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ORIGINAL ARTICLE

The anionic ring-opening polymerization of five-membered cyclic carbonates fused to the cyclohexane ring

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The anionic polymerization of five-membered cyclic carbonates fused to a cyclohexane ring, that is, the *trans*- and *cis*-cyclohexane-1,2-diyl carbonates (*trans*- and *cis*-1, respectively), were examined as a model polymerization example to reveal the origin of the unusually good polymerizability of the previously reported methyl 4,6-*O*-benzylidene-2,3-*O*-carbonyl-α, D-glucopyranoside. The *tert*-BuOK-initiated anionic polymerization of *trans*-1 produces polymers with M_n values of 11 000, whereas no polymeric products were obtained from *cis*-1. The structure of the poly(*trans*-1) was confirmed by comparison with the model carbonate (2) based on the ^{13}C NMR spectra as well as the hydrolysis experiments. The poly(*trans*-1) form essentially consists of polycarbonate units; therefore, the polymerization of *trans*-1 was not accompanied by any decarboxylation. The thermodynamic parameters for the polymerization of *trans*-1 were estimated to be $\Delta H_p^\circ = -23\,kJ\,mol^{-1}$ and $\Delta S_p^\circ = -63\,J\,K^{-1}\,mol^{-1}$.
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Keywords: aliphatic polycarbonate; anionic polymerization; ring-opening polymerization; thermodynamic

INTRODUCTION

Aliphatic polycarbonates are biocompatible and biodegradable materials.[1–3] For their synthesis, various procedures have been used, that is, (i) the polycondensation between the carbonate derivatives and diols,[4] (ii) the ring-opening polymerization of cyclic carbonates,[5–19] and (iii) the alternating polymerization of epoxides with carbon dioxide. Among these procedures, the ring-opening polymerizations of cyclic carbonates have the potential to control the molecular weight and to induce copolymerization with other cyclic monomers.

The anionic ring-opening behavior of the cyclic carbonates is known to depend on the ring size. Six-membered cycles (or larger) using anionic initiators tend to polymerize smoothly, yielding the corresponding polycarbonate at a lower temperature ($<100\,^\circ C$).[5–19] In contrast, the anionic ring-opening polymerization of the five-membered ring is thermodynamically unfavorable and proceeds at a higher temperature ($>150\,^\circ C$), causing the elimination of carbon dioxide to produce a copolymer that consists of both carbonate and ether linkages.[20–25] However, we reported that the anionic ring-opening polymerization of a five-membered cyclic carbonate (MBCG) (Figure 1) possessing the α,D-glucopyranoside structure proceeded even at $0\,^\circ C$ to produce an aliphatic polycarbonate without the elimination of carbon dioxide.

Additionally, MBCG was found to have corresponding polymerizability to L-lactide (LL), because the copolymerization of MBCG with LL almost produces random copolymers. We attributed the high polymerization tendency of MBCG to the ring strain of the five-membered carbonate ring, which is attached to the pyranoside ring in the trans fashion.

To confirm the high polymerizability of the *trans*-fused cyclic carbonate, we examined the anionic ring-opening polymerization of the model compounds, that is, the *trans*- and *cis*-cyclohexane-1,2-diyl carbonates (*trans*- and *cis*-**1**, respectively) (Figure 1). In this study, we report the anionic polymerization behavior of *trans*- and *cis*-**1** and compare their polymerization abilities.

EXPERIMENTAL PROCEDURE

Measurements

^1H and ^{13}C NMR spectra were measured in $CDCl_3$ or C_6D_6 using a JEOL JNM-ECX 400 spectrometer (JEOL, Tokyo, Japan; 400 MHz for ^1H and 100 MHz for ^{13}C) at room temperature. The chemical shift values were recorded in p.p.m. downfield from tetramethylsilane (0.0 p.p.m.) and $CDCl_3$ (77.0 p.p.m.) or C_6D_6 (128.0 p.p.m.), which were used as the internal standard for the ^1H and ^{13}C measurements, respectively. The number-average (M_n) and weight-average (M_w) molecular weights were estimated by size-exclusion chromatography (SEC) using a Tosoh DP-8020 pump (Tosoh, Tokyo, Japan), a Viscotek TDA MODEL-300 refractive index detector and polystyrene gel columns (Tosoh, TSK gels G2500H, G3000H, G4000H and GMH) in THF or chloroform.

