

Electronic Supplementary Information

Multicomponent tandem polymerization of alkynes, CO₂, alkyl bromide, and thiol toward functional poly(β -thioacrylate)s

*Mengchao Zhang, Sifan Li, Zhaohui Zhang, and Hongkun Li**

Laboratory of Advanced Optoelectronic Materials, Suzhou Key Laboratory of Novel Semiconductor-Optoelectronics Materials and Devices, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Engineering Laboratory of Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China. E-mail: hkli@suda.edu.cn

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Preparation of LCPN films doped with P1a/2/3/CO₂

A homogeneous mixture of 2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (C6M, 473.5 mg), 4-methoxyphenyl 4-((6-(acryloyloxy)hexyl)oxy)benzoate (RM105, 473.5 mg), benzil dimethyl ketal (BDK, 10.0 mg), CA-Acrylate (42.0 mg), and P1a/2/3/CO₂ (1.0 mg) (their molecular structures shown in Chart 1) was ultrasonically dissolved in 2 mL of DCM. The solution was drop-cast onto quartz substrates, followed by solvent evaporation at 85 °C for 3–5 min. After cooling to room temperature, the samples were photopolymerized under 365-nm xenon lamp irradiation (15 W) for 10 s. Finally, freestanding films were obtained by mechanically delaminating the polymerized layers from the substrate using a blade.

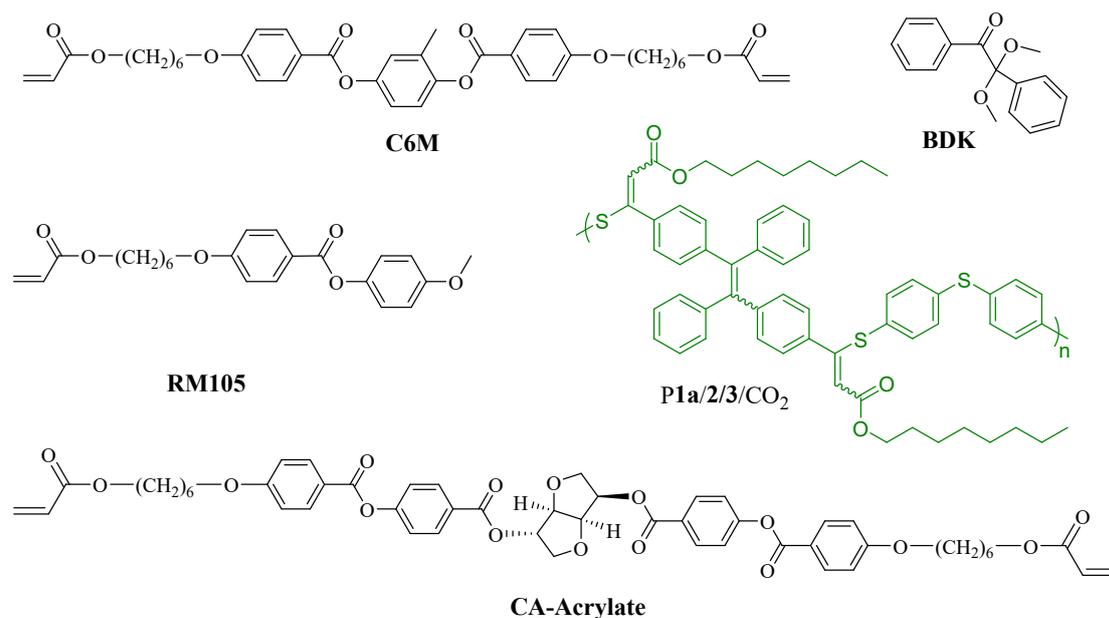


Chart. S1 Molecular structures of the compounds in the polymerizable system.

Table S1 Effect of time on the polymerization of **1a**, CO₂, **2**, and **3**^a

entry	<i>t</i> (h)	<i>M_w</i> ^b	<i>D</i> ^b	Yield (%)
1	8	6800	1.15	34.7
2	16	9800	1.21	45.4
3	20	10500	1.22	50.4
4	24	11200	1.25	52.6
5	48	12000	1.37	53.5

^a [**1a**] = 0.4 mol/L, [**1a**]/[Ag₂WO₄]/[Cs₂CO₃]/[**3**] = 1:0.2:6:1, **1a** and **2** were stirred at 80 °C under CO₂ atmosphere in DMAc for 12 h in the presence of Ag₂WO₄ and Cs₂CO₃, followed by reaction with **3** for different time. ^bEstimated by GPC in THF, *D* = polydispersity index.

Table S2 Solubility properties of P**1a-d/2/3**/CO₂ in different solvents^a

Polymer	chloroform	DCM	THF	DMF	DMAc
P 1a/2/3 /CO ₂	39	38	41	43	47
P 1b/2/3 /CO ₂	35	32	36	33	36
P 1c/2/3 /CO ₂	20	19	21	28	33
P 1d/2/3 /CO ₂	25	22	28	23	26

^a Solubility: mg/100 mg, temperature: 20 °C.

Table S3 Solubility properties of **P1a-d/2/3/CO₂/4** in different solvents^a

Polymer	Chloroform	DCM	THF	DMF	DMAc
P1a/2/3/CO₂/4	62	60	54	59	62
P1b/2/3/CO₂/4	53	49	48	46	49
P1c/2/3/CO₂/4	32	29	34	35	40
P1d/2/3/CO₂/4	39	37	35	31	35

^a Solubility: mg/100 mg, temperature: 20 °C**Table S4** Comparison on CPL properties of the LCPN films

Sample Parameter	S-TPE- CLC ^[1]	R-PN- TPE/BFN ^[2]	S-PN- TAE/TPEB ^[3]	S-PN-2 ^[4]	PN- TPAP ^[5]	This work
λ (nm)	485	620	610	550	505	500
g_{\max}	0.58	-0.71	0.85	0.70	-0.93	-0.88

[1] B. Ni, Y. Li, W. Liu, B. Li, H. Li and Y. Yang, *Chem. Commun.*, 2021, **57**, 2796.

[2] F. Shi, F. Han, W. Zhang, Y. Yang and H. Li, *Dyes Pigm.*, 2024, **222**, 111910.

