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Synthesis of Fully Alternating Polycarbonate with Low T_g from Carbon Dioxide and Bio-based Fatty Acid

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The selective copolymerization of CO_2 and epoxide with fully alternating degree was a great challenge via the catalysis of zinc-cobalt (III) double metal cyanide complex [Zn-Co(III) DMCC]. For the first time, we described the perfectly alternating copolymerization of CO_2 with a bio-based epoxide. The resultant polycarbonate (PC) had pretty low T_gs of -38~-44°C and two end hydroxyl groups, which was further
10 employed to initiate ring-opening polymerization (ROP) of L-lactide via metal-free catalysis, affording a biodegradable triblock copolymer. This study provides a new platform copolymer for making various advanced polymers with biodegradable properties.

Introduction

Recent years have witnessed an increasing demand on the
15 sustainable utilization of renewable natural resources as raw chemical materials due to the depletion of the oil reserves along with the environmental issues.[1] Bio-based plastics, produced from renewable feedstock such as biomass, could decrease our dependency on petroleum and positively impact efforts to curb
20 global warming. Furthermore, the utilization of renewable raw materials, fully taking advantage of the synthetic potential of nature, can meet the principle of green and sustainable chemistry very well.[2] Plant oils are considered as the most important renewable raw materials for the production of bio-based polymers
25 for their renewable property, world wide availability, relatively low price, abundant application possibilities. Castor oil, a non-edible oil extracted from the seeds of the castor bean plant, as many other plant oils, is abundantly available and potentially capable of transforming into various value-added monomers.[3]
30 For instance, 10-undecenoic acid can be obtained by heating ricinoleic acid under vacuum[4], or efficiently produced by hydrolysis of methyl undecenoate[5] at 558–638°C with yields of 44.6–45.7%. Therefore, 10-Undecenoic acid could be potentially used as a valuable precursor for making chemicals and materials,
35 such as antitumor compounds, antibiotics[6], Nylon 11[7] and polyurethane (PU)[8]. A complete review about the possible applications of undecylenic acid was comprehensively summarized by Marijke Van der Steen and Christian V. Stevens.[4]
40 On the other hand, as a renewable natural C1 feedstock, carbon dioxide (CO_2) is low cost, nontoxic and a promising resource for chemical synthesis, especially for polymer synthesis.[9] Recently, a lot of researches were focused on the utilization of CO_2 as C1 building block for making polymers, of these, polycarbonates
45 represent a promising class of materials. Since the landmark discovery of $ZnEt_2/H_2O$ system for CO_2/propylene oxide (PO) copolymerization by Inoue et al in 1969,[10] much progress has

been made in developing various epoxides and catalyst systems for CO_2 copolymerization with epoxides.[11] However, nearly all
50 investigations were focused on the copolymerization of the petrochemically derived epoxides with CO_2. Only few literatures were reported the copolymerization of bio-renewable epoxides. For example, Coates and co-workers reported the alternating copolymerization of limonene oxide and CO_2 using β-diiminate
55 (BDI) zinc complexes, affording a polycarbonate with a high glass transition temperature (T_g) of 113.9°C.[12] To date, many kinds of fully alternating CO_2-epoxide copolymers were reported with relatively high T_gs, such as the poly(indene carbonate)s, from the coupling of indene oxides with CO_2 using bifunctional
60 cobalt(III) catalysts, with a T_g of 138°C was reported by Darensbourg et al.[13] Lu and coworkers recently reported the selective synthesis of high T_g(140°C) CO_2 copolymers from 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (CXO) in perfectly alternating nature by the enantiopure dinuclear Co(III)-complex-
65 mediated desymmetrization copolymerization.[14] The other direction of CO_2-based copolymers is the synthesis of more "soft" or functional copolymers, such as polycarbonates diol with low molecular weights and low T_g.[15] Yamada and co-workers described the alternating polymerization of propylene oxide,
70 terminated epoxides with long side chains and CO_2 using cobalt(III) complex catalysts.[15f] T_g of the obtained polymers could be tuned by varying the feeding ratios the epoxides as well as the length of the long side group.[15f] These CO_2-based copolymers could be potentially applied as the precursors for
75 making rubber or elastomers. In this case, it is necessary to develop low T_g polycarbonate with at least two end –OH groups, which are helpful for the next reactions. To the best of our knowledge, up until now, the lowest T_g of polycarbonate was -22°C and reported by Coates and co-workers, namely poly(l,2-
80 hex-5-ene carbonate)[16] catalyzed by β-diiminate (BDI) zinc complexes, which was obtained from the copolymerization of CO_2 with a petrochemically-derived epoxide.

