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Catalytic synthesis and physical properties of CO₂-based cross-linked poly(cyclohexene carbonate)s†

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Bifunctional aluminum porphyrins (0.001 mol%) catalyzed the terpolymerization of cyclohexene oxide (CHO), bis(CHO), and CO₂ to give cross-linked polycarbonates (CLPs) under solvent-free conditions. A small amount of bis(CHO) acted as a cross-linking agent, and the use of only 0.1 mol% bis(CHO) to CHO produced polymers of quite large sizes. The thermal and mechanical properties of CLPs could be altered by changing the structure and amount of bis(CHO), and the CLPs showed improved thermal stability and tensile strength as compared to linear poly(cyclohexene carbonate)s (PCHCs). The degradation of the CLPs was also investigated, and the selective cleavage of the cross-links was achieved by UV light irradiation to give linear PCHCs. The present study disclosed the potentials of cross-linking terpolymerization for the preparation of various CLPs with a constant CO₂ content (31 wt%).

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Introduction

Conversions of carbon dioxide (CO₂) into value-added materials are important molecular technologies.¹ Synthesis of polycarbonates from epoxides and CO₂ is one of the most important CO₂ fixations with 100% atom economy, and a variety of catalysts have been reported since the discovery of this reaction by Inoue in 1969.^{2–4} In particular, poly(cyclohexene carbonate)s (PCHCs) have received considerable attention partly because they can be prepared directly *via* the copolymerization of cyclohexene oxide (CHO) and CO₂ and because they exhibit good physical properties such as high glass transition temperature and tensile strength. Recently, the terpolymerization of CHO, CO₂, and different comonomers has been extensively studied to control the properties of the PCHC-based polymers.⁵ Various comonomers such as different epoxides, cyclic acid anhydrides, lactones, and heteroallenes have been used.^{6–9} The physical properties of such terpolymers have significantly changed with an increase in the content of the comonomer. In most cases, however, such terpolymers have lower CO₂ contents than PCHC.

Synthesis of cross-linked polycarbonates (CLPs) *via* CO₂ terpolymerization is a practical method to prepare large polymers without the loss of the CO₂ content because the

incorporation of a small amount of cross-linkers causes a drastic increase in the molar masses (Fig. 1). Several cross-linked poly(propylene carbonate)s (PPCs) have been synthesized *via* the terpolymerization of propylene oxide, CO₂, and cross-linking agents such as diepoxides¹⁰ and cyclic acid anhydride oligomers,¹¹ and the CLPs exhibited the enhanced thermal and mechanical properties as compared to linear PPCs. On the other hand, despite the potentiality of cross-linked PCHCs, there have been no reports on the terpolymerization of CHO, CO₂, and diepoxides as far as we know.¹² A highly active and robust catalyst is required to elongate a large network of branched polymers in a possible viscous reaction mixture even at high temperature.

Previously, we have reported highly active and robust bifunctional metalloporphyrin catalysts for the synthesis of cyclic carbonates and polycarbonates.^{13,14} Bifunctional aluminum porphyrin **1d** (Fig. 1) was used for the synthesis of PCHC *via* the copolymerization of CHO and CO₂.¹⁴ We envisioned that our highly active bifunctional catalysts might achieve the terpolymerization of CHO, CO₂, and bis(CHO) such as 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (**2a**) and bis(3,4-epoxycyclohexylethylthio)ethane (**2b**) for the synthesis of cross-linked PCHCs (Fig. 1). Here we have found that newly synthesized bifunctional aluminum porphyrin **1b** with tetramethylene chains is the best catalyst for the cross-linking terpolymerization, giving novel CLPs under solvent-free conditions. The structure and amount of the cross-linkers could modulate the thermal and mechanical properties of the CLPs. We have also found that UV photoirradiation can cleave the cross-link moieties (thioether bonds) of CLPs selectively to give linear PCHCs.

