

Supporting Information for

**Composition-dependent emission colors for biomass-based
main-chain luminescent liquid crystalline copolyesters with
excellent tensile properties**

Wei Wang,^a Jing Wang,^b Wenting Li,^a Guangjian Liao,^a Yuan Qiu,^{*a} Guochuan Yin,^a
Yonggui Liao,^{*a} Xiaolin Xie^a

^a Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Engineering Research Center for Biomaterials and Medical Protective Materials, Hubei Key Laboratory of Materials Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

^b National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Materials

1. Experimental

1.1. Materials

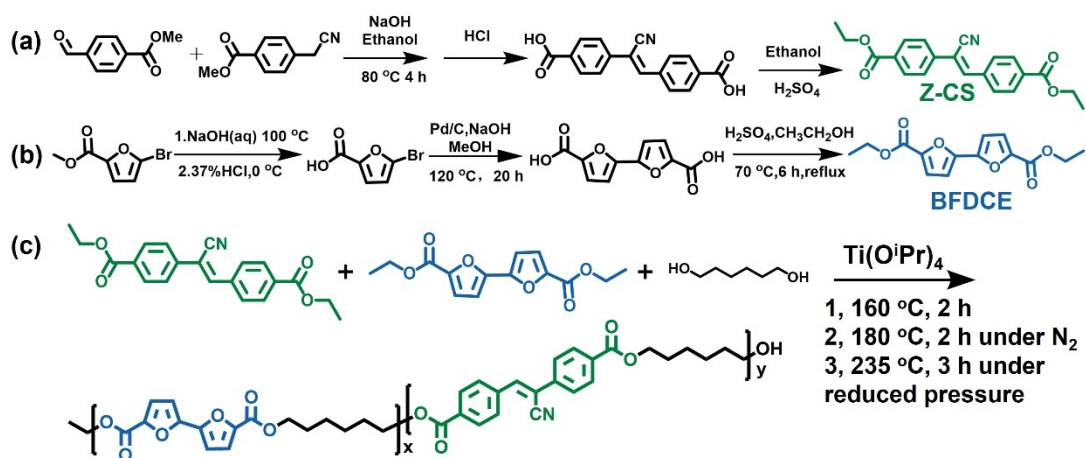
1,6-Hexanediol was purchased from Aladdin Reagent Co., Ltd. 4-Methoxyphenylacetonitrile, 4-methoxybenzaldehyde and tetraisopropyl orthotitanate $\text{Ti}(\text{OiPr})_4$ were obtained from TCI. Diethyl [2,2'-bifuran]-5,5'-dicarboxylate (BFDCE) and (Z)-2,3-bis(4-ethoxyphenyl) acrylonitrile (Z-CS) were synthesized according to previous literatures.¹⁻³

1.2. Characterizations

^1H nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE III-400 NMR instrument at room temperature. Fourier transform-infrared (FT-IR) spectra were taken on a Bruker Equinox 55 spectrometer in the attenuated total reflectance (ATR) mode. The number-average molar masses (M_n) and the polydispersity (M_w/M_n) were measured on the Waters 1515 GPC instrument at 40 °C using chloroform as the eluent at a flow rate of 0.5 mL min⁻¹. The molecular weight calibration curves were obtained with polystyrene standards. UV-vis absorption spectra and fluorescence spectra were recorded using a Shimadzu UV-2550 diode-array spectrophotometer and EDINBURGH FS5 spectrofluorometer at room temperature, respectively. The solutions were tested in 1 cm quartz cuvettes, while the films prepared by spin coating the corresponding chloroform solutions with a concentration of 30 mg mL⁻¹ onto the quartz plate were directly tested. Polarized optical microscopic (POM) observations were carried out using a Zeiss Axio Scope P1 polarizing optical microscope with a hot stage (Linkam THMS 600) at different temperature. Thermogravimetric analyses (TGA) were performed on a Perkin Elmer Diamond

TGA8000 under an argon flow rate of 20 mL min⁻¹. Differential scanning calorimetry (DSC) was run on a DSC2A-01634 instrument at a heating or cooling rate of 10 °C min⁻¹ under an argon atmosphere. X-ray diffraction (XRD) patterns for the as-polymerized samples were recorded on an X-ray diffraction meter (D/max 2500 PC, Rigaku) with a Cu-K α radiation source with a wavelength of 0.154 nm. The mechanical strength measurements were carried out on an UTM2103 testing machine with a transducer-coupled 1 kN load cell. The films with a thickness of 100 ~ 200 μ m were prepared by compression molding for testing, where an appropriate amount of the polymer sample was loaded between two iron plates that were preheated at 180 °C for 5 min.

1.3. Syntheses of Z-CS, BFDCE, and PBFCS



Scheme S1. Synthetic routes for Z-CS (a), BFDCE (b), and PBFCS (c).

The syntheses of Z-CS and copolyesters were carried out according to the synthetic route illustrated in **Scheme S1**.

(Z)-2,3-Bis(4-hydroxyphenyl)acrylonitrile (CS-OH). 4-Methoxybenzaldehyde (0.88 g, 5.0 mmol) and sodium hydroxide (0.40 g, 10.0 mmol) were added to a three-necked flask containing 100 mL of ethanol. The flask was equipped with a reflux condenser,

and the resulting mixture was stirred at 60 °C until it completely dissolved. Subsequently, 4-methoxyphenylacetonitrile (0.82 g, 5.0 mmol) was added to the solution and stirred at 80 °C for 4 h. The mixture was extracted using ethyl acetate and deionized water. The aqueous phase was then acidized by 36.5 wt % hydrochloric acid. After filtration, the residue was washed with deionized water for three times. The obtained product was dried in an oven at 60 °C for 24 h to afford Z-CS as a pale-yellow crystal (0.96 g, 66.3%). ¹H NMR (400 MHz, DMSO-*d*₆) δ = 13.23 (s, 2H), 8.30 (s, 1H), 8.08 (m, 6H), 7.94 (d, *J* = 8.3 Hz, 2H).

(*Z*)-2,3-Bis(4-ethoxyphenyl)acrylonitrile (Z-CS). CS-OH (1.47 g, 5.0 mmol) was added to a three-necked flask equipped with a reflux condenser containing 100 mL ethanol. Then, 1 mL of concentrated sulfuric acid was slowly added to the reaction flask. After stirring at 80 °C for 4 h, the mixture was cooled, extracted, and dried to obtain the desired product as a yellow solid (1.26 g, 72.1%). ¹H NMR (400 MHz, CDCl₃, TMS, ppm): δ = 8.22 (s, 1H), 7.98 (dd, *J* = 8.9, 5.6 Hz, 6H), 7.86 (d, *J* = 8.3 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H).

The synthetic procedures of PBF and the copolyesters are similar. Take the synthesis of P79.5 as an example. BFDCE (1.00 g, 3.60 mmol), Z-CS (0.32 g, 0.90 mmol), 1,6-hexanediol (0.53 g, 4.50 mmol), and a solution of Ti(OiPr)₄ with a concentration of 0.3 wt % relative to the diester in ethylene glycol dimethyl ether (10 wt %) were added to a 50 mL three-necked flask equipped with a mechanical stirrer. The flask was evacuated to a low vacuum (below 100 Pa) and then filled with argon three times to reduce the generation of by-products. The mixture was then heated at 160 °C for 2 h,

followed by 180 °C for 2 h under N₂. The reaction mixture was further heated at 235 °C for 3 h under reduced pressure (less than 100 Pa). After cooling to room temperature, the product was dissolved in a mixture solution of chloroform and trifluoroacetic acid (1:1) and then the solution was poured into ethanol (20 times). The precipitate was collected by centrifugation, and dried at 80 °C in vacuum for 48 h to afford P79.5 as a white block (1.12 g, 79.4%). ¹H NMR (400 MHz, CDCl₃, TMS, ppm): δ = 8.05 (m, 4H), 7.96 (d, 2H), 7.76 (d, 2H), 7.66 (s, 1H), 7.22 (d, 8H), 6.88 (d, 8H), 4.34 (q, 20H), 1.82–1.77 (m, 24H), 1.52–1.48 (m, 17H).

