.4 (NCH_2), 65.1 and 67.9 (OCH_2), 105.5 (acetal-C), 121.8 (carbonyl *o*-C_{Ar}), 123.2 (acetal *p*-C_{Ar}), 130.5 (acetal *o*-C_{Ar}), 131.9 (acetal *ipso*-C_{Ar}), 132.4 (carbonyl *p*-C_{Ar}), 140.8 (carbonyl *ipso*-C_{Ar}), 165.1 (C═O), values denote the chemical shifts where the signals with fine splitting centered; FT-IR (KBr) 1719 ($\nu_{\text{lactam C=O}}$), 1408 (ν_{C-N}), 1070−1000 cm^{-1} (ν_{C-O}); UV λ_{max} in nm [tetrahydrofuran (THF)] (log ϵ in L mol^{-1} cm^{-1}) 244 (1.50), 251 (1.48).

Poly[oxy(2-methyl-2-phthalimidomethyltrimethylene)] (4): ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 0.77 (s-like with fine splitting, 3H, CH_3), 3.13 (s, 4H, OCH_2), 3.58 (s, 2H, NCH_2), 7.60 (s-like with fine splitting, 2H, carbonyl *m*-H_{Ar}), 7.72 (s-like with fine splitting, 2H, carbonyl *o*-H_{Ar}); ^{13}C NMR (100.54 MHz, $CDCl_3$) δ 18.3 (CH_3), 42.0 (C-CH_3), 42.7 (t, $^1J_{CH}$ 140.7 Hz, NCH_2), 75.1 (t, $^1J_{CH}$ 142.5 Hz, OCH_2), 123.0 (carbonyl *o*-C_{Ar}), 132.1 (carbonyl *ipso*-C_{Ar}), 133.6 (carbonyl *m*-C_{Ar}), 168.6 (C═O); FT-IR (KBr) 1775, 1717 ($\nu_{\text{imide C=O}}$), 1393 (ν_{C-N}), 1120−1070 cm^{-1} (ν_{C-O}); UV λ_{max} in nm (THF) (log ϵ in L mol^{-1} cm^{-1}) 291 (1.18), 299 (1.14).

Polymerization of 1 in an NMR Sample Tube. The polymerization was carried out in an evacuated NMR sample tube of 5-mm diameter under dry nitrogen. To the tube containing **1** (125 mg, 0.54 mmol) was added anhydrous $CDCl_3$ (0.5 mL), and the solution was chilled to −30 °C. Then, a $CDCl_3$ solution of $BF_3{\cdot}OEt_2$ (0.06 mL, 0.027 mmol) was added at −30 °C, whereupon neither isomerization nor polymerization took place. The resulting mixture was rapidly heated in an NMR probe thermostated at 25 °C, and the reaction progress was followed by periodically taking the ^{1}H NMR spectrum at this temperature.

Transformation of 3 to 4. Oligomer-freed **3** (M_n 5030, M_w/M_n 2.34, the lowest molecular weight > ca. 2000), purified by reprecipitation from a $CHCl_3$ solution with diethyl ether, was thoroughly dried over P_2O_5 under reduced pressure at 80 °C. To a 25-mL tube equipped with a three-way stopcock, containing **3** (0.25 g, 1.1 mmol as monomer unit) and BnTA (22.5 mg, 0.054 mmol), was added anhydrous PhCl (1.0 mL) by a syringe in a nitrogen stream. The resulting solution was allowed to stand at 130 °C for 24 h. After the addition of anhydrous Et_3N (0.1 mL), the solvents were removed by evaporation to leave **4** quantitatively. The newly produced polymer was analyzed by IR, ^{1}H NMR, and GPC (M_n 1540, M_w/M_n 1.53).

Two-Stage Polymerization of 1. The two-stage polymerization was carried out temperature-stepwise in a 2-fold scale (**1**, 1.0 g) of the above-mentioned polymerization. After the first-stage polymerization with TMSOTf in PhCl at 0 °C was run for 24 h, an aliquot of the reaction mixture was taken out and placed into a small amount of anhydrous Et_3N by a syringe in a dry nitrogen stream. The evaporated sample was subjected to IR, ^{1}H NMR, and GPC analyses to determine the yield, structure, M_n, and M_w of the initially produced polymer. Then, the second stage was continued at 130 °C, and meanwhile aliquots of the polymerization mixture were periodically taken out and put into anhydrous $CDCl_3$. The prepared samples were immediately subjected to ^{1}H NMR analysis using a presaturation method for removing the strong solvent signals due to the PhCl.

Likewise, the temperature step-down polymerization of **1** with BnTA in PhCl was carried out, i.e., at 130 °C for 15 min and then at 25 °C for 3 days.

Copolymerization of 1 and 7. The copolymerization of **1** and **7** in a feed mole ratio of 1:1 was carried out using 5 mol % of $BF_3{\cdot}OEt_2$ in PhCl at 25 °C for 4 days, to give a copolymer composed of the **3** unit and ring-opened **7** unit in a mole ratio of 0.34:0.66. The conversions of **1** and **7** were 36% and 85%, respectively.

Hydrolysis of Acetalic Products. When a polymer mixture of **3** and **4** or a copolymer composed of both structural units was produced, a small amount of the crude products was treated with a few drops of 1 mol L^{-1} hydrochloric acid in THF (5 mL). After 12 h at 25 °C, the solvents were evaporated to dryness. During this procedure, **3** (units) was quantitatively cleaved to 2-methyl-2-(phthalimidomethyl)propane-1,3-diol (**5**). If the crude products contained **2**, it was also hydrolyzed to **5**.[6] The content of **4** remaining unchanged in the resulting residue was determined by ^{1}H NMR, and the samples before and after the hydrolysis were subjected to GPC analysis to examine the change in their M_ns and M_w/M_ns.

5: colorless plates; mp 117−118 °C (CH_2Cl_2−carbon tetrachloride); ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 0.88 (s, 3H, CH_3), 3.38, 3.49 (each dd-like, J_1 11.1 Hz, J_2 7.2 and 5.9 Hz, each 2H, OCH_2), 3.53 (dd-like overlapping OCH_2 signals, J_1 7.2 Hz, J_2 5.9 Hz, 2H, OH), 3.82 (s, 2H, NCH_2), 7.78, 7.89 (each dd, J_1 5.4 Hz, J_2 2.9 Hz, each 2H, carbonyl *m*- and *o*-H_{Ar}); ^{13}C NMR (100.54 MHz, $CDCl_3$) δ 17.9 (CH_3), 40.4 (NCH_2), 42.2 (C-CH_3), 67.6 (t, $^1J_{CH}$ 143.4 Hz, OCH_2), 123.7 (carbonyl *o*-C_{Ar}), 131.6 (carbonyl *ipso*-C_{Ar}), 134.8 (carbonyl *m*-C_{Ar}), 170.0 (C═O); FT-IR (KBr) 3403 (ν_{OH}), 1769, 1703, 1692 ($\nu_{\text{imide C=O}}$), 1056, 1032 cm^{-1} (ν_{C-O}); HRMS found, *m/e* 249.1017 (calcd for $C_{13}H_{15}NO_4$, *m/e* 249.1002). Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.67; H, 6.22; N, 5.44.

