Substituent Effect on the Anionic Equilibrium Polymerization of Six-Membered Cyclic Carbonates

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ABSTRACT: Anionic equilibrium polymerization behavior of several six-membered cyclic carbonates was examined. The conversions of the monomers reached a constant below 100%, and the final conversion decreased in the order of 1,3-dioxan-2-one (**1**) > 5,5-dimethyl-1,3-dioxan-2-one (**2**) > 5,5-diethyl-1,3-dioxan-2-one (**3**) ≥ 5-methyl-5-phenyl-1,3-dioxan-2-one (**4**) > 5-ethyl-5-phenyl-1,3-dioxan-2-one (**5**). The reactions of 2,2-disubstituted-1,3-propanediols were carried out with phosgene dimer to find that the cyclic carbonate (**5**) was formed quantitatively in the reaction of 2-ethyl-2-phenyl-1,3-propanediol, while the corresponding polycarbonate was formed in the reaction of 2,2-diethyl-1,3-propanediol in 24% yield besides **3**. Thermodynamic parameters were estimated in the anionic ring-opening polymerizations of cyclic carbonates (**1**−**5**) by Dainton's equation. The obtained ΔH_p value in the ring-opening polymerization of each cyclic carbonate reflected the polymerizability. Molecular orbital calculations of the model compounds of the polymers were carried out to find that the polymerizabilities of the cyclic carbonates correlated with the stabilities of the corresponding polymer structures. The concentrations of the monomers formed in the depolymerizations well agreed with the equilibrium monomer concentrations in the anionic ring-opening polymerizations.

Introduction

It has been reported that anionic ring-opening polymerization of cyclic carbonates efficiently proceeds to afford the corresponding linear polycarbonates,[1a−h,m] while cationic ring-opening polymerization is always accompanied by elimination of carbon dioxide to yield polycarbonates containing ether units.[1i−l] We have reported that six-membered cyclic carbonates undergo cationic polymerization without decarboxylation by alkyl halide initiators such as methyl iodide and benzyl bromide.[1n,o] Further, we have found that six-membered cyclic carbonates undergo volume expansion on polymerization, and this volume expansion can be accounted for by the difference in strength of the intermolecular interaction between the monomers and polymers. That is, strong interactions in the monomers and weak interactions in the polymers eventually cause the volume expansion.[2] Recently, we have reported the anionic and cationic ring-opening polymerizations of an aliphatic seven-membered cyclic carbonate, 1,3-dioxepan-2-one.[3] The seven-membered cyclic carbonate showed a higher polymerizability than a six-membered one, 1,3-dioxan-2-one, which might be explained by the difference of their ring strains. As described above, cyclic carbonates can be expected to be one of the attractive monomers from the viewpoints of polymer synthesis and the function.

It has been reported that the anionic ring-opening polymerization of a six-membered cyclic carbonate shows an equilibrium character,[1b] which is similar to common heterocyclic compounds.[4] Although some studies have been reported on the anionic ring-opening polymerization of cyclic carbonates with various substituents,[1b−h] there are only few reports on the equilibrium polymerization. Monomers which undergo equilibrium polymerization are useful, because they are expected to be applied to chemical recycling of polymeric materials.[5] In this paper, we report on the substituent effect on the anionic equilibrium polymerization of cyclic carbonates.

Experimental Section

Measurements. Melting points (mp) were measured by a Yanaco micro melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-EX400 and JNM-EX90 spectrometers (400 or 90 MHz for ^{1}H and 100 or 22.5 MHz for ^{13}C NMR), using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) at 27 °C. IR spectra were obtained with a JASCO FT/IR-5300 spectrometer at 27 °C. Molecular weights (M_n and M_w: number- and weight-average molecular weights) and the distributions (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCP & 8000 system, equipped with a refractive index detector and polystyrene gel columns (Tosoh TSK gels G2500H and G3000H) using tetrahydrofuran (THF) as an eluent, with a flow rate of 1.0 mL/min by polystyrene calibration at 30 °C.

Materials. THF was purified by distillation over sodium and benzophenone under nitrogen. *N*,*N*-Dimethyl formamide (DMF) was distilled over calcium hydride under nitrogen. Triethylamine and pyridine were dried over KOH and distilled. Reagents, 2,2-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, ethyl chloroformate, ethyl bromide, formaldehyde, 2-phenylpropionaldehyde, diethyl phenylmalonate, and potassium *tert*-butoxide (1.0 M solution in THF, from Aldrich Co.) were used as received. Diols 2-methyl-2-phenyl-1,3-propanediol[6] and 2-ethyl-2-phenyl-1,3-propanediol[7,8] were synthesized according to the literature.

Synthesis of 2-Methyl-2-phenyl-1,3-propanediol. To a solution of 2-phenylpropionaldehyde (20 mL, 0.15 mol) and formaldehyde (30.1 g, 0.37 mol) in methanol (60 mL) was added 45% aqueous KOH solution (24 mL). The reaction mixture was refluxed for 7 h. After removal of the solvent, the residue was washed with 2-propanol. The filtrate was concentrated by rotary evaporation, and the residue was recrystallized from benzene−*n*-hexane to afford white crystals. Yield: 15.7 g (63%). Mp 78 °C (lit.[6] mp 75 °C). ^{1}H NMR ($CDCl_3$): δ 1.30 (−CH_3, s, 3H), 2.12 (−OH, broad s, 2H), 3.96 (−CH_2−, q, J = 10.8 Hz, 4H), 7.24−7.44 (−C_6H_5, m, 5H) ppm.

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^{13}C NMR ($CDCl_3$): δ 142.87, 128.70, 126.73, 126.63, 70.09, 44.58, 20.73 ppm. IR (KBr): 4407, 4054, 3317, 3069, 2974, 2947, 2922, 2874, 2364, 1956, 1874, 1813, 1751, 1599, 1579, 1560, 1501, 1474, 1443, 1393, 1273, 1204, 1186, 1159, 1138, 1078, 1057, 1035, 1024, 995, 953, 903, 839, 770, 698, 619, 577, 490 cm^{-1}.