In this work, we describe the synthesis of a new polycarbonate derived from C1 feedstock and bio-renewable monomer of epoxy methyl 10-undecenoate (EMU) by using a zinc-cobalt (III) double metal cyanide complex [Zn-Co(III) DMCC] (scheme 1) and its application for synthesizing C1- and bio-based triblock copolymer. The resultant polycarbonate showed fully alternating nature (carbonate linkage content was estimated to be > 99%) with two end –OH groups and a pretty low T_g of –44°C.
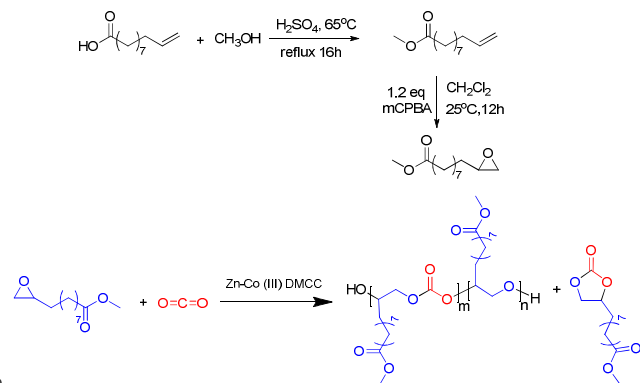
Scheme 1. Synthesis of bio-based epoxide from 10-undecenoic acid and alternating copolymerization of epoxy methyl 10-undecenoate and CO_2.

Experimental Section

Materials

10-undecenoic acid (95%), m-chloroperbenzoic acid (mCPBA), sulphuric acid (98%), anhydrous sodium sulfate, sodium chloride, methanol, dichloromethane (DCM) were purchased from Aladdin and used without further purification. L-lactide was recrystallized from ethanol, dried under vacuum at 40°C overnight. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was purchased from Aladdin and distilled under reduced pressure over CaH$_2$. THF was distilled from sodium and stored under nitrogen. Carbon dioxide with 99.995% was used as received.

Characterization

^{1}H and ^{13}C NMR spectra of the products were performed on a Bruker Advance DMX 500-MHz spectrometer. Chemical shift values were referenced to TMS as internal standard at 0.0 ppm for ^{1}H NMR (500 MHz) and against CDCl$_3$ at 77.0 ppm for ^{13}C NMR (100 MHz). Molecular weights and polydispersity index (PDI) of the polycarbonates were determined by using a PL-GPC220 chromatograph (Polymer Laboratories) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with THF with 1.0 mL/min at 40°C. The sample concentration was approximately 0.3wt % and the injection volume was 50μL. Calibration was performed using monodisperse polystyrene standards covering the molecular-weight range from 500 to 500,000 Da. Infrared spectra were obtained by using a Bruker Vector 22 FT-IR spectrophotometer. Differential scanning calorimetric (DSC) tests were conducted on a TAQ200 instrument (New Castle, DE) with a heating rate of 10 ^{o}C/min from -80-220°C under N$_2$ atmosphere. T_g and T_m was determined from the second run. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 1 instrument at a

heating rate of 10°C/min from room temperature to 500°C under N$_2$ atmosphere. Samples for thermal analyses were all purified. ESI−MS analyses were performed by using an Esquire3000 plus mass spectrometer with mixed methylene chloride/methanol as solvent for dissolving the copolymer. Water content in EMU was determined using a MaxTitra20Q moisture meter (Shanghai Tianmei Scientific Instruments Co., Ltd. China) based on coulometric method.