Crystallography of 2. A single crystal of **2** (approximate dimensions, 0.34 × 0.25 × 0.43 mm) grown from acetone was used for the unit-cell determinations and the data collections of a Rigaku AFC-5R four-circle diffractometer controlled by the MSC/AFC program package, using graphite-monochromated Mo Kα radiation (λ 0.71069 Å) in the $2\theta-\omega$ scan mode. Crystal data of **2**: $C_{13}H_{13}NO_3$; FW 231.10; orthorhombic, space group $P2_12_12_1$, Z 4 with a 10.1154(9) Å, b 18.521(2) Å, c 6.081(2) Å; V 1139.3(3) Å^3, and D_{calc} 1.348 g cm^{-3}. All calculations were performed using the TEXSAN TEXRAY crystallographic software package of Molecular Structure Corp., and the structure was solved by the SIR program.[14] The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located from the difference Fourier map and refined with isotropic temperature factors. The final R and R_w factors after full-matrix least-squares refinements were 0.045 and 0.052, respectively, for 1076 observed reflections [$I > 3.0\sigma(I)$]. Fractional atomic coordinates for all the atoms and their thermal parameters are given in Table 1.

Measurements. Gel permeation chromatography (GPC) was performed on a Shimadzu LC-10A high-speed liquid chromatography system equipped with a differential refractometer and a UV detector operated at 310 nm, using THF as eluent with a flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes. Infrared spectra were recorded on a JASCO model FT/IR-3 or A-202 infrared spectrometer using a KBr disk method. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ using TMS as an internal standard on a JEOL JNM GX-400 NMR or JEOL JNM FX-100S spectrometer.

Results and Discussion

Preparation of Monomers: 1 and 2. The oxetane phthalimide (**1**) was prepared from 2-hydroxymethyl-2-methylpropane-1,3-diol through several steps, according to our previously reported method.[4,6] The overall yield was 64% based on the starting alcohol. The other monomer was bicyclic acetal (**2**), which was prepared in 91% yield by the Lewis acid-catalyzed isomerization of **1**.[6] The excellent catalyst was trimethylaluminum, in that the reaction was accompanied by no polymerization of **1**. These monomers were colorless crystals and

Table 1. Fractional Atomic Coordinates and Isotropic Thermal Parameters of 2[a,b]

atom[c]	x	y	z	B_{eq}, Å^2
O(1)	0.5289(3)	0.0103(1)	0.3848(6)	5.2(2)
O(2)	0.2515(2)	0.1328(2)	0.8120(4)	3.7(1)
O(3)	0.3393(2)	0.2125(1)	0.5628(4)	3.3(1)
N(1)	0.3715(3)	0.0890(2)	0.5125(5)	3.2(1)
C(1)	0.0328(5)	0.1308(3)	0.3060(8)	4.2(2)
C(2)	0.1597(3)	0.1352(2)	0.4400(6)	2.8(1)
C(3)	0.2571(4)	0.0759(2)	0.3742(7)	3.3(2)
C(4)	0.4931(4)	0.0578(2)	0.5119(7)	3.4(2)
C(5)	0.5676(3)	0.0924(2)	0.6932(7)	3.3(2)
C(6)	0.4889(3)	0.1444(2)	0.7911(6)	2.9(2)
C(7)	0.3589(3)	0.1469(2)	0.6735(6)	2.7(1)
C(8)	0.2285(4)	0.2075(2)	0.4113(7)	3.3(2)
C(9)	0.1295(4)	0.1278(2)	0.6843(7)	3.5(2)
C(10)	0.6944(4)	0.0780(2)	0.769(1)	4.6(2)
C(11)	0.7382(5)	0.1172(2)	0.9493(9)	4.9(2)
C(12)	0.6595(4)	0.1686(3)	1.0483(8)	4.5(2)
C(13)	0.5328(4)	0.1833(2)	0.9716(7)	3.7(2)
H(1a)	−0.013(4)	0.084(2)	0.338(8)	5(1)
H(1b)	0.048(4)	0.133(2)	0.147(8)	5(1)
H(1c)	−0.034(5)	0.165(2)	0.346(8)	6(1)
H(3a)	0.221(4)	0.026(2)	0.410(7)	4(1)
H(3b)	0.281(3)	0.079(2)	0.216(7)	3.0(8)
H(8a)	0.163(3)	0.249(2)	0.452(6)	2.9(8)
H(8b)	0.260(4)	0.215(2)	0.260(7)	3.3(8)
H(9a)	0.087(4)	0.084(2)	0.716(8)	4(1)
H(9b)	0.066(4)	0.172(2)	0.731(7)	5(1)
H(10)	0.743(5)	0.037(2)	0.717(9)	6(1)
H(11)	0.832(5)	0.107(2)	1.00(1)	6(1)
H(12)	0.692(5)	0.195(3)	1.174(8)	7(1)
H(13)	0.476(3)	0.220(2)	1.034(6)	3.2(8)

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit. [b] The hydrogen atoms were located from a difference Fourier map and refined as independent isotropic atoms. [c] Numberings of all atoms are given in Figure 1.

were used for polymerization after purification by recrystallization. The above yields were those after recrystallization.

The structures of **1** and **2** were well-characterized from the ^{1}H and ^{13}C NMR, IR, high-resolution mass spectra, and the analytical data. Additionally, the stereostructure of **2** was analyzed by X-ray crystallography. The ORTEP view of **2** and the bond lengths and angles of significance are shown in Figure 1, which indicates that the five-membered lactam ring is in almost planar geometry.

Monomer-Isomerization Polymerization of 1. The results of the polymerization of **1** with Lewis acids, alkylating or silylating agents (Et_3OBF_4, BnTA, and TMSOTf), and a Brϕnsted acid (*d*-camphorsulfonic acid) as catalysts (5 mol % to **1**) are summarized in Table 2. The cationic and proton catalysts all caused more or less polymerization. *d*-Camphorsulfonic acid and metal chlorides such as $SnCl_4$ and $TiCl_4$ were less suitable because of their poor catalytic activity and/or a competitive nucleophilic ring opening by the chloride anion.[15] The polymerization proceeded at various temperatures from −10 to 130 °C, although no reaction took place at −30 °C and below. Interestingly, the polymerizations under different conditions resulted in either of two geometrically isomeric polymers, polyacetal **3** or polyether **4**. The former was very sensitive toward moisture in the presence of an acid; therefore, it was isolated after neutralizing the acid catalyst with anhydrous triethylamine. In most cases, **3** and **4** had low number-averaged molecular weights (M_n) below 1500. However, the substantially high M_ns of **3** were obtained in the polymerization using toluene or chlorobenzene as a solvent, although these reaction systems became heterogeneous after moderate conversions. In addition, the cycloacetalized isomer of **1**, i.e., 5,6-benzo-1-methyl-8,11,3-dioxazatricyclo[5.2.2.0^{3,7}]undeca-5-en-4-one (**2**),[6] was always formed together with the polymer products.

