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Structure-induced catalytic activity of Co-Zn double-metal cyanide complexes for terpolymerization of propylene oxide, cyclohexene oxide and CO$_2$

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The application of Co-Zn double-metal cyanide (DMC) complexes as catalysts for selective terpolymerization of propylene oxide, cyclohexene oxide and CO$_2$ producing polycarbonates is reported for the first time. DMC complexes were prepared with and without using a co-complexing agent. The complex with monoclinic/rhombohedral crystal structure and strong Lewis acidity, prepared without using a co-complexing agent, showed higher initial activity than that with a cubic structure prepared using a co-complexing agent. Interestingly, no induction period in the terpolymerization reaction was observed. The terpolymer has 75.5% of carbonate fraction in its composition and an average molecular weight of 22,700 and polydispersity index of 2.97. It is characterized by a T$_g$ of 55°C. This structure-induced catalytic activity of DMC can open up new avenue for its application in other reactions. The influence of process parameters on the catalytic activity of DMC was investigated.

Introduction

Polycarbonates have applications in lithography, environmentally friendly packaging materials, adhesives and binders for ceramics.[1] These bulk applications of polycarbonates are significantly influenced by their mechanical and thermal properties. Poly(propylene carbonate) (PPC) is decidedly preferred over poly(cyclohexene carbonate) (PCHC) due to superior tensile strength, elasticity and fast biodegradability. However, low glass transition temperature (T$_g$) of PPC (30—40°C) compared to PCHC (100—120°C) hampers its broad utility.[2] Terpolymerization of propylene oxide (PO), cyclohexene oxide (CHO) and CO$_2$ improves the T$_g$ property (Scheme 1). The concept of terpolymerization is chemically more challenging due to difference in the reactivity of PO and CHO which makes very difficult to control the composition of the terpolymer (polycarbonate). Some successful reports are available with single-site homogeneous catalysts.[3] But, such reports using solid catalysts are scarce in the open literature,[4] due to further challenges in the heterogeneous nature of the active sites. Although, there are reports on the individual copolymerizations of PO-CO$_2$ and CHO-CO$_2$ over double-metal cyanide (DMC) catalysts,[5] information on terpolymerization of two epoxides with CO$_2$ is not documented as yet. The objective of this study is to report the successful synthesis of a terpolycarbonate from PO, CHO and CO$_2$ over a solid Co-Zn DMC catalyst and also to explore the influence of catalyst preparation method and structure on the polymerization activity of DMC. Co-polymerization of CO$_2$ and epoxides demonstrates a low energy process for the efficient utilization of greenhouse gas CO$_2$ to environmentally adaptable polymeric materials.[6]
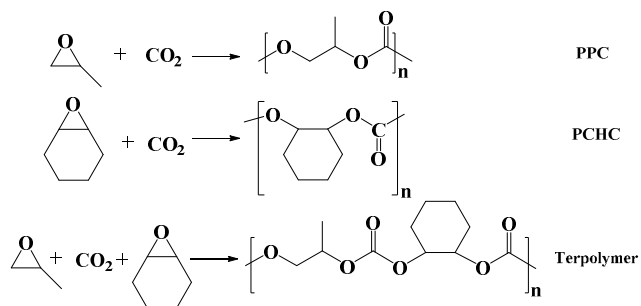
Scheme 1 Polymerization of epoxides and CO$_2$.

Experimental

Catalyst preparation

DMC-I was prepared in the presence of complexing and co-complexing agents (tert.-butanol and polyethylene glycol of molecular weight 4000 – PEG-4000, respectively).[7] In its synthesis, solution 1 was prepared by dissolving 3.32 g of K$_3$[Co(CN)$_6$] in 40 ml of deionized water. Solution 2 was prepared by dissolving 13.6 g of ZnCl$_2$ in deionized water (18 ml) and tert.-butanol (20 ml) mixture. Solution 3 was made by dissolving 15 g of PEG-4000 in 2 ml of water and 40 ml of tert.-butanol. Solutions 2 and 3 were mixed and then, added to solution 1 over 1 h at 50°C while stirring. Then the slurry was aged for another 1 h at the same temperature while continuing the stirring. Solid cake formed was separated by filtration, washed with deionized water (500 ml) and dried at 25°C for 2 to 3 days to a constant weight. Specific surface area of DMC-I = 486 m^2/g, total pore volume = 0.518 ml/g and average pore diameter = 2.1 nm.

DMC-II was prepared in the absence of a co-complexing agent (PEG-4000).[7] In a typical preparation, solution 1 was prepared by dissolving 4 gm of K$_3$[Co(CN)$_6$] in 70 ml of deionized water and

solution 2 was made by dissolving 12.5 g of $ZnCl_2$ in 20 ml of deionized water. Solution 3 was a mixture of tert.-butanol (50 ml) and water (50 ml), and solution 4 was 1 ml of tert.-butanol in 100 ml of deionized water. Then, solution 2 was added to solution 1 maintained at 50°C over a period of 1 h. To this, solution 3 was added immediately and stirred for 10 min. Solution 4 was then added to the above slurry and kept for aging at 50°C for 1 h while stirring was continued. The solid cake was then filtered and suspended in a mixture of tert.-butanol (70 ml) and deionized water (30 ml). It was stirred for 10 min at 50°C and filtered. The solid was then suspended in pure tert.-butanol (100 ml), stirred for 10 min at 50°C and filtered. The catalyst was dried at 25°C for 2 to 3 days to a constant weight. Specific surface area of DMC-II was 235 m^2/g; total pore volume = 0.243 ml/g and average pore diameter = 2.1 nm.