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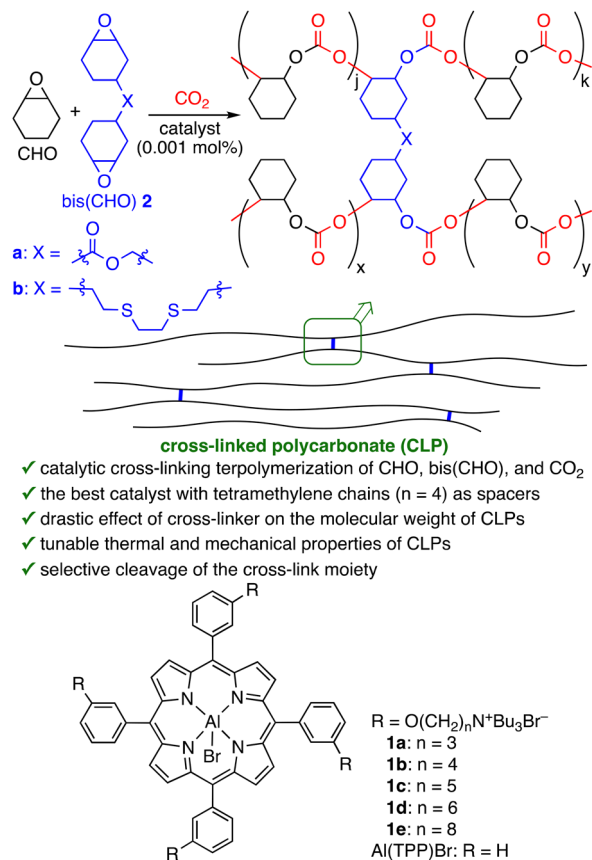


Fig. 1 Terpolymerization of CHO, bis(CHO) **2**, and CO₂ catalyzed by the aluminum porphyrin catalysts.

Results and discussion

First, we screened catalysts **1a–e** with different methylene chain lengths for the terpolymerization of CHO, bis(CHO) **2a**, and CO₂ (2 MPa) in a ratio of 1 : 400 : 100 000 (**1** : **2a** : CHO) at 130 °C for 24 h under solvent-free conditions (Table 1). Interestingly, the catalytic activities highly depended on the methylene chain lengths, and **1b** with tetramethylene chains

showed the highest conversion (entries 1–5). It should be noted that the weight-average molar masses (M_w) significantly increased, and the dispersity (D) values were high. In addition, **1b** and **1c** produced insoluble polymers, which suggested the formation of the high-molar mass cross-linked PCHCs. In sharp contrast, a binary catalytic system composed of Al(TPP)Br and tetrabutylammonium bromide (TBAB) was inactive under otherwise identical reaction conditions (entry 6).¹⁵

We further investigated the terpolymerization by changing the amount of bis(CHO) **2a** using the best catalyst **1b** (0.001 mol%), and the polymer products were analyzed by SEC (Table 2, entries 1–4 and Fig. 2). In contrast to the bimodal peaks observed for PCHC,^{14,16} surprisingly, the CLPs synthesized by using only 0.1 mol% of **2a** to CHO showed a broad SEC profile, which indicated the formation of higher-molar mass polymers as compared with typical linear PCHC.¹⁷ The fraction at 11–12 min significantly increased with an increase of **2a**, and the M_n reached 558 kg mol⁻¹. A further increase of **2a** to more than 0.4 mol% produced polymers showing poor solubility. These results suggest that the larger polymers consist of several PCHC chains cross-linked with the ester linkage of **2a**. The number of the PCHC chains included in the CLPs with a M_n of 558 kg mol⁻¹ was roughly calculated to be 8 by comparing this M_n value with that of linear PCHC. The intrinsic viscosity of the CHCl₃ solution of the polymers increased with an increase in the content of **2a** (Table 2). Electrospray ionization mass spectra were measured to confirm the incorporation of **2a** into the polymers. CHO and **2a** were heated in the presence of **1b** under a CO₂ pressure of 2 MPa at 130 °C for 5 min. Mass spectra of the mixture confirmed the ion peaks of the terpolymers as well as typical PCHC (Fig. S1 in ESI[†]); only one epoxide of **2a** was ring-opened, and the other epoxide moiety remained intact because of the early reaction stage. This result together with the SEC analysis strongly suggests that cross-linking occurs at the later stage of the polymerization. It should also be noted that the copolymerization of **2a** and CO₂ (without CHO) did not proceed well probably because of the steric hindrance of **2a**. We also performed the terpolymerization using bis(CHO) **2b** with the thioether bonds (Table 2, entries 5–7). The successful synthesis of the corresponding CLPs was confirmed by the SEC analysis and the intrinsic viscosity measurements.

