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Synthesis of bis(cyclic carbonate) and propylene carbonate *via* a one-pot coupling reaction of CO_2, bisepoxide and propylene oxide†

Ren-jian Wei, Xing-hong Zhang,* Bin-yang Du, Zhi-qiang Fan and Guo-rong Qi

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The effective transformation of carbon dioxide (CO_2) into valuable products is promising in green and sustainable chemistry. The coupling reaction of CO_2 with epoxides to afford cyclic carbonates is an atom-economic pathway for CO_2 fixation. Many catalysts have been developed for this coupling reaction, however, very few of them were reported for the coupling reaction of CO_2 with bisepoxides. This work describes an efficient one-pot coupling reaction of CO_2, propylene oxide (PO) and bisepoxides without the addition of external organic solvents by using a nanolamellar zinc-cobalt double metal cyanide complex (Zn–Co(III) DMCC) as the catalyst and cetyltrimethyl-ammonium bromide (CTAB) as the co-catalyst. Propylene carbonate (PC) and bis(cyclic carbonate)s were obtained at the same time with high monomer conversions (PO: 93.6%, bisepoxides: 82.9%). The *in situ* produced PC acted as a good solvent for the coupling reaction of CO_2 with bisepoxides. Two products could be easily separated by distillation or precipitation. The application of the obtained bis(cyclic carbonate)s was also preliminarily investigated. A non-isocyanate route for synthesizing polyurethanes with massive hydroxyl groups was proposed.

Introduction

Carbon dioxide (CO_2) is an important C1 feedstock in industry as it is abundant and inexpensive. The fixation of CO_2 into valuable chemicals has attracted much attention. Among all the reported CO_2 fixation routes, the coupling reaction of CO_2 with epoxides to afford five-membered cyclic carbonates is one of the most promising routes.[1] The resultant cyclic carbonates have a broad variety of applications, such as aprotic polar solvents, electrolytes in lithium batteries, and intermediates for the production of biodegradable polymers.[2]

Numerous effective catalyst systems[3] have been developed for the coupling reaction of CO_2 with epoxides. Some of the catalyst systems, such as the $ZnBr_2/PPh_4PI$ system,[4] bifunctional metal tetraphenylporphyrin complexes[5] and starch grafted nickel/TBAB system,[6] presented high catalytic activities for this coupling reaction. However, most studies have focused on the coupling reaction of CO_2 with mono-epoxides.[7] The studies on the coupling reaction of CO_2 with epoxides containing two or more oxirane groups are very limited.[8–10] By the coupling reaction of CO_2 with epoxides containing two or more oxirane groups, di- or polyfunctional cyclic carbonates could be obtained. Di- and polyfunctional cyclic carbonates can react with di- and polyfunctional primary alkyl amines, leading to polyurethanes (PU) with massive hydroxyl groups, which might be an alternative and attractive green route for synthesizing PU materials without using toxic isocyanates or phosgene. It is thus meaningful to develop new efficient way to synthesise di- and polyfunctional cyclic carbonates.[8f]

Endo and co-workers[8] had reported that homogeneous alkali metal halides, especially lithium bromide (LiBr), could effectively catalyze the coupling reaction of CO_2 with bisepoxides or poly (glycidyl methacrylate) at 80–100 °C with 1-methyl-2-pyrrolidone as an organic solvent to afford di- or polyfunctional carbonates. Mülhaupt *et al.*[9] reported the coupling reaction of limonene dioxide, epoxidized soybean oil and epoxidized linseed oil with CO_2 catalyzed by silica-supported 4-pyrrolidinopyridinium iodide. The conversion of limonene dioxide was up to 78% at 140 °C and 3.0 MPa within 120 h, while the epoxides could be completely converted to the products at 140 °C and 3.0 MPa within 45 h. Wang and co-workers[10] disclosed that a composite catalyst system of $SnCl_4$ and tetrabutylammonium bromide could catalyze the coupling reaction of the epoxidized soybean oil with CO_2 under 140 °C and 1.0 MPa within 20 h by using N, N-dimethylformamide as a solvent. The carbonated soybean oil with 95% conversion was obtained.

In this work, we reported an efficient one-pot coupling reaction of bisepoxides, PO and CO_2 without the addition of external organic solvents for the synthesis of bis(cyclic

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MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China. E-mail: xhzhang@zju.edu.cn; Fax: +86-571 87953732; Tel: +86-571 87953732

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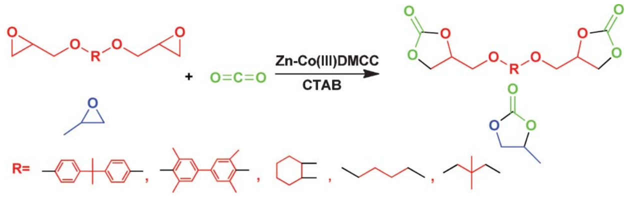


Scheme 1 The one-pot coupling reaction of PO, bisepoxide and CO_2 catalyzed by the Zn–Co(III) DMCC/CTAB binary catalyst system.

carbonate)s, which was catalyzed by a nanolamellar zinc-cobalt double metal cyanide complex (Zn–Co(III) DMCC) in the presence of cetyltrimethyl-ammonium bromide (CTAB), as shown in Scheme 1. Propylene carbonate (PC) and bis(cyclic carbonate)s could be obtained at the same time with high monomer conversions.

