

Random terpolymer of CO₂, 1,3-butadiene and epoxides: synthesis, topology, fluorescence and degradability

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Abstract

The utilization of carbon dioxide (CO₂) as a feedstock is consistently attractive, especially in the preparation of sustainable polymeric materials. Here, a terpolymer of CO₂, 1,3-butadiene (BD) and epoxides is synthesized via an intermediate named α -ethylidene- δ -vinyl- δ -valerolactone (EVL). The terpolymer with number-average molecular weight (M_n) up to 7.8 kg/mol and dispersity (\mathcal{D}) of 2.4 is obtained from cationic ring-opening copolymerization of EVL with cyclohexene oxide (CHO). The reactivity ratios of EVL and CHO are determined as 0.01 and 1.07, respectively, suggesting random characteristic of the terpolymer. The preserved C=C double bonds from BD allow further topology alternation of the terpolymer by photoinitiated crosslinking. The yielded networks are fluorescent and degradable. This method offers enhanced versatility to the synthesis and additional functionalization of CO₂-based polymers.

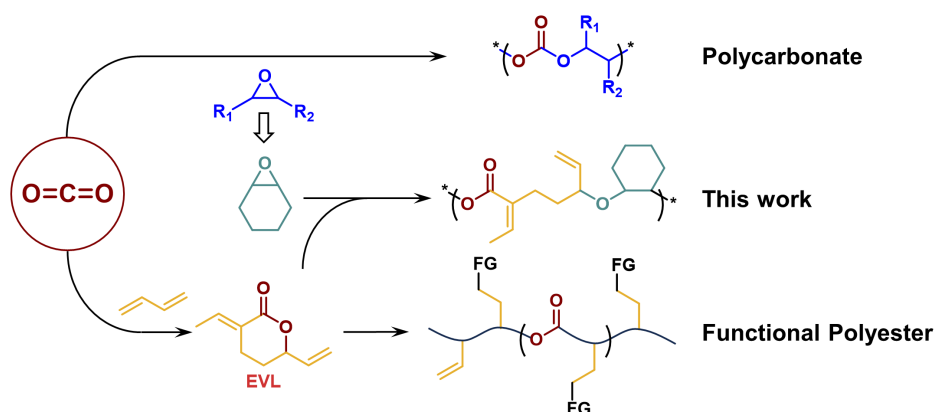
Introduction

Carbon dioxide (CO₂), the main culprit of the greenhouse effect, is also an abundant and renewable C1 resource. Accordingly, it has been of great value to utilize CO₂ in the synthesis of sustainable polymers.^[1-4] However, the inherent inertness of CO₂ makes the incorporation of CO₂ into polymers quite challenging, leading to limited choices in this field. The mainstream method is the copolymerization of CO₂ with epoxides that produces polycarbonate, which has been extensively studied.^[5-10]

Another effective method is the copolymerization of CO₂ with olefins via a promising intermediate, α -ethylidene- δ -vinyl- δ -valerolactone (EVL, Scheme 1).^[11-16] The di-substituted lactone obtained from the telomerization of CO₂ with 1,3-butadiene (BD) contains two C=C double bonds derived from BD and serves as a monomer in the synthesis of several functional polymers. Various ester-functionalized polyolefins are prepared by radical and coordinate (co)polymerizations on the C=C double bonds.^[17-23] On the other hand, the C=C double bonds remain in the polyesters prepared by ring-opening polymerization (ROP) so that functional polyesters were accessible via post-polymerization modifications.^[24-29] Our group grafted polysarcosine onto poly(EVL-co- β -butyrolactone) backbone by thiol-ene click reaction to produce amphiphilic polymers.^[24] Tonks and co-workers introduced

quaternary amine side chains to provide polyesters, which is generated from the ROP of hydrogenated EVL derivatives, with antimicrobial properties.^[27] Polyesters with same structure was also synthesized by Lin and co-workers and functionalized by 4-(trifluoromethyl)thiophenyl to offer fluorescent polyesters.^[29]

In this work, a novel functional terpolymer is synthesized from CO₂, BD and epoxides using EVL as an intermediate. With a number-average molecular weight (M_n) of 7.8 kg/mol and a dispersity (D) of 2.4, the resulted terpolymer bears all the double bonds derived from BD, enabling post-polymerization modification and functionalization. Cross-linked terpolymer is transformed from the linear one via photoinitiated radical reaction on the preserved C=C double bonds. The obtained terpolymer networks that exhibit fluorescence with maximum emission wavelength of 444 nm are alcoholically degraded.



Scheme 1. Overview of two mentioned methods to produce CO₂-based polymers and the synthesis of terpolymer of CO₂, BD and epoxides reported in this work. FG: functional groups.

Experimental Section

Materials

EVL was synthesized according to the literature,^[30] purified by column chromatography and then distilled twice under reduced pressure over calcium hydride. CHO from J&K Scientific Co., Ltd. and propylene oxide (PO) from Sinopharm Chemical Reagent were distilled over calcium hydride. Sc(OTf)₃ was synthesized according to the literature and dried in vacuum (<0.5 mmHg) at 200 °C for 48 hours.^[31] Benzophenone was purchased from Aladdin. All other chemicals were purchased from Sinopharm Chemical Reagent and used as received.

Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DMX 400 spectrometer, a Bruker Avance DMX 500 spectrometer and an Agilent DD2-600 One spectrometer and were referenced versus solvent shifts (CDCl₃, $\delta = 7.26$ ppm in ¹H NMR and $\delta = 77.16$ ppm in ¹³C NMR). Correlation spectroscopy (COSY), heteronuclear single-quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) technique were used to assist in the assignment of ¹H and ¹³C NMR spectra. Diffusion-ordered spectroscopy (DOSY) was recorded on a 500 MHz Bruker Avance DMX 500

spectrometer. The number-average molecular weights (M_n s) and the dispersities (D_s) of the polymers were determined by size exclusion chromatography (SEC) using a Waters-1515 apparatus equipped with Waters Styragel HR3, HR4 and HR5 columns and a Water 2414 refractive index detector. THF was used as eluent with a flow rate of 1.0 ml/min at 40 °C, and commercial polystyrene samples were used as calibration standards. Matrix assisted laser desorption ionization-time of flight mass spectra (MALDI-TOF MS) were recorded on a Bruker rapiflex MALDI Tissue typer in reflector mode. 2,5-Dihydroxybenzoic acid (DHB) and CF_3COOK were used as the matrices and the cationic agent, respectively. Differential scanning calorimetry (DSC) analyses were performed on a TA Q200 instrument. Samples were scanned in the temperature range from -80 to 130 °C at a heating rate of 20 °C/min under nitrogen flow and data were collected from the second heated run to erase the thermal history. UV irradiation experiments were carried out through a Hamamatsu LC-8 light source equipped with a mercury xenon lamp of 2 kW. Fluorescence spectra were recorded on a PTI QM-40 spectrofluorometer with excitation wavelength of 350 nm. Network films directly used for fluorescence measurement.

Typical procedure for terpolymerization of CO_2 , BD and CHO via EVL as an intermediate

All polymerizations were conducted using standard Schlenk techniques under argon atmosphere in a flame-dried ampoule. In a typical polymerization procedure, $\text{Sc}(\text{OTf})_3$ (0.0047 g, 0.0095 mmol) was added into a 10 mL ampoule under dry argon and dissolved in EVL (0.163 g, 1.09 mmol) added with a dry syringe. Then CHO (0.0975 g, 0.993 mmol) was added into the ampoule using a dry syringe to start the polymerization. The mixture was heated and stirred at 40 °C for 30 min. The mixture was dissolved in CDCl_3 and a small portion was removed for ^1H NMR analysis to calculate the monomer conversions. The polymerization was terminated by the addition of ether with trace amount of water and then dried with a rotary evaporator. The quenched mixture was dissolved in CHCl_3 and precipitated in n-hexane at -20 °C. The dissolution and precipitation were repeated three times and the obtained PCBE was dried under vacuum.

