

Supporting Information

High Elastic and Degradable Thermoset Elastomers from CO₂-Based Polycarbonates and Bioderived Polyesters

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Materials

All experiments that sensitive to air- and/or water were performed in a glovebox or with the standard Schlenk techniques under N₂. 4-Vinyl-cyclohexene 1, 2-epoxide (VCHO, 98%, TCI), Cyclohexene oxide (CHO, 98%, Energy Chemical) were distilled over CaH₂ prior to use. Dry carbon dioxide was purchased from Hangzhou Jingong Gases, which was supplied in a high-pressure cylinder and equipped with a liquid dip tube. β -di-iminate zinc (II) acetate catalyst [(bdi)Zn(OAc)] and γ -methyl- ϵ -caprolactone (MCL) were prepared according to literature procedures^{1, 2}. MCL was used after purified by distillation over CaH₂ under reduced pressure. Toluene was distilled from sodium/benzophenone under N₂. β -Mercaptoethanol (98%, TCI), stannous octoate (95%, Energy Chemical), 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO, 98%, Energy Chemical), 4,4'-Diphenylmethane Diisocyanate (MDI) (98%, Energy Chemical), ditin butyl dilaurate (98%, Energy Chemical) and other reagents were used as received.

Characterization Methods

¹H NMR spectra. Spectra were recorded on a Bruker Avance III 400 MHz type spectrometer from CDCl₃ solutions under room temperature. Chemical shifts are referenced to an internal standard (TMS) shifts at 0 ppm.

Gel Permeation Chromatography (GPC). GPC data was obtained at 35 °C using a system equipped with a Waters Chromatography, Inc. model 1515 isocratic pump, a model 2414 differential refractometer, and a three-column set of Polymer Laboratories, Inc. Styragel columns (PLgel 5 μm Mixed C, 500 Å, and 104Å, 300×7.5 mm columns). The mobile phase was THF (1.00 mL/min flow rate). The molar mass reported were determined using polystyrene standards.

Differential Scanning Calorimetry (DSC). A NETZSCH DSC 214 Polyma instrument (NETZSCH, Germany) was used to determine thermal transitions. The glass transition temperatures (T_g) values were obtained from the second heating run, using a heating rate of 10 K min⁻¹.

Thermogravimetric Analysis (TGA). TGA measurements were performed on a TA-Q500 analyzer. Samples of about 5 mg were heated from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

Fourier transform infrared (FTIR). FT-IR spectroscopy were performed in the solid state using a Bruker Tensor E spectrometer equipped with a DTGS detector in the transmission mode at a resolution of 4 cm⁻¹. And the spectra were collected with 32 scans.

Swell tests. Gel fraction of the elastomers was determined by extractions of soluble (sol) fractions using DCM. A small amount of each cross-linked elastomer (ca. 50-100 mg) was immersed in DCM for 48 h. Then the solvent was removed and the swollen elastomer was dried in a vacuum oven at 50 °C for 48 h before the final mass was measured. The gel fraction was calculated by taking the ratio of the final mass to

the initial mass.

Mechanical Tensile Property Tests. Prior to mechanical test, the elastomers films were cut as dog-bone shaped specimens [ca. 1 mm (T) × 2.5 mm (W) × 30 mm (L)]. Tensile tests were carried on a testing machine (CMT 4204, Shenzhen SANS Test Machine Co. Ltd., China) at a test speed of 50 mm/min at 25 °C. Three replicates for each sample were performed to determine the mechanical properties. For cyclic tests, all samples were extended up to strains of 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500% at a constant strain rate of 50 mm·min⁻¹. No delay between two cycles.

Synthetic Methods

Terpolymerization of CO₂, CHO and VCHO. [(bdi)Zn(OAc)] (41.6 mg, 0.086 mmol, 1 equiv) , CHO(4 g, 41 mmol, 475 equiv), VCHO(0.267 g, 2.15 mmol, 25 equiv) were added into a 50 mL predried autoclave (Anhui Kemi Machinery Technology Co., Ltd., China). Then the system was pressurized CO₂ with a pressure of 2.0 MPa. After the reaction at 50 °C for 24 h, the CO₂ pressure was released. The crude polymer was dissolved in CHCl₂ and precipitated into methanol. White polymer was obtained by vacuum-drying. Conversion: 71 %, yield: 4.1 g, 67 %.