Materials

Tetrahydrofuran (THF, Kanto Chemicals, Akishima, Japan) was refluxed over sodium-benzophenone ketyl and was distilled immediately prior to use.

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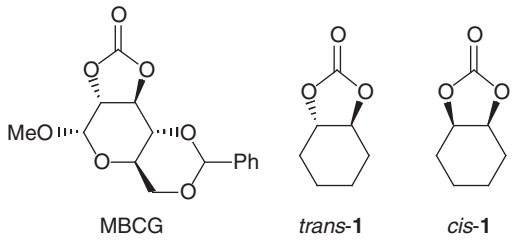

Figure 1 The structures of MBCG, *trans*-**1** and *cis*-**1**.

Potassium *tert*-butoxide (^{t}BuOK) was purchased as a 1.0 M solution in THF (Aldrich, Tokyo, Japan) and was used as received. The *trans*- and *cis*-cyclohexane-1,2-diols were prepared from cyclohexene according to the literature.[26,27] All other chemicals were commercially available and used as received.

Monomer synthesis

*trans-Cyclohexane-1,2-diyl carbonate (trans-**1**).* Ethyl chloroformate (240 ml, 2.52 mol) was added drop-wise at 5 °C to a solution of *trans*-cyclohexane-1,2-diol (10 g, 86 mmol) in 1,4-dioxane (120 ml). A solution of triethylamine (85 ml, 0.61 mol) in toluene (400 ml) was then slowly added so that the temperature of the solution did not exceed 20 °C. The resulting white suspension was further stirred for 1 h at 5 °C. Filtration was used to remove the formed salt, and the filtrate was washed with 1 wt% aqueous hydrochloric acid until acidified, and then with water to neutralize. The organic layer was dried over $MgSO_4$ and was concentrated under reduced pressure. The residue was recrystallized from n-hexane to give colorless needles. Yield 7.1 g (50 mmol, 58%). MP 57–58 °C (lit. 53–54 °C).[28,29] ^{1}H NMR (400 MHz, $CDCl_3$): δ (p.p.m.) = 4.14–3.97 (m, 2H, CH), 2.39–2.13 (m, 2H, equatorial H-3 and H-6), 2.07–1.82 (m, 2H, axial H-3 and H-6), 1.81–1.52 (m, 2H, axial H-4 and H-5), 1.52–1.23 (m, 2H, equatorial H-4 and H-5). ^{13}C NMR (100 MHz, $CDCl_3$): δ (p.p.m.) = 155.1 (C = O), 83.5 (CH), 28.2 (C-3 and C-6), 23.2 (C-4 and C-5).

*cis-Cyclohexane-1,2-diyl carbonate (cis-**1**).* *Cis*-**1** was prepared from *cis*-cyclohexane-1,2-diol (2.0 g, 17 mmol) according to a procedure that was similar to that used for the *trans*-**1**. Pure *cis*-**1** was obtained as colorless needles after recrystallization from ethyl acetate-petroleum ether. Yield 1.5 g (11 mmol, 61%). MP 40–41 °C (lit. 35–37 °C).[30] ^{1}H NMR (400 MHz, $CDCl_3$): δ (p.p.m.) = 4.74–4.67 (m, 2 H, CH), 1.91–1.87 (m, 4H, CH_2), 1.70–1.36 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ (p.p.m.) = 155.4 (C = O), 75.7 (CH), 26.5 (C-3 and C-6), 18.9 (C-4 and C-5).

Polymerization

The following describes a typical polymerization procedure. In a test tube equipped with a three-way stopcock and filled with nitrogen, *trans*-**1** (0.57 g, 4.0 mmol) was melted at 60 °C using an oil bath. An initiator, ^{t}BuOK (1.0 M solution in THF, 0.16 ml, 0.16 mmol) was added via syringe. The mixture was stirred at this temperature for 3 h. Acetic acid (12 µl) was added to quench the reaction, and the solution was then poured into petroleum ether (50 ml). The white precipitate was collected by filtration, reprecipitated from $CHCl_3$-petroleum ether and dried in vacuo at room temperature. Yield 0.49 g (83%). M_n = 11 000 (SEC). M_w/M_n = 3.9.