Kinetic study for terpolymerization of CO_2 , BD and CHO via EVL

$\text{Sc}(\text{OTf})_3$ (0.0787 g, 0.160 mmol) was dissolved in EVL (2.43 g, 16.0 mmol) in a 10 mL ampoule under dry argon. The mixture was then evenly divided into 16 ampoules and CHO (1.57 g, 16.0 mmol) was evenly added to these ampoules with a dry syringe. The mixture in each ampoule was heated and stirred at 40 °C. After a predetermined time, the ampoule was opened and 0.6 mL CDCl_3 was added for ^1H NMR analysis to calculate the monomer conversions.

Photoinitiated crosslinking of PCBE

The following is a typical procedure. The copolymer (0.200 g, Entry 20 in Table 1, containing 0.65 mmol EVL units) and the photoinitiator benzophenone (0.006 g, 0.033 mmol) was dissolved in dioxane or DMF. The mixture was spread out on a teflon plate and exposed to UV light for 1 h. The obtained

product was immersed in THF overnight for three times and dried under vacuum.

Photoinitiated crosslinking through one-pot method

Sc(OTf)₃ (0.021 g, 0.043 mmol) and benzophenone (0.012 g, 0.066 mmol) were dissolved in EVL (0.640 g, 4.21 mmol) in a flamed dried 10 mL Schlenk tube under dry argon. CHO (0.471 g, 4.79 mmol) was then added with a dry syringe to start the polymerization. The mixture was heated and stirred at 40 °C under UV irradiation for 1 h. Then the Schlenk tube was opened and CHCl₃ was added to dissolve residual monomer and copolymer. The obtained crosslinked product was immersed in CHCl₃ overnight for three times and dried under vacuum.

Results and discussion

The ROP of EVL is fraught with difficulties due to the conjugated tiglate ester, the sterically hindered allylic ester linkages and the low ring-strain of the six-membered ring.^[32] EVL could not homopolymerize in the presence of Sc(OTf)₃ (Entry 1, Table 1), showing its inertness in polymerization. Epoxides such as CHO and PO are generally suitable for cationic ROP with high ring-strain and sufficient reactivity to propel the polymerization.^[33,34]

The ROP of EVL with PO is successful catalyzed by Sc(OTf)₃ (Entry 2-5, Table 1). The ¹H nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC) results of the obtained terpolymer of poly(CO₂-butadiene-epoxide) (PCBE) are shown in Figure S1 and S2. However, even after 24 h of reaction, the product mixture with low viscosity was obtained. Despite the high monomer conversions, the low yields after precipitation and low molecular weights of PCBE suggest that the products are mostly oligomers. In comparison, CHO is a better comonomer and mainly used in the following studies due to its potential to prepare polymers with high molecular weights.

After the introduction of CHO, high-viscous products are obtained in merely 30 min (Entry 9, Table 1). The conversions of EVL and CHO reach 39% and 67%, respectively, and the EVL content in the terpolymer is 41 mol% according to the ¹H NMR spectrum (Figure S3). The isolated terpolymer has a number-average molecular weight (*M_n*) of 6.5 kg/mol with a dispersity (*D*) of 2.2. Its SEC curve shows a symmetrically single peak, indicating that the terpolymer has a single sort of propagation species (Figure S4). The effects of reaction conditions are studied and the results are presented in Table 1. The increase of temperature significantly accelerates the polymerization and increases the conversions of the two monomers and the *M_n*s of the products (Entry 7-10, Table 1). Nevertheless, when the temperature reaches 50 °C, the *M_n* no longer increases and the distribution widens due to more frequent chain transfer reaction. The content of EVL in the products increases with the initial feed ratio of EVL (Entry 11-15, Table 1). More Sc(OTf)₃ catalyst accelerates the polymerization and results in a lower *M_n* and a broader *D* (Entry 16, Table 1). When the catalyst concentration is low (Entry 17-19, Table 1), no obvious difference is observed in *M_n* or *D*, suggesting that the transfer reactions are unavoidable and thus lead to a non-linear relationship between feed ratio of [monomers]/[Sc(OTf)₃] and *M_n*. For the effect of the polymerization time (Entry 20-24, Table 1), the *M_n* of the terpolymer reaches 3.5 kg/mol within 5 min. The subsequent propagation gets slower and the *M_n* barely increases after 30 min while the dispersity becomes broad.

Table 1. Terpolymerization of CO₂, BD and epoxides via EVL as an intermediate.^a

Entry	[Sc(OTf) ₃] ₀ / [EVL] ₀ /[CHO] ₀	Temp. (°C)	Time (min)	Yield (%) ^b	Conv. (%) ^c		Content of EVL (%) ^c	M _n (kg/mol) ^d	D ^d
					EVL	CHO			
1	1:100:0	40	120	0	0	-	-	-	-
2 ^e	1:40:60	40	1440	40	88	>99	36	2.6	1.8
3 ^e	1:50:50	40	1440	35	77	>99	44	2.3	1.7
4 ^e	1:60:40	40	1440	35	63	>99	49	2.2	1.8
5 ^e	1:70:30	40	1440	25	50	>99	54	2.4	1.6
6	1:0:100	40	30	70	-	70	-	18.7	2.8
7	1:100:100	20	30	20	21	37	35	4.2	2.0
8	1:100:100	30	30	37	32	60	35	5.4	2.0
9	1:100:100	40	30	45	39	67	41	6.5	2.2
10	1:100:100	50	30	61	56	89	43	6.6	2.7
11	1:60:140	40	30	40	32	51	16	5.0	2.4
12	1:80:120	40	30	42	37	54	32	6.6	2.1
13	1:120:80	40	30	49	39	75	41	5.3	2.4
14	1:140:60	40	30	48	45	91	49	4.7	2.3
15	1:160:40	40	30	31	38	90	57	2.4	2.0
16	1:50:50	40	30	49	56	88	38	3.7	3.4
17	1:150:150	40	30	40	34	55	38	7.2	2.6
18	1:200:200	40	30	36	29	46	40	7.8	2.4
19	1:300:300	40	30	37	29	44	38	7.5	2.5
20	1:100:100	40	5	27	21	42	36	3.5	1.9
21	1:100:100	40	10	32	27	49	36	3.8	2.2
22	1:100:100	40	20	41	36	61	37	4.5	2.5
23	1:100:100	40	40	49	52	84	39	5.4	2.6
24	1:100:100	40	60	66	56	87	39	5.1	3.0

^a Polymerizations were conducted in bulk. ^b Determined by weight. ^c Determined by ¹H NMR of the product mixture (Figure S3). ^d Determined by SEC. ^e PO was used as the comonomer.

The obtained terpolymer PCBE is characterized in detail by NMR spectra. The ¹H NMR spectrum is shown in Figure 1A. The proton signals of the unsaturated C=C double bonds (H_h, δ = 6.87 ppm, H_f, δ = 5.58-5.92 ppm, H_g, δ = 5.53 and 5.05-5.24 ppm) on EVL units keeps 1:3 proportions (H_h :H_f + H_g) the same as those in EVL monomer, indicating that the two double bonds do not participate in polymerization and are preserved. Through the analysis of NMR spectra (¹H, ¹³C, ¹H-¹H COSY, HSQC and HMBC, Figure S5-S9), the methine protons (H_j, δ = 4.84 ppm) on CHO units attached to the ester group as well as the methine protons (H_e, δ = 3.75-4.14 ppm) on EVL units attached to the ether group are clearly identified, demonstrating the occurrence of ring-opening copolymerization. Furthermore, the signal at 4.55 ppm (H_e) is identified as the methine protons on EVL units adjacent to the ester group, which suggests the existence of EVL-EVL dyads in the copolymer. The typical signals of the methine protons of CHO-CHO dyads are observed at 2.98-3.63 ppm (H_k and H_{k'}).^[33-35] The integral ratios of H_j and H_{k, k'} is 1:3, indicating a 1:1 ratio of CHO-EVL dyads to CHO-CHO dyads. The DOSY NMR spectrum (Figure S10) proves all repeating units in the terpolymer backbone by the identical diffusion coefficient of all EVL and CHO protons.