P86.7. Yield: 76.0%. ¹H NMR (400 MHz, CDCl₃, TMS, ppm): δ = 8.12 (m, 4H), 7.96 (d, 2H), 7.76 (d, 2H), 7.66 (s, 1H), 6.88 (d, 13H), 4.33 (t, 30H), 1.82–1.77 (m, 37H), 1.54–1.23 (m, 23H).

P88.6. Yield: 85.1%. ¹H NMR (400 MHz, CDCl₃, TMS, ppm): δ = 8.12 (m, 4H), 7.96 (d, 2H), 7.77 (d, 2H), 7.66 (s, 1H), 7.22 (d, 15H), 6.88 (d, 15H), 4.33 (t, 39H), 1.82–1.77 (m, 33H), 1.52–1.48 (m, 36H).

P90.5. Yield: 91.3%. ¹H NMR (400 MHz, CDCl₃, TMS, ppm): δ = 8.12 (m, 7.0 Hz, 4H), 7.96 (d, 2H), 7.76 (d, 2H), 7.66 (s, 1H), 7.23 (d, 19H), 6.88 (d, 19H), 4.33 (q, 48H), 1.82–1.77 (m, 46H), 1.53–1.48 (m, 39H).

P96.0. Yield: 87.4%. ¹H NMR (400 MHz, CDCl₃, TMS, ppm): δ = 8.17 (m, 4H), 7.96 (d, 2H), 7.77 (d, 2H), 7.66 (s, 1H), 7.23 (d, 48H), 6.88 (d, 48H), 4.33 (q, 118H), 1.79 (m, 92H), 1.52–1.48 (m, 116H).

PBF. Yield: 86.7%. ¹H NMR (400 MHz, CDCl₃, TMS, ppm): δ = 7.22 (d, 2H), 6.88 (d, 2H), 4.33 (t, 4H), 1.79 (t, 4H), 1.52–1.48 (m, 4H).

1.4. Preparation of samples for latent fingerprints

Firstly, a fingertip was pressed onto ethanol-cleaned glass slides. Secondly, a PBFCS solution in chloroform was gradually added into silica powder, which was continuously stirred until a uniform mixture formed. Finally, after chloroform was evaporated completely, a small amount of the prepared powder was then gently applied to the fingerprinted surface of the glass slides, and the excess powder was removed to obtain the latent fingerprints.

2. Supporting data

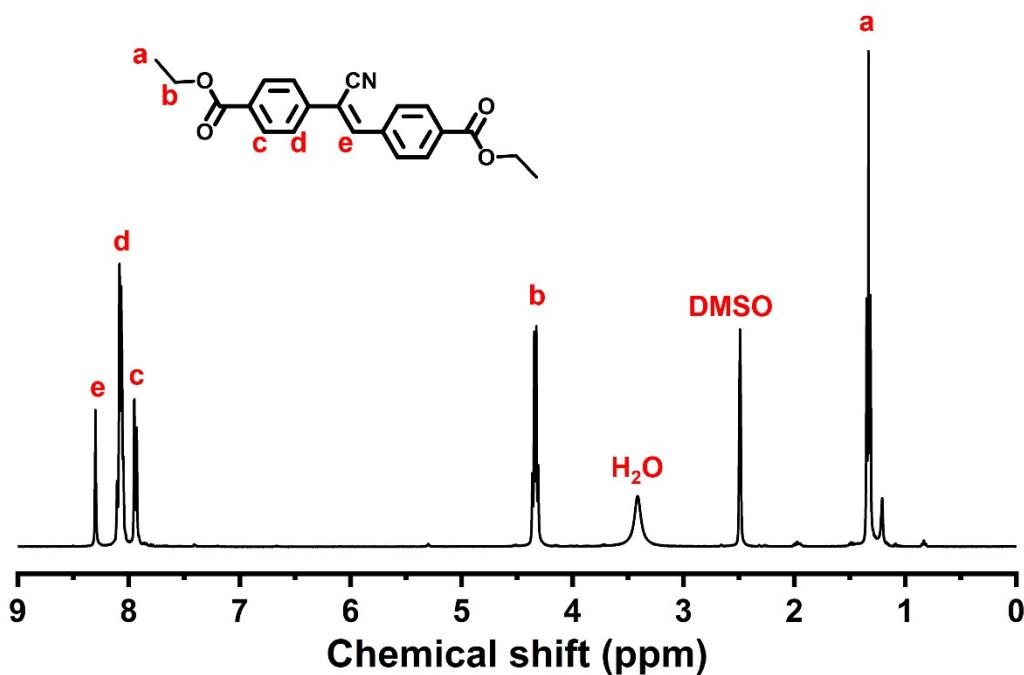


Figure S1. ¹H NMR spectrum of Z-CS in DMSO-*d*₆ at room temperature.

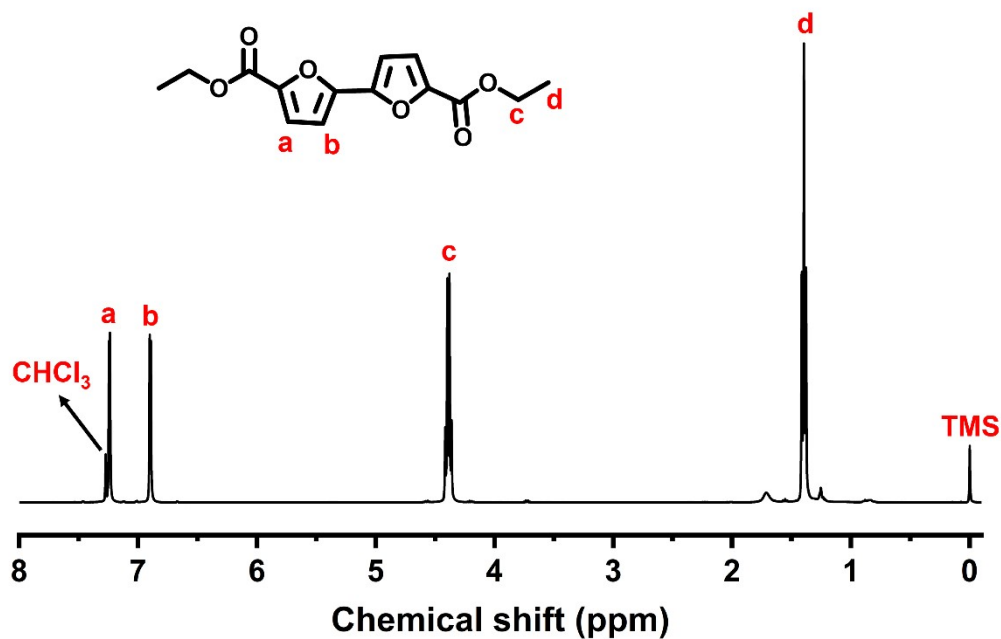


Figure S2. ^1H NMR spectrum of BFDCE in CDCl_3 at room temperature.

