



Synthesis of CO₂-derived polycarbonates with high glass transition temperatures

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Abstract

To synthesize CO₂-derived polycarbonates with high T_g values, epoxides having rigid and bulky 2-norbornyl or 1-adamantyl substituents were selected as comonomers. The alternating copolymer obtained from 1-adamantylethylene oxide showed a T_g above 150 °C. This is the highest T_g among those observed for alternating copolymers obtained from CO₂ and a terminal epoxide.

Introduction

Carbon dioxide (CO₂) is a renewable carbon resource, making it a potentially useful raw material in synthetic chemistry [1, 2]. New methodologies for the direct use of CO₂ have focused on methods for CO₂ reduction [1, 2]. One of the direct utilizations of CO₂ in the production of organic materials, reported by Inoue et al. [3, 4] involves the synthesis of polycarbonates by the alternating copolymerization of CO₂ and epoxides. Since then, the copolymerization of CO₂ with various epoxides and the properties of their copolymers have been investigated [5–11]. For example, poly(propylene carbonate) (PPC; Fig. 1a, R¹ = H, R² = CH₃) is synthesized by the alternating copolymerization of CO₂ and propylene oxide, and 43% of the polymer by mass is derived from CO₂. In addition, the thermal decomposition temperature range of PPC is narrow; hence, PPC has been utilized as a binder [12]. The effects of molecular weight [13], molecular weight distribution, stereoregularity [14], regioregularity [15, 16], and topology [17, 18] of the copolymer on the

thermal properties have been studied. However, despite these investigations, the T_g values of the PPCs are not expected to be above 50 °C. This feature prevents us from using PPC in molding materials. Therefore, we have started to study the synthesis of polycarbonates with much higher T_g values than that of PPC.

It is well known that polymers with high T_g values can be obtained by introducing large and/or rigid side chains [19]. Previously, epoxides with rigid substituents have been investigated as comonomers to give CO₂-derived polycarbonates with rigid side chains. For example, cyclohexene oxide [20], indene oxide [21], and limonene oxide [22] (Fig. 1b) have been employed to produce copolymers with high T_g values. Among the copolymers obtained from these epoxides, the T_g of poly(indene carbonate), which is the alternating copolymer of CO₂ and indene oxide, was 138 °C. More recently, Kleij et al. [23] reported that the T_g of poly(limonene)dicarbonate was up to 180 °C. This value is the highest T_g of all the reported CO₂-derived polycarbonates. Although the T_g values of copolymers with internal epoxides are higher than those of PPC, the reactivities of internal epoxides in the copolymerizations with CO₂ are generally low [24]. Hence, the scope of epoxides that can be copolymerized with CO₂ is limited.