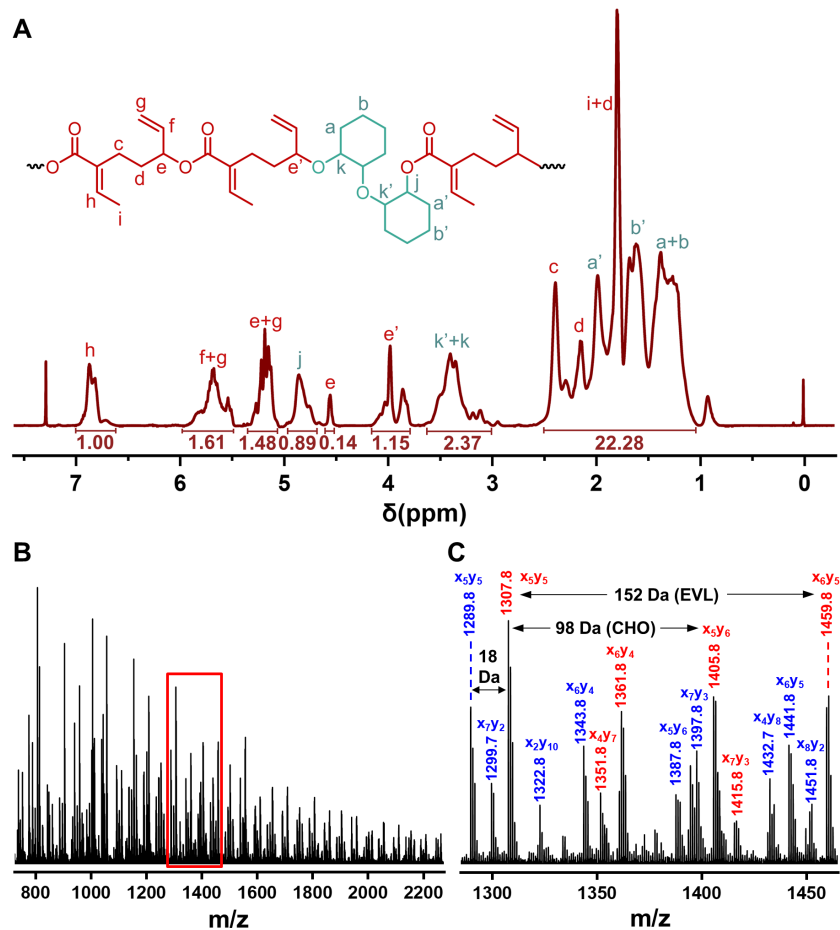


Figure 1. Chemical structure and ^1H NMR spectrum of the terpolymer PCBE (Entry 21, Table 1) (A). MALDI-TOF MS spectrum of PCBE (Entry 11, Table 1) (B). Zoom-in view of the MALDI-TOF MS spectrum (C).

The MALDI-TOF MS results are shown in Figure 1B and 1C. Both mass intervals of EVL (152 Da) and CHO (98 Da) are clearly observed. The masses of the populations are represented as the sum of x of EVL units, y of CHO units, counter-ion K^+ (39 Da) with different end groups terminated by water (red, 18 Da) or transfer reaction (blue, 0 Da). The major populations correspond to the chains terminated by transfer reactions. According to the Figure 1C, polymers with x greater than $y + 1$ prove the existence of EVL-EVL dyads even if both end groups of the polymer are EVL unit, which is consistent with the NMR analysis.

To better understand the mechanism, the polymerization kinetics has been investigated. The time-dependent conversions of EVL and CHO are shown in Figure 2A. At the beginning of polymerization, the reaction rate is so fast that the conversions of EVL and CHO reach 21 % and 42 %, respectively, within only 5 min (Entry 20, Table 1), indicating that both monomers have high reactivities. The consumption rate of CHO is about twice that of EVL, resulting in a nearly 1:1 ratio of CHO content to BD content in the terpolymer during the polymerization (Figure 2A). Based on Fineman-Ross equation (Figure S11), the reactivity ratios (r) of EVL and CHO at 40 °C are determined as 0.01 and 1.07 (Figure 2B), respectively, indicating a random copolymerization. The extremely low r_{EVL} is responsible for the difficulty of its homopolymerization, while r_{CHO} of 1.07 leads to the very close probabilities of its

copolymerization and homopolymerization, which explains the consumption rates of the two monomers and the 1:1 ratio of CHO-EVL to CHO-CHO dyads in the product.

The results of differential scanning calorimetry (DSC) also support the randomness of terpolymerization. PCBE exhibits a single glass transition temperature (T_g) of $-17.4\text{ }^\circ\text{C}$, which is significantly lower than that of CHO homopolymer PCHO of $29.2\text{ }^\circ\text{C}$ (Figure S12).

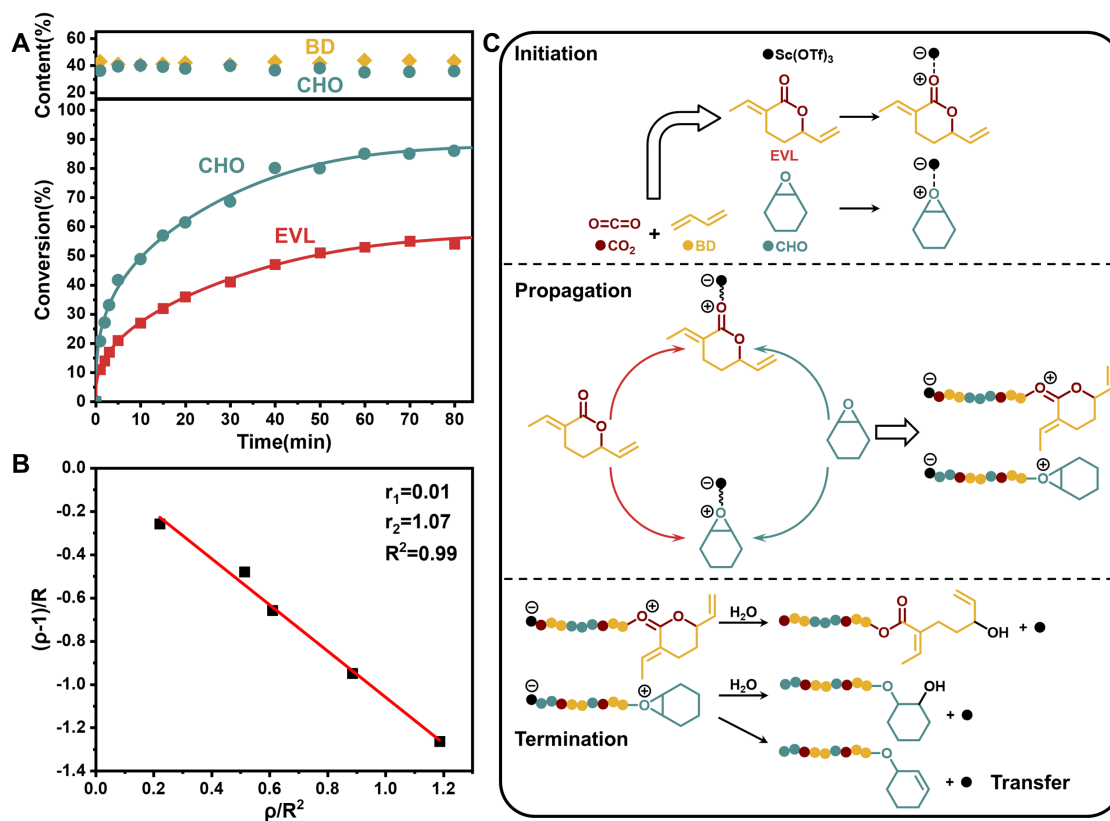


Figure 2. Time-dependent conversions of EVL and CHO (A), and the corresponding content of BD and CHO in the terpolymer. Calculation of reactivity ratios (r) of EVL (r_1) and CHO (r_2) at 40°C (B). Proposed mechanism of terpolymerization (C).