[3] F. Shi, L. Xu, J. Zhao, Z. Li, W. Zhang, Y. Yang and H. Li, *Chem. Commun.*, 2024, **60**, 11096.

[4] P. Guan, F. Shi, C. Xu, Y. Yang and H. Li, *J. Phys. Chem. Lett.*, 2025, **16**, 10142.

[5] P. Guan, S. Yu, Y. Yang and H. Li, *Chem. Commun.*, 2025, **61**, 17133.

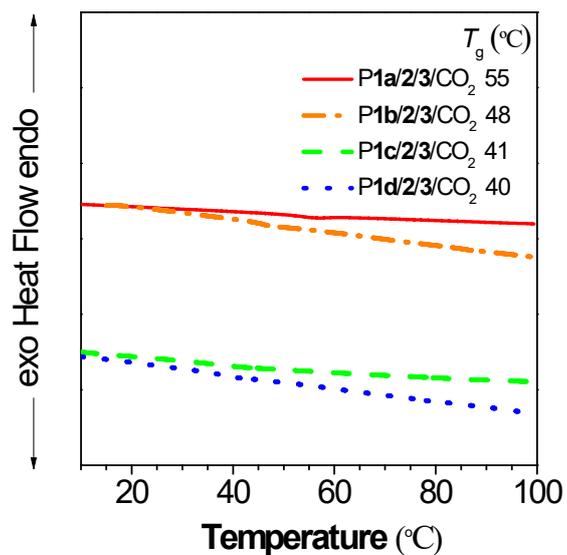


Fig. S1 DSC Curves of P1a–d/2/3/CO₂ under nitrogen at a heating rate of 10 °C min⁻¹.

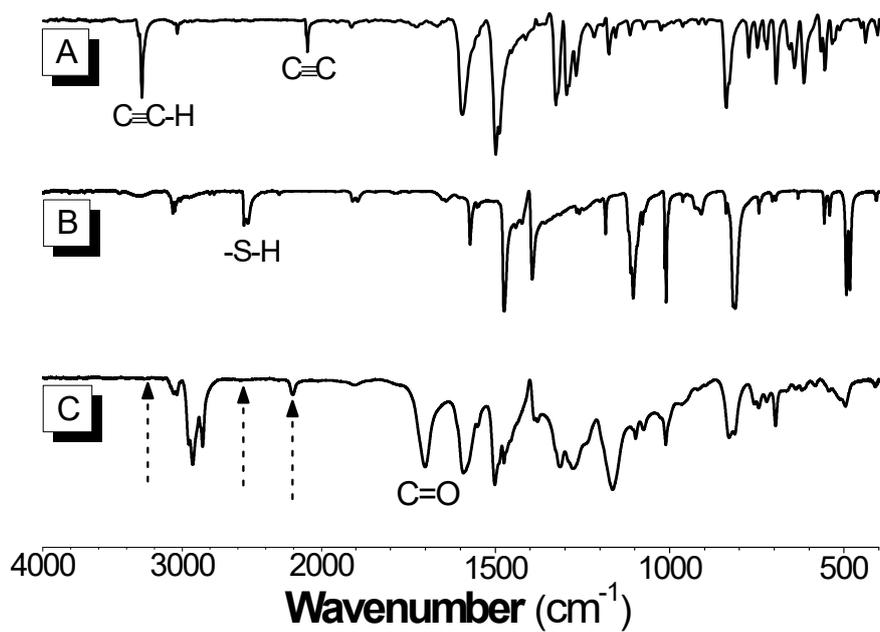


Fig. S2 IR spectra of monomer 1b (A), 2 (B) and polymer P1b/2/3/CO₂ (C).

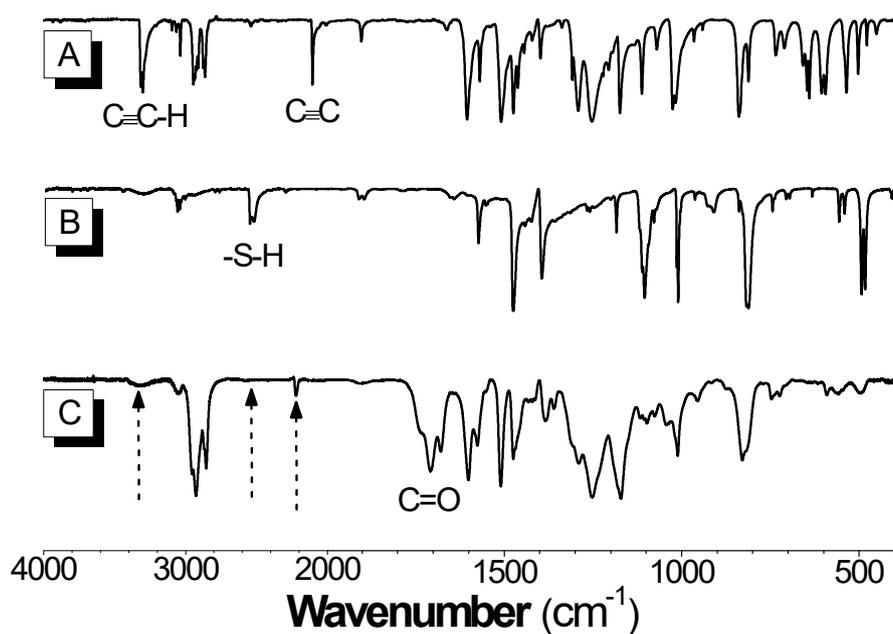


Fig. S3 IR spectra of monomer **1c** (A), **2** (B) and polymer **P1c/2/3/CO₂** (C).