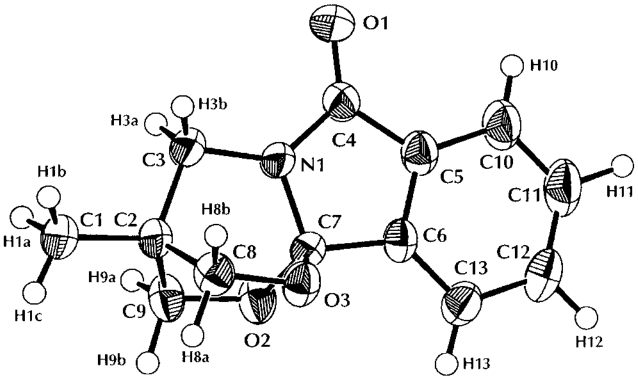


Figure 1. ORTEP view of **2** with the atom-numbering scheme. The non-hydrogen atoms are represented by 30% probability thermal ellipsoids. Selected bond lengths (l/Å) and angles (ϕ/deg) are as follows: O2−C7 1.399(4), O2−C9 1.461(4), O3−C7 1.403(4), O3−C8 1.453(4), C3−H3a 1.02(4), C3−H3b 1.00(4), C8−H8a 1.04(4), C8−H8b 0.98(4), C9−H9a 0.94(4), C9−H9b 1.08(4), O2−C7−O3 109.9(3), C3−N1−C4 130.4(3), C3−N1−C7 116.3(3).

Inspection of the polymerization conditions employed seemed to suggest the strong influence of the reaction temperature on the polymer structure. To investigate the temperature effect, the polymerization of **1** was carried out at various temperatures using TMSOTf, which exhibited good catalytic activity over a wide temperature range. The results are depicted in Figure 2. The polymer produced at temperatures below 50 °C was identified as **3**, the yield of which increased with a decrease of the reaction temperature. In contrast, **4** was produced at 80 °C and above, and the yield increased with an increase of the reaction temperature. In a thermal boundary region from 60 to 70 °C, polymers composed of both units were produced and the yields became minimal.

The polymer structures of **3** and **4** were determined by IR and ^{1}H and ^{13}C NMR spectroscopic techniques. The structural difference between them was best characterized by the IR spectra. The adsorption pattern of **3** shown in the top of Figure 3 closely resembled that of **2**.[6] Thus, a single carbonyl stretching band at 1719 cm^{-1} was ascribed to the lactam carbonyl groups of **3**. In sharp contrast, two carbonyl stretching bands appeared at 1775 and 1717 cm^{-1} (the bottom spectrum), originating from the imide pendant groups of **4**. In addition, the C−O stretching region from 1000 to 1150 cm^{-1} was informative of the structure of main chain, in that the acetalic linkage for **3** changed into an ether linkage for **4**. In fact, **3** was easily hydrolyzed with a trace amount of dilute hydrochloric acid to give 2-methyl-2-(phthalimidomethyl)propane-1,3-diol (**5**) quantitatively, whereas **4** was stable under these hydrolytic degradation conditions.

The ^{1}H and ^{13}C NMR spectra of **3** and **4** are shown in Figures 4 and 5, respectively. The very simple ^{1}H−^{13}C hetero COSY spectrum of **4** clearly supported the expected chemical structure. The signal assignment is consistent with that of an analogous polyether prepared by the usual cationic ring-opening polymerization of 3-methyl-3-(6-phthalimido-2-oxahexyl)oxetane (**6**). On the other hand, the ^{1}H NMR spectrum of **3** is rather complicated, but it at least indicates that **3** contains

Table 2. Monomer-Isomerization Polymerization of 1 with Two Ring-Opening Courses

run no.	catalyst[a]	solvent[b]	temp, °C	time, h	yield, %[c] 1	2	polymer	polymer structure[d]	M_n[e] (MWD)[f]
1	BF_3·OEt_2	CH_2Cl_2	25	24	0	54	46	**3**	850 (1.59)
2	BF_3·OEt_2	CH_2Cl_2	0	48	0	29	71	**3**	1090 (1.63)
3	BF_3·OEt_2	CH_2Cl_2	−10	72	0	18	82	**3**	1270 (1.59)
4	BF_3·OEt_2	$CHCl_3$	25	24	0	53	47	**3**	810 (1.48)
5	BF_3·OEt_2	PhCl	25	24	0	45	55	**3**	13.9 × 10^3 (1.85)
6	BF_3·OEt_2	$PhCH_3$	25	24	0	28	72	**3**	26.2 × 10^3 (1.66)
7	Et_3OBF_4	CH_2Cl_2	0	72	0	40	60	**3**	1130 (1.55)
8	Et_3OBF_4	PhCl	130	12	0	63	37	**4**	710 (1.27)
9	$SnCl_4$	PhCl	0	24	85	9	3		
10	$SnCl_4$	PhCl	110	12	0	32	60	**4**	1050 (1.38)
11	$TiCl_4$	PhCl	25	24	40	31	27	**3**	530 (1.42)
12	$TiCl_4$	PhCl	130	12	0	72	14		350 (1.12)
13	BnTA[g]	PhCl	130	10	0	19	81	**4**	1370 (1.53)
14	*d*-CSA[h]	CH_2Cl_2	25	72	6	47	47	**3**	790 (1.36)
15	*d*-CSA[h]	PhCl	130	24	24	68	8		470 (1.10)
16	TMSOTf[i]	CH_2Cl_2	25	2	0	57	43	**3**	880 (1.28)
17	TMSOTf[i]	PhCl	70	24	0	86	14	**3** + **4**	700 (1.36)
18	TMSOTf[i]	PhCl	130	12	0	54	46	**4**	580 (1.14)

[a] Five mole percent of each initiator was used per 0.5 g (2.2 mmol) of **1**. [b] $[\mathbf{1}]_0 = 0.83$ mol L^{-1}. [c] Determined by ^1H NMR. [d] Determined by IR. [e] Calibrated by polystyrene standards. [f] Molecular weight dispersion. [g] Benzylthiolanium hexafluoroantimonate. [h] *d*-Camphorsulfonic acid. [i] Trimethylsilyl trifluoromethanesulfonate.

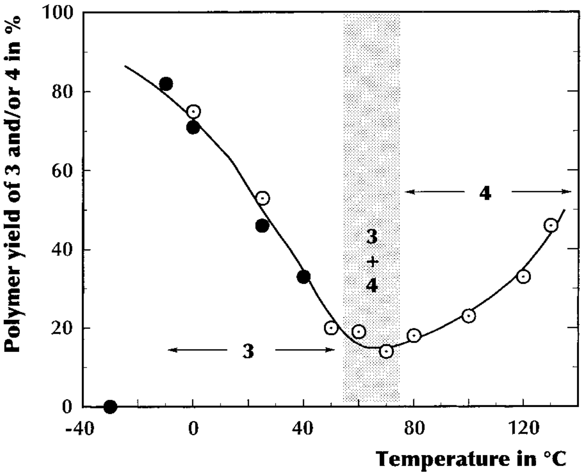


Figure 2. Effect of the reaction temperature on the yield and structure of the polymer obtained in the polymerization of **1** with TMSOTf: (○) in PhCl; (●) in CH_2Cl_2; The other conditions are denoted in the legend of Table 2. **3** and **4** were produced below 50 °C and above 80 °C, respectively. Polymers formed in the thermal boundary (shadowed) consisted of both units.