Experimental

Materials

$K_3Co(CN)_6$ (Lianyang Chemical Co., Ltd, Yixing, China) was recrystallized in de-ionized water before use. $ZnCl_2$, *tert*-butanol (*t*-BuOH), PO, 1,6-hexamethylenediamine, cetyltri-methyl-ammonium bromide (CTAB), tetrahydrofuran(THF), dioxane, N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP), dichloromethane (DCM), and propylene carbonate (PC) were analytical grade and used without further purification. Carbon dioxide with 99.995% was used as received. Bisphenol A diglycidyl ether (BisAG, epoxy value: 0.54 mol 100 g^{-1}), cyclohexanediol diglycidyl ether (epoxy value: 0.59 mol 100 g^{-1}), 1,4-butanediol diglycidyl ether (epoxy value: 0.65 mol/100 g), 4,4-bis(2,3-epoxypropoxy)-3,3,5,5-tetramethylbiphenyl (epoxy value: 0.42 mol/100 g), neopentyl glycol diglycidyl ether (epoxy value: 0.58 mol/100 g) (Kingboard Co., Ltd, Kunshan, China) were commercial products and used without further purification.

Characterization

The morphology of the nano-sized Zn–Co(III) DMCC catalyst was observed by using scanning electron microscopy (SEM) (JEOL JSM 840A instrument) under vacuum after being sputter-coated with gold at 10 mA for 1 min. The specific surface area was measured by using the BET method (Quantachrome automated gas sorption system (AUTOSORB-1-C)) and was determined by N_2 adsorption isotherms (at liquid nitrogen temperature). The pore size distribution was calculated by analyzing the adsorption/desorption branches of the isotherm using the Barrett–Joyner–Halenda (BJH) method. Fourier transform infrared spectra (FT-IR) were measured by using a Brucker Vector 22 FT-IR spectrophotometer. Elemental analyses were performed by using an ICP-AES instrument (Leeman Labs) and a Vario MACRO instrument (Elementar). ^{1}H NMR spectra of the products were obtained on a Bruker Advance DMX 400 MHz spectrometer using TMS as the internal reference. The number-averaged molecular weight (M_n) and polymer distribution index (PDI) were determined by using gel permeation chromatography (PL-GPC 220) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with DMF solution containing 0.05 M LiBr at 1.0 mL min^{-1} at 40 °C. The sample concentration was approximately 0.3 wt% and the injection volume was 100 μL. Calibration was performed using mono-dispersed poly(methyl methacrylate).

Preparation of nanolamellar Zn–Co(III) DMCC

A nanolamellar Zn–Co(III) DMCC catalyst was synthesized according to the reported literature:[11] the given amount of $ZnCl_2$ (8.0 (g) were dissolved in the mixed solution of de-ionized water (10 mL) and *t*-BuOH (10 mL). The aqueous solution of $K_3Co(CN)_6$ (6.6 g in 10 mL de-ionized water) was added dropwise into $ZnCl_2$ solution over 30 min at 30 °C under vigorous stirring. The precipitation reaction was then heated to 75 °C and agitated greatly for 3 h. The resulting white precipitate was separated by pressure filtration and reslurried in a mixture of *t*-BuOH and water (v/v = 1/1) under vigorous stirring over 2 h. Once again, the precipitation was isolated and reslurried in a mixture of *t*-BuOH and water. With increasing proportions of *t*-BuOH over water, the precipitate was washed several times to remove potassium ion. Finally the precipitate was reslurried in neat *t*-BuOH, which was then separated and dried at 70 °C under vacuum to a constant weight. The elemental analysis result of the catalyst: Co: 12.48; Zn: 27.30; N: 16.57; C: 23.38; H: 2.27; Cl: 9.52.

One-pot BisAG/CO_2 coupling reaction

A 100 mL autoclave equipped with a mechanical stirrer was dried under vacuum at 80 °C for 2 h, and given amounts of Zn–Co(III) DMCC, CTAB and BisAG were then transferred into the autoclave, which was dried for another 2 h. After the autoclave was cooled down to 25 °C, organic solvent (30 mL) was injected into the autoclave using a syringe under negative pressure. CO_2 was then filled and adjusted to certain system pressure at a desired temperature with stirring of 500 r min^{-1}. After the reaction, the autoclave was cooled in an ice-water bath and the pressure was slowly vented. If THF was used as the solvent, the produced bis(cyclic carbonate) (denoted as BisAC) was just purified by filtration. If other solvents were used, the resultant products were first evaporated to get rid of the solvents and then poured into THF. The final products were obtained by filtration.