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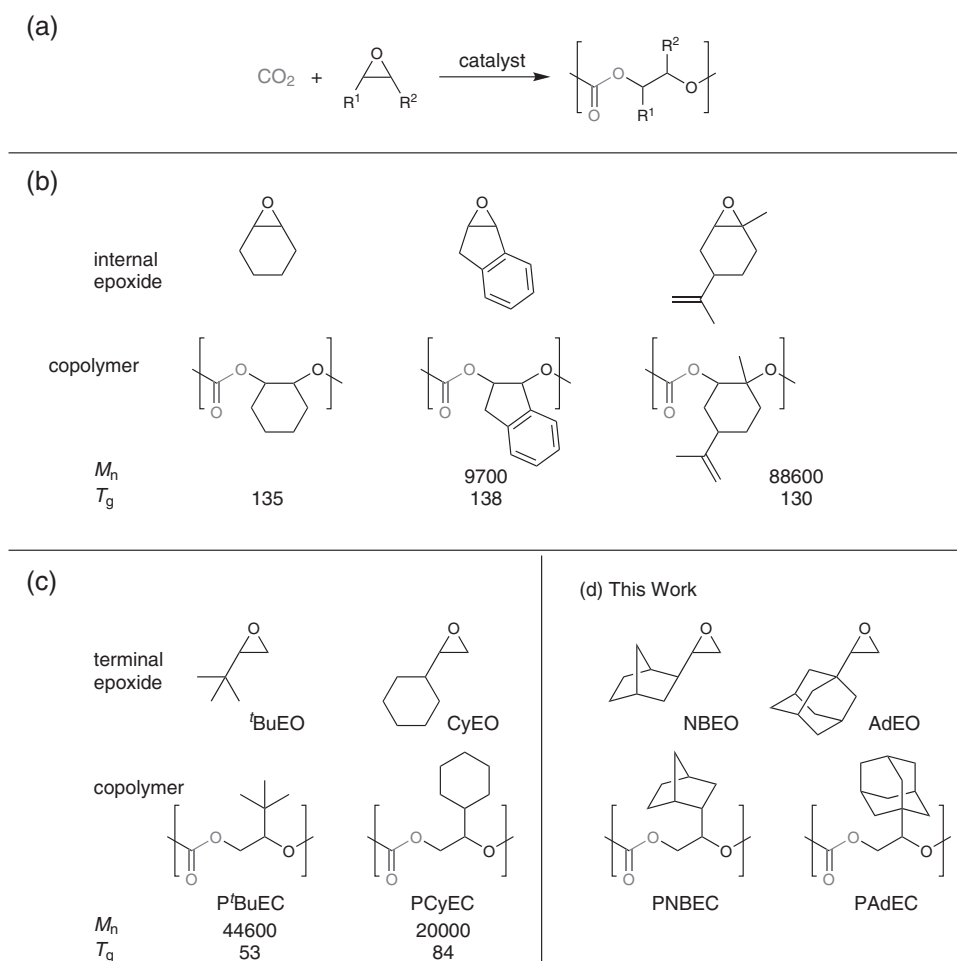
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Fig. 1 **a** Copolymerization of CO₂ and epoxides. **b** Internal epoxides and their copolymers with CO₂. **c** Terminal epoxides and their copolymers with CO₂. **d** Rigid and bulky terminal epoxides and their copolymers with CO₂



In contrast to the above, terminal epoxides are more reactive than internal epoxides, and thus various terminal epoxides have been employed as comonomers in copolymerizations with CO₂. For example, the copolymerizations of CO₂ and epoxides having bulky alkyl groups on their side chains have been reported to show T_g values that were higher than that of PPC (Fig. 1c) [25]. We anticipated that polycarbonates derived from CO₂ and terminal epoxides bearing large side groups should show higher T_g values than PPC.

To synthesize CO₂-derived polycarbonates with higher T_g values, epoxides with substituents that are more rigid and bulky than cyclohexyl were selected as comonomers. The copolymers were synthesized by alternating copolymerization of CO₂ and epoxides with 2-norbornyl (NB) or 1-adamantyl (Ad) groups as substituents (Fig. 1d), and the T_g values of the obtained copolymers were measured. As expected, we herein report that the alternating copolymerization of CO₂ and various terminal epoxides with increasing steric bulk provides copolymers with much higher T_g values than that of PPC (high glass transition temperature photoimageable polycarbonate polymers with pendent polycyclic functional groups Patent WO2014134373A1. This patent differs from this paper in

which cobalt salen complex was used as a catalyst for the alternating copolymerization).

Experimental section

Materials

Commercially available CO₂ was used without further purification. Propylene oxide (PO) was purchased from NACALAI TESQUE, INC., and *tert*-butylethylene oxide (^tBuEO) was synthesized according to the literature method [26]. All epoxides, including cyclohexylethylene oxide (CyEO), *exo*-2-norbornylethylene oxide (NBEO), and 1-adamantylethylene oxide (AdEO), the syntheses of which are described below, were distilled over CaH₂ under a nitrogen atmosphere before use. Tetraphenylporphyrinacobalt (III) chloride ((TPP)CoCl) was synthesized according to the reported procedure [27]. 4-(Dimethylamino)pyridine (DMAP) was recrystallized from toluene. CH₂Cl₂, when used as a polymerization solvent, was washed sequentially with concentrated H₂SO₄, water, aqueous NaHCO₃, and brine, dried over CaCl₂, and distilled over CaH₂ under

nitrogen. Other commercially available reagents were used as received.