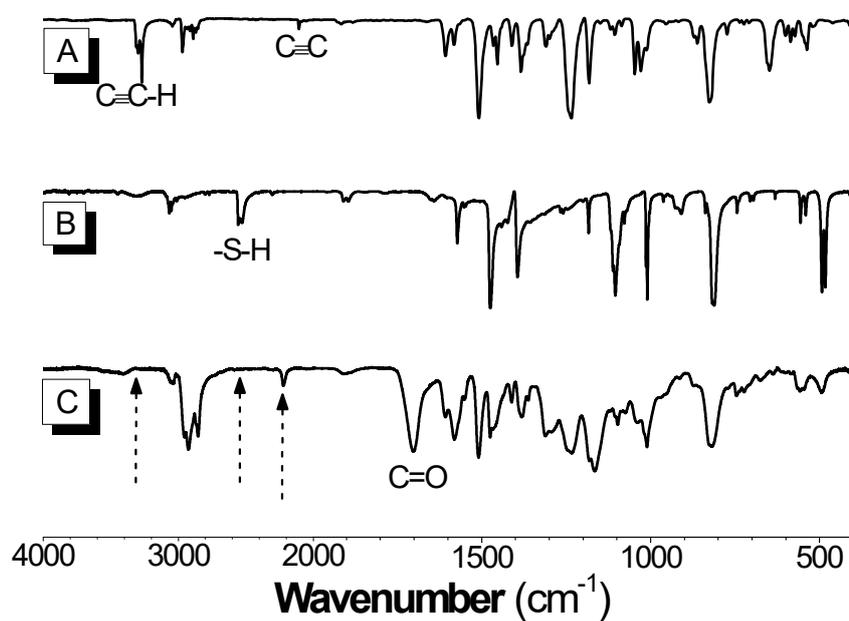


Fig. S4 IR spectra of monomer **1d** (A), **2** (B) and polymer **P1d/2/3/CO₂** (C).

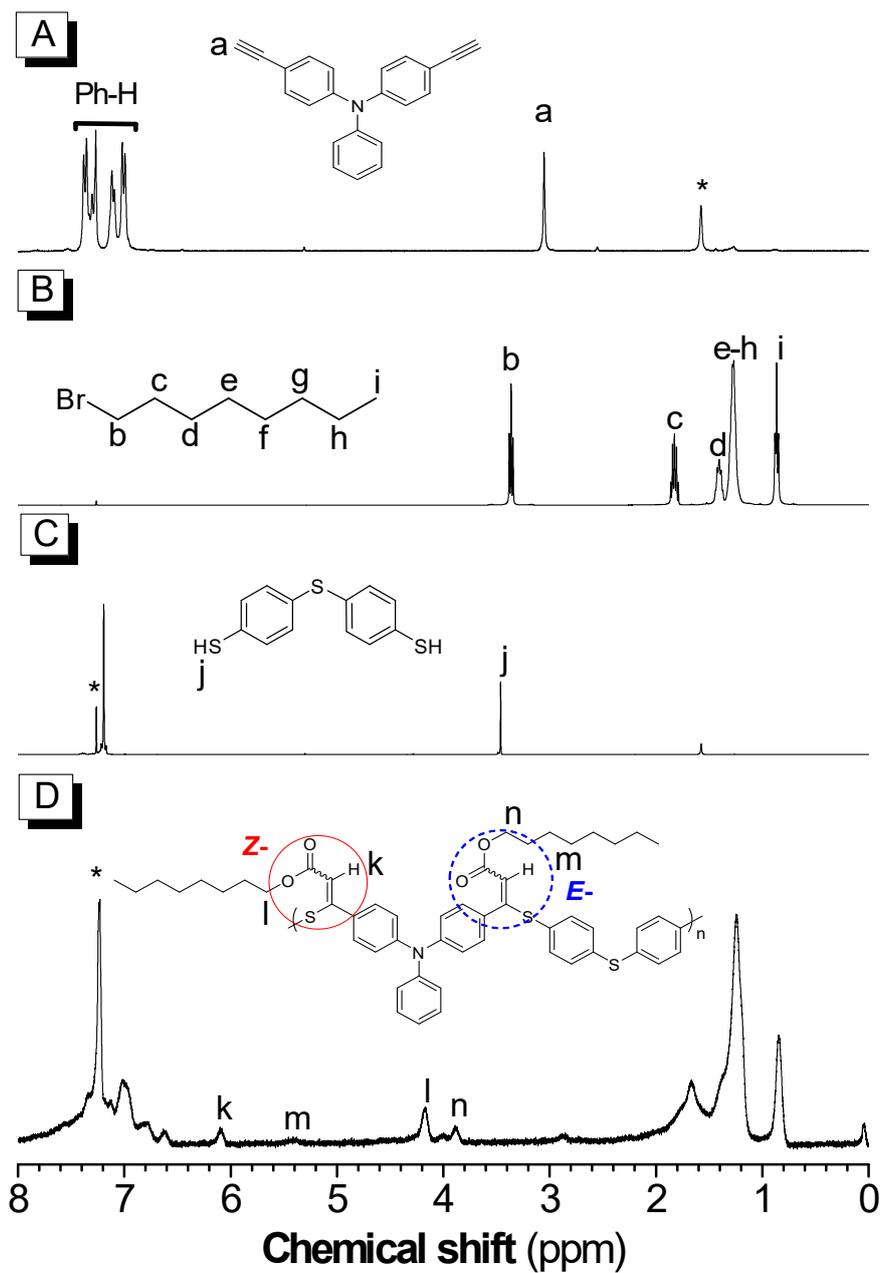


Fig. S5 ^1H NMR spectra of monomer **1b** (A), **2** (B), **3** (C) and polymer **P1b/2/3/CO₂** (D) in CDCl_3 . The solvent peaks are marked with asterisks.