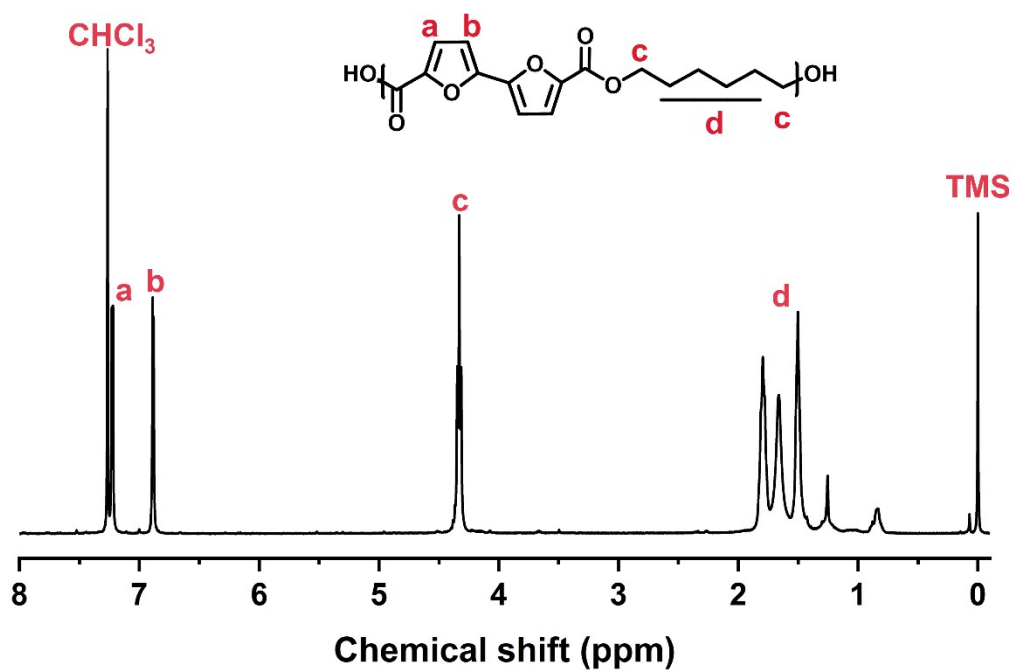


Figure S3. ^1H NMR spectrum of PBF in CDCl_3 at room temperature.

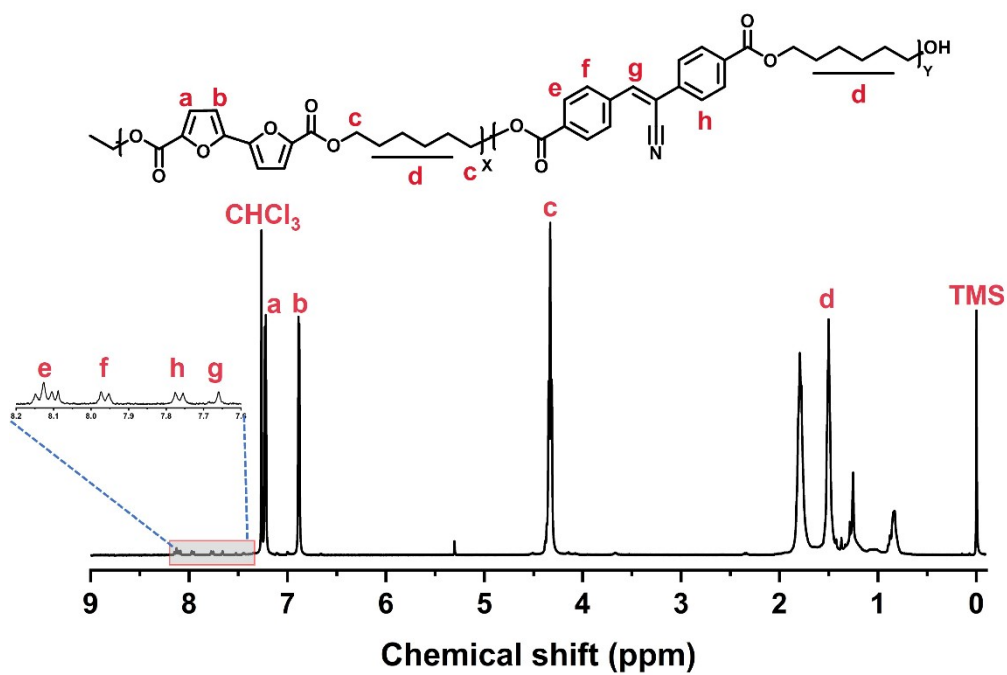


Figure S4. ^1H NMR spectrum of P96.0 in CDCl_3 at room temperature.

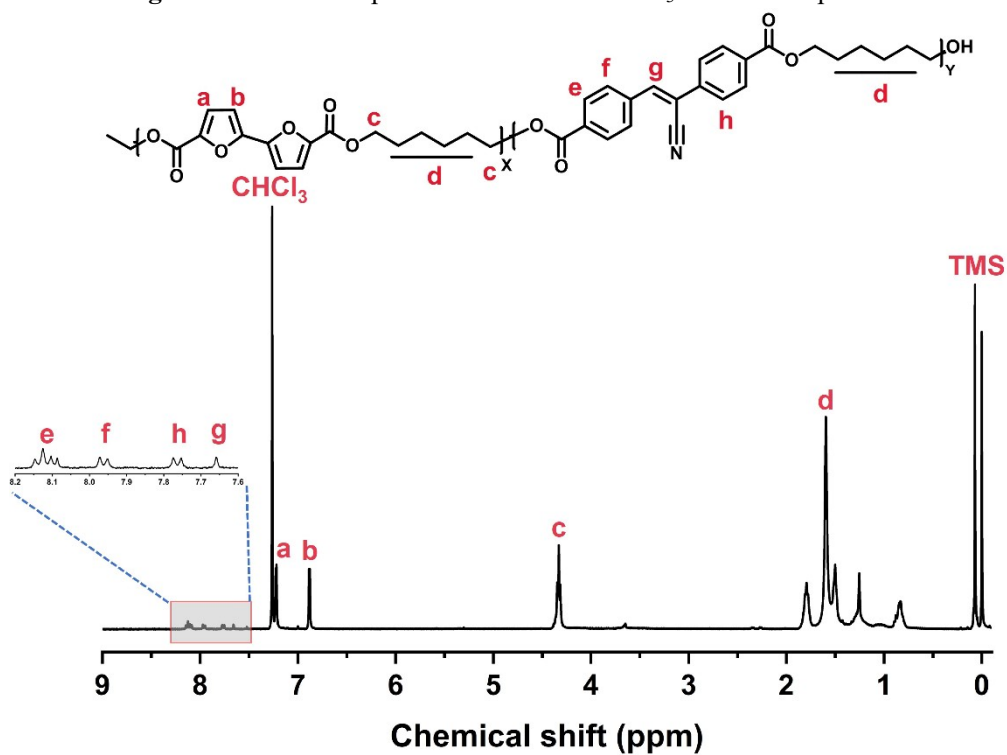


Figure S5. ^1H NMR spectrum of P90.5 in CDCl_3 at room temperature.

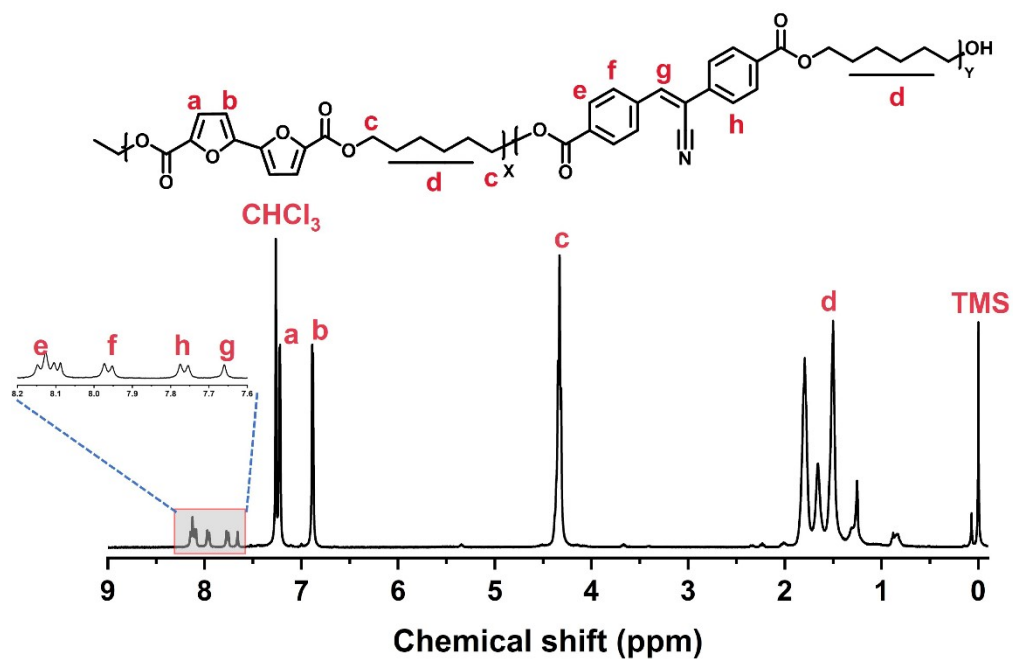


Figure S6. ^1H NMR spectrum of P88.6 in CDCl_3 at room temperature.

