Supporting information

Cost-effective synthesis of poly(ether ester) via polycondensation of terephthalic acid and 1,3-propanediol at the sulfonic acids-participating catalysis

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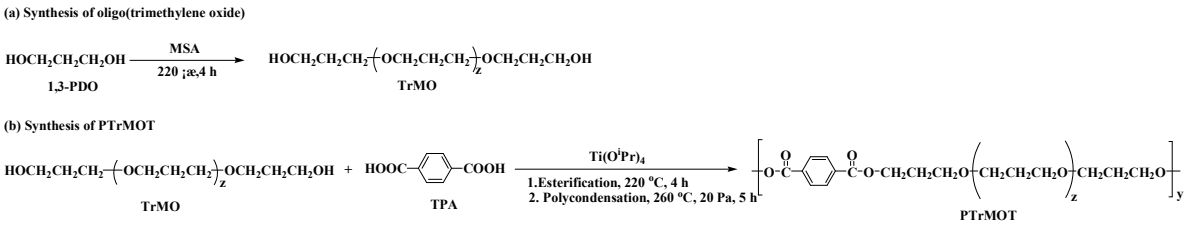
Synthesis of PTT. All the operations were similar to the synthesis of PTT-*co*-PDPT-*co*-PTrMOT, except TPT (109 mg, 0.38 mmol) used only.

Synthesis of dipropylene glycol. The 1,3-PDO (8.56 g, 0.11 mol) was placed in a three-necked flask, and aqueous sodium hydroxide solution (46.4 wt%) was dropped into the 1,3-PDO under ice bath, followed by reacting for 30 min. Then, with rising to 100 °C, 3-chloro-1-propanol (10.40 g, 0.11 mol) was dropped into the above mixture, and the reaction lasted for 8 h. Then the mixture was dissolved in deionized water and transferred into a separating funnel, adding chloroform to extraction, and then through rotary evaporation (35 °C) to obtained a crude product. Finally the crude product was purified by silica gel column (chloroform and anhydrous methanol (v/v = 8/1). The compound was isolated as light yellow liquid in a yield of 20 %. ^{1}H NMR ($CDCl_3$, 500 MHz, δ ppm): 3.75 (t, J = 5.7 Hz, 1H, CH_2), 3.61 (t, J = 5.8 Hz, 1H, CH_2), 1.90-1.78 (m, 4H, CH_2).

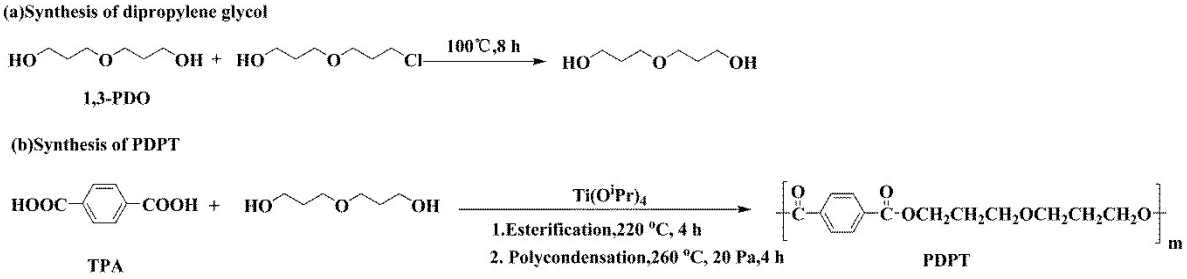
Synthesis of PDPT. TPA (2.58 g, 0.016 mol), dipropylene glycol (3.9 g, 0.029 mol) and TPT (39 mg, 0.14 mmol) were added to the three-necked flask under N_2 atmosphere. Similar polycondensation operation was performed in the following. Finally, PDPT was dissolved in trichlorochloride, precipitated with ether, and dried under vacuum.

Synthesis of oligo(trimethylene oxide). 1,3-PDO (10 g, 0.13 mol) and MSA (133 mg, 1.38 mmol) were added to the three-necked flask, conducted at 220-240 °C for 4 h in N_2 atmosphere, and oligo(trimethylene oxide) will be obtained.