Synthesis of Diethyl 2-Ethyl-2-phenylmalonate. To a suspension of dry DMF (170 mL) and NaH (7.0 g, 0.17 mol) was added diethyl 2-phenylmalonate (25 mL, 0.12 mol) under nitrogen. After the mixture was stirred at 85 °C for 90 min, ethyl bromide (15.5 mL, 0.21 mol) was slowly added at 70 °C. The reaction mixture was stirred at 70 °C for 1 h. After aqueous 0.05 M H_2SO_4 solution was added to the reaction mixture, it was extracted with ethyl acetate, and the organic layer was dried over anhydrous $MgSO_4$. Diethyl 2-ethyl-2-phenylmalonate was isolated from the reaction mixture by silica gel column chromatography using ethyl acetate and *n*-hexane (volume ratio 1:25) as an eluent. Yield: 28.4 g (93%). ^{1}H NMR ($CDCl_3$): δ 0.88 ($-CH_3$, t, J = 7.2 Hz, 3H), 1.23 ($-CH_3$, t, J = 7.0 Hz, 6H), 2.40 ($-CH_2-$, q, J = 7.0 Hz, 2H), 4.25 ($-CH_2-$, q, J = 7.0 Hz, 4H), 7.25−7.51 ($-C_6H_5$, m, 5H) ppm. ^{13}C NMR ($CDCl_3$): δ 170.45, 136.84, 127.90, 127.81, 127.12, 62.92, 61.08, 28.75, 13.74, 9.05 ppm. IR (NaCl): 3547, 3061, 2928, 2940, 2378, 1732, 1545, 1499, 1449, 1389, 1368, 1304, 1238, 1125, 1096, 1026, 860, 729, 698, 482, 413 cm^{-1}.

Synthesis of 2-Ethyl-2-phenyl-1,3-propanediol. To a suspension of $LiAlH_4$ (3.88 g, 0.10 mol) in dry THF (150 mL) was added a solution of diethyl 2-ethyl-2-phenylmalonate (15 g, 0.056 mol) in THF (40 mL) at room temperature, followed by refluxing for 7 h. Carefully addition of saturated aqueous Na_2SO_4 (24 mL) resulted in forming a white mass. The mixture was filtered off and washed with THF, and the combined filtrate was dried over anhydrous $MgSO_4$. 2-Ethyl-2-phenyl-1,3-propanediol was isolated by recrystallization from benzene−*n*-hexane. Yield: 7.2 g (71%). Mp: 76 °C (lit.[8] mp 78−79 °C). ^{1}H NMR ($CDCl_3$): δ 0.68 ($-CH_3$, t, J = 7.4 Hz, 3H), 1.69 ($-CH_2-$, q, J = 7.4 Hz, 2H), 2.28 ($-$OH, t, J = 5.8 Hz, 2H), 4.10 ($-CH_2-$, q, J = 5.8 Hz, 4H), 7.23−7.40 ($-C_6H_5$, m, 5H) ppm. ^{13}C NMR ($CDCl_3$): δ 141.19, 128.68, 127.11, 126.52, 68.51, 47.41, 26.82, 7.89 ppm. IR (KBr): 4396, 4059, 3241, 3027, 2944, 2880, 2074, 1950, 1873, 1802, 1748, 1601, 1580, 1501, 1458, 1381, 1304, 1262, 1209, 1167, 1134, 1103, 1078, 1059, 1040, 1017, 993, 978, 907, 855, 760, 721, 696, 627, 592, 577, 503, 480, 453 cm^{-1}.

Synthesis of Six-Membered Cyclic Carbonates. Typical Procedure. To a solution of 1,3-propanediol (10 g, 0.13 mol) and ethyl chloroformate (28.4 g, 0.26 mol) in THF (260 mL) was added a solution of triethylamine (26.5 g, 0.26 mol) in THF (65 mL) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 2 h. Precipitated triethylamine hydrochloride was filtered off, and the filtrate was concentrated under vacuum. 1,3-Dioxan-2-one (**1**) was isolated from the reaction mixture by silica gel column chromatography using ethyl acetate and *n*-hexane (volume ratio 3:1) as an eluent and recrystallized from THF and ether. Yield: 7.9 g (60%). Mp: 45 °C (lit.[6] mp 45 °C).

1,3-Dioxan-2-one (1). ^{1}H NMR ($CDCl_3$): δ 2.14−2.17 ($-CH_2-$, m, 2H), 4.47 ($-CH_2O-$, t, J = 6.0 Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 148.42 (C=O), 67.89 (CH_2O), 21.66 (CH_2) ppm. IR (KBr): 2924, 2854, 1736, 1639, 1477, 1421, 1253, 1190, 1147, 1120, 771 cm^{-1}.

5,5-Dimethyl-1,3-dioxan-2-one (2). Yield: 68%. Mp: 105 °C (lit.[6] mp 109−110 °C). ^{1}H NMR ($CDCl_3$): δ 1.13 ($-CH_3$, s, 6H), 4.08 ($-CH_2O$, s, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 148.07 (C=O), 77.42 (CH_2O), 28.35 (CH_3), 21.00 ($C_{quatern}$) ppm. IR (KBr): 2969, 2915, 2882, 2780, 2594, 2521, 2421, 2375, 2211, 1989, 1910, 1752, 1661, 1566, 1537, 1474, 1410, 1377, 1321, 1296, 1240, 1223, 1196, 1121, 1005, 955, 924, 826, 801 cm^{-1}.

5,5-Diethyl-1,3-dioxan-2-one (3). Yield: 68%. Mp: 45 °C (lit.[6] mp 44−45 °C). ^{1}H NMR ($CDCl_3$): δ 0.91 ($-CH_3$, t, J = 7.3 Hz, 6H), 1.49 ($-CH_2-$, q, J = 7.3 Hz, 4H), 4.14 ($-CH_2O-$, s, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 148.51(C=O), 74.81 (CH_2O), 33.40 (CH_2), 22.56 ($C_{quatern}$), 6.98 (CH_3) ppm. IR (KBr): 2975, 2876, 2377, 1763, 1535, 1480, 1414, 1383, 1323, 1256, 1186, 1128, 1061, 1013, 984, 951, 812, 795, 768, 689, 594, 532, 424 cm^{-1}.