Synthesis of (PCHC-co-PVCHC)-OH by thiol-ene click reaction. PCHC-co-PVCHC (3.0 g, 1.22 mmol C=C), β-Mercaptoethanol (1.9 g, 24.4 mmol, 20 equiv) and TPO (41.8 mg, 0.12 mmol, 0.1 equiv) were dissolved in 50 mL THF in a 100 mL round bottle flask under N₂. The solution was kept under UV (365 nm, 15 Watt) irradiation for 6 hours. Then the solution was concentrated and precipitated in methanol for several times to totally removed β-Mercaptoethanol. Conversion: 100 %, yield: 2.8 g, 90 %.

Synthesis of graft block copolymers by “grafting from” method. The grafting-from strategy was employed to synthesize graft block copolymers via ROP of MCL using (PCHC-co-PVCHC)-OH as

macroinitiator. For instance, MCL (2.4 g, 18.75 mmol), (PCHC-*co*-PVCHC)-OH (0.6 g, 0.07 mmol), and Sn(Oct)₂ (15 mg, 0.038 mmol) were added to a dry pressure flask under a nitrogen atmosphere in a glovebox. The vessel was sealed, taken out of the glovebox, and heated under 130 °C for 1.5 h. After that, the vessel was cooled and the mixtures were dissolved in dichloromethane, precipitated into methanol (×3) and dried under vacuum for 2 days. Conversion: 70 %, yield: 1.95 g, 65%.

Post-polymerization of (PCHC-*co*-PVCHC)-*g*-PMCL. MDI was used to post-polymerize (PCHC-*co*-PVCHC)-*g*-PMCL for crosslinking. Take **CO₂E-2** for example, (PCHC-*co*-PVCHC)-*g*-PMCL (3g, 0.35 mmol hydroxyl groups, 1 equiv) and MDI (43.8 mg, 0.5 equiv) were dissolved in CH₂Cl₂, followed by the addition of the catalyst ditin butyl dilaurate (0.2 wt%). Then the solution was transferred into a Teflon mold. After 24 h at room temperature, the elastomers were obtained after the removal of solvents under vacuum dry at 60 °C for 2 h.

Calculation of parameters of polymers. Molar percentage of VCHO incorporated in PCHC-*co*-PVCHC was calculated by PVCHC mol % = $I_c / (I_{a,b} / 2)$, where the I_c and $I_{a,b}$ stand for integrals, corresponding to peaks c and a&b in Fig1a. The molar percentage of VCHO incorporated was calculated to be 6 %.

The mass ratio of PCHC-*co*-PVCHC/PMCL were determined using ¹H NMR spectroscopy by integration of peaks at 4.56-4.87 ppm (peaks a&b) and 4.04-4.17 ppm (peak h) in Fig1c, where the wt % PMCL = $(M_{MCL} \times I_h) / [(M_{PCHC} \times 94 \% + M_{PVCHC} \times 6 \%) \times I_{a,b}]$; M_{MCL} , M_{PCHC} , and M_{PVCHC} refers to the molar mass of MCL, chain unit of PCHC, and chain unit of PVCHC, respectively; I_h and $I_{a,b}$ stand for integrations of peak h and a&b, respectively.

The theory molecular weights of (PCHC-*co*-PVCHC)-*g*-PMCL were acquired by using $M_{n,theory} = (DP_n \text{ of the side chain}) \times M_{MCL} \times \text{number of hydroxyl groups in (PCHC-}co\text{-PVCHC)-OH} + M_{n,PCHC-co-PVCHC}$, where the DP_n of the side chain was calculated by the ratio of the integration area of the methylene protons (f) at 2.71 ppm to the methylene protons (h) at 4.10 ppm in Fig. 1c, $M_{n,MCL}$ refers to the molar mass of MCL, and the number of hydroxyl groups in (PCHC-*co*-PVCHC)-OH were calculated by molar percentage of VCHO to the DP_n of the PCHC-*co*-PVCHC.