Catalyst characterization techniques

Powder X-ray diffraction (PXRD) patterns of the catalysts were recorded in the 2θ range of 5- 50° at a scan speed of 2°/min on a Philips X'Pert Pro diffractometer using Cu-K$_\alpha$ radiation (λ = 0.15406 nm) and a proportional counter detector. Fourier transform infrared (FTIR) spectra of the catalysts, as KBr pellets, were performed on a Shimadzu 8201 PC spectrophotometer in the wavenumber region of 450 to 4000 cm^{-1}. FT-Raman spectra were measured on a Horiba JY LabRaman HR800 MicroRaman spectrometer using 630 nm wavelength generated by a He-Ne laser operating at 20 mV. Chemical composition of the catalysts was determined by energy dispersive X-ray analyzer (FEI, Quanta 200 3D dual beam ESEM; 30 kV, resolution = 3 nm). The type and density of acid sites were determined by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy of adsorbed pyridine and temperature-programmed ammonia desorption (NH_3-TPD) techniques. Specific surface area, pore volume and pore diameter of the catalysts were determined from N_2 adsorption-desorption isotherms measured at -196°C using a Quantachrome USA (Autosorb-1C) equipment. Prior to N_2 adsorption, the samples were evacuated at 180°C for 3 h. A reference alumina sample (supplied by Quantachrome, USA) was used to calibrate the instrument.

Reaction procedure

Terpolymerization of PO, CHO and CO_2: Terpolymerization was carried out in a 100 ml stainless-steel Parr reactor (Parr Instrument Co., Parr 4871) equipped with a mechanical stirrer and an automatic temperature controller system. The reactor was charged with 5.8 ml of CHO (Aldrich Co.), 4.2 ml of PO (Merck), 0.226 g of Co-Zn DMC catalyst and 10 ml of toluene. The molar ratio of PO: CHO was 1:1. Initially, the reactor was flushed twice with CO_2 (laboratory grade) and then, pressurised to 30 bar. Polymerization was conducted at 85°C for 11 h. At the end of the reaction, left out CO_2 was vented out and the catalyst was separated by centrifugation (9000 rpm, 5 min) followed by decantation. Toluene was distilled out over a rotary evaporator and the crude elastic polymer was isolated (yield = 11.7 g). It was purified by dissolving in dichloromethane (24 ml) and re-precipitating by adding excess methanol (117 ml). The solid terpolymer was separated from the solution, dried (yield = 7.37 g) and subjected to characterization (M_w = 46900, PDI = 4.98, T_g = 58°C using DMC-I and M_w = 22700, PDI = 2.97, T_g = 55°C using DMC-II).

Copolymerization of CHO and CO_2 – Poly(cyclohexene carbonate) (PCHC): In this reaction, 10 ml each of CHO and toluene were charged into the Parr reactor along with 0.25 g of the DMC catalyst. The reactor was flushed twice with CO_2 and then, pressurised to 30 bar. Polymerization was conducted at 85°C for 11 h. At the end of the reaction, the gas was vented out and the catalyst was separated by centrifugation (9000 rpm, 5 min) followed by decantation. The polymer was then isolated by removing toluene by rotary evaporation (isolated yield = 11.9 g). The solid polymer thus obtained was purified by dissolving in dichloromethane (24 ml) and re-precipitated by adding excess methanol (120 ml). The solid polycarbonate was then separated from the solution, dried (yield = 63.1 wt%) and subjected to characterization (M_w = 11800, PDI = 2.3).

Copolymerization of PO and CO_2 – Poly(propylene carbonate) (PPC): Copolymerization of PO and CO_2 was performed in the same manner as that of CHO-CO_2 copolymer. The polymer obtained was viscous (isolated yield = 9.2 g). It was purified by dissolving in dichloromethane (18.5 ml). Then excess of methanol (92.5 ml) was added. The elastomeric formed was separated, dried (yield = 15.7 wt%) and subjected to characterization (M_w = 15800, PDI = 3.13).

Polymer characterization

[1]H nuclear magnetic resonance (NMR) spectroscopy was used to calculate the percentage incorporation of CO_2 (F_{CO2}) in the polycarbonates produced. Measurements were done on a Bruker Avance 200 MHz spectrometer using $CDCl_3$ as solvent. In the case of PCHC, methine (C**H**) protons near to the carbonate linkages were observed at δ = 4.2 to 4.6 ppm and those near to the ether linkages were found at δ = 3.2 to 3.6 ppm (ESI[†]). F_{CO2} was calculated by integrating the C**H** peaks (A) attached to carbonate and ether linkages and using the formula given below.[8]

$$F_{CO2} = \frac{A_{4.2-4.6}}{A_{4.2-4.6} + A_{3.2-3.6}} \times 100$$

F_{CO2} in PPC was calculated by integrating the peaks at 5.1 and 4.2 ppm (C**H$_2$/CH** attached to carbonate units), 3.5 ppm (C**H$_2$/CH** attached to ether linkages) and 4.5 ppm (C**H$_2$/CH** of cyclic propylene carbonate) (ESI[†]) using the formula reported by Chen et al.[9]

$$F_{CO2} = \frac{(A_{5.1} + A_{4.2} - 2 \times A_{4.5})}{(A_{5.1} + A_{4.2} - 2 \times A_{4.5}) + A_{3.5}}$$