PO/bisepoxides/CO_2 one-pot coupling reactions

By taking PO/BisAG/CO_2 as an example: the experimental procedure was similar to that of the BisAG/CO_2 system but without using any organic solvent. Instead, PO was injected into the autoclave. After the reaction, CO_2 was vented and the unreacted PO was removed by a rotary evaporator. The solid catalyst was removed by pressure filter or centrifugation. Afterwards, the mixture was put into cool water and the solid precipitate (BisAC) was collected and washed with THF. The propylene carbonate (PC) was collected by evaporating the water from the remaining mixture. The reaction and purification procedure of one-pot PO/4,4-bis(2,3-epoxypropoxy)-3,3,5,5-tetramethylbiphenyl/CO_2 coupling reaction was the same with that of the PO/BisAG/CO_2 system [the corresponding bis(cyclic carbonate) was denoted as BisCC-1].

For the coupling reaction of cyclohexanediol diglycidyl ether, butanediol diglycidyl ether and neopentyl glycol diglycidyl ether with PO and CO_2, the purification of PC and corresponding bis(cyclic carbonate)s (denoted as BisCC-2, BisCC-3 and BisCC-4 respectively) was as follows: after removing the solid catalyst by pressure filter or centrifugation, the mixture was put into cool water, viscous products were precipitated and dissolved into acetonitrile, which were then separated by flash column chromatography to provide colourless products of glutinous oil. The resultant PC was again collected by evaporating the water from the remaining mixture.

BisAC: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 7.09 (d, 4H), 6.82 (d, 4H), 5.09 (s, 2H), 4.58 (t, 2H), 4.34 (m, 2H), 4.16 (m, 4H), 1.54 (s, 6H).

BisCC-1: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 7.27 (s, 4H), 5.11 (s, 2H), 4.64 (t, 2H), 4.47 (m, 2H), 4.02 (m, 4H), 2.26 (s, 12H).

BisCC-2: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 4.88 (m, 2H), 4.53 (t, 2H), 4.23 (m, 2H), 3.50–3.90 (m, 4H), 3.19 (s, 2H), 1.86 (s, 2H), 1.55 (s, 2H), 1.19 (d, 4H).

BisCC-3: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 4.90 (m, 2H), 4.51 (t, 2H), 4.24 (m, 2H), 3.35–3.80 (m, 8H), 1.50 (m, 4H).

BisCC-4: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 4.89 (m, 2H), 4.51 (t, 2H), 4.25 (m, 2H), 3.40–3.85 (m, 6H), 3.17 (m, 2H), 0.79(s, 6H).

PC: ^{1}H NMR ($CDCl_3$, TMS, 400 MHz): δ (ppm) = 4.90–5.10 (m, 1H), 4.50 (t, 1H), 4.00 (t, 1H), 1.50 (d, 3H).

Polyaddition of bis(carbonate)s with 1,6-hexamethylenediamine

Polyurethane could be synthesized by the polyaddition of the obtained bis(carbonate) with 1,6-hexamethylenediamine. Briefly, bis(cyclic carbonate) (0.05 mmol), 1,6-hexamethylenediamine (0.05 mmol), CTAB (0.005 mmol) and NMP (4 mL) were transferred to a 50 mL round-bottomed flask. The mixture was heated to 60 °C for 5 h under magnetic stirring. After the reaction, the mixture was poured into ethylether, and the insoluble precipitate was collected by filtration and dried at 80 °C at reduced pressure to a constant weight.

The resultant PUs from BisAC, BisCC-1, BisCC-2, BisCC-3 and BisCC-4 were noted as PAU, PU**1**, PU**2**, PU**3** and PU**4** respectively.

PAU: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 7.18 ($-\mathrm{N}H$), 6.70–7.15 ($-\mathrm{C}_6H_4-$), 5.08 ($-\mathrm{CH_2O}H$), 4.85 ($-\mathrm{OC}H(\mathrm{CH_2OH})\mathrm{CH_2}-$), 3.70–4.30 ($\mathrm{ArOC}H_2-$, $-\mathrm{C}H_2\mathrm{OH}$, $-\mathrm{OC}H_2\mathrm{C}H(\mathrm{O}H)\mathrm{C}H_2\mathrm{O}-$), 3.00–3.21 ($-\mathrm{NHC}H_2-$), 1.50 ($-\mathrm{C}H_3$), 1.10–1.45 ($-\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2-$).

PU**1**: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 7.18 ($-\mathrm{N}H$), 7.22 ($-\mathrm{Ar}H$), 5.08 ($-\mathrm{CH_2O}H$), 4.85 ($-\mathrm{OC}H(\mathrm{CH_2OH})\mathrm{CH_2}-$), 3.70–4.25 ($\mathrm{ArOC}H_2-$, $-\mathrm{C}H_2\mathrm{OH}$, $-\mathrm{OC}H_2\mathrm{C}H(\mathrm{O}H)\mathrm{C}H_2\mathrm{O}-$), 2.90–3.15 ($-\mathrm{NHC}H_2-$), 2.20 ($-\mathrm{C}H_3$), 1.10–1.45 ($-\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2-$).