Synthesis of methyl 10-undecenoate

A 250-mL three-necked round-bottomed flask equipped with a water cooled condenser was charged with 60ml 10-undecenoic acid, an excess of methanol (110ml). 15ml concentrated sulphuric acid was added dropwise by a dropping funnel within 30min. The reaction mixture was heated at 65°C for 16 h under magnetic stirring. The mixture was then washed with 10% sodium bicarbonate solution followed by Brine water until the solution were neutral, the upper layer liquid was collected and dried over anhydrous magnesium sulfate, and filtered to obtain methyl 10-undecenoate.Yield: 95%; FT-IR: 1640 cm^{-1} (C=C), 1742 cm^{-1} (COOCH$_3$), 3077 cm^{-1} (C=C-H); ^{1}H NMR (CDCl$_3$, 500 MHz, δ ppm): 1.40-1.17 (m, 10H), 1.67-1.52 (m, 2H), 2.05-1.93 (q, 2H), 2.33-2.21 (t, 2H), 3.63 (s, 3H), 5.01-4.84 (m, 2H), 5.85-5.68 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz, δ ppm): 174.2 (1C), 139.1 (1C), 114.2 (1C), 51.4 (1C), 34.1 (1C), 33.9 (1C), 29.4-29.0 (5C), 25.0 ppm (1C).

Epoxidation of methyl 10-undecenoate (MUD)

A 500mL bottomed flask was charged with 30ml methyl 10-undecenoate (0.13mol). A 250ml mCPBA/DCM solution (0.16mol mCPBA) was added in small portions at 0°C. The reaction mixture was then stirred at room temperature for 12h. After the reaction, 10% (wt/v) of saturated aqueous solution of sodium sulfite was added followed by saturated aqueous solution of sodium hydrogen carbonate and brine water. The organic phase was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to obtain the epoxy methyl 10-undecenoate (EMU). Yield: 93 %; FT-IR: 1741 cm^{-1} (COOCH$_3$), 837 cm^{-1} (epoxy); ^{1}H NMR (CDCl$_3$, 500 MHz, δ ppm): 1.34-1.22 (m, 10H), 1.52-1.46 (m, 2H), 1.66-1.53 (m, 2H), 2.31-2.23 (t, 2H), 2.91-2.83 (m, 1H), 2.76-2.69 (m, 1H), 2.90-2.83 (m, 1H), 3.64 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz, δ ppm): 174.1(1C), 52.3 (1C), 51.4 (1C), 47.0 (1C), 34.0 (1C), 32.5 (1C), 29.4-29.1 (4C), 26.0 (1C), 25.0 ppm (1C).

Preparation of nanolamellar Zn-Co (III) DMCC catalyst

The catalyst was synthesized according to our method reported.[20] The elemental analysis result of the catalyst: Co: 12.48; Zn: 27.29; N: 16.57; C: 23.34; H: 2.27; Cl: 9.50.

Representative copolymerization of CO_2 and epoxy methyl 10-undecenoate (EMU)

A 10 ml autoclave with a small magnetic stirrer was dried at 120°C for 3 h, and cooled to room temperature in a closed desiccator. 16.0 mg Zn-Co (III) DMCC catalyst and 2.0 ml EMU were transferred into the autoclave. The autoclave was sealed and filled with CO_2, then heated to the target temperature in a pre-

heated oil bath. The system was adjusted to the set pressure and kept stirring for the set time. After the copolymerization, the autoclave was cooled with ice-water bath and the pressure was slowly vented. A small amount of crude product was collected for [5] ^{1}H NMR spectroscopy. The remained products were dissolved with small amounts of methylene dichloride and precipitated by excess methanol, dried at 60°C under vacuum to constant weight. The obtained copolymer was colorless and viscous.