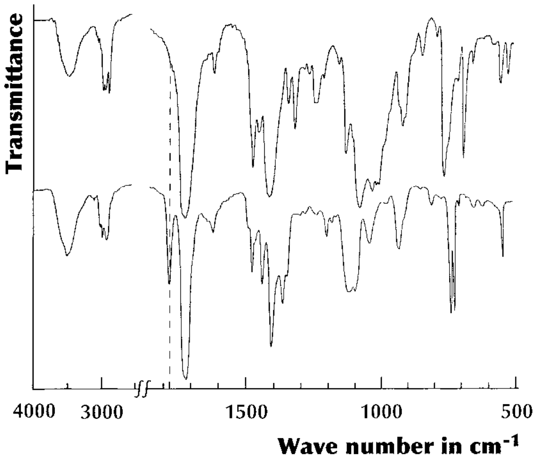


Figure 3. IR (KBr) spectra of the polymers **3** (top) and **4** (bottom).

unsymmetrically substituted aromatic rings. The signal assignment was made by comparing it to the spectrum of **2**.[6] The fully decoupled carbon signals of **3** split finely, although the examined sample was free from oligomeric parts and had a substantially high M_n of ca. 5000. This phenomenon might be caused by the variety of stereosequences between the repeating units of **3**, because two asymmetric quaternary carbons are expected in the postulated repeating structure. The carbon signals of **3** were assigned on the basis of the DEPT (distortionless enhancement by polarization transfer) spectrum shown in the middle of Figure 4.

The Fate of 2: Polymerization of 1 in an NMR Tube. From the above-mentioned results, **1** was found to bring about two routes of polymerizations leading to **3** and **4**, as well as isomerization to **2**. These three processes were not competitive, since either **3** or **4** was individually produced in most cases and the yields continued to increase after **1** was consumed. To investigate in more detail the fate of **2**, the reaction progress of **1** with BF_3·Et_2O in deuterated chloroform at 25 °C was followed by ^1H NMR. The product distribution observed periodically is plotted in Figure 6. As can be seen from Table 2 (runs 1 and 4), almost no solvent effect on the overall reaction was observed between dichloromethane and chloroform. The isomerization of **1** proceeded rapidly at the beginning of the reaction, and then the cycloacetalized **2** was gradually converted into **3**. These results clearly indicate that **2** is the real monomer common to both polymerizations, leading to **3** and **4**. Therefore, **3** and **4** are the products in the single and double ring-opening polymerization of **2**, respectively.

Thus, the polymerization was carried out using **2** in place of **1** as a feed monomer. Indeed, the results were very similar to those of the polymerization started from **1**, as shown in Table 3. Namely, **3** was produced at 0 °C and below, while **4** was yielded at 130 °C (runs 19 and 22). Unlike **1**, however, **2** brought about the single ring-opening polymerization even at −30 °C, and a quantitative yield of **3** was observed at −78 °C (runs 20 and 21). The reason no polymerization of **1** took place below −30 °C is that the isomerization of **1** to **2** did not proceed at such low temperatures. Increased reaction temperatures, at least −10 °C, would be required to attain a reasonable isomerization rate.

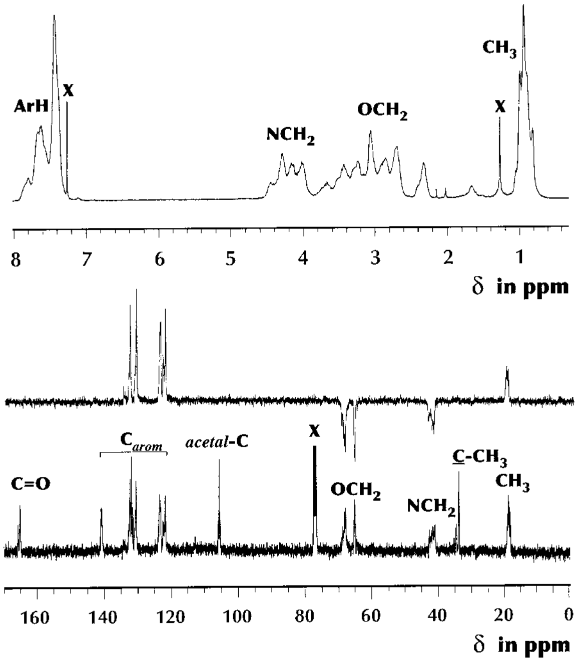


Figure 4. ^{1}H and ^{13}C NMR spectra of the polymer **3** in $CDCl_3$: 400-MHz ^{1}H (top); 100-MHz ^{13}C DEPT ($\theta = 3/4\pi$) (middle); 100-MHz ^{13}C BBD (bottom).

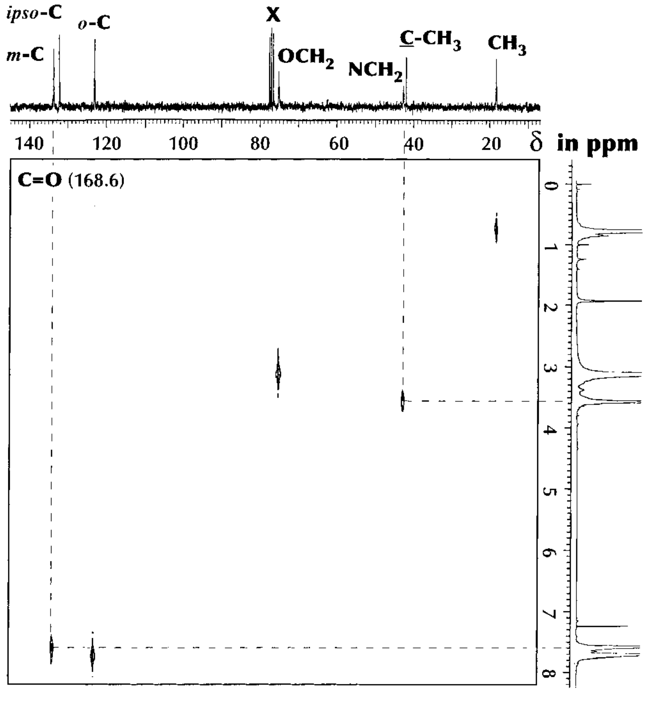


Figure 5. ^{1}H−^{13}C COSY spectra of the polymer **4** in $CDCl_3$.

On the basis of the observed yields in Figure 6, the pseudo-first-order rate constant of isomerization of **1** (k_i) and the initial rate constant of single ring-opening polymerization of **2** ($k_{p(app)}$) were estimated to 8.7×10^{-4} and 2.8×10^{-5} s^{-1}, respectively. The broken curves represent the yields calculated from these rate constants. The observed yields are in good agreement with the calculated ones up to 200 min, after which, however, they begin to deviate. Experimentally, the formation of **3** gradually slowed as the reaction time progressed, and the yield no longer changed after 24 h.