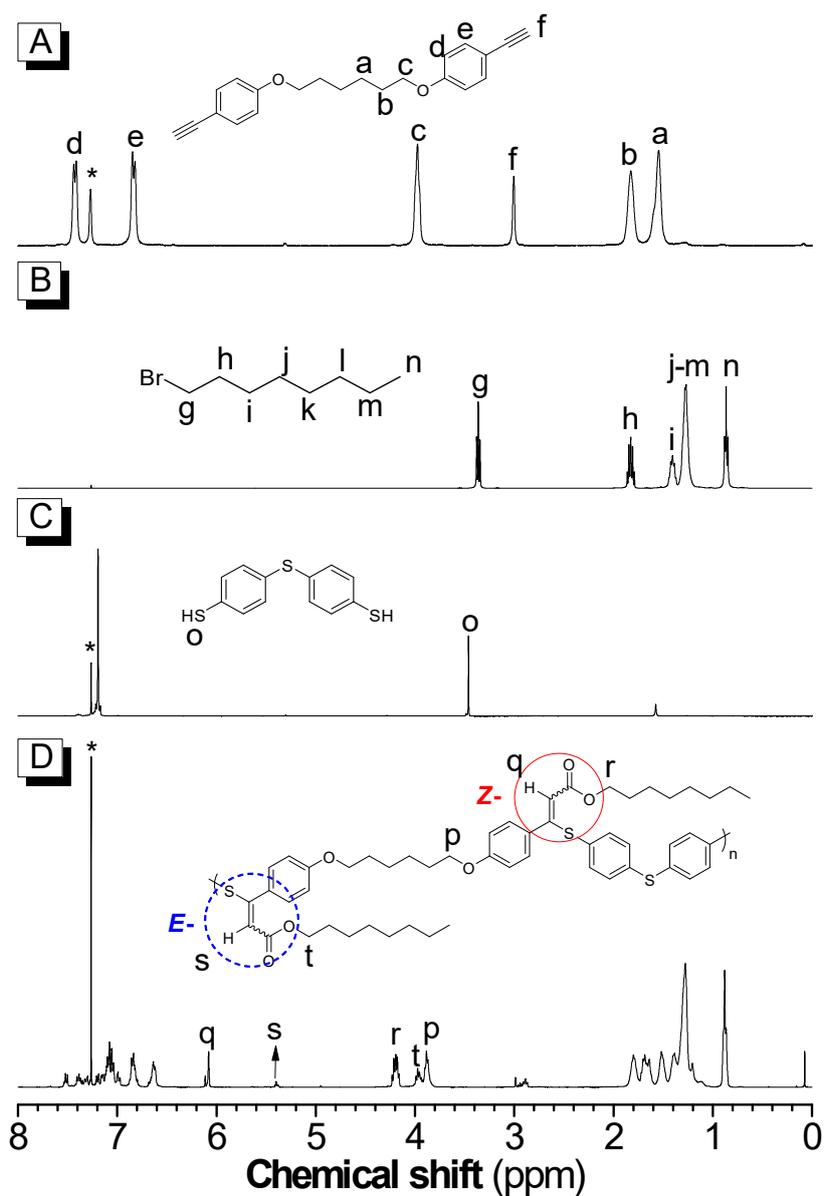


Fig. S6 ^1H NMR spectra of monomer **1c** (A), **2** (B), **3** (C) and polymer **P1c/2/3/CO₂** (D) in CDCl_3 . The solvent peaks are marked with asterisks.

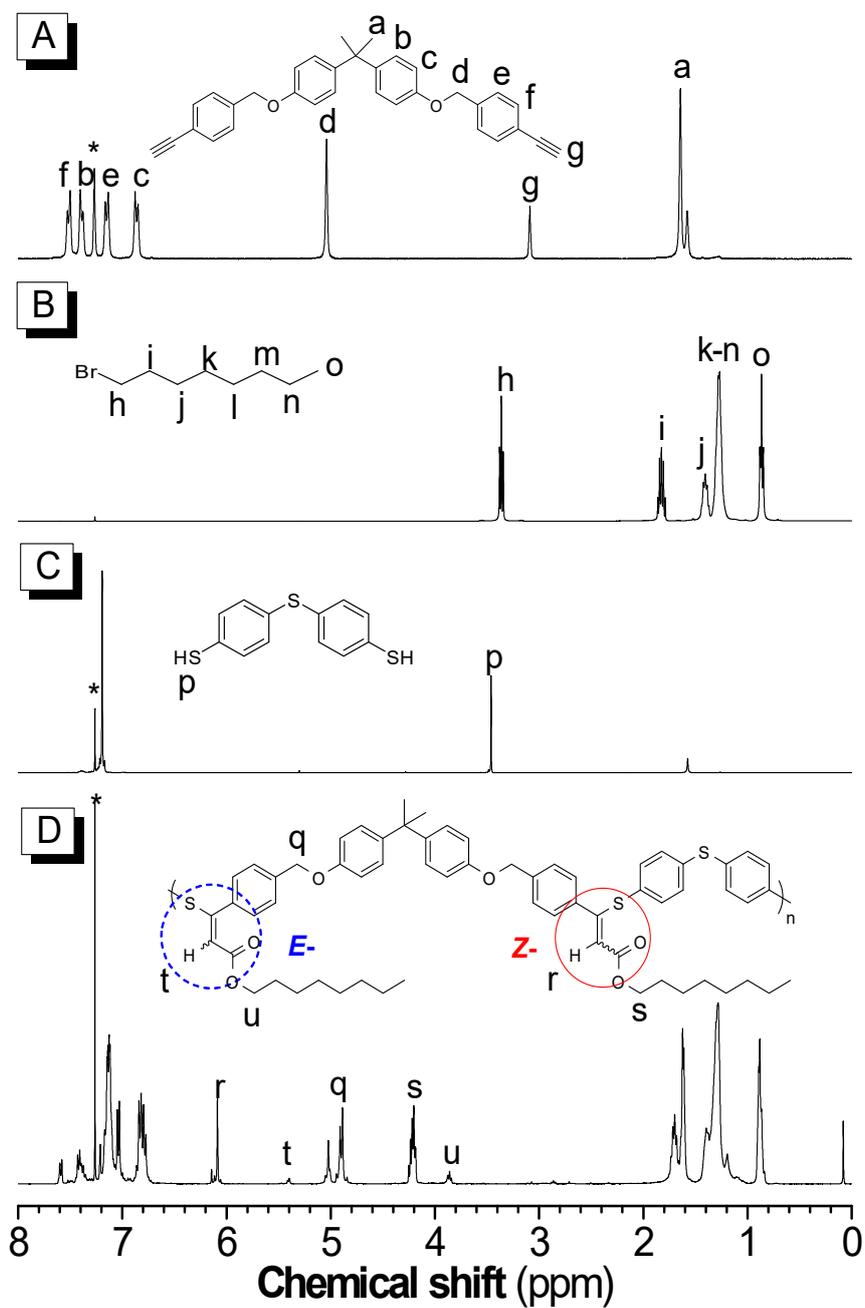


Fig. S7 ^1H NMR spectra of monomer **1d** (A), **2** (B), **3** (C) and polymer **P1d/2/3/CO₂** (D) in CDCl_3 . The solvent peaks are marked with asterisks.

