

Electronic Supplementary Information

Development of completely furfural-based renewable polyesters with controllable properties

Haiyan Zhang,^{a,c} Min Jiang,^{b,c} Yuanpeng Wu,^{*a} Lu Li,^{b,c} Zhipeng Wang,^{b,c} Rui Wang,^{*b,c} and Guangyuan Zhou,^{*b,c}

^a School of New Energy and Materials, State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, 610500, China.

^b Division of Energy Materials (DNL22), Dalian Institute of Chemical Physics of the Chinese Academy of Sciences, Dalian, 116023, China;

^c Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renmin Street 5625, 130022 Changchun, P. R. China.

*Corresponding author E-mail address:

ypwu@swpu.edu.cn; wangrui87@dicp.ac.cn; gyzhou@dicp.ac.cn

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■ Materials

Succinic anhydride (SA, purity > 99%), 1,4-butanediol (1,4-BDO, purity > 99%), 2-furoic acid (FCA, purity > 98%), maleic anhydride (MA, purity > 99%) and tetrabutyl titanate (TBT, purity > 99%) were purchased from Acros Organics (Belgium). Various inorganic salts (NaNO_2 , KNO_3 , NaNO_3 , KHCO_3 , NaHCO_3 , KOAc , NaOAc and HCOONa) and furan (purity > 99%) were purchased from Beijing InnoChem Science & Technology Co., Ltd.. Potassium carbonate (K_2CO_3 > 99%), potassium phosphate (K_3PO_4 > 99%), potassium permanganate (KMnO_4 , purity > 99%), tert-butyl alcohol (TBA, purity > 99%), and paraformaldehyde ($(\text{CH}_2\text{O})_n$, purity > 96%) were purchased from Tianjin Guangfu Fine Chemical Research Institute. Diethyl ether (Et_2O), methanol (MeOH), and ethyl acetate (EtOAc) were purchased from Beijing Chemicals Works. All reagents were used as received without any purification.

■ General Methods

The ^1H NMR spectra, ^{13}C NMR spectra, 2D COSY and HMBC spectra were recorded on a Bruker spectrometer (^1H 600 MHz, ^{13}C 150 MHz or ^1H 400 MHz, ^{13}C 100 MHz) at 25 °C with tetramethylsilane (TMS) as an internal reference and the sample (10 mg for ^1H NMR and 30 mg for ^{13}C NMR, respectively) was dissolved in 0.5 mL of dimethylsulfoxide-*d* ($\text{DMSO-}d_6$), chloroform-*d* (CDCl_3), and trifluoroacetic acid-*d* (TFA-*d*). ^1H NMR chemical shifts are referenced to residual solvent peaks in TFA-*d*, CDCl_3 , $\text{DMSO-}d_6$ at 11.37, 7.20 and 2.50 ppm, respectively. ^{13}C NMR chemical shifts are referenced to residual solvent peaks in TFA-*d*, CDCl_3 and $\text{DMSO-}d_6$ at 162.68-161.82 ppm, 77.36-76.72 ppm and 46.62-39.37 ppm, respectively.

Fourier Transform Infrared (FTIR) spectra were reported by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) with VERTEX 70 spectrophotometer (Bruker, Germany) equipped with a zinc selenide (ZnSe) crystal in the wavenumber region of 500-4000 cm^{-1} , and the ATR-FTIR spectra were carried out at a resolution of 4 cm^{-1} and 128 co-added scans.

Size-Exclusion Chromatography (SEC) was recorded on a Waters 1515 HPLC apparatus to test number-average molecular weight (M_n), weight-average molecular weight (M_w) and its distribution (PDI). Hexafluoroisopropanol (HFIP) with sodium trifluoroacetate (CF_3COONa , 5 mmol/L) was used as an eluent (1.0 mL/min, 35 °C) to evaluate relative molecular weight of different polyesters, and polymethyl methacrylate (PMMA) standards was used to establish a calibration curve.

Thermogravimetric Analysis (TGA) was performed on a Mettler-Toledo TGA/DSC 1 Instrument to evaluate the thermal stability of copolyesters. About 5-10 mg of each sample was heated from 30 to 600 °C at a heating rate of 10 °C/min under a nitrogen flow of 20 mL/min and the weight loss of 5% ($T_{d,5\%}$) is a criterion to estimate that thermal stability of polymers and the maximum decomposition rate (T_{dmax}) is evaluated as well from TGA curves.

Differential Scanning Calorimetry (DSC) measurement was conducted by a Mettler-Toledo DSC 3 to investigate the thermal transition behaviors of copolyesters. The specific testing parameters were as follows: appropriately 5-10 mg of each sample was tested under a standard heat-cool-heat cycle from -60 to 200 °C or 0 to 200 °C depending on the samples. Both heating and cooling rate were 10 °C/min, and the temperature at 200 °C was held for 3 min after first heating to eliminate the thermal history. The relevant results were obtained

from TA Universal Analysis. For isothermal crystallization experiments, the treatment of samples was the following: similarly, the thermal history was removed by heating up to 200 °C and held for 3 min, and then cooled to the selected crystallization temperature of samples, where it was left to crystallize until saturation.

The Polarized Optical Microscope (POM) (ZEISS, Axio Imager A2) was conducted to observe the morphology of spherulites of crystal polyesters, equipped with a Linkam hot stage (THMS600). The samples were first melted at 180-200 °C for 3 min to diminish thermal history, and quenched to the selected crystallization temperature at -60 °C/min until crystallization completed.

Wide-angle X-ray Diffraction (WAXD) patterns were recorded on a Bruker (D8 ADVANCE) X-ray diffractometer from 5° to 60° at room temperature with Cu K α radiation and the scan rate of 2°/min. The films of copolyesters were prepared by hot-press molding at different temperature ranging from 80 °C to 200 °C. Before testing, the films were conditioned at room temperature for two days.

Tensile Properties were carried out with Instron-1121 tester at 25 °C in accordance with ASTM D638. Dumbbell-shaped specimens with width and thickness of 10 mm and 0.5 mm were prepared via hot-pressing, and the crosshead speed was 5 mm/min. The relevant parameters, including tensile strength (σ_m), elongation at break (ϵ_b), and Young's modulus (E_t), were obtained.

Gas Barrier Properties were examined by Labthink VAC-V2 gas permeability tester using thin films (150-200 μ m) from the melt-press/quench procedures and they were conducted at 23.0 °C with the relative humidity (RH) of 0%. The purity of CO₂ reached over 99.99%. The

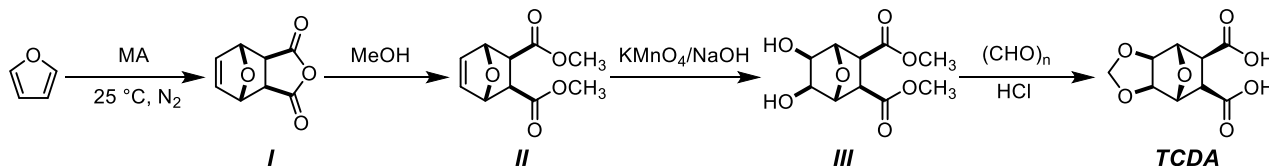
samples were cut into circular discs with a diameter around 3.0 cm, and were measured at three times to ensure the accuracy of the results.

Ultraviolet-visible (UV-vis) spectra were recorded on SHIMADZU UV-2600 spectrophotometer, and the absorption spectra (200-800 nm) from melt-pressed films of polyesters and solutions of monomers TCDA and FDCA (1 mg/100 mL dimethyl sulfoxide) were obtained.

■ Monomers Preparation

Synthesis of tricyclic acid monomer TCDA.

The synthesis of TCDA was according to our previous reports as follows.¹



Diels-Alder reaction for the preparation of I. Maleic anhydride (98.1 g, 1.0 mol) was dispersed into furan (362.10 mL, 5.0 mol), and stirred at room temperature under N₂ atmosphere for 24 h. The crystallized product in the solvent was filtered, washed with cool Et₂O and dried under dry nitrogen atmosphere to afford a white crystal (143.9 g, yield 86%).
¹H NMR (400 MHz, DMSO-*d*₆): δ 6.58 (s, 2 H), 5.34 (s, 2 H), 3.31 (s, 2 H).

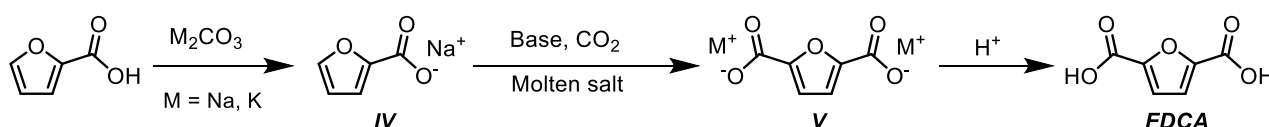
Esterification reaction for the preparation of II. Concentrated sulfuric acid (25.0 mL) was added dropwise to the 800 mL MeOH with anhydride I (83.07 g, 0.5 mol), and stirred for 16 h. After concentrating under the vacuum, the precipitate was filtered, washed with ice MeOH

and dried in the vacuum to afford **II** (88.2 g, yield 83%) as a white crystal. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.46 (s, 2 H), 5.27 (s, 2 H), 3.71 (s, 6 H), 2.83 (s, 2 H).

Oxidation reaction for the preparation of **III**. A solution of potassium permanganate (18.9 g, 76.0 mmol) in 300 mL water was added to a mixture solution of **II** (20.56 g, 120.0 mmol) and 0.4 M NaOH in tertbutyl alcohol (200 mL) under the ice bath. The mixture was stirred for 10 min and then quenched with a saturated aqueous solution of sodium metabisulfite. After filtering the tert-butyl alcohol was removed from in vacuo. The solution was extracted with boiling ethyl acetate repeatedly, and the combined organic layers dried over anhydrous sodium sulphate, filtered, and concentrated in vacuo to afford a white crystal (7.7 g, yield 26%). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 4.81 (s, 2 H), 4.32 (s, 2 H), 3.77 (s, 2 H), 3.53 (s, 6 H), 3.02 (s, 2 H).

Acetal reaction for the preparation of **TCDA**. Paraformaldehyde (50.0 g) and **III** (50.0 g, 0.20 mol) were dissolved in 360 mL concentrated hydrochloric acid and refluxed at 105 °C for 6 h. The precipitate was filtered, washed with ice water and dried in vacuum to afford a white solid powder (35.82 g, yield 78%). $^1\text{H NMR}$ (600 MHz, $\text{DMSO-}d_6$): δ 12.26 (s, 2 H), 4.94 (s, 1 H), 4.74 (s, 1 H), 4.56 (s, 2 H), 4.28 (s, 2 H), 2.86 (s, 2 H). $^{13}\text{C NMR}$ (150 MHz, $\text{DMSO-}d_6$): δ 172.19, 96.86, 81.86, 81.02, 46.09.

Synthesis of 2,5-furan-dicarboxylic acid (FDCA) monomer.



Neutralization reaction for the preparation of **IV**. Potassium carbonate (K_2CO_3 , 1.0 mmol,

138 mg) or sodium carbonate (Na_2CO_3 , 1.0 mmol, 106 mg) was dissolved in minimal deionized water. Then, furoic acid (2.0 mmol, 224 mg) was added in the alkaline solution. After removing the water by rotary evaporation, the resulted furoate was dried under vacuum at 100 °C for 2 h.

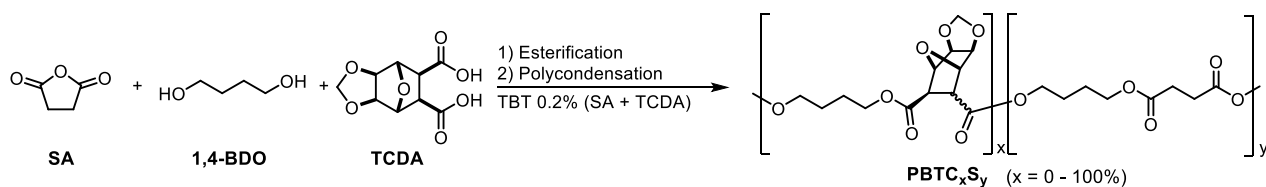
C-H activation reaction for the preparation of V. In a typical experiment, dry sodium furancarboxylate ($\text{FCA}\cdot\text{Na}^+$, 2 mmol, 288 mg), K_2CO_3 (2.5 mmol, 345 mg) and sodium formate (HCOONa , 30 wt% of K_2CO_3 and $\text{FCA}\cdot\text{Na}^+$, 190 mg) were loaded into a 100 mL Parr reactor. The reactor was degassed and flushed with CO_2 for three times at 150 °C. Subsequently, the mixture was heated to 280 °C for 6 h at 8 atm of flowing CO_2 . Once the programmed sequence had completed, the reaction was cooled to room temperature and the solid product mixture was dissolved in D_2O and analyzed by ^1H NMR spectrum. ^1H NMR (600 MHz, D_2O): δ 8.35 (s, 0.72 H), 7.48 (s, 0.93 H), 6.89 (s, 11.62 H), 6.43 (s, 1 H), 3.02 (s, 0.56 H), 1.80 (s, 2.20 H).

Large-scale C-H activation reaction for the preparation of FDCA. The mixture of $\text{FCA}\cdot\text{Na}^+$ (0.25 mol, 36.0 g), K_2CO_3 (0.31 mmol, 43.12 g) and HCOONa (30 wt% of K_2CO_3 and $\text{FCA}\cdot\text{Na}^+$, 23.7 g) prepared as previously described were loaded into a 10 L Parr reactor. The reactor was degassed and flushed with CO_2 at 180 °C for an overnight. The mixture was gradient heated up to 280 °C during 10 h, and then reacted at this temperature for 15 h under 8 atm of flowing CO_2 . Once the programmed sequence had completed, the reaction was cooled to room temperature and the solid product mixture was dissolved in a minimum of H_2O . After decolorizing with activated carbon, the filtrate was acidified by concentrated hydrochloric acid to pH of 1-2, and the product precipitated from the solution was collected

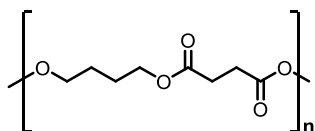
on a Büchner funnel. After dried in vacuum to afford FDCA as an off-white powder (20.0 g, yield 51%). In order to obtain the polymerization grade monomer, the FDCA production was further purified by washing with hot ethyl acetate repeatedly. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 13.64 (s, 2 H), 7.32 (s, 2 H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 159.35, 147.47, 118.85.

■ Melt co-Polymerizations

Polymerization of SA and TCDA with 1,4-BDO.

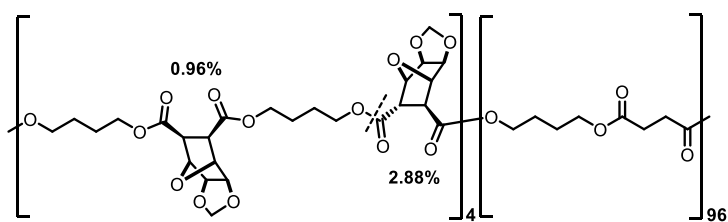


100% SA synthesized homopolymer PBS.



SA (2.00 g, 20 mmol), 1,4-BDO (4.5 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, and 180 °C for 4 h. Then the polycondensation reaction was performed under vacuum at 230 °C for 5.5 h. After cooling to room temperature, the resultant polymer was obtained as white solid material without further purification. ^1H NMR (600 MHz, $\text{TFA-}d$): δ 4.12 (s, 4 H), 2.67 (s, 4 H), 1.67 (s, 4 H). ^{13}C NMR (150 MHz, $\text{TFA-}d$): δ 176.95, 66.73, 29.33, 24.95.

95% SA and 5% TCDA synthesized PBTC₄S₉₆.



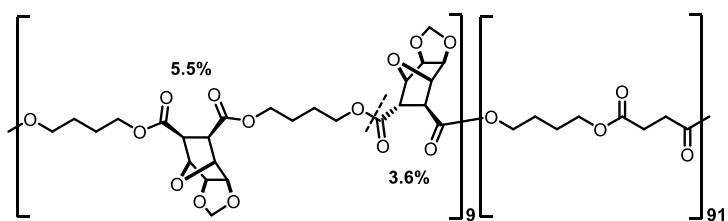
SA (1.90 g, 19 mmol), TCDA (0.23 g, 1.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 3.5 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 5.02 – 5.11 (m, 0.11 H), 4.83 – 4.85 (m, 0.03 H), 4.49 – 4.54 (m, 0.08 H), 4.14 – 4.21 (m, 4.16 H), 3.61 (s, 0.03 H), 3.16 (s, 0.05 H), 2.70 (s, 4 H), 1.69 (s, 4.16 H). ¹³C NMR (150 MHz, TFA-*d*): δ 176.96, 174.44, 173.84, 172.47, 84.48, 81.45, 79.71, 66.73, 47.86, 47.32, 46.31, 29.33, 24.95.

$$\text{PBS [\%]} = (I_{2.70} / 4) / (I_{2.70} / 4 + I_{4.49-4.54} / 2) \times 100\% = 96.1\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.16} - I_{3.61}) / 2] / (I_{2.70} / 4 + I_{4.49-4.54} / 2) \times 100\% = 1.0\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.61} / (I_{2.70} / 4 + I_{4.49-4.54} / 2) \times 100\% = 2.9\%.$$

90% SA and 10% TCDA synthesized copolyester PBTC₉S₉₁.



SA (1.80 g, 18 mmol), TCDA (0.46 g, 2.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a

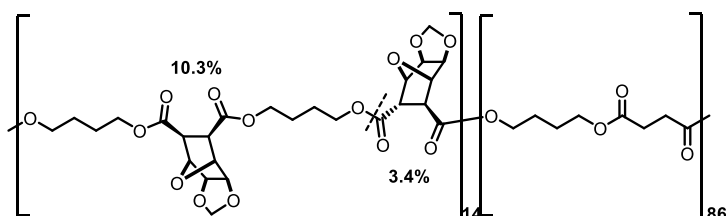
stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 3.5 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 5.07 – 5.13 (m, 0.30 H), 4.82 – 4.84 (m, 0.09 H), 4.48 – 4.55 (m, 0.20 H), 4.13 – 4.20 (m, 4.40 H), 3.61 (s, 0.04 H), 3.17 (s, 0.16 H), 2.68 (s, 4 H), 1.68 (s, 4.40 H). ¹³C NMR (150 MHz, TFA-*d*): δ 176.95, 174.49, 173.84, 172.46, 97.38, 97.17, 84.48, 82.59, 81.43, 79.71, 67.68, 66.73, 47.93, 47.22, 46.30, 29.32, 24.95.

$$\text{PBS [\%]} = (I_{2.68} / 4) / (I_{2.68} / 4 + I_{4.48-4.55} / 2) \times 100\% = 90.9\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.17} - I_{3.61}) / 2] / (I_{2.68} / 4 + I_{4.48-4.55} / 2) \times 100\% = 5.5\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.61} / (I_{2.68} / 4 + I_{4.48-4.55} / 2) \times 100\% = 3.6\%.$$

85% SA and 15% TCDA synthesized copolyester PBTC₁₄S₈₆.



SA (1.70 g, 17 mmol), TCDA (0.69 g, 3.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 3.5 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600

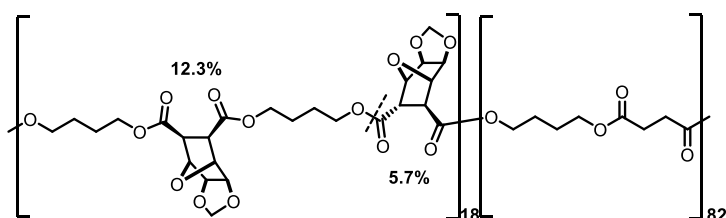
MHz, TFA-*d*): δ 5.01 – 5.14 (m, 0.50 H), 4.82 – 4.85 (m, 0.16 H), 4.49 – 4.54 (m, 0.33 H), 4.14 – 4.20 (m, 4.66 H), 3.61 (s, 0.04 H), 3.18 (s, 0.28 H), 2.69 (s, 4 H), 1.69 (s, 4.66 H). ^{13}C NMR (150 MHz, TFA-*d*): δ 176.97, 174.45, 173.86, 172.48, 97.41, 97.19, 82.62, 81.45, 67.70, 66.66, 47.95, 47.24, 46.33, 29.34, 24.97.

$$\text{PBS [\%]} = (I_{2.69} / 4) / (I_{2.69} / 4 + I_{4.49-4.54} / 2) \times 100\% = 85.8\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.18} - I_{3.61}) / 2] / (I_{2.69} / 4 + I_{4.49-4.54} / 2) \times 100\% = 10.3\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.61} / (I_{2.69} / 4 + I_{4.49-4.54} / 2) \times 100\% = 3.4\%.$$

80% SA and 20% TCDA synthesized copolyester PBTC₁₈S₈₂.



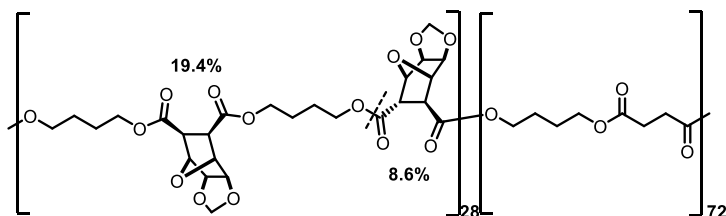
SA (1.60 g, 16 mmol), TCDA (0.92 g, 4.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ^1H NMR (600 MHz, TFA-*d*): δ 4.99 – 5.13 (m, 0.66 H), 4.81 – 4.84 (m, 0.22 H), 4.47 – 4.53 (m, 0.44 H), 4.13 – 4.18 (m, 4.88 H), 3.60 (s, 0.07 H), 3.16 (s, 0.37 H), 2.68 (s, 4 H), 1.67 (s, 4.88 H). ^{13}C NMR (150 MHz, TFA-*d*): δ 170.85, 168.33, 167.73, 166.36, 91.29, 91.07, 78.38, 75.34, 73.62, 61.57, 60.63, 41.83, 41.12, 40.20, 23.22, 18.84.

$$\text{PBS [\%]} = (I_{2.68} / 4) / (I_{2.68} / 4 + I_{4.47-4.53} / 2) \times 100\% = 82\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.16} - I_{3.60}) / 2] / (I_{2.68} / 4 + I_{4.47-4.53} / 2) \times 100\% = 12.3\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.60} / (I_{2.68} / 4 + I_{4.47-4.53} / 2) \times 100\% = 5.7\%.$$

70% SA and 30% TCDA synthesized copolyester PBTC₂₈S₇₂.



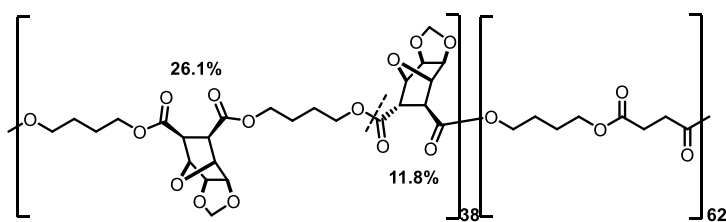
SA (1.40 g, 14 mmol), TCDA (1.38 g, 6.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 5.03 – 5.16 (m, 1.24 H), 4.85 – 4.88 (m, 0.39 H), 4.51 – 4.56 (m, 0.78 H), 4.16 – 4.23 (m, 5.64 H), 3.63 (s, 0.12 H), 3.20 (s, 0.66 H), 2.72 (s, 4 H), 1.71 (s, 5.64 H). ¹³C NMR (150 MHz, TFA-*d*): δ 177.00, 174.48, 173.88, 172.51, 97.44, 97.22, 84.53, 82.64, 81.49, 79.77, 67.72, 66.78, 47.98, 47.27, 46.35, 29.37, 24.99.

$$\text{PBS} [\%] = (I_{2.72} / 4) / (I_{2.72} / 4 + I_{4.51-4.56} / 2) \times 100\% = 72\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.20} - I_{3.63}) / 2] / (I_{2.72} / 4 + I_{4.51-4.56} / 2) \times 100\% = 19.4\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.63} / (I_{2.72} / 4 + I_{4.51-4.56} / 2) \times 100\% = 8.6\%.$$

60% SA and 40% TCDA synthesized copolyester PBTC₃₈S₆₂.



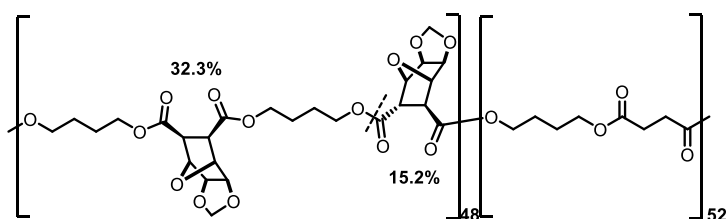
SA (1.20 g, 12 mmol), TCDA (1.84 g, 8.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 5.03 – 5.16 (m, 1.88 H), 4.85 – 4.87 (m, 0.61 H), 4.51 – 4.56 (m, 1.22 H), 4.16 – 4.23 (m, 6.47 H), 3.63 (s, 0.19 H), 3.20 (s, 1.03 H), 2.72 (s, 4 H), 1.71 (s, 6.48 H). ¹³C NMR (150 MHz, TFA-*d*): δ 176.91, 174.40, 173.80, 172.41, 97.36, 97.14, 82.54, 81.41, 79.68, 67.64, 66.70, 66.60, 47.89, 47.19, 46.28, 29.28, 24.91.

$$\text{PBS [\%]} = (I_{2.72} / 4) / (I_{2.72} / 4 + I_{4.51-4.56} / 2) \times 100\% = 62.1\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.20} - I_{3.63}) / 2] / (I_{2.72} / 4 + I_{4.51-4.56} / 2) \times 100\% = 26.1\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.63} / (I_{2.72} / 4 + I_{4.51-4.56} / 2) \times 100\% = 11.8\%.$$

50% SA and 50% TCDA synthesized copolyester PBTC₄₈S₅₂.



SA (1.00 g, 10 mmol), TCDA (2.30 g, 10.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a

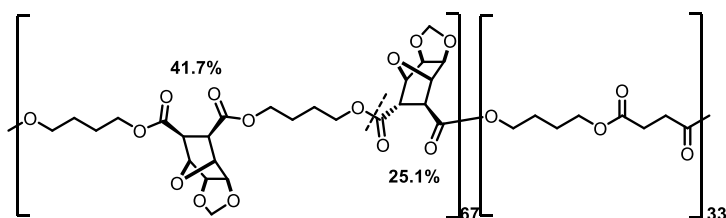
stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 5.05 – 5.17 (m, 2.72 H), 4.86 – 4.88 (m, 0.90 H), 4.51 – 4.57 (m, 1.81 H), 4.17 – 4.24 (m, 7.62 H), 3.64 (s, 0.29 H), 3.20 (s, 1.52 H), 2.73 (s, 4 H), 1.72 (s, 7.62 H). ¹³C NMR (150 MHz, TFA-*d*): δ 176.97, 174.45, 173.84, 172.47, 97.41, 97.20, 84.52, 82.62, 81.46, 79.69, 67.70, 66.76, 66.66, 47.95, 47.24, 46.33, 29.34, 24.97.

$$\text{PBS [\%]} = (I_{2.73} / 4) / (I_{2.73} / 4 + I_{4.51-4.57} / 2) \times 100\% = 52.5\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.20} - I_{3.64}) / 2] / (I_{2.73} / 4 + I_{4.51-4.57} / 2) \times 100\% = 32.3\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.64} / (I_{2.73} / 4 + I_{4.51-4.57} / 2) \times 100\% = 15.2\%.$$

30% SA and 70% TCDA synthesized copolyester PBTC₆₇S₃₃.



SA (0.60 g, 6 mmol), TCDA (3.22 g, 14.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz,

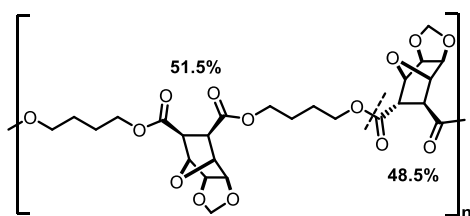
TFA-*d*): δ 5.05 – 5.18 (m, 6.16 H), 4.87 – 4.90 (m, 2.04 H), 4.53 – 4.58 (m, 4.06 H), 4.18 – 4.25 (m, 12.23 H), 3.66 (s, 0.76 H), 3.22 (s, 3.29 H), 2.74 (s, 4 H), 1.74 (s, 12.21 H). ^{13}C NMR (150 MHz, TFA-*d*): δ 176.95, 174.43, 173.82, 172.45, 97.41, 97.19, 84.51, 82.61, 81.46, 79.70, 67.68, 67.57, 66.65, 47.93, 47.23, 46.32, 29.32, 24.95.

$$\text{PBS [\%]} = (I_{2.74} / 4) / (I_{2.74} / 4 + I_{4.53-4.58} / 2) \times 100\% = 33\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.22} - I_{3.66}) / 2] / (I_{2.74} / 4 + I_{4.53-4.58} / 2) \times 100\% = 41.7\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.66} / (I_{2.74} / 4 + I_{4.53-4.58} / 2) \times 100\% = 25.1\%.$$

100% TCDA synthesized homopolymer PBTC.

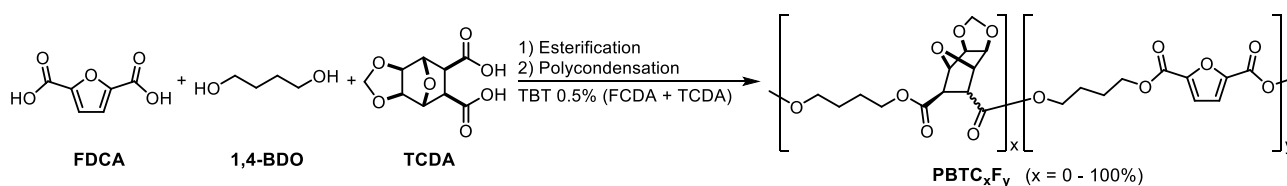


TCDA (4.60 g, 20 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h, 220 °C for 3.5 h and 230 °C for 1 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ^1H NMR (600 MHz, TFA-*d*): δ 5.03 – 5.16 (m, 3 H), 4.85 – 4.87 (m, 1 H), 4.50 -4.56 (m, 2 H), 4.18 -4.23 (m, 4H), 3.63 (s, 0.48 H), 3.19 (s, 1.50 H), 1.74 (s, 4 H). ^{13}C NMR (150 MHz, TFA-*d*): δ 174.40, 173.76, 172.41, 97.39, 97.17, 84.49, 82.57, 81.44, 79.71, 67.63, 67.53, 47.91, 47.20, 46.30, 24.94, 24.87, 24.77.

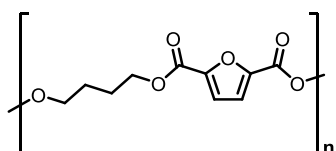
$$\text{PBTC}_{\text{exo-exo}} [\%] = (I_{3.19} - I_{3.63}) / (I_{3.19} + I_{3.63}) \times 100\% = 51.5\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = 2 I_{3.63} / (I_{3.19} + I_{3.63}) \times 100\% = 48.5\%.$$

Polymerization of FCDA and TCDA with 1,4-BDO

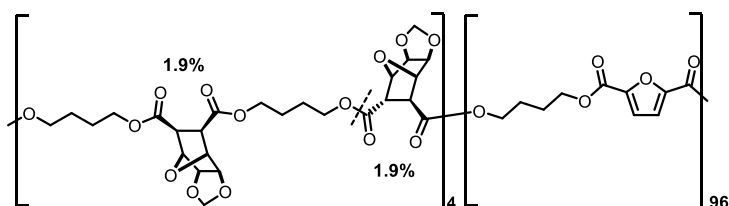


100% FDCA synthesized homopolymer PBF.



FDCA (3.12 g, 20.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h, 220 °C for 3.5 h and 230 °C for 1 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.20 (s, 2 H), 4.38 (s, 4 H), 1.85 (s, 4 H). ¹³C NMR (150 MHz, TFA-*d*): δ 161.49, 147.08, 120.21, 67.18, 24.89.

95% FDCA and 5% TCDA synthesized copolymer PBTC₄F₉₆.



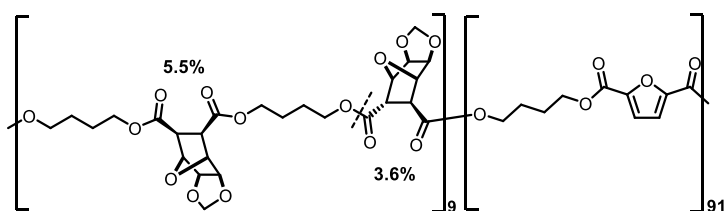
FDCA (2.96 g, 19.0 mmol), TCDA (0.23 g, 1.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (39 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h, 220 °C for 3.5 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.23 (s, 2 H), 5.01 – 5.13 (m, 0.12 H), 4.82 – 4.85 (m, 0.04 H), 4.17 – 4.49 (m, 4.25 H), 3.62 – 3.68 (m, 0.02 H), 3.19 (s, 0.06 H), 1.81 – 1.89 (m, 4.16 H). ¹³C NMR (150 MHz, TFA-*d*): δ 161.61, 147.21, 120.34, 82.59, 81.42, 67.63, 67.31, 47.30, 25.02.

$$\text{PBF [\%]} = (I_{7.23} / 2) / [I_{7.23} / 2 + (I_{3.19} + I_{3.62-3.68}) / 2] \times 100\% = 96.1\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.19} - I_{3.62-3.68}) / 2] / [I_{7.23} / 2 + (I_{3.19} + I_{3.62-3.68}) / 2] \times 100\% = 1.9\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.62-3.68} / [I_{7.23} / 2 + (I_{3.19} + I_{3.62-3.68}) / 2] \times 100\% = 1.9\%.$$

90% FDCA and 10% TCDA synthesized copolyester PBTC₉F₉₁.



FDCA (2.81 g, 18 mmol), TCDA (0.46 g, 2.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed

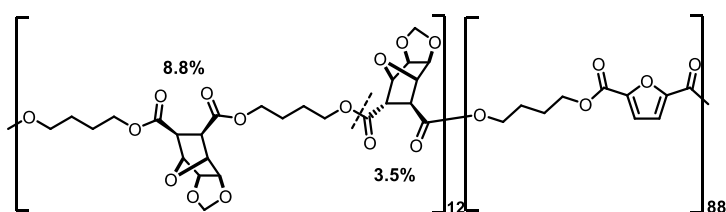
under vacuum at 190 °C for 1 h and 220 °C for 2 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.22 (s, 2 H), 5.00 – 5.12 (m, 0.28 H), 4.81 – 4.84 (m, 0.08 H), 4.48 – 4.53 (m, 0.20 H), 4.16 – 4.41 (m, 4.39 H), 3.61 (s, 0.04 H), 3.18 (s, 0.16 H), 1.76 – 1.88 (m, 4.40 H). ¹³C NMR (150 MHz, TFA-*d*): δ 174.47, 173.86, 161.64, 147.23, 120.37, 97.40, 97.18, 84.49, 82.61, 81.46, 79.73, 67.65, 67.33, 47.97, 47.24, 46.33, 25.05, 24.84.

$$\text{PBF [\%]} = (I_{7.22} / 2) / (I_{7.22} / 2 + I_{4.48-4.53} / 2) \times 100\% = 90.9\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.18} - I_{3.61}) / 2] / (I_{7.22} / 2 + I_{4.48-4.53} / 2) \times 100\% = 5.5\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.61} / (I_{7.22} / 2 + I_{4.48-4.53} / 2) \times 100\% = 3.6\%.$$

85% FDCA and 15% TCDA synthesized copolyester PBTC₁₂F₈₈.



FDCA (2.65 g, 17 mmol), TCDA (0.69 g, 3.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 2 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.26 (s, 2 H), 5.04 – 5.17 (m, 0.42 H), 4.85 – 4.88 (m, 0.14 H), 4.20 – 4.57 (m, 4.88 H), 3.65 (s, 0.04 H), 3.21 (s, 0.24 H), 1.84 – 1.91 (m, 4.60 H). ¹³C NMR (150 MHz, TFA-*d*): δ 173.82, 161.61, 147.17, 120.28, 82.53, 81.45, 67.58, 67.25, 47.16,

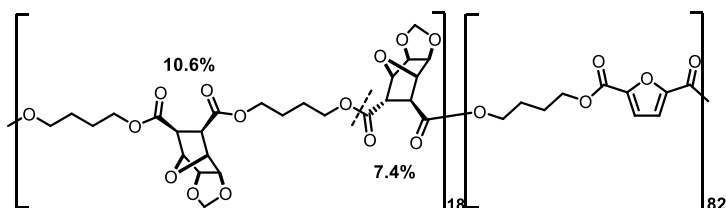
24.96, 24.83, 24.75.

$$\text{PBF [\%]} = (I_{7.26} / 2) / [I_{7.26} / 2 + (I_{3.21} + I_{3.65}) / 2] \times 100\% = 87.7\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.21} - I_{3.65}) / 2] / [I_{7.26} / 2 + (I_{3.21} + I_{3.65}) / 2] \times 100\% = 8.8\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.65} / [I_{7.26} / 2 + (I_{3.21} + I_{3.65}) / 2] \times 100\% = 3.5\%.$$

80% FDCA and 20% TCDA synthesized copolyester PBTC₁₈F₈₂.



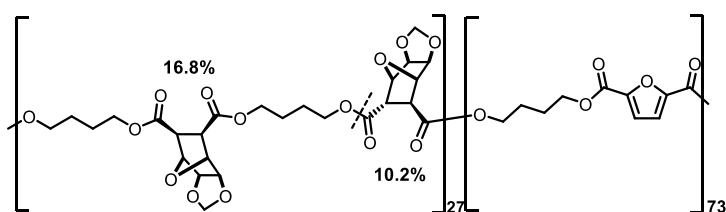
FDCA (2.50 g, 16 mmol), TCDA (0.92 g, 4.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.25 (s, 2 H), 5.02 – 5.15 (m, 0.66 H), 4.83 – 4.86 (m, 0.21 H), 4.50 – 4.56 (m, 0.44 H), 4.18 – 4.43 (m, 4.88 H), 3.64 (s, 0.09 H), 3.17 – 3.20 (m, 0.35 H), 1.73 – 1.90 (m, 4.88 H). ¹³C NMR (150 MHz, TFA-*d*): δ 174.43, 173.83, 172.46, 161.61, 147.20, 120.59, 97.37, 97.15, 84.45, 82.58, 81.42, 67.62, 67.30, 67.20, 47.93, 47.21, 46.30, 25.01, 24.80.

$$\text{PBF [\%]} = (I_{7.25} / 2) / (I_{7.25} / 2 + I_{4.50-4.56} / 2) \times 100\% = 82.0\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.17-3.20} - I_{3.64}) / 2] / (I_{7.25} / 2 + I_{4.50-4.56} / 2) \times 100\% = 10.6\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.64} / (I_{7.25} / 2 + I_{4.50-4.56} / 2) \times 100\% = 7.4\%.$$

70% FDCA and 30% TCDA synthesized copolyester PBTC₂₇F₇₃.