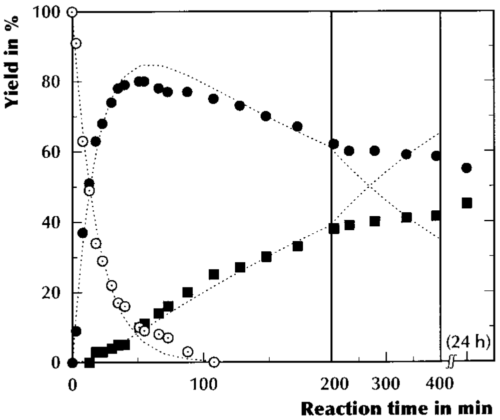


Figure 6. Time−yield plots in the polymerization of **1** with $BF_3 \cdot OEt_2$ in $CDCl_3$ at 25 °C [**1** (125 mg, 0.54 mmol), $BF_3 \cdot OEt_2$ (0.06 mL of 0.43 mol L^{-1} in $CDCl_3$, 0.027 mmol), $CDCl_3$ (0.5 mL)]: (○) **1**; (●) **2**; (■) **3**. The broken curves represent the calculated yields based on the pseudo-first-order rate constant of isomerization of **1**, $k_i = 8.7 \times 10^{-4}$ s^{-1}, and the initial rate constant of single ring-opening polymerization of **2**, $k_{p\,(app)} = 2.8 \times 10^{-5}$ s^{-1}.

Equilibrium Polymerization of 2. As can be seen from Figure 2 and Table 3, the polymerization of **1** or **2** at low temperatures from 50 to −78 °C always gave **3**. In these cases, characteristic behavior was observed in support of an equilibrium polymerization. The final yield of **3** was independent of the reaction time but increased with a decrease of temperature. To investigate the influence of the reaction temperature on the yield of **3**, the polymerization of **1** with $BF_3 \cdot OEt_2$ in dichloromethane was performed for a few days to attain equilibrium. The ^{1}H NMR spectra of the reaction mixtures revealed that no unreacted **1** remained in all cases and that the products were **2** and **3** only. After the complete consumption of **1**, therefore, the following stoichiometric balance is satisfied

$$[\mathbf{2}] = [\mathbf{1}]_0 - [\mathbf{3}] = [\mathbf{1}]_0 \frac{100 - \mathrm{CY}_3}{100} \qquad (1)$$

where $[\mathbf{1}]_0$ and CY_3 are the initial concentration of **1** and the percent yield of **3**, respectively. By assuming $[\mathbf{2}]_0 = [\mathbf{1}]_0$, the following Dainton's equation[16] should be expressed by the term of the concentration of **2**

$$\ln\,[\mathbf{2}]_e = \Delta H^\circ_{ss}/RT - \Delta S^\circ_{ss}/R \qquad (2)$$

where $[\mathbf{2}]_e$, T, ΔH°_{ss}, and ΔS°_{ss} are the concentration of **2** at equilibrium, the polymerization temperature in K, and the standard enthalpy and entropy changes in solution, respectively. The Dainton's plots illustrated in Figure 7 gave a good linear correlation between ln $[\mathbf{2}]_e$ and T^{-1}. In addition, when **1** was polymerized at 0 °C for 24 h and then the resulting mixture was warmed at 35 °C, approximately half of the **3** produced at 0 °C back to **2**. The resulted concentration of **2** is in fair agreement with $[\mathbf{2}]_e$ at 35 °C predicted from the straight line, as shown in Figure 7. These results clearly indicate that **2** is equilibrated with **3** via ring-opening polymerization and ring-closure depolymerization. Such an equilibrium polymerization is a general phenomenon in the ring-opening polymerization of different classes of monomers having more than four atoms in the ring, such as spiro- or bicyclo-ortho esters[10,17] and THF.[18] Apparently, **2** as well as these ortho esters may be classified into the same category as cyclic acetals.

By applying eq 2 to the straight line in Figure 7, the thermodynamic parameters such as ΔH°_{ss} and ΔS°_{ss}

Table 3. Polymerization of 2 with Two Ring-Opening Courses

run no.	catalyst[a]	solvent[b]	temp, °C	time, h	yield, %[c]		polymer structure[d]	M_n[e](MWD)[f]
					2	polymer		
19	BF_3·OEt_2	CH_2Cl_2	0	24	33	67	**3**	1160 (1.53)
20	BF_3·OEt_2	CH_2Cl_2	−30	72	13	87	**3**	1210 (1.82)
21	BF_3·OEt_2	CH_2Cl_2	−78	72	0	100	**3**	1230 (1.56)
22	BnTA[g]	PhCl	130	10	0	100	**4**	2160 (1.89)

[a] Five mole percent of each initiator was used per 0.5 g (2.2 mmol) of **2**. [b] $[\mathbf{2}]_0 = 0.83$ mol L^{-1}. [c] Determined by ^1H NMR. [d] Determined by IR. [e] Calibrated by polystyrene standards. [f] Molecular weight dispersion. [g] Benzylthiolanium hexafluoroantimonate.

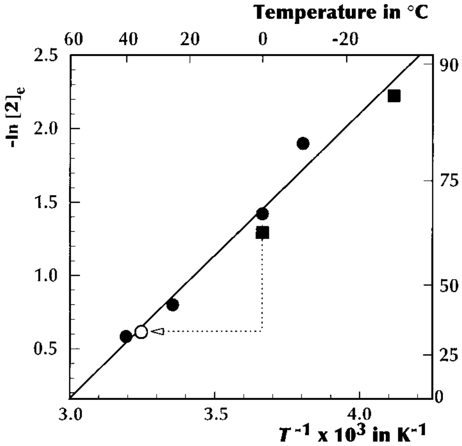


Figure 7. Dainton's plots obtained in the polymerization of **1** or **2** with BF_3·OEt_2 in CH_2Cl_2: (●) [**1**] = 0.83 mol L^{-1} and [BF_3·OEt_2] = 0.04 mol L^{-1} (No unreacted **1** was detected in each reaction mixture); (○) After being equilibrated at 0 °C, the polymerization system was warmed at 35 °C; (■) **2** was used as a feed monomer.

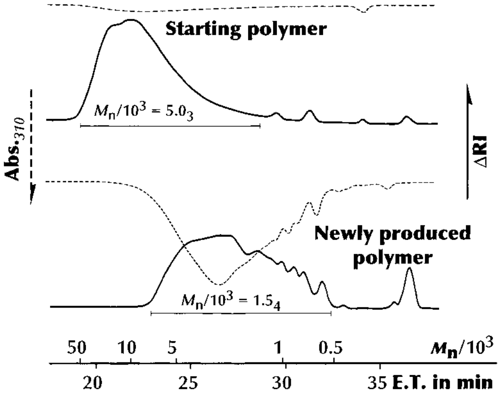


Figure 8. UV (at 310 nm) and RI double-detection GPC curves before and after the reaction of **3** with BnTA in PhCl at 130 °C for 24 h: **3** (0.25 g, 1.1 mmol, M_n $5.0_3 \times 10^3$), BnTA (22.5 mg, 0.054 mmol), PhCl (1.13 mL).