PU**2**: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 7.20 ($-\mathrm{N}H$), 5.04 ($-\mathrm{CH_2O}H$), 4.85 ($-\mathrm{OC}H(\mathrm{CH_2OH})\mathrm{CH_2}-$), 3.60–4.10 ($-\mathrm{OC}H_2\mathrm{CH}(\mathrm{CH_2OH})O-$, $-\mathrm{C}H_2\mathrm{OH}$, $-\mathrm{OC}H_2\mathrm{C}H(\mathrm{O}H)\mathrm{C}H_2\mathrm{O}-$), 3.25 (methine protons in cyclohexyl), 3.05–3.12 ($-\mathrm{NHC}H_2-$), 1.00–1.8 ($-\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2-$, methylene protons in cyclohexyl).

PU**3**: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 7.20 ($-\mathrm{N}H$), 5.04 ($-\mathrm{CH_2O}H$), 4.86 ($-\mathrm{OC}H(\mathrm{CH_2OH})\mathrm{CH_2}-$), 3.61–4.12 ($-\mathrm{OC}H_2\mathrm{CH}(\mathrm{CH_2OH})O-$, $-\mathrm{C}H_2\mathrm{OH}$, $-\mathrm{OC}H_2\mathrm{C}H(\mathrm{O}H)\mathrm{C}H_2\mathrm{O}-$), 3.51 ($-\mathrm{OC}H_2\mathrm{CH_2CH_2C}H_2\mathrm{O}-$), 2.90–3.10 ($-\mathrm{NHC}H_2-$), 1.56 ($-\mathrm{OCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2O}-$), 1.10–1.45 ($-\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2-$).

PU**4**: ^{1}H NMR (d_6-DMSO, TMS, 400 MHz): δ (ppm) = 7.20 ($-\mathrm{N}H$), 5.03 ($-\mathrm{CH_2O}H$), 4.87 ($-\mathrm{OC}H(\mathrm{CH_2OH})\mathrm{CH_2}-$), 3.63–4.15 ($-\mathrm{OC}H_2\mathrm{CH}(\mathrm{CH_2OH})O-$, $-\mathrm{C}H_2\mathrm{OH}$, $-\mathrm{OC}H_2\mathrm{C}H(\mathrm{O}H)\mathrm{C}H_2\mathrm{O}-$), 3.24 ($-\mathrm{OC}H_2\mathrm{C(CH_3)_2C}H_2\mathrm{O}-$), 3.03–3.10 ($-\mathrm{NHC}H_2-$), 1.10–1.45 ($-\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2-$), 0.91 ($-\mathrm{OCH_2C}(\mathrm{C}H_3)_2\mathrm{CH_2O}-$)

Result and discussion

Zn–Co(III) DMCC is a typical solid catalyst for many epoxide-involved reactions with high catalytic activity, such as ring-opening polymerization (ROP) of epoxides,[12] copolymerization of epoxides/CX_2(X = O, S),[13] and the terpolymerization of epoxides/CO_2/cyclic anhydride.[14] It was also demonstrated to be a highly efficient catalyst for the coupling reaction of various mono-epoxides and CO_2.[15] Zn–Co(III) DMCC catalyst was traditionally prepared through a precipitation reaction of excess $ZnCl_2$ and $K_3Co(CN)_6$ in water/*t*-BuOH solution at room temperature. An excess $ZnCl_2$ and an appropriate amount of *t*-BuOH are indispensable for the high catalytic activity of the Zn–Co(III) DMCC catalyst. The typical formula of the Zn–Co(III) DMCC catalyst is $Zn_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot yt\text{-}BuOH \cdot zH_2O$. Structurally, Zn–Co(III) DMCC has a three-dimensional backbone in which zinc and cobalt are linked by cyanide bridges, and the local active site of the Zn–Co(III) DMCC catalyst was demonstrated to be Zn–OH structure (Fig. 1d) on its surface which was confirmed by our recently reported works.[13d,16]

Herein, a nanolamellar Zn–Co(III) DMCC catalyst was prepared according to our developed method.[13d] The obtained

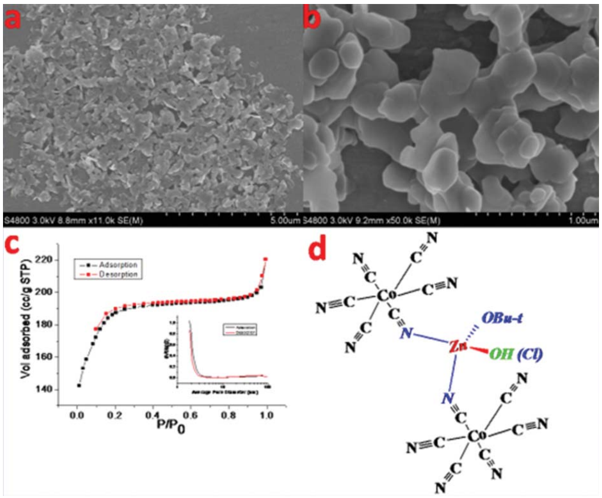


Fig. 1 SEM images (a,b), nitrogen adsorption–desorption isotherm and pore size distribution (c) and the proposed local active site of the Zn–Co(III) DMCC catalyst (d).