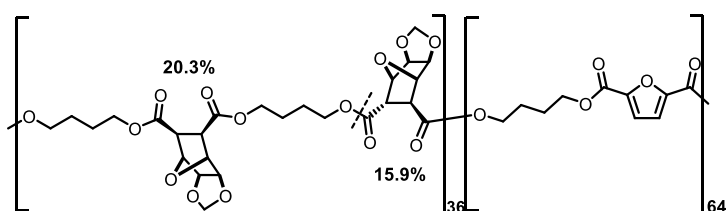
FDCA (2.18 g, 14 mmol), TCDA (1.38 g, 6.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.26 (s, 2 H), 5.04 – 5.13 (m, 1.11 H), 4.84 – 4.87 (m, 0.37 H), 4.20 – 4.56 (m, 6.30 H), 3.64 (s, 0.14 H), 3.20 (s, 0.60 H), 1.83 – 1.91 (m, 5.49 H). ¹³C NMR (150 MHz, TFA-*d*): δ 168.34, 167.73, 166.35, 155.51, 141.11, 114.24, 91.27, 91.05, 78.38, 76.49, 75.33, 73.61, 61.20, 41.82, 41.12, 40.21, 18.92, 18.78, 18.71.

$$\text{PBF [\%]} = (I_{7.26} / 2) / [I_{7.26} / 2 + (I_{3.20} + I_{3.64}) / 2] \times 100\% = 73.0\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.20} - I_{3.64}) / 2] / [I_{7.26} / 2 + (I_{3.20} + I_{3.64}) / 2] \times 100\% = 16.8\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.64} / [I_{7.26} / 2 + (I_{3.20} + I_{3.64}) / 2] \times 100\% = 10.2\%.$$

60% FDCA and 40% TCDA synthesized copolyester PBTC₃₆F₆₄.



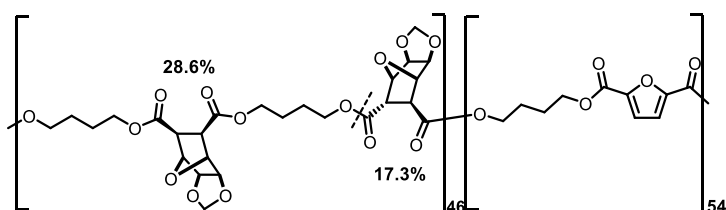
FDCA (1.87 g, 12 mmol), TCDA (1.84 g, 8.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.27 (s, 2 H), 5.04 – 5.17 (m, 1.71 H), 4.85 – 4.88 (m, 0.57 H), 4.52 – 4.57 (m, 1.15 H), 4.21 – 4.45 (m, 6.38 H), 3.65 (s, 0.25 H), 3.21 (s, 0.89 H), 1.74 – 1.92 (m, 6.37 H). ¹³C NMR (150 MHz, TFA-*d*): δ 174.45, 173.85, 172.48, 161.63, 147.23, 120.37, 97.41, 97.20, 82.60, 81.46, 79.74, 67.65, 67.33, 67.23, 47.97, 47.24, 46.33, 25.11, 24.91, 24.83.

$$\text{PBF [\%]} = (I_{7.27} / 2) / (I_{7.27} / 2 + I_{4.52-4.57} / 2) \times 100\% = 63.5\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.21} - I_{3.65}) / 2] / (I_{7.27} / 2 + I_{4.52-4.57} / 2) \times 100\% = 20.3\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.65} / (I_{7.27} / 2 + I_{4.52-4.57} / 2) \times 100\% = 15.9\%.$$

50% FCDA and 50% TCDA synthesized copolyester PBTC₄₆F₅₄.



FDCA (1.56 g, 10 mmol), TCDA (2.30 g, 10.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h,

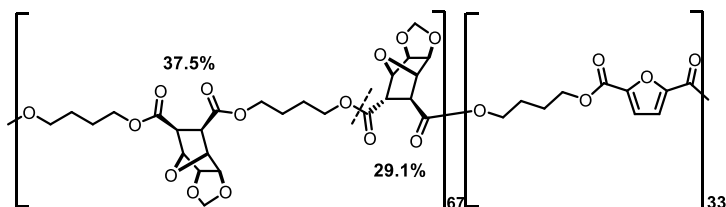
180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.26 (s, 2 H), 5.03 – 5.16 (m, 2.55 H), 4.84 – 4.87 (m, 0.84 H), 4.51 – 4.56 (m, 1.70 H), 4.19 – 4.44 (m, 7.41 H), 3.64 (s, 0.32 H), 3.18 – 3.25 (m, 1.38 H), 1.73 – 1.91 (m, 7.41 H). ¹³C NMR (150 MHz, TFA-*d*): δ 174.34, 173.75, 172.38, 161.54, 147.14, 120.28, 97.31, 97.09, 82.52, 81.36, 81.27, 67.57, 67.24, 67.14, 47.85, 47.15, 46.24, 25.02, 24.96, 24.82, 24.75.

$$\text{PBF [\%]} = (I_{7.26} / 2) / (I_{7.26} / 2 + I_{4.51-4.56} / 2) \times 100\% = 54.1\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.18-3.25} - I_{3.64}) / 2] / (I_{7.26} / 2 + I_{4.51-4.56} / 2) \times 100\% = 28.6\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.64} / (I_{7.26} / 2 + I_{4.51-4.56} / 2) \times 100\% = 17.3\%.$$

30% FDCA and 70% TCDA synthesized copolyester PBTC₆₇F₃₃.



FDCA (0.47 g, 6 mmol), TCDA (3.22 g, 14.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.27 (s, 2 H), 5.04 – 5.17 (m, 5.99 H), 4.86 – 4.94 (m, 1.99 H),

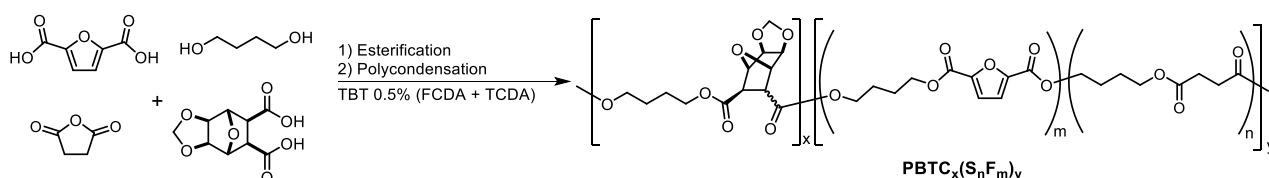
4.52 – 4.57 (m, 3.98 H), 4.19 – 4.41 (m, 12.18 H), 3.65 (s, 0.87 H), 3.21 (s, 3.11 H), 1.75 – 1.92 (m, 12.19 H). ¹³C NMR (150 MHz, TFA-*d*): δ 174.36, 173.75, 172.95, 172.37, 161.61, 147.16, 120.31, 97.33, 97.11, 82.53, 81.38, 81.28, 67.58, 67.50, 67.15, 47.86, 47.16, 46.25, 25.04, 24.97, 24.84, 24.76.

$$\text{PBF [\%]} = (I_{7.27} / 2) / (I_{7.27} / 2 + I_{4.52-4.57} / 2) \times 100\% = 33.4\%;$$

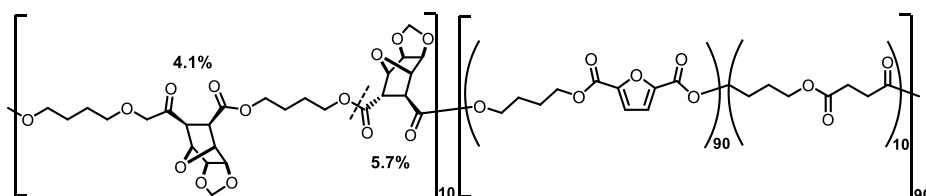
$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.21} - I_{3.65}) / 2] / (I_{7.27} / 2 + I_{4.52-4.57} / 2) \times 100\% = 37.5\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.65} / (I_{7.27} / 2 + I_{4.52-4.57} / 2) \times 100\% = 29.1\%.$$

Polymerization of SA, FCDA and TCDA with 1,4-BDO.



9% SA, 81% FDCA and 10% TCDA synthesized copolyester PBTC₁₀(S₁₀F₉₀)₉₀.



SA (0.18 g, 1.8 mmol), FDCA (2.53 g, 16.2 mmol), TCDA (0.46 g, 2.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.23 (s, 2 H), 5.00 – 5.13 (m, 0.36 H), 4.82

– 4.85 (m, 0.12 H), 4.14 – 4.49 (m, 5.15 H), 3.62 (s, 0.07 H), 3.18 (s, 0.17 H), 2.70 (s, 0.44 H), 1.69 – 1.89 (m, 4.91 H). ¹³C NMR (150 MHz, TFA-*d*): δ 176.87, 174.33, 173.74, 172.34, 161.61, 147.47, 120.26, 97.29, 97.08, 84.38, 82.50, 81.36, 79.62, 67.53, 67.22, 66.62, 47.86, 47.12, 46.22, 29.26, 24.94, 24.84, 24.76.

$$\text{PBF [\%]} = (I_{7.23} / 2) / [I_{7.23} / 2 + I_{2.70} / 4 + (I_{3.18} + I_{3.62}) / 2] \times 100\% = 81.3\%;$$

$$\text{PBS [\%]} = (I_{2.70} / 4) / [I_{7.23} / 2 + I_{2.70} / 4 + (I_{3.18} + I_{3.62}) / 2] \times 100\% = 8.9\%;$$

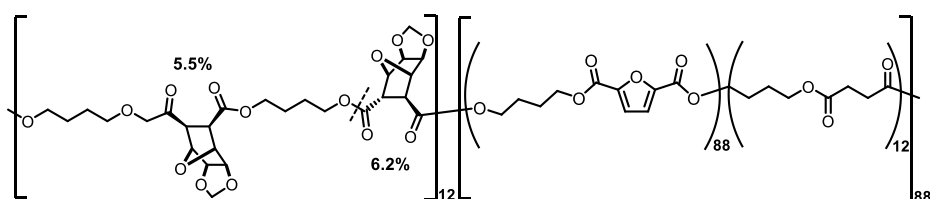
$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.18} - I_{3.62}) / 2] / [I_{7.23} / 2 + I_{2.70} / 4 + (I_{3.18} + I_{3.62}) / 2] \times 100\% = 4.1\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.62} / [I_{7.23} / 2 + I_{2.70} / 4 + (I_{3.18} + I_{3.62}) / 2] \times 100\% = 5.7\%;$$

$$\text{PBF in PBSF [\%]} = (I_{7.23} / 2) / [I_{7.23} / 2 + I_{2.70} / 4] \times 100\% = 90.1\%;$$

$$\text{PBS in PBSF [\%]} = (I_{2.70} / 4) / [I_{7.23} / 2 + I_{2.70} / 4] \times 100\% = 9.9\%.$$

10.5% SA, 77.5 % FDCA and 12% TCDA synthesized copolyester PBTC₁₂(S₁₂F₈₈)₈₈.



SA (0.211 g, 2.11 mmol), FDCA (2.42 g, 15.49 mmol), TCDA (0.55 g, 2.4 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 2.5 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.24 (s, 2 H), 5.01 – 5.14 (m, 0.38 H), 4.82-4.85 (m, 0.12 H), 4.38 – 4.54 (m, 4.15 H), 4.18 (s, 1.08 H), 3.62 (s, 0.08 H), 3.19 (s, 0.22 H), 2.71 (s, 0.52 H), 1.70 – 1.89 (m, 5.04 H). ¹³C NMR (150 MHz, TFA-*d*): δ 176.64,

173.53, 161.31, 146.91, 120.03, 97.08, 96.85, 84.17, 82.29, 81.13, 79.40, 67.33, 67.00, 66.41, 47.64, 46.92, 46.01, 29.02, 24.72, 24.60, 24.51.

$$\text{PBF [\%]} = (I_{7.24} / 2) / [I_{7.24} / 2 + I_{2.71} / 4 + (I_{3.19} + I_{3.62}) / 2] \times 100\% = 78.1\%;$$

$$\text{PBS [\%]} = (I_{2.70} / 4) / [I_{7.24} / 2 + I_{2.71} / 4 + (I_{3.19} + I_{3.62}) / 2] \times 100\% = 10.1\%;$$

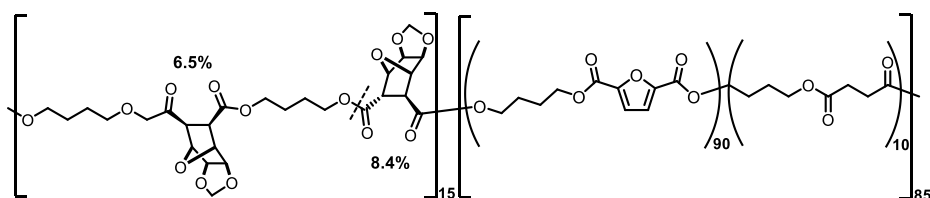
$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.19} - I_{3.62}) / 2] / [I_{7.24} / 2 + I_{2.70} / 4 + (I_{3.19} + I_{3.62}) / 2] \times 100\% = 5.5\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.62} / [I_{7.24} / 2 + I_{2.70} / 4 + (I_{3.19} + I_{3.62}) / 2] \times 100\% = 6.2\%;$$

$$\text{PBF in PBSF [\%]} = (I_{7.24} / 2) / [I_{7.24} / 2 + I_{2.70} / 4] \times 100\% = 88.5\%;$$

$$\text{PBS in PBSF [\%]} = (I_{2.70} / 4) / [I_{7.24} / 2 + I_{2.70} / 4] \times 100\% = 11.5\%.$$

8.5% SA, 76.5 % FDCA and 15% TCDA synthesized copolyester PBTC₁₅(S₁₀F₉₀)₈₅.



SA (0.17 g, 1.7 mmol), FDCA (2.39 g, 15.3 mmol), TCDA (0.69 g, 3.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 4 h. After cooling to room temperature, the resultant polymer was obtained as light yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.22 (s, 2 H), 5.00 – 5.10 (m, 0.54 H), 4.81 – 4.84 (m, 0.19 H), 4.17 – 4.47 (m, 5.41 H), 3.61 (s, 0.11 H), 3.17 (s, 0.28 H), 2.70 (s, 0.44 H), 1.69 – 1.87 (m, 5.02 H). ¹³C NMR (150 MHz, TFA-*d*): δ 176.76, 174.25, 173.65, 172.27, 161.61, 147.03, 120.15, 97.20, 96.98, 84.28, 82.41, 81.25, 79.53, 67.44, 67.12, 66.52, 47.76, 47.03, 46.13, 29.15, 24.84, 24.72, 24.63.

$$\text{PBF [\%]} = (I_{7.22} / 2) / [I_{7.22} / 2 + I_{2.70} / 4 + (I_{3.17} + I_{3.61}) / 2] \times 100\% = 76.6\%;$$

$$\text{PBS [\%]} = (I_{2.70} / 4) / [I_{7.22} / 2 + I_{2.70} / 4 + (I_{3.17} + I_{3.61}) / 2] \times 100\% = 8.4\%;$$

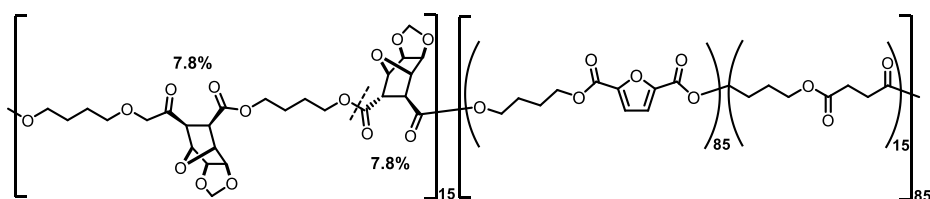
$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.17} - I_{3.61}) / 2] / [I_{7.22} / 2 + I_{2.70} / 4 + (I_{3.17} + I_{3.61}) / 2] \times 100\% = 6.5\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.61} / [I_{7.22} / 2 + I_{2.70} / 4 + (I_{3.17} + I_{3.61}) / 2] \times 100\% = 8.4\%;$$

$$\text{PBF in PBSF [\%]} = (I_{7.22} / 2) / [I_{7.22} / 2 + I_{2.70} / 4] \times 100\% = 90.1\%;$$

$$\text{PBS in PBSF [\%]} = (I_{2.70} / 4) / [I_{7.22} / 2 + I_{2.70} / 4] \times 100\% = 9.9\%.$$

12.7% SA, 72.3 % FDCA and 15% TCDA synthesized copolyester PBTC₁₅(S₁₅F₈₅)₈₅.



SA (0.255 g, 2.55 mmol), FDCA (2.25 g, 14.45 mmol), TCDA (0.69 g, 3.0 mmol), 1,4-BDO (4.50 g, 50.0 mmol) and TBT (34 mg, 0.10 mmol) were added into a 25 mL three neck round bottom flask equipped with a stirring paddle. The air in the apparatus was evacuated and replaced with nitrogen (99.99%). The esterification reaction was conducted under nitrogen flow at 160 °C for 1 h, 180 °C for 1 h and 190 °C for 2.5 h. Then the polycondensation reaction was performed under vacuum at 190 °C for 1 h and 220 °C for 2.5 h. After cooling to room temperature, the resultant polymer was obtained as lightly yellow solid material without further purification. ¹H NMR (600 MHz, TFA-*d*): δ 7.23 (s, 2 H), 5.00 – 5.10 (m, 0.50 H), 4.85 (s, 0.17 H), 4.41 – 4.48 (m, 4.44 H), 4.17 (s, 1.44 H), 3.61 (s, 0.10 H), 3.18 (s, 0.30 H), 2.70 (s, 0.70 H), 1.69 – 1.88 (m, 5.49 H). ¹³C NMR (150 MHz, TFA-*d*): δ 176.23, 173.71, 173.11, 171.73, 161.61, 146.50, 119.62, 96.66, 96.44, 83.75, 81.87, 80.72, 78.99, 66.91, 66.59, 65.99, 47.23, 46.50, 45.59, 28.61, 24.31, 24.19, 24.11.

$$\text{PBF [\%]} = (I_{7.23} / 2) / [I_{7.23} / 2 + I_{2.70} / 4 + (I_{3.18} + I_{3.61}) / 2] \times 100\% = 72.7\%;$$

$$\text{PBS [\%]} = (I_{2.70} / 4) / [I_{7.23} / 2 + I_{2.70} / 4 + (I_{3.18} + I_{3.61}) / 2] \times 100\% = 12.7\%;$$

$$\text{PBTC}_{\text{exo-exo}} [\%] = [(I_{3.18} - I_{3.61}) / 2] / [I_{7.23} / 2 + I_{2.70} / 4 + (I_{3.18} + I_{3.61}) / 2] \times 100\% = 7.8\%;$$

$$\text{PBTC}_{\text{exo-endo}} [\%] = I_{3.61} / [I_{7.23} / 2 + I_{2.70} / 4 + (I_{3.18} + I_{3.61}) / 2] \times 100\% = 7.8\%;$$

$$\text{PBF in PBSF} [\%] = (I_{7.23} / 2) / [I_{7.23} / 2 + I_{2.70} / 4] \times 100\% = 85.1\%;$$

$$\text{PBS in PBSF} [\%] = (I_{2.70} / 4) / [I_{7.23} / 2 + I_{2.70} / 4] \times 100\% = 14.9\%.$$

■ Optimized the Synthesis of 2,5-Furandicarboxylic salt (FDCA²⁻)

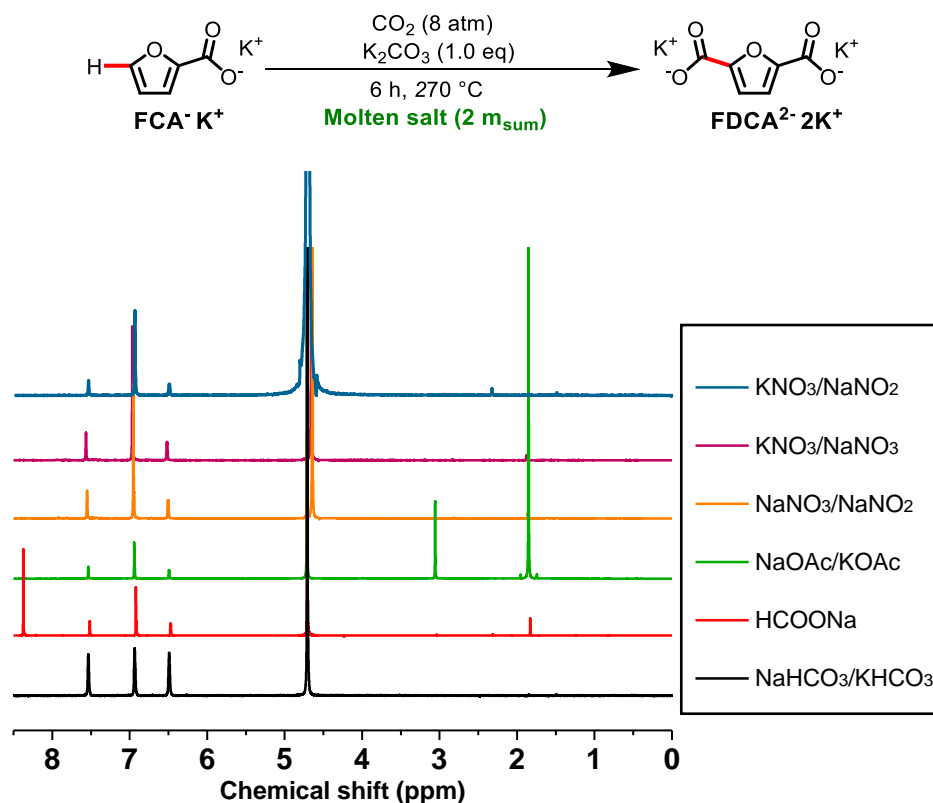


Figure S1. ¹H NMR spectrum of FDCA²⁻ synthesized by different molten salt.

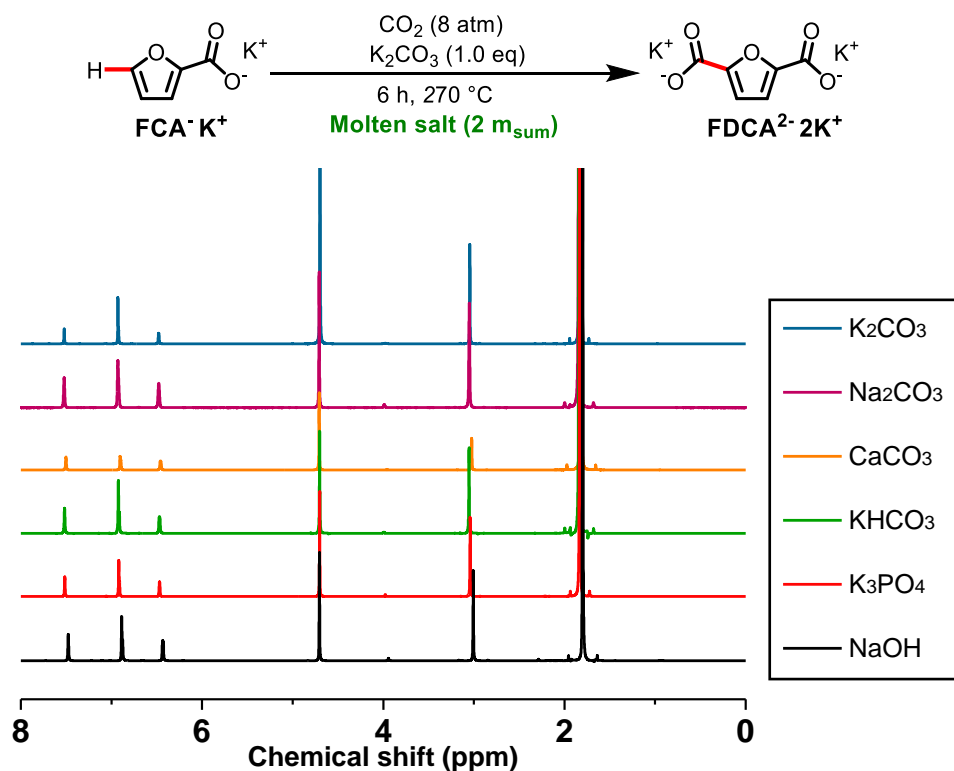


Figure S2. ¹H NMR spectrum of FDCA²⁻ synthesized by different catalysts.

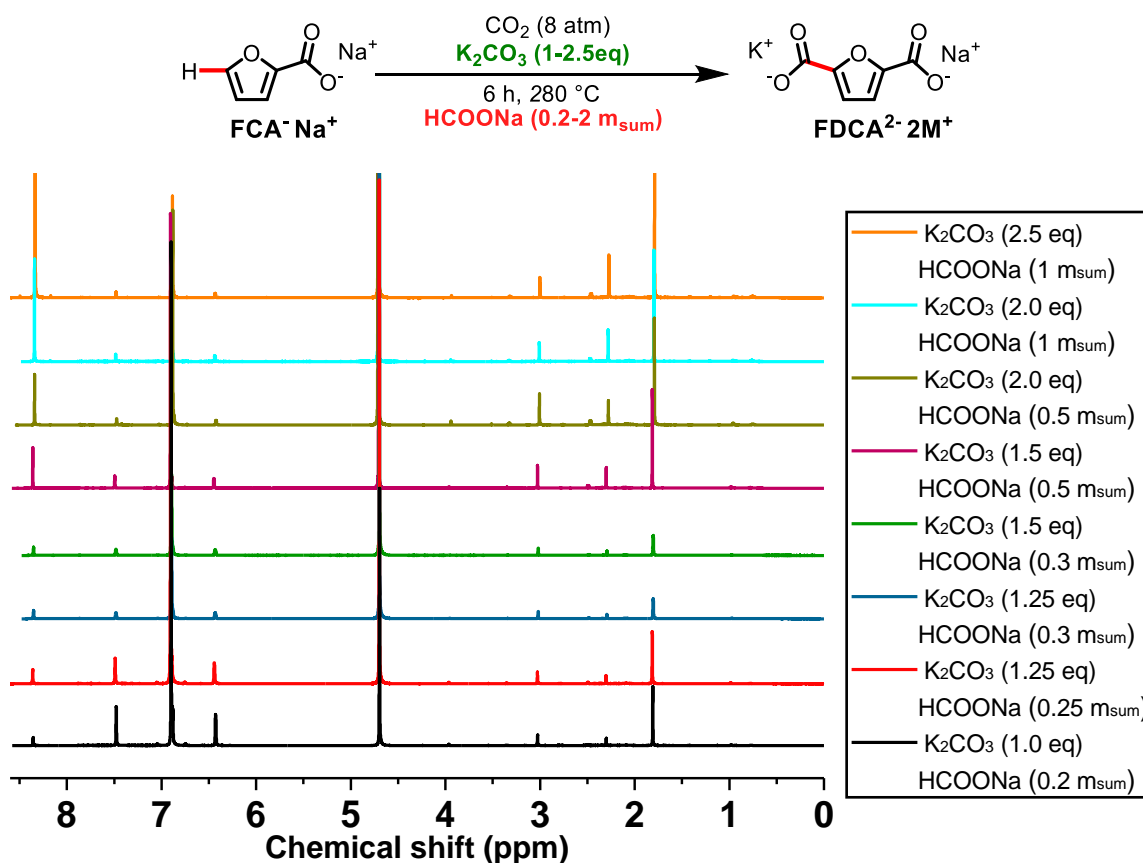


Figure S3. ¹H NMR spectrum of FDCA²⁻ optimizing in the HCOONa.

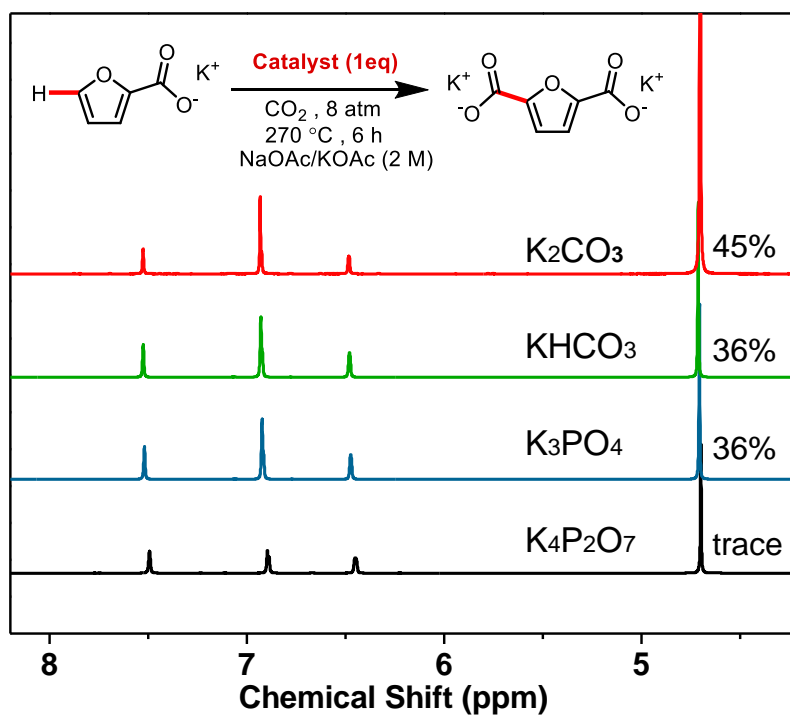


Figure S4. Carboxylation activities by K₂CO₃ and K₃PO₄ under KOAc/NaOAc by ¹H NMR spectrum.

When K_2CO_3 and K_3PO_4 were used as catalysts, the intermediate products were KHCO_3 and K_2HPO_4 , respectively, which could be further decomposed to K_2CO_3 and $\text{K}_4\text{P}_2\text{O}_7$ at high temperatures (**Equation S1 - S4**).



Thus, we hypothesized that the different catalytic activity between KHCO_3 and $\text{K}_4\text{P}_2\text{O}_7$ lead to the effect on carboxylation of furoate by using K_2CO_3 was greater than that of K_3PO_4 . To confirm this, a control experiment was conducted using 1 eq of KHCO_3 and $\text{K}_4\text{P}_2\text{O}_7$ as catalysts under the unified condition (**Figure S4**). A 36% conversion of FCA^-K^+ for KHCO_3 as catalyst, compared with a trace amount of the desired carboxylation catalyzed by $\text{K}_4\text{P}_2\text{O}_7$ (**Figure S4, Equation S5**). This result suggests that the continuous conversion between HCO_3^- and CO_3^{2-} by K_2CO_3 lead to a superior activity to that of K_3PO_4 .

■ Reactivity Ratio of TCDA and SA with 1,4-BDO

The reactivity ratio obtained by kinetics experiments according to the basic data in **Table**

S1 revealed that r_{SA} and r_{TCDA} are 1.136 and 0.880, respectively.

Table S1. The data of kinetics calculation.

SA (2.5 mmol)	SA : BDO = 1 : 1		C ~ t	
Time	$C_{t=0}$ (mol/L)	Conv.	C_t (mol/L)	$[C_{t=0} - C_t]$ (mol/L)
60 s	6.47	2.53%	0.1636	6.3064
80 s	6.47	3.19%	0.2063	6.2637
90 s	6.47	3.98%	0.2574	6.2126
100 s	6.47	5.74%	0.3712	6.0988
TCDA (1 mmol)	TCDA : BDO = 1 : 1		C ~ t	
Time	$C_{t=0}$ (mol/L)	Conv.	C_t (mol/L)	$[C_{t=0} - C_t]$ (mol/L)
120 s	4.31	5.67%	0.2442	4.0658
180 s	4.31	7.41%	0.3191	3.9909
240 s	4.31	10.87%	0.4681	3.8419
300 s	4.31	12.43%	0.5353	3.7747

The reactivity ratios were calculated using Mayo-Lewis equation (**Equation S6**), usually applied to chain-growth copolymerization deduced from free radical copolymerization (FRCP). Mayo-Lewis equation was also able to be used as mathematically applicable to the step-growth copolymerization, even though the reaction mechanism of step-growth copolymerization is different from FRCP.² The relevant parameters calculated with $r_{SA} = 1.136$ and $r_{TCDA} = 0.880$ were listed in **Table S2**. Then, the molar composition of PBTC_xS_y according to the ¹H NMR and Mayo-Lewis equation were showed in **Figure S5**. It suggested that the calculated result is agree well with the copolymerization result.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_1 f_1^2} \quad (S6)$$

Table S2. Calculation for the determination of reactivity ratios of r_1 and r_2 and the root mean square (RMS) error.^a

SA feed	SA incorp. (¹ H NMR)	f_1	f_2	F_1 calc.	$F_1 \cdot 100$	diff.	square
100	100.00	1.00	0.00	1.0000	100.00	0.000000	0.000000
95	96.15	0.95	0.05	0.9557	95.57	0.577854	0.333915
90	90.91	0.90	0.10	0.9109	91.09	-0.18075	0.032671
85	86.20	0.85	0.15	0.8655	86.55	-0.35482	0.125898
80	81.97	0.80	0.20	0.8196	81.96	0.006665	4.44E-05
70	71.68	0.70	0.30	0.7261	72.61	-0.92949	0.863945
60	62.30	0.60	0.40	0.6302	63.02	-0.72051	0.519134
50	52.63	0.50	0.50	0.5319	53.19	-0.55725	0.310529
30	33.22	0.30	0.70	0.3275	32.75	0.471217	0.222045
0	0.00	0.00	1.00	0.0000	0.00	0.000000	0.000000
AVE							2.408181
RMS error							1.55183149

a: $r_1 = r_{SA}$ = the reactivity ratio of SA; $r_2 = r_{TCDA}$ = the reactivity ratio of TCDA; f_1 = the feed fraction of SA; f_2 = the feed fraction of TCDA; F_1 = the composition fraction of SA; $F_2 = 1 - F_1$, the composition fraction of TCDA; $r_1 = r_{SA} = k_{11}/k_{12}$; $r_2 = r_{TCDA} = k_{22}/k_{21}$; The chain end for SA and TCDA are nearly identical with both ending $O=CO(CH_2)_4OH$, thereby, $r_1 = r_{SA} = k_1/k_2$; $r_2 = r_{TCDA} = k_2/k_1$; k_1 = the reaction rate constant of any chain end with SA; k_2 = the reaction rate constant of any chain end with TCDA;

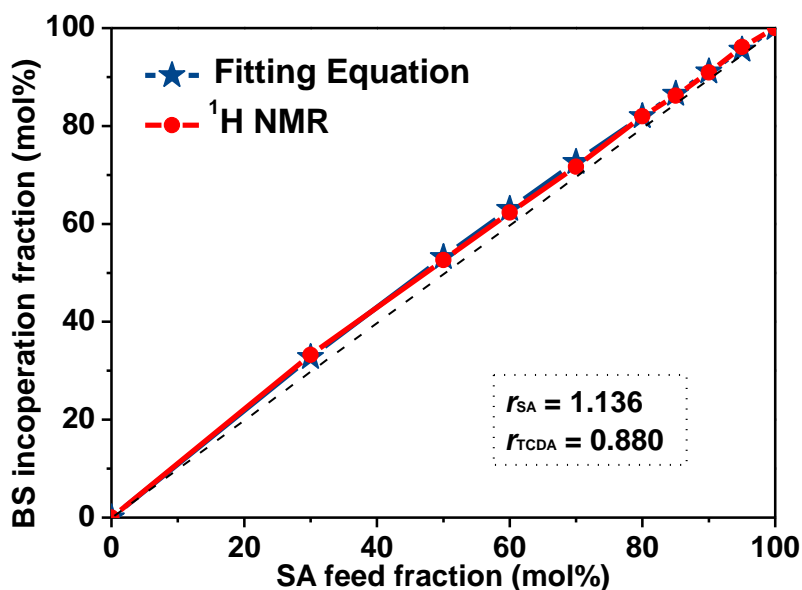


Figure S5. The “SA” incorporation fraction (%) determined by ¹H NMR (Red) and calculated by Mayo-Lewis equation (Blue).