5-Methyl-5-phenyl-1,3-dioxan-2-one (4). Yield: 67%. Mp: 98 °C (lit.[6] mp 100 °C). ^{1}H NMR ($CDCl_3$): δ 1.44 ($-CH_3$, s, 3H), 4.38−4.66 ($-CH_2O-$, m, 4H), 7.32−7.40 ($-C_6H_5$, m, 5H) ppm. ^{13}C NMR ($CDCl_3$): δ 147.74 (C=O), 139.25, 129.18, 127.86, 125.45, 76.01 (CH_2O), 35.40 (CH_3), 21.7 ($C_{quatern}$) ppm. IR (KBr): 3459, 3090, 3065, 3029, 2984, 2917, 2583, 2550, 2427, 2361, 2209, 1971, 1904, 1888, 1738, 1605, 1582, 1557, 1535, 1501, 1489, 1474, 1445, 1406, 1323, 1285, 1252, 1213, 1186, 1152, 1105, 1074, 1038, 978, 916, 802, 777, 761, 702, 619, 592, 559, 530, 509, 449 cm^{-1}.

5-Ethyl-5-phenyl-1,3-dioxan-2-one (5). Yield: 67%. Mp: 97 °C (lit.[6] mp 99−100 °C). ^{1}H NMR ($CDCl_3$): δ 0.72 ($-CH_3$, t, J = 7.4 Hz, 3H), 1.84 ($-CH_2-$, q, J = 7.4 Hz, 2H), 4.48−4.68 ($-CH_2O-$, m, 4H), 7.23−7.43 ($-C_6H_5$, m, 5H) ppm. ^{13}C NMR ($CDCl_3$): δ 147.96 (C=O), 137.46, 129.21, 127.82, 125.96, 74.66 (CH_2O), 38.91 (CH_2), 27.75 ($C_{quatern}$), 7.71 (CH_3) ppm. IR (KBr): 3464, 3096, 3059, 3036, 2978, 2928, 2884, 2868, 2593, 2548, 2436, 2363, 2199, 1981, 1960, 1944, 1883, 1738, 1603, 1582, 1532, 1505, 1481, 1412, 1395, 1385, 1352, 1319, 1254, 1202 cm^{-1}.

Anionic Ring-Opening Polymerization of Six-Membered Cyclic Carbonates. Typical Procedure. All glass vessels were heated in vacuo before use, filled with dry nitrogen, and handled in a stream of dry nitrogen. To a solution of a monomer (4.8 mmol) in THF (6.1 mL) was added a solution of *t*-BuOK in THF (1 M, 48 μL, 0.048 mmol) at 0 °C. After the reaction time at the desired conditions, a solution of methanol/phosphoric acid (volume ratio 9:1, 0.1 mL) was added to the reaction mixture. The monomer conversion was estimated by ^{1}H NMR spectroscopy.[9] The reaction mixture was poured into methanol (500 mL) to isolate the polymer.

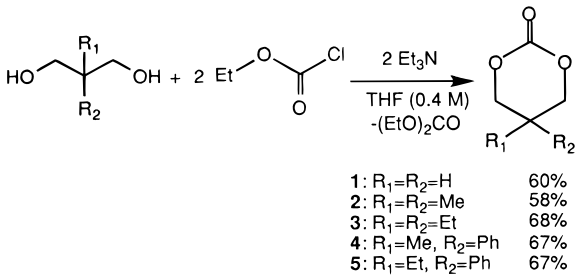
Poly(**1**): ^{1}H NMR ($CDCl_3$) δ 2.02−2.08 ($-CH_2-$, m, 2H), 4.24 ($-CH_2O-$, t, J = 5.6 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$) δ 154.58 (C=O), 64.03 (CH_2O), 27.71 (CH_2) ppm, IR (KBr) 3474, 2970, 2912, 2368, 1747, 1585, 1462, 1410, 1244, 1095, 1033, 929, 790, 567, 457 cm^{-1}. Poly(**2**): ^{1}H NMR ($CDCl_3$) δ 0.97 ($-CH_3$, s, 6H), 3.93 ($-CH_2O-$, s, 4H) ppm; ^{13}C NMR ($CDCl_3$) δ 155.29 (C=O), 72.43 (CH_2O), 35.14 (CH_3), 21.37 ($C_{quatern}$) ppm; IR (KBr) 3470, 2967, 2346, 2218, 2027, 1742, 1584, 1476, 1389, 1263, 1098, 1020, 968, 791, 737, 617, 527, 503, 426 cm^{-1}. Poly(**3**): ^{1}H NMR ($CDCl_3$) δ 0.84 ($-CH_3$, t, J = 7.3 Hz, 6H), 1.37 ($-CH_2-$, q, J = 7.3 Hz, 4H), 4.00 ($-CH_2O-$, s, 4H) ppm; ^{13}C NMR ($CDCl_3$) δ 148.51 (C=O), 74.81 (CH_2O), 33.40 (CH_2), 22.56 ($C_{quatern}$) 6.98 (CH_3) ppm; IR (KBr) 2967, 2749, 2348, 2232, 1752, 1591, 1460, 1406, 1256, 1098, 1065, 1044, 980, 870, 820, 791, 613, 557, 492, 421 cm^{-1}. Poly(**4**): ^{1}H NMR ($CDCl_3$) δ 1.33 ($-CH_3$, s, 3H), 4.26 ($-CH_2O-$, s, 4H), 7.22−7.29 ($-C_6H_5$, m, 5H) ppm; ^{13}C NMR ($CDCl_3$) δ 154.85 (C=O), 140.97, 128.50, 127.09, 126.23, 71.61 (CH_2O), 42.13 (CH_3), 20.25 ($C_{quatern}$) ppm; IR (KBr) 3476, 3094, 3061, 3029, 2978, 2909, 2365, 2216, 1954, 1877, 1744, 1603, 1582, 1501, 1474, 1449, 1389, 1256, 1096, 961, 860, 787, 766, 700, 594, 561 cm^{-1}. Poly(**5**): ^{1}H NMR ($CDCl_3$) δ 0.60−0.63 ($-CH_3$, broad s, 3H), 1.52−1.69 ($-CH_2-$, broad s, 2H), 4.41−4.43 ($-CH_2O-$, broad s, 4H), 7.16−7.32 ($-C_6H_5$, broad s, 5H) ppm; ^{13}C NMR ($CDCl_3$) δ 154.85 (C=O), 139.55, 128.46, 126.84, 126.43, 69.17 (CH_2O), 45.25 (CH_2), 26.05 ($C_{quatern}$), 7.56 (CH_3) ppm; IR (KBr) 3464, 3061, 3030, 2971, 2884, 2369, 1748, 1605, 1501, 1468, 1400, 1233, 1098, 1042, 957, 785, 760, 698, 583 cm^{-1}.