Reactivity ratios of copolymerization

Terpolymerization of CO₂, CHO and VCHO was performed at 50 °C with various monomer feed compositions (<10 % conversion). The reactivity ratios can be obtained by using Eq. 1 (the Fineman-Ross method),³ for which the reactivity ratio of VCHO (r_{VCHO}) is the negative value of the slope and reactivity ratio of CHO (r_{CHO}) is the intercept.

$$(f-1)/F = -r_{VCHO} \times f/F^2 + r_{CHO} \quad (1)$$

The values of various parameters for calculating reactivity ratios of VCHO and CHO are summarized in Table S1. Figure S1 shows the plot of $(f-1)/F$ versus f/F^2 . From data fitting by the least-squares regression, the obtained reactivity ratios of CHO (r_{CHO}) and VCHO (r_{VCHO}) are 0.66 and 1.42, respectively.

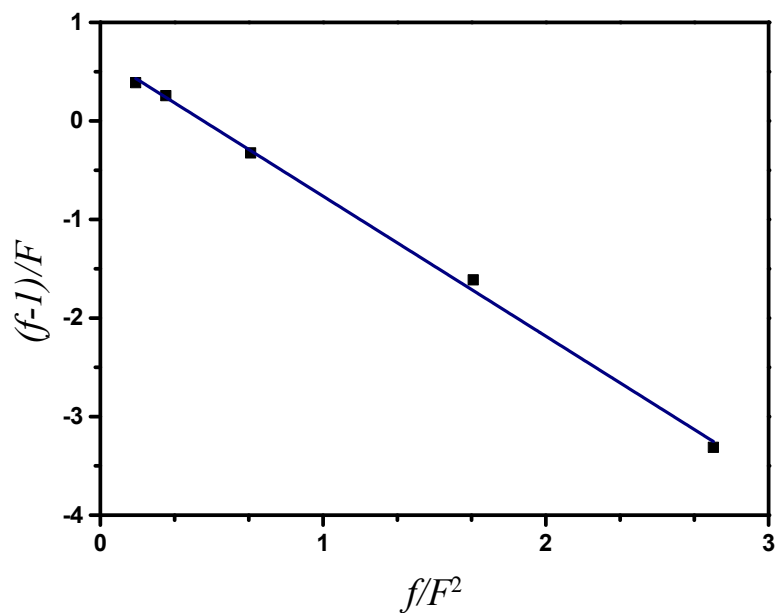


Fig.S1 Fineman-Ross plot for the terpolymerization of CHO/VCHO/CO₂.

Table.S1 Various Parameters for Calculating Reactivity Ratios of CHO and VCHO.

Feed ratio(CHO/VCHO)	$f(\text{CHO/VCHO})$ in polymer	$F(\text{CHO/VCHO})$ in feed	f/F^2	$(f-1)/F$
8:2	2.55	4	0.159	0.388
7:3	1.6	2.333	0.294	0.257
5:5	0.675	1	0.675	-0.325
3:7	0.308	0.429	1.674	-1.613
2:8	0.172	0.25	2.752	-3.312