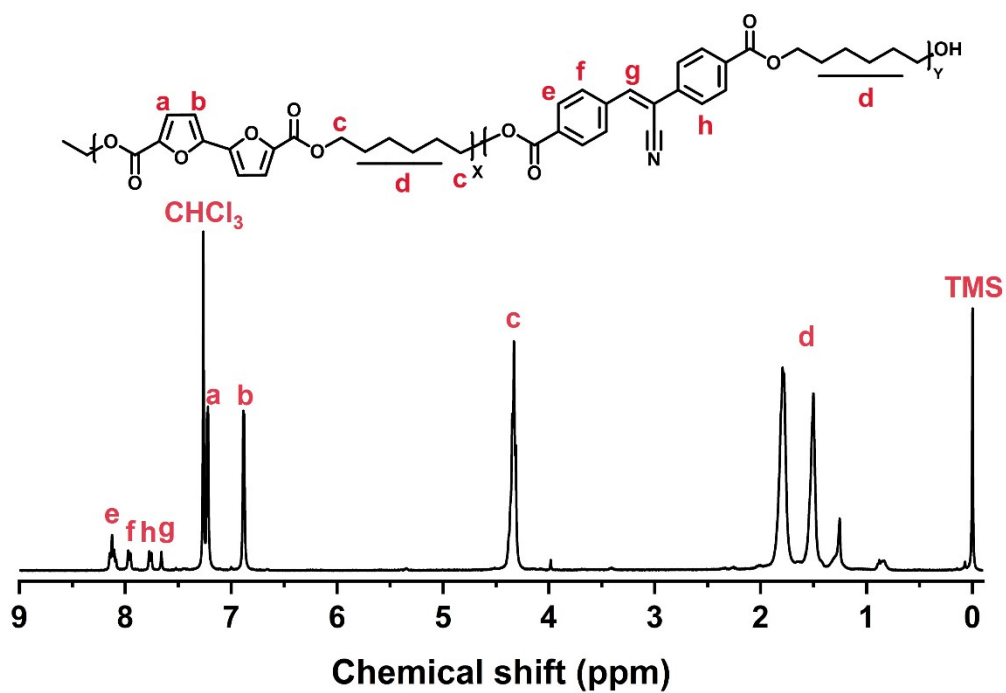


Figure S7. ^1H NMR spectrum of P86.7 in CDCl_3 at room temperature.

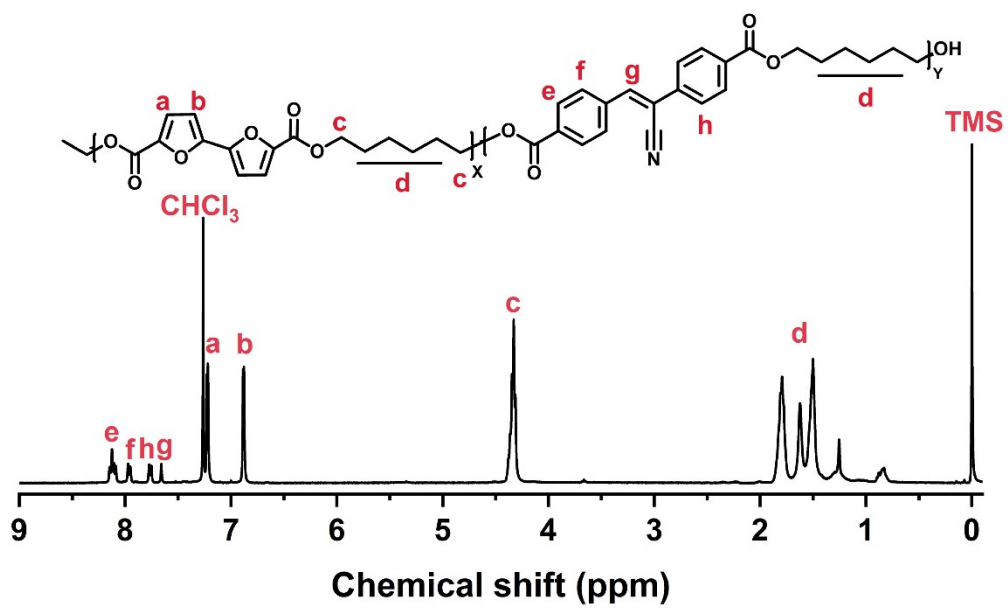


Figure S8. ¹H NMR spectrum of P80.5 in CDCl₃ at room temperature.