Depolymerization. Typical Procedure. To a solution of a polymer (0.97 mmol) in THF (2.1 mL) was added a solution of *t*-BuOK in THF (1 M, 9.7 μL, 0.0097 mmol) at 20 °C. After 24 h, a solution of methanol/hydrochloric acid (36%) (volume ratio 9:1, 0.05 mL) was added to the reaction mixture. The obtained monomer concentration was estimated by ^{1}H NMR spectroscopy.

Results and Discussion

Monomer Syntheses. The cyclic carbonates (**1**−**5**) were synthesized from ethyl chloroformate and the corresponding diols according to the literature in 58−68% yields (Scheme 1).[1n,o]

Scheme 1



1: $R_1=R_2=H$ 60%
2: $R_1=R_2=Me$ 58%
3: $R_1=R_2=Et$ 68%
4: $R_1=Me$, $R_2=Ph$ 67%
5: $R_1=Et$, $R_2=Ph$ 67%

Scheme 2

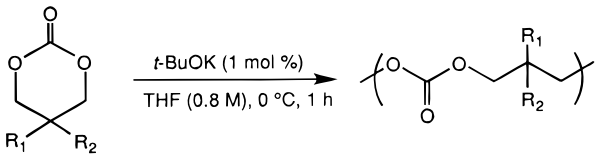


Table 1. Anionic Ring-Opening Polymerizations of Cyclic Carbonates[a]

run	monomer	yield[b] (%)	M_n[b,c]	M_w/M_n[b,c]
1	1	75	32 600	1.5
2	2	90	54 000	1.4
3	3	85	48 100	1.4
4	4	74	51 900	1.4
5	5	46	12 700	1.5

[a] Conditions: initiator, *t*-BuOK (1 mol %); time, 1 h; solvent, THF (0.8 M); temperature, 0 °C. [b] MeOH-insoluble part. [c] Estimated by GPC based on polystyrene standards.

Anionic Ring-Opening Polymerization of Cyclic Carbonates. Anionic ring-opening polymerizations of cyclic carbonates (**1**−**5**) were carried out at 0 °C for 1 h in THF (0.8 M) with *t*-BuOK (1 mol %) as an initiator (Scheme 2) to obtain polycarbonates with M_ns 12 700−54 000 in 46−90% yields, as summarized in Table 1.

Next, equilibrium behavior was examined in the polymerizations of **1**−**5**. Figure 1 illustrates the time−conversion relationships in the anionic ring-opening polymerizations of **2**−**5** at 20 °C in 0.6 and 0.45 M concentrations. The conversions of **2**−**5** reached a constant after 30 min, but **1** was converted quantitatively above 0.45 M concentration. The polymerization of **1** was carried out in THF at a lower monomer concentration (0.05 M) to investigate the possibility of a polymerization equilibrium. As a result, the conversion of **1** also reached a constant at that concentration. These results may support strongly that there is an equilibrium between the polymer and monomer. Table 2 summarizes the average conversions of **1**−**5** and the equilibrium monomer concentrations calculated therefrom.[9] In the polymerizations of **3** and **4**, the lower initial monomer concentration resulted in the higher equilibrium monomer concentration as reported in the equilibrium polymerization of THF.[10] The polymerizability, judged by the monomer conversion, decreased in the order of **1** > **2** > **3** ≥ **4** > **5**. These results show that the equilibrium monomer concentration increases with the degree of substitution.

In general, polymers which are synthesized by ring-opening polymerization can be also synthesized by polycondensation. Sarel et al. have reported the substituent effect on the polycondensation of 1,3-propanediol derivatives with diethyl carbonate. They suggested that the substituents at the 2-position of 1,3-propanediol suppressed the polycondensation but enhanced the formation of cyclic carbonates, because the steric repulsion of the substituent was larger in the polymer than that in cyclic carbonate.[1a] However, the reaction of the diols was not examined with phosgene, which has higher reactivity than diethyl carbonate. It seems that the cyclic structure is more preferable than the linear polymer, if the cyclic carbonate is selectively formed in the reaction of the diols with phosgene dimer. The reactions of 2,2-diethyl-1,3-propanediol and 2-ethyl-2-phenyl-1,3-propanediol were carried out with phosgene dimer to find that the cyclic carbonate (**3**) and poly(**3**) were formed in the reaction of 2,2-diethyl-1,3-propanediol in 76 and 24% yields, respectively, while the cyclic carbonate (**5**) was produced quantitatively in the reaction of 2-ethyl-2-phenyl-1,3-propanediol (Scheme