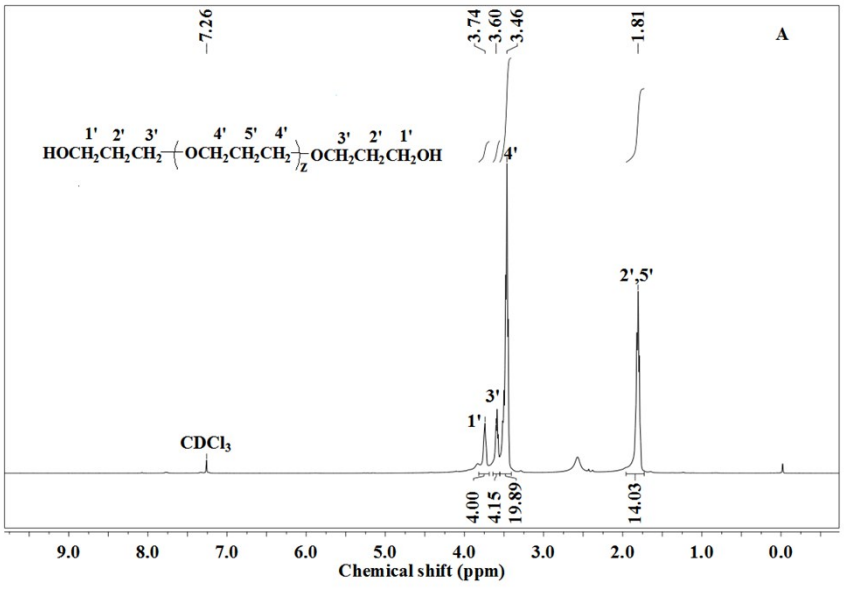
Synthesis of PTrMOT. TPA (5 g, 0.03 mol), oligoether (13.7 g, 0.054 mol) and TPT (112 mg, 0.40 mmol) were added to the three-necked flask under N_2 atmosphere. The esterification and polycondensation operation were identical to the synthesis of PTT-*co*-PDPT-*co*-PTrMOT. Finally, PTrMOT was dissolved in trichlorochloride, precipitated with ether, and dried under vacuum.



Scheme S1. (a) Synthetic route of oligo(trimethylene oxide). (b) Synthetic route of PTrMOT.



Scheme S2. (a) Synthetic route of dipropylene glycol. (b) Synthetic route of PDPT.



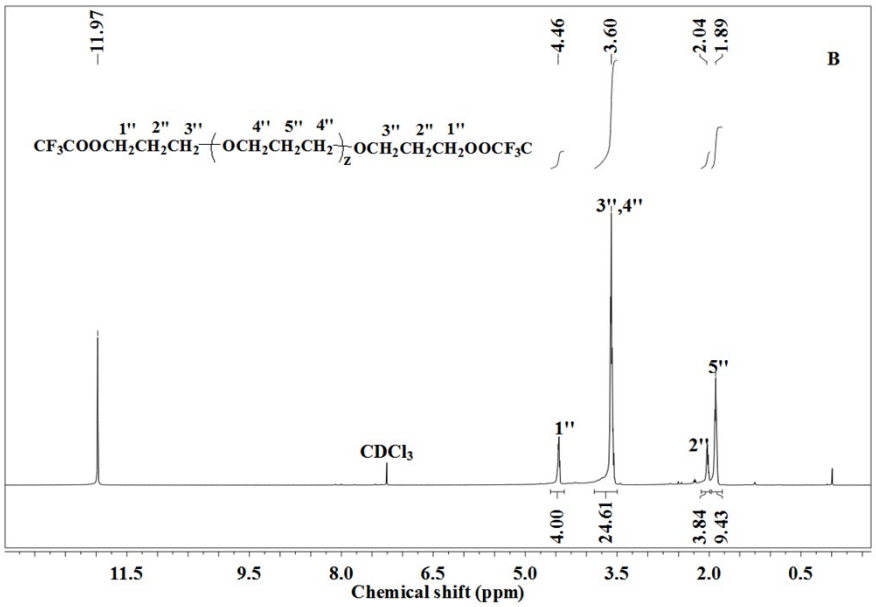


Figure S1. ^{1}H NMR spectra of oligo(trimethylene oxide) (A) and after adding one droplet of trifluoroacetic anhydride (B).