Zn–Co(III) DMCC catalyst had a lamellar structure with an edge length of approximately 100–500 nm and a thickness of 20–50 nm, as shown in Fig. 1a and 1b. Fig. 1c shows that the nanolamellar Zn–Co(III) DMCC catalyst had a high BET surface area of 653 m^2 g^{-1}. Such one-dimensional nanostructure and high surface area may physically have a better dispersion in the monomers and better exposure of active sites to the reactants, which were proven in the present work to be favorable to the coupling reactions of bisepoxides/CO_2 and bisepoxides/PO/CO_2 in the presence of CTAB as the co-catalyst.

Firstly, the effects of various solvents on the bisepoxides/CO_2 coupling reaction catalyzed by the binary catalyst system of nanolamellar Zn–Co(III) DMCC/CTAB were investigated. Bisphenol A diglycidyl ether (BisAG) was chosen as the model bisepoxide because it was completely soluble in all of the solvents studied here. The experimental results indicated that for the bisepoxides/CO_2 coupling reaction, the use of organic solvents (entries 2–8, Table 1) improved the productivity of the bis(cyclic carbonate), which was much higher than that of the control experiment without using any solvents (entry 1, Table 1). For the seven solvents studied, propylene carbonate (PC) was the best solvent for the coupling reaction of BisAG/CO_2, as seen entry 8 in Table 1. The maximum conversion of BisAG was 84.2%. It is worth noting that the structure of PC was similar with that of the resultant bis(cyclic carbonate) (BisAC).

Interestingly, it was found that the produced bis(cyclic carbonate) (BisAC) from BisAG/CO_2 coupling reaction was not dissolved in tetrahydrofuran (THF). Hence, BisAC could be purified by washing with THF several times and then being completely dried. Fig. 2 and 3 show the FT-IR and ^{1}H NMR spectra of BisAG and BisAC, respectively. In the FT-IR spectrum of BisAC, the strongest peak at 1793 cm^{-1} could be ascribed to the carbonyl group of BisAC. The small but wide FT-IR band at about 3500 cm^{-1} in both BisAG and BisAC could be assigned to small amounts of hydroxyl groups in their structures. Fig. 3 shows that the chemical shifts of the methylene and methine protons of epoxy group in BisAG at 2.68, 2.77 and 3.28 ppm disappeared completely after the coupling reaction, and the new peaks at 5.09, 4.58 and 4.34 ppm (line 2 in Fig. 3) appeared. These results indicated the successful synthesis of BisAC.

Table 1 The effect of additional solvent on BisAG/CO_2 coupling reaction catalyzed by Zn–Co(III) DMCC/CTAB binary catalyst system[a]

Entry	Solvent	BisAC (g)	BisAG conversion (%)
1[b]	—	3.8	30.2
2	Dioxane	6.7	53.2
3	THF	7.9	62.8
4	DMSO	8.2	65.1
5	DCM	8.4	66.7
6	DMF	8.7	69.1
7	NMP	9.1	72.3
8	PC	10.6	84.2
9[c]	PC	5.2	41.5
10[d]	PC	8.8	70.4

[a] Reaction condition: Zn–Co(III) DMCC: 20.0 mg, CTAB: 150.0 mg, BisAG: 10.0 g, solvent: 30.0 mL, 120 °C, 4.0 MPa, 9.0 h. [b] No solvent was added. [c] Only 20.0 mg Zn–Co(III) DMCC catalyst was employed. [d] 150 mg CTAB was employed.

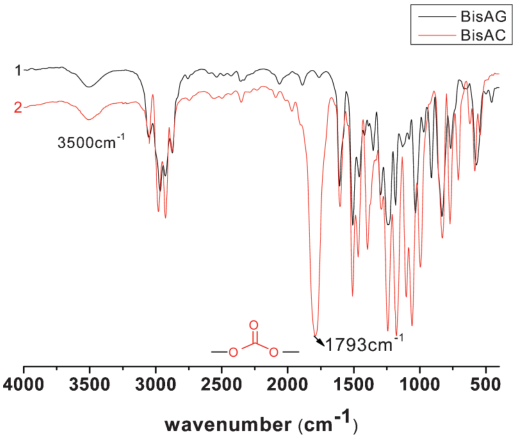


Fig. 2 FT-IR spectra of the BisAC derived from BisAG and CO_2.