Polymer products were purified by reprecipitation with CH₂Cl₂/MeOH to remove the remaining monomers and a small amount of cyclic carbonates (<1%). The thermal properties of the purified polymers were characterized by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (Table 2). TGA indicated that all the samples of cross-linked and linear PCHCs showed a large weight loss at ca. 320 °C, which suggests the cleavage of the carbonate linkages. When 50% weight loss temperatures (T_{50}) were compared, importantly, the CLPs showed higher T_{50} than linear PCHC, which suggests that the cross-linkers especially containing the thioether bonds improved the thermal stability. DSC analysis revealed slight changes in the glass transition temperature (T_g): 127 °C for CLPs with the

Table 1 Terpolymerization of CHO, **2a**, and CO₂^a

Entry	Catalyst	Conv ^b (%)	M_n^c (kg mol ⁻¹)	M_w^c (kg mol ⁻¹)	D^c
1	1a	20	37	122	3.3
2 ^d	1b	58	61	219	3.6
3 ^d	1c	39	58	222	3.8
4	1d	40	30	93	3.1
5	1e	17	14	42	3.0
6 ^e	Al(TPP)Br	<1	—	—	—

^a Reaction conditions: CHO (29 mmol), **2a** (0.12 mmol), catalyst (0.29 μmol, 0.001 mol% based on CHO), CO₂ (2.0 MPa), 130 °C, 24 h in an autoclave. ^b Conversion based on CHO determined by ¹H NMR spectroscopy using mesitylene as an internal standard. ^c Determined by SEC analysis. ^d Insoluble polymer products formed. The ratios of the soluble to insoluble polymers were 74 : 26 (entry 2) and 89 : 11 (entry 3). ^e 1.2 μmol of TBAB was used as a cocatalyst.



Table 2 Terpolymerization of CHO, **2**, and CO₂ using catalyst **1b** (0.001 mol%)^a

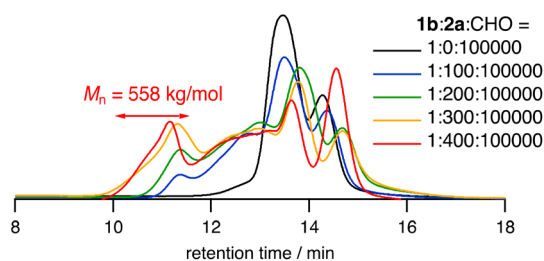
Entry	Bis (CHO)	1b : 2 : CHO	Conv ^b (%)	M_n^c (kg mol ⁻¹)	D^c	Intrinsic viscosity ^d (mL g ⁻¹)	T_{50}^e (°C)	T_g^f (°C)	E^g, h (MPa)	$\sigma^{g, i}$ (MPa)	$\epsilon^{g, j}$ (%)
1	—	1 : 0 : 100 000	58	49	1.3	37	312	125	2780 (±90)	34 (±1)	1.4 (±0.02)
2	2a	1 : 100 : 100 000	66	57	1.8	44	318	127	2940 (±160)	36 (±2)	1.5 (±0.1)
3	2a	1 : 200 : 100 000	52	50	2.5	51	314	127	3100 (±200)	41 (±2)	1.7 (±0.1)
4 ^k	2a	1 : 300 : 100 000	52	57	3.6	68	314	127	2900 (±280)	33 (±1)	1.3 (±0.1)
5	2b	1 : 100 : 100 000	44	53	1.6	47	321	124	2870 (±140)	35 (±2)	1.4 (±0.1)
6	2b	1 : 200 : 100 000	55	57	2.0	50	323	124	2950 (±150)	36 (±2)	1.5 (±0.2)
7	2b	1 : 300 : 100 000	48	50	2.1	53	321	125	2990 (±90)	35 (±2)	1.4 (±0.02)

^a Reaction conditions: CHO (29 mmol), **2** (0–87 μmol), **1b** (0.29 μmol, 0.001 mol% based on CHO), CO₂ (2.0 MPa), 130 °C, 24 h in an autoclave.

^b Conversion based on CHO determined by ¹H NMR spectroscopy using mesitylene as an internal standard. ^c Determined by SEC analysis.