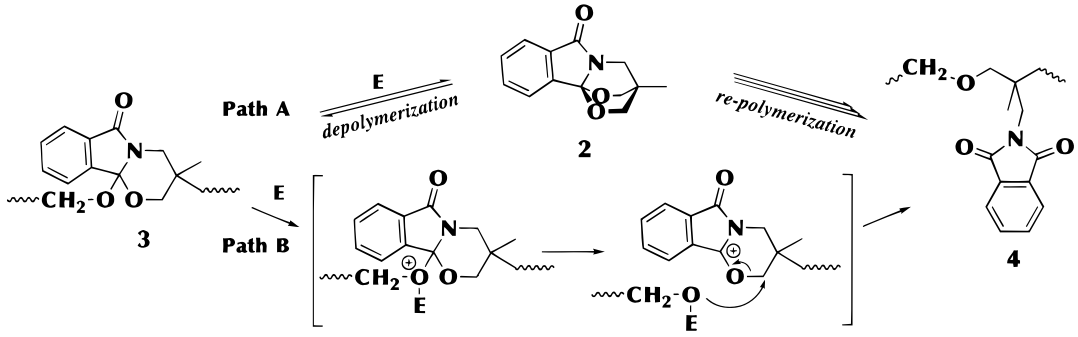
were estimated to be −15.8 kJ mol^{-1} and −46.0 J mol^{-1} K^{-1} ($r = 0.97$), respectively, for the single ring-opening polymerization of **2** in dichloromethane. From these values, the ceiling temperature (T_c) for 1 mol L^{-1} solution could be also calculated as 70.1 °C. Generally, in equilibrium polymerization, no polymer can exist at T_c and above, since the equilibrium lies well away from the monomer state. As shown in Figure 2, however, unnegligible amounts of polymer were produced even at 59.1 °C, which is the T_c calculated for the initial monomer concentration in this experiment (0.83 mol L^{-1}). This strongly suggests that the formation of the other polymer **4** begins at or near the T_c.

Transformation of 3 to 4. Oligomer-freed **3** was treated with BnTA in chlorobenzene at 130 °C as a temperature sufficiently higher than the T_c. After 24 h, however, a different polymer from the starting one was obtained quantitatively. The newly produced polymer was found to be **4**. Figure 8 shows the change of the molecular weight distributions before and after this treatment. The difference between the UV-detected curves apparently reflected a structural change from **3** to **4**, since **4** responded to 310-nm light while **3** was almost silent. In addition, the RI-detected curves showed a substantial decrease of M_n from 5030 to 1540. This suggested that the isomerization of polymer involved scission of the main chain of **3**. Thus, two pathways, as shown in Scheme 3, are applicable to such isomerization of polymer. One is an indirect process involving the ring-closure depolymerization of **3** followed by the repolymerization of **2** in the double ring-opening manner (path A). The other is a direct isomerization via acid-catalyzed inter- and/or intramolecular polymer reaction (path B).[19]

To clarify the more detailed mechanism, the polymerization of **1** was carried out at two temperatures. In the first stage, the polymerization was done at 0 °C for 24 h to give an equilibrium mixture consisting of **2** and **3** in 25 and 75% yields, respectively. The resulting mixture was immediately heated at 130 °C, and the isomerization process of the produced **3** was followed by ^1H NMR. Figure 9 shows the change of the product distribution during the second stage. As soon as the second stage was started, **3** began to rapidly revert back to **2**. In this case, **3** was the living species, and therefore the depolymerization is assumed to proceed via a zipping mechanism.[10b] After the yield of **2** reached its maximum, 74%, it decreased gradually to 40% after 7 h. On the other hand, not all polymer components disappeared, but the yield began to increase after 1 h. Finally, the prepolymer **3** formed in the first stage was entirely replaced by pure **4**, the yield of which was 60%. Furthermore, the change of the polymer composition was determined by utilizing the hydrolysis of **3** units to **5** with dilute hydrochloric acid. The content of unhydrolyzed **4** units is also plotted in Figure 9. The results reveal that the formation of **4** units started just after the beginning of the second stage and that the polymer composition was almost completely altered from **3** to **4** within the initial 1 h. This supports path A as an actually occurring process. The isomerization of **3** to **4** is regarded as a unique polymerization using a depolymerizable polymer as a monomer source.

Copolymerization of 1. The two-stage polymerization of **1** using BnTA was carried out in a reversed temperature mode, i.e., at 130 °C for 15 min and then at 25 °C for 3 days. In the first stage, the prepolymer **4** with $M_n = 635$ ($M_w/M_n = 1.2$) was formed in 13% yield by the double ring-opening polymerization of **2**. The remainder was **2** alone. After the second stage, both the yield and M_n of polymer increased to 62% and 1460 ($M_w/M_n = 2.5$), respectively. At 25 °C, of course, the single ring-opening polymerization of **2** took place selectively to form only **3** units. Consequently, the postpolymer was composed of both **3** and **4** units in a ratio of 0.79:0.21.

Scheme 3



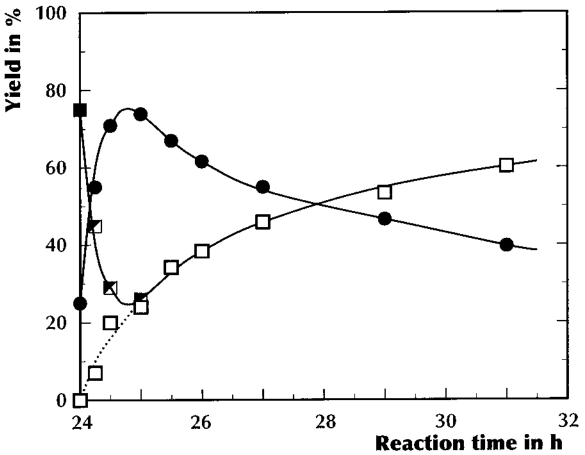


Figure 9. Time–conversion curves in the second-stage polymerization of **1** at 130 °C after the first stage at 0 °C for 24 h [**1** (1.0 g, 4.3 mmol), TMSOTf (0.5 mL of 0.43 mol L^{-1} in PhCl, 0.22 mmol), PhCl (4.0 mL)]: (●) **2**; (■) **3**; (□) unhydrolyzed polymer, **4**; (◩) total polymer of **3** and **4**.