The weight percentage (W_{PC}) of cyclic propylene carbonate (side product) in the crude polymer was calculated using the formula:

$$W_{PC} = \frac{102 \times A_{1.5}}{58 \times A_{1.14} + 102 \times (A_{1.33} + A_{1.50})}$$

Microstructural analysis of PCHC, PPC and terpolymer in terms of tacticity was analyzed by inverse-gated ^{13}C NMR spectrum recorded on a 500 MHz Bruker Avance spectrometer using $CDCl_3$ as solvent (ESI[†]). Differential scanning calorimetric (DSC) analyses of the polymer samples were done on a DSC Q100TA instrument in the temperature region of -80 to 145°C with a ramp rate of 10°C/min. Thermogravimetric analysis of the samples were recorded on a Perkin Elmer STA 6000 instrument in the temperature range of 25 to 500 °C and with a ramp rate of 10°C/min (ESI[†]).

The average molecular weight (M_w) and polydispersity index (PDI) of polycarbonates were determined on a PL 220 HT gel permeation chromatography equipped with Styragel columns at 25°C using chloroform as eluent. The sample concentration was 3 mg/ml. The columns were calibrated with monodispersed polystyrene standards of different molecular weights.
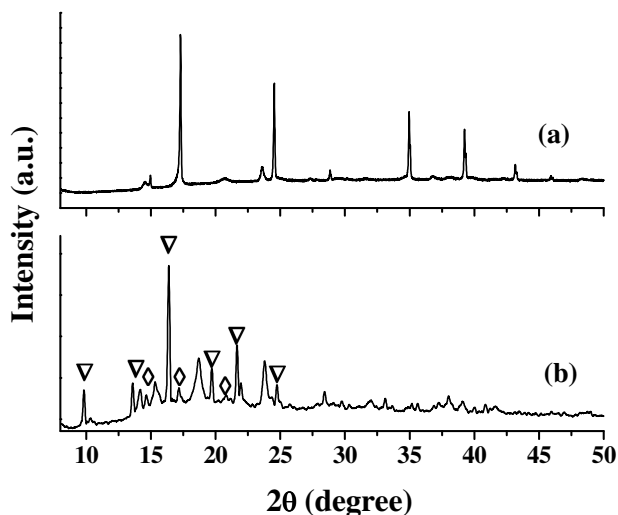

Figure 1 PXRD patterns of (a) DMC-I and (b) DMC-II. Peaks marked with ▽ correspond to rhombohedral phase and those with ◊ stand for a monoclinic phase.

Results and discussion

Structural characterization

Figure 1 shows PXRD patterns of Co-Zn DMC catalysts investigated in this study. DMC-I prepared using both complexing and co-complexing agents showed X-ray peaks characteristic of a cubic structure (Figure 1, trace a).[10] On the contrary, DMC-II synthesized without using a co-complexing agent showed peaks which could be indexed to rhombohedral[11] (peaks at 2θ = 9.8, 14.3, 16.4, 19.6, 21.6 and 24.8° marked by ▽) and monoclinic[10] (peaks at 2θ = 14.6, 17.1, 20.8 and 23.7° marked by ◊) structures (Figure 1, trace b). Average crystallite sizes of rhombohedral and monoclinic phases were estimated by the Debye-Scherrer formula and found to be 44 and 51 nm, respectively. The average crystallite size of DMC-I was 87 nm. Interestingly, the cubic phase was absent in the sample (DMC-II) prepared by the modified procedure without using a co-complexing agent.

Raman spectroscopy too confirmed the presence of two crystalline phases in DMC-II showing splitting in CN⁻ stretching band (2200, 2220, 2210 and 2226 cm⁻¹) (Figure 2, trace b). While the first two bands are assigned to the monoclinic phase, the latter are corresponded to the rhombohedral phase. DMC-I with cubic structure showed these stretching bands at 2184 and 2205 cm⁻¹ (Figure 2, trace a). Differences in band positions point out differences in the structure and bonding of bridging cyanide groups. Increase in stretching frequency corresponds to increase in the amount of electron donation from cyanide to metal ions. Thus, the appearance of cyanide bands at higher frequency in the case of DMC-II than in DMC-I suggest higher amount of electron transfer from CN⁻ to Co³⁺ in the case of the former than in the latter complex.
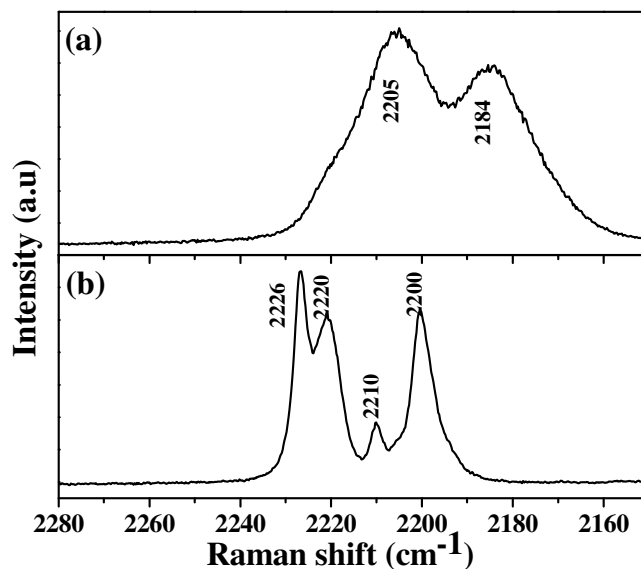

Figure 2 FT-Raman spectra of (a) DMC-I and (b) DMC-II.