FT-IR: 3450 cm^{-1} (OH), 1741 cm^{-1} (COOCH$_3$); ^{1}H NMR (CDCl$_3$, [10] 500 MHz, δ ppm): 1.43-1.16 (m, 10H), 1.70-1.49(m, 4H), 2.33-2.21 (t, 2H), 3.64 (s, 3H), 4.42-3.95(m, 2H), 4.86(s, 1H) . ^{13}C NMR (CDCl$_3$, 100 MHz, δ ppm): 174.3 (1C), 154.7 (1C), 75.8 (1C), 68.2 (1C), 51.5 (1C), 34.1 (1C), 30.5 (1C), 29.2 (4C), 25.0 ppm (2C).

[15] **Representative procedure for synthesis of triblock copolymers from L-lactide**

0.1645g polycarbonate (M_n = 4400g/mol), L-lactide (5.586mmol, 0.805g) were placed in a 25ml Schlenk flask under a nitrogen atmosphere and dissolved in THF (3 mL). Then DBU (45μl) in 2 [20] mL CH$_2$Cl$_2$ was added to prepare the triblock polymer. Stirring was continued for 3h, benzoic acid was added to quench the reaction. The crude polymer was precipitated from methanol three times, and white polymer was obtained and dried under vacuum. ^{1}H NMR (CDCl$_3$, 500 MHz, δ ppm): 1.26 (s), 1.55 (m), [25] 2.27 (t), 3.64 (s, 3H), 4.42-3.95 (m), 4.86 (s), 5.13 (q). ^{13}C NMR (CDCl$_3$, 100 MHz, δ ppm): 174.3 (1C), 169.5(1C), 154.7 (1C), 75.8 (1C), 68.2 (1C), 68.9(1C), 51.5 (1C), 34.1(1C), 30.5(1C), 29.2 (4C), 25.0 (2C), 16.6 (3C).

Results and Discussion

[30] Zn-Co(III) DMCC catalyst is a typical catalyst and has been developed to an highly efficient catalyst for CO$_2$-epoxide copolymerization.[17] The basic structure of Zn-Co(III) DMCC is that the zinc and cobalt atoms are associated with cyanide bridges, affording a three dimensional backbone. The empirical [35] formula of the catalyst prepared at below 40°C in the presence of tert-butanol (t-BuOH) was denoted as Zn$_3$[Co(CN)$_6$]$_2$·xZnCl$_2$·yt-BuOH·zH$_2$O (x,y and z are varied based on the preparation conditions).[17f, 18] We have reported a nanolamellar Zn-Co(III) DMCC catalyst synthesized at 75°C. The Zn/Co molar ratio of [40] this catalyst was 2.0 based on the elemental analysis.[17b] The catalytic center of this catalyst was confirmed to be Zn-OH bond in the surface of the catalyst, as shown in Figure S1.[19] For Zn-Co(III) DMCC catalyzed CO$_2$-epoxide copolymerization, it is still a big challenge to get fully alternating copolymer. The best [45] record was 99.4% alternating degree of the styrene oxide-CO2 copolymer from Zn-Co (III) DMCC, as our recent report.[20] This kind of Zn-Co(III) DMCC catalyst exhibited nanolamellar structures with thickness of ca. 20−80 nm and high surface areas of ca.600 m^2/g, which could provide more active sites than the [50] traditional one.[20] Herein, we applied this nanolamellar Zn-Co (III) DMCC catalyst directly for the copolymerization of CO$_2$ with epoxy methyl 10-undecenoate (EMU). Polycarbonate with perfectly alternating structure would be expected because of the long bulky side group of EMU (Scheme 1).

