SUPPORTING INFORMATION

One-Pot Synthesis and Postpolymerization Functionalization of Cyclic Carbonate/Epoxide-Difunctional Polycarbonates Prepared by Regioselective Diepoxide/CO2 Copolymerization

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1. General Materials.

Unless otherwise special, all reagents were purchased from commercial suppliers and used without further purification. All manipulations involving air- and/or water-sensitive compounds were carried out with the standard Schlenk and vacuum line techniques under argon atmosphere. 4-vinyl-1-cyclohexene diepoxide (VCHDEP) was was stirred over powered CaH_2 at room temperature over 48 h and vacuum-distilled before use. Bis(triphenylphosphine) iminium chloride($[PPN]^+$=$[Ph_3P\text{-}N{=}PPh_3]^+$) (PPNCl) (Acros) was dissolved dissolved in acetone, precipitated by an excess amount of ether, and then the precipitate was dried under vacuum. SalenCrCl (salen-H_2=*N, N*-bis(3,5-*di-tert*-butylsalicylidene)-1,2-cyclohexanediamine) was purchased from Acros and used directly. 4-dimethylaminopyridine (DMAP) was recrystallized from toluene and dried before use. (ONSO)CrCl complexes were synthesized as described in our previous work.[1] Carbon dioxide (99. 995% purity) was used without further purification.

2. *Characterization*

^1H and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer at frequencies of 400 MHz (^1H) and 100 MHz (^{13}C), respectively. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^1H NMR and against the solvent. Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} (16 scans collected). The glass transition temperature (T_g) of copolymers were determined at a heating rate of 10 ^oC/min on Perkin-Elmer Diamond Differential Scanning Calorimetry instrument. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT/Q 600 at a scanning speed of 10 °C/min (from room temperature to 400 °C) under a nitrogen atmosphere with a purge rate of 80 mL/min. Molecular weight of polymer was determined by using gel permeation chromatography (GPC) on a PL-GPC 220 instrument with a refractive index detector, calibrated with polystyrene standards. The columns used was MIXED-B 300×7.5mm columns held at 40 °C, using THF as eluent at a flow rate of 1.0 mL/min.

General Copolymerization of VCHDEP and CO_2. The copolymerizations were carried out in a 100 mL stainless-steel autoclave equipped with a magnetic stirrer. Desired amounts of (ONSO)CrCl/PPNCl or salenCrCl/DMAP (1:5 molar ratio) were transferred into the dried autoclave and dried at 60 ^oC for 2 h

under vacuum. The autoclave was heated to the target temperature in a pre-heated oil bath, filled with CO_2 to a set pressure and was kept stirring for the desired time. After the reaction, the unreacted CO_2 was slowly released. Then the methanol was added. The solid was filtered and washed with hot methanol three times. The whole methanol solution were collected. The isolated solid was dried at 45 ^oC in vacuum. The dried copolymer was subjected to NMR analysis. The pendant cyclic carbonate (CC) and epoxide (EP) functional groups along the polycarbonate chain were calculated according to ^1H NMR data The fotmula is as follows: $CC/EP=[1-(7A_{2.59\text{-}2.81}/3A_{1.00\text{-}2.25})]/[7A_{2.59\text{-}2.81}/3A_{1.00\text{-}2.25}]$.

In addition, the whole collected-methanol solution was condensed under vaccum to remove the methanol. The residual solution was subjected to the ^1H NMR for the determination of percentage of cyclic carbonate A and B and unreacted diepoxide. According to the the percentage and mass of residual solution, the mass and TOF of the cyclic carbonate A and B were estimated.

Hydrolysis of side epoxides functional group on the copolymer. [2] Coploymer (CC/EP =50/50, M_n=4, 300 g mol^{-1}, MWD=6.48) (1.24 g) was dissolved in 8.0 mL DMSO and 1.5 mL HCl aq (1mol/L) was added, and the mixture was stirred for 9 h at 25 ^oC. After the reaction, the mixture was poured into a saturated aqueous solution of $NaHCO_3$ (100 mL) and the precipitate was washed with water three times and then deeped in 100 mL methanol for 6 h. The precipitate was collected by filtration and dried at 60 ^oC under reduced pressure.