The plausible mechanism of the terpolymerization is shown in Figure 2C. The polymerization follows a typical cationic ROP mechanism. EVL and CHO first coordinate with $\text{Sc}(\text{OTf})_3$ to generate the cationic active species, followed by propagation via nucleophilic attack of the monomers on the cationic oxonium chain ends. The major side reactions are backbiting cyclization and β -proton elimination, both of which are well-known in cationic polymerization of CHO and lead to the absence of mass of the end groups in MALDI-TOF MS spectrum.^[32] Moreover, the coupling signal of the chain end protons ($\text{H}_q\text{-H}_p$ and $\text{H}_r\text{-H}_s$) is observed in the $^1\text{H}\text{-}^1\text{H}$ COSY spectrum (Figure S7), supporting the occurrence of β -proton elimination.

Since PCBE contains an abundance of unsaturated C=C double bonds available for post-polymerization modification, we use photoinitiated crosslinking as a convenient and efficient way to change linear PCBE to networks and demonstrated its application potential. Under UV irradiation, the C=C double bonds of PCBE are crosslinked by radicals in the presence of photoinitiator benzophenone. As illustrated in Figure 3A and 3B, a pattern “ZJU” is written by a pen on one side of the slide and the reverse side is coated with a dioxane solution of PCBE and benzophenone. A beam of UV light (365 nm with 3000 mW/cm²) is directed from the patterned side. After 2 h of UV irradiation and the removal of cover, the pattern “ZJU” is clearly observed on the PCBE network with sharp edges (Figure 3C).

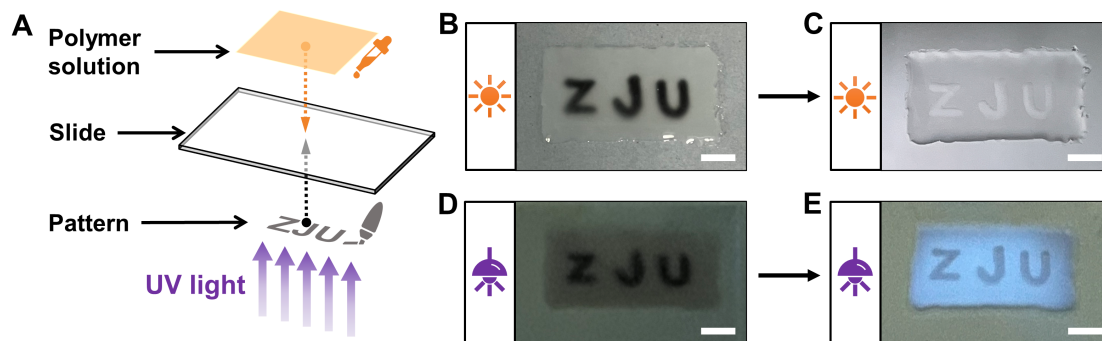


Figure 3. Photopatterning procedure of crosslinked network (A). Before UV irradiation, the pattern “ZJU” was written on the slide to block UV light (B)(D). After UV irradiation, curing and the removal of the written pattern (C)(E), the photopatterned “ZJU” was observed under sunlight (B)(C) and the sample showed fluorescence under 365 nm UV light (D)(E). Scale bar is 5 mm in (B-E).

It is worth mentioning that the process of crosslinking through double bonds is orthogonal to the cationic ROP. The two reactions can be carried out at the same time to produce the crosslinked PCBE directly via a one-pot-one-step procedure. Benzophenone is added together with the monomers and catalyst to produce the crosslinked network with UV irradiation during polymerization (Figure S13). This method makes the preparation of crosslinked network convenient and provides a flexible way to control the topology of the terpolymer.

The crosslinked network exhibits strong fluorescence under 365 nm UV light (Figure 3E) while linear PCBE and benzophenone do not (Figure 3D). Under the excitation, the maximum emission wavelengths of the crosslinked sample and the decomposed benzophenone are 444 nm and 409 nm (Figure S14), respectively, indicating that the fluorescence of crosslinked product is produced by its own through the reaction rather than the decomposed photoinitiator. Therefore, the consumption of C=C double bonds of EVL units is responsible for the fluorescence of the crosslinked PCBE, which is a new sample of aggregation-induced emission.

Chemical degradation of the network has been carried out. Linear and crosslinked PCBE are immersed in basic ethanol solution containing 1 mol/L NaOH, heated and stirred at 40 °C for 48 h. Both samples are completely degraded and no polymeric species are observed through SEC measurement (Figure S15).

Conclusions

The cationic ROP of EVL with PO and CHO is catalyzed by Sc(OTf)₃ to prepare a terpolymer from CO₂, BD and epoxides. The resulted random terpolymer PCBE, featuring an EVL content of 41 mol%, M_n of 6.5 kg/mol and D of 2.2, contains a significant number of C=C double bonds, according to the NMR spectra. The kinetic study, the reactivity ratios ($r_{\text{EVL}}=0.01$ and $r_{\text{CHO}}=1.07$) and DSC analysis support the random distributions of repeating units in the terpolymer. Photoinitiated crosslinking of PCBE through C=C double bonds yields degradable network with fluorescence and designable crosslinked region. This work introduces a new strategy towards novel polymers from CO₂ with considerable application potential and expands the methodology to prepare CO₂-based polymeric materials.

Acknowledgments

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Supporting information

Random terpolymer of CO₂, 1,3-butadiene and epoxides: synthesis, topology, fluorescence and degradability

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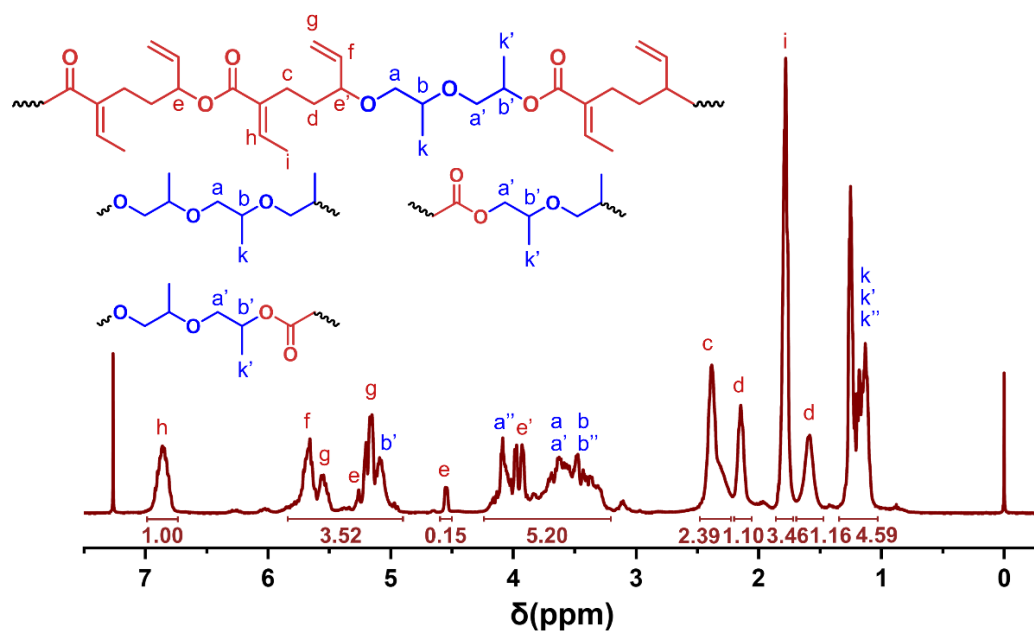