[55] The bio-based epoxide, epoxy methyl 10-undecenoate (EMU), was synthesized from 10-undecenoic acid by two methods [21]

that are often used in the laboratory, as shown in Scheme 1. Firstly, the esterification of 10-undecenoic acid with methanol was carried out using sulphuric acid as the catalyst.[21a] [60] Afterwards, the methyl 10-undecenoate (MUD) was oxidized by an oxidant of m-chloroperbenzoic acid at 25°C for 12h using dichloromethane as solvent. The FT-IR (Fig. S2) and ^{1}H NMR spectra (Fig. S3) proofed the successful synthesis of epoxy methyl 10-undecenoate (EMU) with a yield of 93%.[21b] Note that [65] this epoxy monomer could be synthesized by sustainable methods, for example, direct pyrolysis of methyl ricinoleate to give methyl 10-undecenoate[4-5] and the employment of an environmentally friendly oxidants for the epoxidation, such as hydrogen peroxide [22].
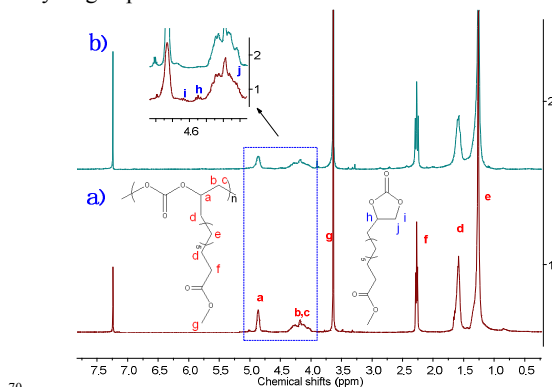

[70] **Figure 1.** Selected ^{1}H NMR spectra of a) the crude product and b) the purified copolymer of entry 3 in Table 1 (CDCl$_3$, 500 MHz).

Table 1. The copolymerization of EMU with CO$_2$ catalyzed by nanolamellar Zn-Co (III) DMCC catalyst at various conditions [a].

Entry	Temp (°C)	Press (MPa)	EMU[b] (conv%)	F_{CO2}[c] (%)	Wcc[c] (wt%)	Mn[d] (kg/mol)	PDI	T_g[e] (°C)
1	30	5	ND	ND	ND	ND	ND	ND
2	40	5	78	> 99	4.8	18.6	2.1	-40
3	50	5	100	> 99	7.4	17.7	2.4	-40
4	60	5	100	> 99	14.5	16.6	2.6	-38
5	70	5	100	> 99	15.3	11.8	2.1	-39
6	80	5	100	> 99	16.7	9.9	2.8	-40
7	90	5	100	92	18.0	8.5	2.8	-42
8	100	5	100	90	20.0	7.1	2.9	-44
9	50	3	100	> 99	1.9	3.7	2.2	-41
10	50	4	100	> 99	3.9	4.2	2.3	-41
11	50	5	100	> 99	5.7	4.4	2.3	-41

[75] [a] Reactions were performed in a 10 ml dry autoclave for 12 h, 2.0 ml EMU, 16.0 mg Zn-Co(III) DMCC catalyst. Water contents of entries 1-8 and entries 9-11 were 120 ppm and 400 ppm, respectively. [b] EMU converted to both poly(carbonate-co-ether) and cyclic carbonate, and EMU was not observed from ^{1}H NMR spectra of entries 3-11(Figure S5-[80] S13). [c] F_{CO2} (%) indicates the molar fraction of carbonate linkages in the produced polymer. F_{CO2} (%) = A$_{4.9}$ / [A$_{4.9}$ + (A$_{3.4-3.8}$ − A$_{3.6}$) / 3]; Wcc (wt%) indicates the weight percentage of cyclic carbonate in the total crude product, determined by using ^{1}H NMR spectra. Wcc (wt%) = 258A$_{4.5}$ / [258A$_{4.5}$ + 258A$_{4.9}$ + 214(A$_{3.4-3.8}$ − A$_{3.6}$) / 3](Figure S4-S13) [d] [85] Determined by gel permeation chromatography in THF, 40°C, calibrated with standard monodispersed polystyrene. [e] Data obtained from the second DSC scan (10°C/min, N$_2$).