Aminolysis of the polymer obtained by the hydrolysis of copolymer.[2] The polymer obtained by the aforementioned hydrolysis (0.63 g) was dissolved in DMSO (6.0 mL) and *n*-propylamine (0.80g, 15 mmol) was added. The mixture was stirred for 24 h at 70 ^oC. After the reaction, the mixture was poured into 50 ml diethyl ether. The precipitate was collected by filtration and washed with water. The isolated solid was dried at 70 ^oC under reduced pressure.

Azidolysis and aminolysis of the polymer by sodium azide and *n*-propylamine. The azidolysis the copolymer was accoring to the slightly modified procedure.[3] 0.62 g copolymer (CC/EP =50/50, M_n=4,300 g mol^{-1}, MWD=6.48) was dissolved in 15 mL of dried DMF. Sodium azide (0.29 g, 4.5 mmol) and

ammonium chloride (0.24 g, 4.5 mmol) were added to the solution, and the mixture was stirred at 50 ^{o}C for 24 h.

The above mixture was filtrated and the solution was added *n*-propylamine (0.80g, 15 mmol). After stirred at 70 ^{o}C for 24 h, the solution was poured into 100 mL diethyl ether. The precipitate was filtrated, washed with water, and dried at 70 ^{o}C under vacuum.

References

1. B. Han, L. Zhang, S. J. Kyran, B. Y.Liu, and D. J. Darensbourg, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, DOI:10.1002/pola.28052.

2. B. Ochiai, Y. Hatano, and T. Endo, *Macromolecules* 2008, **41**, 9937-9939

3. C. Z. Zhao, D. X. Wu, X. M. Lian, Y. Zhang, X. H. Song, and H. Y. Zhao, *J. Phys. Chem. B*, 2010, **114**, 6300–6308

Entry	Cross-linked	$CHCl_3$	DMSO	DMF	THF	Acetone	toluene	CH_3OH	Diethyl Ether
1	×	√	√	√	√	√	×	×	×
2	×	√	√	√	√	√	×	×	×
3	×	√	√	√	√	√	×	×	×
4	×	√	√	√	√	√	×	×	×
5	×	√	√	√	√	√	×	×	×
6	√	×	×	×	×	×	×	×	×
7	×	√	√	√	√	√	×	×	×
8	√	×	×	×	×	×	×	×	×
9	×	√	√	√	√	√	×	×	×
10	×	√	√	√	√	√	×	×	×

Table S1 Solubility of copolymers
Conditions: 5 mg copolymer, 2 mL solvent, 25°C. "×" insoluble, "√"soluble. The order of Entry is corresponidng to number in the Table 1.

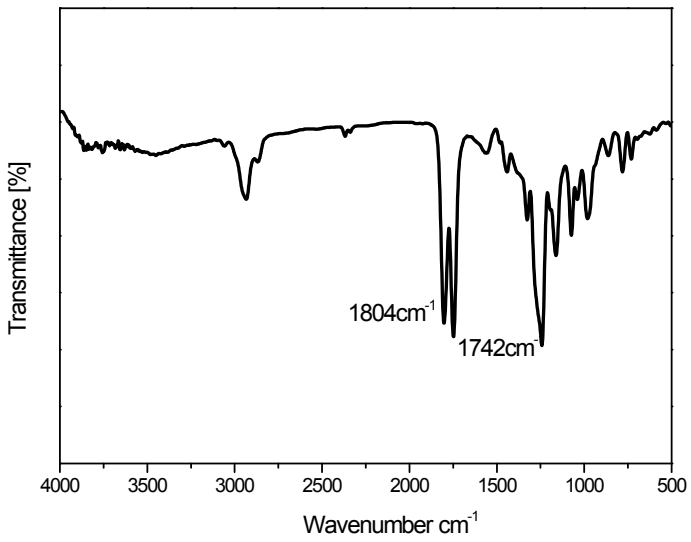
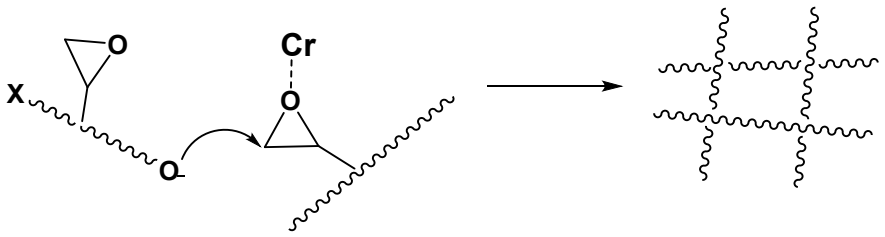