Furthermore, a clear cooperative effect of Zn–Co(III) DMCC and CTAB on the coupling reaction was observed. If only nanolamellar Zn–Co(III) DMCC was used, the BisAG conversion could be only up to 41.5% (entry 9, Table 1). If only CTAB was used, the BisAG conversion could reach to 70.4% (entry 10, Table 1). However, an improved BisAG conversion of 84.2% was obtained with the binary catalysts of nanolamellar Zn–Co(III) DMCC and CTAB (entry 8, Table 1).

The above results suggested that the propylene carbonate (PC) could be the best solvent for the BisAG–CO_2 coupling reaction (Table 1). It was also proven that PC could be efficiently synthesized by the coupling reaction of PO and CO_2 with a 97.8% PO conversion by using the same binary catalyst system (entry 1, Table 2). Thus, one might expect that propylene carbonate (PC) and bis(cyclic carbonate)s could be synthesized at the same time with high monomer conversion

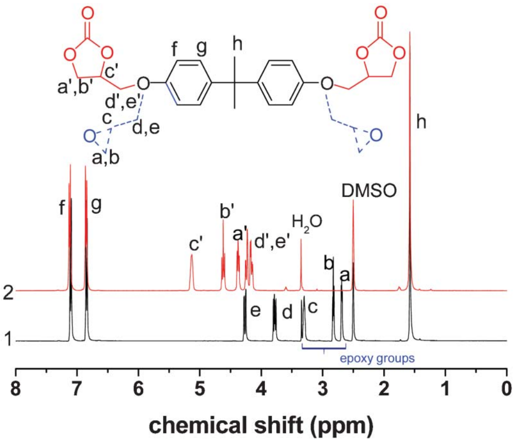


Fig. 3 ^{1}H NMR spectra of the bis(cyclic carbonate) (line 2) derived from BisAG and CO_2, and BisAG monomer (line 1).

Table 2 The effects of reaction temperatures and pressures on the one-pot coupling reaction of PO, BisAG and CO_2[a]

Entry	Temp. (°C)	Pressure (MPa)	BisAC (g)	PC (g)[b]	Conversion of BisAG	Conversion of PO
1[c]	120	4.0	—	41.3	—	97.8%
2	120	5.0	10.5	37.4	81.6%	85.4%
3	120	4.0	8.3	33.1	65.9%	75.6%
4	100	4.0	7.2	29.5	57.2%	67.4%
5	80	4.0	6.0	24.8	47.7%	56.6%
6	120	3.0	6.5	30.1	51.6%	68.7%
7	120	2.0	4.8	27.2	38.1%	62.1%
8	120	1.0	3.2	26.6	25.4%	60.7%

[a] Reaction condition: Zn–Co(III) DMCC 20.0 mg, CTAB 150.0 mg, BisAG 10.0 g (0.03 mol), PO 30 mL, 9.0 h. [b] The weight of the isolated product after distillation under reduced pressure. [c] No BisAG was added.

via the one-pot coupling reaction of PO, CO_2 and bisepoxides by using the binary catalyst system of the nanolamellar Zn–Co(III) DMCC/CTAB. In this protocol, CO_2 was the common monomer for the coupling reactions of PO/CO_2 and bisepoxides/CO_2. The *in situ* generated PC could then serve as the solvent of bis(cyclic carbonate). As a result, no external organic solvent was required to achieve the high monomer conversion. The coupling reaction of PO, CO_2 and BisAG was carried out under the same conditions as entry 8 in Table 1. After the reaction, the solid catalyst was firstly separated by pressure filter or centrifugation. The resultant PC was then distilled out under reduced pressure from the crude solution. Afterwards, the remaining mixture was poured into THF for purifying the obtained BisAC. The experimental results indicated that 75.6% of PO and 65.9% of BisAG were converted to PC and BisAC, respectively (entry 3, Table 2). Note that water could be used for the separation of BisAC and PC because PC could dissolve into water very well while BisAC could not. This is a much greener route for separation because the amounts of THF for purifying BisAC could be reduced.

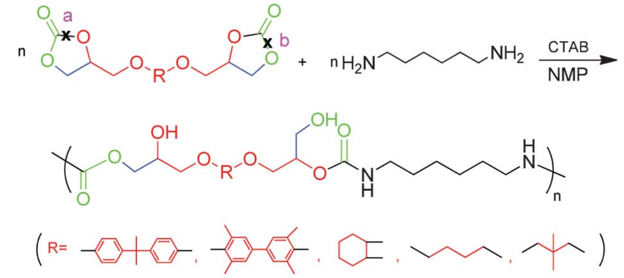
The CO_2 pressure and reaction temperature played important roles in this one-pot coupling reaction. As shown in Table 2, the conversions of PO and BisAG decreased from 85.4% and 81.6% to 60.7% and 25.4% (entries 2–3 and 6–8), respectively, with decreasing CO_2 pressure from 5.0 MPa to 1.0 MPa. When the temperatures decreased from 120 °C to 80 °C, the conversions of BisAG and PO were reduced from 65.9% and 75.6% to 47.7% and 56.6% (entries 3–5, Table 2), respectively, which indicated that the coupling reactions were thermodynamically favourable. High reaction temperature and high CO_2 pressure are favorable for the production of PC and BisAC.

