Supporting Information

Carbon Dioxide/Epoxide Copolymerization via a Nanosized Zinc-Cobalt(III) Double Metal Cyanide Complex: Substituent Effects of Epoxides on Polycarbonate Selectivity, Regioselectivity and Glass Transition Temperatures

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Experimental section

Materials

$K_3Co(CN)_6$ (Yixing City Lianyang Chemical Co., Ltd, China, 99%) was recrystallized in de-ionized water before use. $ZnCl_2$, *tert*-BuOH were analytical grade and used without further purification. Epoxides **B-H**, **J** were refluxed over calcium hydride for 12 h and then distilled out for use. Thereof, epoxides **I, K** were prepared from vinylcyclohexane and allylbenzene, respectively, while other epoxides were directly purchased from Aldrich. Carbon dioxide with 99.995% was used as received.

Preparation of 2-benzyloxirane (K) and 2-cyclohexyloxirane (I)

An amount of 1-allylbenzene or vinylcyclohexane (10.0 mL, 0.075 mol) was dissolved in 150 mL dichloromethane (DCM). 3-chloroperoxybenzoic acid (20.7 g, 0.113 mol) dissolved in 200 mL DCM was added slowly into 1-allylbenzene/DCM or vinylcyclohexane/DCM solution under vigorous stirring at 0 ^oC within 20 min. The reaction system was then heated to 20 ^oC and stirred for 12 h. After the reaction, the resultant viscous solution was filtered with reduced pressure and the solution was neutralized by 400 mL sodium hydrogen carbonate solution (10.0 g, 0.119 mol). The organic layer was separated and washed with massive deionized water for 3 times. The organic layer

was then dried over anhydrous magnesium sulfate for 24 h and filtered. DCM was removed by rotary evaporator below 40 ^{o}C. Epoxides **K** or **I** were then obtained after drying process.

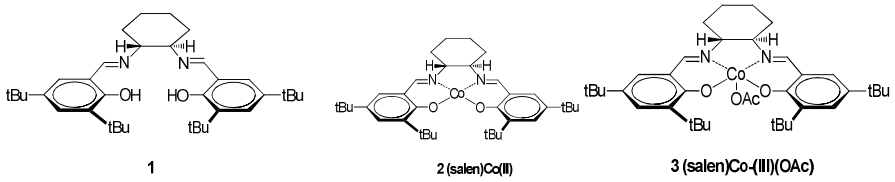
Nanolamellar Zn-Co (III) DMCC catalysts preparation

The catalyst used in this work was the same catalyst used our recent work (R.-J. Wei, X.-H. Zhang, B.-Y. Du, X.-K. Sun, Z.-Q. Fan and G.-R. Qi, Macromolecules, 2013, 46, 3693-3697). An amount of $ZnCl_2$ (8.0 g) was dissolved in the solution of de-ionized water (10 mL) and *tert*-BuOH (10 mL). $K_3Co(CN)_6$ (6.6 g) in 10 mL deionized water was added dropwise into $ZnCl_2$ solution over 30 min at room temperature under vigorous stirring. Then the precipitation reaction was heated to 75 °C and stirred for 3 h. The resulting white precipitate was separated by pressure filtration and reslurried in a mixture of *tert*-BuOH and water (v/v=1/1) with vigorous stirring over 2 h. Once again the precipitation was isolated and reslurried in a mixture of alcohol and water. With increasing proportion of alcohol over water, the precipitate was washed several times to remove potassium ion. Finally the deposition was reslurried in neat *tert*-BuOH to remove water, and separated and dried at 70 °C under vacuum to a constant weight. The elemental analysis result of the catalyst: Co: 12.48; Zn: 27.29; N: 16.57; C: 23.34; H: 2.273; Cl: 9.50. BET surface area of the catalyst is 653 m^2/g. The SEM images of this catalyst could be found in our previous work (R.-J. Wei, X.-H. Zhang, B.-Y. Du, X.-K. Sun, Z.-Q. Fan and G.-R. Qi, Macromolecules, 2013, 46, 3693-3697).