Tert.-butanol (complexing agent) was included in the DMC structure. Confirmation towards this was obtained from FTIR spectroscopy which showed characteristic bands at 2955 and 1465 cm⁻¹ due to CH stretching and scissoring vibrations, 1370 cm⁻¹ due to OH bending and 1190 cm⁻¹ due to C-O stretching vibrations, and from the elemental analysis (ESI†). Crystals of DMC-I and DMC-II differ in their morphology (Figure 3). While DMC-I possess mainly octahedron shaped crystals, DMC-II has agglomerated crystals of no definite shape.
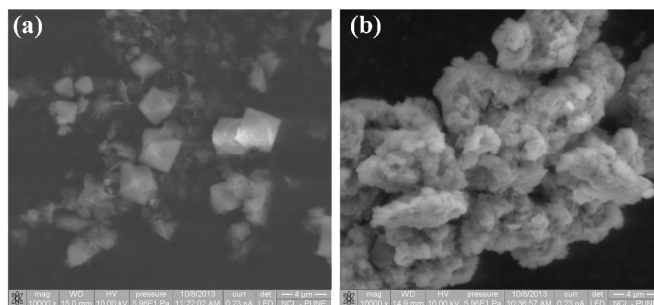

Figure 3. SEM images of (a) DMC-I and (b) DMC-II.

DRIFT spectroscopy of adsorbed pyridine revealed that Co-Zn DMC is Lewis acidic (ESI†). DMC prepared without using a complexing agent (DMC-II) has higher overall acidity of 2.27 mmol/g than the complex prepared by using a co-complexing agent (1.79 mmol/g) (ESI†). DMC-II has a Zn/Co molar ratio of 2.8 which is higher than the theoretical prediction of 1.5 corresponding to a molecular formula of $Zn_3[Co(CN)_6]_2$. The sample contained also K⁺ (2 at.%) and Cl⁻ (11.3 at.%) ions in its composition. Based on the chemical composition determined from energy dispersive X-ray analysis (EDX), the molecular formula of DMC-II is described as $Zn_3[Co(CN)_6]_2.mZnCl_2.xH_2O$.[12] DMC-I has a Zn/Co molar ratio of 1.6 and K⁺ of 0.19 at.% and Cl⁻ of 0.17 at.%. All these characterization studies thus reveal that the method of synthesis has an influence on the structure DMC catalysts.
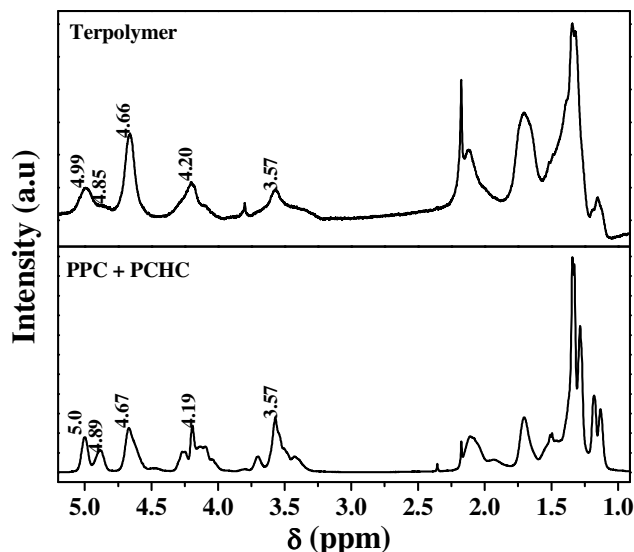
Figure 4 ^{1}H NMR spectra of PO-CHO-CO$_2$ terpolymer and PPC + PCHC physical blend synthesised over DMC-II.

DMC structure-catalytic activity correlations

Figure 4 shows ^{1}H NMR spectra of a purified terpolymer product (top panel) and a physical blend of PPC and PCHC (bottom panel). NMR signals at 4.19(m), 4.89(s) and 5.0(s) ppm for the physical blend are due to **CH$_2$/CH** groups of PPC component (ESI†). The signal at 4.67 ppm is due to the **CH** proton of PCHC (ESI†). While polycarbonate formation is the preferred reaction, etherification forming ether linkages (PEP) would also occur under these polymerization conditions. ^{1}H NMR spectroscopy is a powerful tool to identify and distinguish these ether units from carbonate units. The multiplet pattern at 3.57 ppm in spectrum for the physical blend is due to **CH/CH$_2$** groups involved in the ether linkages. The **CH$_3$** of PPC and ring **CH$_2$** (not involved in carbonate linkages) of PCHC showed NMR signals in the chemical shift region of 1.2 – 2.3 ppm (Figure 4; bottom panel). All these signals of the physical blend are present also in the NMR spectrum of PO-CHO-CO$_2$ terpolymer (Figure 4; top panel). But, broader linewidth and loss in fine-structure originally present in the mixture point out that the PO-CHO-CO$_2$ product is not a physical mixture of PPC and PCHC copolymers. Also, it is not a –(PPC-PCHC-PPC)$_n$- block-copolymer. Copolymerization of PO and CO$_2$ over the same catalyst produced an elastomeric product (PPC). The terpolymerization product of this study contained all the ^{1}H NMR signals of **CH/CH$_2$/CH$_3$** groups of PPC but was a white solid with no elastomeric component. These observations unequivocally confirm that the reaction of PO, CHO and CO$_2$ over Co-Zn DMC catalyst produced a terpolymer and not a physical mixture of PPC/PCHC or block-copolymer.