■ Crystallization Behaviors

Isothermal crystallization behavior of PBTC_xS_y and PBTC_xF_y were evaluated by DSC. The evaluation of the relative crystallinity, X_c vs the half-time of crystallization ($t_{1/2}$) for the two series of polyesters at different temperatures were recorded in **Figures S6-S10**. Since crystallization could not be carried out at the same temperature for these polyesters due to the large differences in crystallization rates, leading to directly comparing the crystallization of these polyesters is unfeasible.³ However, a relative evaluation of the crystallizability of the two series of polyesters could be obtained by plotting $t_{1/2}$ against the crystallization supercooling defined as $[T_m^0 - T_c]$, where T_m^0 is the equilibrium melting temperature and T_c is the crystallization temperature. T_m^0 can be obtained *via* Hoffman-Weeks plot of T_m vs T_c , as shown in **Figures S6-S9**. Firstly, the exothermal curves were recorded as a function of crystallization time (**Figure S6A**, **Figure S7A**, **Figure S8A** and **Figure S9A**), and the crystallization rate becomes slower and the exothermic peaks become broader for tested samples. Meanwhile, double-melting endotherms can be observed in DSC curves after isothermal crystallization, exception for isothermal crystallization behavior of PBS at 80 °C, and the low-temperature melting endotherm visibly shift to higher temperature. However, the high-temperature melting temperature slightly shift to higher temperature. Thus, T_m^0 of homopolyesters PBS and PBF is 114 and 175 °C, respectively, though the values of PBS and PBF are lower than those reported in the literatures (T_m^0 of PBF and PBS is 184.5 and 128.0 °C, respectively).^{4, 5} As expected, T_m^0 values display the same trend with composition as was observed for the T_m measured, because of the decrease of crystallization after the incorporation of TCDA units. A comparison of PBS and PBTC₉S₉₁ reveal that the $t_{1/2}$ of polyesters increases enormously from 1.8 min to 9.7 min for relatively small amounts of

TCDA incorporated into the polyesters under the same supercooling ($T_m^0 - T_c = 30\text{ }^\circ\text{C}$, more than five times for 9% of TCDA) (**Figure S10A**). This variation trend was also observed for PBF and PBTC₄F₉₆, and the $t_{1/2}$ values increases from 5.9 min to 15.2 min with the increase of TCDA units under the same supercooling ($T_m^0 - T_c = 35\text{ }^\circ\text{C}$) shown in **Figure S10B**. This result may be interpreted as the decreased chain mobility and the difficulty in chain packing by incorporation tricyclic units, and this behavior is accordance with the results of DSC and WAXD data. In addition, kinetic data afforded by the Avrami analysis of the results obtained at the selected crystallization temperatures are summarized in **Table S3**. The corresponding Avrami data plots $\log[-\ln(1-X_c)]$ vs $\log(t-t_0)$ for the illustrative crystallization temperature are shown in **Figure S10C** and **S10D**. the Avrami exponent n is composed of the time dimension which is related to the nucleation mode (homogeneous or heterogeneous) and growth dimension of crystal. For the two series, the Avrami exponent n ranged from 2.18 to 2.86, indicating a similar crystallization mechanism, which is attributed to the heterogeneous nucleation with two to three dimensional growth. The Avrami parameters k are indicative of the crystallization rates,^{5, 6} and as was expected, they decreased after the incorporation of TCDA.

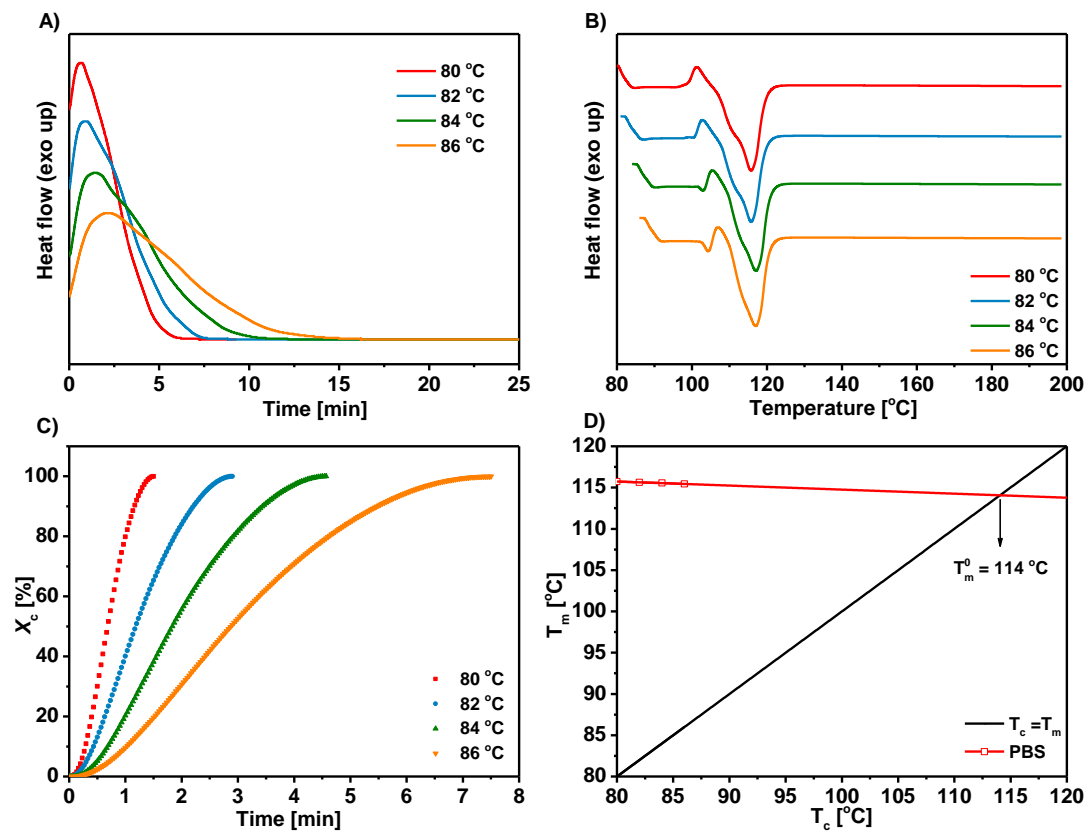


Figure S6. (A) DSC curves of isothermal crystallization at different temperature for PBS; (B) DSC heating scans for PBS crystallized at different temperature from the melt; (C) Development of relative crystallinity with crystallization time at different temperature for PBS; (D) Hoffman-Weeks plots of T_m vs T_c for PBS.

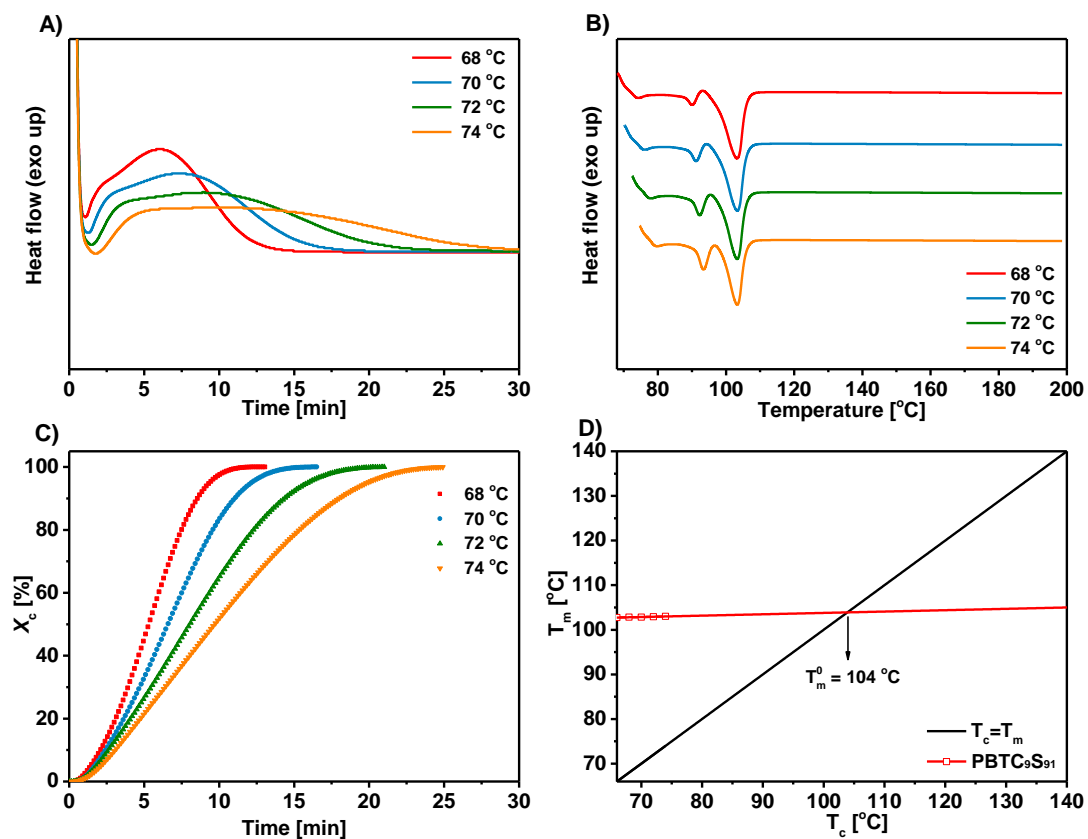


Figure S7. (A) DSC curves of isothermal crystallization at different temperature for PBTC₉S₉₁; (B) DSC heating scans for PBTC₉S₉₁ crystallized at different temperature from the melt; (C) Development of relative crystallinity with crystallization time at different temperature for PBTC₉S₉₁; (D) Hoffman-Weeks plots of T_m vs T_c for PBTC₉S₉₁.

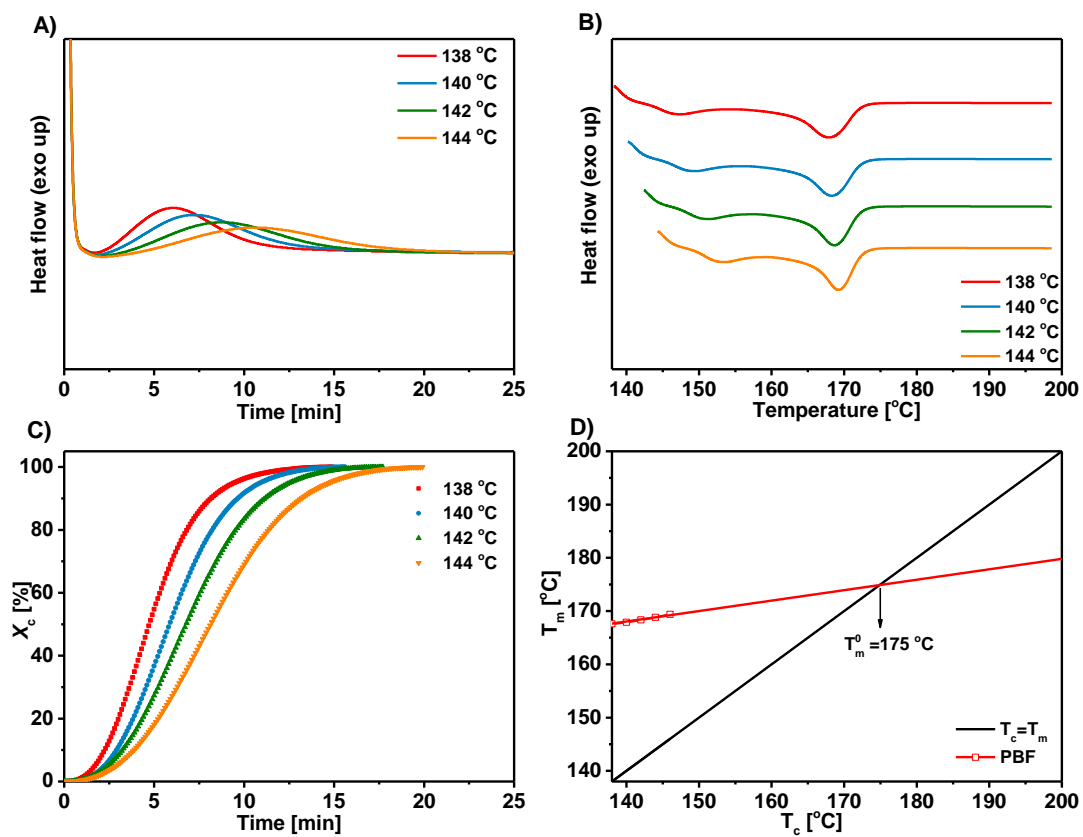


Figure S8. (A) DSC curves of isothermal crystallization at different temperature for PBF; (B) DSC heating scans for PBF crystallized at different temperature from the melt; (C) Development of relative crystallinity with crystallization time at different temperature for PBF; (D) Hoffman-Weeks plots of T_m vs T_c for PBF.

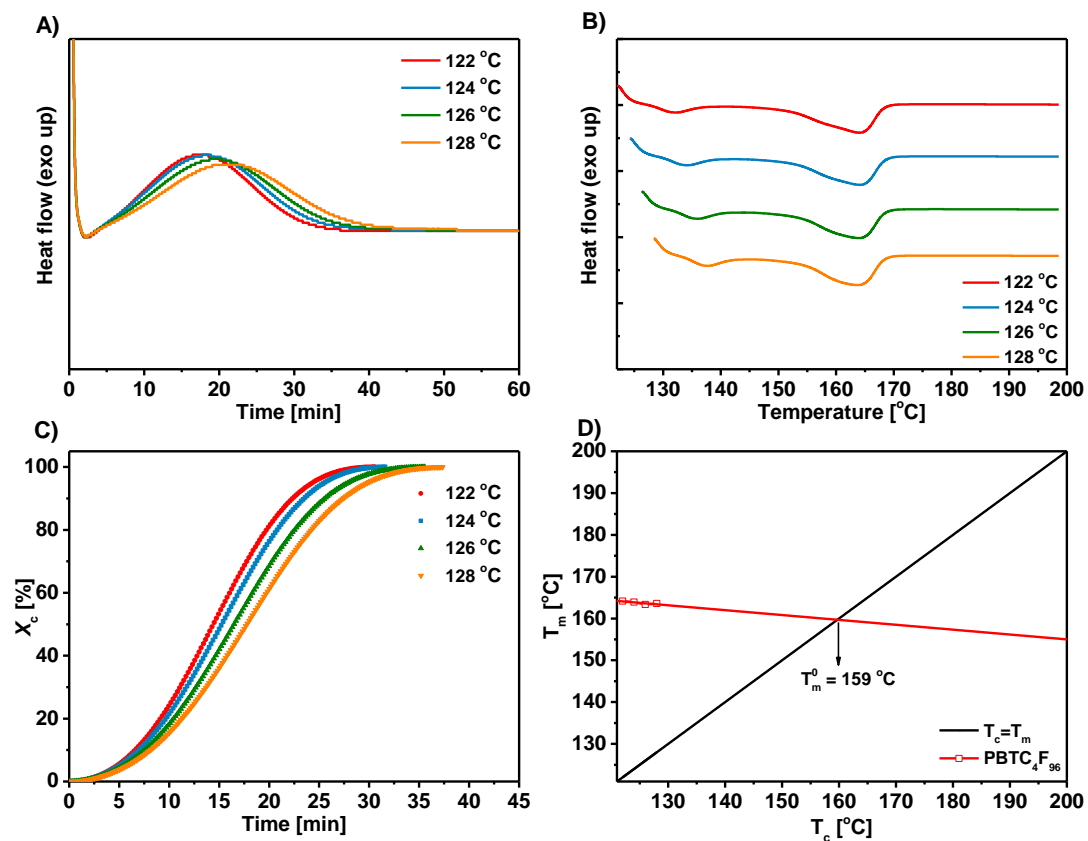
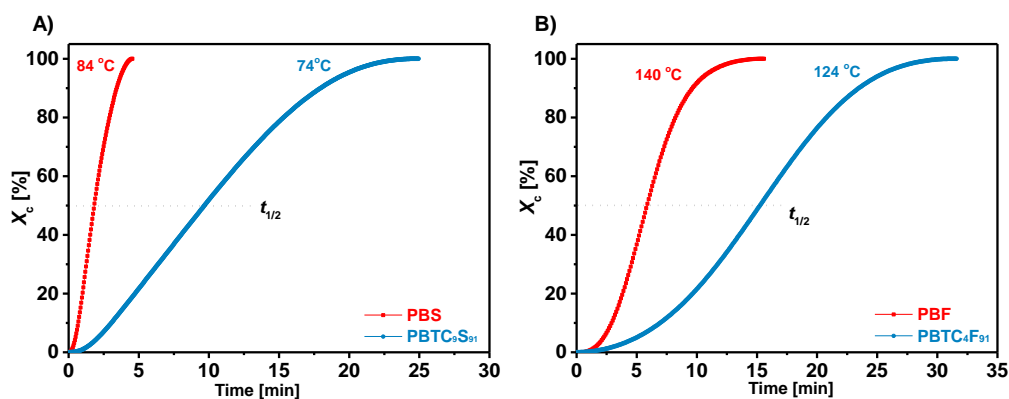


Figure S9. (A) DSC curves of isothermal crystallization at different temperature for PBTC₄F₉₆; (B) DSC heating scans for PBTC₄F₉₆ crystallized at different temperature from the melt; (C) Development of relative crystallinity with crystallization time at different temperature for PBTC₄F₉₆; (D) Hoffman–Weeks plots of T_m vs T_c for PBTC₄F₉₆.



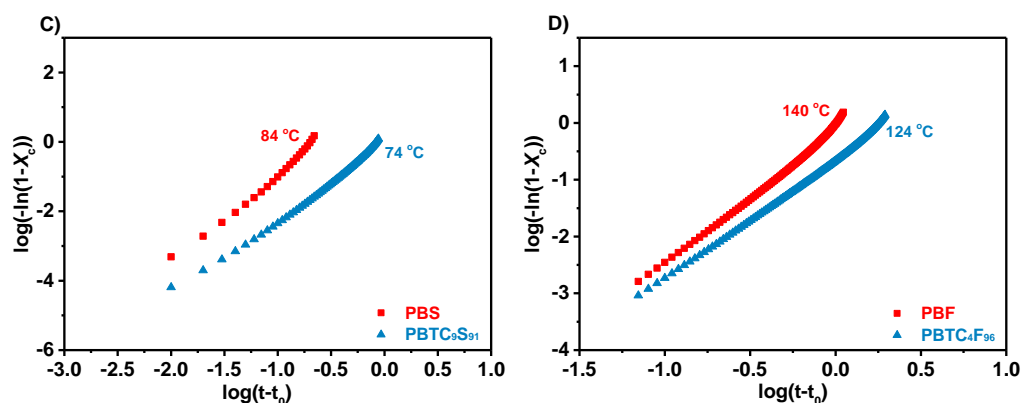


Figure S10. Isothermal crystallization under the same supercooling of PBS/PBTC₉S₉₁ and PBF/PBTC₄F₉₆. Evaluation of the relative crystallinities with $t-t_0$ (A and B). Avrami plots (C and D).

Table S3. The relevant parameters of isothermal crystallization behavior of polyesters.

Polyester	T_c [°C]	T_m^0 [°C]	$T_m^0 - T_c$ [°C]	$t_{1/2}$ [min]	n	log k
PBS	84	114	30	1.8	2.86	1.885
PBTC ₉ S ₉₁	74	104	30	9.7	2.43	0.061
PBF	140	175	35	5.9	2.43	-0.082
PBTC ₄ F ₉₆	124	159	35	15.2	2.18	-0.620

WAXD was used to study the effect of TCDA moiety on the crystal structure of PBF and PBS. The main diffraction peaks of PBF crystal located at 2θ values are 17.9° , 22.6° and 25.0° , and diffraction peaks of PBS are 19.6° , 21.9° and 22.6° . There are no additional diffraction peaks were observed for the two series co-polyesters, indicated TCDA moiety does not damage the monoclinic crystal structure of PBF and PBS (**Figures S11**).

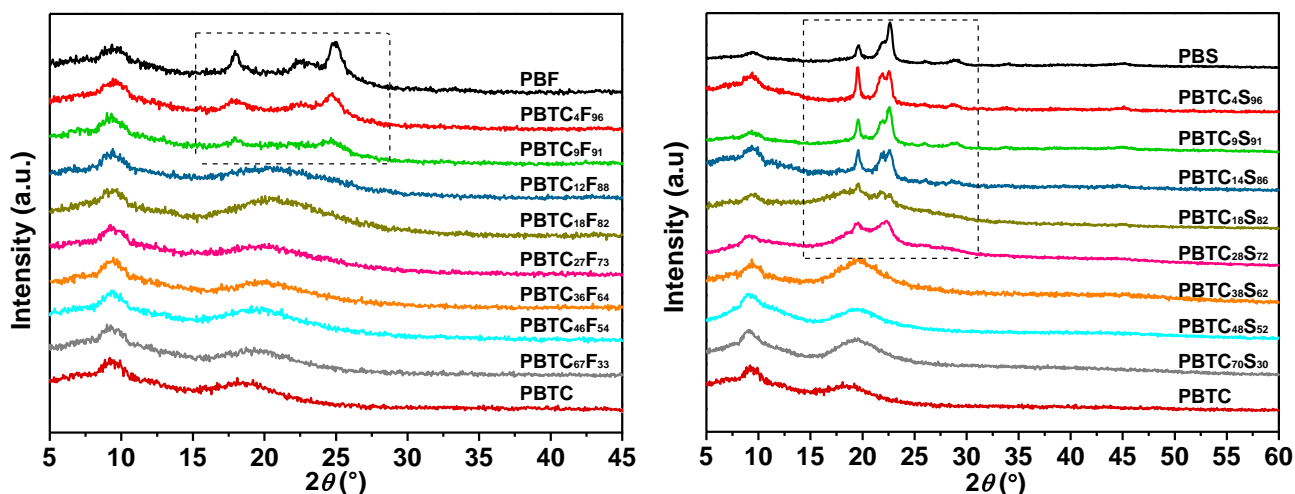


Figure S11. WAXD curves of PBTC_xF_y (left) and PBTC_xS_y (right).

The intensity of the diffraction peaks gradually weakened with the increase of TCDA moiety, which disturb the crystalline phase of the PBS or PBF. While the percentage of TCDA moiety exceed 15 mol%, only two broad peaks are found for PBTC_xF_y series, revealing that these *co*-polyesters are poorly crystalline or amorphous. This phenomenon was observed for the PBTC_xS_y series as TCDA moiety exceed 30 mol%.

Furthermore, Polarizing Optical Microscope (POM) was conducted to investigate the influence of TCDA moiety on the of PBTC_xF_y and PBTC_xS_y. Maltese crosses and concentric annulus extinction, namely, spherulites was observed for PBF, and the spherulite diameter of PBF is about 38 μm before impinging with each other (**Figure S12A**). However, the lower crystallization of PBTC_xF_y compared with PBF lead to the size of spherulites dramatically decrease (less than 10 μm) with increase of TCDA moiety (**Figures S12B and C**), and very small spherulites with blurry boundaries are observed for PBTC₉F₉₁. In contrast, accumulative spherulites are formed because of the high nucleation density of PBS, and the sizes of spherulites increase with the improving the contents of TCDA (**Figures S12D-F**). The spherulite diameter of PBS is about 35 μm because of the impingement of spherulites with each other. With the incorporation of TCDA units, the PBTC_xS_y copolyesters

show ring-banded spherulites, and the band spacing decrease with the increase of TCDA units. In addition, the spherulite density decrease with the increase of TCDA units while the spherulite sizes increase (e.g., about 86 μm of PBTC₉S₉₁) with higher TCDA content in PBTC_xS_y copolyesters. The reason of this phenomenon may be interpreted that the supercoiling and chain regularity of copolyesters decrease by incorporating stiffness units, and distorted lamellae and coarse bands are formed.⁷

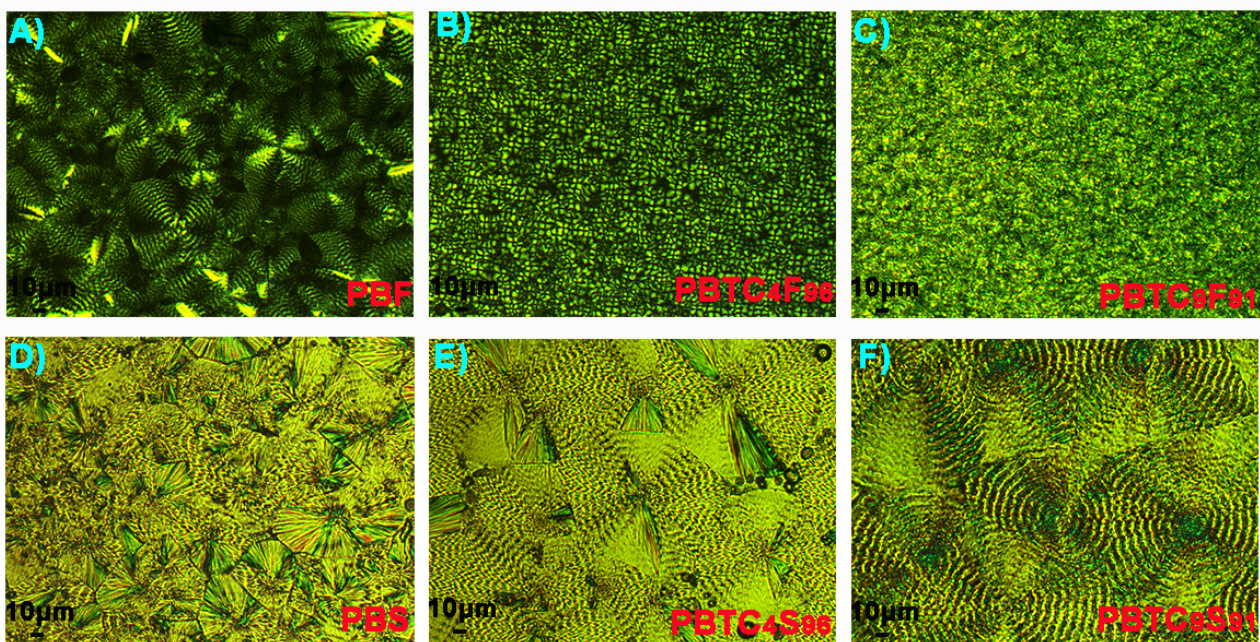


Figure S12. Crystalline morphology of polyesters isothermally crystallized.

■ Thermal and Mechanical Behaviors

Table S4. Thermal stability and mechanical properties of ternary-polyesters.

Polyester	TGA		Mechanical property		
	T _{d,5%} [°C]	T _{d,max} [°C]	E _t [MPa]	σ _m [MPa]	ε _b [%]
PBTC_xS_y					
PBS	333.3	396.1	400±48	33.0±3.8	20.1±4.5
PBTC ₄ S ₉₆	331.5	393.7	218±36	23.6±1.9	120.3±10
PBTC ₉ S ₉₁	328.8	390.0	312±45	27.1±0.6	160.8±9.2
PBTC ₁₄ S ₈₆	325.8	385.6	145±12	22.3±4.9	665.3±75
PBTC ₁₈ S ₈₂	323.8	386.6	132±20	19.1±4.9	1200.8±41
PBTC ₂₈ S ₇₂	318.9	386.6	73±12	8.9±0.6	2000.6±100
PBTC ₃₈ S ₆₂	315.2	383.2			
PBTC ₄₈ S ₅₂	312.6	383.3			
PBTC ₆₇ S ₃₃	306.4	377.8	10±3	19.6±7.6	8.6±2.7
PBTC	305.8	368.4			
PBTC_xF_y					
PBF	354.9	387.9	1600±50	67.7±5.4	12.4±4.1
PBTC ₄ F ₉₆	351.2	387.1	1480±48	65.4±10.4	48.2±8.4
PBTC ₉ F ₉₁	344.3	373.6	1490±75	56.0±7.6	110.4±10.3
PBTC ₁₂ F ₈₈	341.0	377.5	1408±52	49.5±6.7	60.5±5.7
PBTC ₁₈ F ₈₂	337.5	374.8	958±42	51.4±3.8	25.0±3.0
PBTC ₂₇ F ₇₃	331.5	378.1	1030±70	53.2±5.2	13.0±3.2
PBTC ₃₆ F ₆₄	327.9	378.5	930±69	55.8±4.6	16.0±4.0
PBTC ₄₆ F ₅₄	318.6	385.8			
PBTC ₆₇ F ₃₃	308.5	372.4			

Table S5. Thermal behavior of ternary-polyesters.

Polyester	DSC							WAXD ^b	
	1 st Heating		Cooling		2 nd Heating			X_c^a [%]	X_c [%]
	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]	T_g [°C]	T_m [°C]	ΔH_m [J/g]		
PBTC_xS_y									
PBS	117.5	75.8	73.3	70.1	-37.5	116.0	72.2	36.1	39.4
PBTC ₄ S ₉₆	108.8	53.7	62.0	53.2	-27.0	104.8	52.0	24.3	26.2
PBTC ₉ S ₉₁	103.1	39.2	31.8	13.7	-24.5	102.9	38.1	16.4	24.5
PBTC ₁₄ S ₈₆	93.7	24.4	nd.	nd.	-23.8	91.0	17.9	7.1	22.9
PBTC ₁₈ S ₈₂	85.8	nd.	nd.	nd.	-22.9	nd.	nd.		19.8
PBTC ₂₈ S ₇₂	58.1	nd.	nd.	nd.	-6.4	nd.	nd.		
PBTC ₃₈ S ₆₂	nd.	nd.	nd.	nd.	4.5	nd.	nd.		
PBTC ₄₈ S ₅₂	nd.	nd.	nd.	nd.	10.7	nd.	nd.		
PBTC ₆₇ S ₃₃	nd.	nd.	nd.	nd.	32.4	nd.	nd.		
PBTC	nd.	nd.	nd.	nd.	78.1	nd.	nd.		
<hr/>									
PBTC_xF_y									
PBF	173.3	39.1	105.0	53.2	36.4	170.8	38.5	29.8	35.1
PBTC ₄ F ₉₆	164.8	38.1	109.0	5.3	39.8	164.0	36.9	27.1	31.6
PBTC ₉ F ₉₁	152.1	21.9	nd.	nd.	42.6	146.5	nd.		23.4
PBTC ₁₂ F ₈₈	138.2	3.1	nd.	nd.	44.4	126.7	nd.		
PBTC ₁₈ F ₈₂	130.1	nd.	nd.	nd.	45.9	nd.	nd.		
PBTC ₂₇ F ₇₃	101.3	nd.	nd.	nd.	50.5	nd.	nd.		
PBTC ₃₆ F ₆₄	nd.	nd.	nd.	nd.	54.1	nd.	nd.		
PBTC ₄₆ F ₅₄	nd.	nd.	nd.	nd.	54.9	nd.	nd.		
PBTC ₆₇ F ₃₃	nd.	nd.	nd.	nd.	59.9	nd.	nd.		

a: Crystallinity index calculated by comparing the ΔH_m with the value of an infinitely large crystal (ΔH_m^0), taken as $\Delta H_m^0=129$ J/g for PBF⁵ $\Delta H_m^0=200$ J/g for PBS⁸ and $X_c = \Delta H_m/\Delta H_m^0/\varphi \times 100\%$, φ is the weight percentage of PBF or PBS in the PBTC_xS_y or PBTC_xF_y.

b: Crystallinity index calculated as the quotient between the crystalline area and total area quantified in the X-ray diffraction profiles.

T_g = glass transition temperature, T_m = transition temperature, T_c = crystallization temperature, and ΔH = enthalpy of transition.

TGA Characterization of Polymers.

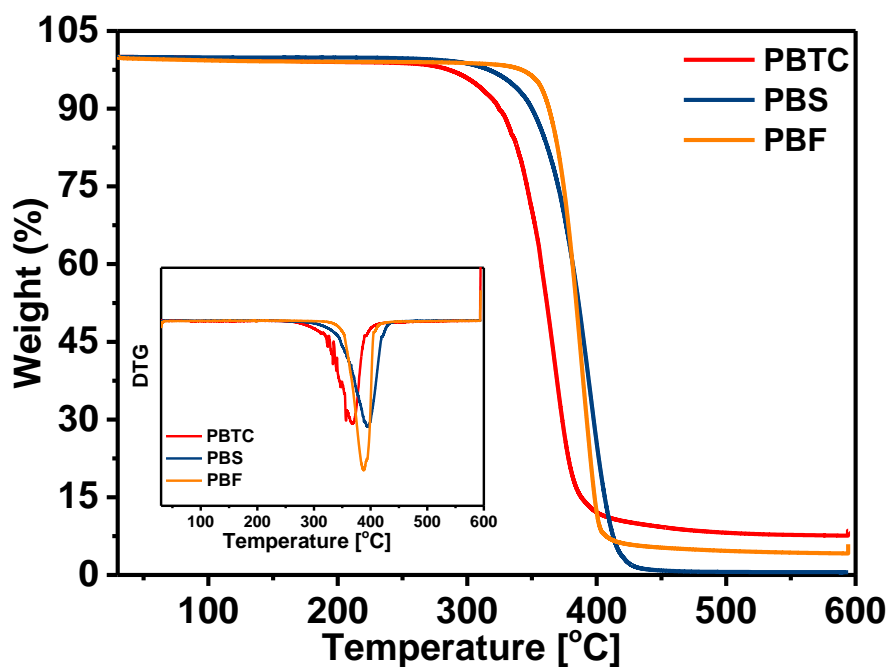


Figure S13. TGA characterization of PBTC, PBS and PBF.

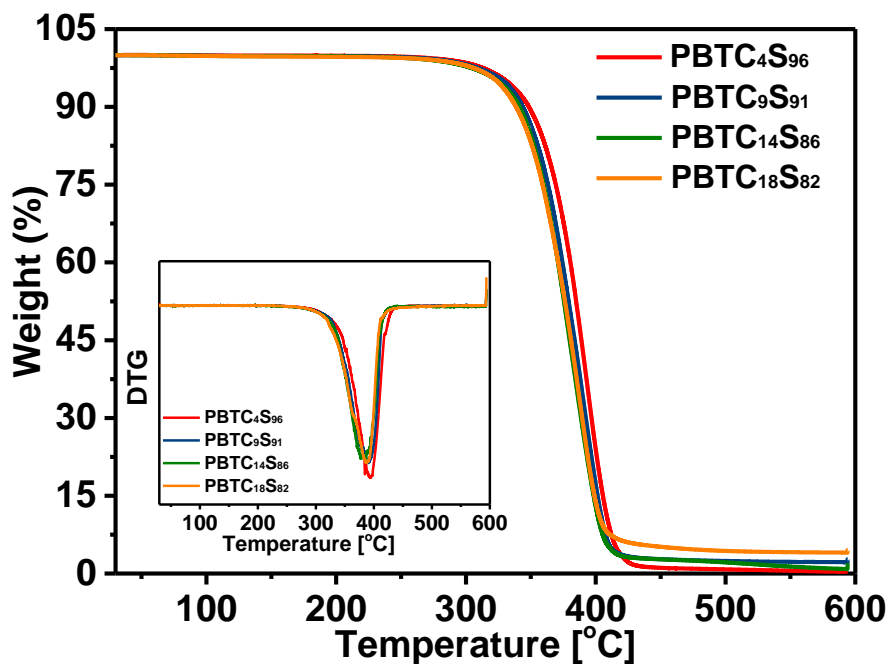


Figure S14. TGA characterization of PBTC₍₄₋₁₈₎S₍₉₆₋₈₂₎.

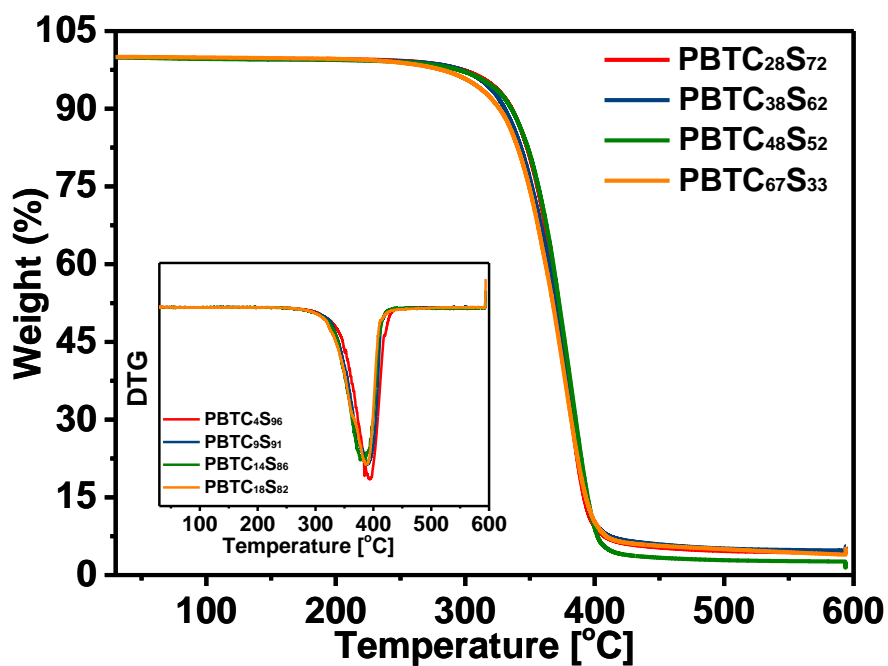


Figure S15. TGA characterization of PBTC₍₂₈₋₆₇₎S₍₇₂₋₃₃₎.

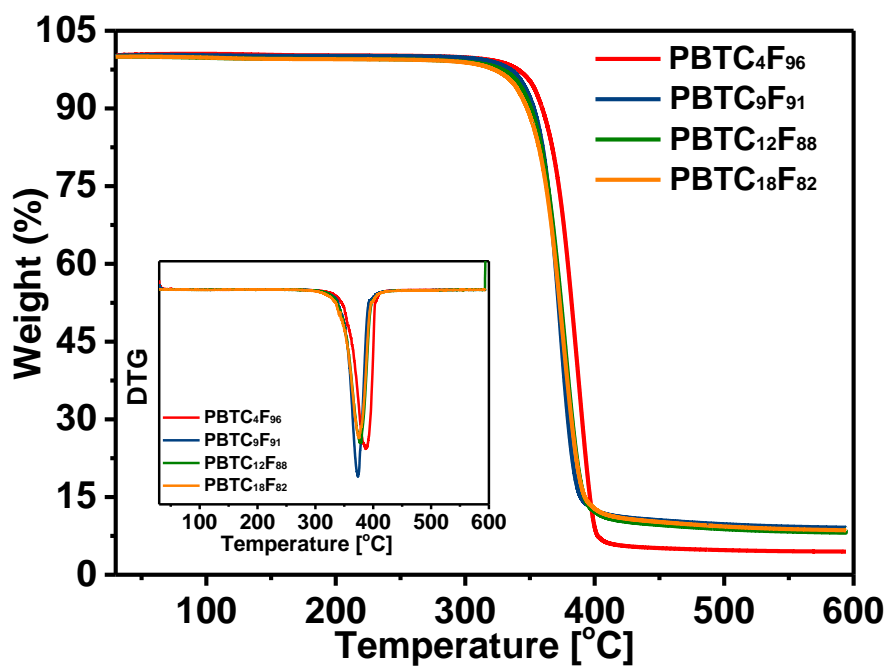


Figure S16. TGA characterization of PBTC₍₄₋₁₈₎F₍₉₆₋₈₂₎.