Model compound

*trans-1,2-bis(ethoxycarbonyloxy)cyclohexane (**2**).* **2** was prepared from *trans*-cyclohexane-1,2-diol (1.3 g, 11 mmol) according to the literature.[31] Pure **2** was obtained as a white solid after performing column chromatography on silica gel with ethyl acetate/n-hexane (1/1, *v/v*). Yield, 1.1 g (4.3 mmol, 39%). ^{1}H NMR (400 MHz, C_6D_6): δ (p.p.m.) = 4.89–4.79 (m, 2 H, CH), 4.04–3.82 (m, 2H, OCH_2), 2.08–1.92 (m, 2H, CH_2), 1.36–1.12 (m, 4H, CH_2), 1.00–0.80 (m, 8H, CH_3 and CH_2). ^{13}C NMR (100 MHz, C_6D_6): δ (p.p.m.) = 155.0 (C = O), 77.0 (CH), 63.7 (OCH_2), 30.0 (C-3 and C-6), 23.1 (C-4 and C-5), 14.1 (CH_3).

Table 1 The anionic polymerization of *trans*- and *cis*-1 with ^{t}BuOK.[a]

Run	Monomer	Solvent	$[M]_0$ (mol l^{-1})	Temp (°C)	Yield[b], (%)	M_n 10^{-3} [c]	M_w/M_n [c]
1	*trans*-**1**	Diglyme	5.0	150	0	—	—
2	*trans*-**1**	Diglyme	5.0	60	0	—	—
3	*trans*-**1**	THF	5.0	60	44	0.4	1.0
4	*trans*-**1**	None	—	150	35	4.3	1.4
5	*trans*-**1**	None	—	60	69	11.0	3.9
6	*cis*-**1**	Diglyme	5.0	150	0	—	—
7	*cis*-**1**	Diglyme	5.0	60	0	—	—
8	*cis*-**1**	THF	5.0	60	0	—	—
9	*cis*-**1**	None	—	150	0	—	—
10	*cis*-**1**	None	—	60	0	—	—

[a] $[M]_0/[I]_0$ = 25, Time; 3 h.
[b] Petroleum-ether-insoluble fraction.
[c] Estimated by SEC eluted in THF with polystyrene standard.

RESULTS AND DISCUSSION

Monomer synthesis

For the monomer synthesis, the corresponding diols were prepared according to the literature. *Trans*-cyclohexane-1,2-diol was synthesized by the oxidation of cyclohexene with H_2O_2 aq, followed by alkaline hydrolysis.[26] *Cis*-cyclohexane-1,2-diol was synthesized by the oxidation of cyclohexene with osmium tetroxide in the presence of *N*-methylmorpholine *N*-oxide.[27] *Trans*- and *cis*-**1** were synthesized from ethyl chloroformate and the corresponding diols. The structures of the monomers were confirmed by ^{1}H and ^{13}C NMR.

Polymerization

Table 1 shows the polymerization results of the *trans*- and *cis*-**1**. The polymerizations were carried out using ^{t}BuOK as the initiator, which is a very common anionic initiator for lactones, including cyclic carbonates. The solution polymerizations of *trans*-**1** were carried out in bis(2-methoxyethyl) ether (diglyme) or tetrahydrofuran (THF) (runs 1, 2 and 3). The polymerization in diglyme gave no polymeric material at either 60 or 150 °C (runs 1 and 2), whereas polymerization in THF produced the petroleum-ether-insoluble material at 44% yield. The products, however, showed only low number-average molecular weights (M_n) of 400; therefore, the solution polymerization of *trans*-**1** hardly proceeded. However, the melt polymerization without solvents produced a polymeric product that was insoluble in petroleum ether (runs 3-5) and exhibited a relatively higher M_n of 11 000 at 60 °C (run 5). The M_n tended to decrease with increasing polymerization temperature (run 4). Such a tendency is often seen during equilibrium polymerizations, that is, a lower monomer concentration and higher temperature lead to suppression of the polymerization progress. The polydispersity index (PDI, M_w/M_n) at 150 °C was 1.4, which was also lower than at 60 °C, despite the common tendency of equilibrium polymerization to become large at higher temperature. It is likely that the polymeric products at 150 °C had a low M_n and significantly dissolved in the petroleum ether during reprecipitation, causing the PDI at 150 °C to be smaller than the actual value. However, the polymerization of *cis*-**1** gave no polymeric products under any conditions (runs 6–10).