Formation of a terpolymer was further confirmed by DSC analysis. The terpolymer exhibited a *single* T$_g$ at 58°C (while using DMC-1) and 55°C (while using DMC-II) which is in between that of PPC (-11°C) and PCHC (96.6°C). Inclusion of PCHC units in PPC increases T$_g$ of the terpolymer (Figure 5). Lower T$_g$ values of the products than expected for 100% pure
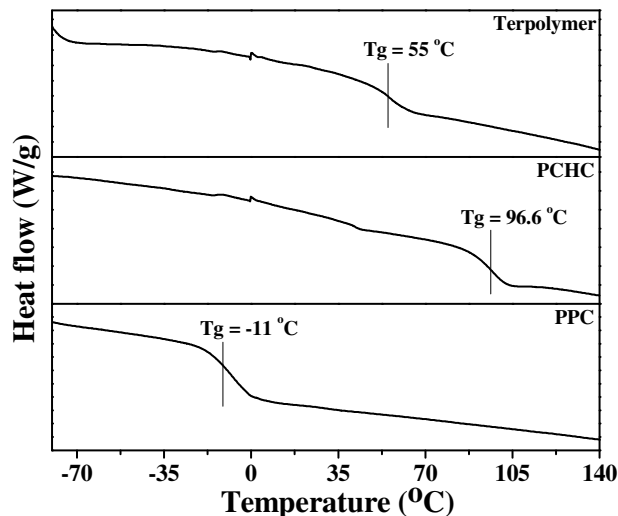

Figure 5 DSC of PPC, PCHC and terpolymer synthesised over DMC-II.

PPC (30—40°C) and PCHC (100—120°C) are due to the presence of some ether (PEP) linkages in the prepared polymers. Also differences were observed in the thermal properties of terpolymer and PPC & PCHC co-polymers. Thermo-gravimetric analysis of the terpolymer showed two weight losses at 207.2°C (6.2 wt%) and 292°C (93.8 wt%). On contrary, PCHC showed these losses at 200.5°C (9.4 wt%) and 286°C (90.6 wt%) and PPC at 263°C (62 wt%) and 338°C (38 wt%), respectively (ESI†). PCHC showed a broad PXRD peak at 2θ = 17.7° while terpolymer exhibited this peak at 18.8°, suggesting differences in polymer configuration (ESI†). PCHC copolymer has block-like morphology while the terpolymer has sheet-like morphology (ESI†).
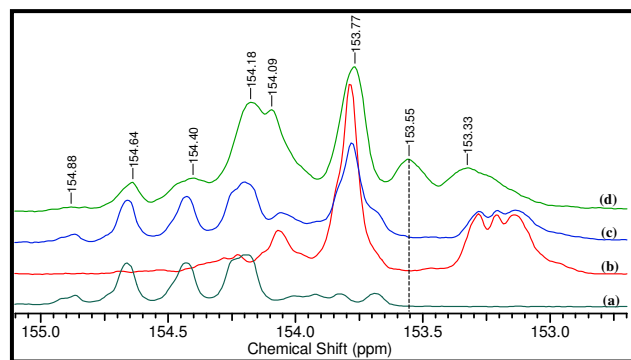
Figure 6 Inverse-gated ^{13}C NMR spectra (in the carbonate region) of polycarbonates: (a) PPC, (b) PCHC, (c) PPC + PCHC and (d) terpolymer.

PPC showed inverse-gated ^{13}C NMR signals (Figure 6) at 153.69 - 154.01, 154.2 - 154.66 and 154.87 ppm corresponding to head-head (HH), head-tail (HT) and tail-tail (TT) tacticity.[13] PCHC showed signals at 153.14 - 153.28 ppm due to syndiotactic isomers (the r-centred tetrads; rrr/rrm/mrm) and 153.8 - 154.23 ppm corresponding to isotactic isomers (m-centred tetrads;

mmm/mmr/rmr;).[14] The terpolymer showed an additional signal at 153.55 ppm confirming regioselective connectivity of CHO and PO around the carbonate unit which was absent for the individual copolymers and their physical mixture (PPC + PCHC; Figure 6).[15]