Representative copolymerization of epoxide and CO_2

A 10 mL autoclave combined with a small magnetic stirrer was dried at 120 °C for 3 h, and cooled to room temperature in desiccators. 10 mg of Zn-Co (III) DMCC catalyst and 3 mL epoxide were transferred into the autoclave. The reactor was then heated to the desired temperature and pressured to a desired pressure. The reaction was performed at the desired temperature and pressure for the whole reaction time with vigorous stirring of 1000 *rpm*. After the copolymerization, the autoclave was cooled with ice-water bath (0 ^{o}C) and the pressure was slowly vented. A small amount of crude product was promptly removed for ^{1}H NMR spectroscopy and gel permeation chromatography (GPC) analysis. The products were dissolved with DCM and precipitated from excess methanol. The products were separated and dried at 60 ^{o}C under vacuum to a constant weight.

Synthesis of (salen)Co-(III)(OAc)



Preparation of **2** (salen)Co(II) (Y. Eddie and K. Ernest, *Journal of the Chemical Society, Dalton Transactions*, 1996, 1229-1236):

To **1** (6 g, 11.01 mmol) in toluene (50 mL) was added dropwise $Co(OAc)_2$ (3.64 g, 11.01 mmol) in aqueous ethanol (100 mL) in an oil-bath at 75 °C. The pink solution turned brown and a copious amount of precipitate was formed. The solid was collected, washed with ethanol and recrystallized from $CHC1_3$-hexane to give red crystals (R,R)-2.

Preparation of **3** (salen)Co(III) OAc (M. Tokunaga, J. F. Larrow, F. Kakiuchi and E. N. Jacobsen, *Science*, 1997, **277**, 936-938.):

A mixture of (R,R)-2 (0.910 g, 1.5 mmol), toluene (10 mL), and acetic acid (0.17 mL, 3.0 mmol, 2 equiv to the catalyst) was stirred for 1 hour at room temperature. The solvent was removed by rotary evaporation, and the brown residue was dried under vacuum.

Representative Procedure for the Hydrolytic Kinetic Resolution of Terminal Epoxides (H).

A 25 mL Schlenk flask was charged with **3** (salen)Co-(III) (OAc) (41.34 mg, 0.062 mmol), 2-*tert*-butyloxirane **H** (3.8 mL, 31.19 mmol) was then added in one portion. The stirred mixture was cooled in an ice-water bath. Water (0.31 mL, 17.16 mmol, 0.55 equiv) was slowly added. The reaction was stirred in an ice-water bath for 15 d. ^{1}H NMR spectrum of the crude product showed no occurrence of the hydrolytic resolution reaction.

Characterization

^{1}H NMR and ^{13}C NMR spectra of the products were obtained on a Bruker Advance DMX 500 MHz and 125-MHz spectrometer using TMS as internal reference, respectively. Number-average molecular weight (M_n) and polydispersity (PDI) were determined using a PL-GPC 220

chromatograph (Polymer Laboratories Ltd.) equipped with an HP 1100 pump from Agilent Technologies. GPC columns were eluted with tetrahydrofuran at 1.0 mL/min at 40 ^{o}C. The sample concentration was approximately 0.3 wt% and the injection volume was 50 μL. Calibration was performed using monodispersed polystyrene standards covering the molecular weight ranging from 580 to 460000 Da. Differential scanning calorimetry (DSC) was taken on a DSCQ200. About 5.0 mg of samples were placed in aluminum pans. The heating rates were 10 ^{o}C /min under N_2 atmosphere.

Figures

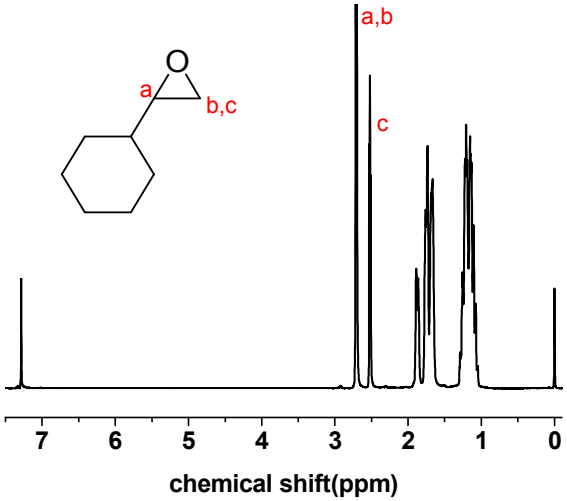


Figure S1. ^{1}H NMR spectrum of the epoxide **I**.