Synthesis of CyEO

3-Chloroperbenzoic acid (460 g, 2.00 mol, <75%) was mechanically stirred with 7300 mL of CH₂Cl₂ inside a 4-neck 12-L flask fitted with a mechanical stirrer, a thermowell, a nitrogen inlet, and an addition funnel. The mixture cooled itself to 7.8 °C before warming to 9.1 °C after 3 min when a turbid but precipitate-free solution formed. The solution was then chilled with ice water to 1.8 °C. Vinylcyclohexane was added rapidly over 10 min via the addition funnel. After that addition, the temperature increased over the next 10 min to 3.6 °C and then cooled gradually to 1.8 °C during the following 2 h. The reaction was stirred and warmed to room temperature overnight. Subsequent gas chromatography (GC) analysis showed no remaining vinylcyclohexane. The reaction mixture was treated with two portions of 10% aqueous NaHSO₃ solution (300 mL and 260 mL) to give a negative KI/starch paper test for peroxide. Then, 3 × 300 mL portions of saturated NaHCO₃ solution were added carefully to the stirred mixture. After the vigorous effervescence subsided, approximately 100 mL of solid NaHCO₃ was added, at which point very vigorous effervescence occurred. After the liquids had become clear, the aqueous phase was found to have a pH of 6. Approximately 100 mL of solid Na₂CO₃ was added, which increased the pH to 9, and the phases were separated. The CH₂Cl₂/aqueous interface was slowly filtered to remove the solids, and the resulting clear phases were separated. The CH₂Cl₂ phase was washed with 1000 mL of brine to achieve a pH of 6–7. The CH₂Cl₂ solution was dried over MgSO₄, filtered, and the volume of solvent was carefully reduced by rotary evaporation at 189 to 91 Torr and 10–20 °C to 262 g of liquid containing a large amount of precipitate. The solids were isolated by filtration and rinsed with pentane. More crystals precipitated from the filtrate, and these were also removed by filtration. The filtrate was repeatedly treated with pentane until the total volume reached 1800 mL and no further precipitation of 3-chlorobenzoic acid occurred. The volume of the pentane solution was carefully reduced by rotary evaporation at 215 to 15 Torr and 10–20 °C to give 198.3 g (97% yield) of a yellow liquid. This crude product was distilled through a 12-inch Hempel column filled with 0.16 × 0.16-inch Pro-Pak metal packing to afford 115.7 g (57% yield) of CyEO (b.p. 109 °C/102 Torr).

Synthesis of NBEO

3-Chloroperbenzoic acid (363 g, 1.58 mol) was mechanically stirred with 4300 mL of CH₂Cl₂ inside a 4-neck 12-L