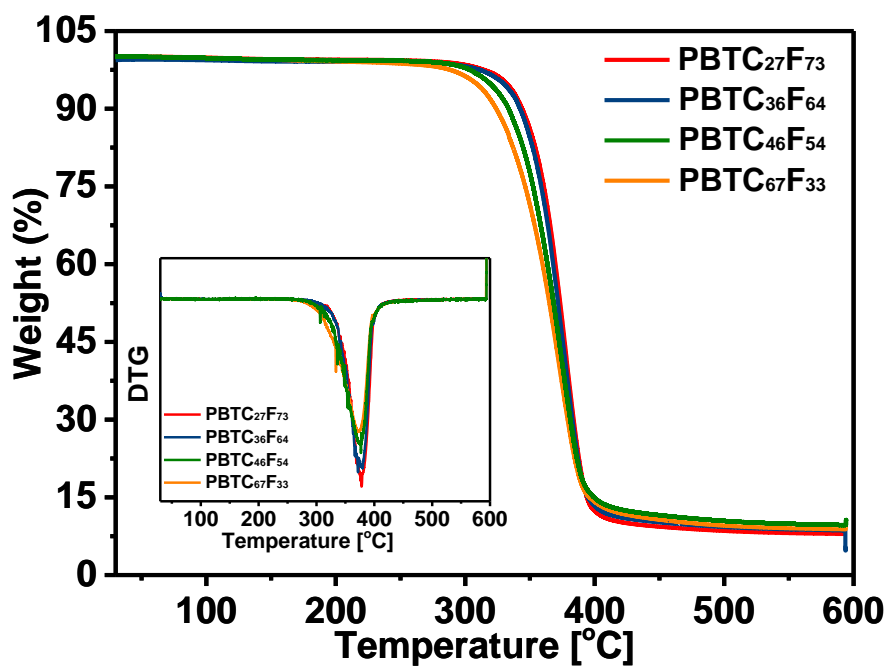


Figure S17. TGA characterization of PBTC₍₂₇₋₆₇₎F₍₇₃₋₃₃₎.

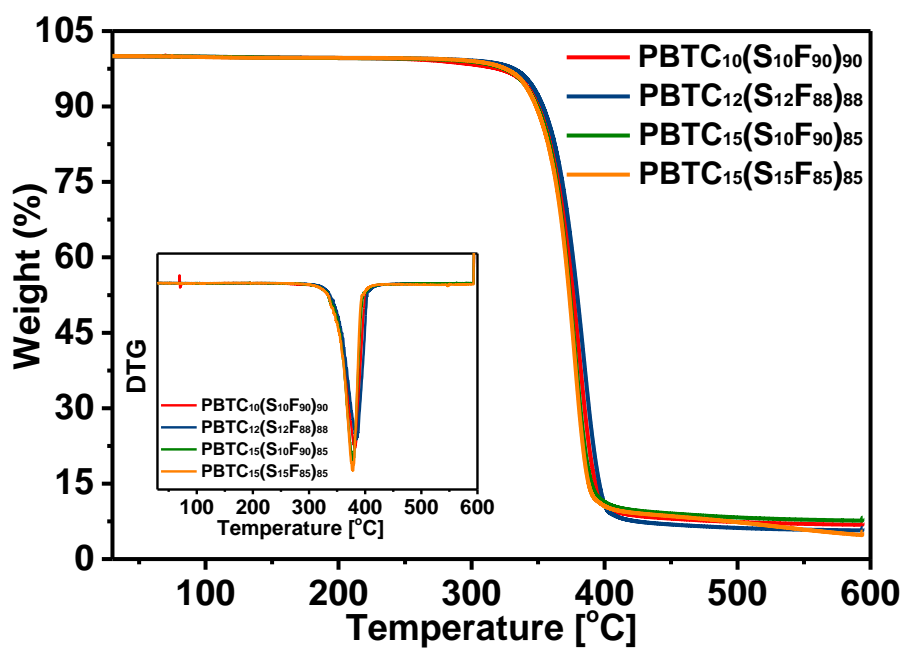


Figure S18. TGA characterization of PBTC_x(S_nF_m)_y.

DSC Characterization of Polymers.

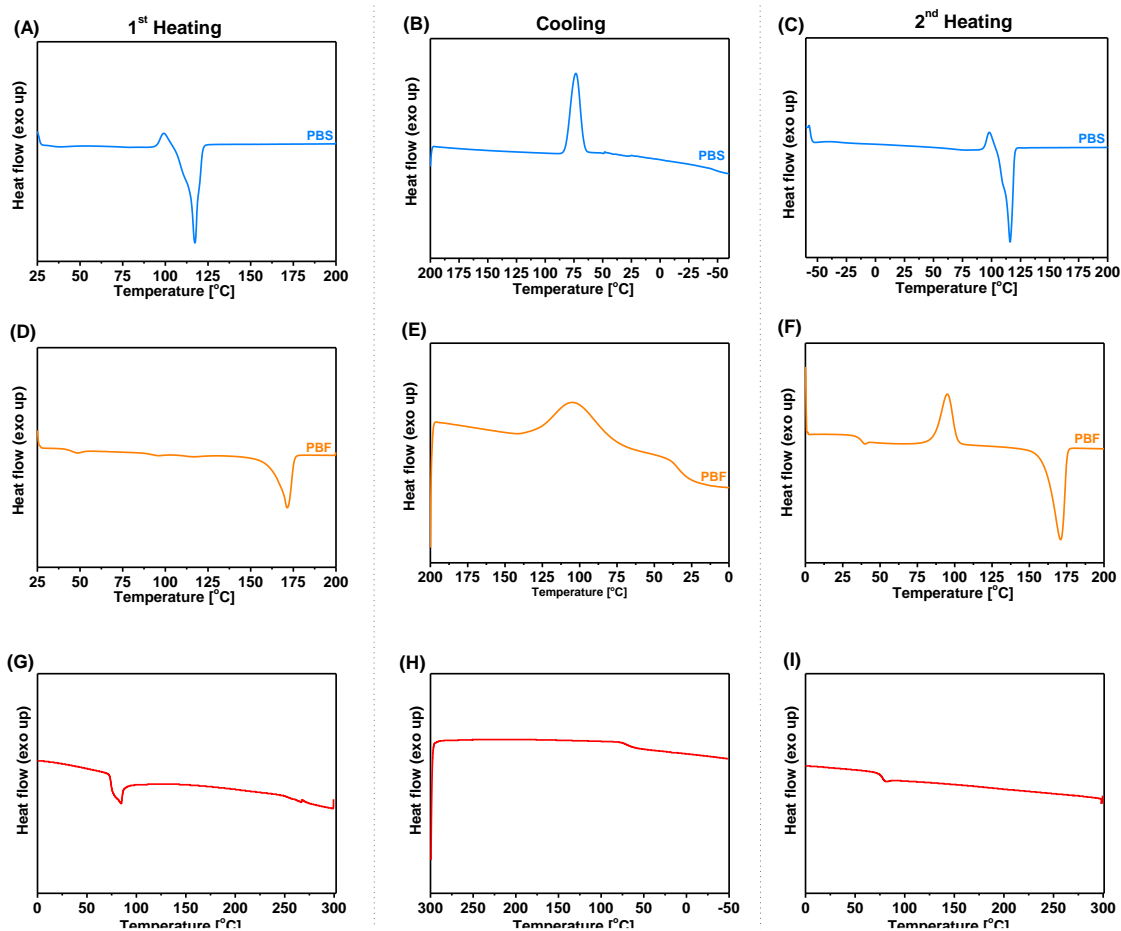


Figure S19. DSC characterization of PBS (A-C), PBF (D-F), and PBTC (G-I).

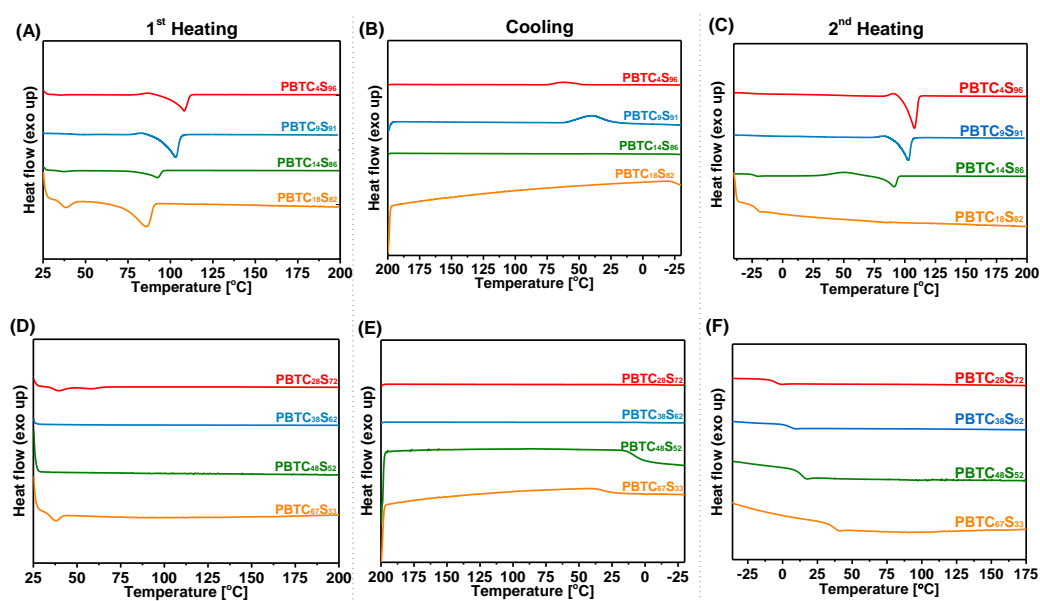


Figure S20. DSC characterization of $\text{PBTC}_{(4-18)}\text{S}_{(96-82)}$ (A-C), and $\text{PBTC}_{(28-67)}\text{S}_{(72-33)}$ (D-F).

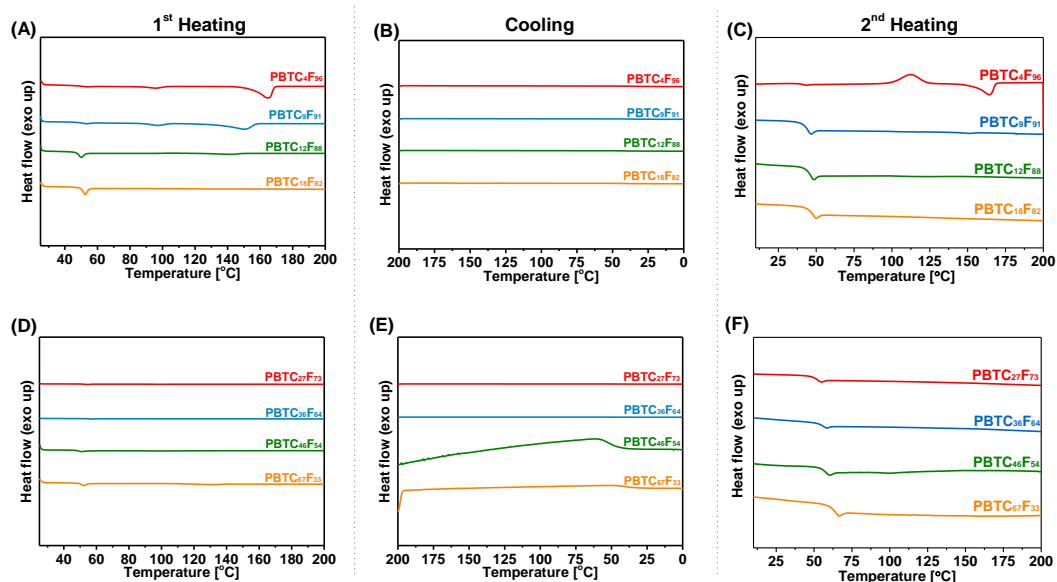


Figure S21. DSC characterization of PBTC₍₄₋₁₈₎F₍₉₆₋₈₂₎ (A-C) and PBTC₍₂₇₋₆₇₎F₍₇₃₋₃₃₎ (D-F).

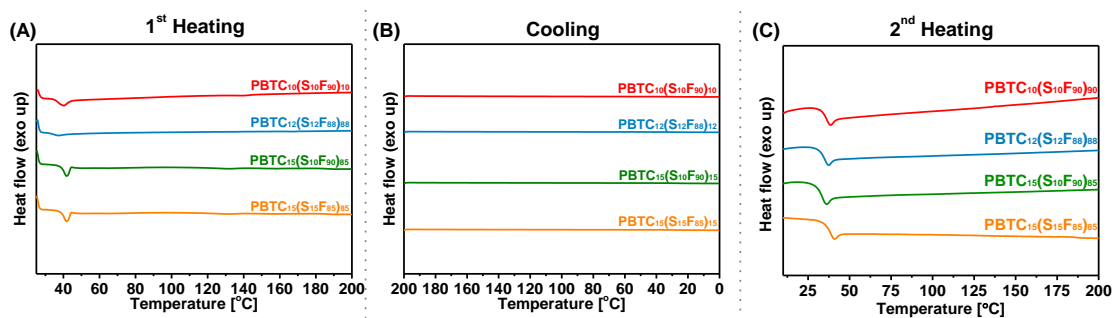


Figure S22. DSC characterization of PBTC_x(S_nF_m)_y.

■ Transparency

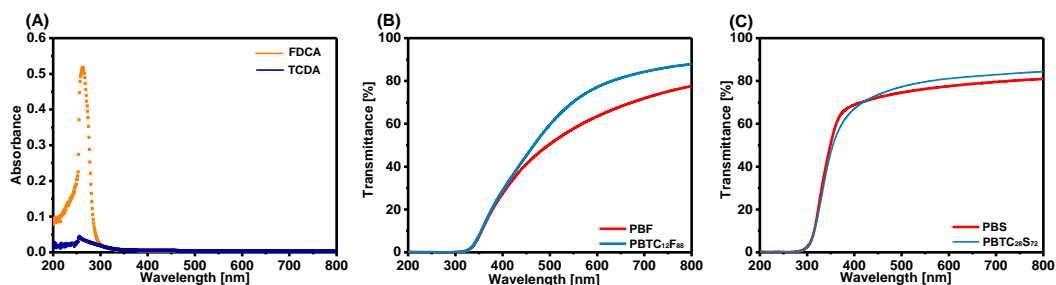


Figure S23. (A) UV-vis absorption of monomers (1 mg/100 mL in dimethyl sulfoxide); (B) UV-vis transmittance of PBF and PBTC₁₂F₈₈ films; (C) UV-vis transmittance of PBS and PBTC₂₈S₇₂ films. The thickness of sample films is around 170 μ m.

Mechanical Property of co-Polyesters.

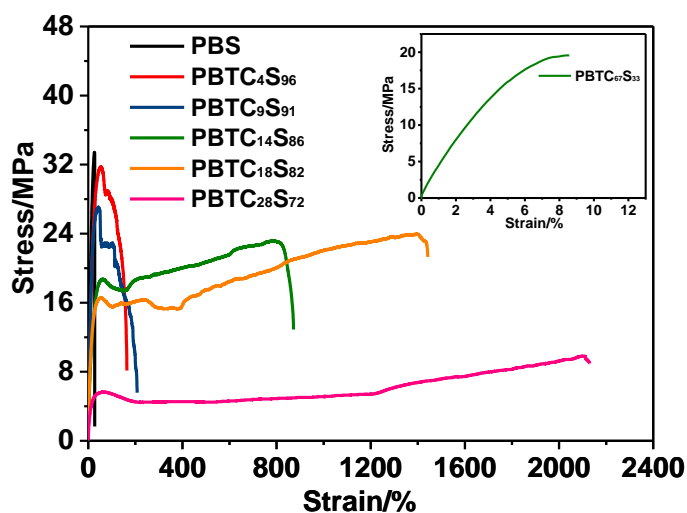


Figure S24. The mechanical property of PBTC_xS_y.

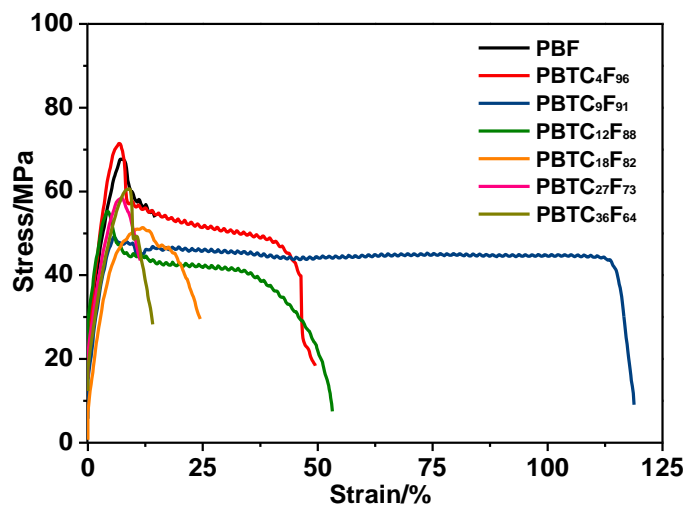


Figure S25. The mechanical property of PBTC_xF_y.

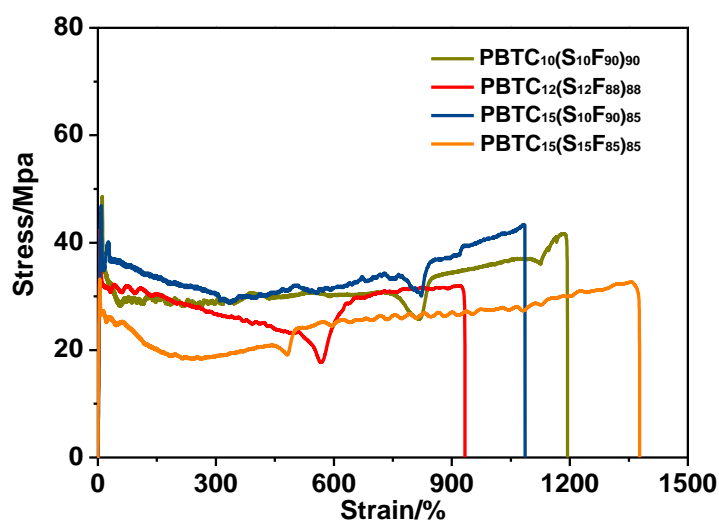


Figure S26. The mechanical property of PBTC_x(S_nF_m)_y.

■ Gas Barrier Properties of Polyesters

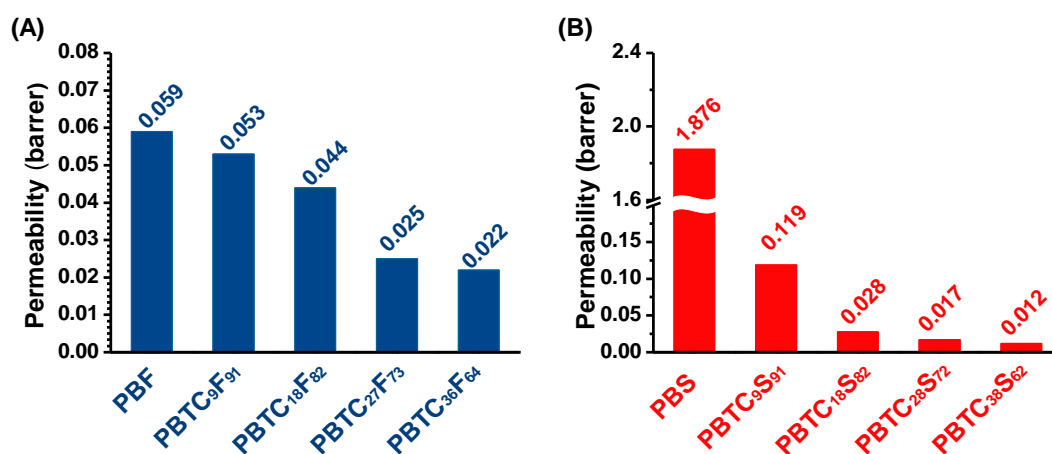


Figure S27. CO₂ barrier properties of (A) PBTC_xF_y series; (B) PBTC_xS_y series. (1 barrer = 10⁻¹⁰ cm³ cm/(cm² s cm Hg)).

■ FTIR Spectra of Monomers and Polyesters

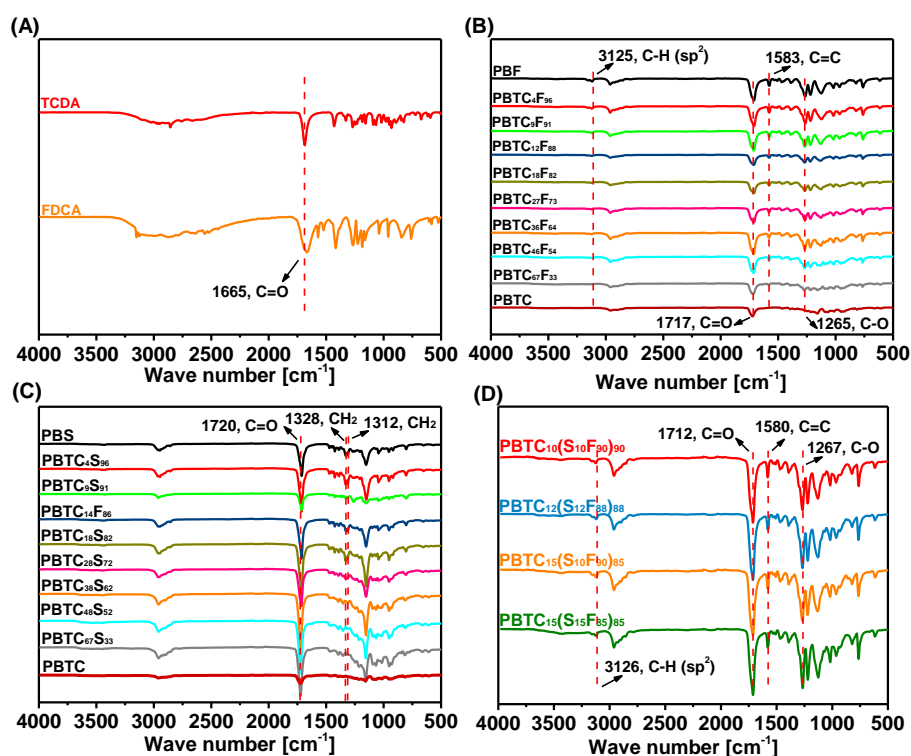


Figure S28. ATR-FTIR spectra of (A) TCDA and FDCA monomers; (B) PBTC_xF_y series; (C) PBTC_xS_y series; (D) PBTC_x(S_nF_m)_y series.

■ NMR Spectroscopic Characterization

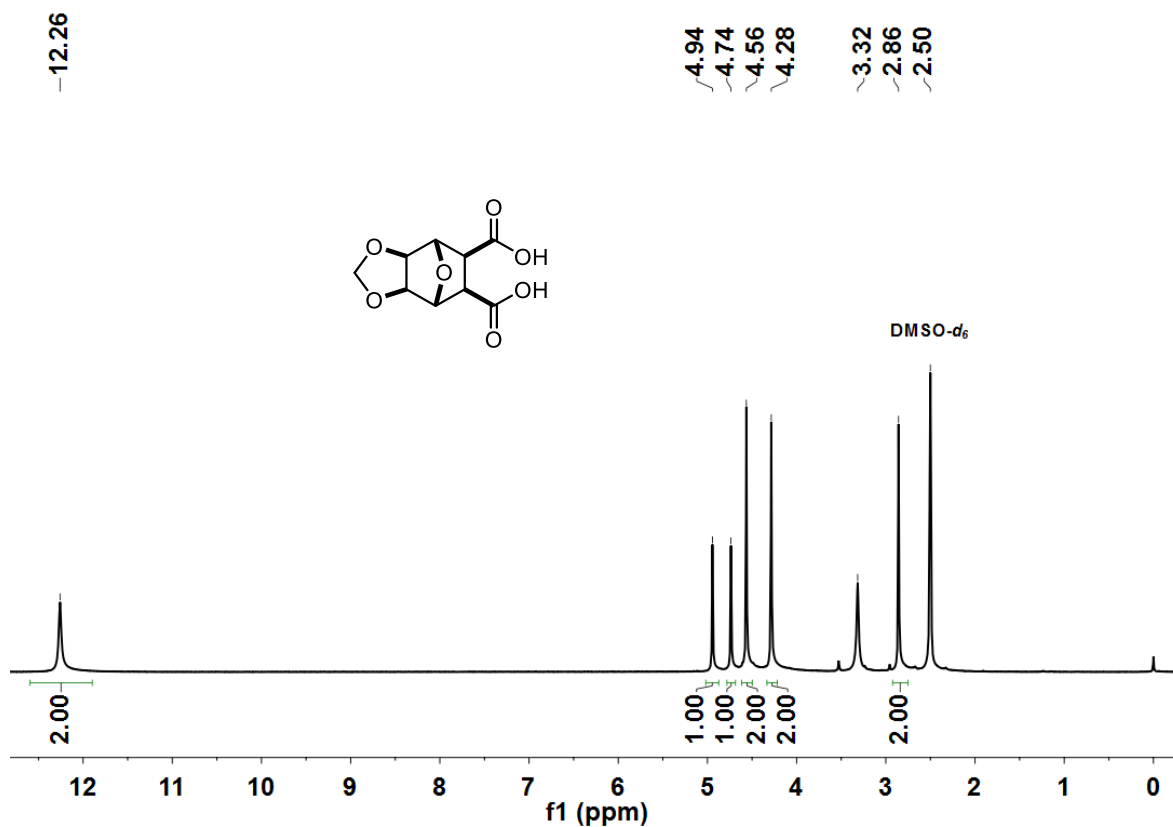


Figure S29. ¹H NMR spectrum of TCDA.

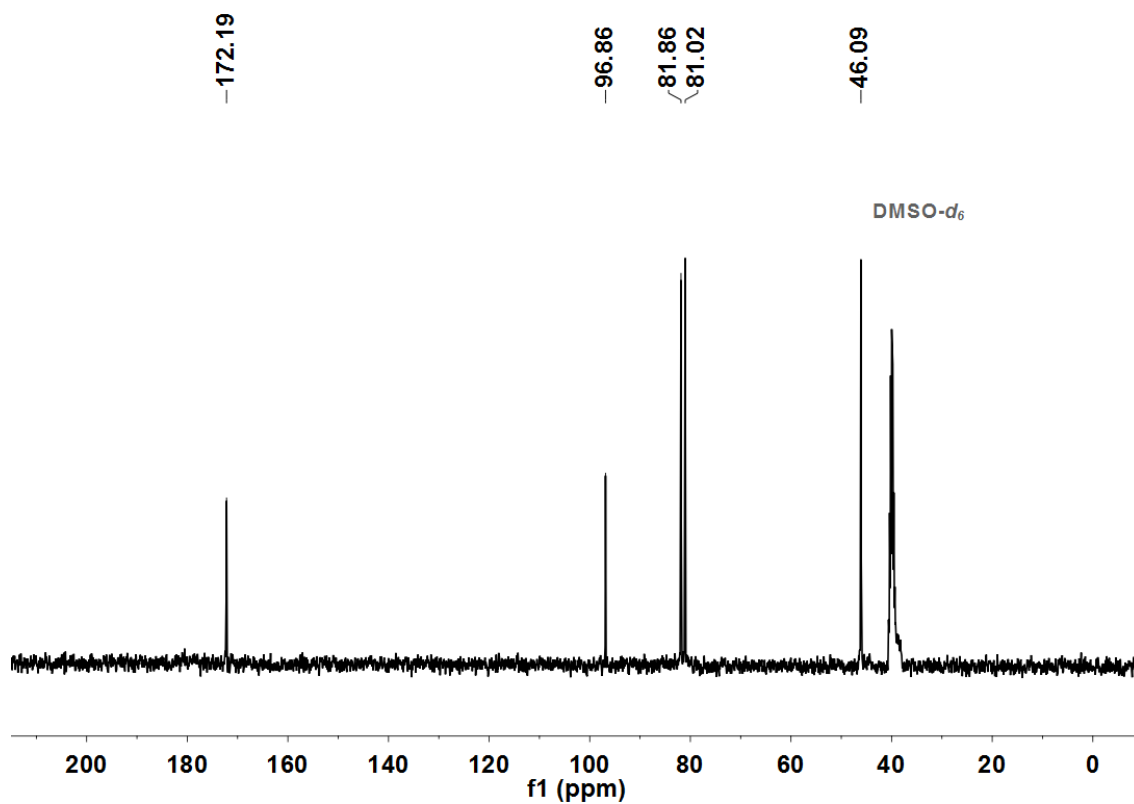


Figure S30. ¹³C NMR spectrum of TCDA.

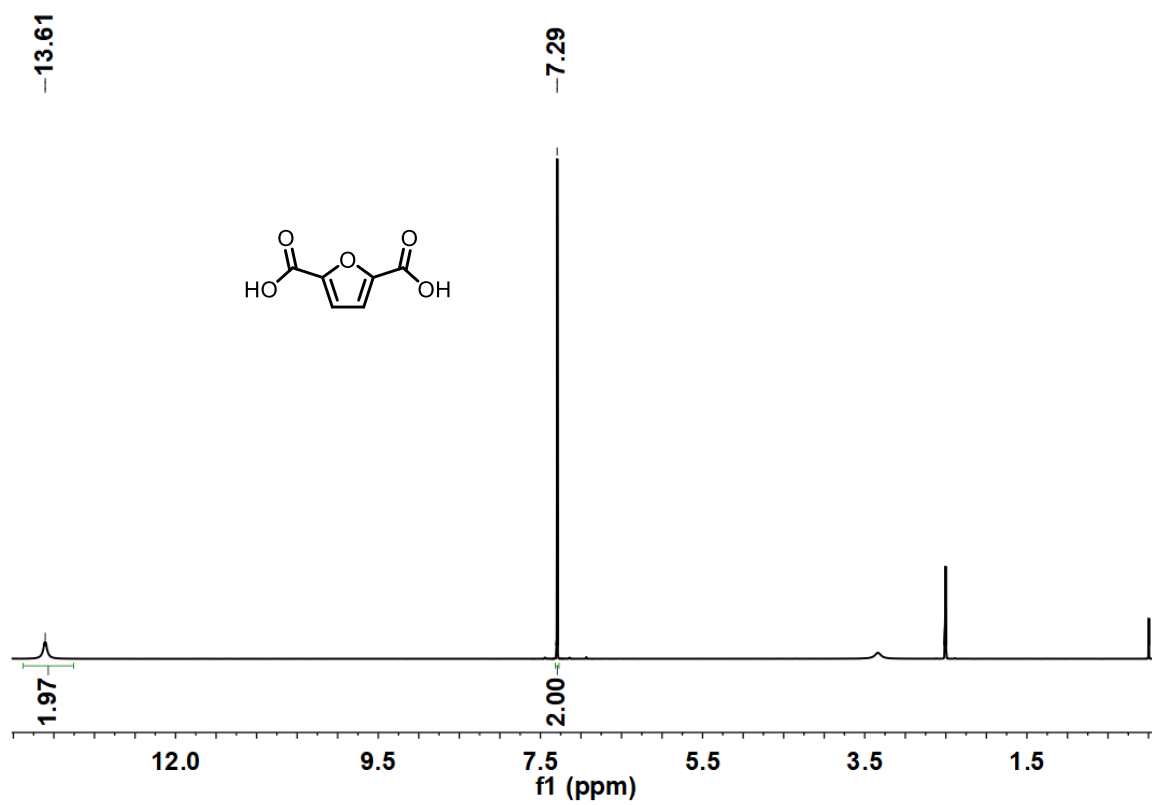


Figure S31. ¹H NMR spectrum of FDCA.

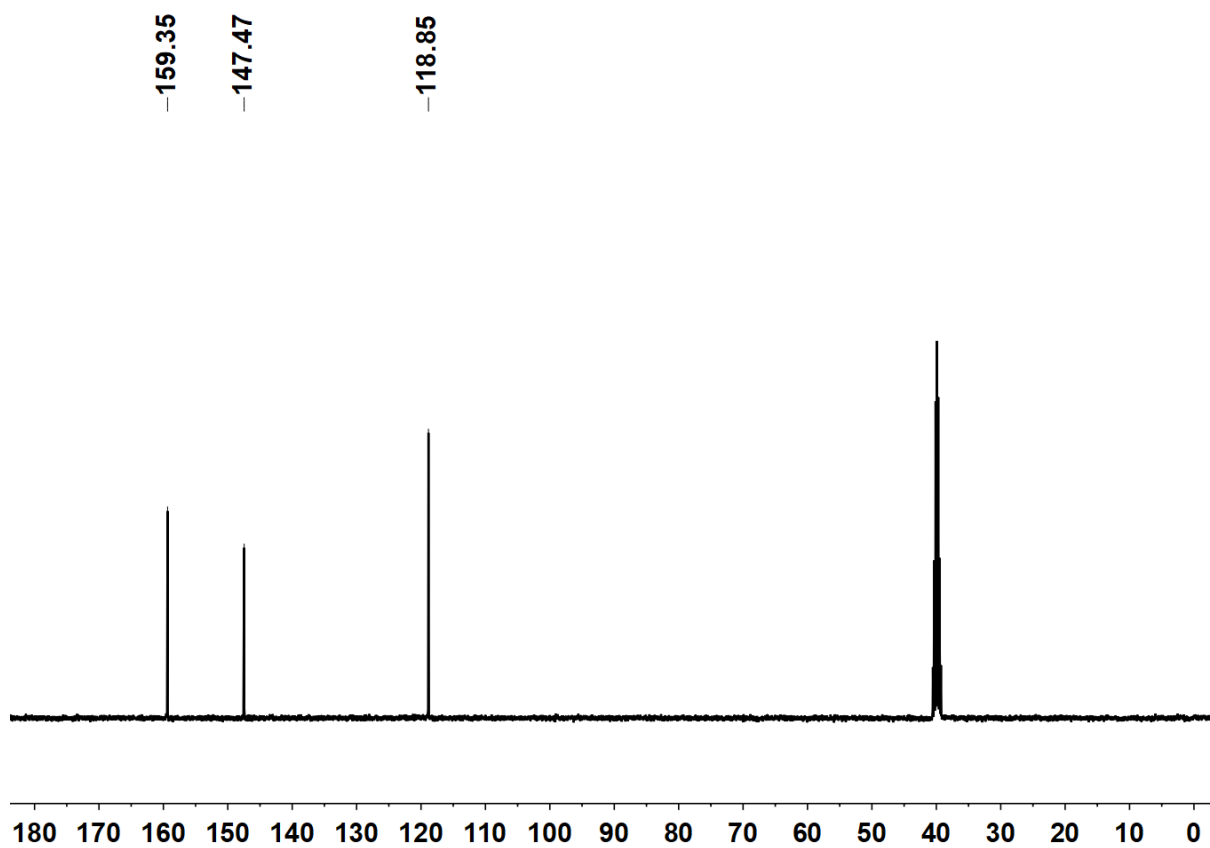


Figure S32. ¹³C NMR spectrum of FDCA.

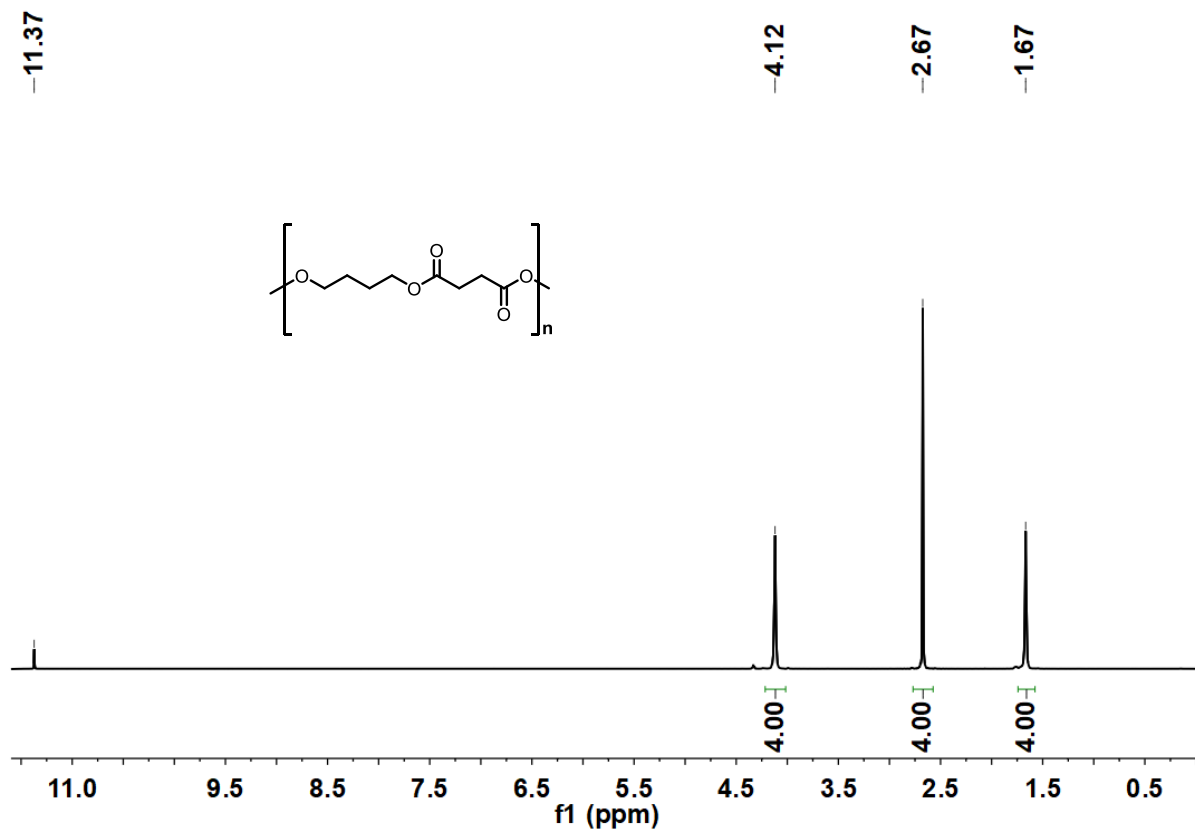


Figure S33. ^1H NMR spectrum of PBS.