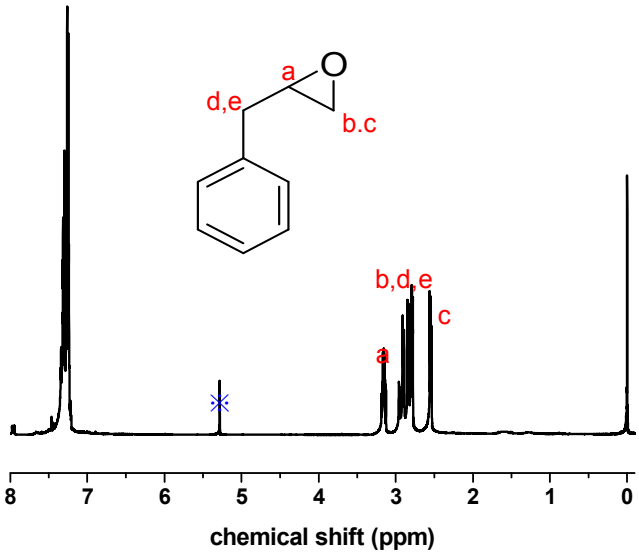


Figure S2. ^{1}H NMR spectrum of the epoxide **K**.

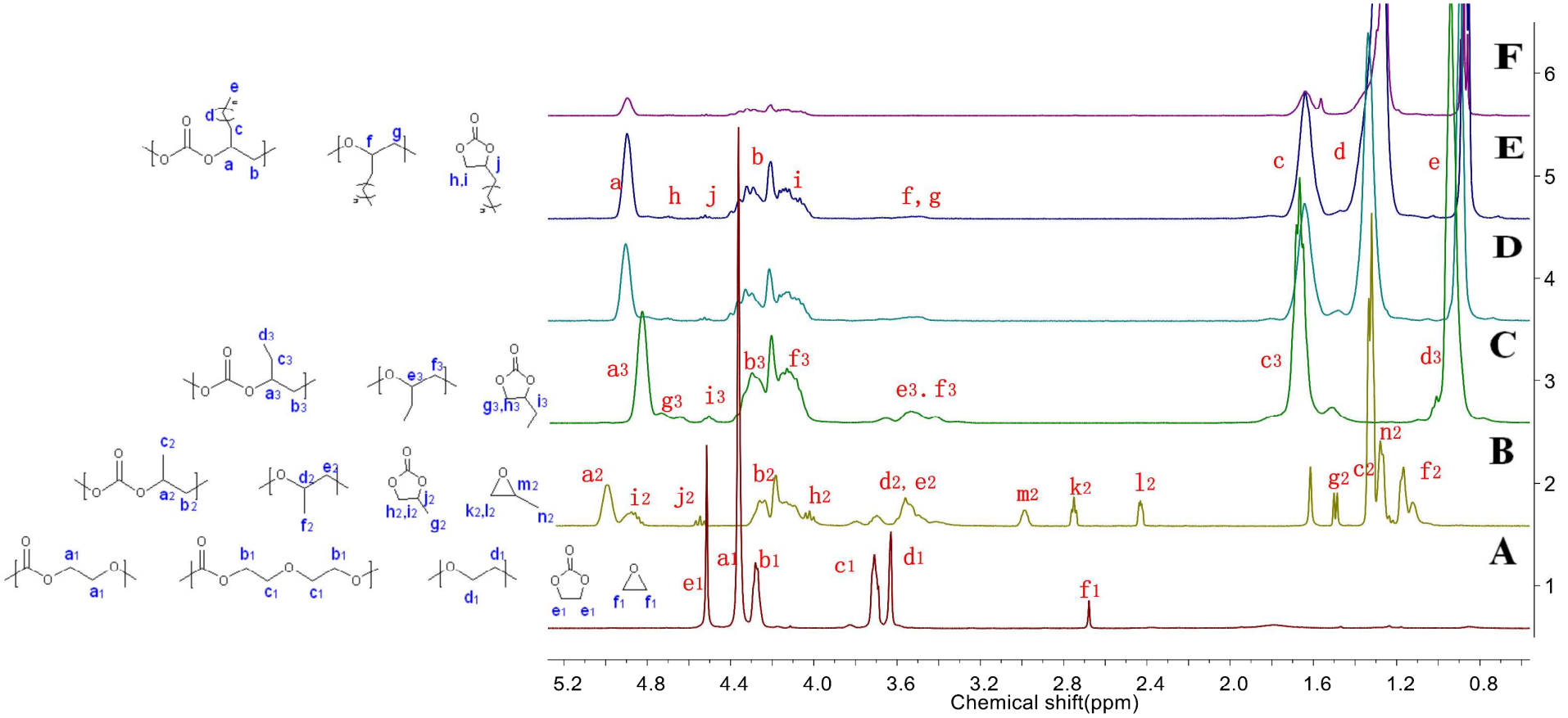


Figure S3. ^{1}H NMR spectra of the crude CO_2-based