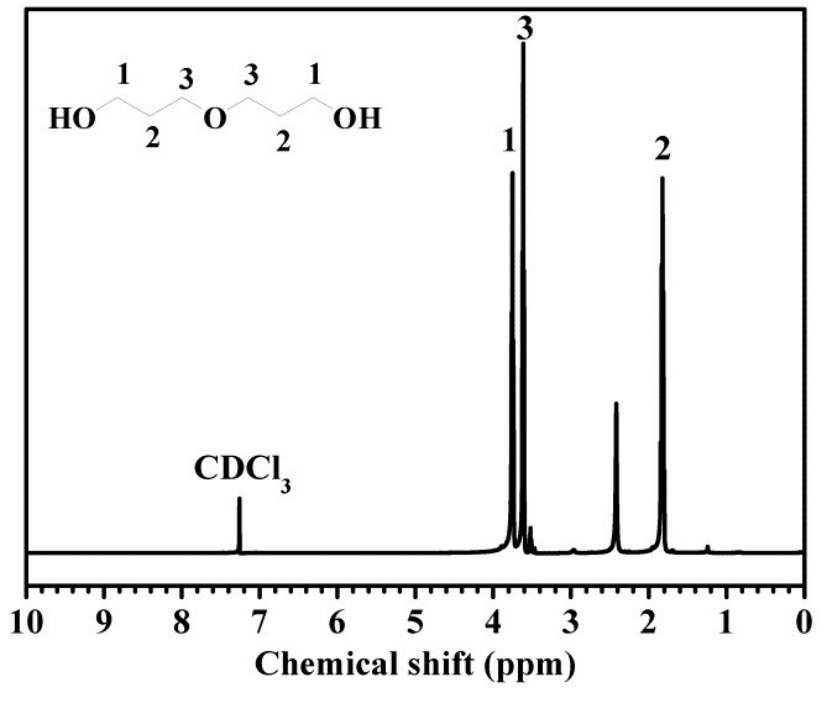


Figure S2. ^{1}H NMR spectrum of PDPT.

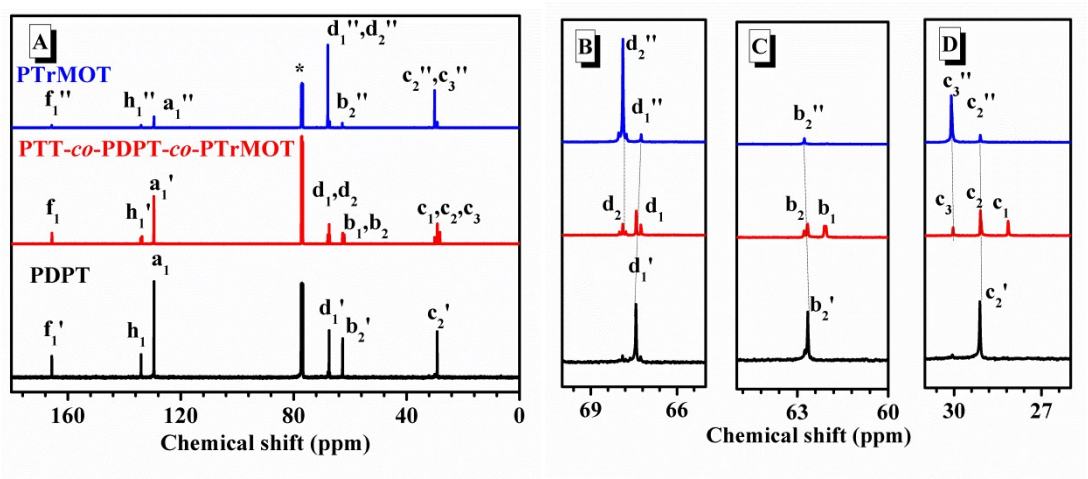


Figure S3. ^{13}C NMR spectra of PDPT, PTrMOT and PTT-*co*-PDPT-*co*-PTrMOT (P-2). The peaks marked as asterisk were $CDCl_3$.