Percentage incorporation of CO_2 in the terpolymer was estimated by integrating the ^1H NMR signals of **CH_2/CH** associated with the carbonate (4.99, 4.85, 4.66 and 4.20 ppm) and ether (3.57 ppm) linkages (Figure 4 and ESI[†]); 77.3 and 75.5 mol% (with DMC-I and DMC-II, respectively) of **CH_2/CH** groups were involved in carbonate linkages. In other words, CO_2 incorporation in the terpolymer was 75.5 – 77.3 mol% and balance was polyether polyol. The relative area of the signal at 4.66 ppm (arising from PCHC) with reference of the total area of signals at 4.99, 4.85 and 4.20 ppm (arising from PPC; 53/47 mol%/mol%; Figure 4) points out that the epoxides (PO and CHO taken in 1:1 molar ratio) were alternatively arranged across the carbonate units in the terpolymer. The percentage distribution of ether fraction from each monomer (PO and CHO) could not be differentiated as the NMR signals corresponding to them appeared at the same position (3.57 ppm; Figure 3). However, from the intensities of –CH_3 (PPC) and –CH (PCHC) peaks near to the ether linkage, we found that the major contribution to the total polyether polyol is from PPC (ESI[†]). This conclusion is supported by the high thermodynamic favourability of homopolymerization of PO.[1] Copolymerization of PO and CO_2 resulted 42 mol% of polyether polyols fraction in the purified PPC copolymer product while that of PCHC contained only 16 mol%. Some amount of cyclic carbonate (19.4 wt%) had also formed under our experimental conditions (ESI[†]). But, the purified terpolymer did not contain this component (see absence of ^1H NMR signals at 4.85 (m), 4.56 (t), 4.05 (t) and 1.5 (d) ppm, Figure 4).
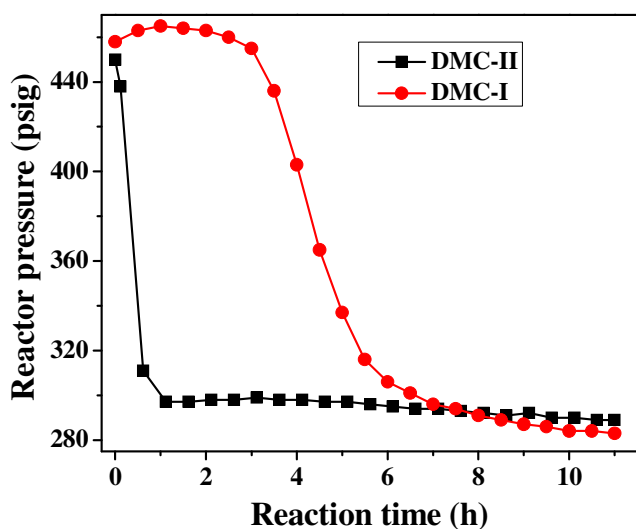

Figure 7 Time on stream activity of Co-Zn DMC catalysts.

Figure 7 shows the reactivity of DMC-I and DMC-II catalysts in terms of CO_2 pressure drop in the reactor as a function of time. Often the known catalysts for polyether-polycarbonate synthesis (through copolymerization) show an induction period in the polymerization reaction.[16] As seen from Figure 7, this is the case also with DMC-I catalyst. Unlike

DMC-I (prepared using co-complexing agent), DMC-II, (prepared by a modified synthetic procedure without using a co-complexing agent) is unique. Surprisingly, DMC-II showed no induction period. Terpolymerization initiated at the zero hour itself. We varied the amount of catalyst from 80 to 226 mg and found that the amount of catalyst has no effect on the induction period in terpolymerizations over DMC-II (ESI[†]). DMC-I exhibited an induction period of 2.5 h in the polymerization reaction (Figure 7). Further it required 4.5 h after the induction period (instead of 1 h) to attain similar conversions of CO_2 as that of DMC-II. The weight average molecular weight (M_W) of terpolymer produced at the end of 11 h run was higher (46900) over DMC-1 than on DMC-II (22700), but PDI which is equally important determining the properties of the polymer is lower (2.97) over DMC-II than on DMC-I (4.89). This unprecedented superior activity of DMC-II of this work (higher initial catalytic activity, no induction period & lower PDI) than DMC-I is correlated to its structural properties. Unlike most of DMCs which are cubic as of DMC-I, the catalyst DMC-II of this study has low-symmetry monoclinic/rhombohedral structure. EDX showed excess amount of Zn^{2+} and retention of Cl^- and K^+ ions in the catalyst composition of DMC-II. This excess Zn exists as $ZnCl_2$ in the DMC-II structure. Hence, DMC-II catalyst of this study is a double-salt with a molecular formulae of $Zn_3[Co(CN)_6]_2.mZnCl_2.xH_2O$. Since Cl^- is electron withdrawing, coordination of it to Zn^{2+} is expected to increase the strength of Lewis acidity which eventually enhances the activity of Zn^{2+} sites and their interaction with epoxides and CO_2. This enhanced activity of Zn^{2+} sites ultimately avoided the induction period of DMC-II catalyst prepared without using a co-complexing agent.

As DMC-II with monoclinic/rhombohedral structure is superior to DMC-I in its catalytic activity, further studies were undertaken with DMC-II catalyst. Table 1 lists the effects reaction parameters on the catalytic activity of DMC-II. Marked effects on the yield (methanol insoluble-high molecular weight fraction of terpolymer), percentage CO_2 incorporation (f_{CO2}), PPC/PCHC distribution, M_w and PDI could be noted.

Effect of reaction temperature. Experiments were conducted at three different temperatures *ca.,* 75, 85 and 95°C while maintaining CO_2 pressure at 30 bar and reaction time at 11 h. As the temperature rose from 75 to 95°C, the yield of polymer (methanol insoluble fraction) decreased from 8.8 to 4.1 g and f_{CO2} decreased from 83.8 to 72.3 mol%. M_w and PDI of terpolymer also decreased from 29000 to 20500 and 3.16 to 2.43, respectively. Only a marginal variation in the yield of cyclic propylene carbonate (PC from 19.1 to 20.9 wt%) was found. An induction of 1 h observed at 75°C got completely vanished at 85°C and above (ESI[†]). Also the distribution of PPC/PCHC in the terpolymer changed from 55.9/44.1 (at 75°C) to 53.5/46.5 (at 95°C). This shift in PPC/PCHC distribution is likely due to preferences for the formation of polyols of PO as well as cyclic carbonate at higher temperatures as against polycarbonate.