copolymers from **A, B, C, D, E, F** (curves 1-6).

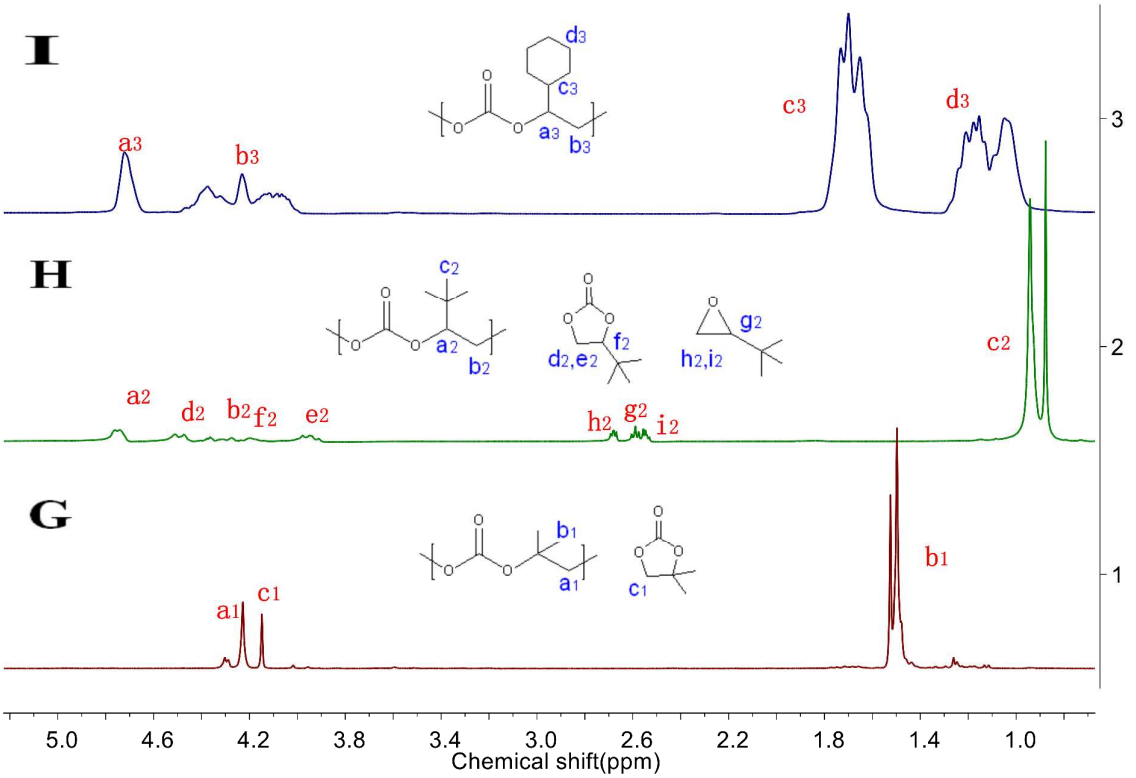


Figure S4. ^{1}H NMR spectra of the crude CO_2-based copolymers from **G, H, I** (curves 1-3).