Figure S1. ¹H NMR spectrum of PCBE (Entry 2, Table 1)

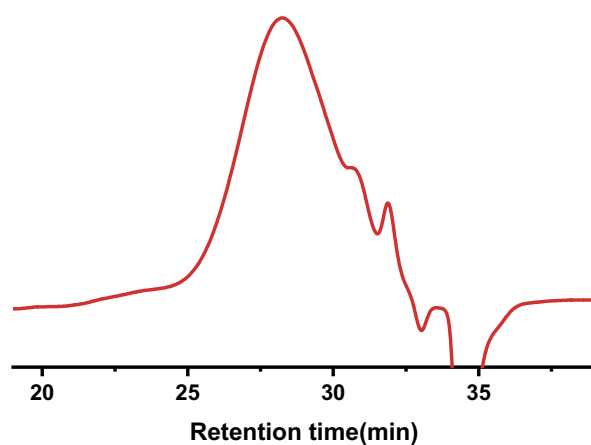


Figure S2. SEC curve of PCBE (Entry 2, Table 1)

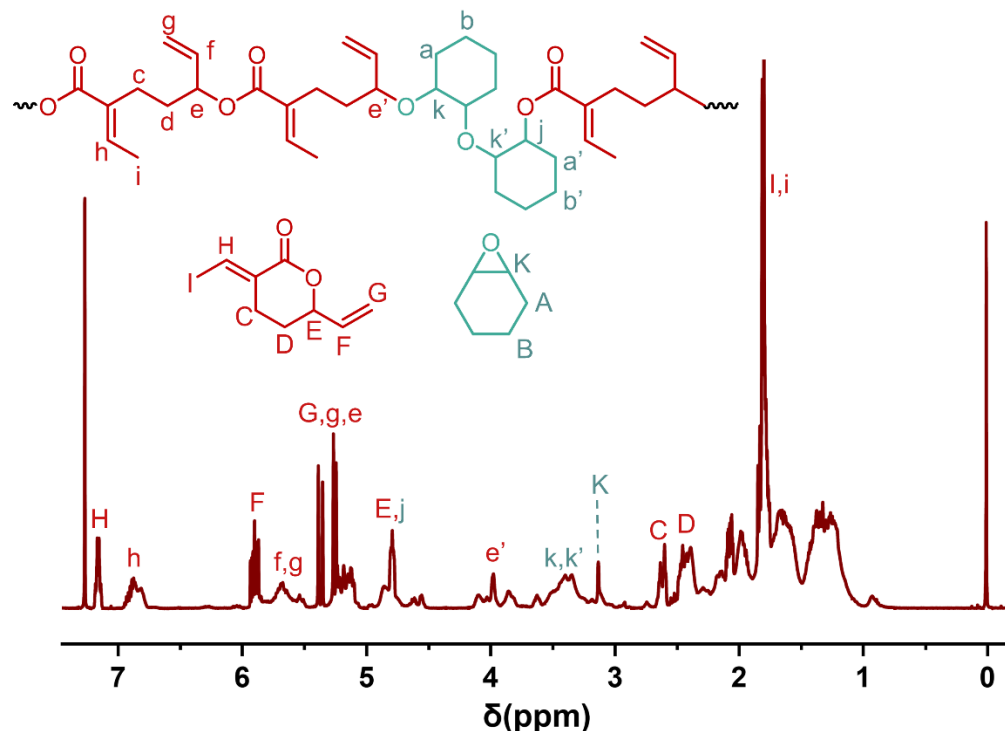


Figure S3. ^1H NMR spectrum for calculating conversion and content of EVL

The conversion of EVL was calculated as follows. The signal (H_H) at $\delta = 7.15$ ppm is attributed to the protons of the conjugated double bond in the residual EVL monomer after polymerization. And the signal (H_h) at $\delta = 6.87$ ppm is attributed to the protons of the conjugated double bond of EVL units in the copolymer. The sum of the two integrals is the total amount of EVL input in the copolymerization, from which the conversion of EVL can be calculated.

$$\text{Conv. EVL} = \frac{I_{6.87}}{I_{7.15} + I_{6.87}}$$

The conversion of EVL was calculated as follows. The signal (H_K) at $\delta = 3.12$ ppm is attributed to the methine protons of the residual CHO monomer. The signals (H_k & $H_{k'}$) at $\delta = 3.17$ - 3.57 ppm and the signal (H_j) at $\delta = 4.84$ ppm are attributed to the methine protons of CHO units in the copolymer. The sum of the integrals of all these signals is the total amount of CHO input in the reaction. However, the signal (H_j) at $\delta = 4.84$ ppm is overlapped with the signal (H_E) at $\delta = 4.78$ ppm attributed to the methine protons of the EVL monomer, which should have approximately the same integral of the signal (H_H) at $\delta = 7.15$ ppm. Therefore, the conversion of CHO can be calculated by the following equation.

$$\text{Conv. CHO} = 1 - \frac{I_{3.12}}{I_{3.17\sim 3.57} + I_{3.12} + I_{4.84} - I_{7.15}}$$

$$\text{EVL. content} = \frac{I_{6.87}}{I_{6.87} + \frac{1}{2}(I_{3.17\sim 3.57} + I_{4.84} - I_{7.15})}$$

I was the integral intensity with a specific chemical shift.

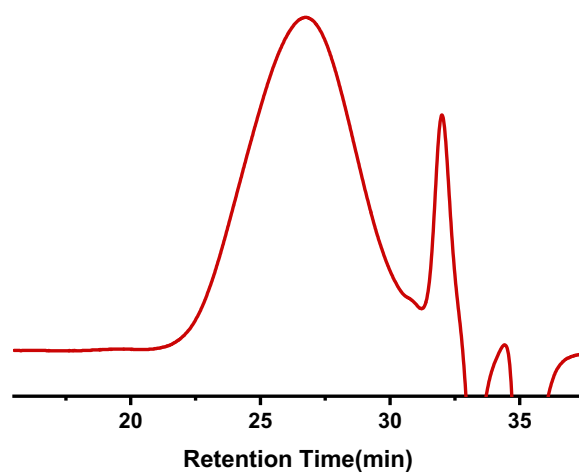
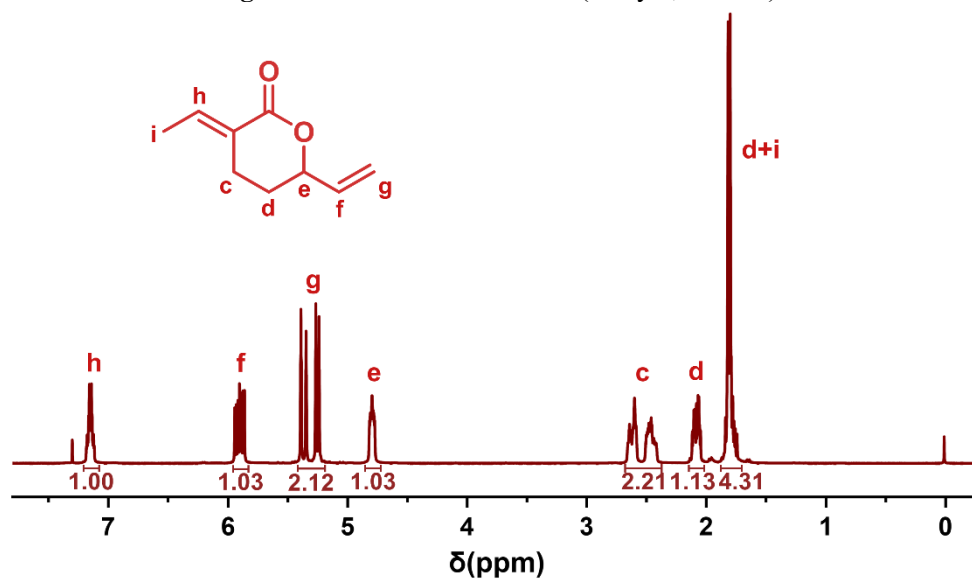