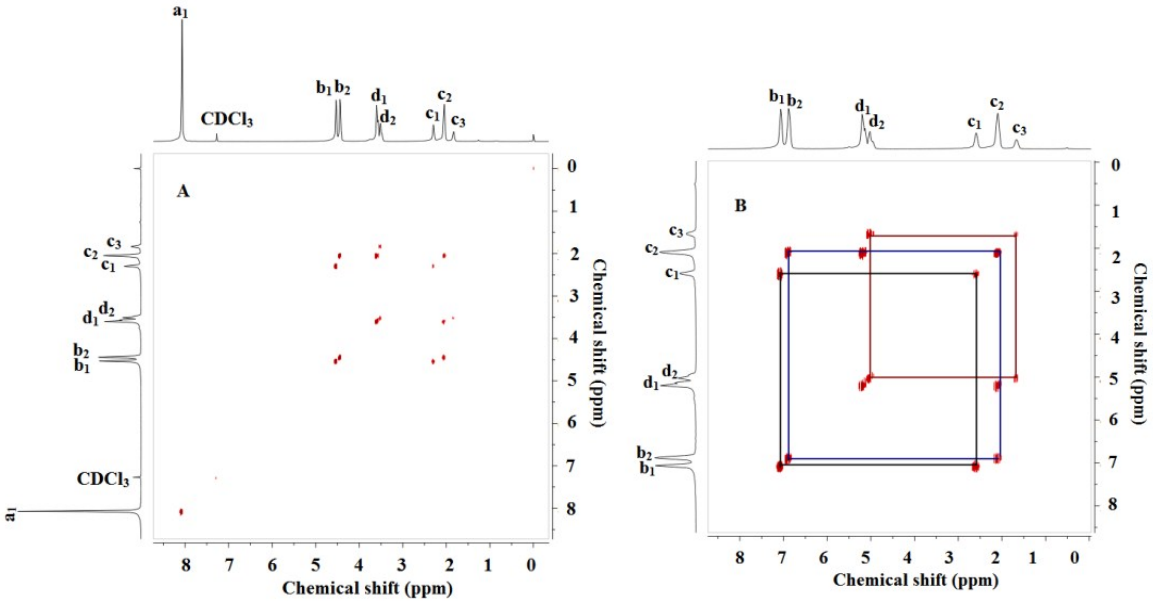


Figure S4. Two dimensional ^{1}H-^{1}H gCOSY spectra of PTT-*co*-PDPT-*co*-PTrMOT obtained via direct polycondensation of TPA and PDO in the presence of MSA. (A) the whole spectrum;(B) the selected enlarged correlated regions.

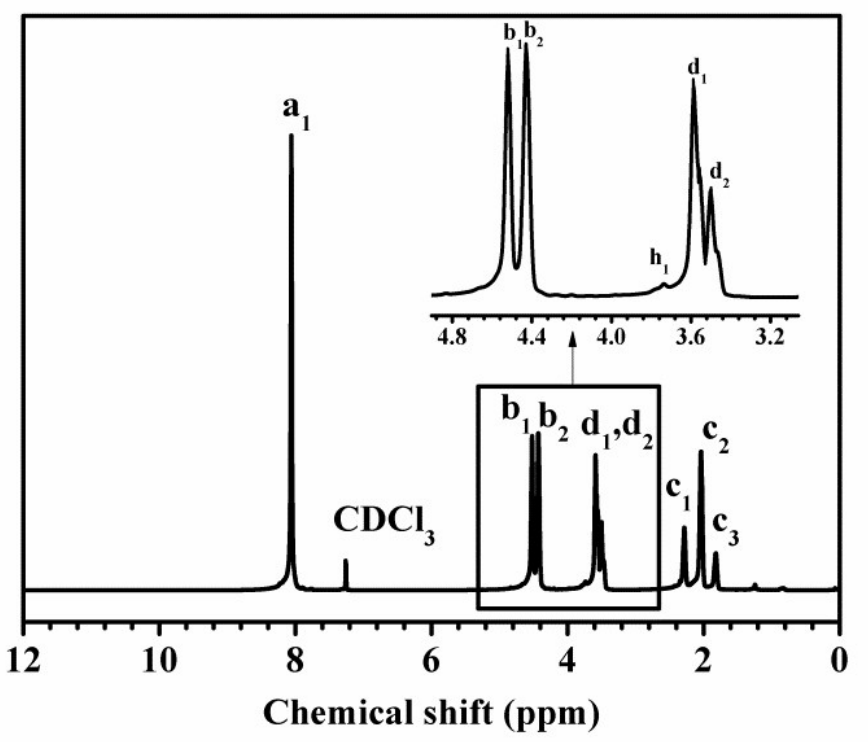


Figure S5. 1D ^{1}H NMR spectrum of P-2.