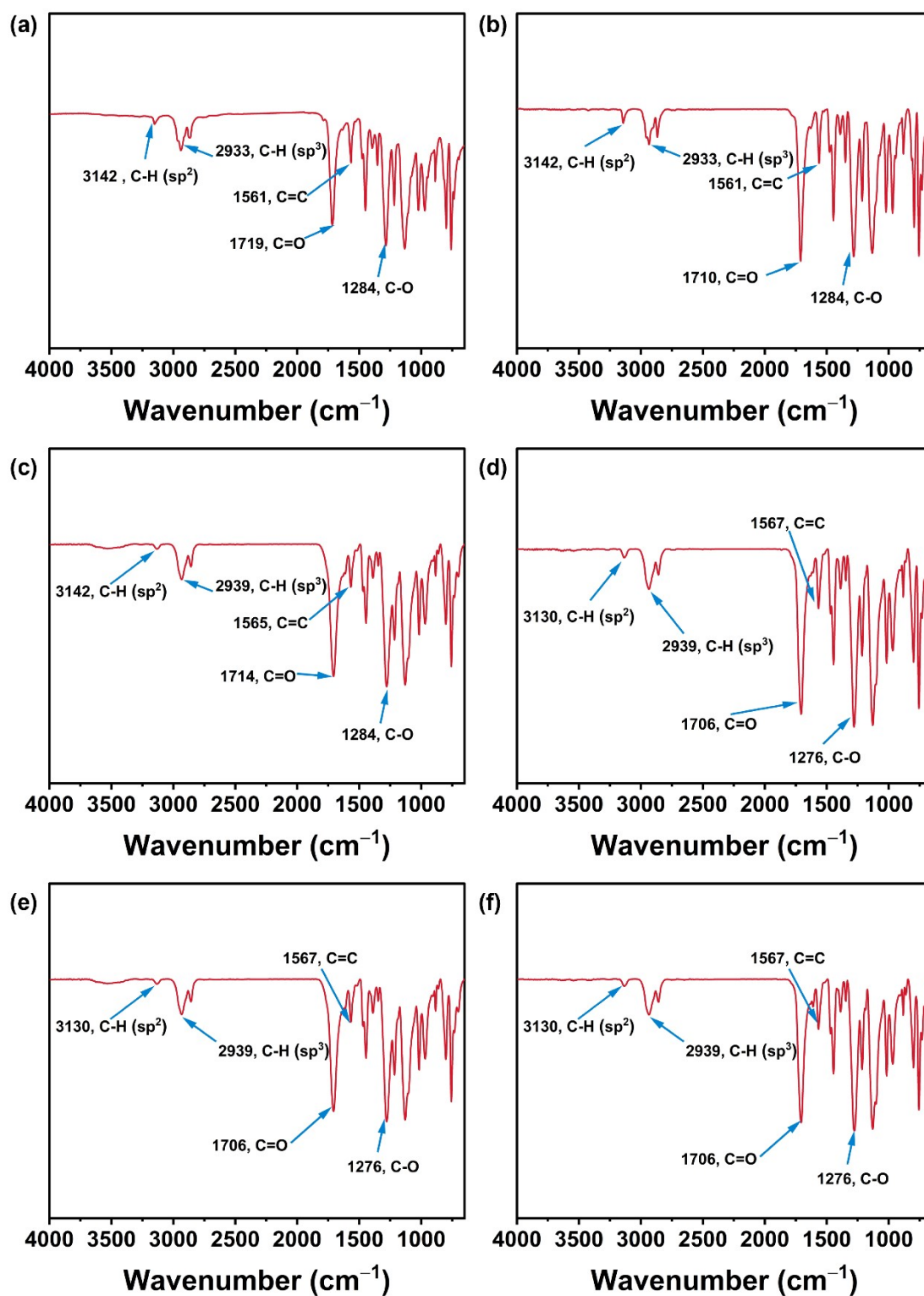


Figure S9. ATR-FTIR spectra of PBF (a), P96.0 (b), P90.5 (c), P88.6 (d), P86.7 (e) and P79.5 (f) in films.

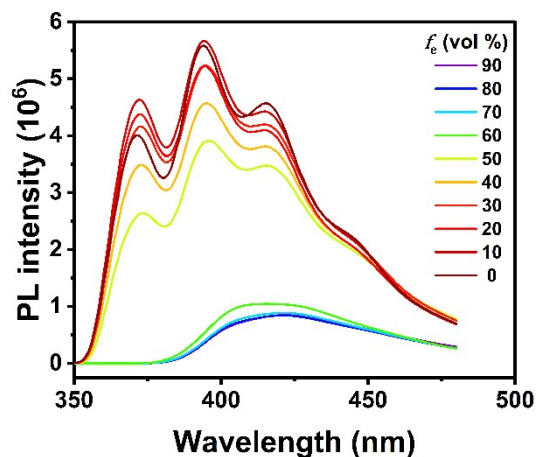


Figure S10. Fluorescence spectra of PBF in DCM/ethanol mixtures with different ethanol volume fraction (f_e) at room temperature.

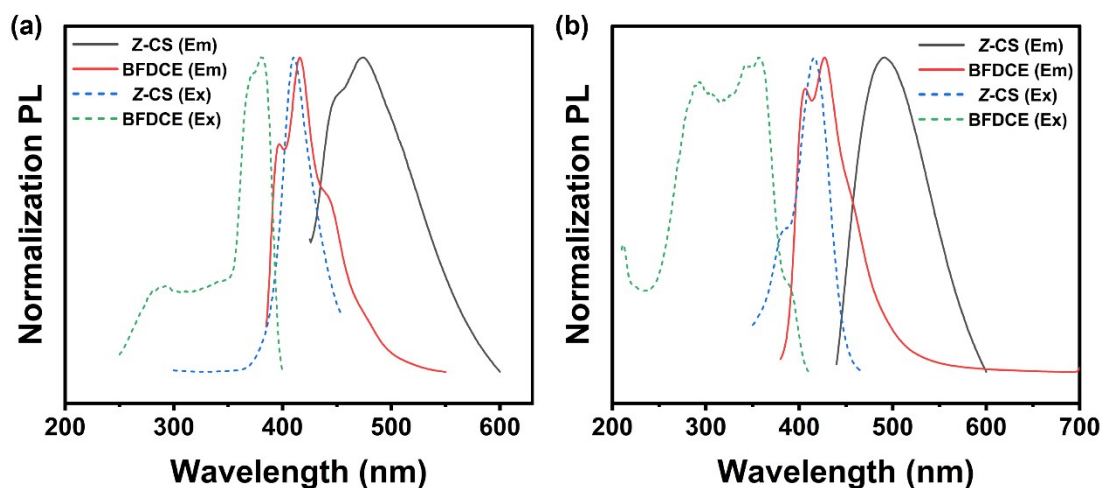


Figure S11. Emission spectra and excitation spectra of Z-CS and BFDCE in CHCl_3 (20 mg/mL) (a) and in solid state (b).

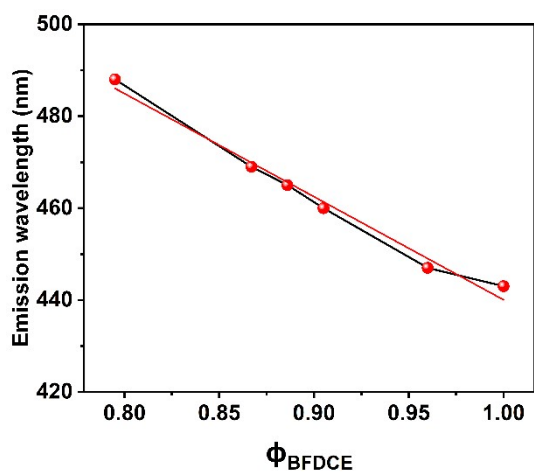


Figure S12. Plot of the maximum emission wavelength of PBFCS versus ϕ_{BFDCE} .

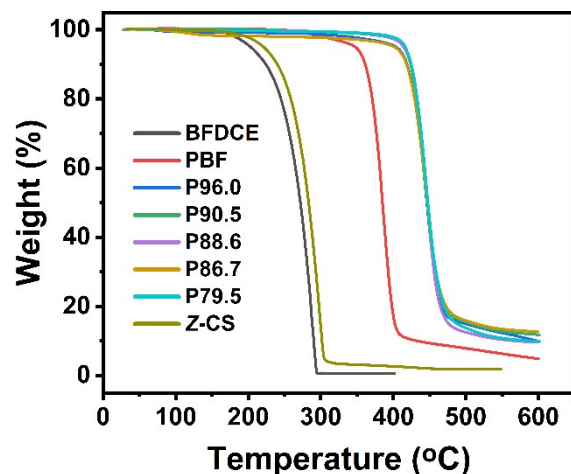


Figure S13. TGA curves of BFDCE, Z-CS, PBF and PBFCS at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere.

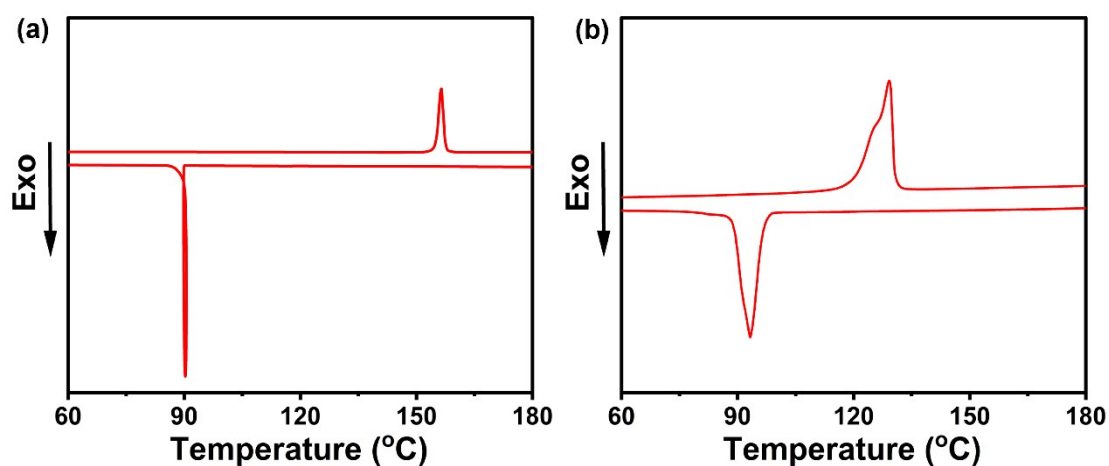


Figure S14. DSC curves of BFDCE (a) and Z-CS (b) at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere.