Figure S4. SEC curve of PCBE (Entry 9, Table 1)



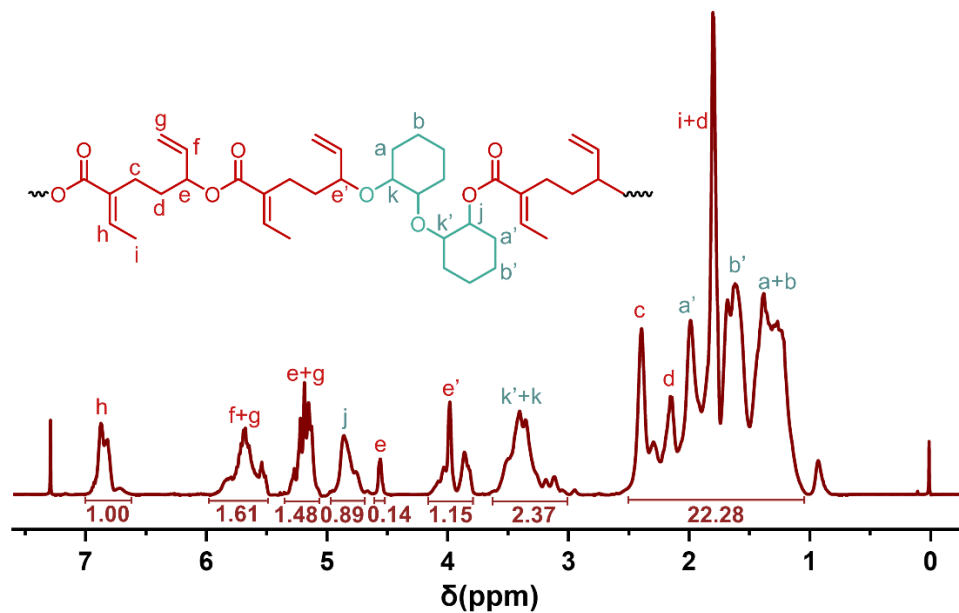


Figure S5. ^1H NMR spectrum of EVL monomer and PCBE (Entry 24, Table 1)

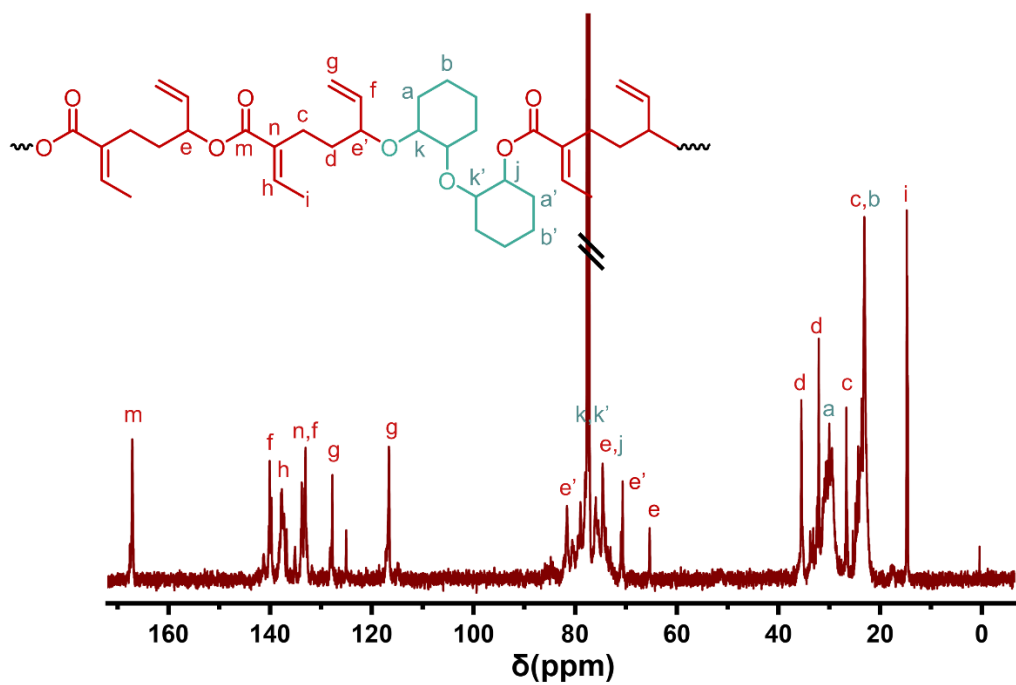


Figure S6. ^{13}C NMR spectrum of PCBE (Entry 24, Table 1)

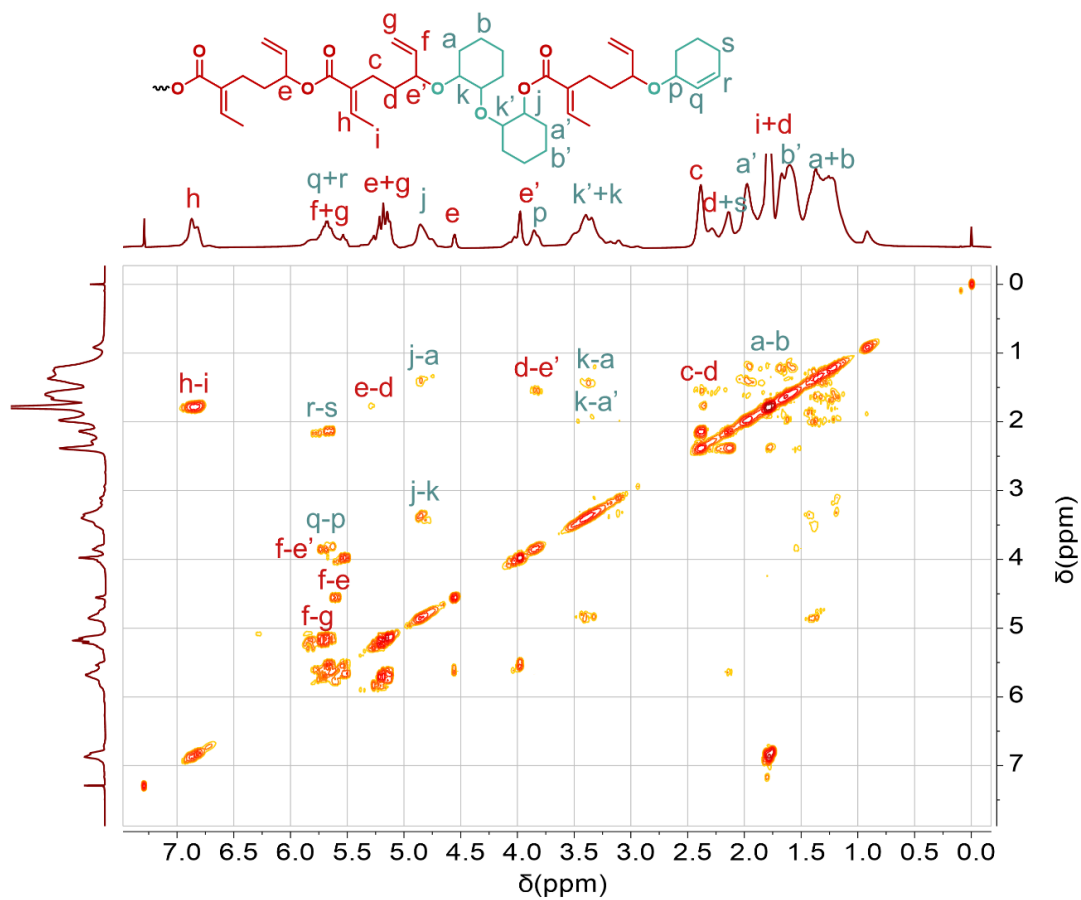


Figure S7. ^1H - ^1H COSY spectrum of PCBE (Entry 24, Table 1)