A series of EMU-CO$_2$ copolymerization were successfully [90] catalyzed by nanolamellar Zn-Co (III) DMCC. The experimental conditions and the results were summarized in Table 1. No products were collected when the reaction temperature was at

30°C (entry 1, Table 1) for 24 h. Increasing the temperature from 40°C to 100°C (entries 2-8) resulted in more production of cyclic carbonate from 4.8 to 20.0 wt% and a decrease of M_n of the resultant copolymer from 18.6 to 7.1 kg mol^{-1}. For obtaining copolymers with relative low M_n, water was used as chain transfer agent in the copolymerization system.[15b] As shown in entries 9-11, when the water content in the monomer was 400ppm, the M_ns of the copolymer was lowered to 3.7-4.4 kg/mol without loss of monomer's conversion at 50°C. In this case, enhancing CO_2 pressure from 3.0 to 5.0 MPa (entries 9-11) resulted in a clear increase of the catalyst productivity, and a slight increase of the weight percentage of cyclic carbonate in the total product (W_{cc}) from 1.9 to 5.7 wt%. Except entries 1-2 in Table 1, EMU in entries 3-11 was completely converted to the product within 12h according to the ^1H NMR spectra of the crude copolymers (Figs.S5-S13). The optimized reaction temperature and CO_2 pressure were 50°C and 3.0MPa because low content of cyclic product was produced, as shown in entries 3, 9-11.

The formation of the ether units is usually thermodynamically favourable during Zn-Co(III) DMCC catalysis,[15b] however, in this case, the alternating degree (F_{CO2}) of all the resultant copolymers obtained at 40-80°C were estimated to > 99% because no ether unit signals were observed from their ^1H NMR spectra (e.g., see Figure 1 and Figure S14-S18). To our knowledge, this is the first example of alternating CO_2-epoxide copolymer with F_{CO2} >99% via Zn-Co(III) DMCC catalysis. The bulky side group led to full alternating copolymerization of EMU with CO_2 via heterogeneous Zn-Co(III) DMCC catalysis. However, such steric effect of bulky group of EMU on F_{CO2} of the resultant copolymer was weakened when the reaction temperature was elevated to 90 and 100°C (as shown in entries 7-8 in Table 1). This is closely accordance with the typical catalytic behaviour of Zn-Co(III) DMCC. Moreover, the resultant copolymer presented regio-irregular structure, as ^{13}C NMR spectra of entry 5 in Table 1 (Fig S24), which means that the attack of propagating species to CH and CH$_2$ sites had nearly equal probability.

The EMU−CO_2 copolymer via Zn−Co(III) DMCC has two end hydroxyl (−OH) groups, which was evidenced by the result of the electrospray ionization-tandem mass spectrometry (ESI-MS) in a positive mode for low M_n copolymer [M_n = 2000 and PDI =2.4(GPC result), F_{CO2} = 95.2%, Fig S25] which was obtained at 90°C for 5h, as seen in Fig S26, in which all captured m/z species in the range of 600-2000 presented two −OH groups. One end −OH group came from the initiation Zn−OH bond, and the other was produced by the chain transfer reaction of the propagating chain to H_2O (or other proton compounds).[19] This was consistent with the results of the copolymerization of other aliphatic epoxides with CO_2 catalyzed by the same Zn-Co (III) DMCC catalyst.[15b, 19]
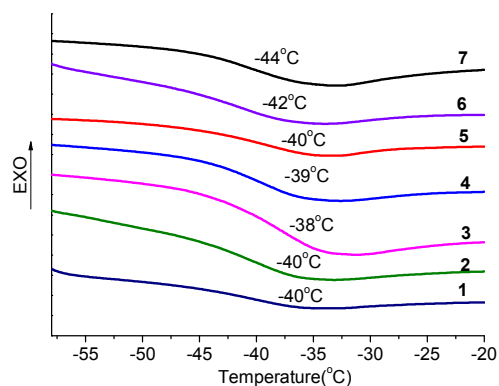

Figure 2. The DSC curves of the CO_2-EMU resultants at various temperatures (curves 1-7 represent entries 2-8 at Table 1).