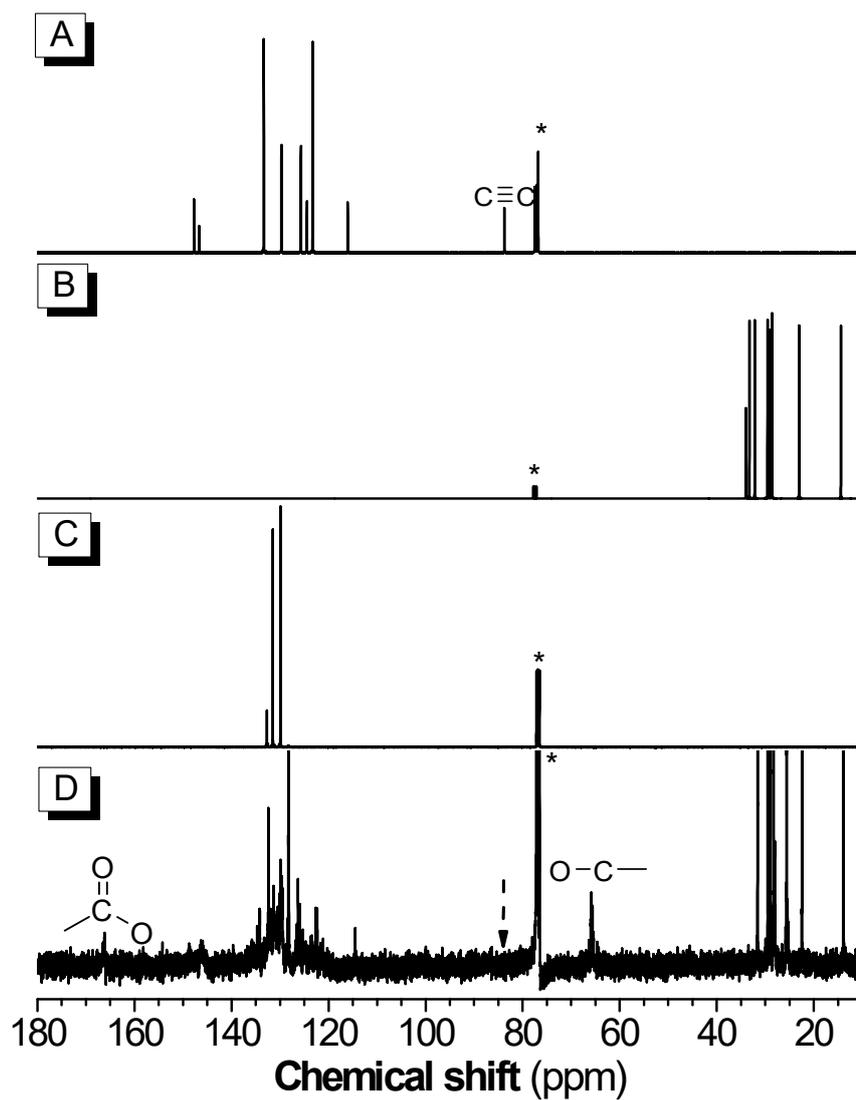


Fig. S8 ^{13}C NMR spectra of monomer **1b** (A), **2** (B), **3** (C) and polymer **P1b/2/3/CO₂** (D) in CDCl_3 . The solvent peaks are marked with asterisks.

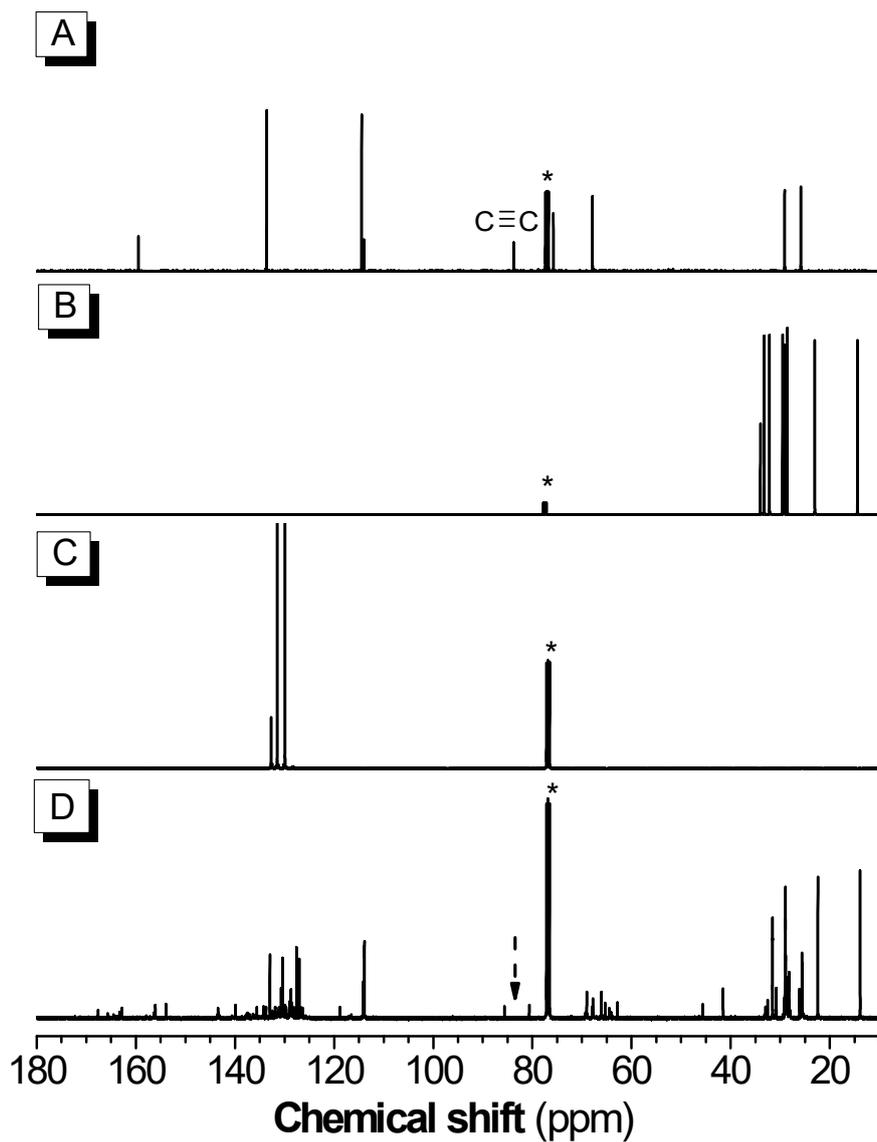


Fig. S9 ^{13}C NMR spectra of monomer **1c** (A), **2** (B), **3** (C) and polymer **P1c/2/3/CO₂** (D) in CDCl_3 . The solvent peaks are marked with asterisks.