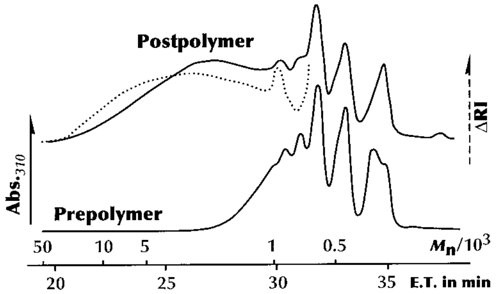
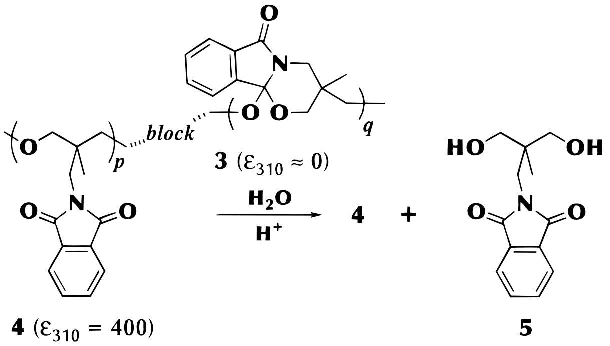


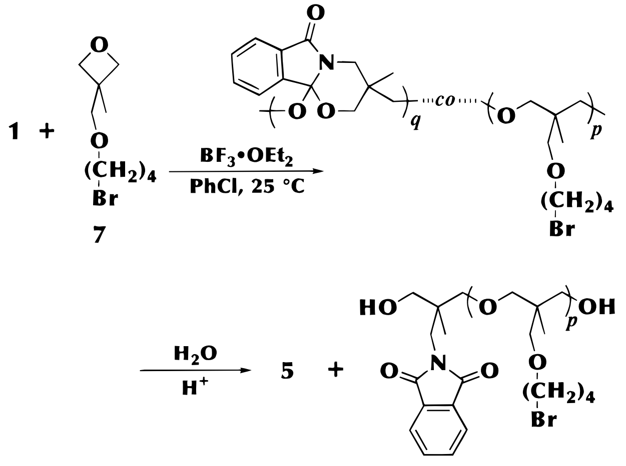
Figure 10. GPC curves of the pre- and postpolymers obtained in the two-stage polymerization of **1** at 130 °C for 15 min and then at 25 °C for 3 days [**1** (1.0 g, 4.3 mmol), BnTA (0.5 mg, 0.22 mmol), PhCl (4.0 mL)].

However, BnTA, if any after the first stage, cannot initiate the polymerization of **2** at 25 °C, because the thermal latent catalyst is virtually inactive below 80 °C.[11,20] This suggested that the block sequences of **3** and **4** were constructed in the second stage. Figure 10 shows the deference between the GPC curves of the pre- and postpolymers thus obtained. The RI-detected curves imply that a high molecular weight part over ca. 1000 in the prepolymer **4** was converted to the main part of the postpolymer. In UV-detected GPC using 310-nm light, the distribution of **4** units in different molecular weight polymer molecules was determined, because only phthalimide pendants were detectable at this wavelength. The UV-detected curve of the postpolymer was almost identical with the RI-detected one, indicating that each molecule of postpolymer contained **4** units.

Scheme 4



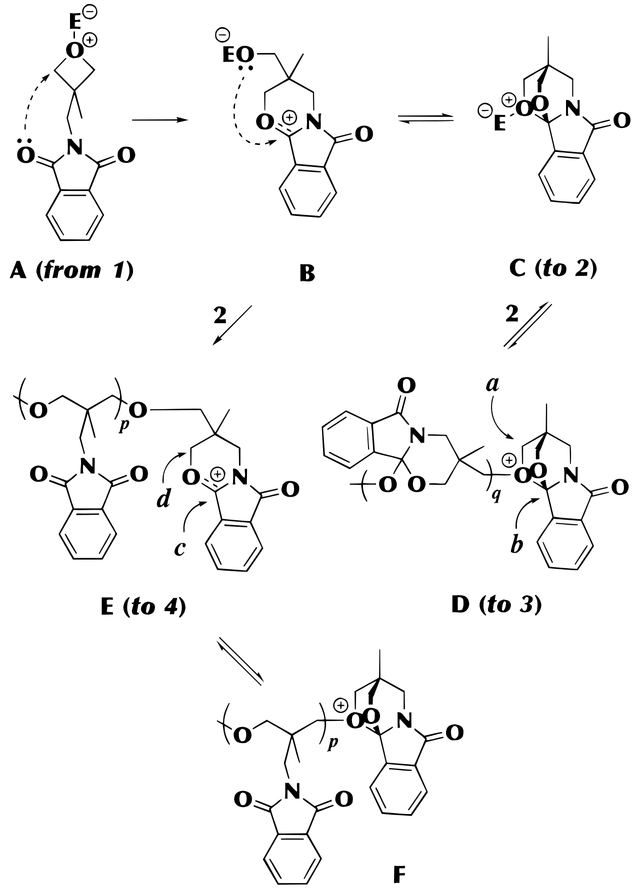
Scheme 5



Accordingly, the postpolymer, as shown in Scheme 4, was a block copolymer having the **3** sequence linked to the **4** sequence formed in the first stage. Indeed, when the **3** sequence in the postpolymer was removed by acid hydrolysis, the resulting polymer showed almost the same GPC curve as that of the prepolymer. It is noticeable that the A–B type block copolymer was produced from the single monomer by a one-pot polymerization.

Moreover, **1** can be copolymerized with a nonisomerizable oxetane, such as 3-(6-bromo-2-oxahexyl)-3-methyloxetane (**7**),[13] in the monomer-isomerization mode. The polymerization of these oxetanes in a feed mole ratio of 1:1 was carried out using BF_3·OEt_2 in chlorobenzene at 25 °C for 4 days, resulting in the 36% and 85% conversions of **1** and **7**, respectively. The obtained copolymer was composed of the **3** units and the ring-opened **7** units in a mole ratio of 0.34:0.66. As shown in Scheme 5, this copolymer was also acid-degradable, so that the hydrolysis of the **3** units in the copolymer caused a great decrease of M_n from 2370 to 1295. The

Scheme 6. Plausible Mechanism for the Monomer-Isomerization Polymerization of 1 with Two Ring-Opening Courses

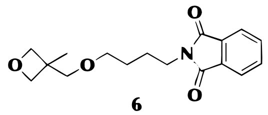


result is additional evidence for the formation of linkages between the **3** and **7** units by copolymerization. The unhydrolyzed chains showed a weak response to 310-nm light, although the original copolymer was silent at this wavelength. This is because that hydrolysis resulted in a polyether of **7** possessing a monoether of **5** as a UV-detectable end group.

Polymerization Mechanism. We have already proposed the mechanism for the Lewis acid-catalyzed isomerization of cyclic imide-substituted oxetanes to the bicyclic acetals via intermediates such as **A**, **B**, and **C** shown in Scheme 6.[6] Thereafter, the ^{1}H NMR-induced chemical shift difference was observed on mixing succinimide-substituted oxetane with MAD.[21] This result clearly demonstrated that the Lewis acid coordinates with the ether oxygen atom rather than the carbonyl one. Furthermore, the closely related isomerization of secondary amide-substituted oxetanes was found to give predominately 4*H*-dihydro-1,3-oxazine derivatives in place of bicyclic acetals.[7] Therefore, the presumed intervention of 1,3-oxazin-2-ylium cation **B** has reality. Although the polymerization mechanism of **1** has not been fully confirmed on the basis of experimental evidence, the above intermediates **B** and **C** are strongly suggestive of the structures of the propagating ends.