Such EMU-CO_2 copolymers exhibited pretty low T_gs at -38°C~-44°C, as shown in Figure 2. This could be attributed to the internal plasticization effect or their micro-Brownian motion[15f] of the long alkyl side chain with ester groups. To the best of our knowledge, it was the first example that CO_2-based polycarbonate with such low T_g. Moreover, T_g of this copolymer is close to the typical commercial bio-compatible polyols such as PEO (T_g is about -54°C)[23] that are widely used as the precursors for functional polymers. At the same time, the EMU-CO_2 copolymers also exhibited high initial thermal decomposition temperature (T_d, 5%) of 240°C (Figure S27), which is clearly higher than that of PEO. Therefore, the EMU-CO_2 copolymer could be potentially used as a platform for making various advanced polymers.
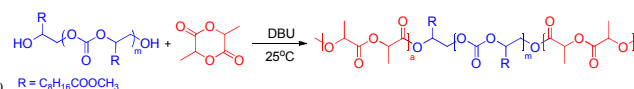
Scheme 2. The synthesis of CO_2- and bio-based triblock copolymer from ROP of L-lactide initiated by EMU-CO_2 copolymer.

Herein, it was demonstrated that the EMU-CO_2 copolymer could be used as a macroinitiator to initiate ring-opening polymerization (ROP) of L-lactide via metal-free catalytic route, as shown in Scheme 2. Note that L-lactide is a common bio-based monomer. DBU (1, 8-diazabicyclo [5.4.0] undec-7-ene) was used as the catalysis for L-lactide ROP at mild temperature of 25°C. The weight percentage of EMU-CO_2 copolymer in this block polymer was 20.1% based on L-lactide conversion. GPC traces of the resultant triblock copolymers and EMU-CO_2 copolymer (Figure 3) showed the clear increase of M_n, while control experiment that L-lactide ROP didn't occur without using EMU-CO_2 copolymer as the initiator under the same reaction conditions. The structure of the triblock copolymer was well revealed by ^1H and ^{13}C NMR spectra (Fig. S28-S29). The thermal properties of the resulting triblock copolymers were determined by Differential scanning calorimetric (DSC) tests (Fig. S30) at a heating rate of 20°C/min. Two T_gs at -35°C and 45°C were observed, which could be attributed to the polycarbonate block and PLLA block, respectively. A cold crystallizing peak at 108°C and two melting peaks at 131°C and 142°C were also observed. The cold crystallizing peak meant confined or incomplete

crystallization of the sample, while the double melting peaks disclosed the existence of dual (or multiple) crystal structures[24] of this sample, because the polycarbonate macroinitiator presented a relative large polydispersity (PDI) of 2.30, which caused the obtained triblock copolymers had different length ratios of poly(EMU-CO$_2$) block and PLLA block. Still, such CO$_2$ and bio-based triblock copolymer, PLLA-PC-PLLA, has prolific thermal transitions and has potential applications as functional materials.
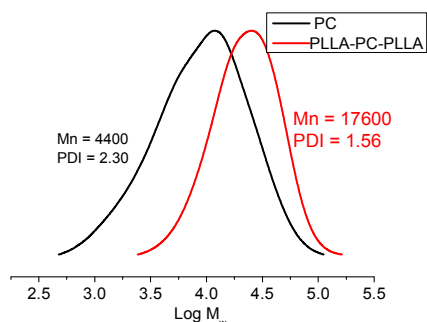

Figure 3. GPC curves of EMU-CO$_2$ copolymer macroinitiator (Table 1, entry 11) and the resultant triblock copolymer, PLLA-PC-PLLA.

Conclusions

In summary, novel biodegradable full alternating polycarbonate and derived triblock copolymer were synthesized from CO$_2$ and renewable platform chemicals. The fully CO$_2$-based polycarbonates with the low T_g and two end hydroxyl groups are good candidates for making thermoplastic elastomers that are not from petroleum resources.

Acknowledgements

Notes and references

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