To examine the influence of time on the polymerization of 1, the polymerization was carried out from 1 h to 24 h. Figure 2 shows the relationship between the polymerization time and the yield of *trans*-**1** at 60 °C and 150 °C. At 60 °C, the yield and M_n increased until 12 h, after which time both values slightly decreased. At 150 °C, the yield

and M_n tended to decrease with increasing polymerization time. The ^{13}C NMR spectrum of the filtrate of poly(*trans*-**1**) at 150 °C is analogous to poly(cyclohexene oxide) and showed no carbonyl carbon signal. This means that at 150 °C, the polycarbonate units were decarboxylated to produce oligoether units, and the M_n decreased. However, the polymerization of *cis*-**1** gave no polymeric products even if the polymerization time was extended.

Polymer structure

As already mentioned, it is well known that the ring-opening polymerizations of cyclic carbonates are accompanied by decarboxylation to produce the polyether repeating unit. To clarify the structure of the obtained polymer, *trans*-1,2-*bis*(ethoxycarbonyloxy)-cyclohexane (**2**) was prepared as a model compound for the carbonate repeating units. Figure 3 shows the ^{13}C NMR spectra of the obtained polymer (run 5 in Table 1) and model compound (**2**). The ^{13}C NMR spectra of the obtained polymer showed sharp signals at 154.6 p.p.m.. These data agreed with that of **2** at 155.0 p.p.m., which was assigned to the carbonyl carbon. Additionally, the signals at 77.7, 30.0 and 23.0 p.p.m. in the polymer spectrum were comparable to the methyne carbon, which appeared at 77.0, and the methylene carbons, which appeared at 30.0 and 23.1 p.p.m. of **2**. Thus, the spectrum of the obtained polymer agreed well with that of **2**. This implies that the polymerizations of *trans*-**1** proceeded without decarboxylation.

To further confirm that the anionic polymerizations of *trans*-**1** proceed without decarboxylation, the alkaline hydrolysis of the poly(*trans*-**1**) was carried out. If carbon dioxide elimination occurred during the anionic polymerization of *trans*-**1**, the resulting polymer should contain polyether repeating units, which should be inert to hydrolysis. The polycarbonate repeating units are likely hydrolyzed to give the *trans*-cyclohexane-1,2-diol. Figure 4 shows the SEC chromatograms of the original polymer, the hydrolysis product, and *trans*-cyclohexane-1,2-diol as a model compound. The peak due to the higher molecular weight in the polymer chromatogram was completely absent in that of the hydrolysis product, which instead showed a sharp peak at a lower weight, corresponding to that of *trans*-cyclohexane-1,2-diol.

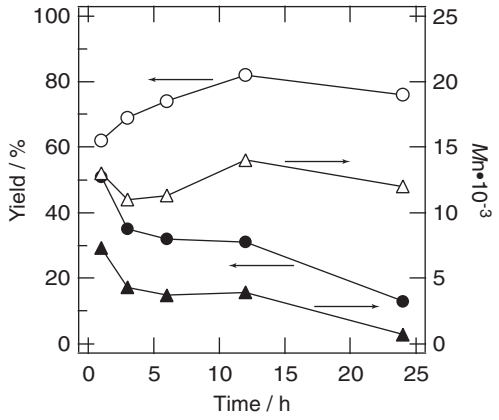

Figure 2 The yield and M_n as a function of time for the bulk polymerization of *trans*-**1**. initiated by ^{t}BuOK. $[M]_0/[I]_0 = 25$. (○) (Δ) = 60 °C, (●) (▲) = 150 °C.

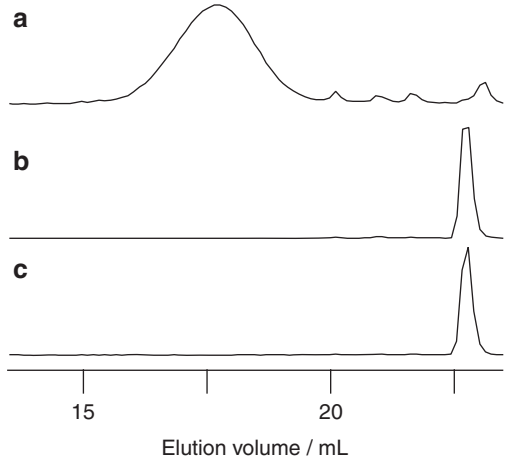

Figure 4 SEC chromatograms of (**a**) the original polymer (run 5 in Table 1), (**b**) their hydrolyzate, and (**c**) *trans*-cyclohexane-1,2-diol eluted with chloroform. The hydrolysis was carried out using KOH in ethanol at room temperature for 3 h.