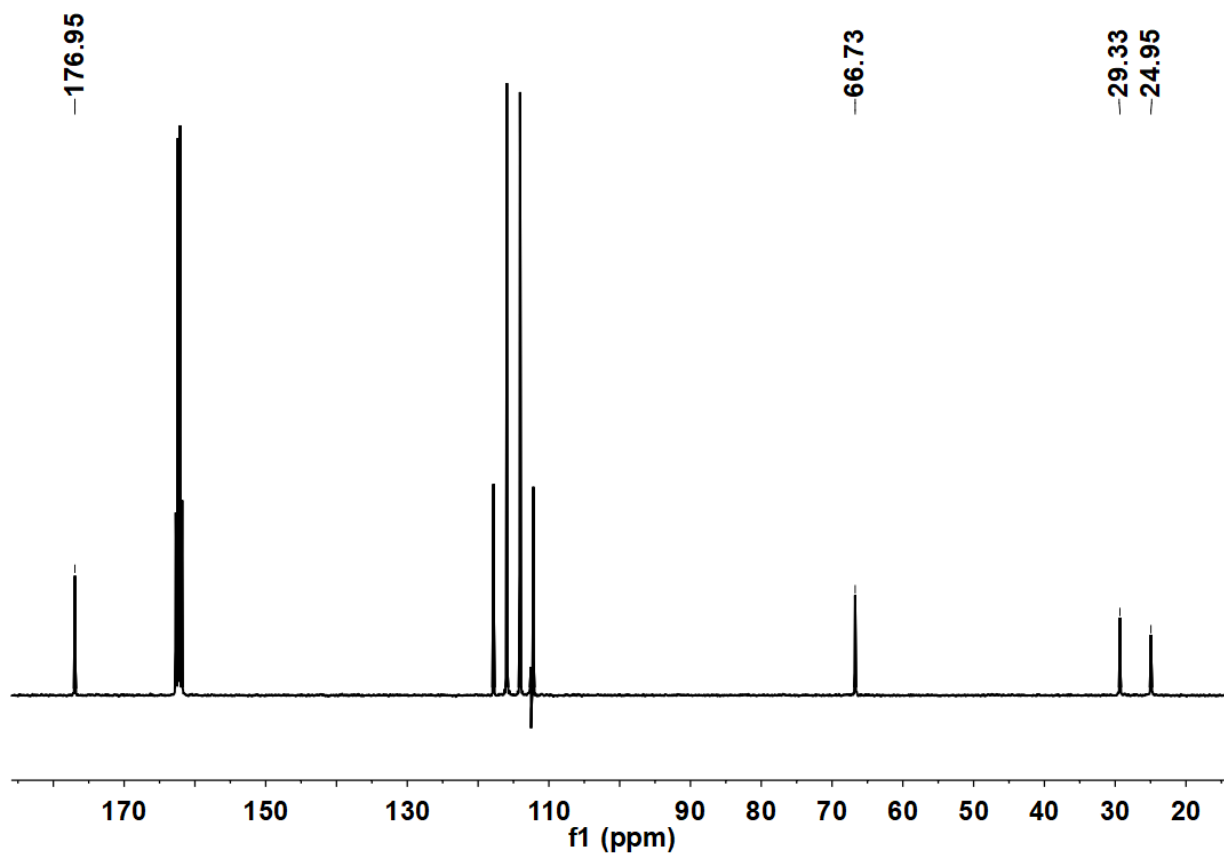


Figure S34. ^{13}C NMR spectrum of PBS.

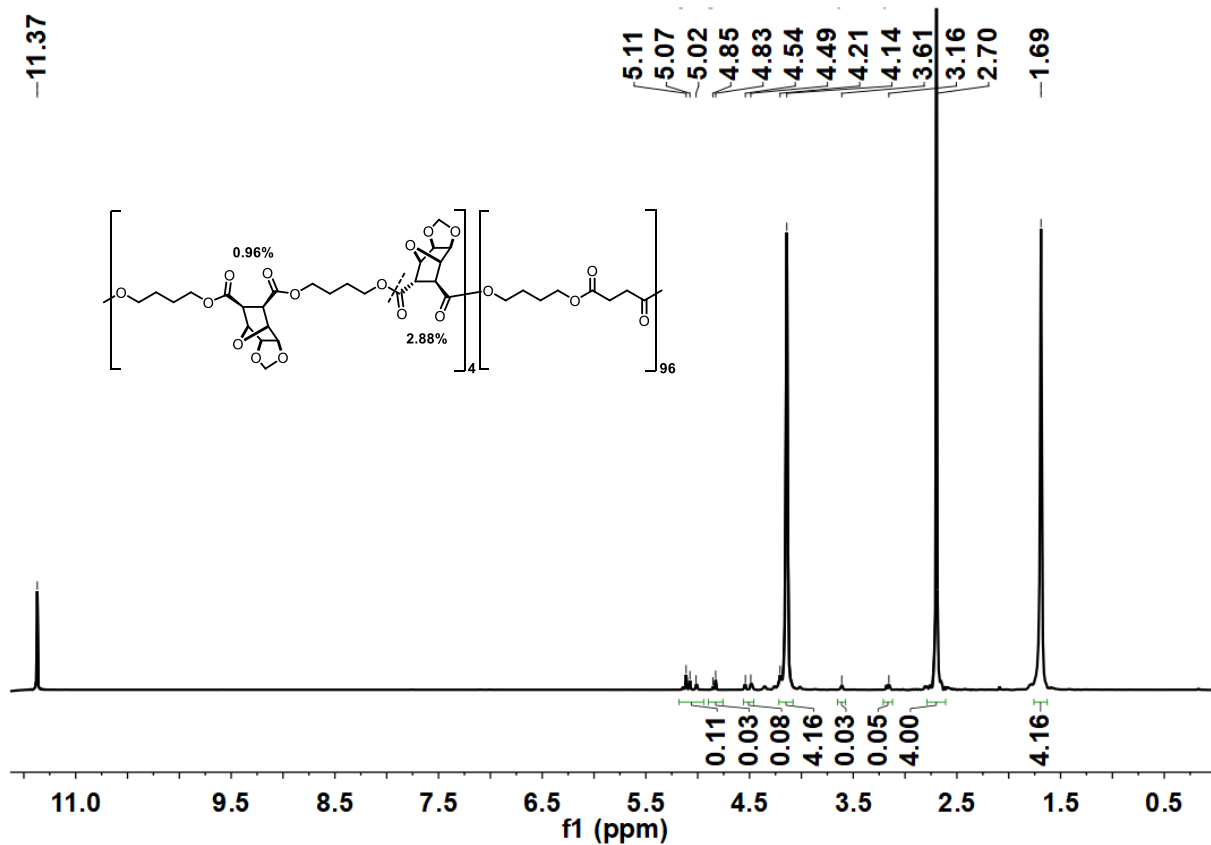


Figure S35. ¹H NMR spectrum of PBTC₄S₉₆.

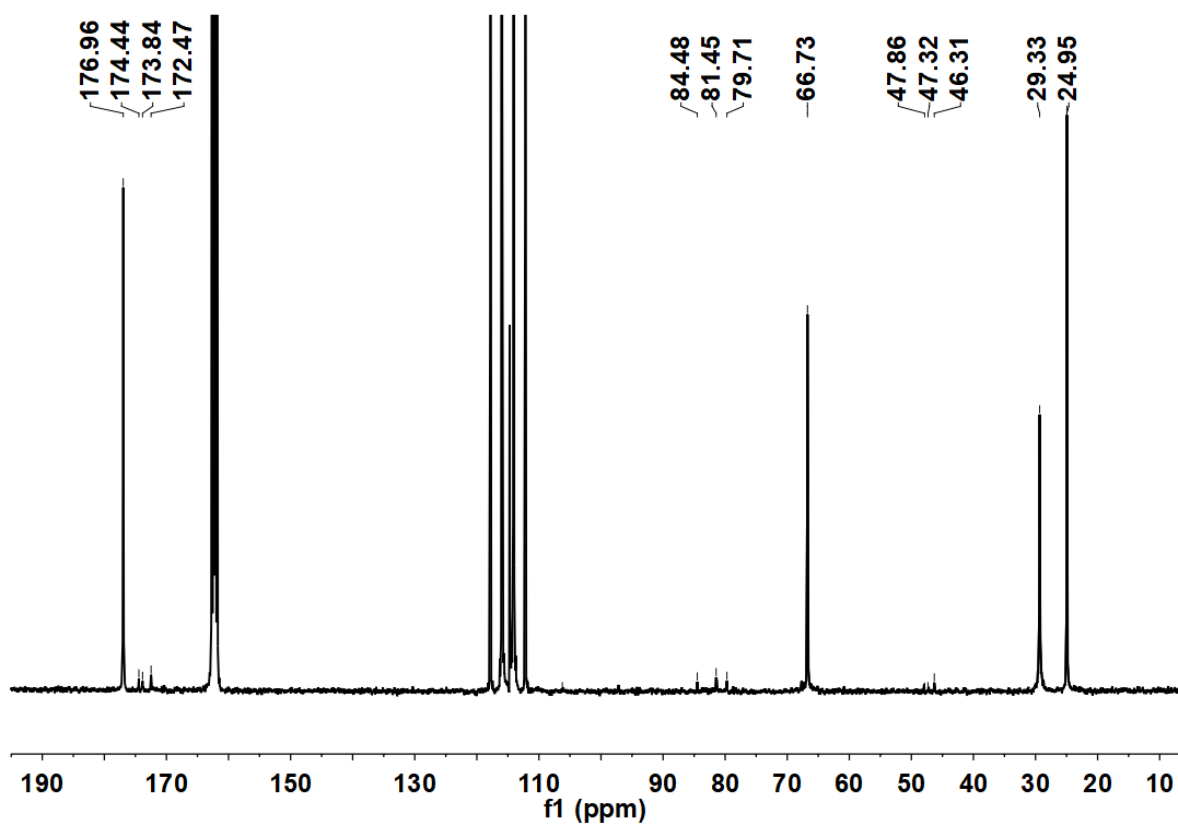


Figure S36. ¹³C NMR spectrum of PBTC₄S₉₆.

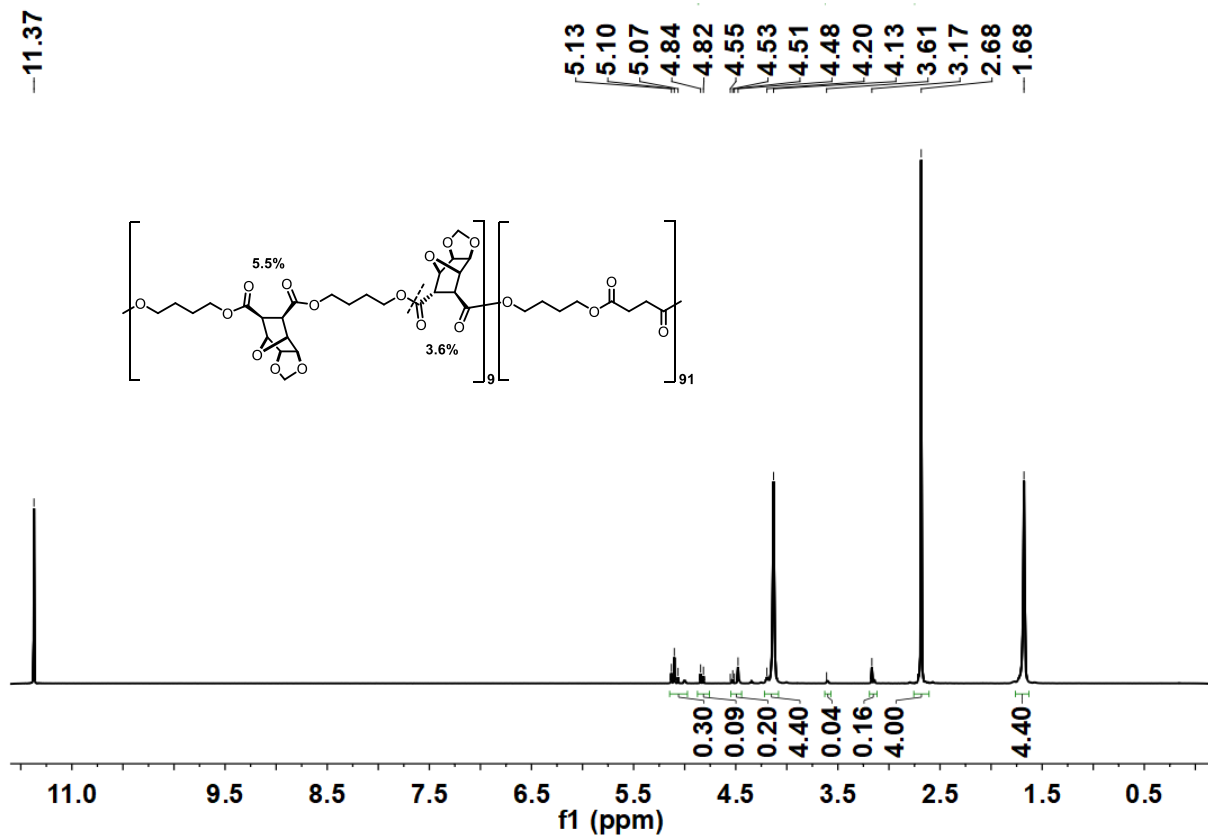


Figure S37. ^1H NMR spectrum of PBTC₉S₉₁.

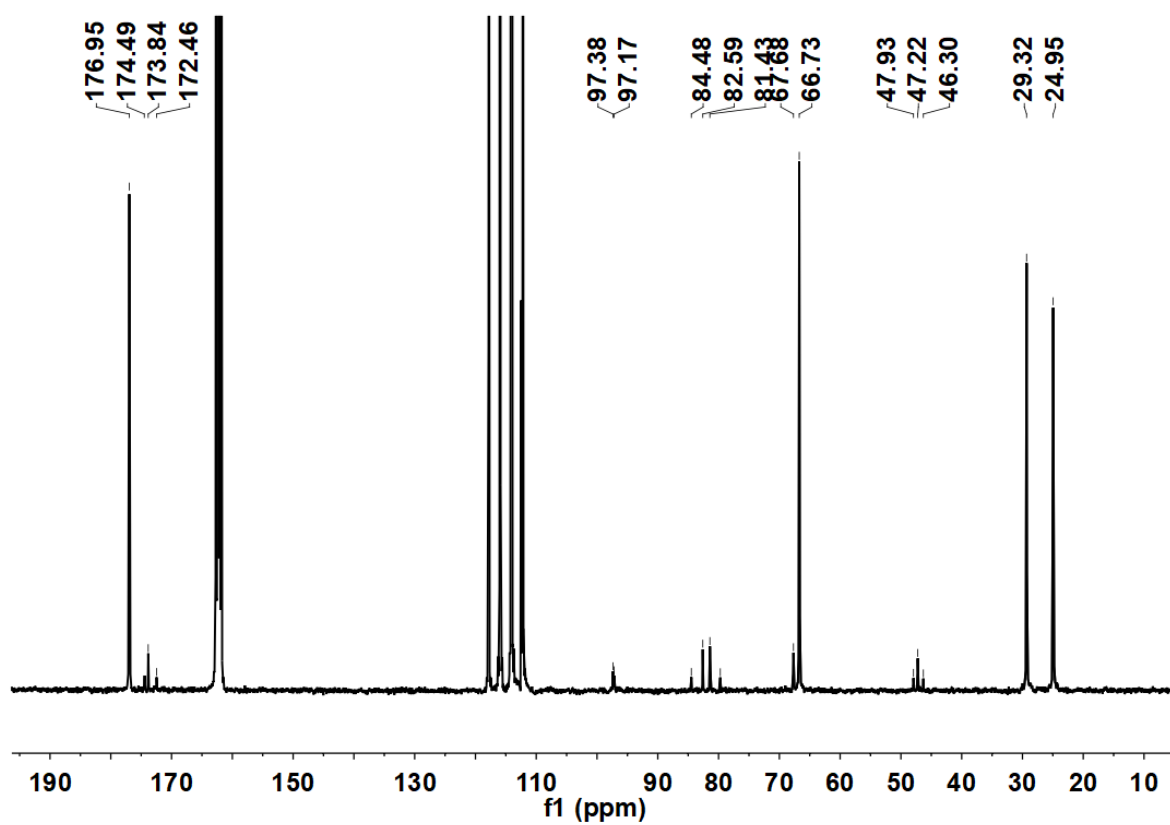


Figure S38. ^{13}C NMR spectrum of PBTC₉S₉₁.

-11.37

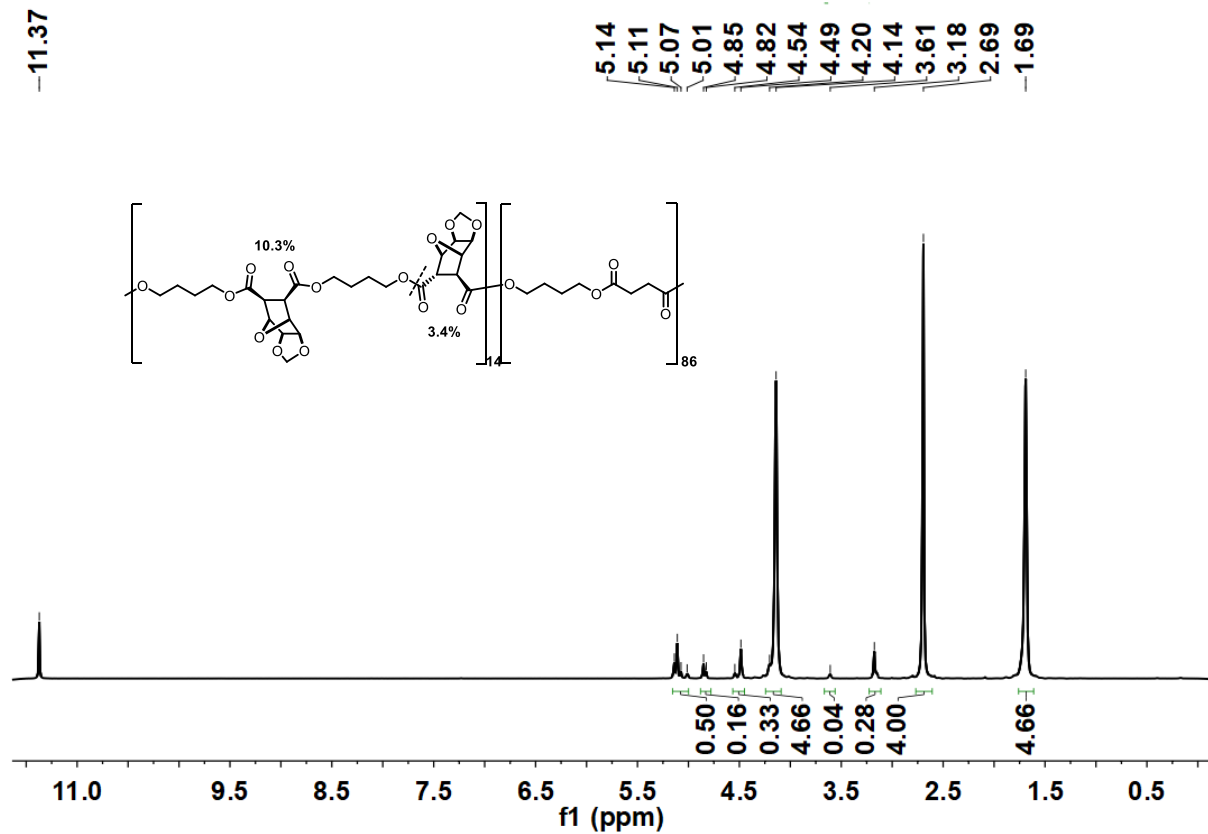


Figure S39. ¹H NMR spectrum of PBTC₁₄S₈₆.

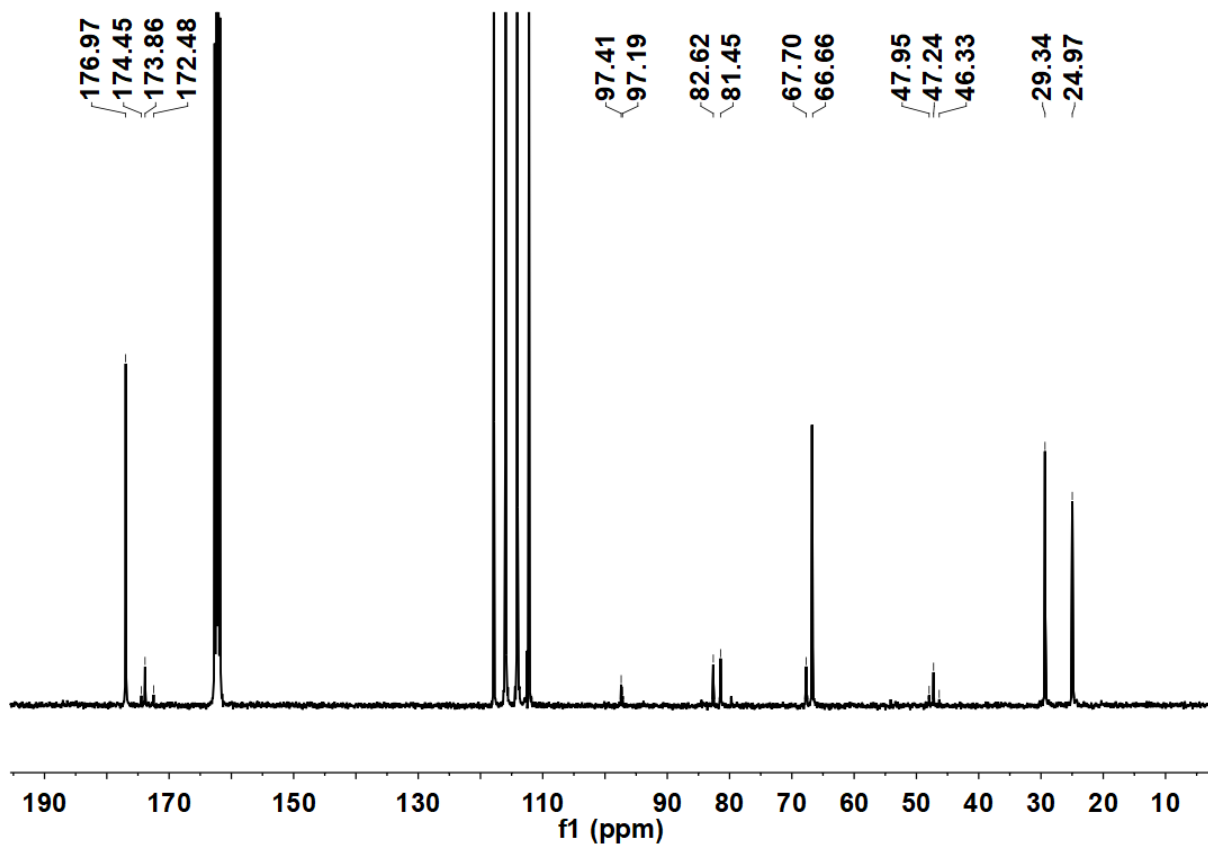


Figure S40. ¹³C NMR spectrum of PBTC₁₄S₈₆.

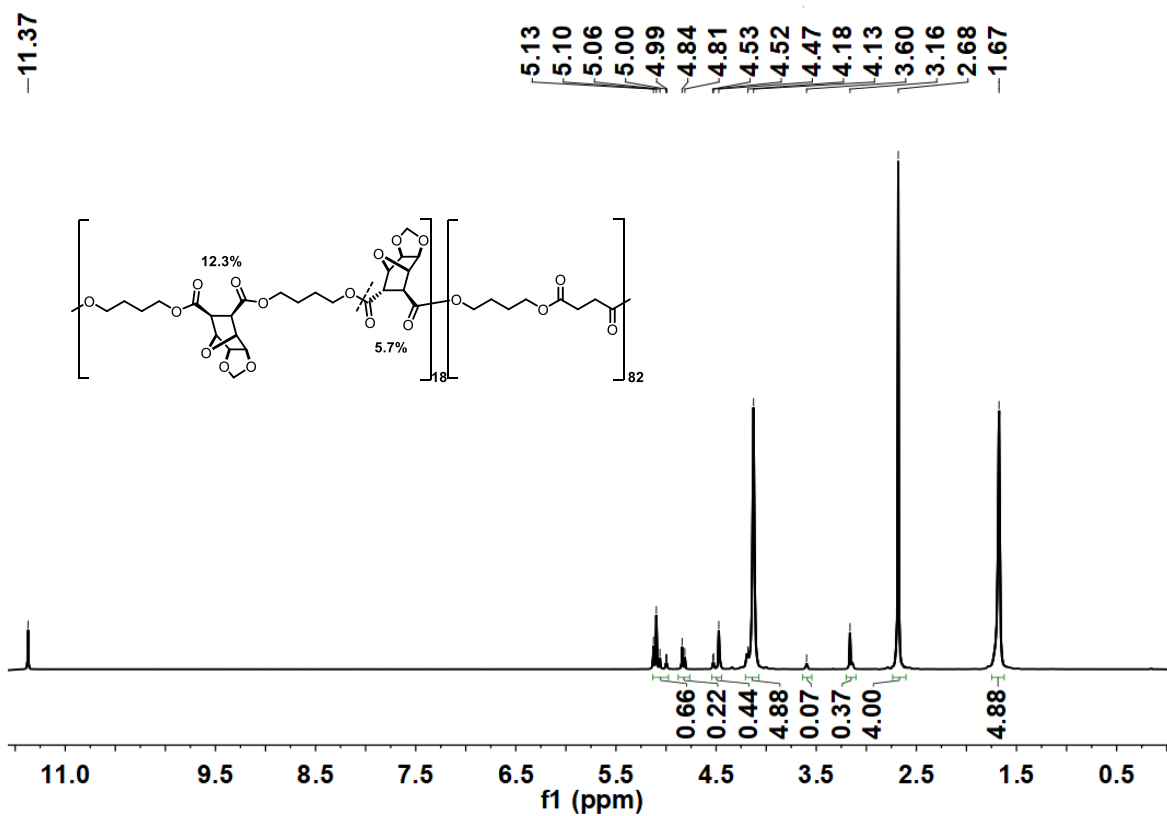


Figure S41. ^1H NMR spectrum of $\text{PBTC}_{18}\text{S}_{82}$.

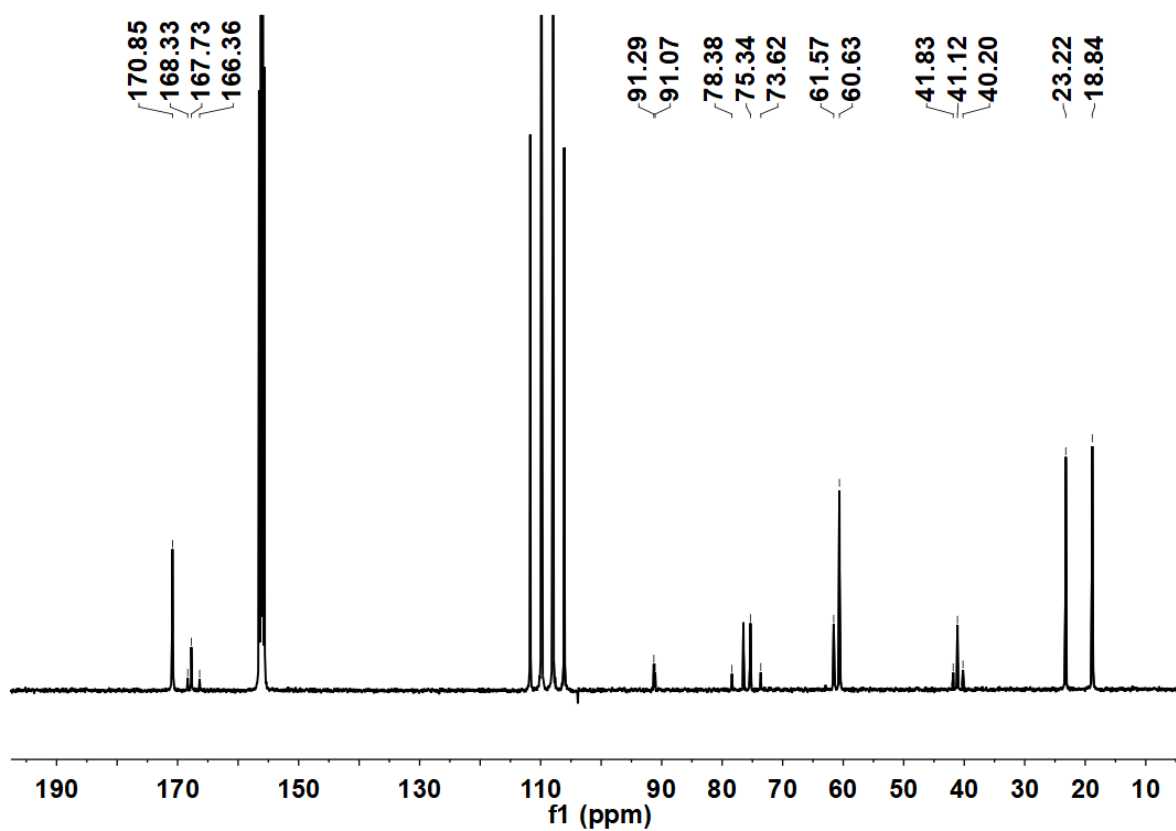


Figure S42. ^{13}C NMR spectrum of $\text{PBTC}_{18}\text{S}_{82}$.

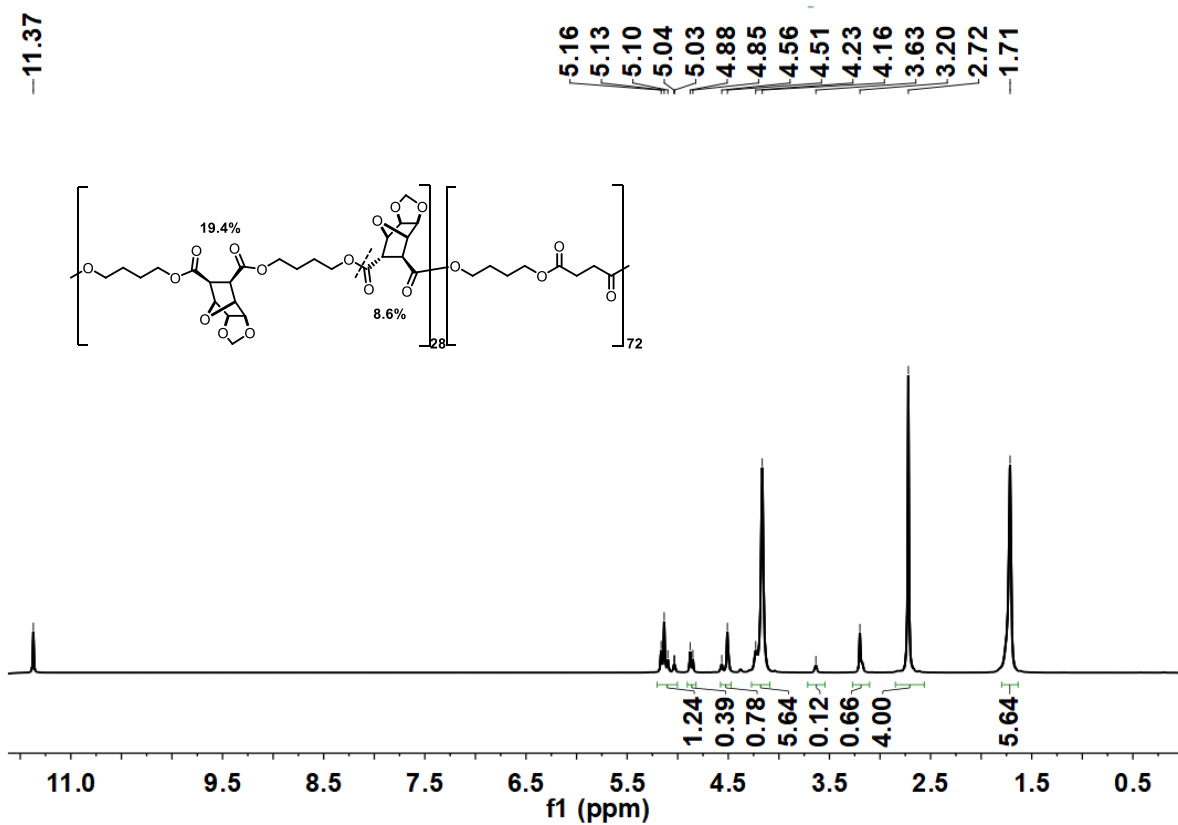


Figure S43. ^1H NMR spectrum of PBTC₂₈S₇₂.

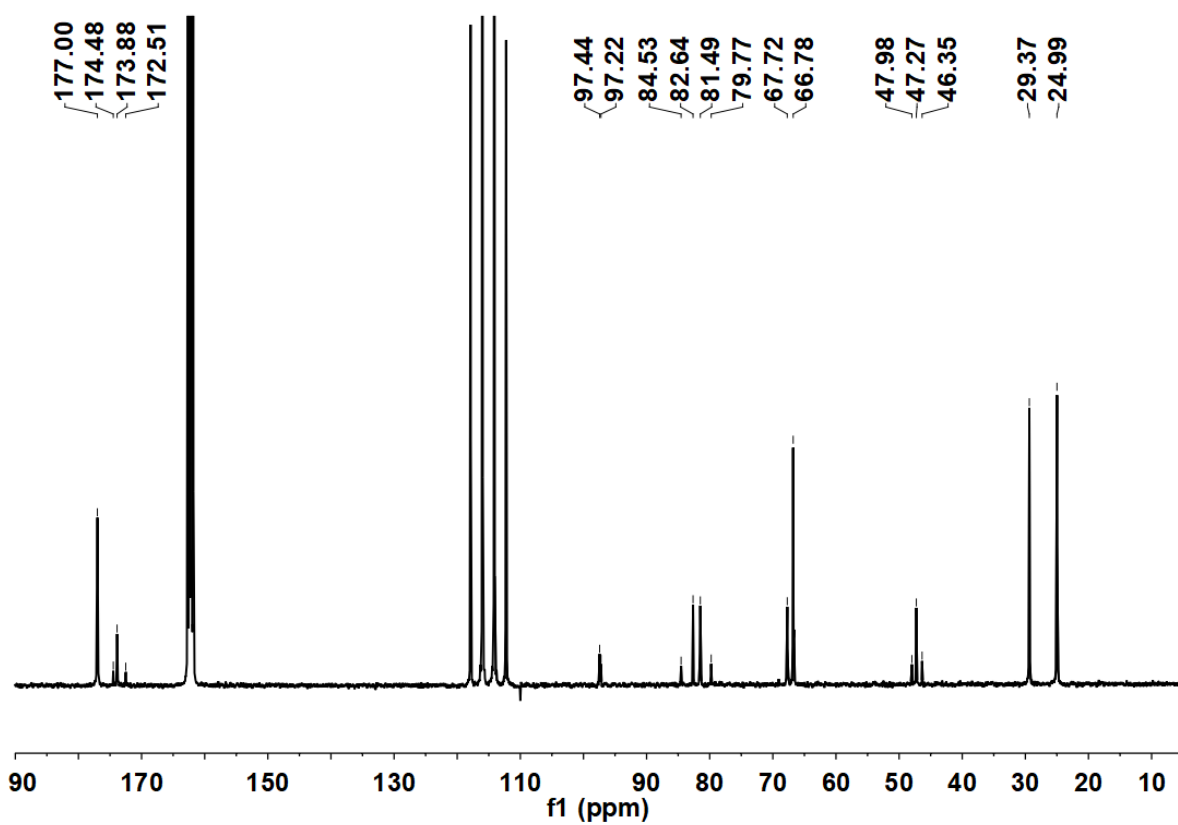


Figure S44. ^{13}C NMR spectrum of PBTC₂₈S₇₂.

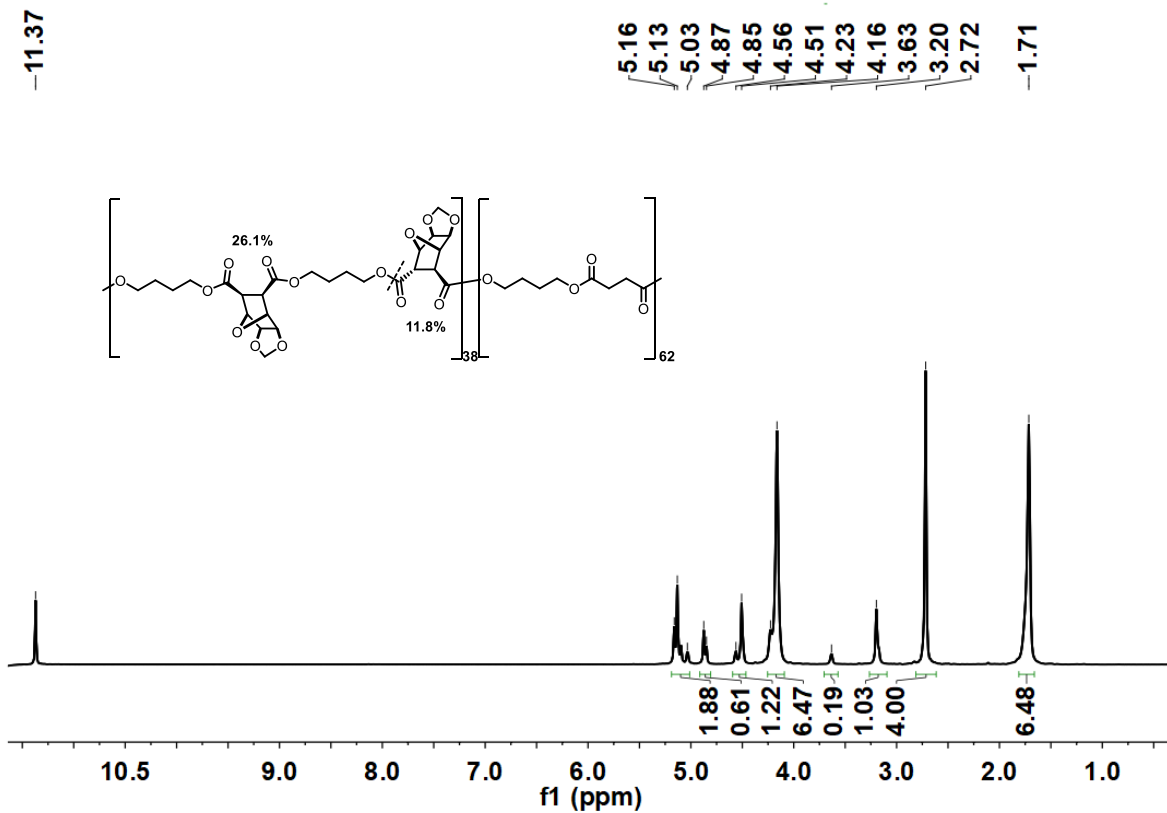


Figure S45. ^1H NMR spectrum of $\text{PBTC}_{38}\text{S}_{62}$.