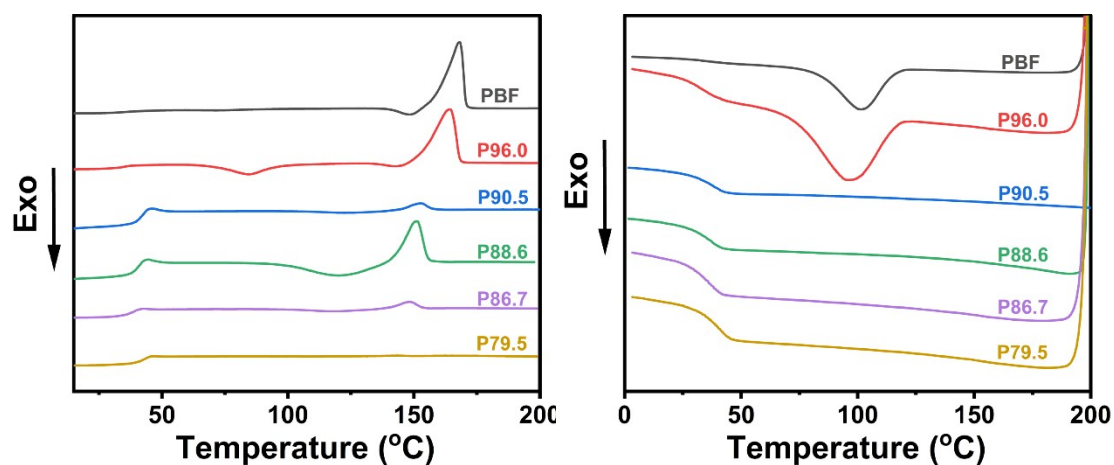


Figure S15. DSC curves of PBF and PBFCS on the second heating scans (a) and first cooling (b) at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere.

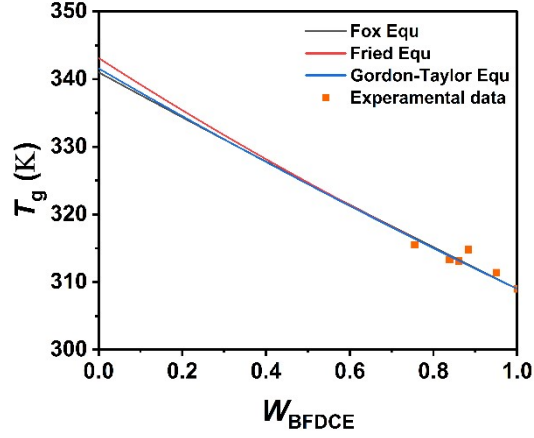


Figure S16. Glass transition temperature of the copolyesters as a function of BFDCE content and the fitting lines from Fox (black line), Fried (red line), and Gordon-Taylor (blue line) equations.

The experimental data can be fitted well by the following equations,

$$\text{Fox Equ.: } \frac{1}{T_{g,\text{copolymer}}} = \frac{W_{\text{BFDCE}}}{T_{g,\text{PBF}}} + \frac{W_{\text{CS}}}{T_{g,\text{PCS}}}$$

(1)

$$\ln(T_{g,\text{copolymer}}/T_{g,\text{PBF}}) = \frac{W_{\text{CS}} \times \ln\left(\frac{T_{g,\text{PCS}}}{T_{g,\text{PBF}}}\right)}{W_{\text{BFDCE}} \times \frac{T_{g,\text{PCS}}}{T_{g,\text{PBF}}} + W_{\text{CS}}}$$

Fried Equ.:

(2)

$$\text{Gordon-Taylor Equ.: } T_{g,\text{copolymer}} = \frac{W_{\text{BFDCE}} \times T_{g,\text{PBF}} + k \times W_{\text{CS}} \times T_{g,\text{PCS}}}{W_{\text{BFDCE}} + k \times W_{\text{CS}}}$$

(3)

where W_{BFDCE} and W_{CS} are the weight fractions of BFDCE and Z-CS, respectively; PBF and PCS represent the corresponding homopolyesters obtained from BFDCE and Z-CS, respectively; k is an adjustable parameter.

Table S1. The fitting parameters of Fox, Fried and Gordon-Taylor equations.

Equation name	Fitted equation	$T_{g,\text{PCS}}$ (K)	R^2
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Fox Equ.	$\frac{1}{T_{g,copolymer}} = \frac{w_{BFDCE}}{309.0} + \frac{w_{PCS}}{341.6}$	341.6 ± 4.1	0.738
Fried Equ.	$\ln\left(\frac{T_{g,copolymer}}{309.0}\right) = \frac{w_{CS} \ln\left(\frac{343.1}{309.0}\right)}{w_{BFDCE} \frac{343.1}{309.0} + w_{CS}}$	343.1 ± 4.6	0.734
Gordon-Taylor Equ.	$T_{g,copolymer} = \frac{309.0w_{BFDCE} + 307.2w_{CS}}{w_{BFDCE} + 0.9w_{CS}}$	341.3 ± 6.1	0.740