Fig. S1. IR spectrum of cross-linked copolymer obtained from SalenCrCl/DMAP (1:5) binary catalyst



Scheme S1 The possible formation of cross-linked copolymer process in the copolymerization of VCHEP and CO_2

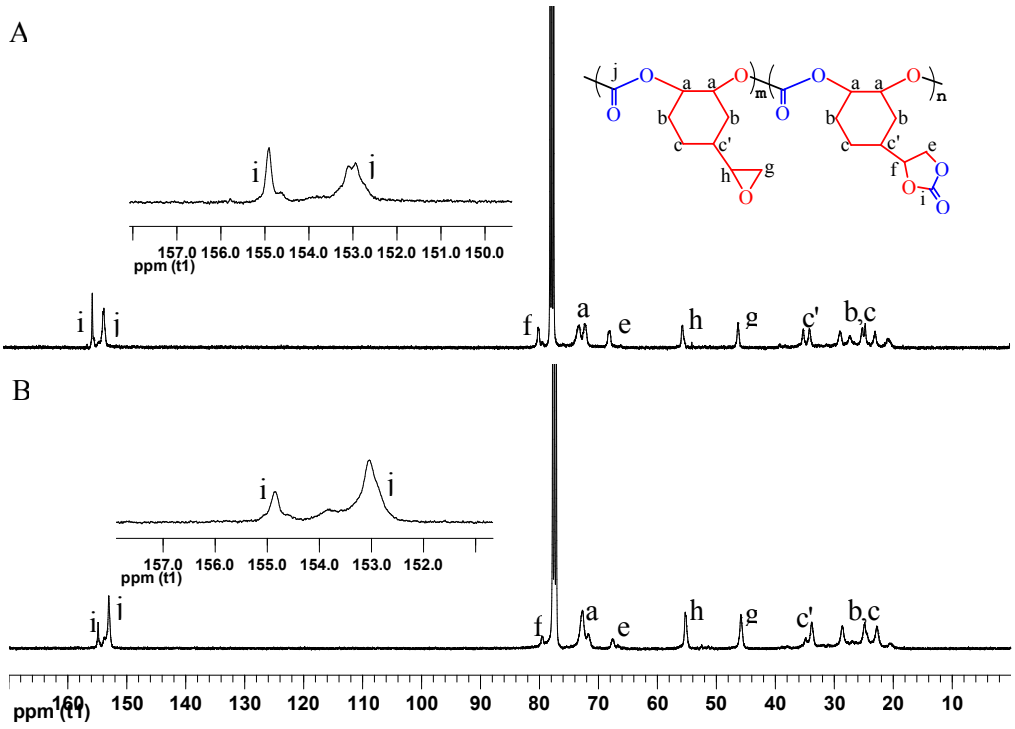


Fig. S2 ^{13}C NMR of copolymer of 4-vinyl-1-cyclohexene diepoxide and CO_2 (A: Entry 9 in Table 1; B: Entry 2 in Table 1)

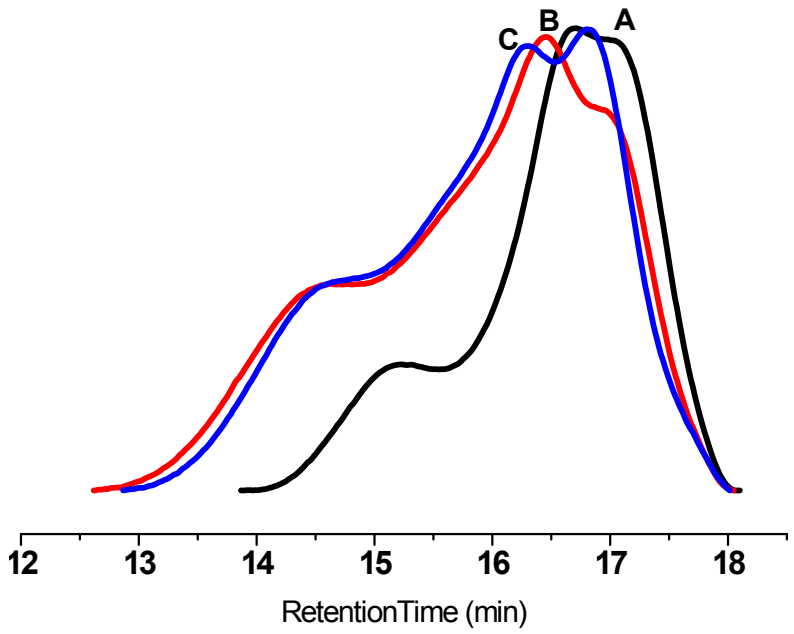


Fig. S3 GPC curves of polycarbonate of entry 1 (A), entry 2 (B), and entry 3 (C) in Table 1