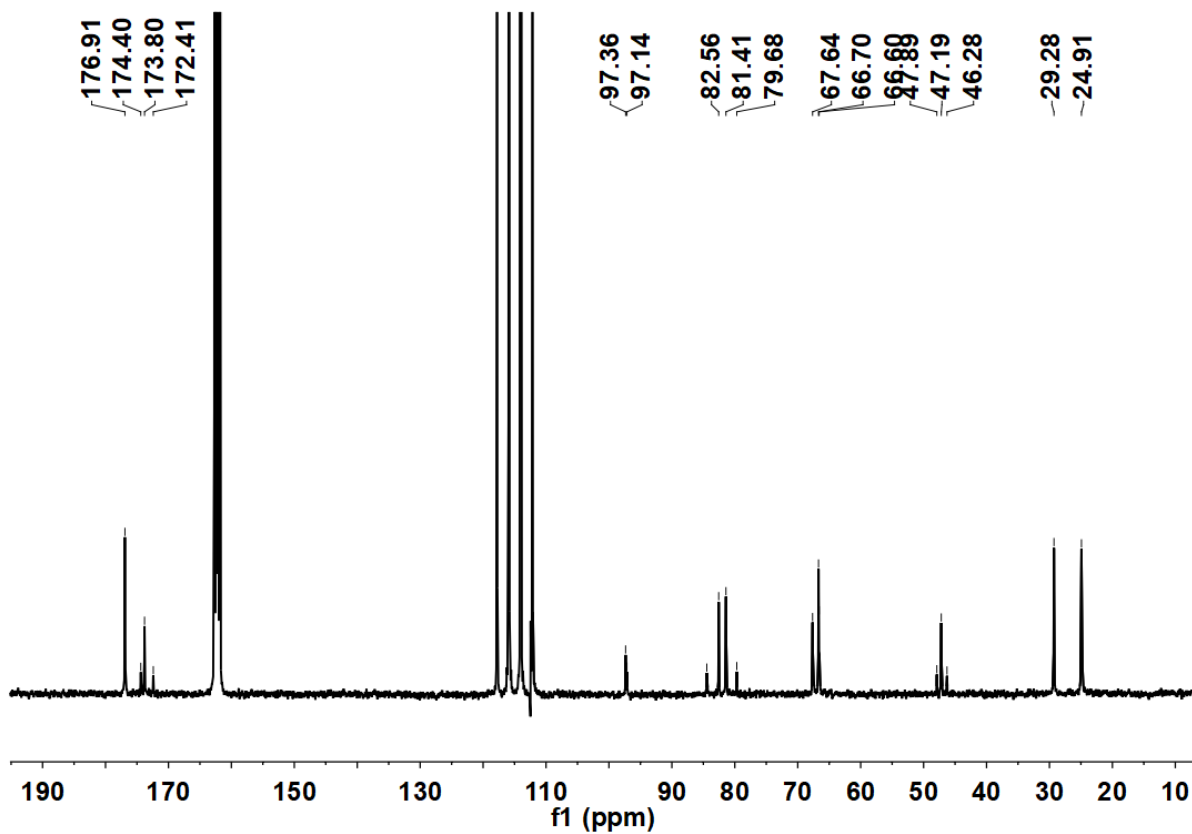


Figure S46. ^{13}C NMR spectrum of $\text{PBTC}_{38}\text{S}_{62}$.

-11.37

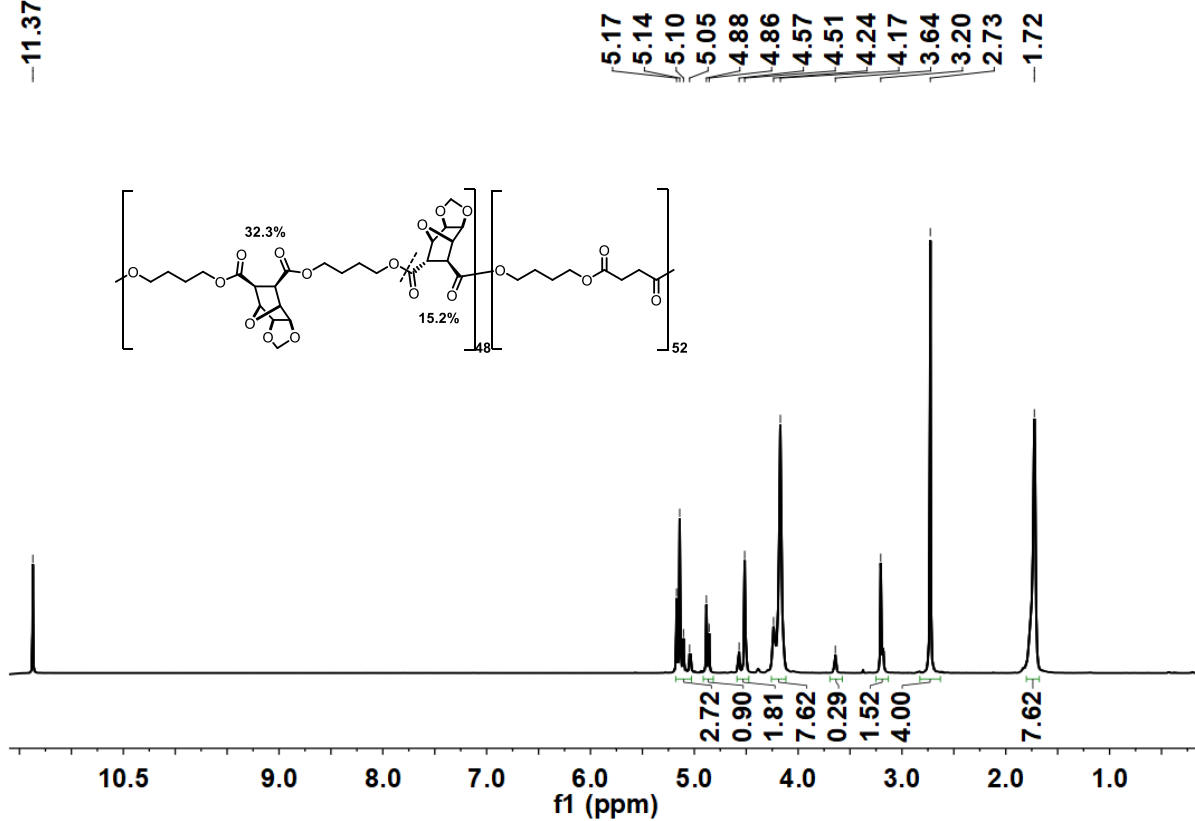


Figure S47. ¹H NMR spectrum of PBTC₄₈S₅₂.

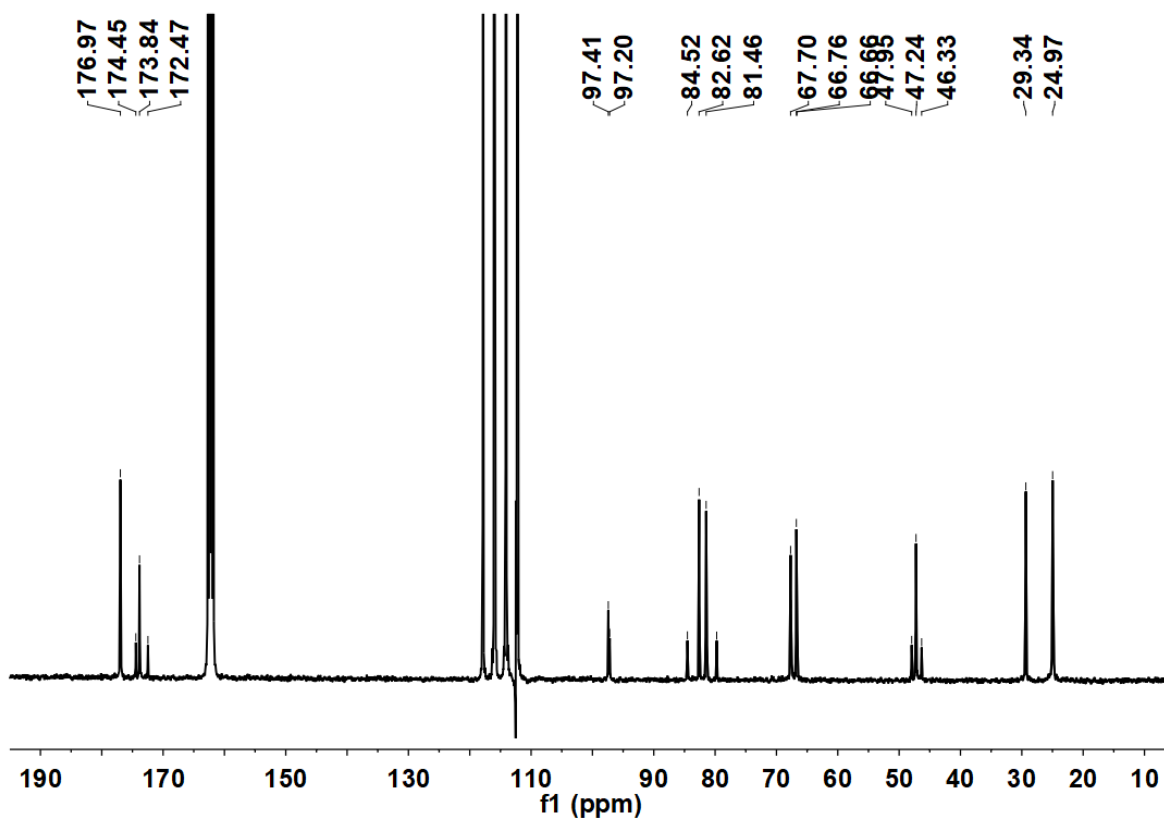


Figure S48. ¹³C NMR spectrum of PBTC₄₈S₅₂.

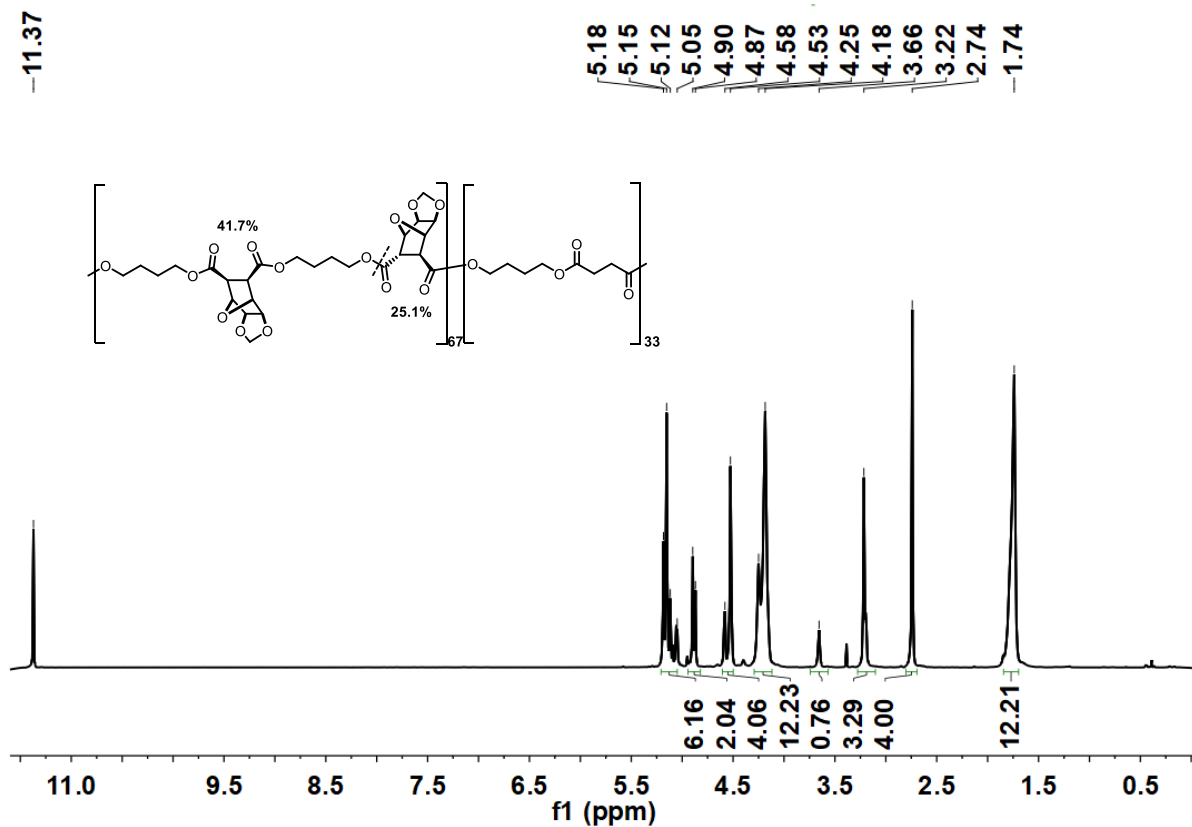


Figure S49. ¹H NMR spectrum of PBTC₆₇S₃₃.

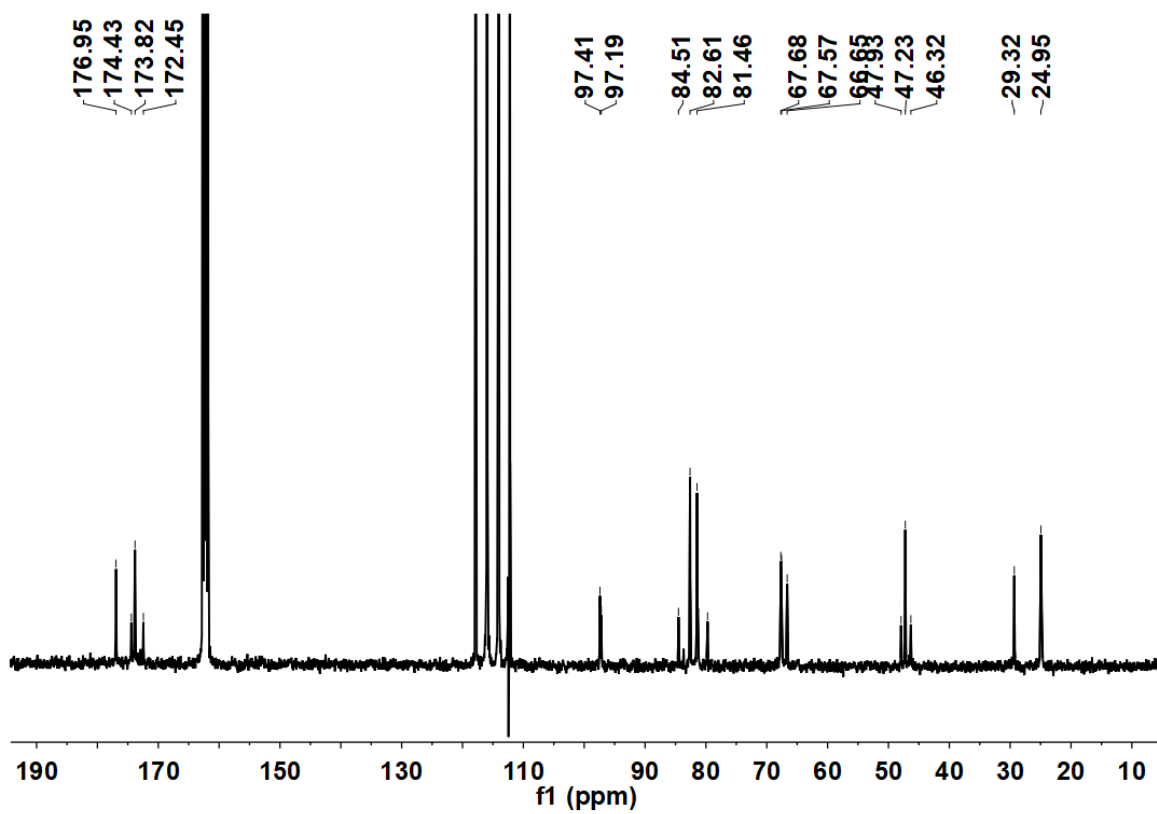


Figure S50. ¹³C NMR spectrum of PBTC₆₇S₃₃.

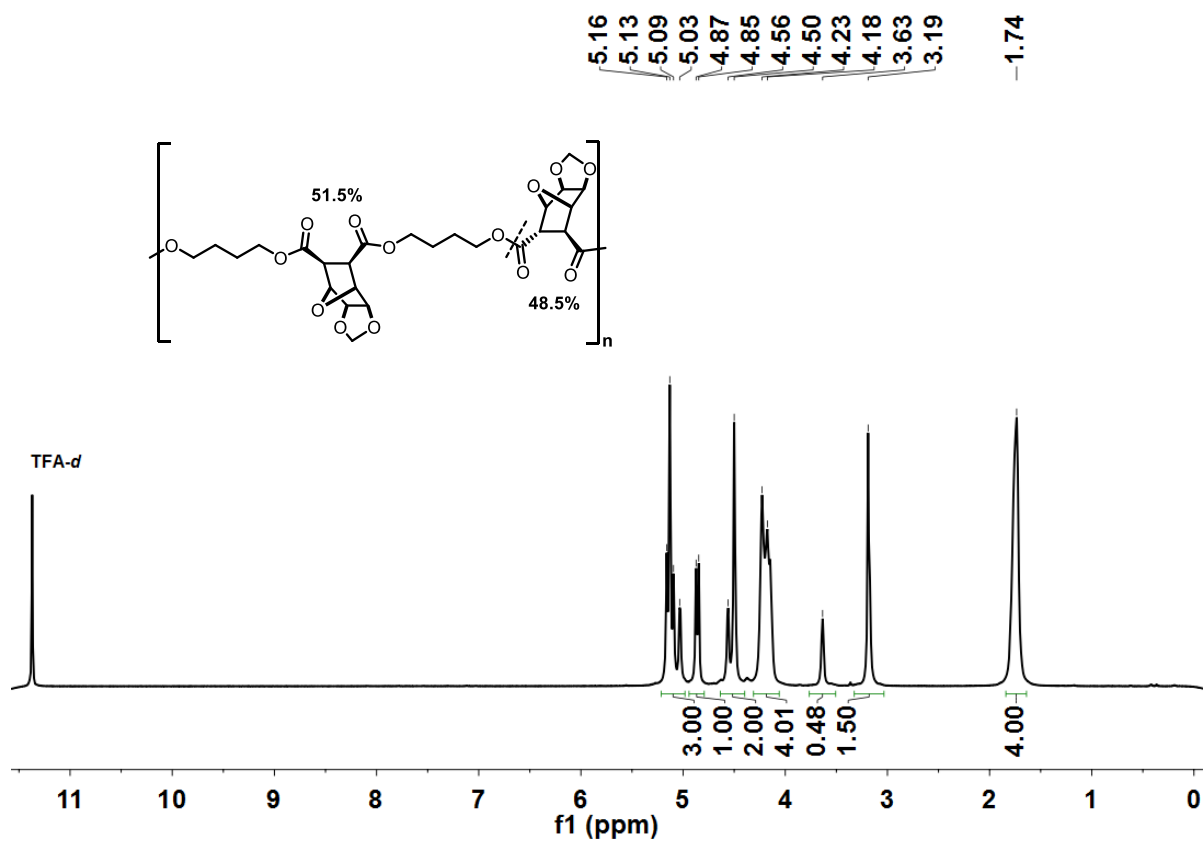


Figure S51. ¹H NMR spectrum of PBTC.

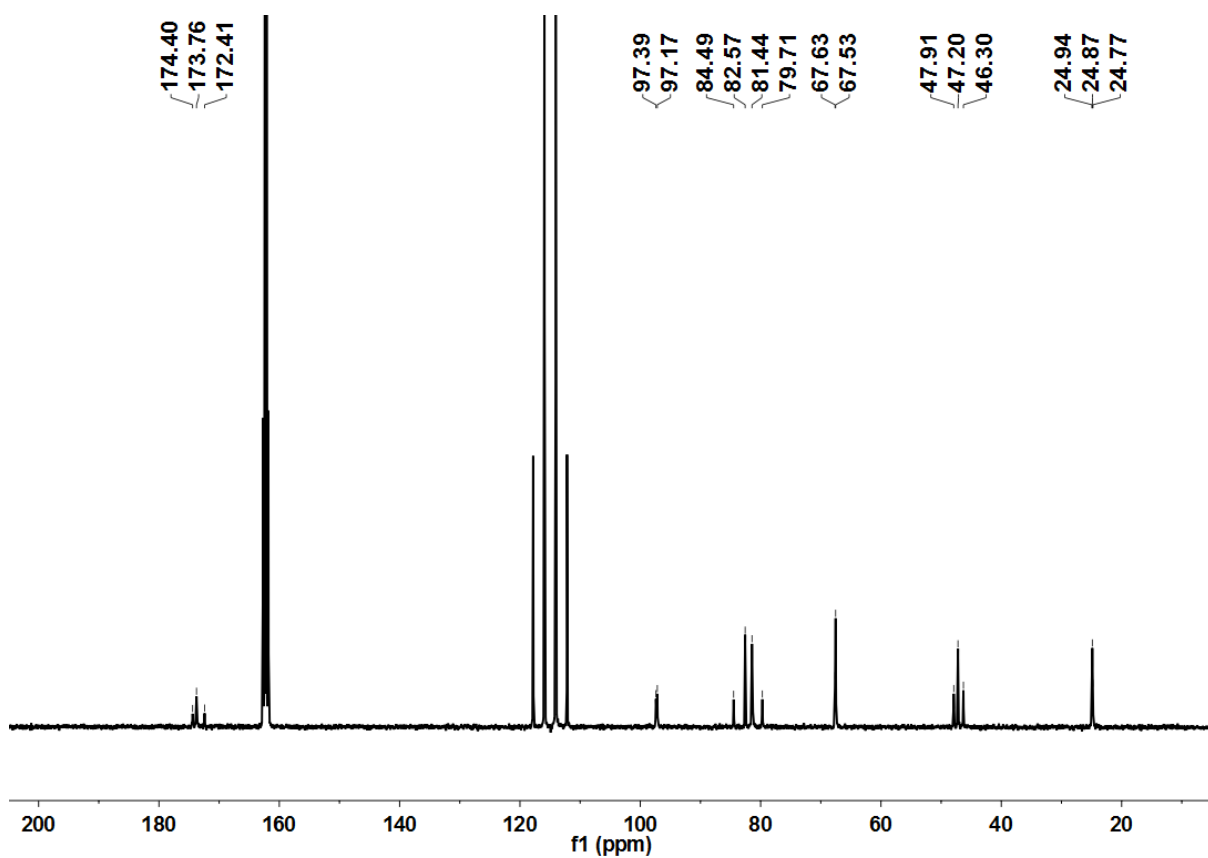


Figure S52. ¹³C NMR spectrum of PBTC.

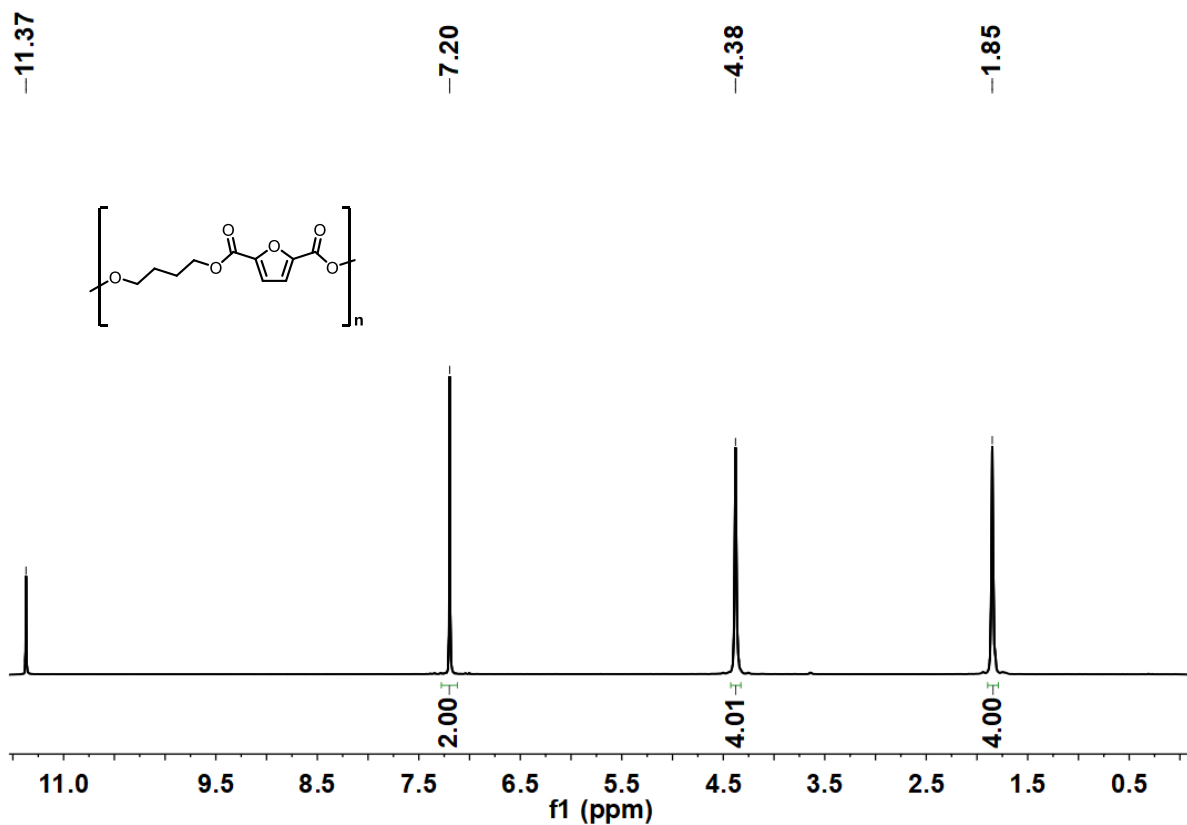


Figure S53. ^1H NMR spectrum of PBF.

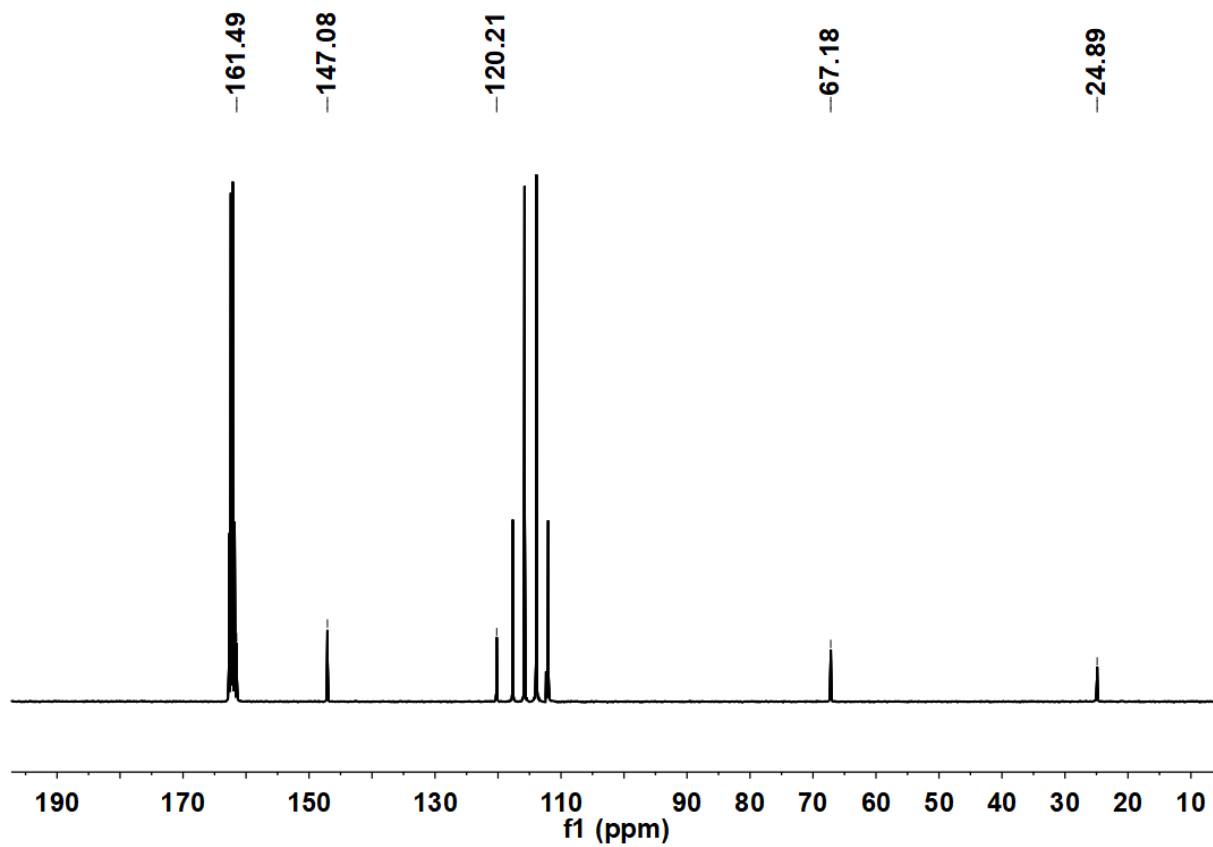


Figure S54. ^{13}C NMR spectrum of PBF.

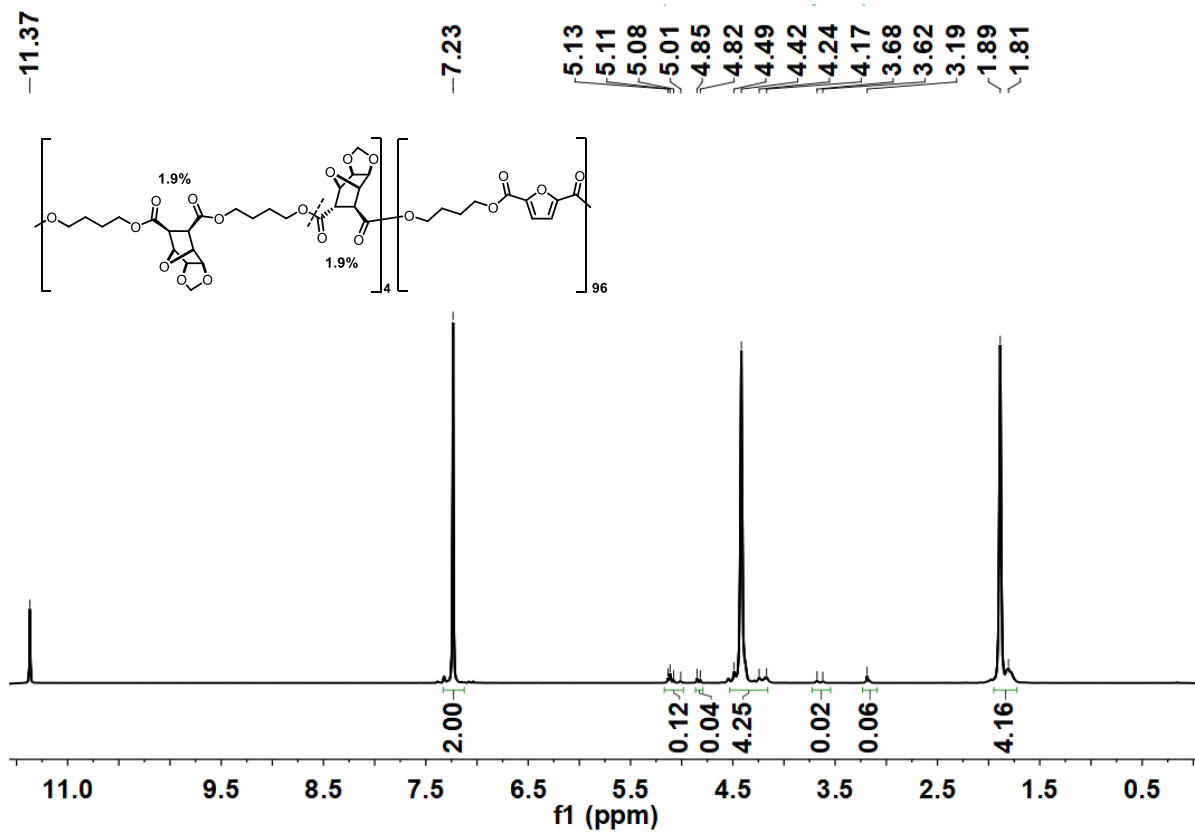


Figure S55. ¹H NMR spectrum of PBTC₄F₉₆.

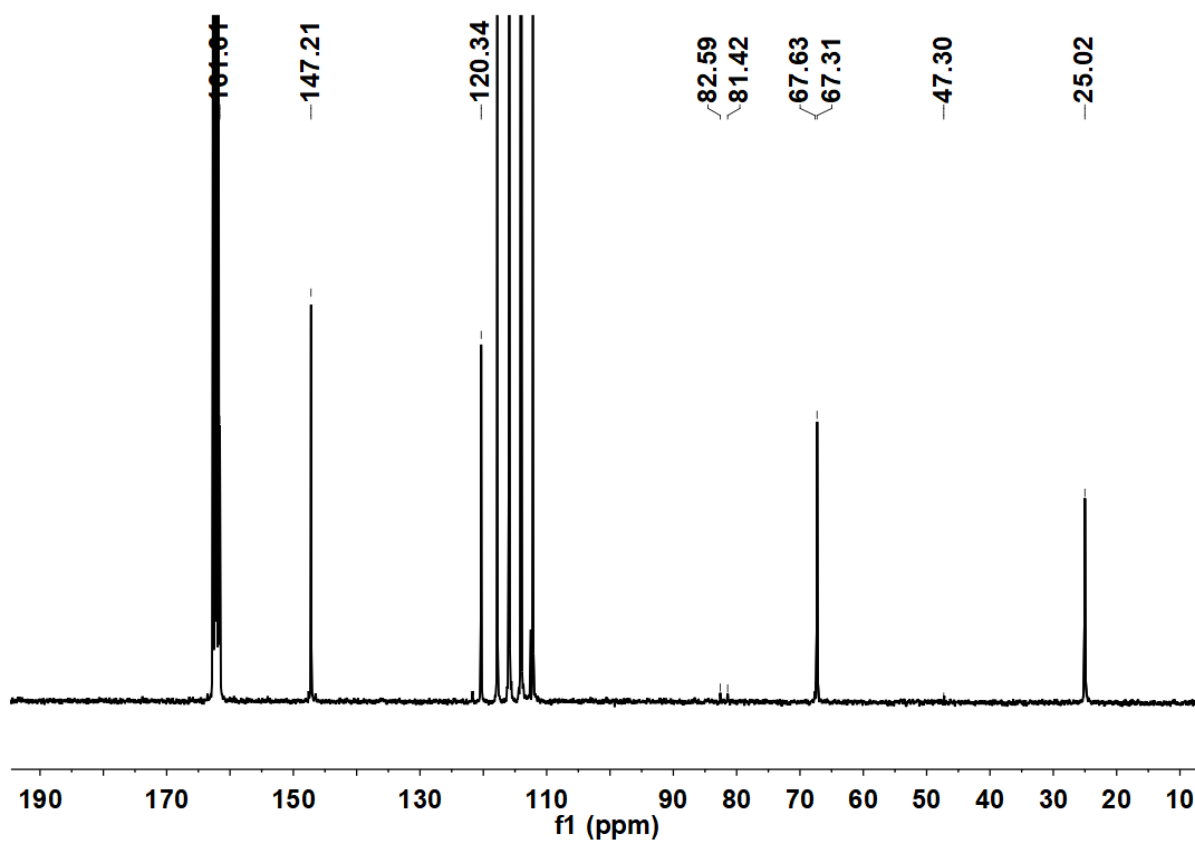


Figure S56. ¹³C NMR spectrum of PBTC₄F₉₆.

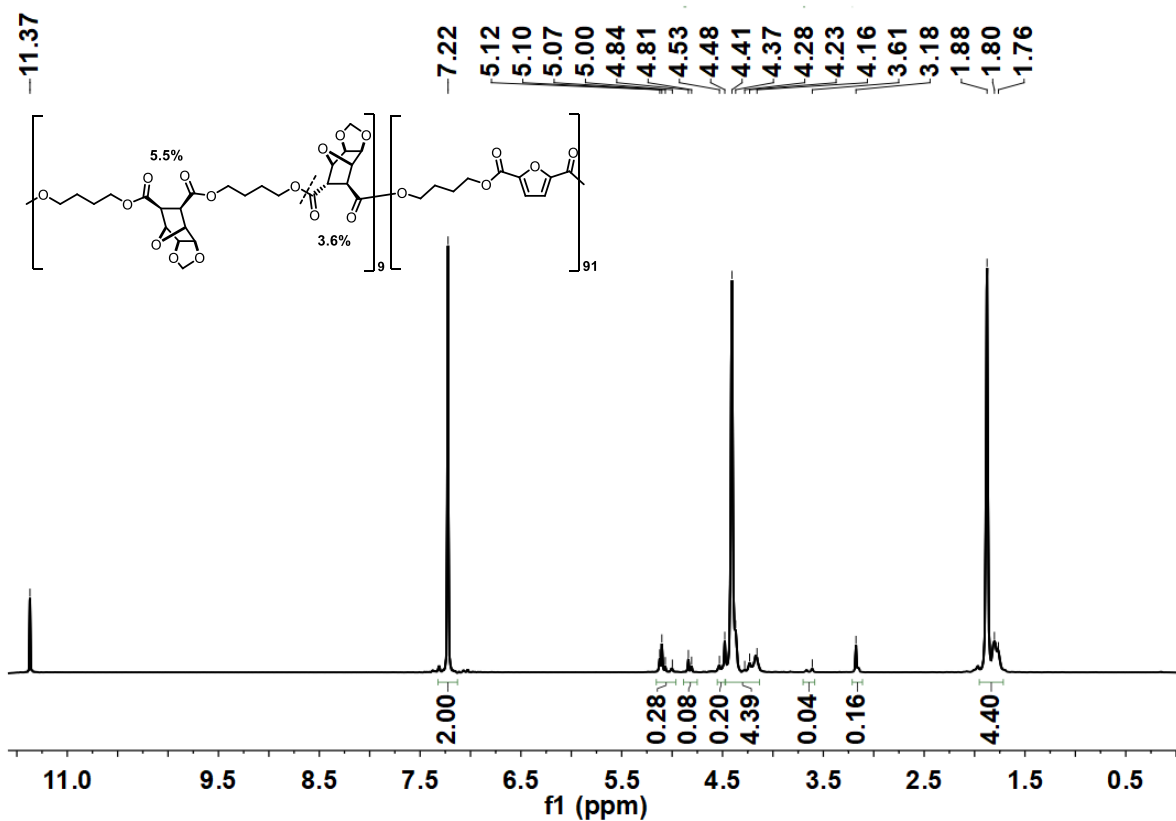


Figure S57. ¹H NMR spectrum of PBTC₉F₉₁.