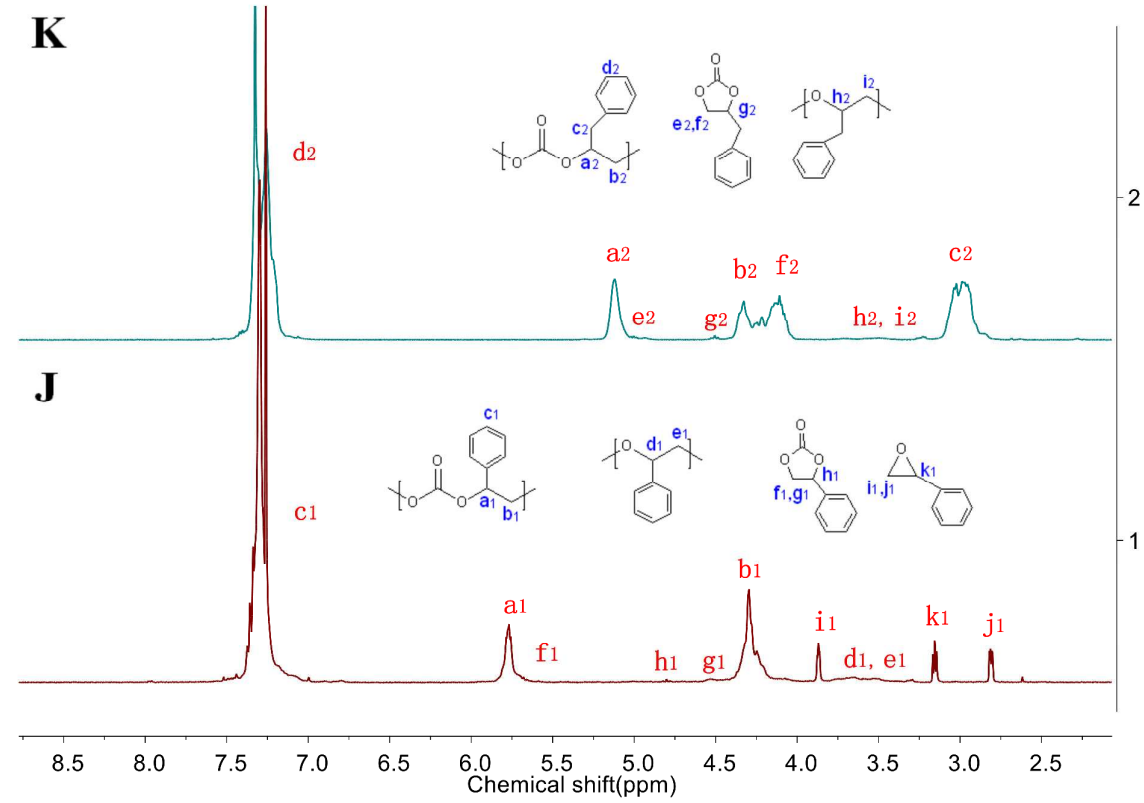


Figure S5. ^{1}H NMR spectra of the crude CO_2-based copolymers from **J** and **K** (curves 1-2).