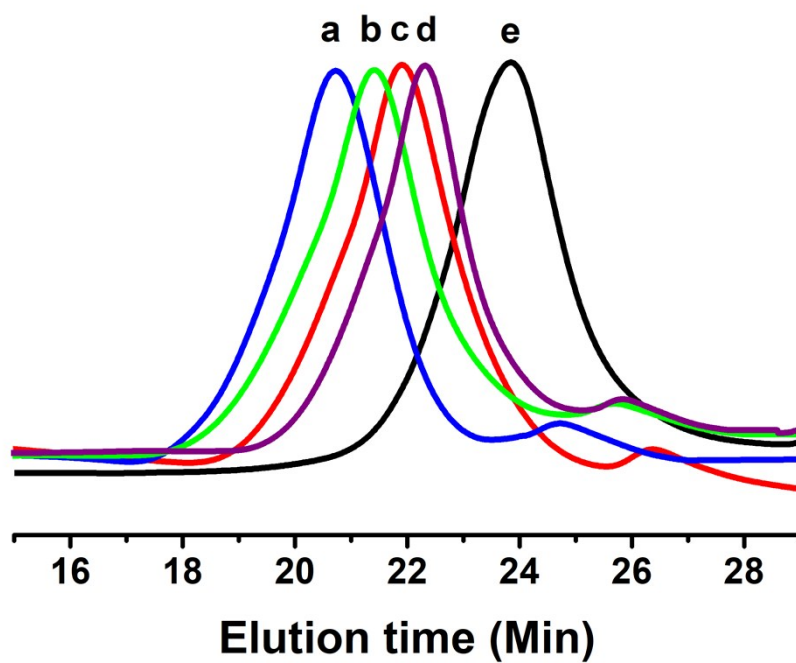


Fig.S2 GPC traces for, (a) (PCHC-*co*-PVCHC)-*g*-PMCL (PCHC-*co*-PVCHC/PMCL = 19/81 in mass ratio.), (b) (PCHC-*co*-PVCHC)-*g*-PMCL (PCHC-*co*-PVCHC/PMCL = 29/71 in mass ratio.), (c) (PCHC-*co*-PVCHC)-*g*-PMCL (PCHC-*co*-PVCHC/PMCL = 40/60 in mass ratio), (d) (PCHC-*co*-PVCHC)-*g*-PMCL (PCHC-*co*-PVCHC/PMCL = 48/52 in mass ratio) and (e) PCHC-*co*-PVCHC.

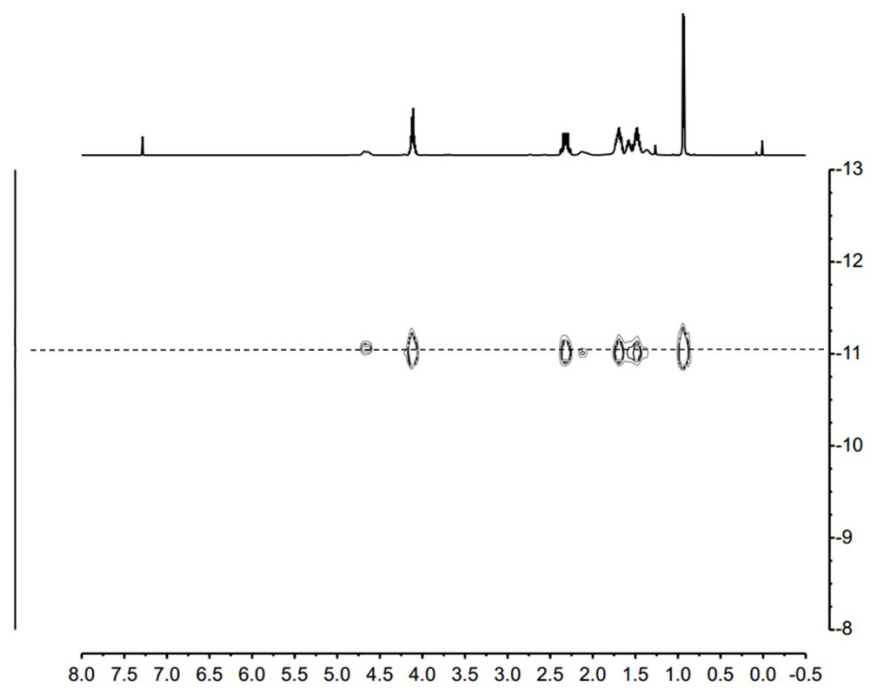


Fig.S3 ¹H DOSY NMR spectrum of (PCHC-*co*-PVCHC)-*g*-PMCL.