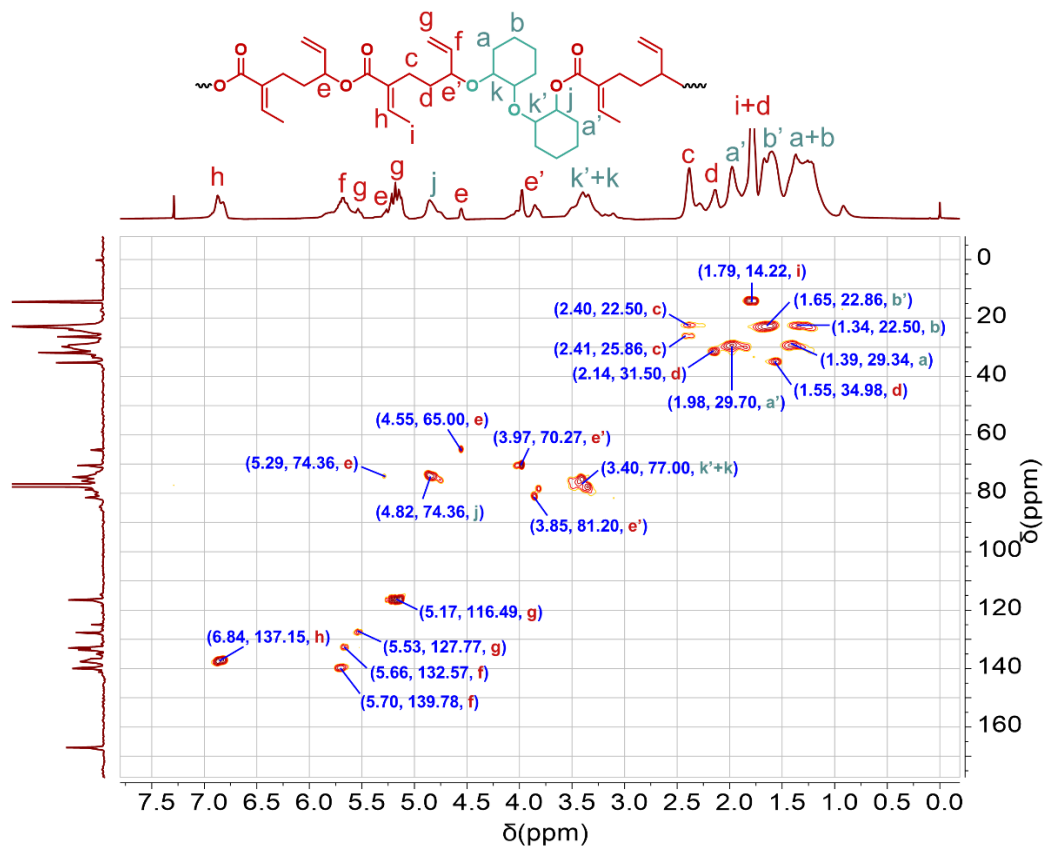


Figure S8. HSQC spectrum of PCBE (Entry 24, Table 1)

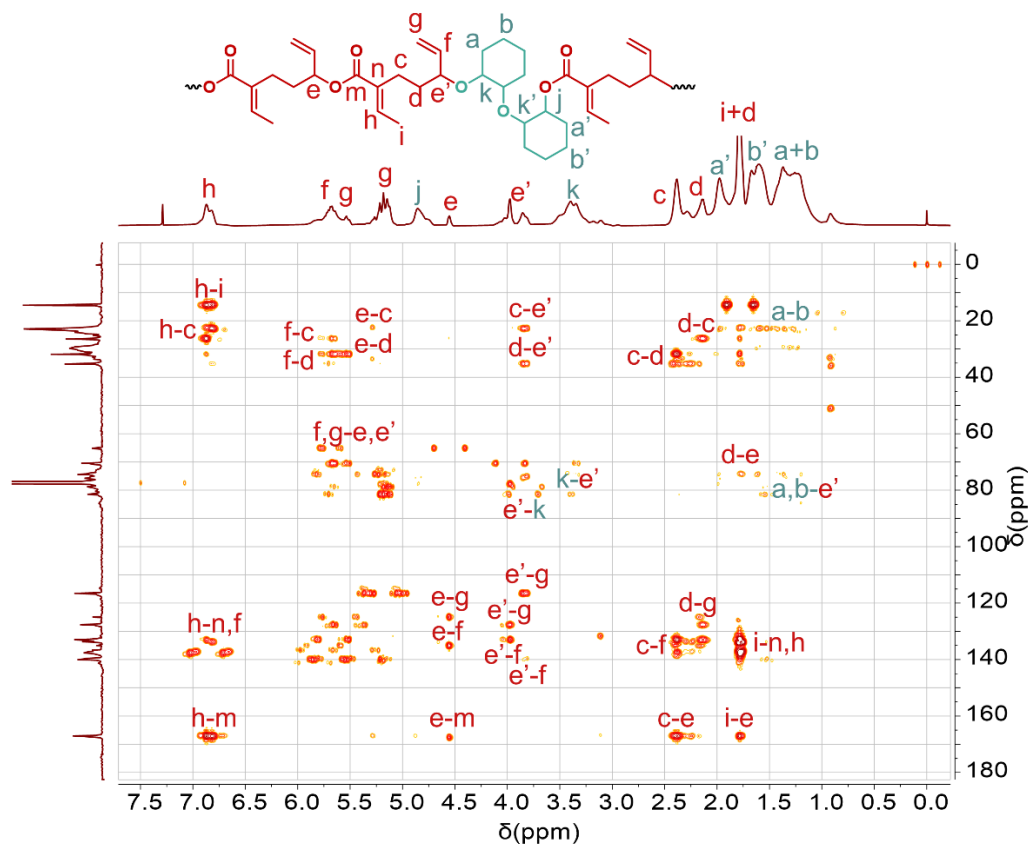


Figure S9. HMBC spectrum of PCBE (Entry 24, Table 1)

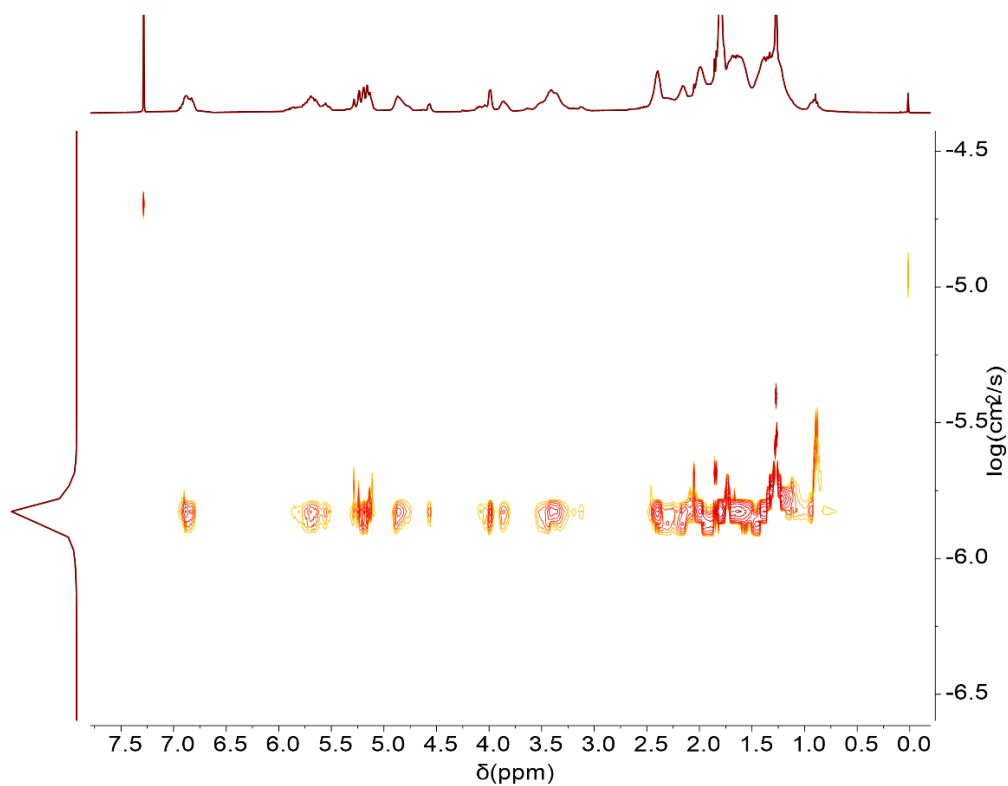


Figure S10. DOSY spectrum of PCBE (Entry 24, Table 1)