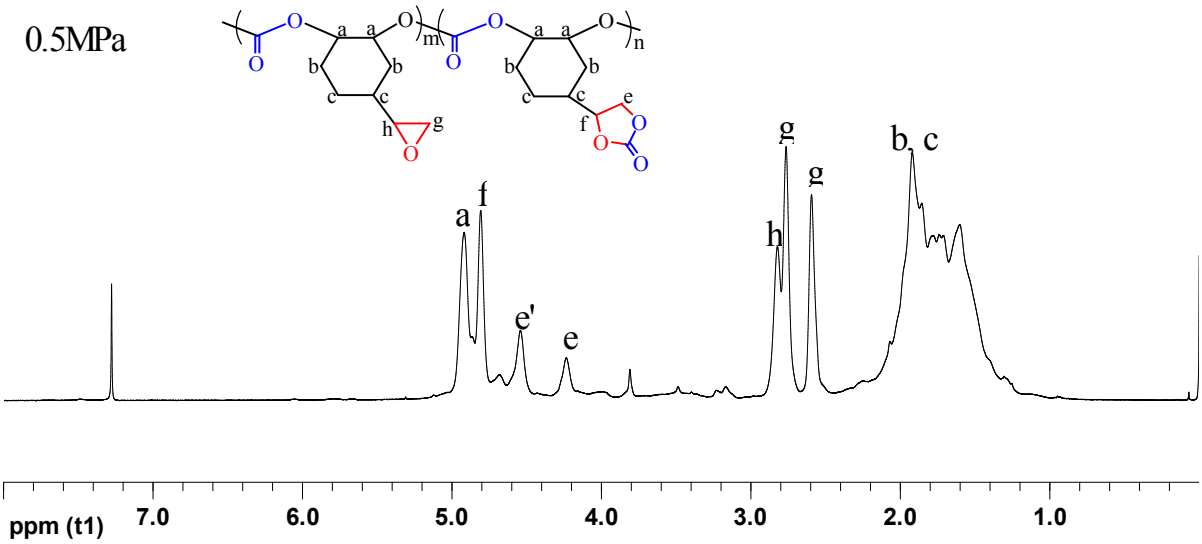


Fig. S4 ^{1}H NMR spectrum of the cyclic carbonate- and epoxide-difunctionalized polycarbonate obtained at 0.5 MPa (Entry 1, Table 1)

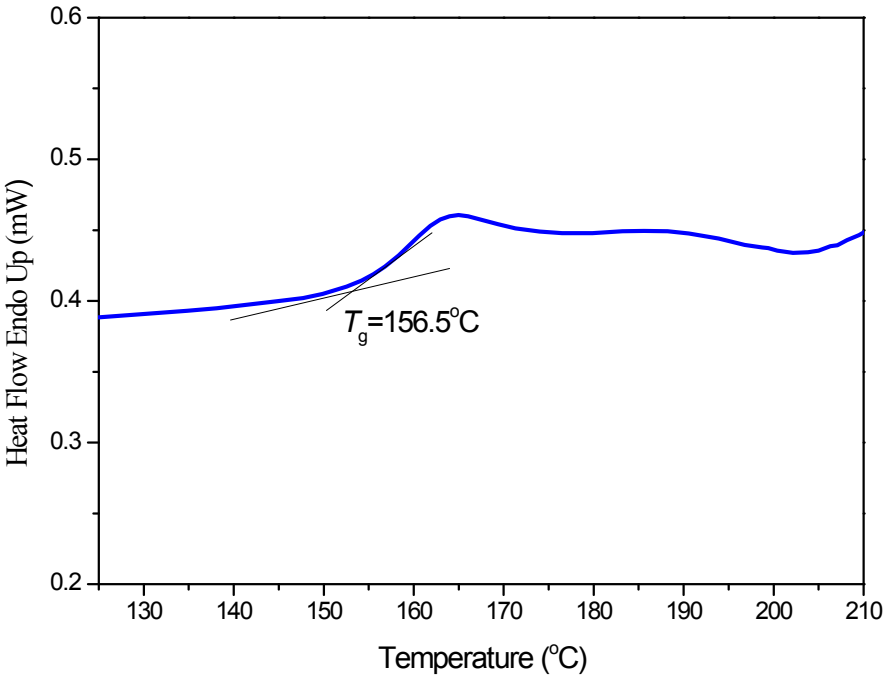


Fig. S5 The DSC curve for sample of entry 9 in Table 1 (heating rate 10°C/min)