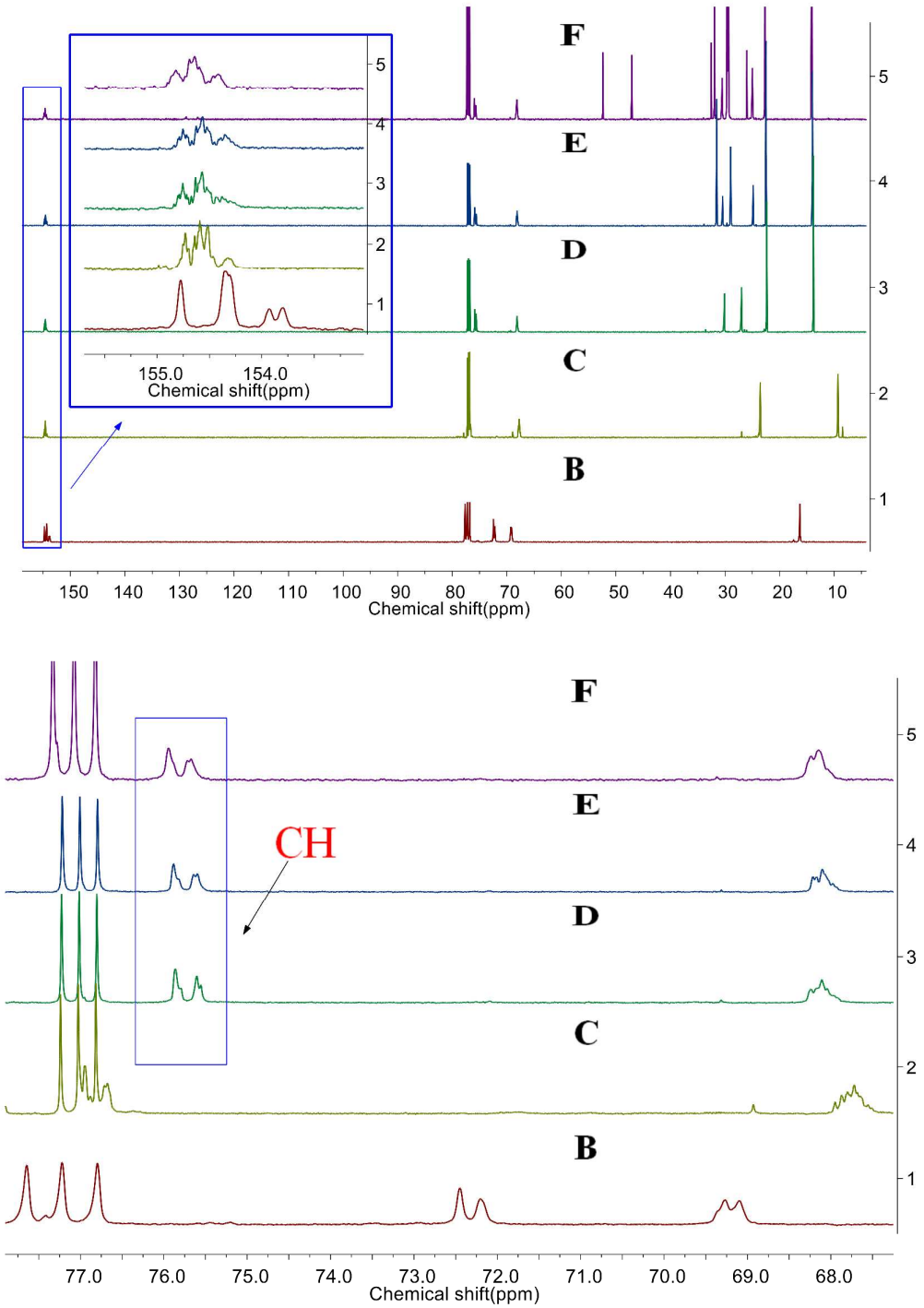


Figure S6. ^{13}C NMR spectra of the copolymers from CO_2 and epoxides of **B, C, D, E, F**(curves 1-5). (**B, C** were provided here for comparing the ^{13}C NMR with **D, E** and **F**).