Effect of CO_2 pressure. Keeping temperature constant at 85°C and reaction time as 11 h, CO_2 pressure was varied from 10 to 20 - 30 bar. The yield of terpolymer increased from 1.2 (at 10 bar CO_2) to 7.4 g (at 30 bar CO_2); f_{CO2} increased from 60.1 to 75.5 mol%; M_w increased from 14700 to 22700 and PDI increased from 2.48 to 2.97. In other words, unlike

Table 1 Catalytic activity of DMC-II in terpolymerization of PO-CHO-CO_2

Reaction Parameter	Isolated yield of polymer (g)	Yield of terpolymer (MeOH insoluble portion; g)	% Incorporation of CO_2 (f_{CO2}; mol%)			PC (wt%)	M_w	PDI
			Total	PPC	PCHC			
Reaction temperature (^oC)^a								
75	11.8	8.8	83.8	55.9	44.1	19.1	29000	3.16
85	11.7	7.4	75.5	53.0	47.0	19.4	22700	2.97
95	11.4	4.1	72.3	53.5	46.5	20.9	20500	2.43
CO_2 pressure (bar)^b								
10	10.0	1.2	60.1	52.7	47.3	13.5	14700	2.48
20	11.5	4.8	65.7	45.1	54.9	20.1	20800	2.81
30	11.7	7.4	75.5	53.0	47.0	19.4	22700	2.97
Catalyst quantity (g)^c								
0.226	11.7	7.4	75.5	53.0	47.0	19.4	22700	2.97
0.113	11.8	6.4	80.2	55.5	44.5	17.9	22300	2.58
0.083	12.7	6.6	85.0	58.1	41.9	20.1	23200	2.83
Reaction time (h)^d								
1	9.5	1.5	60.8	52.0	48.0	20.6	13600	2.77
11	11.7	7.4	75.5	53.0	47.0	19.4	22700	2.97
% Mole fraction of PO^e								
100	9.2	1.4	58.4	100.0	0.0	27.0	15800	3.13
80	10.0	2.0	78.1	79.4	20.5	31.1	27000	2.59
66	10.7	3.9	70.9	64.5	35.5	30.7	20000	2.31
57	11.3	5.2	81.4	59.8	40.2	27.6	23600	2.39
50	11.7	7.4	75.5	53.0	47.0	19.4	22700	2.97
43	10.7	6.5	77.3	45.0	54.9	17.9	14100	2.07
33	12.4	10.1	82.0	38.9	61.0	12.7	22700	2.56
20	12.7	10.2	77.0	25.7	74.2	11.7	15800	2.94
0	11.9	7.5	83.8	0.0	100.0	0.0	11800	2.30

Reaction conditions: (for a) CHO = 5.6 g, PO = 3.5 g, CHO : PO molar ratio = 1:1, catalyst = 0.226 g, toluene = 8.7 g, p_{CO2} = 30 bar, reaction time = 11 h, reaction temperature = 75 - 95°C; (for b) same as for a except reaction temperature = 85°C and p_{CO2} = 10 - 30 bar; (for c) same as for a except, reaction temperature = 85°C and catalyst = 0.083 – 0.226 g; (for d) same as for a except reaction temperature = 85°C and reaction time = 1 or 11 h; (for e) same as for a except reaction temperature = 85°C, %PO = [PO/(PO + CHO)] x100 and catalyst = 2.5 wt% with respect to the amount of highest monomer
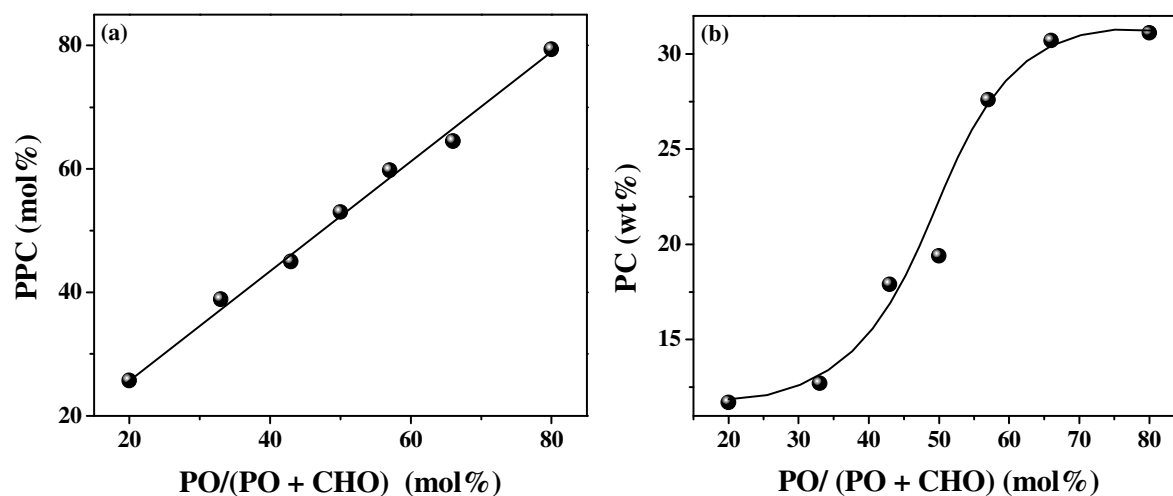
Figure 8 Effect of PO mole fraction on (a) PPC composition in the terpolymer and (b) on the yield of PC.

For temperature, CO_2 pressure has a positive effect on the yield and characteristics of the terpolymer.