flask fitted with a mechanical stirrer, a thermowell, a nitrogen inlet, and an addition funnel. The mixture cooled itself to 9.9 °C before warming to 13.2 °C after 12 min when essentially all solid had dissolved. The solution was chilled with ice water to 2.1 °C. A mixture of vinylnorbornane and ethyl norbornane (240 g) was added rapidly via the addition funnel; the mixture was obtained from the hydrogenation of 5-vinyl-2-norbornene following the literature procedure [27], and it contained approximately 158 g (1.30 mol) of vinylnorbornane. The addition was completed within 3 min. The temperature increased over the next 4 min to 5.3 °C and then cooled steadily to 2.1 °C during the following 2 h. The reaction was allowed to stir and warm to room temperature overnight. Subsequent GC analysis showed no vinylnorbornane remaining. The reaction mixture was treated with 300 mL of 10% aqueous NaHSO₃ solution to give a negative KI/starch paper test for peroxide. Then, 4 × 300 mL portions of saturated NaHCO₃ solution were carefully added to the stirred mixture. After vigorous effervescence, the aqueous phase was found to have a pH of 7. Approximately 100 mL of solid NaHCO₃ was added, which brought the pH to 8, and then the phases were separated. The CH₂Cl₂ phase was filtered to remove the solids and then was washed with 500 mL of saturated NaHCO₃ solution to achieve a pH of 9–10 and 1000 mL of brine to reach a pH of 7–8. The CH₂Cl₂ solution was dried over MgSO₄ and filtered, and then the volume of the solution was reduced by rotary evaporation to give 262 g of liquid. After sitting overnight, crystals of 3-chlorobenzoic acid formed in the solution. These were separated by filtration and rinsed with pentane. More solids crystallized out of the solution and were removed by filtration. The filtrate was repeatedly treated with pentane until the final volume reached 1800 mL and no further crystallization of 3-chlorobenzoic acid occurred. The volume of the pentane solution was reduced by rotary evaporation to give 231 g of liquid. The crude product was distilled through a 12-inch Hempel column filled with 0.16 × 0.16-inch Pro-Pak metal packing to afford 115.9 g (0.85 mol, 65% yield) of *exo*-NBEO (b.p. 91 °C/40 Torr).

Synthesis of AdEO

3-Chloroperbenzoic acid (344 g, 1.51 mol, 1.51 equivalents, <77%) was placed into a 4-neck 5-L flask fitted with a mechanical stirrer, a thermowell, a nitrogen inlet, and an addition funnel. CH₂Cl₂ (2000 mL) was added, and the mixture was stirred. Some but not all of the peracid dissolved. The mixture was chilled to 2.5 °C in a methanol-ice bath. 1-Vinyladamantane (165 g, 1.02 mol) was added dropwise over 27 min during which the temperature ranging from 2.5 to –7.8 °C. When the temperature reached –5.0 °C, the methanol-ice bath was drained and replaced with an ice

water bath. The reaction mixture was stirred for 2 h between -0.4 and 5.0 °C. A mild exotherm occurred within the first hour. The ice bath was removed, and the reaction mixture was allowed to warm to room temperature. The mixture was allowed to stir overnight; after which, GC analysis showed no remaining vinyladamantane. The reaction mixture tested positive with KI/starch paper; thus, 450 mL of 10% aqueous NaHSO_3 solution was added. The quench was exothermic and caused the temperature to increase to ~ 38 °C, which resulted in some unexpected boiling of the CH_2Cl_2 . Following the quench, the KI/starch paper test was negative. The reaction mixture was then filtered. Solids precipitated in the filtrate, so the filtrate was filtered through a filter cake. The filter cake was washed with copious amounts of CH_2Cl_2 , and a clear phase separated out of the filtrate. The upper aqueous phase had a pH of 2. The CH_2Cl_2 phase was stirred as three portions of 100 mL of saturated NaHCO_3 solution were cautiously added. The mixture was then carefully treated with 55, 79, and 58 g portions of solid NaHCO_3 until the effervescence ceased. The aqueous phase was at $\text{pH} = 8-9$. The organic phase contained a large amount of white solid, so it was treated with 300 mL of water. The phases were separated, and the CH_2Cl_2 phase was decanted away from the remaining solids. The solids were treated with 200 mL of water and then returned to the organic phase. The phases were separated again, and the pH of the aqueous phase was 8. The solids at the interface were filtered, and the resulting phases were separated. The organic phases were combined, dried over Na_2SO_4 until clear, filtered, and reduced by rotary evaporation to give 179.6 g of clear, nearly colorless liquid in 99% yield. GC analysis shows the AdEO was 99.1% pure. AdEO can be further purified by vacuum distillation (85 °C/ 3.5 Torr).