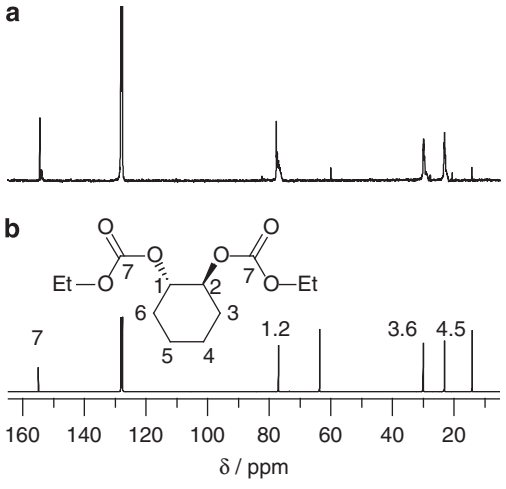

Figure 3 ^{13}C NMR spectra of (**a**) the obtained polymer (run 5 in Table 1) and (**b**) **2** measured in C_6D_6.

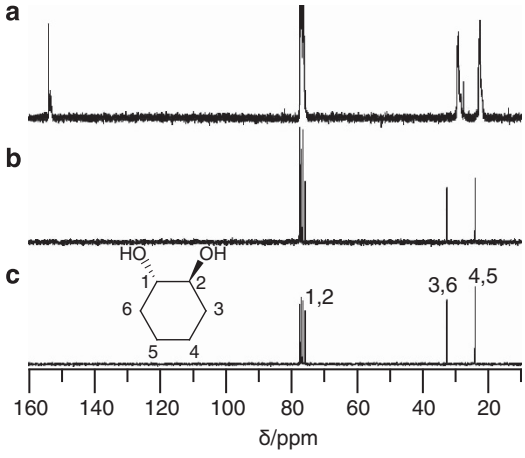

Figure 5 ^{13}C NMR spectra of (**a**) the original polymer (run 5 in Table 1), (**b**) their hydrolyzates, and (**c**) *trans*-cyclohexane-1,2-diol measured in $CDCl_3$.

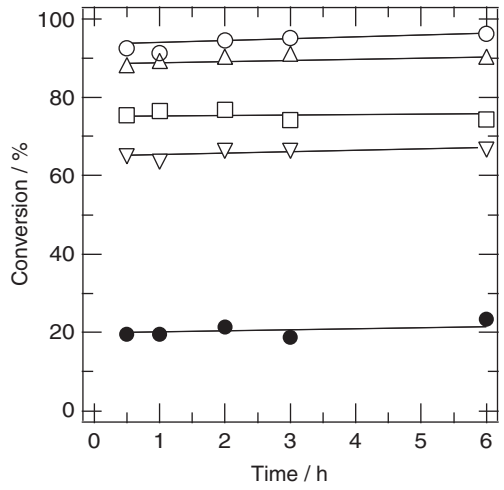

Figure 6 Monomer conversion as a function of the reaction time for the solution. polymerization of *trans*-**1** with ^{t}BuOK. Solvent: THF, $[M]_0 = 0.1$ mol/l, $[M]_0/[I]_0 = 25$. (○) = –60°C, (Δ) = –40°C, (□) = –20°C, (▽) = 0°C, (●) = 30°C.

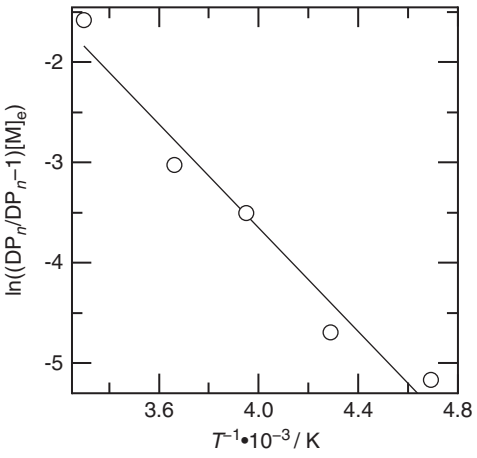

Figure 7 Dainton's plot for the anionic solution polymerization of *trans*-**1**.