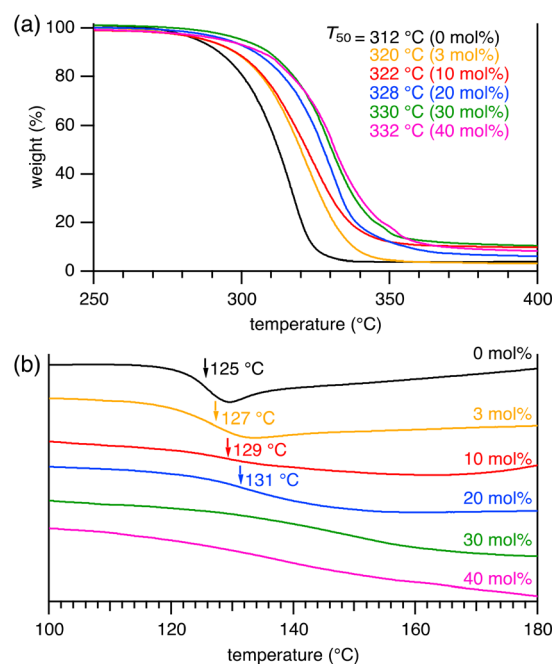
^d Measured by an Ostwald viscometer in CHCl₃ at 30 °C. ^e Temperature at 50% decomposition determined by TGA. ^f Glass transition temperature determined by DSC. ^g Dog-bone-shaped specimens with the thickness of 0.2–0.3 mm were tested with a strain rate of 5 mm min⁻¹. Average values of three measurements are shown. Values in parenthesis are standard deviations. ^h Young's modulus. ⁱ Tensile strength. ^j Elongation at break.

^k Insoluble polymers formed. The ratio of the soluble to insoluble polymers was 96 : 4.

**Fig. 2** SEC charts of polymer samples.

ester cross-linkers (entries 2–4) and 124–125 °C for those with the flexible thioether cross-linkers (entries 5–7). The rigidity of the cross-linkers affects the thermal properties of the polymers.

When we further increased the amount of **2a**, CLPs obtained with 3 mol% of **2a** showed a T_{50} of 320 °C and a broad DSC curve at 127 °C (Fig. 3). We expected the improvement of the thermal properties by the incorporation of a larger amount of cross-linkers. Therefore, CLPs containing more cross-linkers were prepared by the terpolymerization using 10–40 mol% of **2a** under 4 MPa CO₂ pressure for 48 h, which gave insoluble polymers. The products were ground with a mill and washed with MeOH. IR spectra of the resulting powder samples were measured by the attenuated total reflection (ATR) method (Fig. S2 in ESI†). The IR spectra of CLPs showed C–H stretching vibrations at 2942 and 2868 cm⁻¹ and a C=O stretching vibration at 1730 cm⁻¹, which are quite similar to those of PCHC. Careful observations allowed us to find that the C=O stretching vibration of the CLPs was slightly broadened. Since the CLPs contain the ester group, the broadened peak was assigned as the C=O stretching vibrations of both the carbonate and ester groups. In addition, we observed a new peak at 1196 cm⁻¹, which increased with an increase in the content of **2a** and therefore could be assigned as the C–O stretching vibration of the ester bond. These insoluble CLPs prepared from 10–40 mol% of **2a** were investigated by TGA and DSC. The decomposition temperature of the CLPs increased

**Fig. 3** (a) TGA and (b) DSC profiles of polymers. Polymer samples were prepared from **1b** : **2a** : CHO = 1 : x : 100 000 (x = 0, 3000, 10 000, 20 000, 30 000, and 40 000).

with an increase in the content of **2a**, and T_{50} reached 332 °C. In addition, the DSC peaks at 127 °C disappeared and broadened up to 160 °C. Clearly, the thermal properties could be altered by the amount of the cross-linker. Although there are reports on the improved thermal stability of cross-linked PPCs as compared to linear PPC,^{10,11} such high T_{50} and T_g values observed for the cross-linked PCHCs in this work have never been reported.