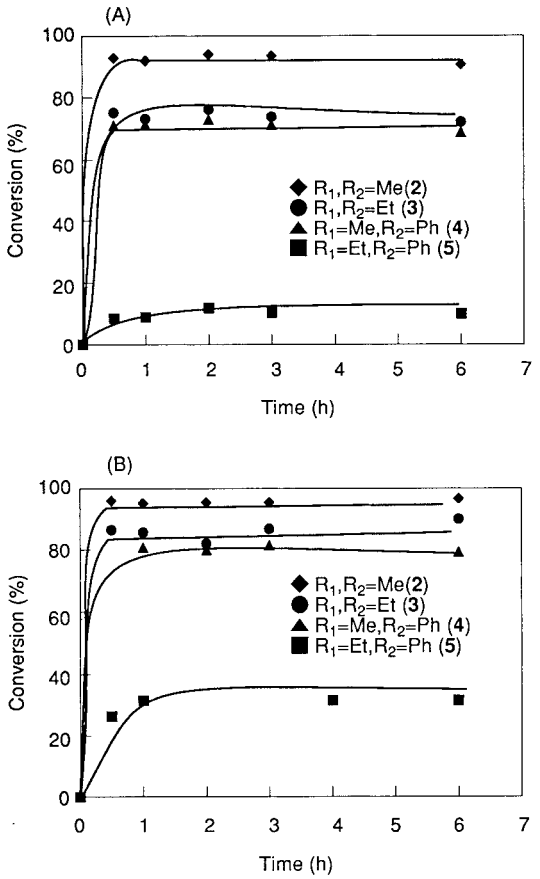


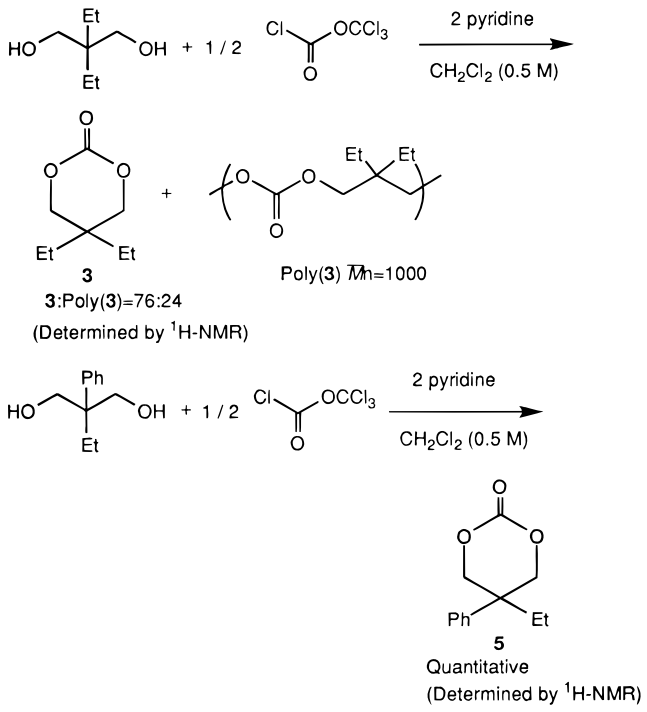
Figure 1. (A) Time−conversion relationships in the anionic ring-opening polymerizations of **2**−**5** in THF (0.45 M) at 20 °C, initiator *t*-BuOK (1 mol %). (B) Time−conversion relationships in the anionic ring-opening polymerizations of **2**−**5** in THF (0.6 M) at 20 °C, initiator *t*-BuOK (1 mol %).

Table 2. Average Conversions of 1−5 in the Anionic Ring-Opening Polymerizations and Equilibrium Monomer Concentrations[a]

run	monomer	concn (M)	av conversion[b] (%)	equil monomer concn (M)
1	**1**	0.05	65	0.02
2	**2**	0.45	93	0.03
3	**2**	0.6	96	0.03
4	**3**	0.45	74	0.12
5	**3**	0.6	86	0.08
6	**4**	0.45	71	0.13
7	**4**	0.6	82	0.11
8	**5**	0.45	10	0.40
9	**5**	0.6	32	0.41

[a] Conditions: initiator, *t*-BuOK (1 mol %); solvent, THF; temperature, 20 °C. [b] Determined by ^{1}H NMR.

Scheme 3



3). These results may support that the cyclic structure is more preferable than the linear structure when the bulky substituent is introduced, although not only a thermodynamic factor but also a kinetic factor may affect the difference of the selectivity between the monomer and polymer.

As usual, the driving force of polymerization is negative enthalpy ($\Delta H_p < 0$) during the polymerization, because polymerization is accompanied by entropy decrease ($\Delta S_p < 0$). In ring-opening polymerization, ring strain of monomers considerably contributes to the negative enthalpy during the polymerization.[5a]

$$\Delta G_p = \Delta H_p - T\Delta S_p$$

$$\Delta H_p < 0 \quad \Delta S_p < 0 \quad |\Delta H_p| > -T\Delta S_p$$

The anionic ring-opening polymerizations of cyclic carbonates **1**−**5** were carried out at 10, 20, and 30 °C to estimate the thermodynamic parameters (Table 3).

The conversion of the cyclic carbonate decreased as the polymerization temperature was raised. Dainton's equation[11] (eq 1) can be applied to this type of equilib-

$$\ln [M_1] = \Delta H^\circ_{ss}/RT - \Delta S^\circ_{ss}/R \qquad (1)$$

rium polymerization, where T, $[M_1]$, ΔH°_{ss}, and ΔS°_{ss} denote the polymerization temperature, the monomer concentration at equilibrium, the standard enthalpy, and the standard entropy change for the polymerization of cyclic carbonates in solution, respectively.

Linear relationships were observed between ln $[M_1]$ and $1/T$ in the polymerizations of cyclic carbonates as shown in Figure 2, supporting the equilibrium polymerization. The ΔH_{ss} and ΔS_{ss} values were calculated from the plots as summarized in Table 4, which were similar to those of the other heterocyclic compounds.[4f,j,12] The absolute value of ΔH_{ss} and ΔG_{ss} decreased in the order of **1** > **2** > **3** ≥ **4** > **5**. The monomer with higher polymerizability showed a larger $|\Delta G_{ss}|$ value. This result suggests that the polymerizabilities of the cyclic carbonates closely correlate to their thermodynamic parameters.

It seems that the substituent effect on the equilibrium polymerization is caused by the difference between the monomer and polymer structures. First, single-crystal X-ray analysis was carried out for the monomers **1**−**5** to examine the conformations (Figure 3). No significant difference could be observed for the steric hindrances by the substituents around the carbonyl groups of **1**−**5** and their ring structures. The difference of the polymerizability could not be simply explained by the difference of the monomer conformation.