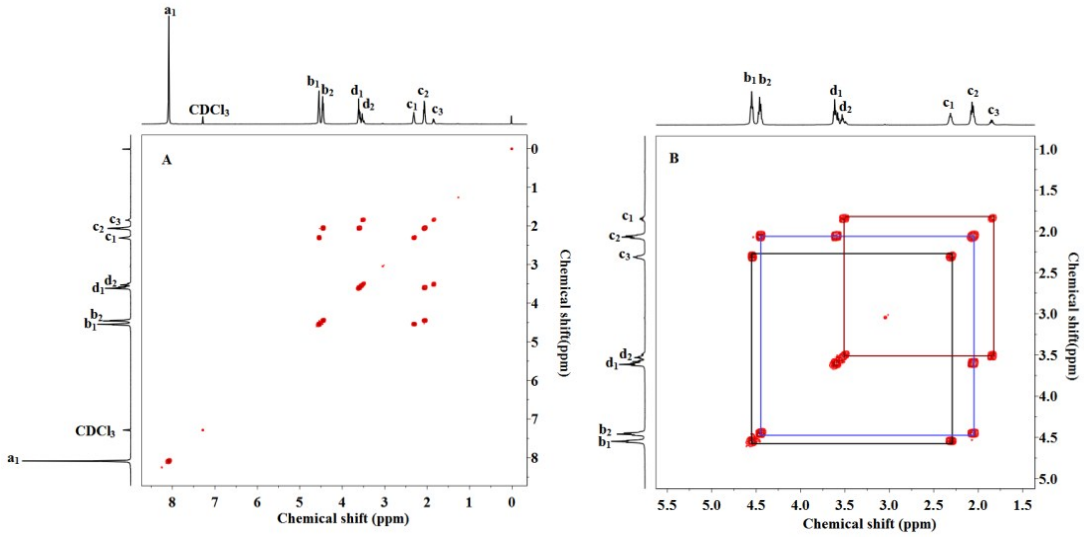


Figure S6. Two dimensional ^{1}H-^{1}H gCOSY spectra of P-3 obtained at the catalysis of TSA and MSA with feeding ratios of 1 to 1. (A) the whole spectrum; (B) the selected enlarged correlated regions.