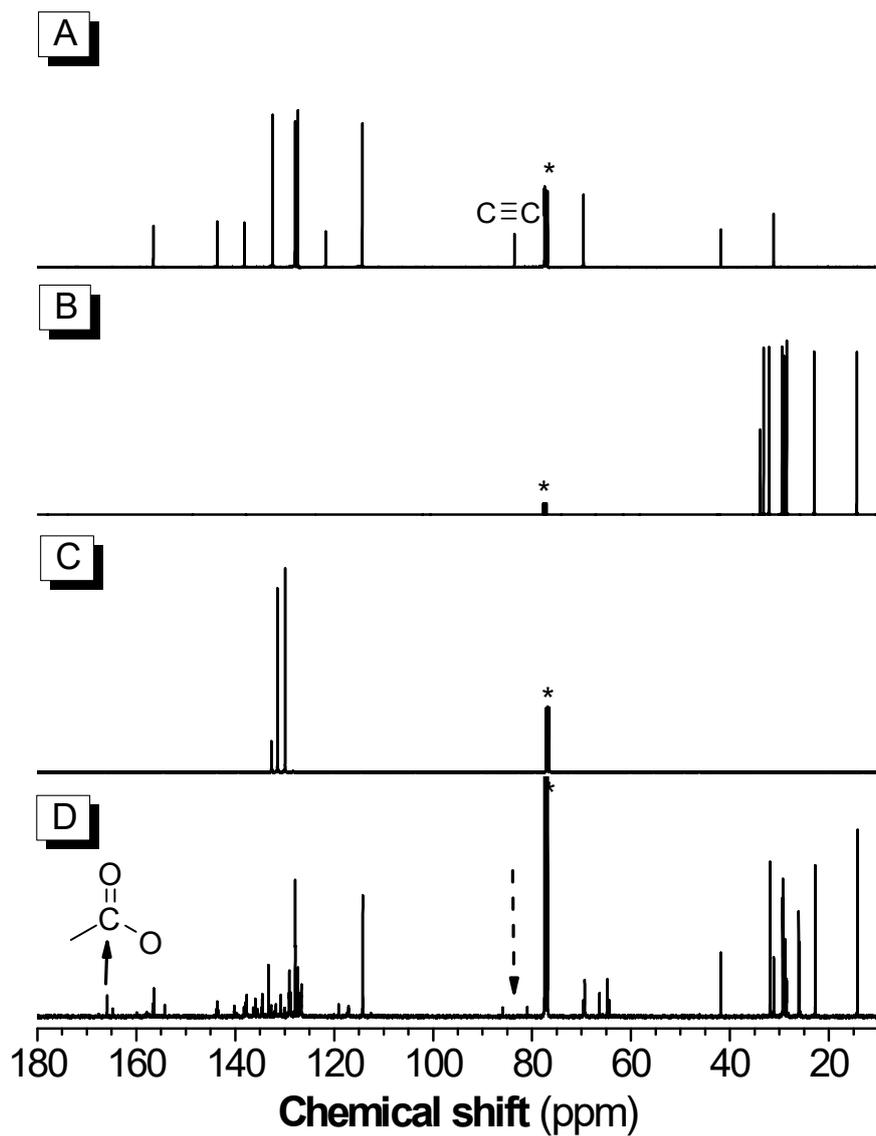


Fig. S10 ^{13}C NMR spectra of monomer **1d** (A), **2** (B), **3** (C) and polymer **P1d/2/3/CO₂** (D) in CDCl_3 . The solvent peaks are marked with asterisks.

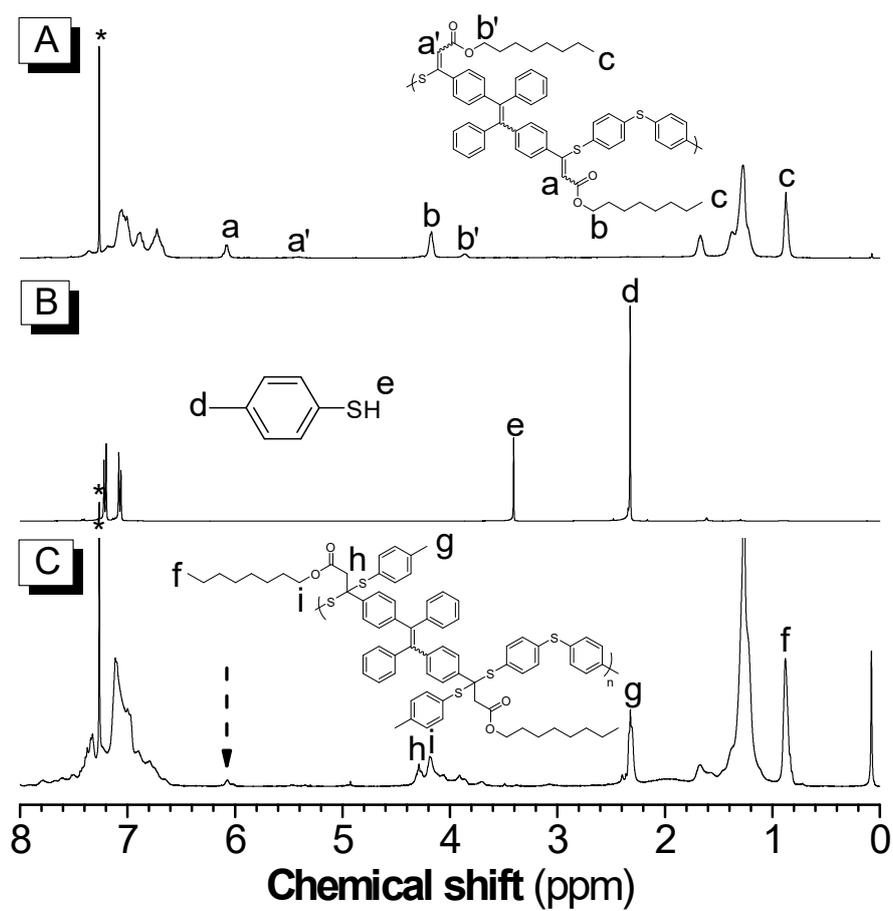


Fig. S11 ^1H NMR spectra of P1a/2/3/CO_2 (A), **4** (B) and polymer $\text{P1a/2/3/CO}_2/4$ (C) in CDCl_3 . The solvent peaks are marked with asterisks.