Next, the conformations of the trimers were analyzed by semiempirical molecular orbital calculations (PM3 method) as the model compounds of the polymers. A trans zigzag structure was used as the starting geom-

Table 3. Temperature Effect on the Equilibrium Monomer Concetration in the Anionic Ring-Opening Polymerization of Cyclic Carbonates[a]

run	monomer	concn (M)	temp (°C)	av conversion[b] (%)	equil monomer concn (M_e)
1	**1**	0.03	10	90	0.30×10^{-2}
2	**1**	0.03	20	82	0.54×10^{-2}
3	**1**	0.03	30	79	0.60×10^{-2}
4	**2**	0.2	10	89	0.02
5	**2**	0.2	20	85	0.03
6	**2**	0.2	30	79	0.04
7	**3**	0.45	10	79	0.10
8	**3**	0.45	20	74	0.12
9	**3**	0.45	30	64	0.16
10	**4**	0.45	10	75	0.11
11	**4**	0.45	20	71	0.13
12	**4**	0.45	30	60	0.18
13	**5**	0.6	10	35	0.39
14	**5**	0.6	20	32	0.40
15	**5**	0.6	30	25	0.45

[a] Conditions: initiator, *t*-BuOK (1 mol %); solvent, THF. [b] Determined by ^{1}H NMR.

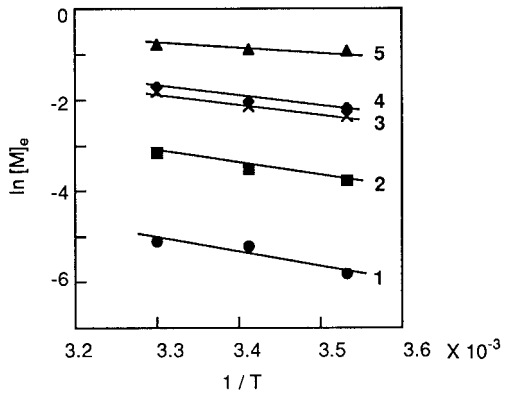


Figure 2. Relationships between ln $[M]_e$ and $1/T$ in the anionic ring-opening polymerization of cyclic carbonates. Polymerization conditions: Table 3.

Table 4. ΔH_{ss}, ΔS_{ss}, and ΔG_{ss} Estimated for the Equilibrium Polymerization of Cyclic Carbonates by Dainton's Equation

monomer	ΔH_{ss} (kcal/mol)	ΔS_{ss} (cal/(K·mol))	ΔG_{ss}[a] (kcal/mol)
1	−6.3	−10.7	−3.1
2	−5.1	−10.5	−2.0
3	−4.4	−10.9	−1.2
4	−4.0	−9.7	−1.2
5	−1.2	−2.4	−0.5

[a] At 20 °C.

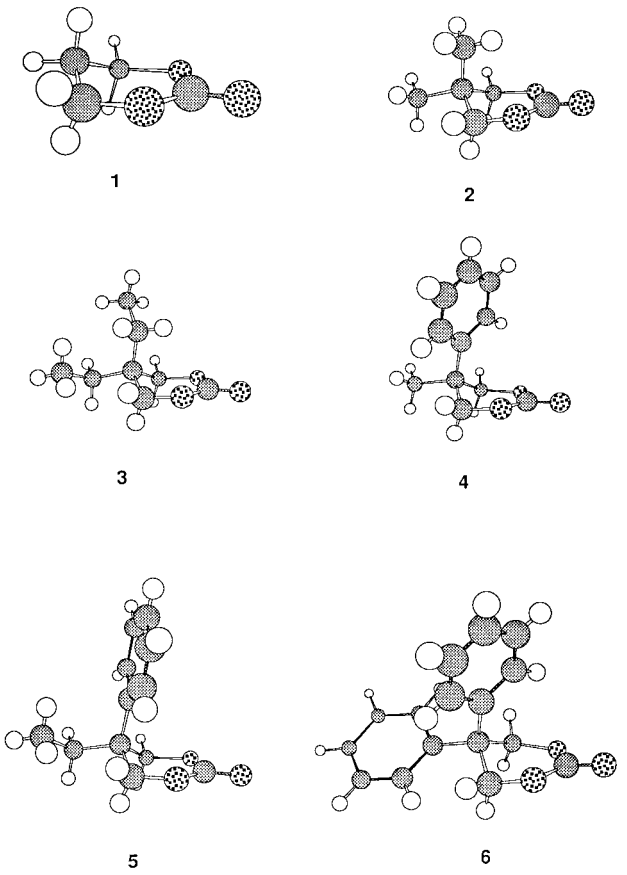


Figure 3. Structures of cyclic carbonates **1**−**6** obtained by single-crystal X-ray structural analyses.

etry, and a syndiotactic structure was adopted as the geometries of the model compounds of poly(**4**) and poly(**5**), because the structure had smaller steric repulsion than the isotactic one. The optimized structures are illustrated in Figure 4. No significant difference was observed between the starting and optimized geometries of poly(**1**), poly(**2**), and poly(**3**) (**I**−**III**). On the other hand, the carbonate moieties of poly(**4**) and poly(**5**) (**IV** and **V**, indicated with boxes in Figure 4) were twisted by the steric repulsion of the substituents. Table 5 summarizes the heats of formation of the model compounds (A) and cyclic carbonates (B), estimated by the PM3 method, and the ratios of A to B, along with the data for 5,5-diphenyl-1,3-dioxan-2-one (**6**).[13] The [A]/[B] value was in the order **1**−**3** > **4**, **5** > **6**, which well agreed with the order of the polymerizability. This result suggests that the steric repulsion of substituents on the polymer chain is responsible for the thermodynamic stability of macromolecules, as reported in the polymerization of spiro ortho ester.[4h]

Depolymerization of Polycarbonate. As described above, the anionic ring-opening polymerization of the cyclic carbonates is the equilibrium one. It is expected that the monomer will be re-formed up to the equilibrium monomer concentration in the depolymerization of the corresponding polycarbonate. The depolymerizations of poly(**2**−**5**) were carried out with *t*-BuOK (1 mol %) in THF (0.45 M) at 20 °C for 24 h (Scheme 4). The reaction mixtures were analyzed by GPC. Figure 5 shows the GPC profiles before and after the depolymerizations of poly(**3**) and poly(**5**), respectively. The peak based on the polycarbonate disappeared after the depolymerization, and the peaks attributable to the monomer and the oligomers appeared.