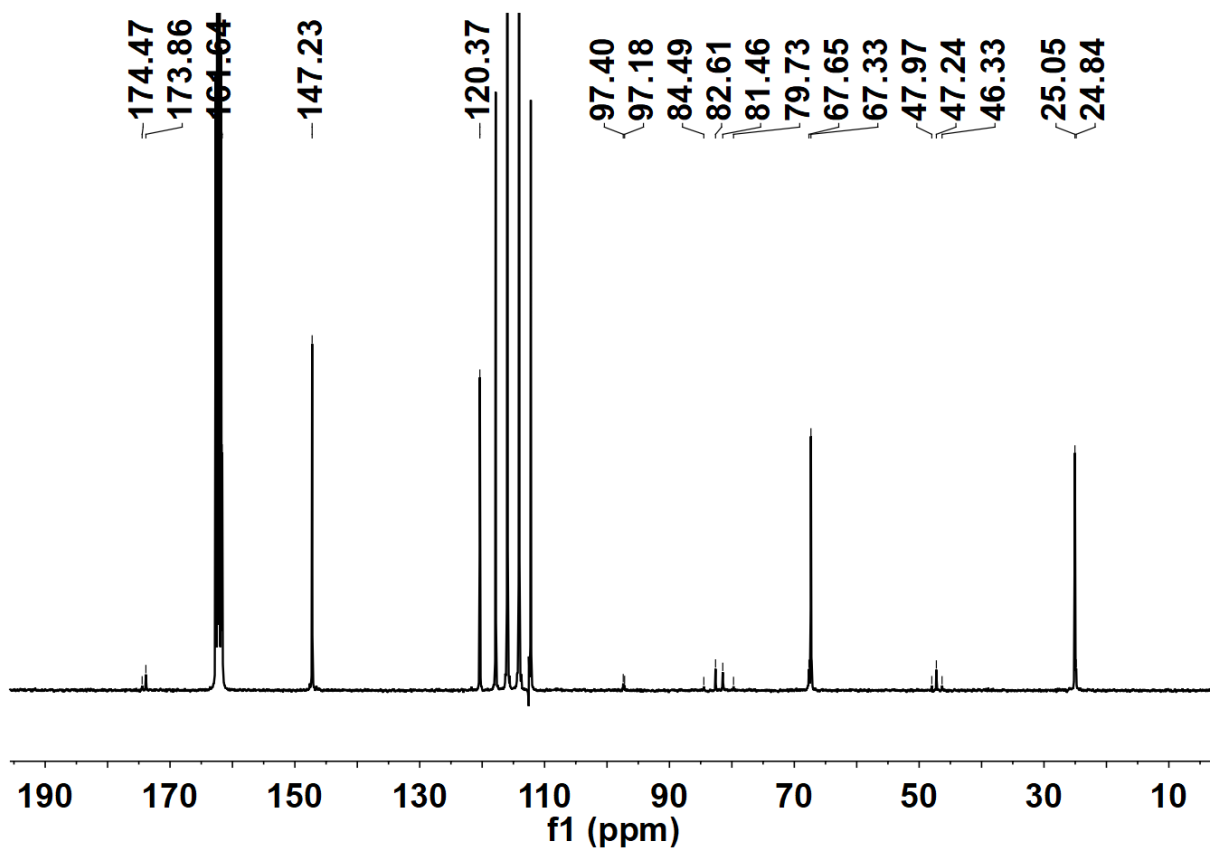


Figure S58. ¹³C NMR spectrum of PBTC₉F₉₁.

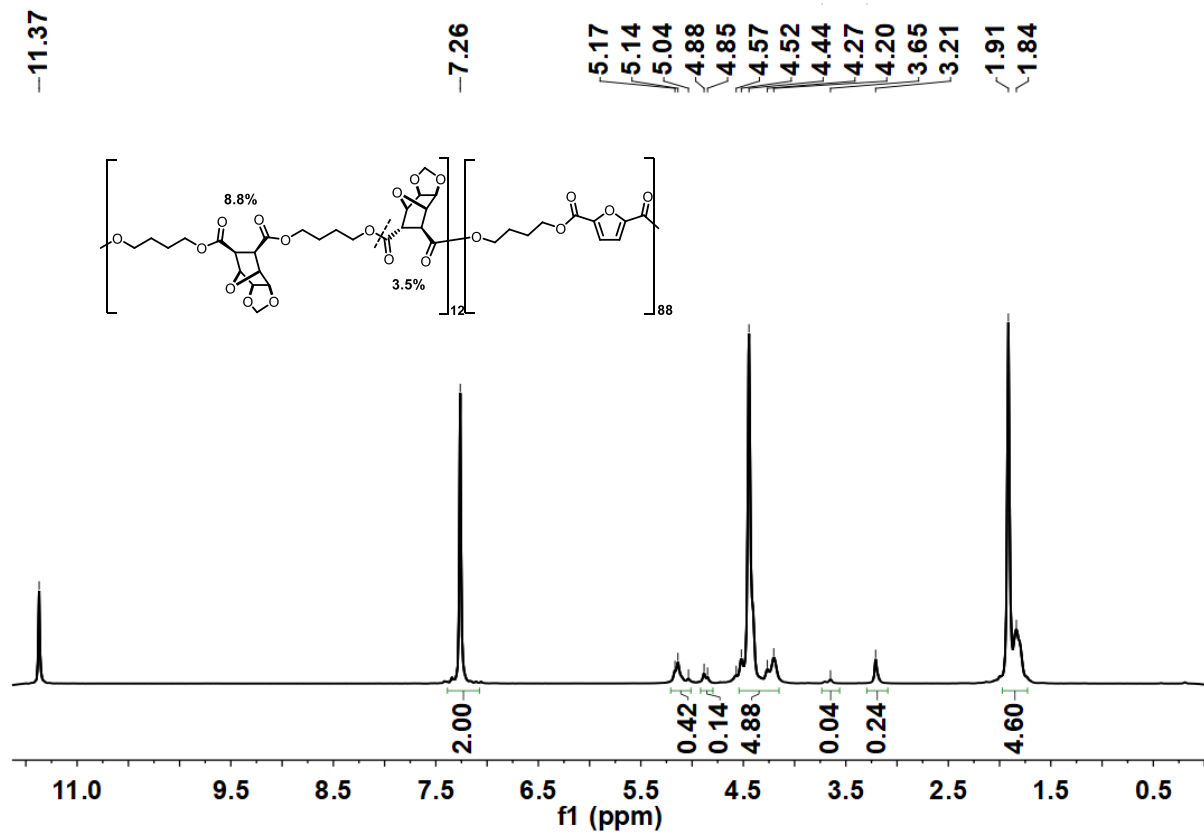


Figure S59. ^1H NMR spectrum of $\text{PBTC}_{12}\text{F}_{88}$.

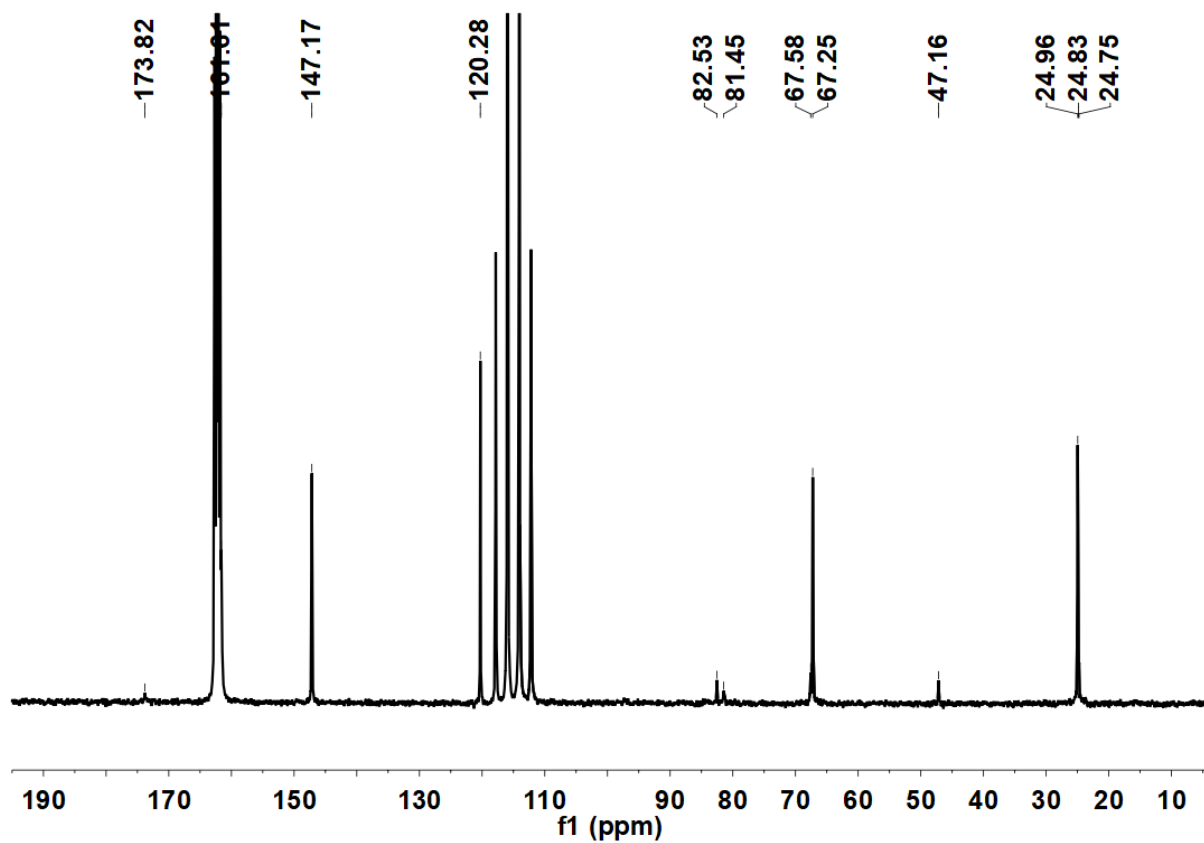


Figure S60. ^{13}C NMR spectrum of $\text{PBTC}_{12}\text{F}_{88}$.

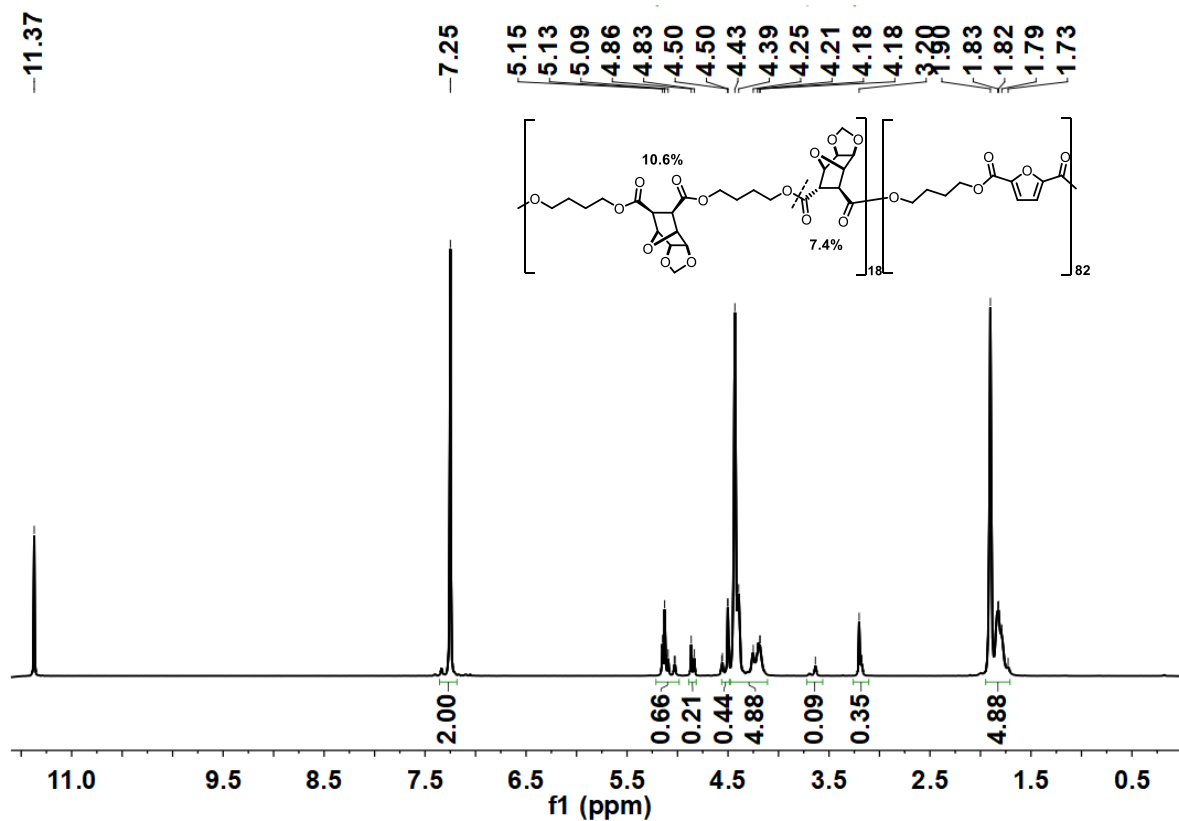


Figure S61. ^1H NMR spectrum of $\text{PBTC}_{18}\text{F}_{82}$.

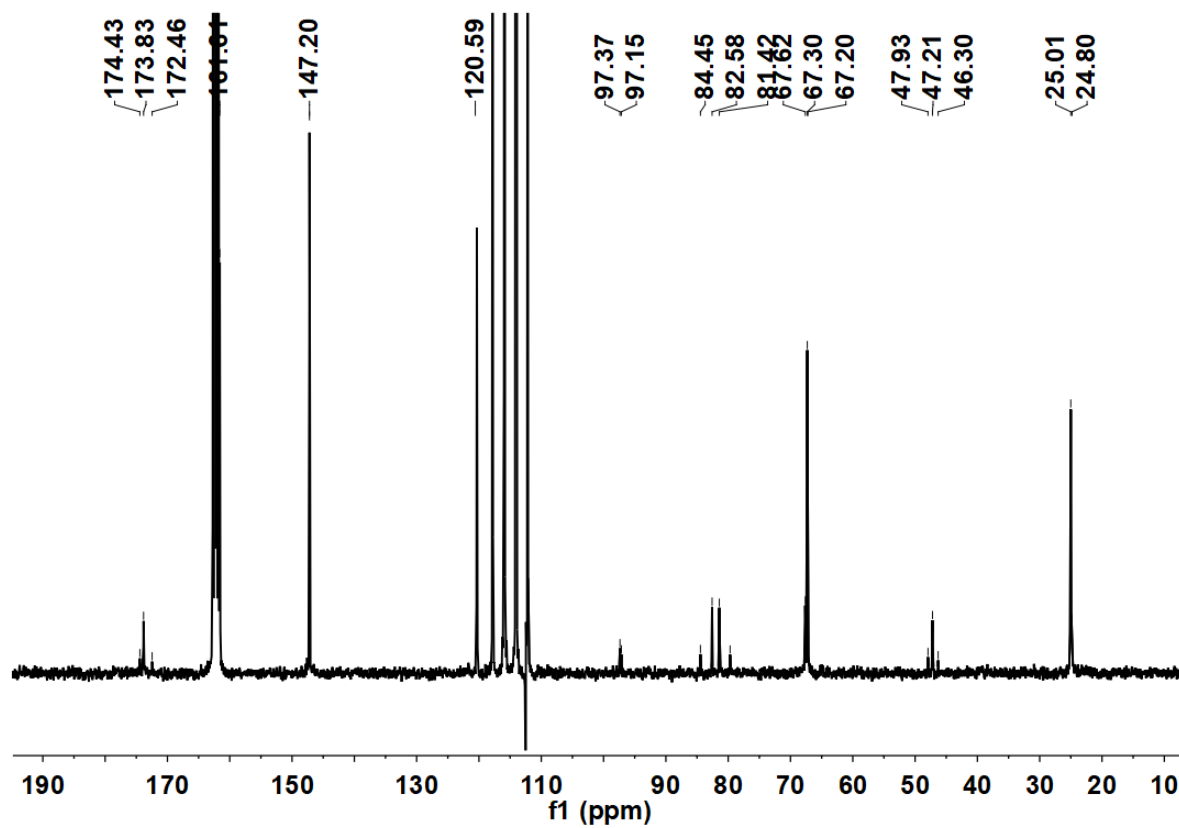


Figure S62. ^{13}C NMR spectrum of $\text{PBTC}_{18}\text{F}_{82}$.

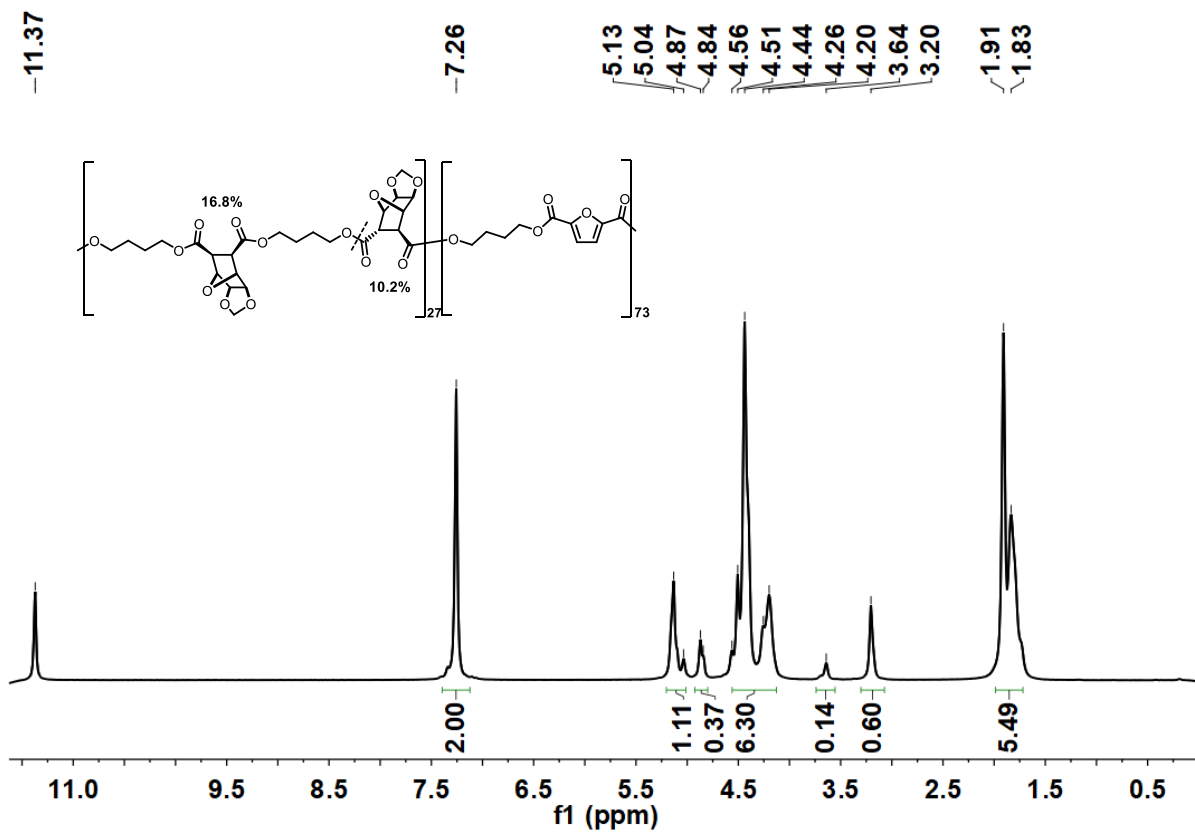


Figure S63. ^1H NMR spectrum of PBTC₂₇F₇₃.

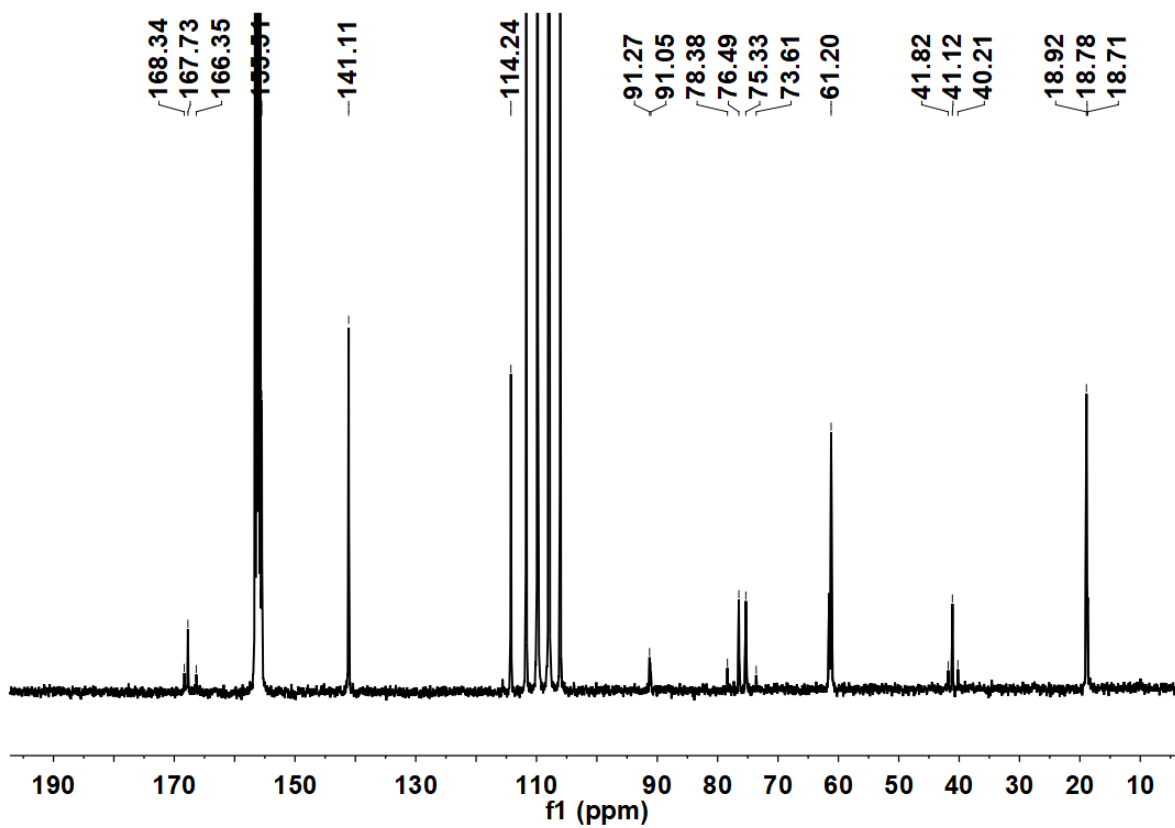


Figure S64. ^{13}C NMR spectrum of PBTC₂₇F₇₃.

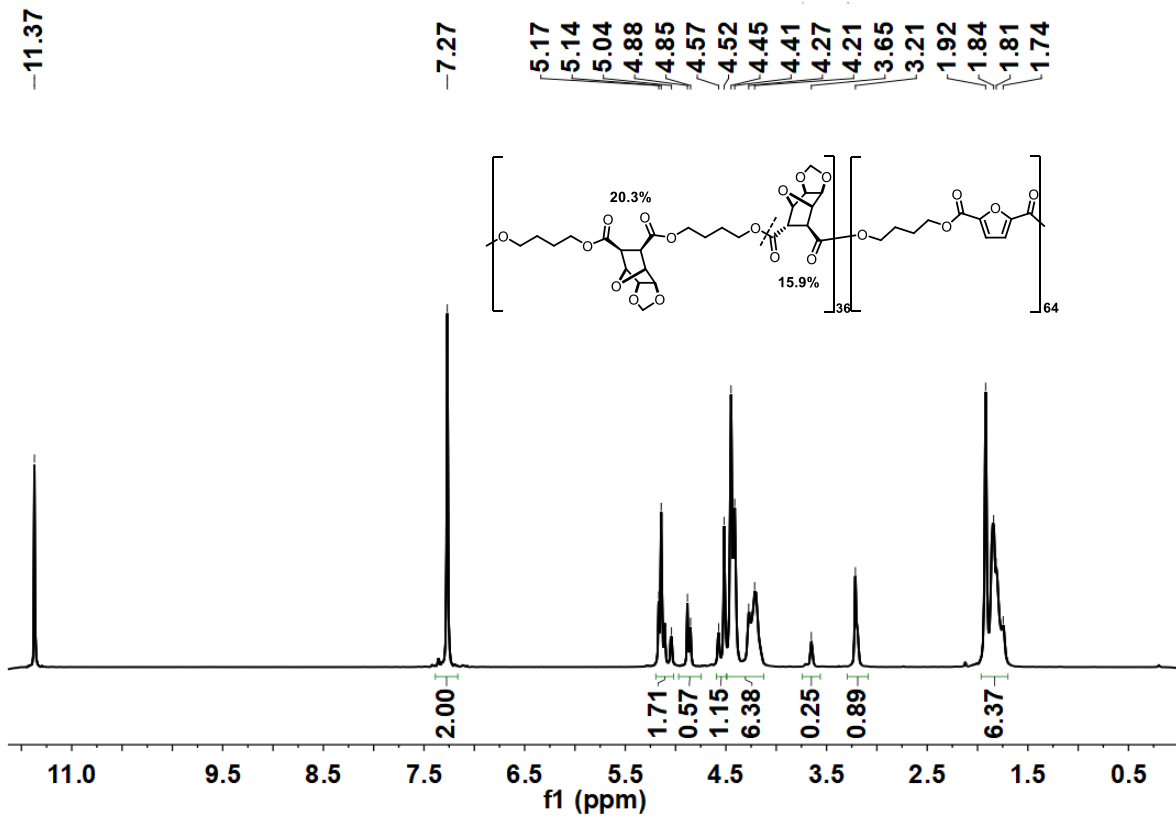


Figure S65. ^1H NMR spectrum of $\text{PBTC}_{36}\text{F}_{64}$.

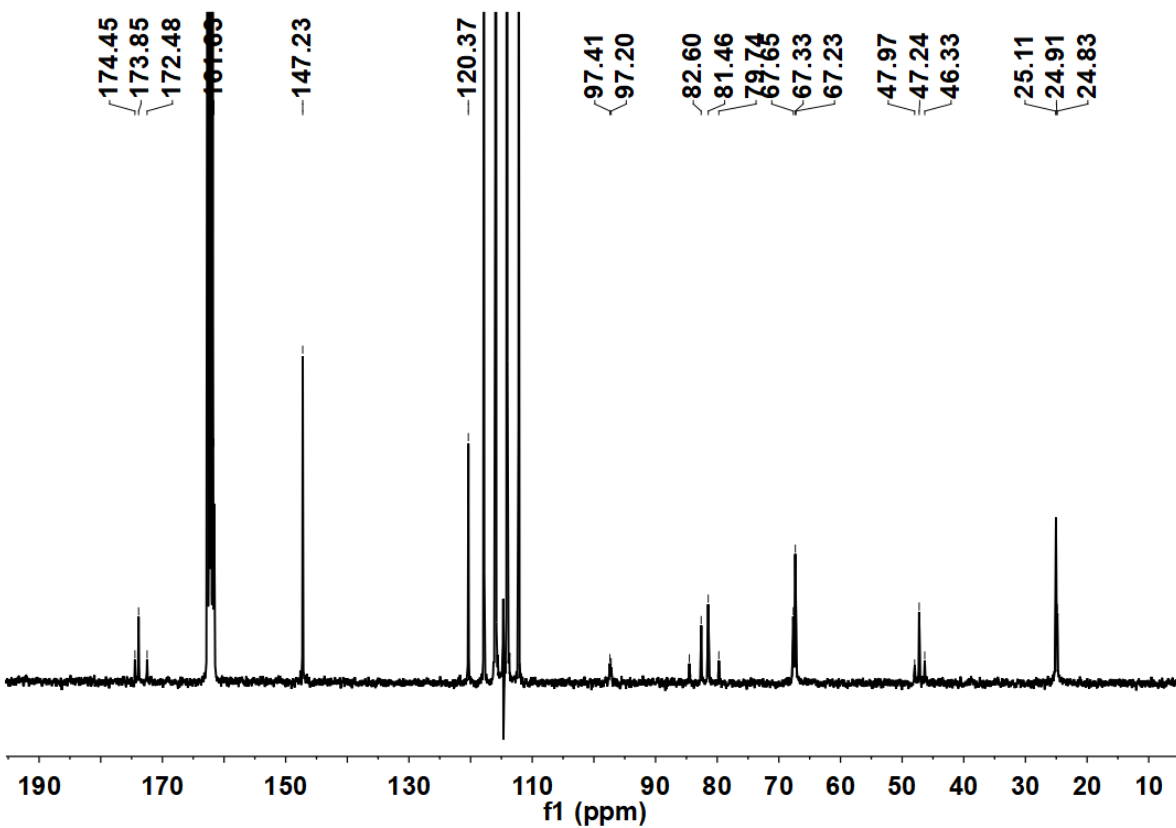


Figure S66. ^{13}C NMR spectrum of $\text{PBTC}_{36}\text{F}_{64}$.

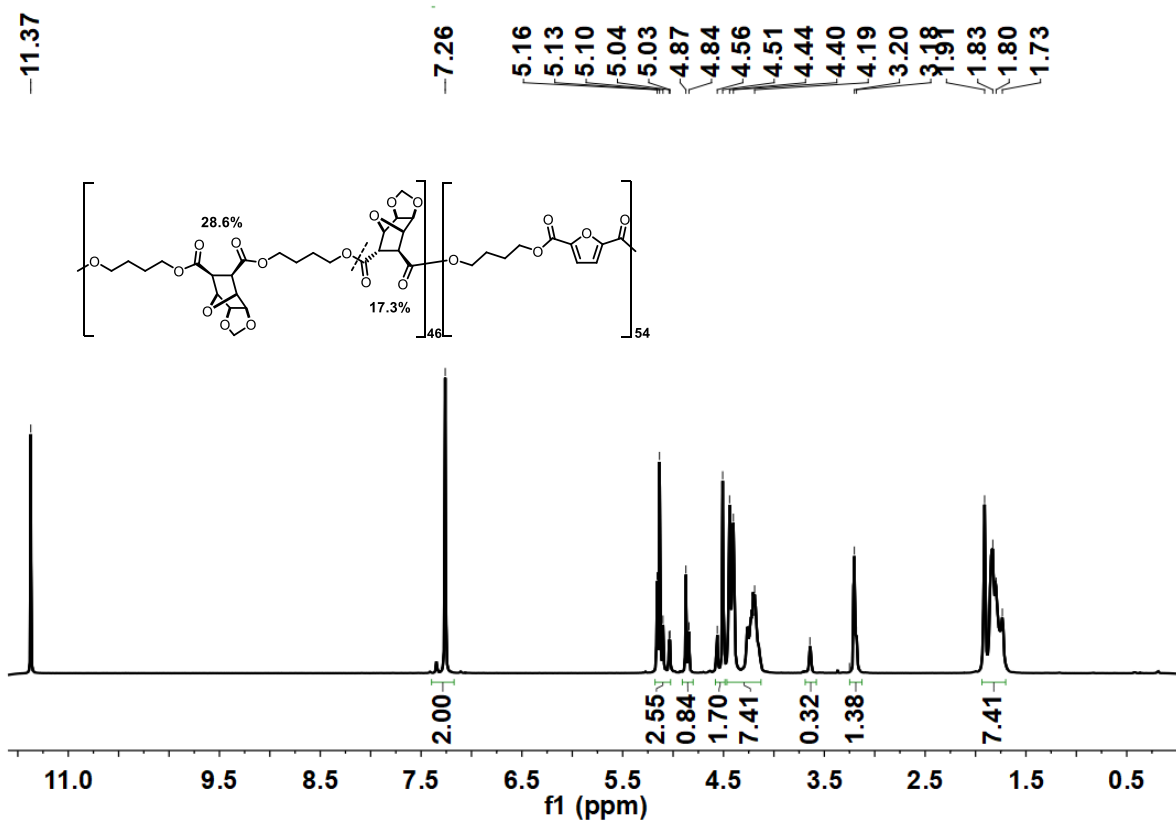


Figure S67. ¹H NMR spectrum of PBTC₄₆F₅₄.

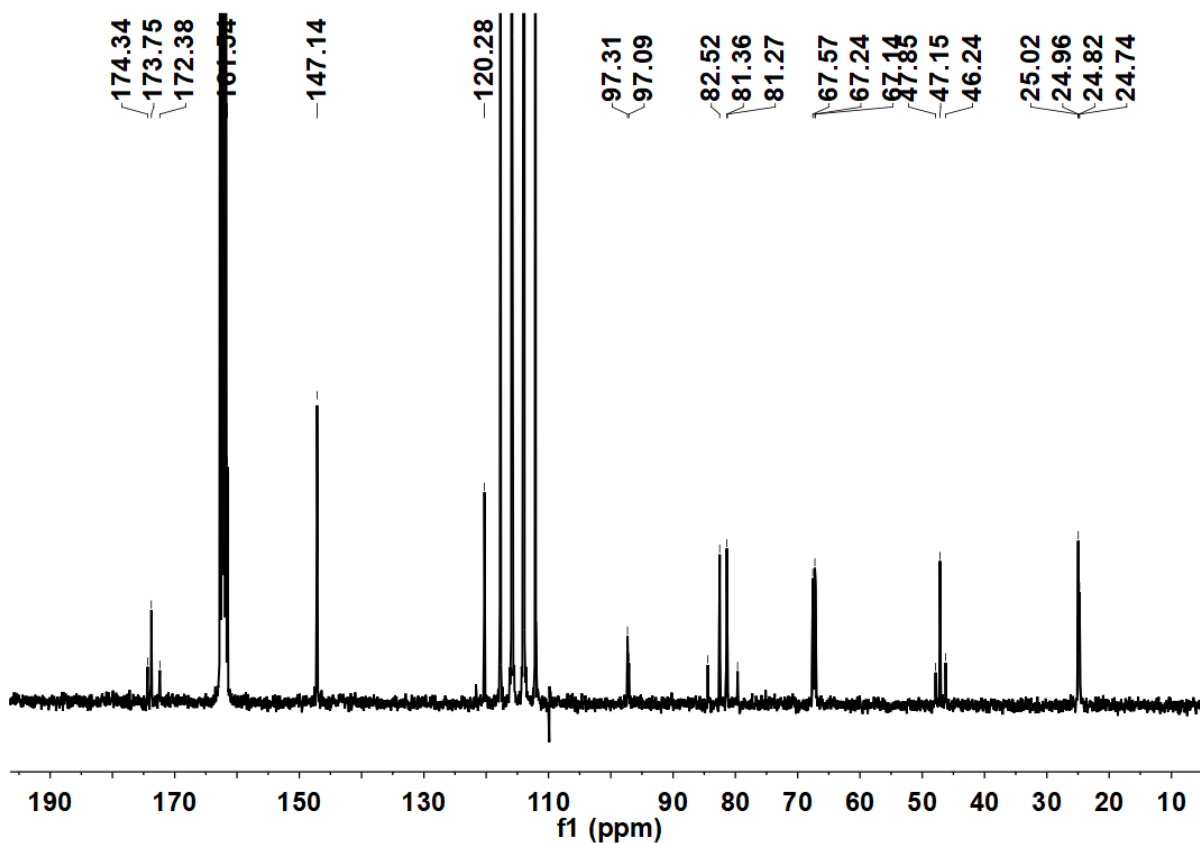


Figure S68. ¹³C NMR spectrum of PBTC₄₆F₅₄.

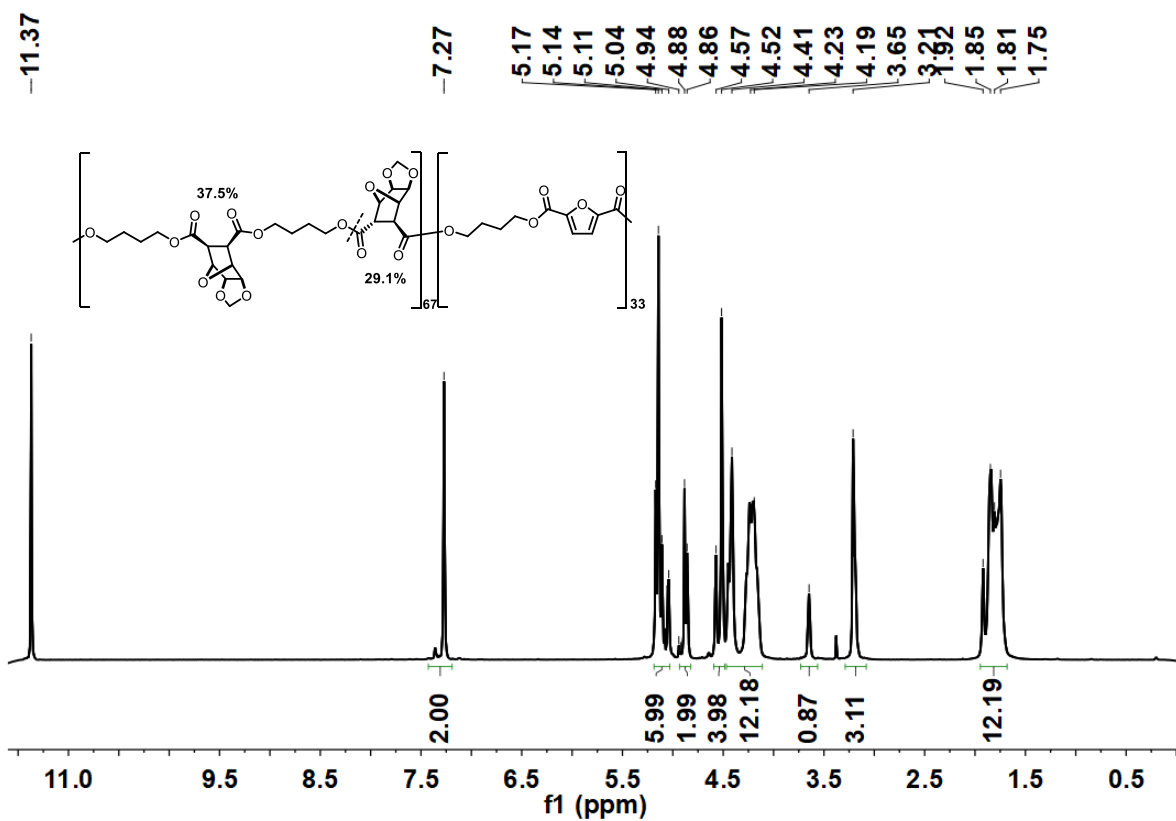


Figure S69. ¹H NMR spectrum of PBTC₆₇F₃₃.