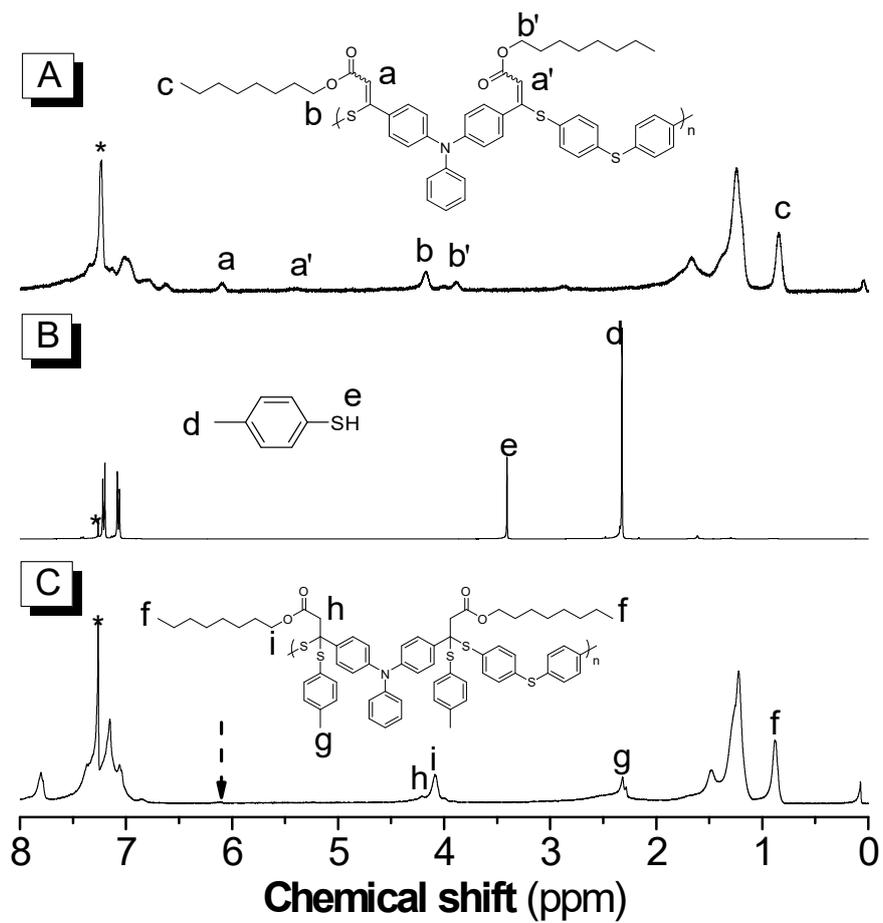


Fig. S12 ¹H NMR spectra of polymer P1b/2/3/CO₂ (A), 4 (B) and polymer P1b/2/3/CO₂/4 (C) in CDCl₃. The solvent peaks are marked with asterisks.

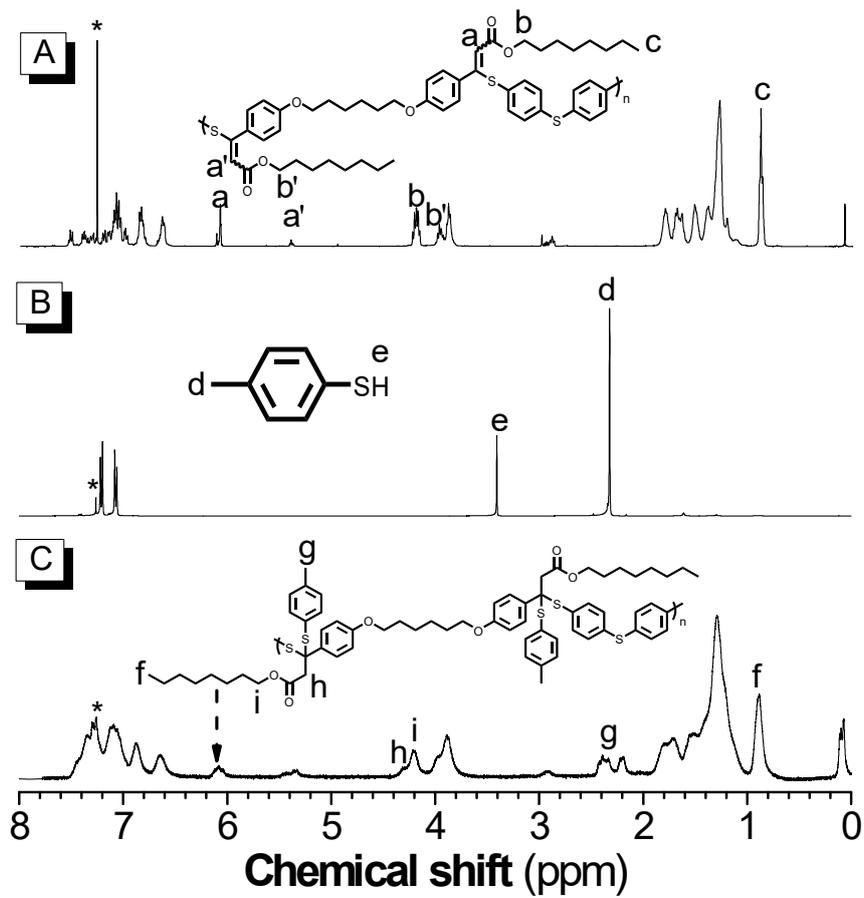


Fig. S13 ^1H NMR spectra of P1c/2/3/CO_2 (A), **4** (B) and polymer $\text{P1c/2/3/CO}_2/4$ (C) in CDCl_3 . The solvent peaks are marked with asterisks.