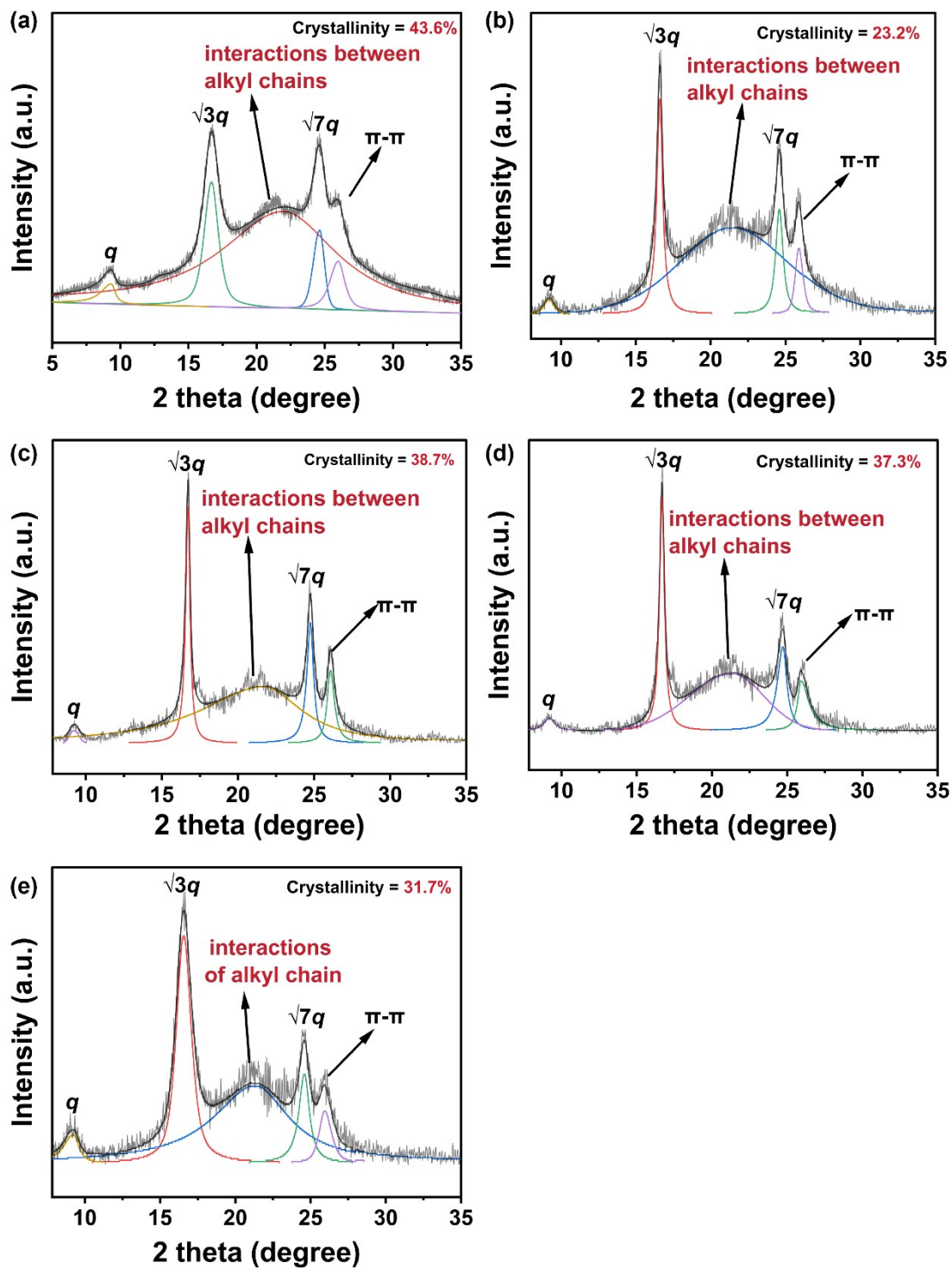


Figure S17. XRD patterns and analysis data for PBF (a), P90.5 (b), P88.6 (c), P86.7 (d), and P80.5 (e).

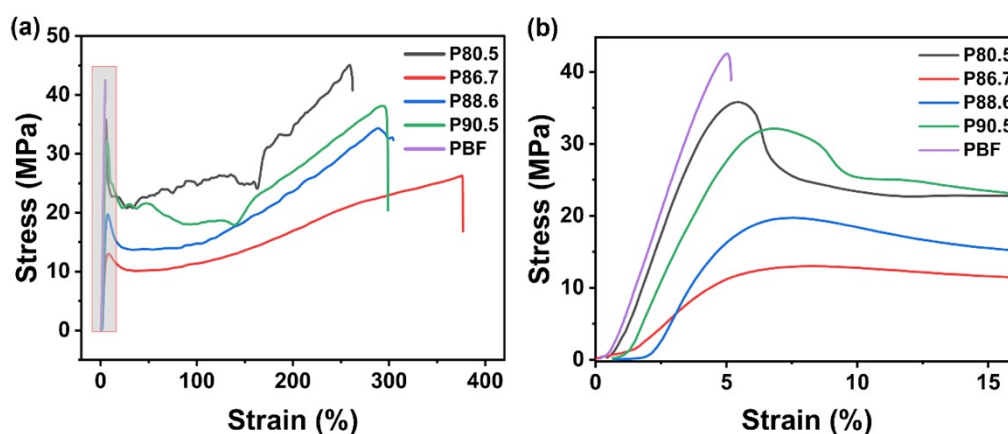


Figure S18. Stress-strain curves (a) and the partial curves (b) of PBFCS.

Table S2. Young's modulus (E), tensile strength at break (σ_b), elongation at break (ϵ_b) of common engineering plastics and general-purpose plastics.^a

sample	conditions	E (MPa)	σ_b (MPa)	ϵ_b (%)
Engineering plastics				
Nylon 6,6	23 °C	3300	82.7-90.3	30-60
	50% relative humidity (23 °C)		62.1-77.2	200- > 300
Polycarbonate	ASTM: D638	2380	62.1	110
Polyoxymethylene	296 K, ASTM D638	2825	60.6	40-75
Poly(butylene terephthalate)	ASTM D638	2600	55	200-300
General-purpose plastics				
Polyethylene, high-density	25 °C	60-290	10-60	18-40
Polyethylene, low-density	D 638	100-310	9-15	100-800
Polystyrene	Unoriented	3200-3400	30-60	1-4
Poly(ethylene terephthalate)		1700	50	180
Acrylonitrile-butadiene elastomers	ACN (20-40%)	2.9-3.6	13.4-17.9	387-466
Polypropylene, isotactic	APAO, Eastoflex™ P1010 and P1023	1.38	/	100-200
Poly(vinyl chloride)	With 10% dioctyl phthalate	2964	55.5	104

^a Source: Data collected in Mark, J. E. *Polymer Data Handbook*. Oxford University Press. 1998.

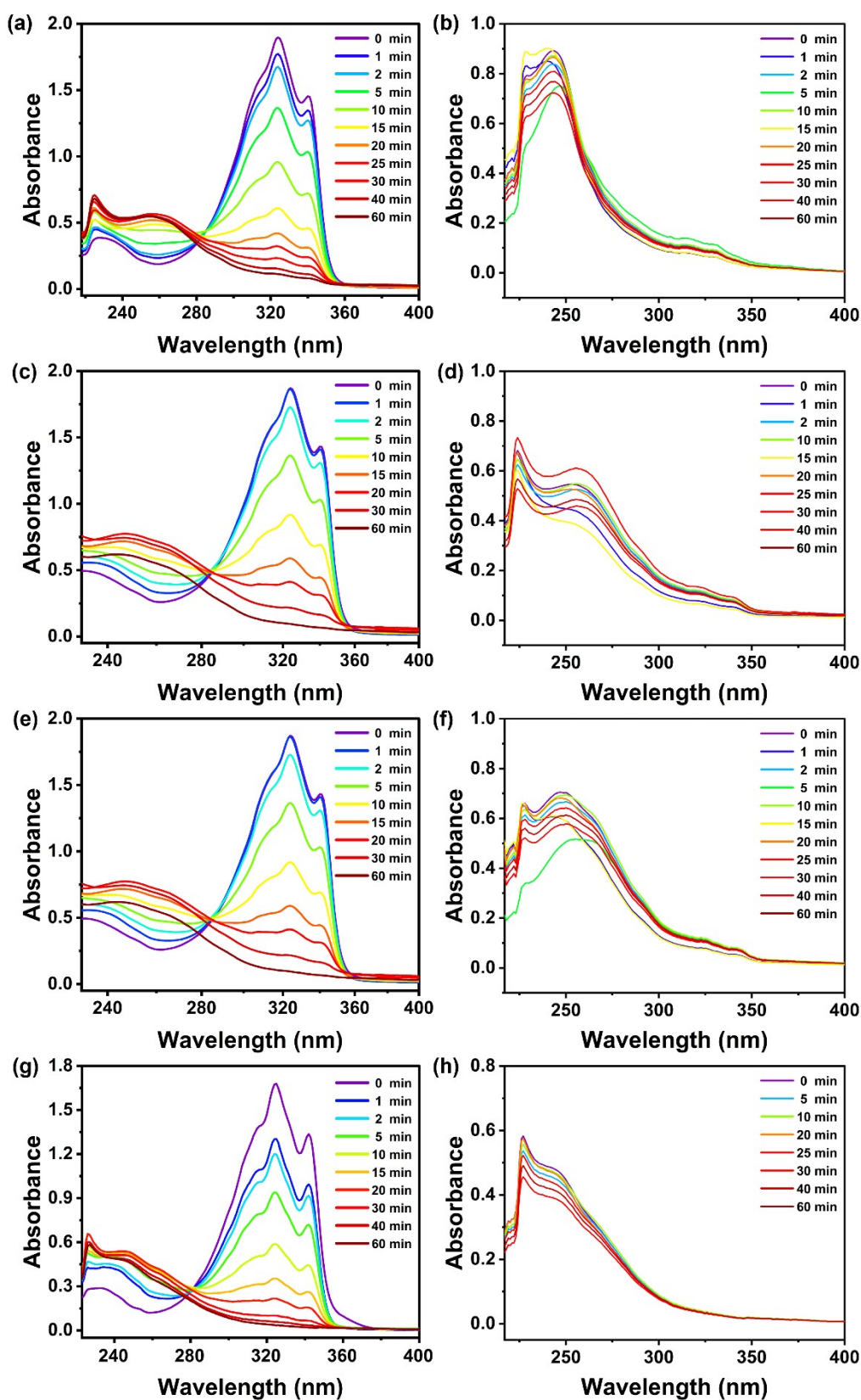


Figure S19. UV-vis absorption spectra of P96.5 (a), P88.6 (c), P86.7 (e), and P79.5 (g) in CHCl_3 upon 365 nm UV irradiation, and P96.5 (b), P88.6 (d), P86.7 (f), and P79.5 (h) in CHCl_3 then by 254 nm UV irradiation for different times at room temperature.