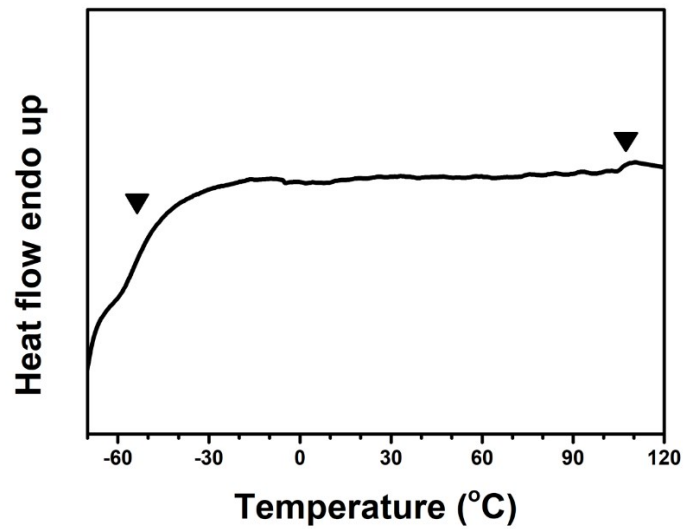


Fig.S4 Representative DSC heating curves of CO₂Es (CO₂E-2), two T_g s (-48 °C and 107°C) were clearly detected. Glass transition temperature were obtained from the second heating scan and the heating rate was 10 °C/min.

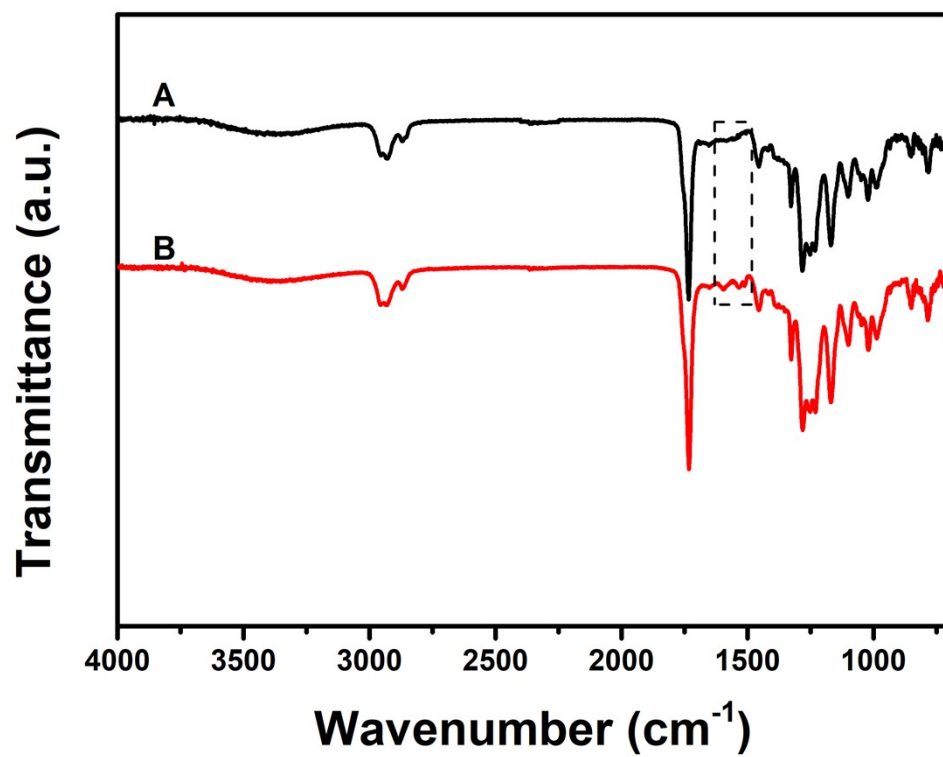


Fig.S5 IR spectra of CO₂E-3 before (A) and after (B) crosslinking.