Measurements

^1H NMR measurements were performed in CDCl_3 at 30 °C on a Bruker DPX-400 spectrometer, and tetramethylsilane ($\delta = 0.00$ ppm) was used as an internal standard. The infrared (IR) spectra of the films polymer cast on an NaCl plate from CHCl_3 solutions were recorded on a JASCO spectrometer FT/IR-4100. Gel permeation chromatography (GPC) was performed at 40 °C on a Tosoh model HLC-8220 high-speed liquid chromatography system equipped with two TSKgel SuperMultiporeHZ-H columns and a differential refractive index detector with THF as the eluent at a flow rate of 0.35 mL min^{-1} . The molecular weight calibration curve was prepared with standard polystyrenes (TSK standard polystyrene from Tosoh Co.); their weight-average molecular weights (M_w 's) by light scattering (weight-average molecular weight/number-average molecular weight (M_w/M_n) by GPC) were 1.90×10^5 (1.04), 3.79×10^4 (1.01), 1.81×10^4 (1.01), 9.1×10^3

(1.02), 5.97×10^3 (1.02). The differential scanning calorimetry (DSC) measurements were performed using a Mettler-Toledo DSC 3 analyzer at a heating and cooling rate of 10 °C min^{-1} . The reported T_g values were determined from the second heating scan.

Copolymerizations of CO_2 and epoxide

A typical procedure for the copolymerization of CO_2 and epoxide by (TPP)CoCl is as follows. A stainless steel autoclave (150 mL) containing (TPP)CoCl (0.05 mmol) and DMAP (0.0375 mmol, dried in vacuo) (Fig. 2) was purged with nitrogen. CH_2Cl_2 (3.0 mL) and epoxide (25 mmol) were added with syringes. The copolymerization was initiated by the pressurization of the solution by CO_2 up to 5.0 MPa. The mixture was stirred at 40 °C. After the prescribed time, the autoclave was cooled, and the excess CO_2 was discharged. CHCl_3 (3 mL for PO, 6 mL for CyEO and t BuEO, 12 mL for NBEO, and 25 mL for AdEO) was added to the reaction mixture, and then the solution was poured into methanol to stop the polymerization and precipitate the produced polymer. After being dried in vacuo, a small portion of the polymer was subjected to ^1H NMR and IR analyses to determine the structure of the polymer, to GPC to estimate the M_n and M_w/M_n and to DSC to determine the glass transition temperature (T_g).

Results and discussion

Copolymerization of CO_2 and epoxide

After CO_2 and PO were reacted in the autoclave for 2 days, the reaction mixture was characterized by ^1H NMR and IR spectroscopy (Table 1, run 1). Based on the ^1H NMR spectrum, the conversion of PO was 74.0% (Figure S1). Absorption bands at 1799 and 1748 cm^{-1} were observed in the IR spectrum (Figure S2). These absorptions are attributed to carbonyl stretching vibrations of cyclic and polycarbonates, respectively. The M_n was 18800 g mol^{-1} (the degree of polymerization (DP) = 184) and the M_w/M_n was

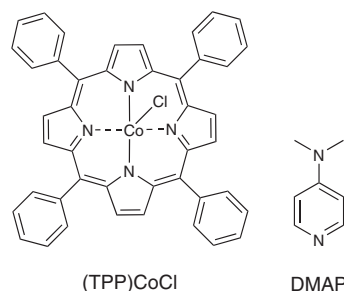


Fig. 2 (TPP)CoCl/DMAP catalytic system

1.21. These M_n and M_w/M_n values are comparable to those reported previously [26]. In the cases of the copolymerization of CO₂ with CyEO or NBEO, the reaction was carried out over 5 days. The conversions were 71.5 and 78.1%, and the M_n s of obtained copolymers were 26400 (DP = 155) and 25900 (DP = 142) (Table 1, runs 2 and 4), respectively. Copolymerizations with ^tBuEO or AdEO gave copolymers with M_n = 32800 (DP = 228) and 9600 (DP = 43) and conversions of 69.4% and 75.6%, respectively. The reactions proceeded very slowly and required 15 and 10 days, respectively, to achieve these conversions (Table 1, runs 3 and 5). In all the copolymerization reactions, consumption of the epoxide stopped at approximately 70% conversion. As polymer growth increased, the fluidity of the reaction mixture was lost, which inhibited the dissolution of CO₂ into the reaction mixture, and thus the rate of the copolymerization reaction dramatically decreased (To maintain the fluidity of the copolymerization media, use of larger amount of solvent provably is one of effective means. However, the thinner concentration causes deceleration of the copolymerization. On the other hand, raising the reaction temperature should certainly accelerate the reaction, but simultaneously promote the side reactions, such as cyclic carbonate formation. Therefore, these common methods for the acceleration of organic reactions cannot be employed in the present study).