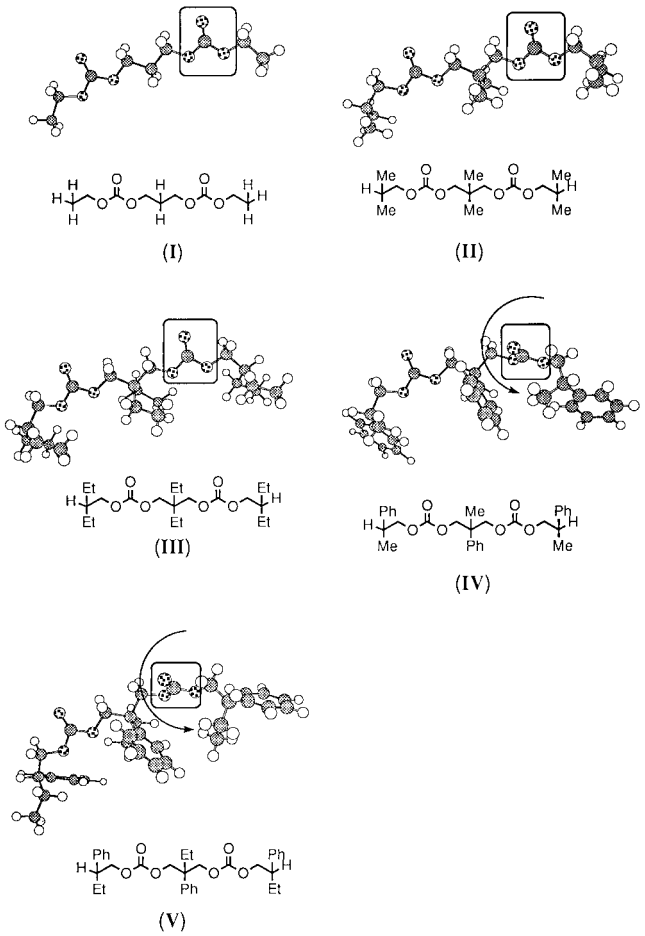
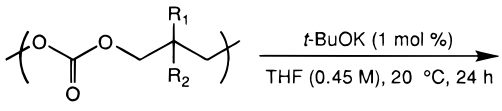


Figure 4. Optimized geometries of polymer models obtained by the PM3 MO method.

Table 5. Heat of Formation (H_f) of Polymer Models (A) and Cyclic Carbonates (B) Estimated by the PM3 Method

polymer model	H_f of polymer model (A) (kcal/mol)	cyclic carbonate	H_f of cyclic carbonate (B) (kcal/mol)	(A)/(B)
I	−271.8	**1**	−128.1	2.12
II	−297.6	**2**	−139.3	2.14
III	−314.3	**3**	−147.4	2.13
IV	−190.2	**4**	−103.0	1.85
V	−196.3	**5**	−106.5	1.84
VI	−76.9	**6**	−65.8	1.17

Scheme 4



R_1=R_2=Me, Poly(**2**)
R_1=R_2=Et, Poly(**3**)
R_1=Ph, R_2=Me, Poly(**4**)
R_1=Ph, R_2=Et, Poly(**5**)

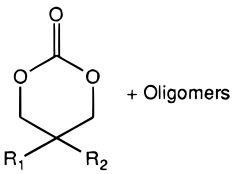


Table 6 summarizes the concentrations of the formed monomers and the equilibrium monomer concentrations calculated therefrom. These values well agreed with the equilibrium monomer concentrations (Table 2) esti-

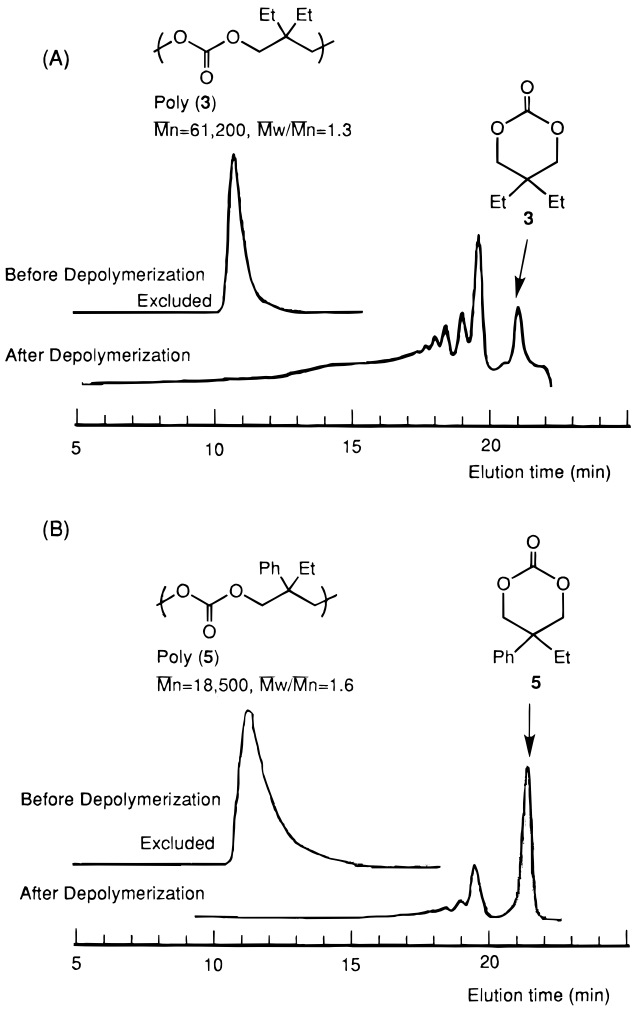


Figure 5. (A) GPC profiles of the reaction mixture before and after depolymerization of poly(**3**) (M_n = 61 200, M_w/M_n = 1.3). The depolymerization was carried out by the addition of *t*-BuOK (1 mol %) in THF (0.45 M) at 20 °C for 24 h. (B) GPC profiles of the reaction mixture before and after depolymerization of poly(**5**) (M_n = 18 500, M_w/M_n = 1.6). The depolymerization was carried out by the addition of *t*-BuOK (1 mol %) in THF (0.45 M) at 20 °C for 24 h.