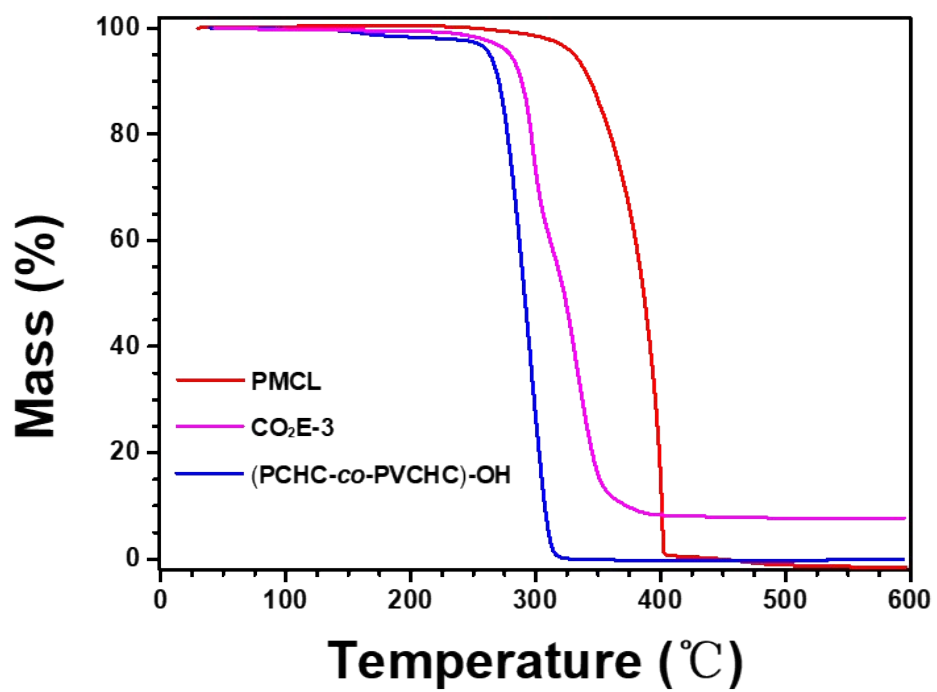


Fig.S6 TGA curves for PMCL, CO₂E-3, (PCHC-co-PVCHC)-OH, at a heating rate of 10 °C/min under a nitrogen atmosphere.

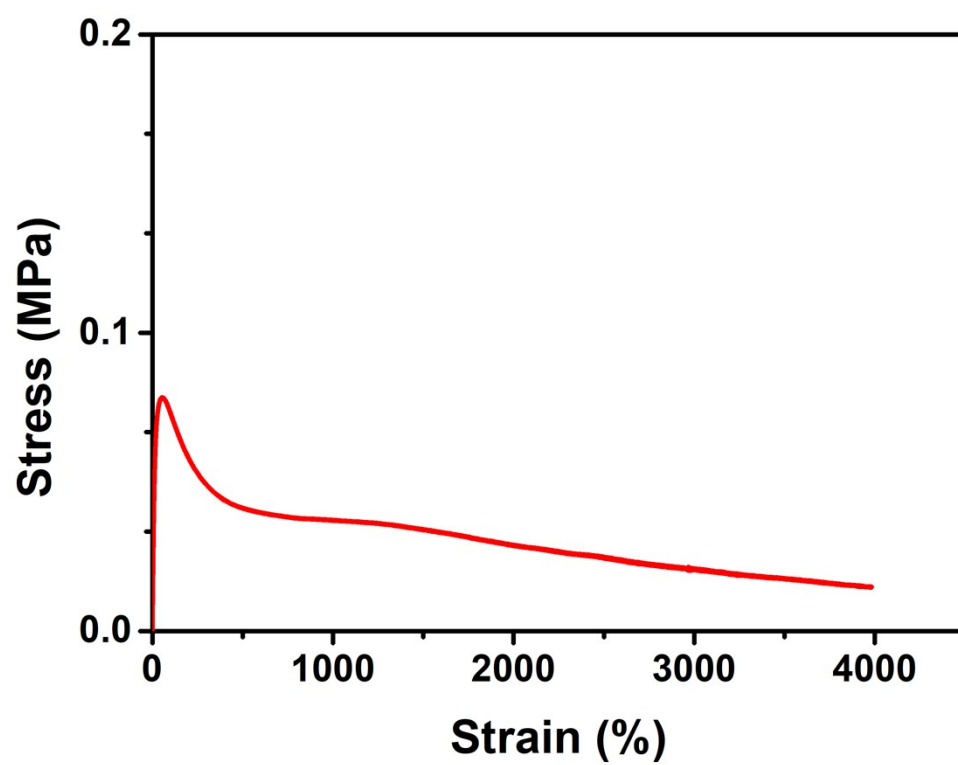


Fig.S7 Tensile test of un-crosslinked prepolymer for CO₂E-3 (PCHC-*co*-PVCHC/ PMCL = 40/60 in mass ratio).