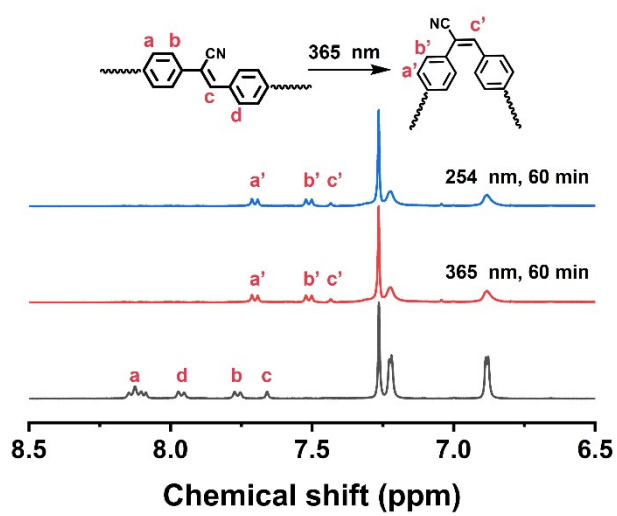


Figure S20. ¹H NMR spectra of P79.5 in CDCl₃ before and after irradiation with 365 nm UV light (20 mW cm⁻²) for 30 min, and subsequent 254 nm UV light (20 mW cm⁻²) for 60 min.

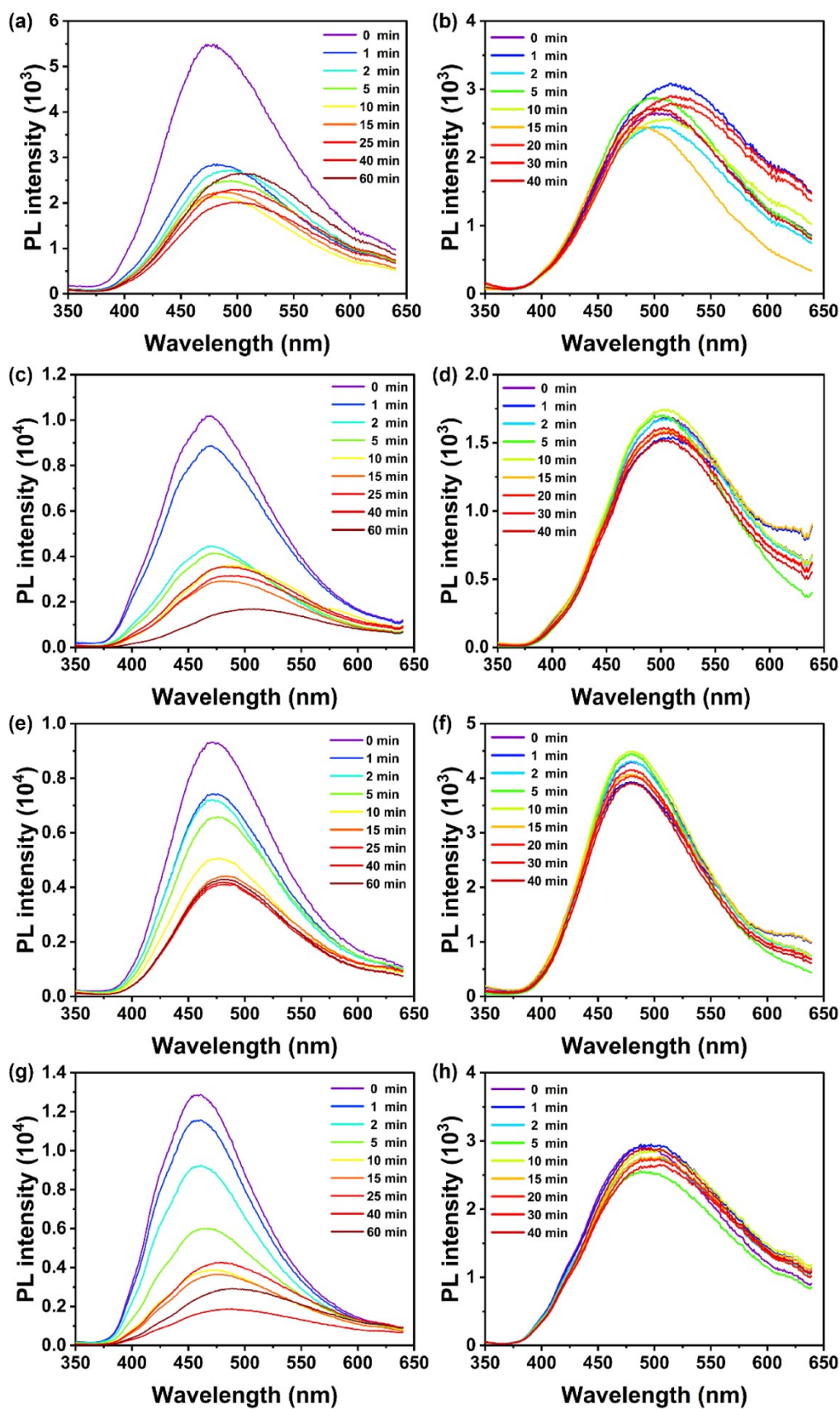


Figure S21. Fluorescence spectra of P96.5 (a), P88.6 (c), P86.7 (e), and P79.5 (g) in films upon 365 nm UV irradiation (20 mW cm^{-2}), and P96.5 (b), P88.6 (d), P86.7 (f), and P79.5 (h) in films then by 254 nm UV irradiation (20 mW cm^{-2}) for different times at room temperature.

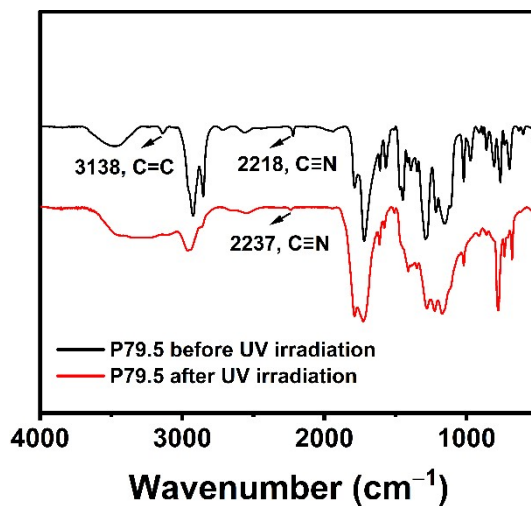


Figure S22. FT-IR spectra of P79.5 before and after 365 nm UV irradiation.

References

- 1 T. Wang, J. Wang, G. Liao, W. Wang, Y. Qiu, G. Yin, Y. Liao; X. Xie Flexible Films of Main-chain Luminescent Liquid Crystalline Polymers Containing Renewable Biobased Bifuran Moieties. *Eur. Polym. J.* **2023**, 199.
- 2 Y. Lei, S. Zhang, G. Shen, J. Zhu, J.-W. Xue, Z. Chen; G. Yin Feasible Synthesis of a Bifuran-Based Monomer for Polymer Synthesis from a Hemicellulose-Derived Platform. *Ind. Eng. Chem. Res.* **2020**, 59, 19876-19883.
- 3 T. P. Kainulainen, T. A. O. Parviainen, J. A. Sirvio, L. J. R. McGeachie; J. P. Heiskanen High Oxygen Barrier Polyester from 3,3'-Bifuran-5,5'-dicarboxylic Acid. *ACS Macro Lett.* **2023**, 12, 147-151.