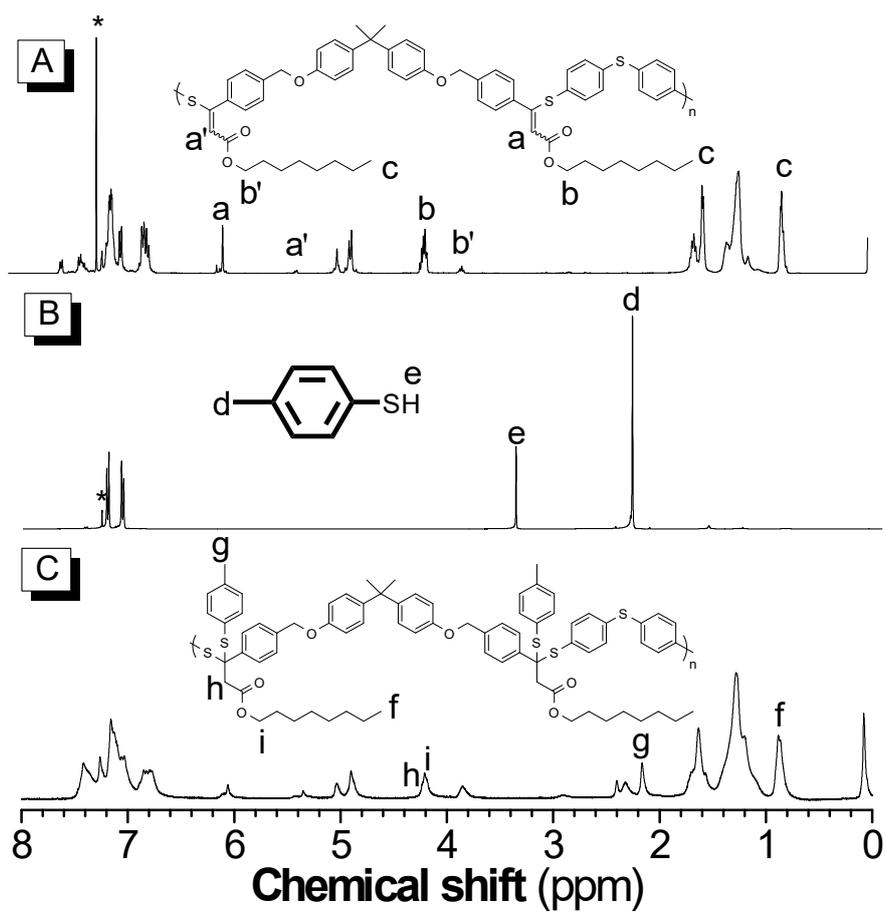


Fig. S14 ^1H NMR spectra of P1d/2/3/CO_2 (A), **4** (B) and polymer $\text{P1d/2/3/CO}_2/4$ (C) in CDCl_3 . The solvent peaks are marked with asterisks.

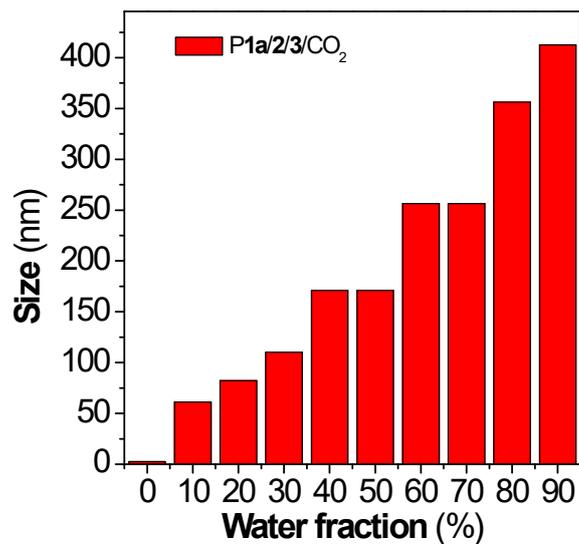


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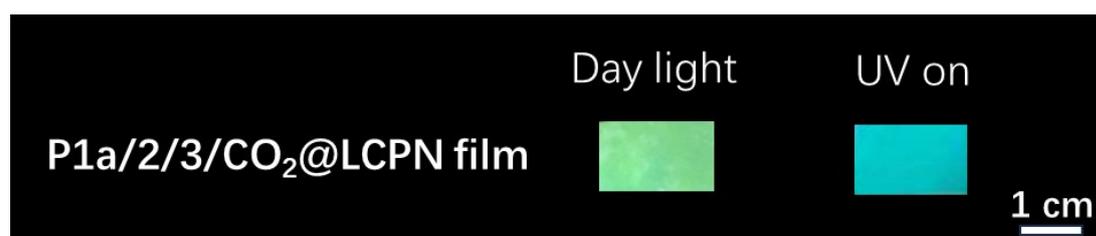


Fig. S16 Photographs of P1a/2/3/CO₂-doped LCPN film under daylight and UV light.

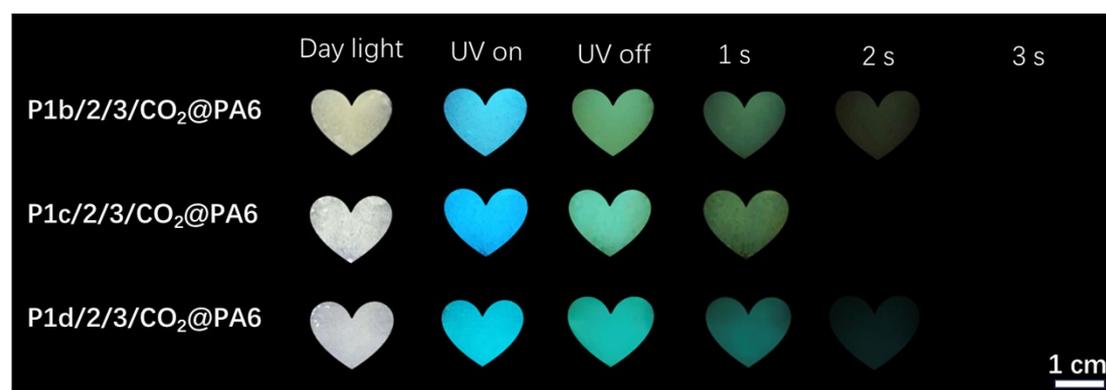


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