Such a one-pot coupling reaction of PO/bisepoxides/CO_2 was further tested for other four bisepoxides. 4,4-Bis(2,3-epoxy-propoxy)-3,3,5,5-tetramethylbiphenyl, cyclohexanediol diglycidyl ether, butanediol diglycidyl ether and neopentyl glycol diglycidyl ether were used to synthesize the corresponding bis(cyclic carbonate) (BisCC-1, BisCC-2, BisCC-3 and BisCC-4, respectively, as denoted in the experimental section). The formation and structures of these bis(cyclic carbonate)s were confirmed by FT-IR and ^{1}H NMR spectra (Fig. S1–S8, ESI†). It can be seen from Table 3 that PO and all bisepoxides were all effectively transformed into PC and the corresponding bis(cyclic carbonate) with high monomer conversions. For instance, in the one-pot coupling reaction of neopentyl glycol diglycidyl ether, PO and CO_2 (entry 4, Table 3), 93.2% of PO and 82.9% of neopentyl glycol diglycidyl ether were carbonated. Moreover, the bisepoxides with aliphatic backbones (entries 2–4, Table 3) presented relative higher monomer conversions in the same monomer to catalyst ratio under the same reaction conditions than those of bisepoxides with aromatic backbone (entry 1, Table 3; and entry 2, Table 2). The obtained bis(cyclic carbonate)s from the coupling reaction of CO_2 with BisAG and 4,4-bis(2,3-epoxy-propoxy)-3,3,5,5-tetramethylbiphenyl were solid powders, while the bis(cyclic carbonate)s derived from aliphatic bisepoxides were viscous liquids (Fig. S9, ESI†).

Table 3 The one-pot coupling reaction of PO, CO_2 and various bisepoxides[a]

Entry	Bisepoxide	Bis(cyclic carbonate) (g)	PC[b] (g)	Bisepoxide Conversion	PO Conversion
1	BisEP **1**	10.7	36.6	80.2	83.6
2	BisEP **2**	7.5	39.6	79.2	90.6
3	BisEP **3**	7.2	39.5	82.5	90.2
4	BisEP **4**	7.6	40.8	82.9	93.2

[a] Reaction condition: PO 30.0 mL, 120 °C, 5.0 MPa, 9.0 h, bisepoxide 0.03 mol, Zn–Co(III) DMCC 20.0 mg, CTAB 150.0 mg. BisEP **1:** 4,4-bis(2,3-epoxy-propoxy)-3,3,5,5-tetramethylbiphenyl, BisEP **2:** cyclohexanediol diglycidyl ether, BisEP **3:** 1,4-butanediol diglycidyl ether, BisEP **4:** neopentyl glycol diglycidyl ether. [b] Isolated weight after distillation under reduced pressure.



Scheme 2 Polyaddition of bis(cyclic carbonate)s and 1, 6-hexamethylenediamine. Note that two ways of ring opening of the carbonate *via* routes a and b occur randomly during reaction, leading to the formation of the secondary and primary hydroxyl groups.

Table 4 Polyaddition of bis(cyclic carbonate)s with 1,6-hexamethylene-diamine catalyzed by CTAB[a]

Entry	Bis(cyclic carbonate)	Yield[b] (%)	M_n[c] (g mol^{-1})	PDI[c]	Primary OH/secondary OH[d]
1	BisAC	85.5	9020	1.5	36/64
2	BisCC-1	84.6	7400	1.4	32/68
3	BisCC-2	83.7	5000	1.5	34/66
4	BisCC-3	84.1	6740	1.5	36/64
5	BisCC-4	84.4	7100	1.4	33/67

[a] Reaction conditions: bis(cyclic carbonate) 0.05 mmol, 1,6-hexamethylenediamine 0.05 mmol, CTAB 0.0015 mmol, NMP 4 mL, 60 °C, 5 h. [b] Isolated yield after precipitation into ether. [c] Determined by GPC eluted with DMF (LiBr 0.05 M). [d] Determined by ^{1}H NMR spectroscopy. Primary OH/secondary OH = $A_{5.08}/[(A_{3.60-4.32} - 4A_{5.08})/6]$.