To confirm the formation of the polycarbonate and cyclic carbonate, IR spectroscopy was carried out to characterize the reaction mixture (Figures S2, S4, S6, S8, and S10). For the copolymerization with CyEO or NBEO, a set of small and large absorptions was observed at 1805 and 1748 cm⁻¹ (CyEO; Figure S4) or at 1809 and 1747 cm⁻¹ (NBEO; Figure S8). These absorptions were attributed to carbonyl stretching vibrations of cyclic carbonate and polycarbonate, respectively.

On the other hand, an absorption at 1749 cm⁻¹ attributable to polycarbonate was observed in the IR spectrum, and an absorption at approximately 1800 cm⁻¹ was not observed for the copolymerization with ^tBuEO (Figure S6). Similarly,

Table 1 Copolymerization of CO₂ and epoxides by the (TPP)CoCl/DMAP system^a

Run	Epoxide	Time Days	conv. ^b %	M_n^c	DP ^c	M_w/M_n^c
1	PO	2	74.0	18800	184	1.21
2	CyEO	5	71.5	26400	155	1.24
3	^t BuEO	15	69.4	32800	228	1.17
4	NBEO	5	78.1	25900	142	1.20
5	AdEO	10	75.6	9600	43	1.39

^a (TPP)CoCl = 0.05 mmol, (epoxide)/((TPP)CoCl)/(DMAP) = 500/1/0.75, CO₂ = 5.0 MPa, solvent = CH₂Cl₂, temperature = 40 °C

^b Estimated from the ¹H NMR spectra

^c Estimated from GPC relative to polystyrene standards

for the copolymerization with AdEO, the large absorption was observed at 1749 cm⁻¹, while the very small absorption was observed at 1812 cm⁻¹ (Figure S10). Cyclic carbonate is formed in the reaction system due to a back-biting reaction from the end of the growing polymer. Introducing bulky substituents such as ^tBu or Ad groups may block the back-biting reaction from the end chain of the growing polymer by steric hindrance. Therefore, only trace cyclic carbonates were produced in these systems.

In the cases of PO, CyEO, and NBEO, the degrees of polymerization were between 142 and 184 with conversions between 71–78%. Since water, a common contaminant in the complex, acts as a bifunctional initiator and/or a chain transfer agent, the DP values do not match the theoretical values [28].

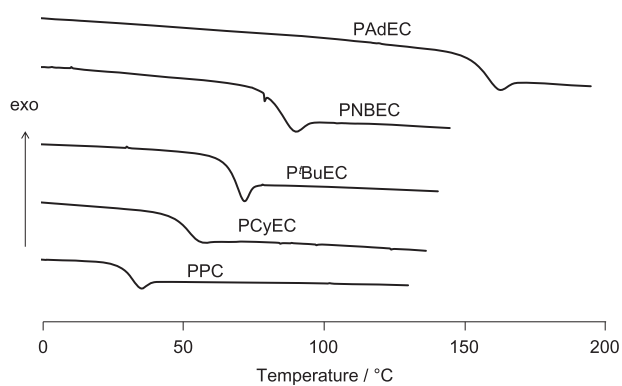
When CyEO, ^tBuEO, and NBEO were used as comonomers, the DP values were 155, 228, and 142 (M_n = 26400, 32800, and 25900; M_w/M_n = 1.24, 1.17, and 1.20), respectively. Compared with the DP of PPC synthesized with the same cobalt porphyrin complex, the DPs of the CyEO and NBEO-containing polymers are adequate. Although the conversion was almost the same, the DP of the ^tBuEO-containing polymer was larger than those of CyEO and NBEO. Because, as described above, cyclic carbonates were not produced during the polymerization, all the epoxide that was consumed was converted into polycarbonate. Much like in the copolymerization of CO₂ and ^tBuEO, only a small amount of cyclic carbonate was produced in the copolymerization of CO₂ and AdEO at a conversion of 75.6% (Figure S10). Nevertheless, the DP of the obtained copolymer of CO₂ and AdEO was smaller (Table 1, run 5, M_n = 9600, DP = 43, M_w/M_n = 1.39). The M_n of PAdEC is possibly underestimated by using GPC calibrated with standard polystyrenes.