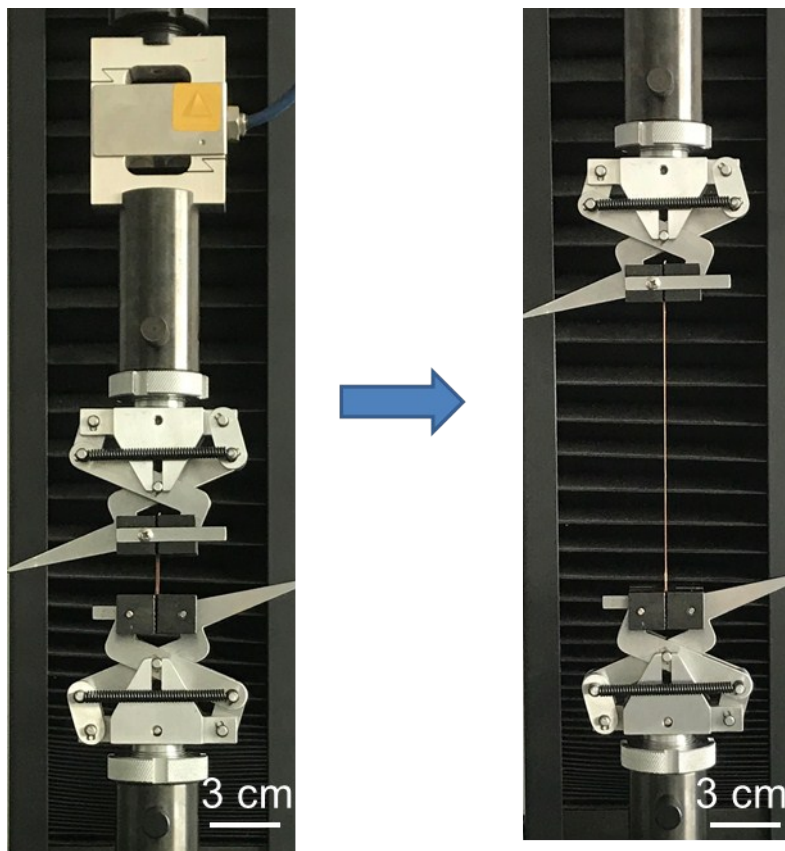


Fig.S8 Photographs showing tensile test of a specimen of elastomers at 50 mm min^{-1} .

The change of entropy between relaxed and stretched state is the driving force for elastic recovery of the CO₂Es. When CO₂Es stretching under an external force, the entropy of the elastomers decreases, the system stores energy. After removal of the external force, the stretched CO₂Es recoil to their relaxed state, and the energy can be released.

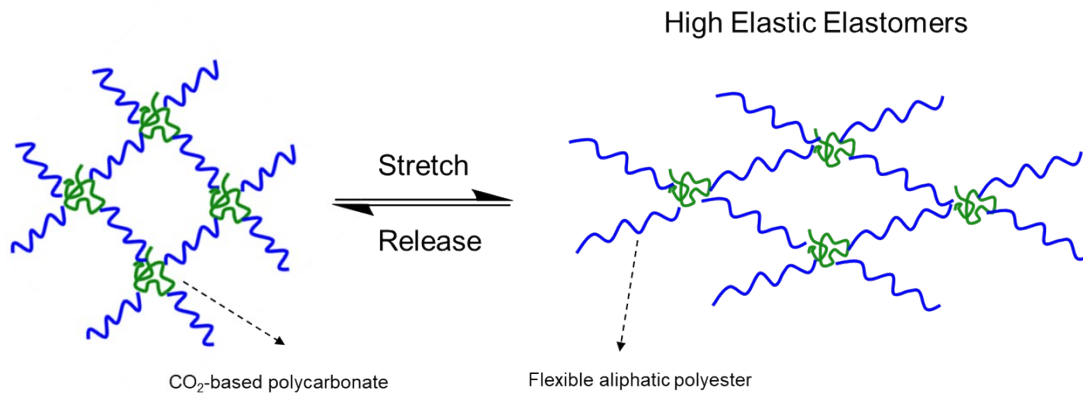


Fig.S9 Proposed micro structure model for the CO₂Es at the stretched and relaxed state

References

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- (2) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky and G. W. Coates, *Journal of the American Chemical Society*, 2001, **123**, 8738-8749.
- (3) Fineman, M.; Ross, S. D. *J. Polym. Sci.*, 1950, 5, 259.