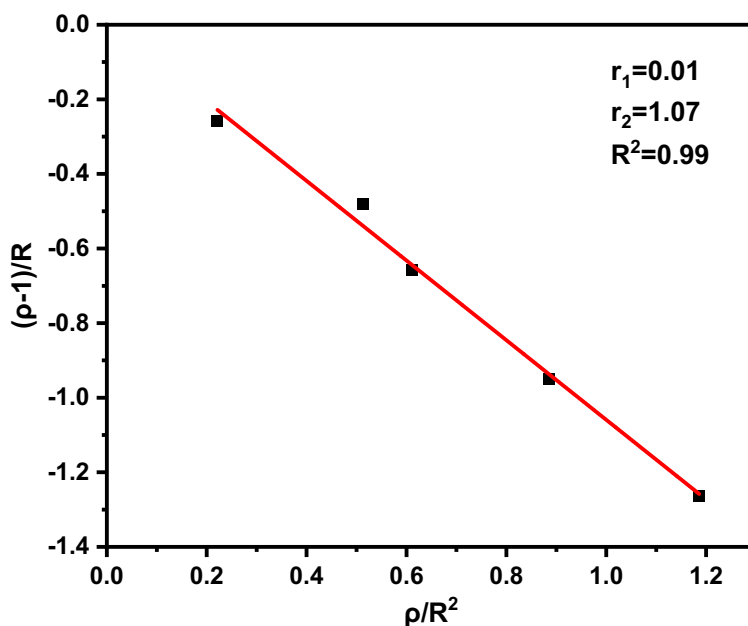


Figure S11. Calculation of reactivity ratios of EVL and CHO at 40 °C.

Reactivity ratios were calculated by the intercept and slope of Fineman-Ross equation derived from the differential equation of binary copolymer composition. Maximum conversions of EVL and CHO are 5% and 13%, respectively. r_1 and r_2 each represent the reactivity ratio of EVL and CHO.

$$\frac{\rho - 1}{R} = r_1 - r_2 \frac{\rho}{R^2}$$
$$\rho = \frac{d[M_1]}{d[M_2]} \quad R = \frac{[M_1]}{[M_2]}$$
$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$

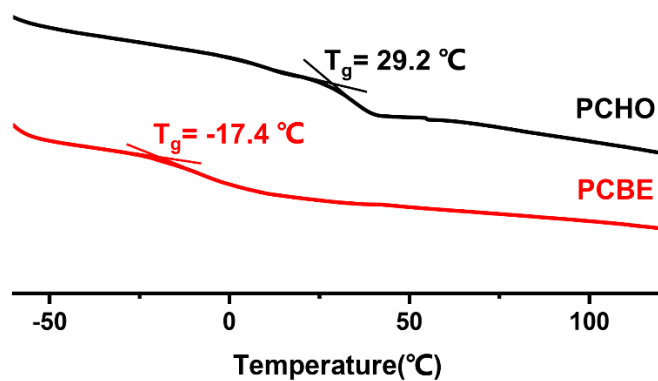


Figure S12. DSC curves of PCHO (Entry 6, Table 1) and PCBE (Entry 9, Table 1)

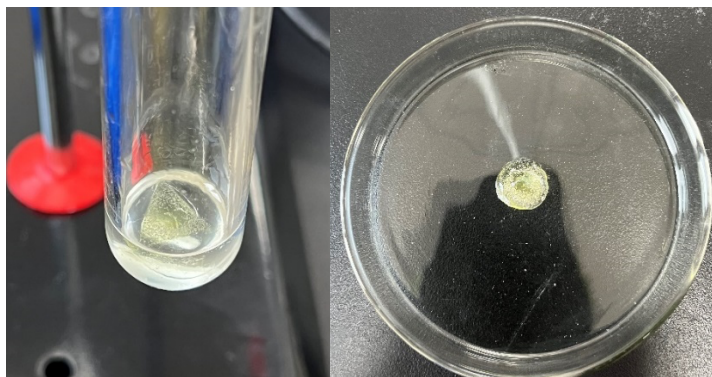


Figure S13. The crosslinked product obtained through the one-pot-one-step method.

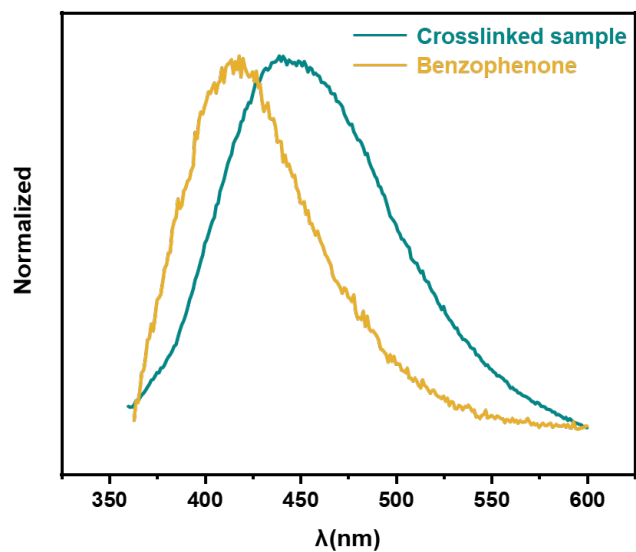


Figure S14. Fluorescence spectrum of crosslinked sample and decomposed benzophenone with excitation wavelength of 350 nm.

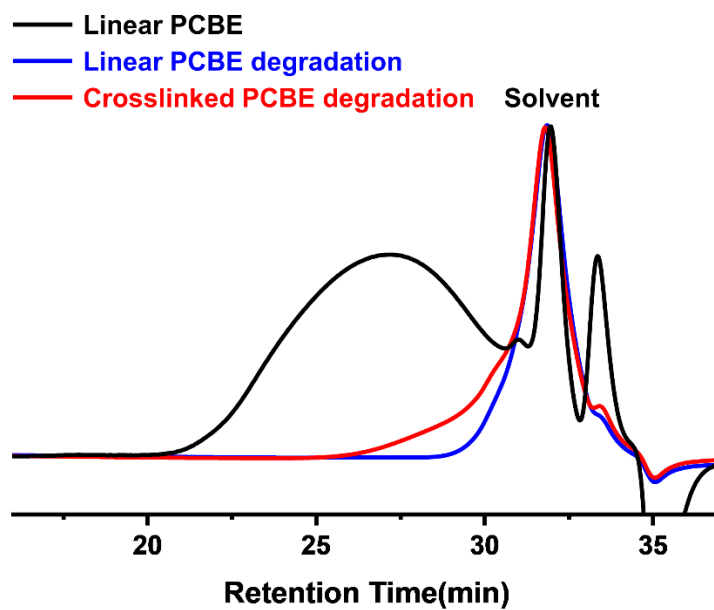


Figure S15. SEC curves of linear PCBE (Entry 24, Table 1), degradation products of linear PCBE and crosslinked PCBE.