Microstructures and T_g values of the copolymers

The products obtained by the copolymerization of CO₂ and epoxides were purified by reprecipitation from chloroform solutions using methanol. In the ¹H NMR spectra, signals between δ 3.0–3.5 ppm due to ether linkages were difficult to observe, which indicates the content of carbonate linkages in the polymer main chain reached 99% (Table 2). The ¹³C NMR spectra suggested that the regioselectivity of PPC was 89% head-to-tail (Figure S12), whereas the contents of H-T structures in the other polymers were almost 100% (Figures S16, S20, S24, and S28). The bulkiness and electron-donating nature of the alkyl groups on the epoxides controlled the mechanism of the epoxide ring-opening, leading exclusively to the β -cleavage of the epoxide ring. The GPC chromatograms of the copolymers were all bimodal (Figures S13, S17, S21, S25, and S29). As already mentioned, these peaks correspond to the high-molecular-

Table 2 Microstructures and T_g values of copolymers^a

Run	-R	M_n^b	DP ^b	M_w/M_n^b	C. L. ^c %	H-T ^d %	T_g^e °C
1	Me	18900	185	1.22	>99	89	29.5
2	Cy	27800	163	1.20	>99	>99	54.7
3	^t Bu	34600	240	1.14	>99	>99	70.4
4	NB	25800	142	1.20	>99	>99	85.3
5	Ad	9300	42	1.42	>99	>99	157.5

^a Isolated and purified polymers^b Estimated from GPC relative to polystyrene standards^c Estimated from the ¹H NMR spectra^d Estimated from the ¹³C NMR spectra^e Measured by DSC**Fig. 3** DSC curves of polycarbonates

weight polymers resulting from water and the low-molecular-weight polymers resulting from interference from the axial ligand of the catalyst complex [29].

The T_g values of the resulting copolymers were measured by DSC (Fig. 3). The T_g of PPC was 29.5 °C, which was consistent with the values reported to date (Table 2, run 1). The T_g values of PCyEC, P'BuEC, and PNBEC were 54.7, 70.4, and 85.3 °C, respectively (Table 2, run 2–4). The increase in the T_g values is believed to be closely related to the bulkiness of the side chains. To our delight, DSC analysis showed the T_g of PAdEC was 157.5 °C (Table 2, run 5). This is the highest T_g among in polycarbonates synthesized by alternating copolymerization of CO₂ and a terminal epoxide.

Conclusions

In conclusion, we synthesized alternating copolymers from CO₂ and terminal epoxides with rigid and bulky alkyl substituents. The copolymerizations provided copolymers

with narrow molecular weight distributions. Except for that of PAdEC, the degrees of polymerization were between 142 and 240. Since the optimized conditions for the alternating copolymerization of CO₂ and PO were adopted for all the copolymerizations investigated here, as the substituents on the epoxides became bulkier, the polymerizations proceeded more slowly and required longer reaction times to reach high epoxide conversions. The rate of polymerization must be increased by changing the reaction temperature and/or pressure. The results of DSC analyses showed that the T_g values of the copolymers are correlated with the rigidity and bulkiness of the substituents on their polymer side chains. Notably, the T_g of PAdEC is 157.5 °C, which is the highest T_g among in alternating copolymers of CO₂ and a terminal epoxide.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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