A plausible mechanism can be illustrated as shown in Scheme 6. The monomer-isomerization process from **1** to **2** can be explained as follows. Oxonium ion **A** generated by coordination of an acid catalyst (E) predominantly undergoes intramolecular nucleophilic attack by one of the imide carbonyl oxygen atoms. Ring closure of the resulting **B** then affords **2** in an oxonium form **C**. Generally **A** may be regarded as an initiating species in the cationic ring-opening polymerization of oxetanes. Thus, there is a possibility that **1** polymerizes in the conventional ring-opening manner or accompanying the isomerization of the propagating end. However, sufficient evidence that **2** is the real monomer has been obtained. A similar oxetane **6** (Chart 1) that carries a phthalimide group separated by a longer spacer CH_2O-$(CH_2)_4$ did not isomerize under the influence of $BF_3{\cdot}OEt_2$ but polymerized in the conventional ring-opening manner. In **A**, the intramolecular nucleophilic attack (isomerization) is preferred over the intermolecular nucleophilic attack (polymerization) of **1**, because of the accessibility between the oxonium α-carbon atom and the properly positioned carbonyl oxygen atom. A second piece of evidence is that the polymerization rate is expressed only by the term of the concentration of **2,** and hence the polymerization of **2** also affords **3** and **4**.

Chart 1



6

The real monomer **2** formed by the isomerization of **1** is accumulated during an early stage of the reaction, because the isomerization rate is much more rapid than the polymerization rates. Oxonium ion **C** probably becomes an initiating species in the present polymerization. In the propagation, there are possibilities of S_N2-like attack of **2** on a cyclic oxonium end and S_N1-like attack on an oxazinium end after one-ring-opening. In addition, **2** could be potentially added to these ends by two incoming courses each. Since the monomer addition leading to the ether linkage is obviously limited only to course d, **E** is the propagating species in the double ring-opening polymerization of **2** at high temperatures. On the other hand, the acetal linkage of **3** can be formed via any of courses a–c, but course c on the **E** end is ruled out by the following experimental results. Other oxetanes having a five-membered cyclic imide group, such as maleimide and succinimide, also polymerized cationically, accompanying the monomer isomerization.[21] The polymerization of maleimide-substituted oxetane also gave both polyether and polyacetal, depending upon temperature. In contrast, the polymerization of the saturated analogue, i.e., succinimide-substituted oxetane, gave no polyether regardless of the conditions but only polyacetal below T_c for a given monomer concentration. This difference in the polymerization behavior implies that conjugative stabilization by the carbon–carbon double bond (for maleimide) or an aromatic ring (for phthalimide) is required to form oxazinium ends leading to polyethers. Since such stabilization effect is absent in the case of the saturated imide-substituted oxetane, no polyether can be formed. On the other hand, polyacetal can be formed via an oxonium end, which is much less susceptible to the substituent effect. For the reason mentioned above, **D** is probably the propagating end in the single ring-opening polymerization of **2** at low temperatures. However, the monomer addition by course b should suffer from more steric repulsion. Consequently, it is the most reasonable that **3** is formed by the monomer addition on **D** by course a.

Discussion of the Polymerization Mechanism. Contrary to the above consideration, Hall et al. reported that, in the course-selective cationic ring-opening polymerization of ortho esters leading to either polyethers or polyacetals,[8c] the one-ring-opened 1,3-dioxan-2-ylium end is always preferred as a single propagating end. The corresponding bicycle in **2** contains a nitrogen atom in place of an oxygen atom. The nitrogen atom, however, possesses amide character, as revealed by X-ray crystallography (Figure 1). This implies that the lone pair electrons of the lactam nitrogen atom would hardly contribute to the resonance stabilization of the oxazinium end **E**. To generate **E**, therefore, the help of the conjugated double bond will be required together with heat. In contrast, the above dioxanium cation end, which is stabilized by two neighboring oxygen atoms, would be much more easily formed, even at low temperatures. Moreover, the ORTEP view of **2** shows that the bond angle of the cyclic acetalic linkage is expanded to 109.9° and the adjacent CH_2-O bonds are rather lengthened to 1.461 and 1.453 Å, compared with the optimum values; for instance, the MM2 calculation adopts 99.9 ° and 1.402 Å, respectively. These strains are attributed to the so-called *rabbit-ear* effect,[22] which refers to dipole−dipole repulsion between the lone pairs parallel standing on the acetalic oxygen atoms. This repulsion serves as an important driving force for the ring-opening polymerization of **2**.

The polymerization of **2** gives two kinds of products. Between 60 and 70 °C, the polymer structure is altered from **3** to **4**. This phenomenon corresponds to a change of the propagating species from **D** to **E**. The propagating species under mild conditions (50 °C and below) is **D** with an oxonium end, which reacts with nucleophilic **2** to form **3**. Since the single ring-opening polymerization is evidently in equilibrium, any propagation via oxonium species is ruled out above a $T_c = 59.1$ °C for the polymerization conditions employed. Moreover, **D** reverts completely to **C** and **2** by the ring-closure depolymerization. However, **C** and **B** are thermally interconvertible. The lowest temperature, where one ring of **C** can open to form **B**, probably exists in the vicinity of the T_c. At increased temperatures (80 °C and above), **B** reacts in turn with **2** to form the other propagating species, **E**. On lowering the reaction temperature, however, the oxazinium end of **E** is transformed to another propagating species, **F**, having an oxonium end. The subsequent attack of **2** on **F** results in the single ring-opening polymerization to form a **3**−**4** block copolymer.

Conclusion. In this paper, the polymerization of 3-phthalimidomethyl-substituted oxetane (**1**) was carried out with several cationic catalysts to afford two kinds of polymers with different structures. One was polyacetal **3**, produced at 50 °C and below, and the other was polyether **4**, produced at 80 °C and above. This new mode of polymerization with two ring-opening courses was found to be accompanied by the monomer isomerization of **1**: it was isomerized to bicyclic acetal (**2**) by the Lewis acid-catalyzed intermolecular nucleophilic attack of the phthalimide carbonyl group and then either of the single and double ring-opening polymerization of **2** as a real monomer took place selectively depending on the reaction temperature. Consequently, some elements constituting the nonpolymerizable phthalimide substituent of the starting monomer **1** was built in into the main chain of **3**. The single ring-opening process of **2** was an equilibrium polymerization. The critical temperature, where the structure of the product polymer changed, was related with a $T_c = 59.1$ °C calculated for the conditions employed. Therefore, **3** was successfully transformed to **4** with a thermal latent catalyst at a higher temperature than T_c through the ring-closure depolymerization of **3** to **2** followed by the repolymerization of **2** in the double ring-opening manner. When **1** was polymerized in a temperature step-down mode, a copolymer with the **3**−**4** block sequence was prepared from the single monomer. Moreover, **1** was copolymerized with a nonisomerizable oxetane, accompanying the monomer isomerization of **1**.

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Supporting Information Available: Details of crystallographic data of **2**: Table S1, giving anisotropic thermal parameters for non-hydrogen atoms, and Tables S2 and S3, listing intramolecular bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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