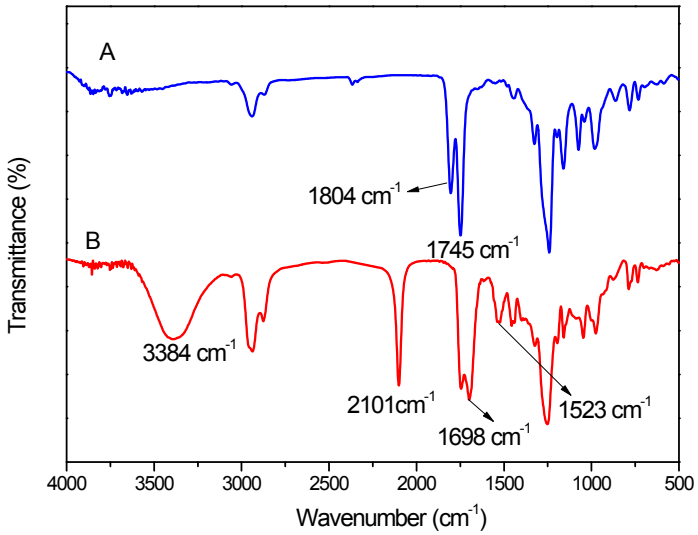


Fig. S6 IR spectra of original functional APCs precursor of entry 9 in Table 1 (A) and modified by sodium azide and *n*-propylene amine (B).

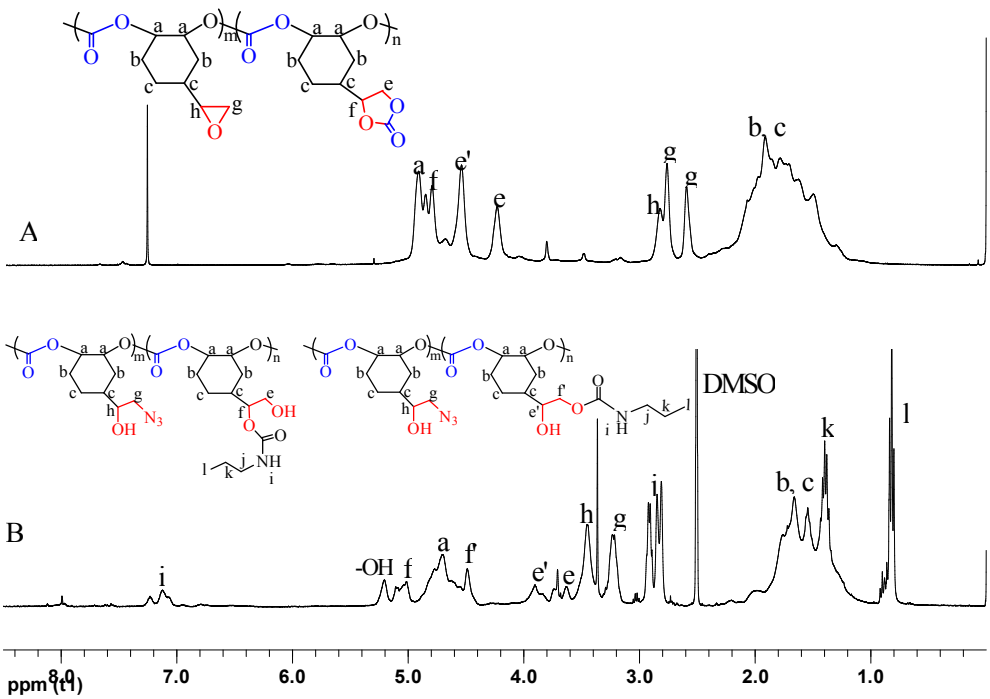


Fig. S7 ^{1}H NMR spectra of original functional APC precursor of entry 9 in Table 1 (A) and modified by sodium azide and then *n*-propylene amine (B).