The mechanical properties of CLPs prepared with 0.1–0.3 mol% of **2** to CHO and linear PCHC were investigated in the film state. Purified polymer powder was hot-pressed at 150 °C to give solvent-free films, and the dog-bone-shaped specimens were prepared by die cutting. Tensile tests of the



specimens were conducted on a universal testing machine (Table 2). The PCHC film showed a Young's modulus (E) of 2780 MPa and a tensile strength (σ) of 34 MPa (entry 1), which were comparable to the values reported by Rieger.^{8d} Interestingly, CLPs with 0.1–0.2 mol% of cross-linkers showed higher values for Young's modulus, tensile strength, and elongation at break (entries 2, 3, 5, and 6), which suggested that the cross-linkers increased the strength of the films. On the other hand, those with 0.3 mol% cross-linkers showed somewhat lower values (entries 4 and 7), probably because the cross-links hampered intermolecular forces between the polymer chains by restricting their mobility. Considering the solubility and processibility of the polymers and the tensile strength of the films, the use of 0.2 mol% cross-linker 2 (entries 3 and 6) is the most suitable for making robust films of the CLPs.

Degradation of polymers is of importance in view of sustainability, and the selective chemical recycling of polycarbonates has been studied.¹⁸ Here, we investigated the selective cleavage of the cross-linkers of the CLPs to give linear polycarbonates (Fig. 4a). We initially attempted the selective hydrolysis of the ester linkers of CLPs prepared from **2a**, which resulted in failure. For example, the base-promoted hydrolysis of the carbonate linkages gave monomers such as CHO and 1,2-cyclohexanediol (Fig. S11a in ESI†). Gratifyingly, we found that photoirradiation selectively cleaved the thioether-containing linkers of CLPs prepared from **2b**. A THF solution of the CLP (Table 2, entry 6) was irradiated by a high-pressure mercury lamp, and the resulting solution was analyzed by SEC. The faster fractions of the multimodal peaks disappeared after photoirradiation for 24 h, and the slower two fractions (bimodal peaks) corresponding to linear PCHC increased (Fig. 4b). In contrast, no changes were observed for the SEC chart of PCHC or the CLPs prepared from **2a** upon irradiation (Fig. S11c and d in ESI†). Clearly, the selective cleavage of the thioether bonds occurred.¹⁹ It should be noted that photoirradiation enabled the highly selective cleavage of the thioether bonds without damaging the other framework of the polymers. Although several examples of the degradation of the backbone of polymers have been reported, the selective cleavage of

specific positions of CO₂-based polymers has been quite rare as far as we know.

Conclusions

In summary, we have prepared cross-linked PCHCs for the first time *via* the terpolymerization of CHO, bis(CHO) **2**, and CO₂ using bifunctional aluminum porphyrins **1** (0.001 mol%) as catalysts under solvent-free conditions. The catalytic activities of **1** were dependent on the methylene chain lengths, and the best catalyst was found to be **1b**. The highly active and robust catalyst **1b** achieved the cross-linking polymerization giving high-molar mass CLPs. Thermal and mechanical properties of the polymers could be altered by the cross-linkers, and enhanced thermal stability and tensile strength were observed. Importantly, the cross-linking terpolymerization reported herein enabled the preparation of polycarbonates of large molecular sizes without the loss of the high CO₂ content (31 wt%), which contrasts with the previously reported terpolymerization methods giving linear terpolymers;^{7–9} for example, when comonomers such as lactones and cyclic acid anhydrides are incorporated, the corresponding PCHC-based terpolymers have lower CO₂ contents than PCHC. Photoirradiation selectively cleaved the thioether linkages of the CLPs, giving linear PCHCs. Further investigation on the development of novel polycarbonates using bifunctional porphyrin catalysts is currently investigated in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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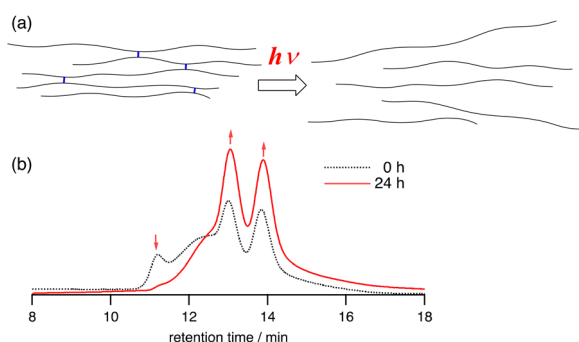


Fig. 4 (a) Schematic representation of the selective cleavage of cross-linkers of CLPs. (b) SEC charts of the CLPs (Table 2, entry 6) before and after photoirradiation.



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