As discussed above, two valuable cyclic carbonates, namely propylene carbonate (PC) and bis(cyclic carbonate), could be simultaneously obtained *via* the one-pot coupling reaction of PO, CO_2 and bisepoxides. The *in situ* produced PC could act as the good solvent for improving the conversion of bisepoxides. No external organic toxic solvent was needed during the reaction. Furthermore, the two resultant cyclic carbonates could be easily separated by distillation or precipitation from water. A possible mechanism was then proposed for this one-pot coupling reaction catalyzed by the binary catalyst system of nanolamellar Zn–Co(III) DMCC/CTAB based on the reported mechanism.[4–6,7a,17] The zinc ions (Zn^{2+}) on the surface of Zn–Co(III) DMCC (Fig. 1d) represented a Lewis acid site, which activated the oxirane groups of the epoxides. Br^- anion of CTAB acted as a stronger nucleophilic reagent, attacked the carbon atom of the activated oxirane groups, promoted the ring-opening reaction of the oxirane groups, and produced a metal (Zn)-oxyalkyl bond. With the following insertion of CO_2 into the Zn–O bond, a metal-carbonate species was obtained by an intramolecular backbiting route, leading to the five-membered cyclic carbonates.

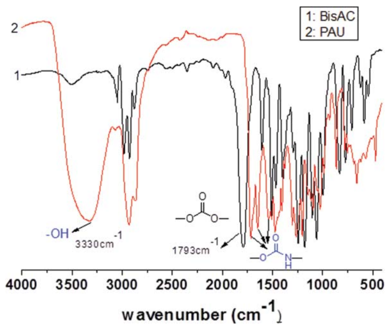


Fig. 4 FT-IR spectra of the PAU derived from 1,6-hexamethylenediamine and BisAC.

The obtained bis(cyclic carbonate)s could be applied to synthesize poly(hydroxyurethanes)s (PUs) *via* a polyaddition with di-and polyfunctional primary alkyl amines. As illustrated in Scheme 2, the polyaddition reactions of the five obtained bis(cyclic carbonate)s and 1,6-hexamethylenediamine were carried out by using NMP as a solvent and CTAB as a catalyst at 60 °C for 5 h, resulting in five linear polyurethanes with different main chains and massive hydroxyl groups. Due to the asymmetrical carbonate group, two ring-opening routes (a or b cleavage in Scheme 2) occurred and led to the formation of the secondary and primary hydroxyl groups. All experimental data were collected in Table 4.

The structures of five polyurethanes were confirmed by FT-IR and ^{1}H NMR spectra (Fig. 4 and 5 and Fig. S11–S18, ESI†). Taking PU prepared from BisAC and 1, 6-hexamethylenediamine as an example, the vibration peak of carbonyl group of BisAC at 1793 cm^{-1} disappeared after polyaddition (curve 1, Fig. 4). The new peaks at 3330 (–OH, –NH), 1710, 1654 and 1540 cm^{-1} that appeared after the polyaddition were assigned to the groups of –OC(=O)NH– (curve 2, Fig. 4), indicating the production of poly(hydroxyurethanes).[9] Fig. 5 shows the ^{1}H NMR spectrum of the produced PAU with characteristic chemical shifts that could be assigned to the protons of amines (δ = 1.10–1.45 ppm, 3.00–3.21 ppm and 7.18 ppm) as well as the protons of the newly formed hydroxyl groups (5.08 ppm and 3.84 ppm)[8b,8d]. The chemical shifts of the methylene and methine protons of carbonate groups at δ = 5.09, 4.58, and 4.34 ppm disappeared (*cf.* curve 2, Fig. 3). The number-average molecular weights (M_ns) of the obtained PUs were 5000–9020 and narrow molecular weight distributions of 1.4–1.5 were measured by GPC (Fig. S19, ESI†). Moreover, the molar ratios of the primary OH and secondary OH were varied at the ranges

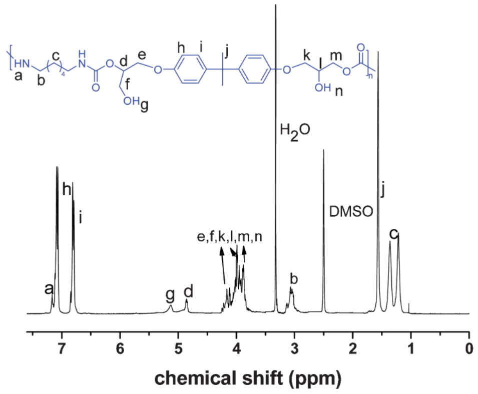


Fig. 5 ^{1}H NMR spectrum of PAU derived from BisAG and 1,6-hexamethylenediamine.

of 32–36 to 64–68, which were consistent with the reported values.[8b,8d]

Conclusions

Propylene carbonate (PC) and bis(cyclic carbonate)s were successfully synthesized with high monomer conversions *via* an efficient one-pot coupling reaction of PO, CO_2 and various bisepoxides catalyzed by using a binary catalyst system of nanolamellar Zn–Co(III) DMCC/CTAB. The obtained bis(cyclic carbonate)s could be used to prepare polyurethanes with massive side –OH groups *via* the polyaddition reaction with 1,6-hexamethylenediamine.

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