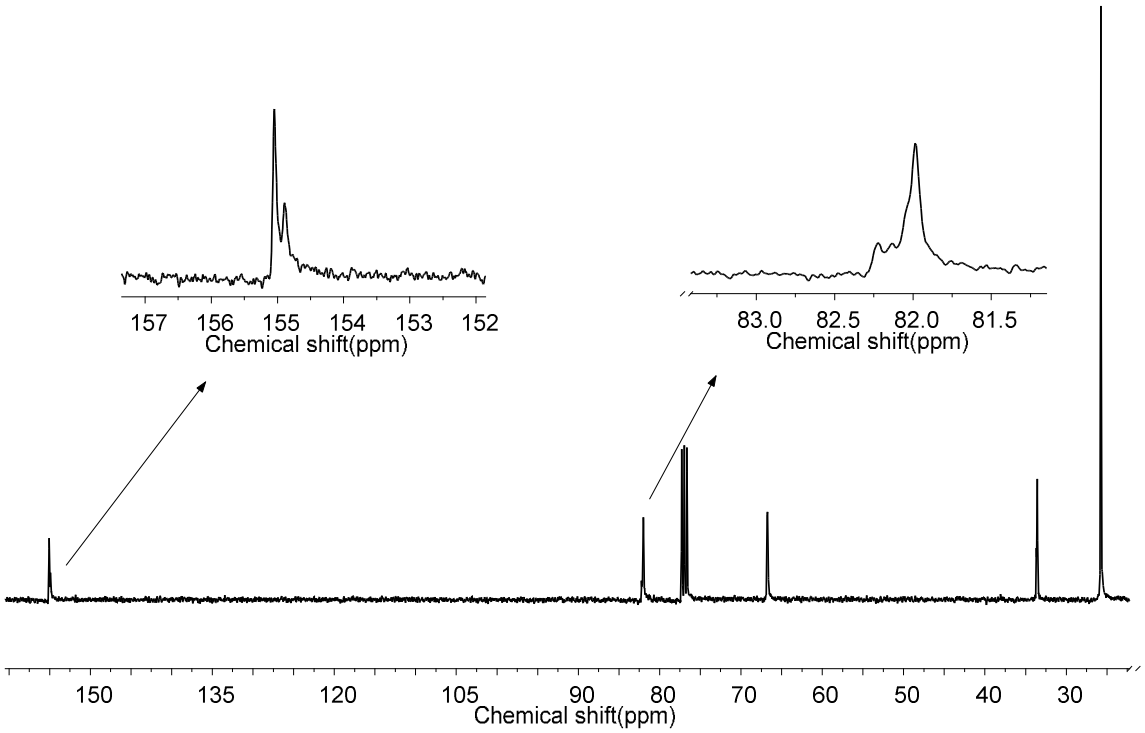


Figure S7. ^{13}C NMR spectra of the copolymers from CO_2 and **H**.

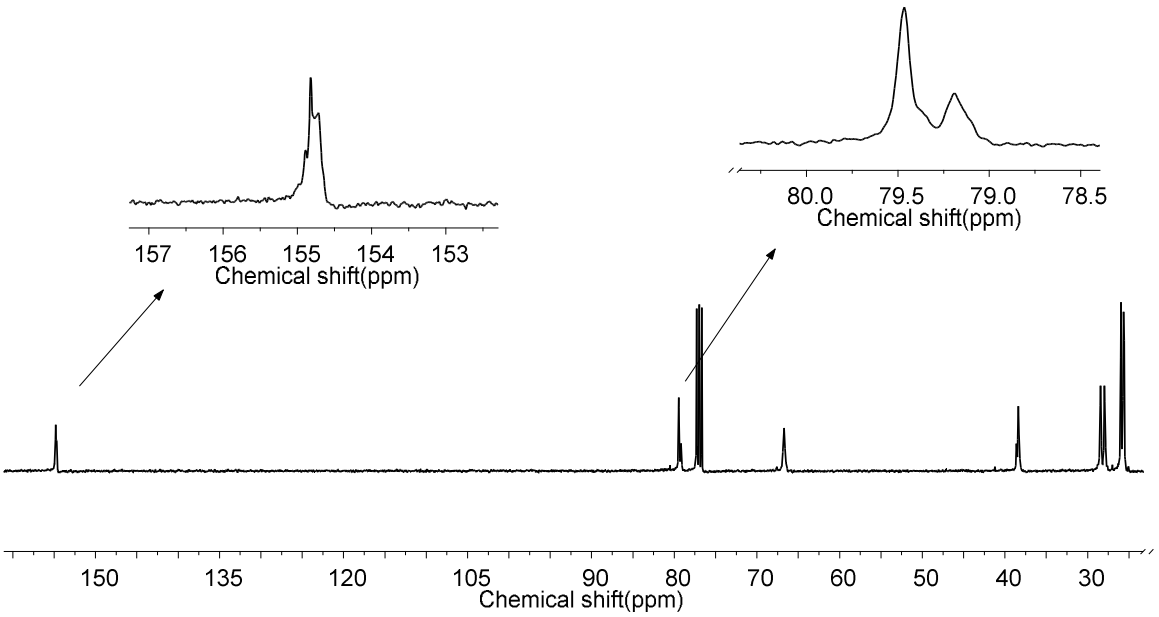


Figure S8. ^{13}C NMR spectra of the copolymers from CO_2 and epoxide **I**.