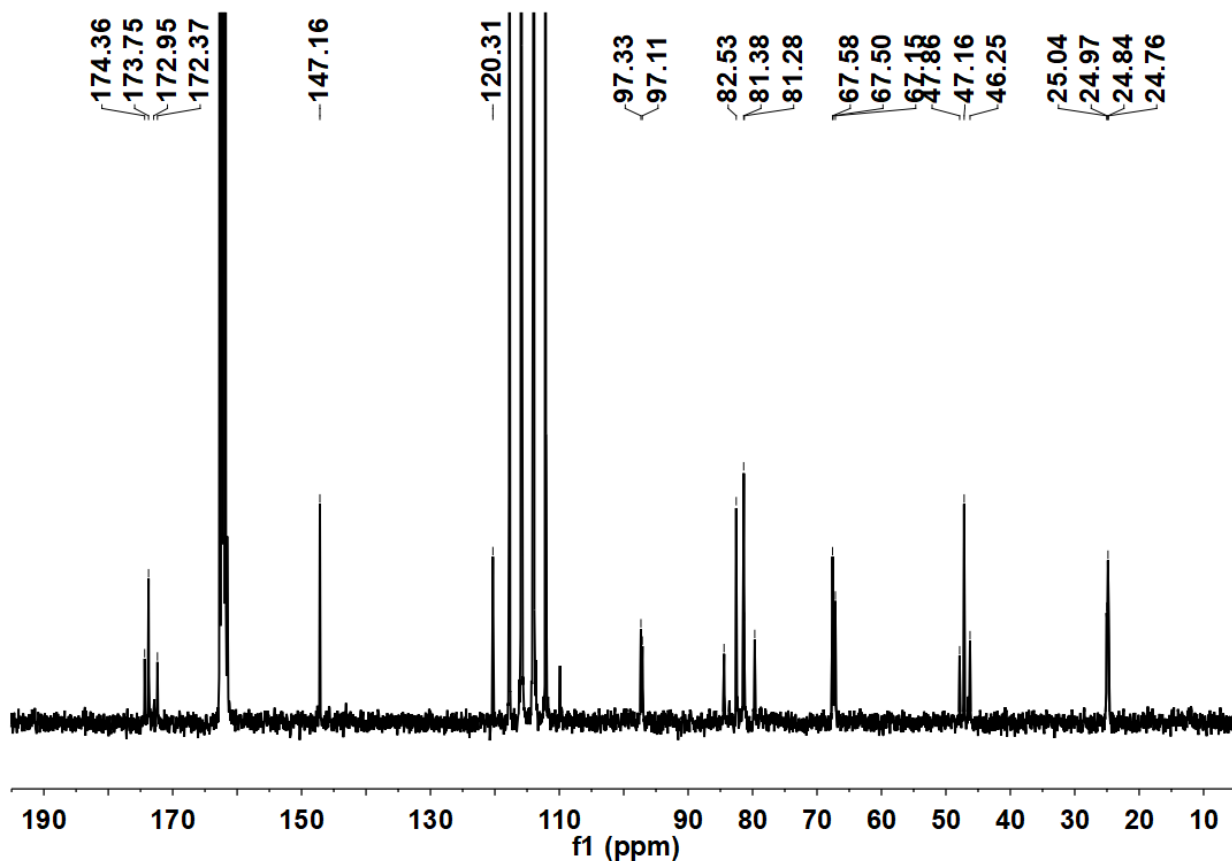


Figure S70. ¹³C NMR spectrum of PBTC₆₇F₃₃.

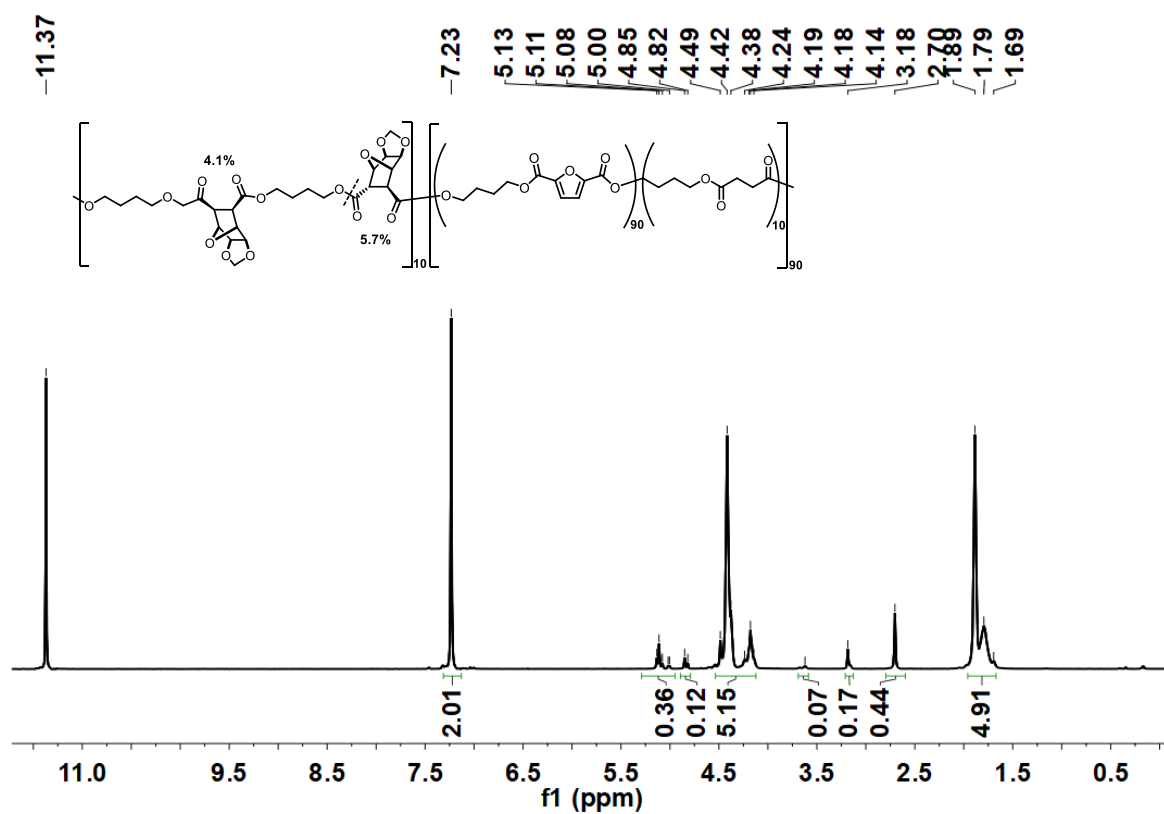


Figure S71. ¹H NMR spectrum of PBTC₁₀(S₁₀F₉₀)₉₀.

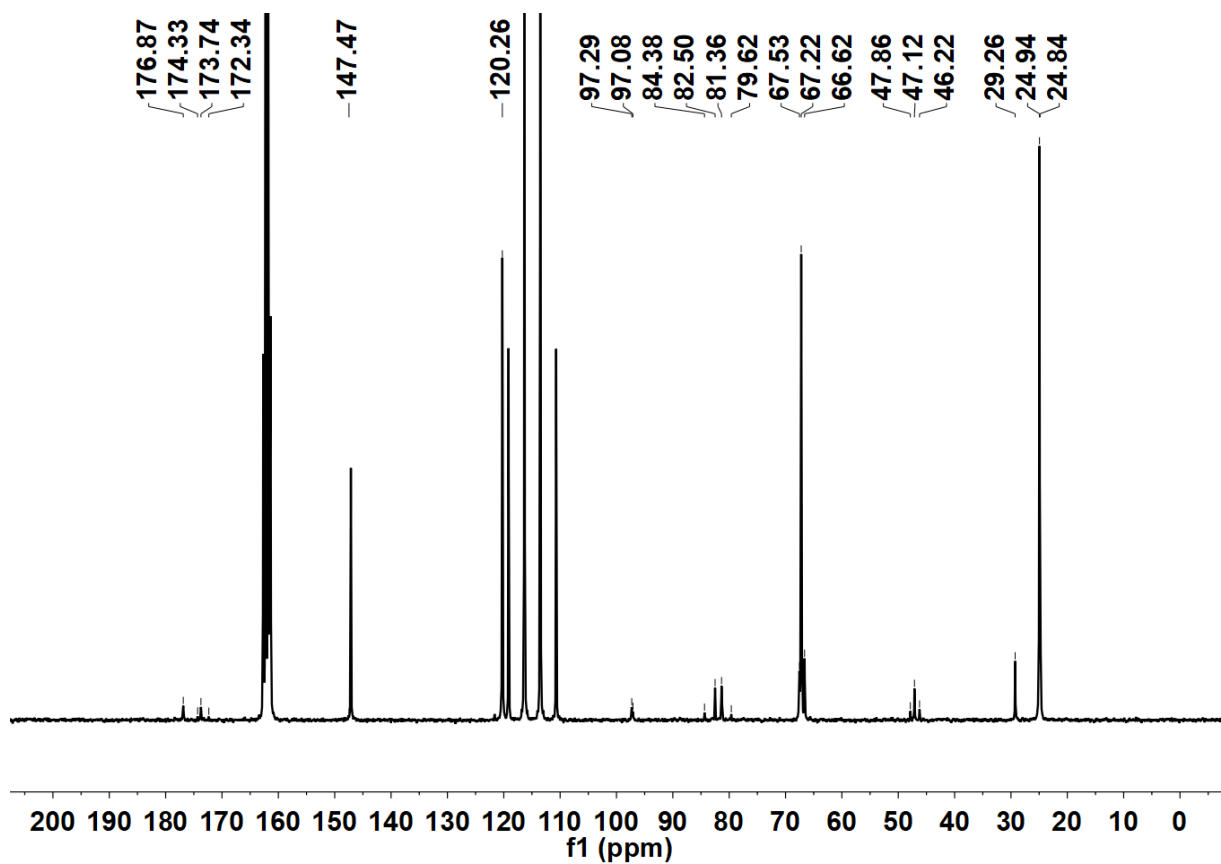
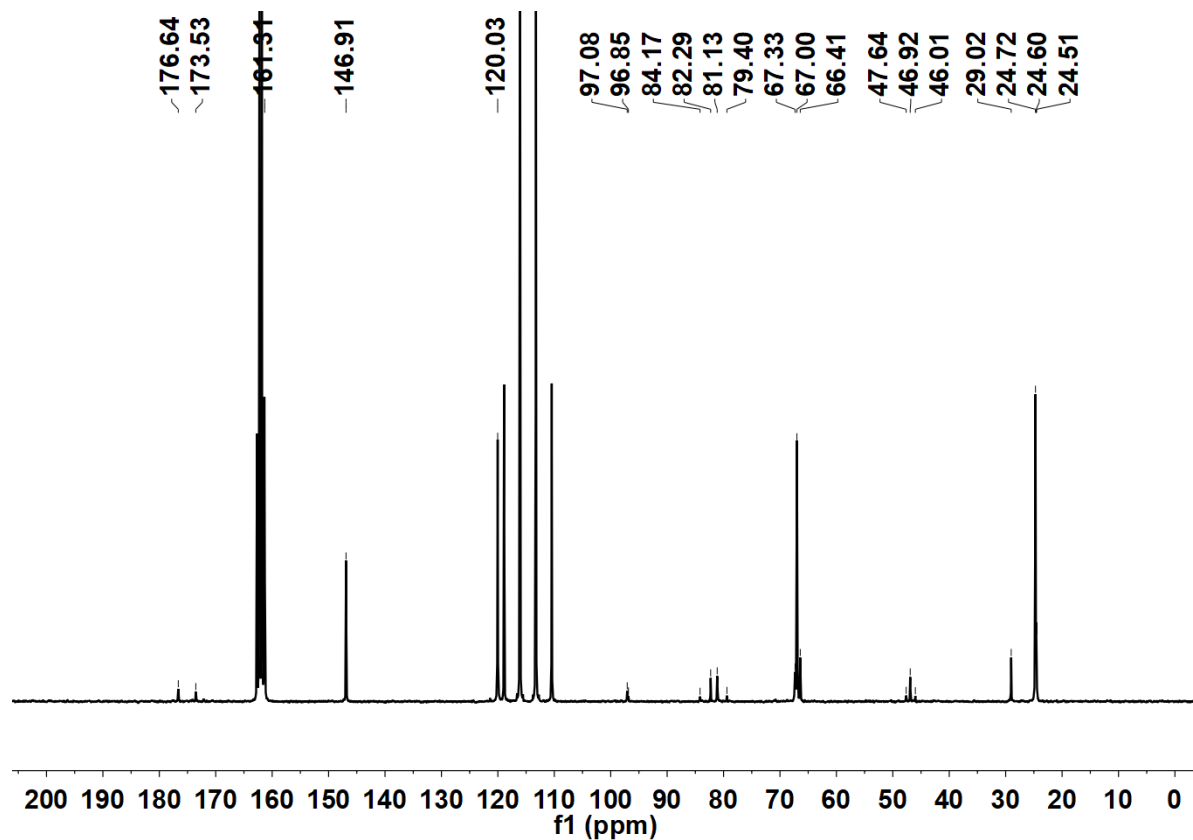
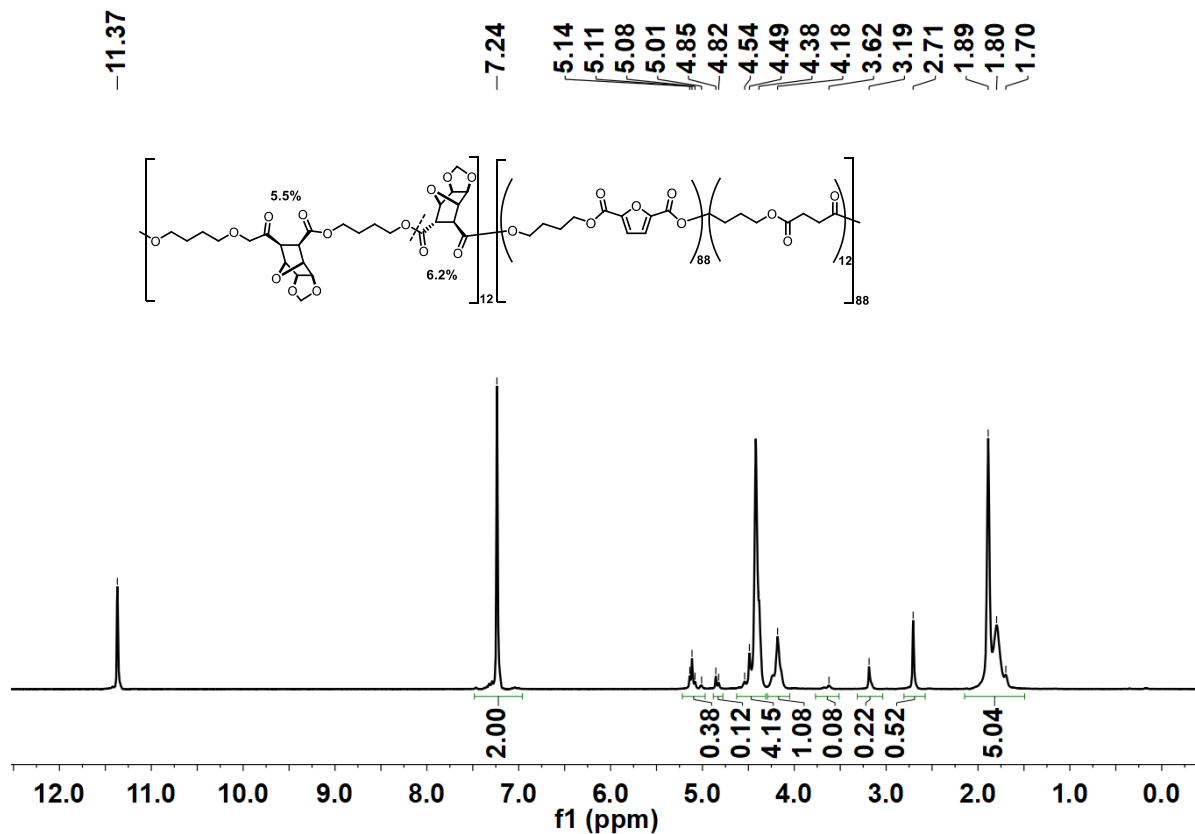
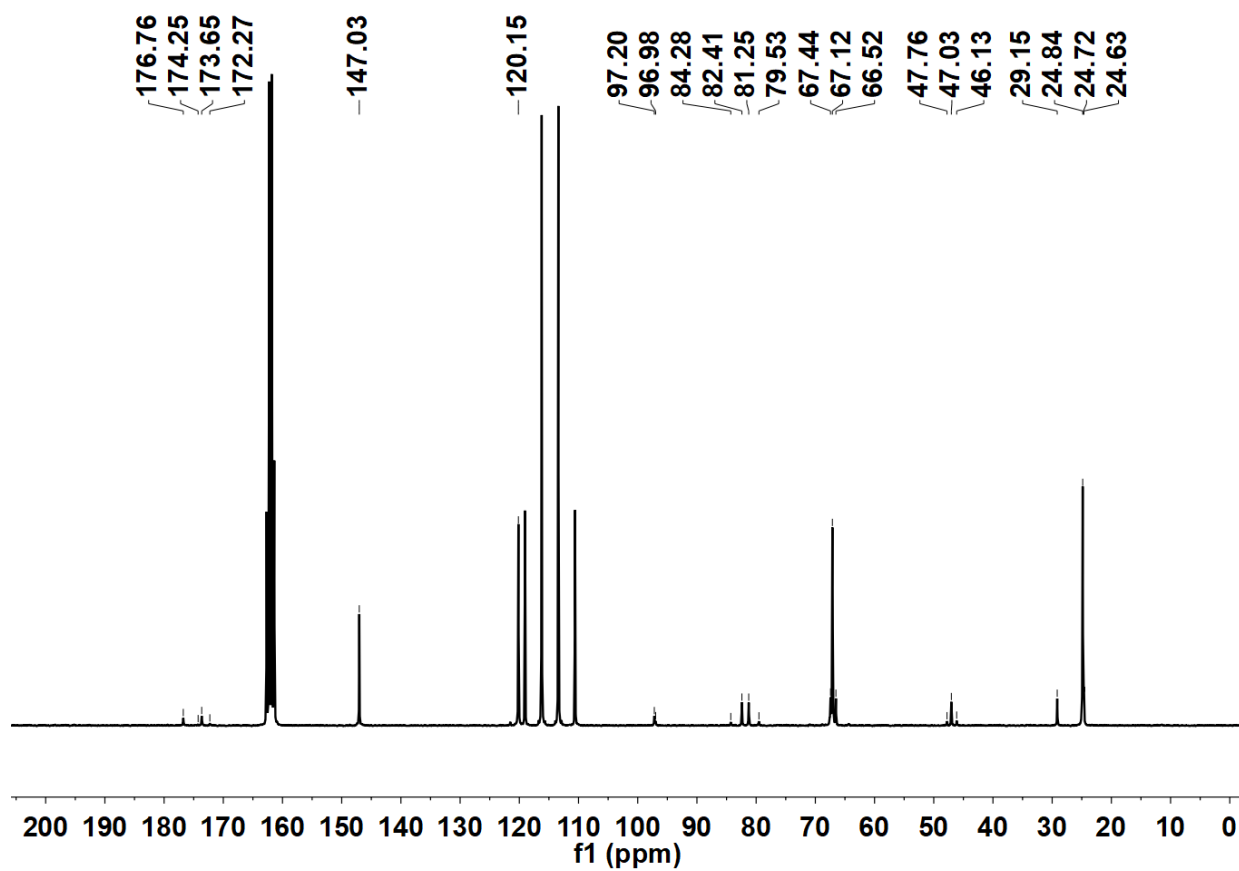
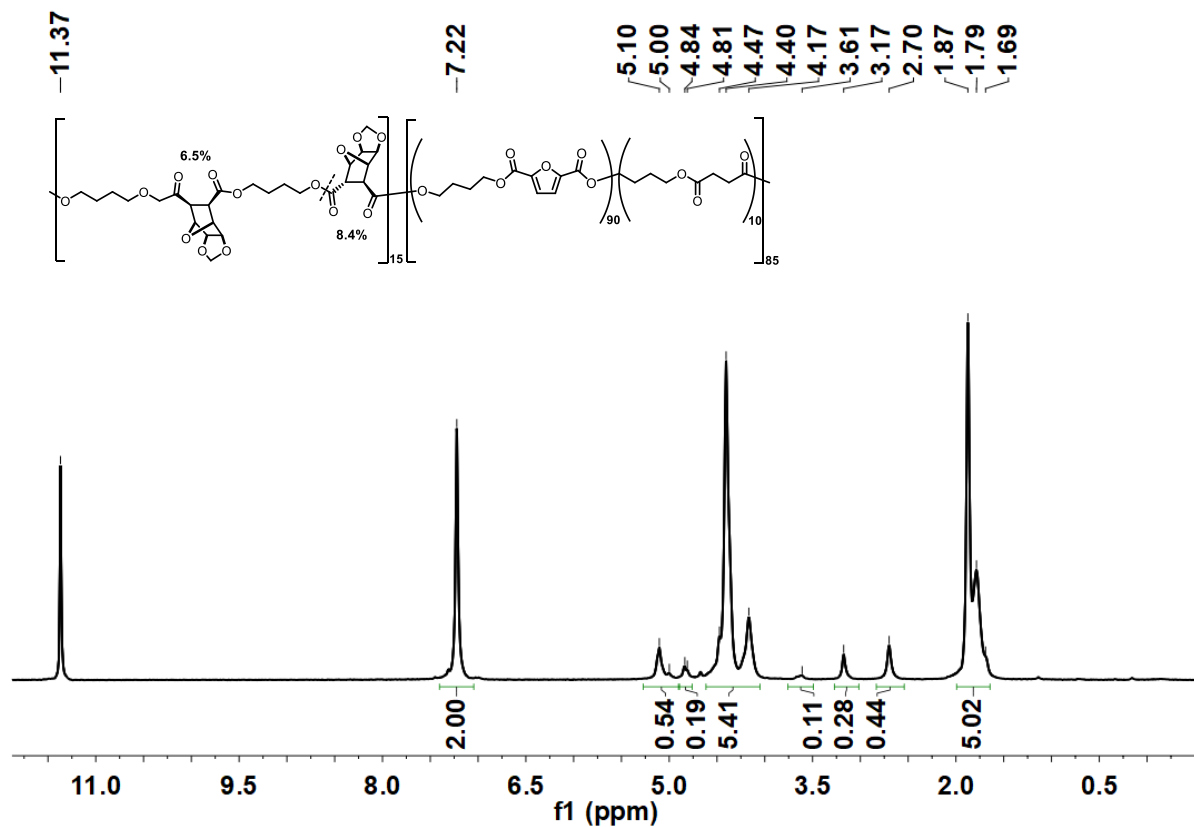


Figure S72. ¹³C NMR spectrum of PBTC₁₀(S₁₀F₉₀)₉₀.





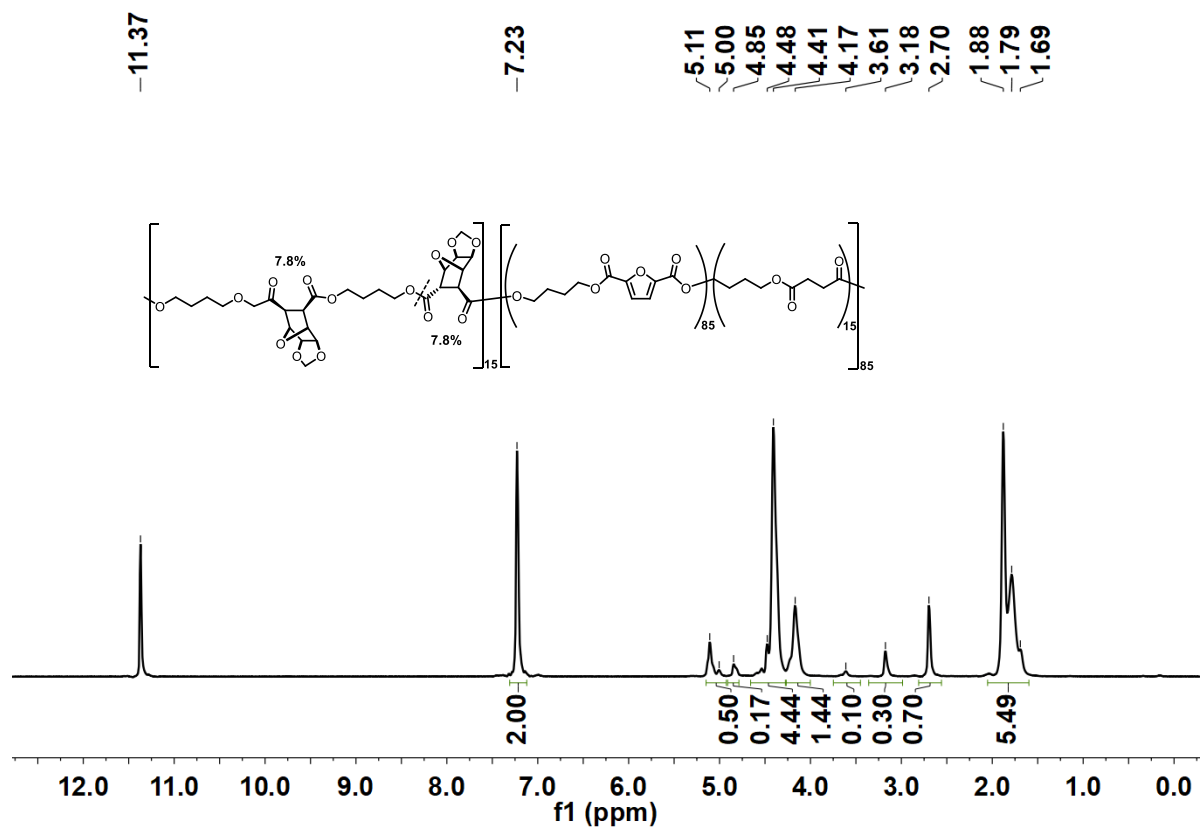


Figure S77. ¹H NMR spectrum of PBTC₁₅(S₁₅F₈₅)₈₅.

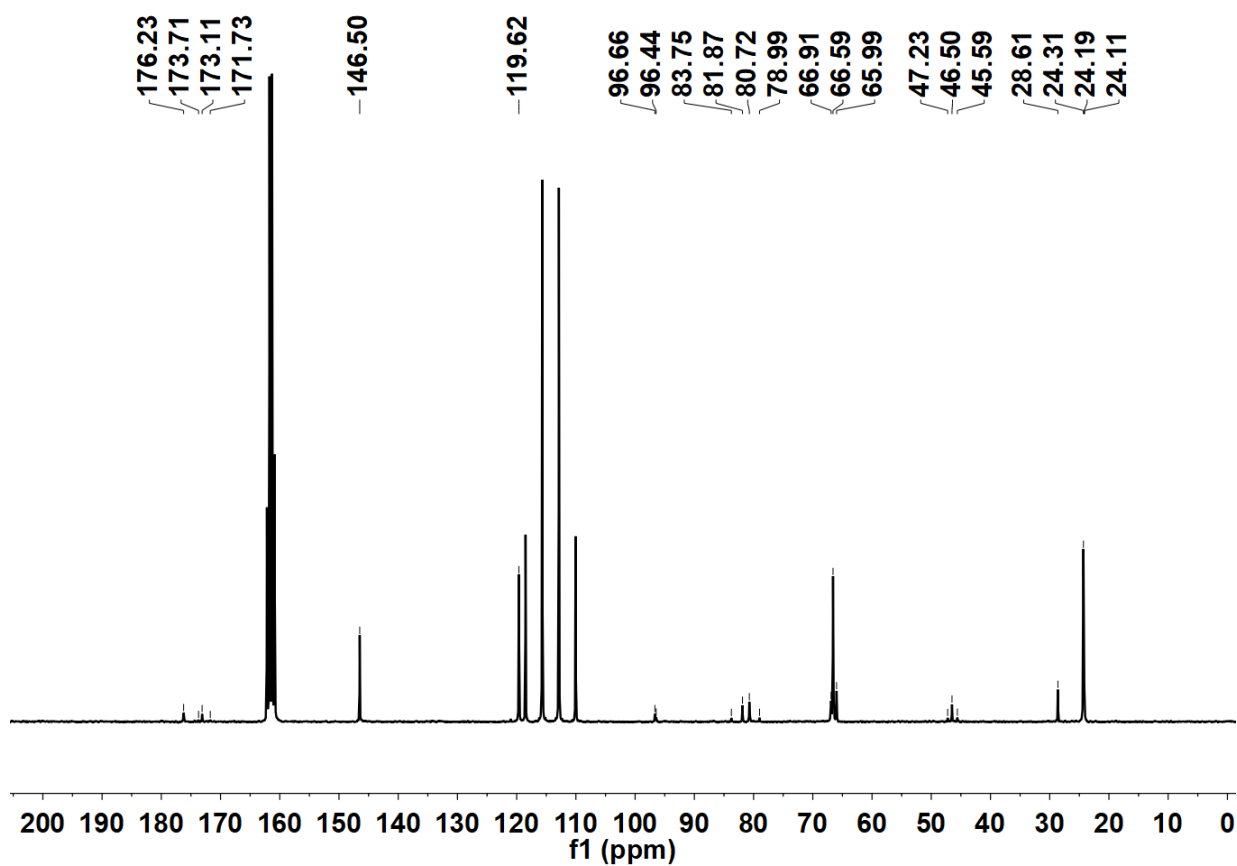


Figure S78. ¹³C NMR spectrum of PBTC₁₅(S₁₅F₈₅)₈₅.

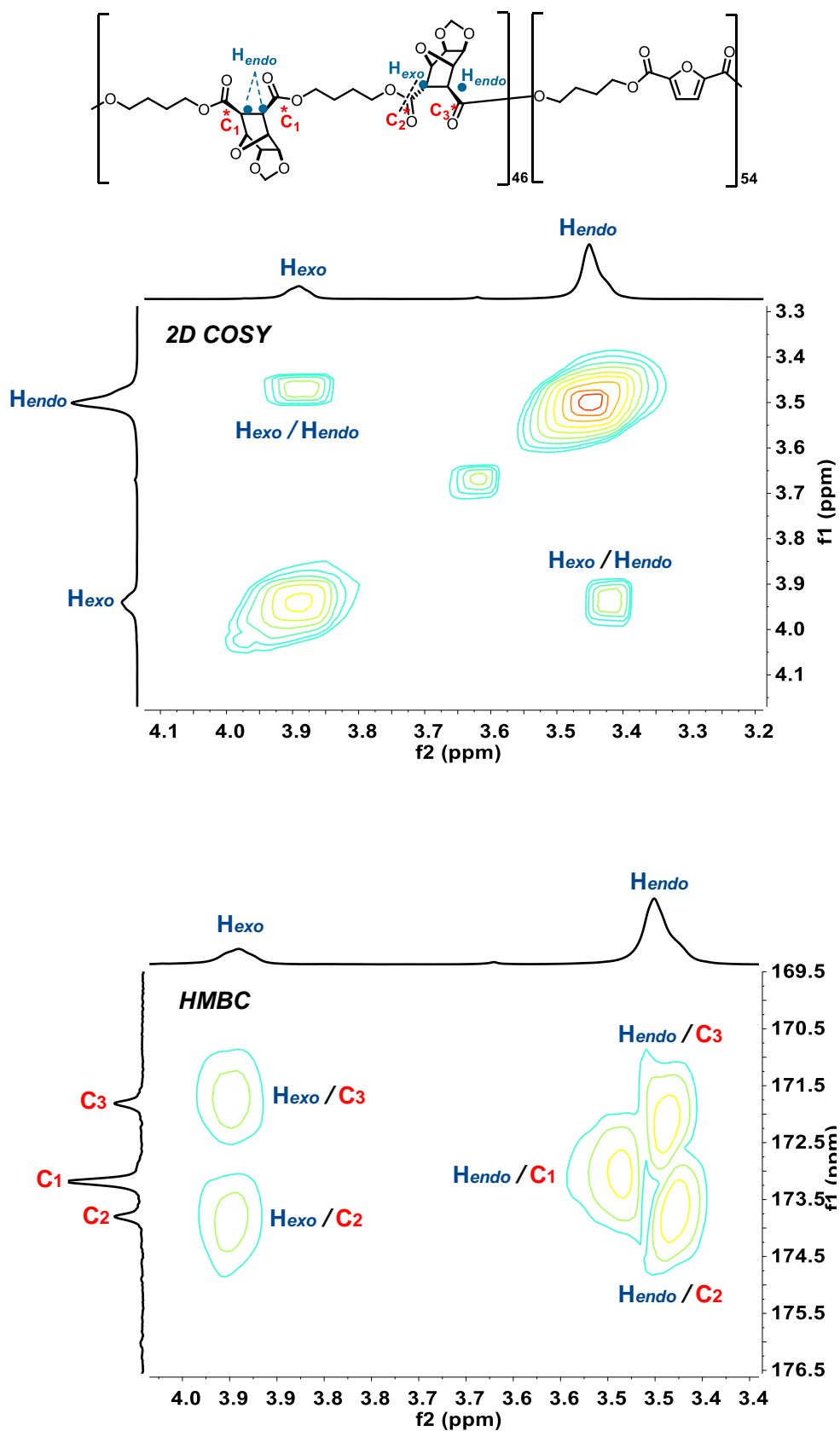


Figure S79. Section of 2D COSY and HMBC spectra of PBTC₄₆F₅₄.

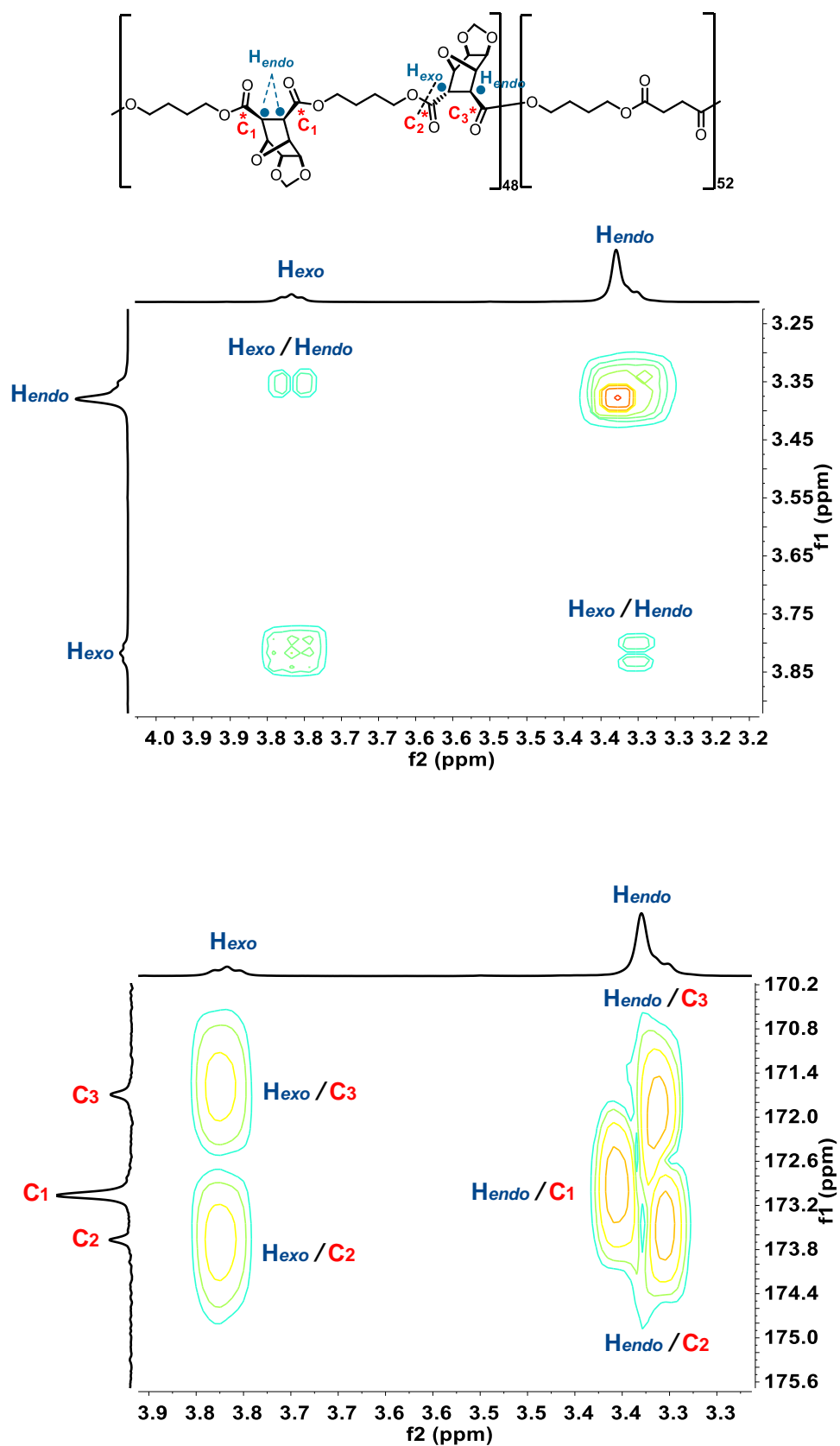


Figure S80. Section of 2D COSY and HMBC spectra of PBTC₄₈S₅₂.

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