Effect of PO-CHO molar ratio. The percentage mole fraction of PO in PO-CHO reactant mixture was varied from 0 to 100%. While 0 and 100% fractions of PO led to PCHC and PPC co-polymers, respectively, other fractions resulted in

terpolymers of varying compositions. The isolated yield of terpolymer increased with decreasing mole fraction of PO in the reactants. This could be due to difference in the molecular weights of epoxides used and their reactivities towards polycarbonate versus polyol formations at chosen conditions. Some variation in the characteristics of the polymer was noted but no systematic correlation with PO mole fraction could be drawn. PPC/PCHC composition in the terpolymer goes parallel with PO mole fraction and cyclic propylene carbonate formation shows an S-shaped curve with increasing percentage fraction of PO in the feed (Figure 8). M_w of the terpolymer was higher than that of the individual copolymers – PPC and PCHC.

Effects of catalyst amount and reaction time. While the yield of polymer (methanol insoluble portion) increased, f_{CO2} and M_w showed a reverse trend with increase in the catalyst amount. Polymer yield, f_{CO2}, and M_w showed parallel variations with the reaction time. The time versus reactor pressure (reactivity) plots for DMC-II at different reaction conditions are shown in ESI[†].

Reaction temperature of 85°C, 30 bar CO_2 pressure and PO:CHO molar ratio of 1:1 were found optimum conditions for high yield of terpolymer with high M_w and PPC/PCHC composition of near unity. Reaction took place with no induction period at those conditions. The catalyst was reusable. Upon use the catalyst broke down to smaller particles and decrease in average crystallite size of DMC-II (44 to 20.7 nm) was found (see PXRD of spent catalyst; ESI[†]). But the rhombohedral/monoclinic structure of pristine catalyst was preserved even after reuse. Copolymerization of CHO and CO_2 were conducted in presence of related DMC catalysts prepared using $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ instead of $K_3Co(CN)_6$ (30 bar CO_2, 85°C and 11 h). Reaction didn't occur to a notable extent with these Fe-Zn DMC catalysts. Copolymer yields of 0.213 and 0.148 g were obtained using Fe-Zn DMC catalysts while the analogous Co-Zn DMC (i.e, DMC-II) enabled a polymer yield of 11.9 g at the same reaction conditions. Fe-Zn DMC shows two NH_3-TPD peaks at 150 and 188°C corresponding desorptions from weak and strong acid sites.[17] These desorptions for DMC-II occurred at 161 and 192°C (ESI[†]). Further, the content of strong acid sites was higher in DMC-II than in Fe-Zn DMC. These differences in strength and density of acid sites are responsible for the higher catalytic performance of DMC-II compared to the related systems.
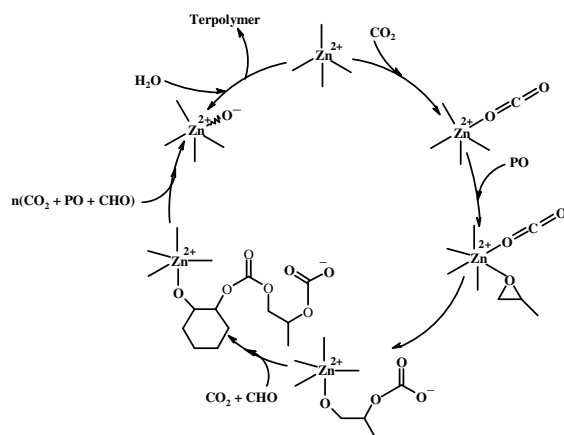

Figure 9 Tentative mechanism for terpolymerization of PO, CO2 and CHO.

Figure 9 shows a tentative mechanism for terpolymerization over DMC-II catalyst. In the initiation step, CO_2 is activated at tetrahedrally coordinated, Lewis acidic Zn^{2+} active centers by coordination through its oxygen atom and converting to a monodentate carbonate species. In the next step, PO is activated at the same Zn^{2+} site. The activated CO_2 facilitates ring-opening followed by its insertion in the epoxide (PO) forming an alkylene carbonate linkage. Subsequent insertion of another CO_2 molecule and CHO results in the formation of a terpolymer repeating unit. Alternative addition of these monomers in the propagation step result the desired polymer chain. Water (added externally or present in trace quantities in the feed) is responsible for chain termination and active site regeneration. Formation of undesired cyclic carbonate (PC) by backbiting reaction can occur either from a dead polymer or from a growing polymer. Alkali metals are expected to accelerate the backbiting in dead polymer by ionising the terminal –OH functionalities of carbonate and alcohol groups. Simultaneous addition of PO or CHO or both lead to ether linkages in the polymer.

Conclusions

Co-Zn DMC catalysts showed high activity for terpolymerization of PO, CHO and CO_2 producing polyether-polycarbonates. Method of preparation of DMC influenced its structure, composition and catalytic activity. The catalyst prepared in the presence of both complexing and co-complexing agents (DMC-I) had a cubic structure whereas the one prepared without using co-complexing agent (DMC-II) had monoclinic and rhombohedral crystal phases. DMC-II showed higher catalytic activity than DMC-I. Moreover, in the polymerization reactions using DMC-II catalyst no induction period was noted. The influence of reaction parameters on the catalytic activity of DMC-II was investigated. DMC-II was reusable. To the best of our knowledge, this is the first report on the structure-induced terpolymerization activity of Co-Zn DMC catalysts.

Acknowledgements

Notes and references

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