Table 6. Monomer Yield Recovered in the Depolymerization of Polycarbonates and Equilibrium Monomer Concentration[a]

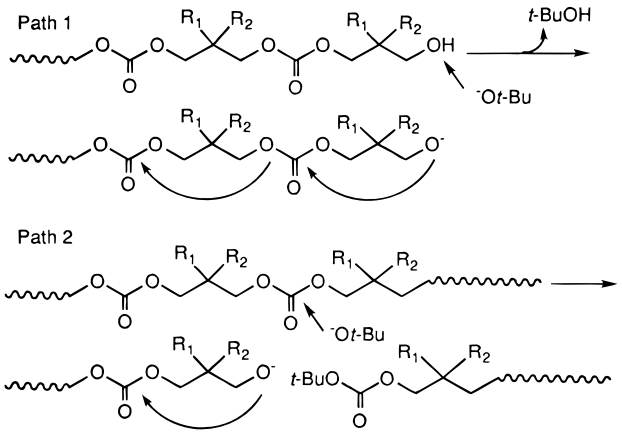
run	polycarbonate	M_n (M_w/M_n)[b]	monomer recovered[c] (%)	equil monomer concn (M)
1	poly(**2**)	54 000 (1.4)	7	0.03
2	poly(**3**)	61 200 (1.3)	19	0.08
3	poly(**4**)	25 300 (1.5)	32	0.15
4	poly(**5**)	18 500 (1.6)	71	0.32

[a] Conditions: initiator, *t*-BuOK (1 mol %); solvent, THF (0.45 M); temperature, 20 °C; time, 24 h. [b] Estimated by GPC based on polystyrene standards. [c] Determined by ^{1}H NMR.

mated from the time−conversion relationships in Figure 1. The cyclic carbonate with more bulky substituents showed the higher equilibrium monomer concentration.

Two initiation reactions are plausible in the depolymerization as shown in Scheme 5. In path 1, the anionic initiator extracts the proton of the end hydroxy group, and the formed alkoxide attacks the carbonate moiety in the main chain. In path 2, the initiator randomly attacks the carbonate moiety in the polymer main chain. Path 2 may be more plausible, since large

Scheme 5



amounts of oligomers were formed in the depolymerizations as shown in Figure 5.

Summary

In this article, the anionic equilibrium polymerization behavior was studied on the six-membered cyclic carbonates (**1**−**5**). The conversions of **1**−**5** reached constant values below 100%, and the final conversions decreased in the order of **1** > **2** ≥ **3** > **4** > **5**. In the reaction of 2-ethyl-2-phenyl-1,3-propanediol and phosgen dimer, the cyclic carbonate (**5**) was formed quantitatively, while, in the reaction of 2,2-diethyl-1,3-propanediol with phosgene dimer, poly(**3**) was formed in 24% yield besides **3**. These results may suggest that the formation of a cyclic monomer with more bulky substituents is more preferable than that of the linear polymer. The thermodynamic parameters were estimated by Dainton's equation in the anionic ring-opening polymerization of cyclic carbonates. The ΔH_{ss} value in the ring-opening polymerization of each cyclic carbonate reflected the polymerizability. X-ray analysis of the cyclic carbonates and MO calculations of the model compounds of the polymer were carried out to study the difference in the polymerizability. No significant difference was observed in the monomer conformation, but some torsion of the main chain was confirmed in the model compound with bulky substituents. It seemed that the polymerizabilities of the cyclic carbonates correlated with the stabilities of the corresponding polymers. The concentrations of the formed monomers in the depolymerization well agreed with the equilibrium monomer concentrations in the anionic ring-opening polymerization.

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(9) Conversion of **1** = the integral ratio of poly(**1**) (CH_2O, 4.24 ppm, 4H)/[the integral ratio of poly(**1**) (CH_2O, 4.24 ppm, 4H) + the integral ratio of **1** (CH_2O, 4.47 ppm, 4H)] × 100. Conversion of **2** = the integral ratio of poly(**2**) (CH_2O, 3.93 ppm, 4H)/[the integral ratio of poly(**2**) (CH_2O, 3.93 ppm, 4H) + the integral ratio of **2** (CH_2O, 4.08 ppm, 4H)] × 100. Conversion of **3** = the integral ratio of poly(**3**) (CH_2O, 4.00 ppm, 4H)/[the integral ratio of poly(**3**) (CH_2O, 4.00 ppm, 4H) + the integral ratio of **3** (CH_2O, 4.14 ppm, 4H)] × 100. Conversion of **4** = [the integral ratio of poly(**4**) (CH_2O, 4.26−4.49 ppm, 4H) − the integral ratio of **4** (CH_2O, 4.65 ppm, 2H)]/[the integral ratio of poly(**4**) (CH_2O, 4.26 ppm, 4H) + the integlation ratio of **4** (CH_2O, 4.40 ppm, 2H) + the integral ratio of **4** (CH_2O, 4.65 ppm, 2H)] x 100. Conversion of **5** = [the integral ratio of poly(**5**) (CH_2O, 4.43−4.53 ppm, 4H) − the integral ratio of **5** (CH_2O, 4.68 ppm, 2H)/[the integral ratio of poly(**5**) (CH_2O, 4.43 ppm, 4H) + the integral ratio of **5** (CH_2O, 4.48 ppm, 2H) + the integral ratio of **5** (CH_2O, 4.68 ppm, 2H)] × 100.

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(12) The thermodynamic parameters were reported for some cyclic monomers in ref 4f,j. δ-Valerolactone: $\Delta H_{lc} = -6.6$ kcal/mol; $\Delta S_{lc} = -15.5$ cal·mol^{-1}·K^{-1}. L-Lactide: $\Delta H_{lc} = -5.5$ kcal/mol; $\Delta S_{lc} = -6.0$ cal·mol^{-1}·K^{-1}. δ-Valerolactam: $\Delta H_{lc} = -1.7$ kcal/mol; $\Delta S_{lc} = -6.6$ cal·mol^{-1}·K^{-1}. THF: $\Delta H_{lc} = -3.0$ kcal/mol; $\Delta S_{lc} = -9.8$ eu. 1,3-Dioxepan: $\Delta H_{ss} = -3.2$ kcal/mol; $\Delta S_{ss} = -9.3$ eu. Subscripts denote the state of monomer and polymer (l = liquid, c = condensed, s = solution).

(13) In another paper, we have reported that **6** does not polymerize at all: Matsuo, J.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.*, submitted for publication.

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