Figure 5 shows the ^{13}C NMR spectra of the original polymer (run 5 in Table 1), the hydrolysis product, and *trans*-cyclohexane-1,2-diol. The peak at 153.8 p.p.m. was derived from the carbonate units and completely disappeared after hydrolysis, and the spectra of the hydrolysis product and *trans*-cyclohexane-1,2-diol completely agreed each other over the entire spectral range. These results indicate that hydrolysis proceeded to completion and that the hydrolysis product did not contain polyether units, that is, the anionic polymerization of *trans*-**1** proceeded without decarboxylation, and the obtained polymer consisted of only polycarbonate units.

Thermodynamics

The polymerizability of cyclic monomers is strongly related to the enthalpy change (ΔH_p°) and entropy change (ΔS_p°) of the ring-opening process. The equilibrium monomer concentration ($[M]_e$) is related to the enthalpy and entropy of polymerization (Equation (1)).[32]

$$\ln\left(\frac{DP_n}{DP_n - 1}[M]_e\right) = \frac{\Delta H_p^\circ}{RT} - \frac{\Delta S_p^\circ}{R} \quad (1)$$

$[M]_e$ can be calculated based on the monomer conversion at equilibrium. However, we could not obtain $[M]_e$ for the melt polymerizations, because the monomer conversions reached ~100% within 1 h at high temperature. Therefore, the polymerizations were carried out in a dilute (0.1 M) solution. The monomer conversions were calculated using the area ratio of the signals of the methyne proton of *trans*-**1** and poly(*trans*-**1**), which appeared at 4.06 and 4.65 p.p.m., respectively, in the ^{1}H NMR spectra. The DP_ns were also estimated from the ^{1}H NMR spectra using the methyne protons of the repeating and terminal units. Figure 6 shows the plotted monomer conversion versus the polymerization time during the solution polymerization at polymerization temperatures ranging from −60 °C to 30 °C. The monomer conversion reached a constant value immediately after initiation. With respect to the period after the constant conversions, where the polymerization was in equilibrium, the $[M]_e$ values were calculated from the conversions. According to Equation (1), the $\ln((DP_n \cdot [M]_e)/(DP_n–1))$, the calculated and obtained $[M]_e$ and DP_n values were plotted versus T^{-1} in Figure 7.

Table 2 ΔH_p° **and** ΔS_p° **of the ring-opening polymerization of cyclic carbonates**

Monomer	ΔH_p°/kJ mol^{-1}	ΔS_p°/J mol^{-1} K^{-1}
trans-**1**	−23	−63
Ethylene carbonate	125.6[24]	—
Trimetylene carbonate	−26[15]	−44.8[15]

We obtained a good linearity, and we estimated $\Delta H_p^\circ = -23$ kJ mol^{-1} and $\Delta S_p^\circ = -63$ J K^{-1} mol^{-1} from the slope and *y*-intercept, respectively. Table 2 shows the ΔH_p° and ΔS_p° values of the cyclic carbonates, including the values of *trans*-**1**. The ΔH_p° of *trans*-**1** showed negative values, which were close to that of trimethylene carbonate; the latter has good ring-opening polymerizability in comparison to the common five-membered cyclic carbonates, such as ethylene carbonate. This indicates that *trans*-**1** has an unusually high ring strain among the five-membered cyclic carbonates. Owing to this high ring strain, *trans*-**1** has a good ring-opening polymerizability, whereas the ring-opening polymerization of *cis*-**1** does not proceed under these conditions.

From the anionic ring-opening polymerization of *trans*- and *cis*-**1**, we conclude that the five-membered cyclic carbonate fused to a six-membered ring in the *trans*-fashion has sufficient ring-strain to produce the aliphatic polycarbonate without the elimination of CO_2 during the polymerization. The good ring-opening polymerizability of MBCG might be due to the *trans*-fused cyclic carbonate attached to the pyranose ring.

Summary

The ring-opening polymerizations of *trans*- and *cis*-**1** were carried out. The ring-opening polymerizations of *trans*-**1** proceeded without the elimination of CO_2. The calculation of the thermodynamic parameters of the anionic polymerization of *trans*-**1** gave $\Delta H_p^\circ = -23$ kJ mol^{-1} and $\Delta S_p^\circ = -63$ J K^{-1}mol^{-1}. The negative value of ΔH_p° indicates that *trans*-**1** has a different ring strain in comparison to that of other five-membered cyclic carbonates.

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