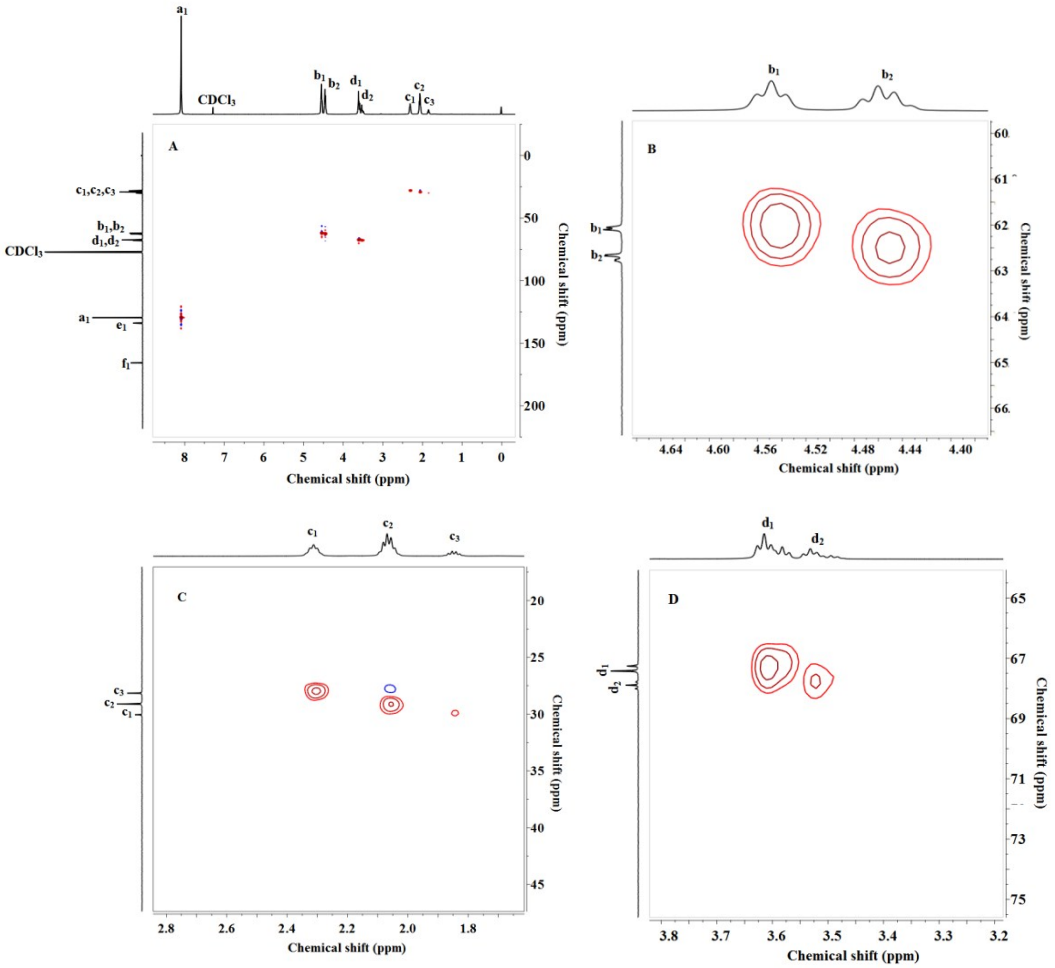


Figure S7. Two dimensional ^{1}H-^{13}C gHSQC spectra of P-3 . (A) the whole spectrum; (B-D) the selected enlarged correlated regions.

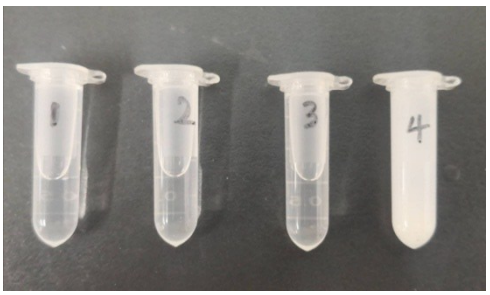


Figure S8. The images of the equimolar mixture of TPT and ESA (1), TSA (2), PheSA (3) and STSA (4) in water.

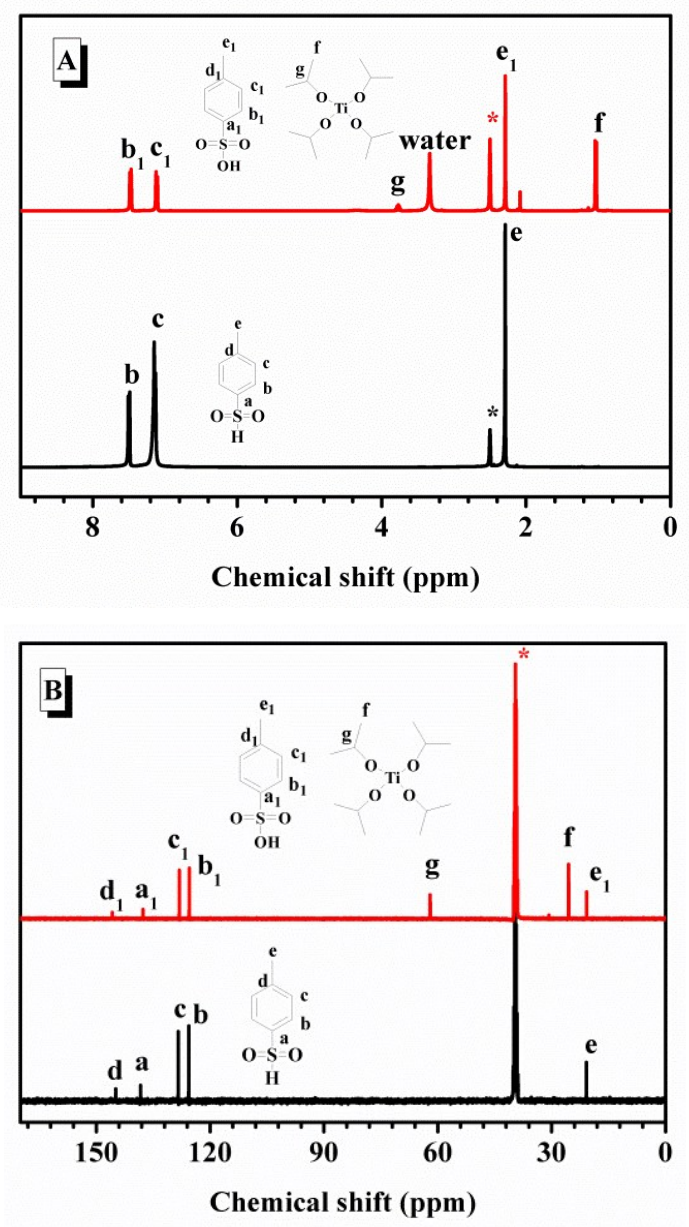


Figure S9. NMR spectra of TSA and the mixture of TSA and MSA with feeding ratio of 1 to 1. (A) ^{1}H NMR spectra. (B) ^{13}C NMR spectra. The peaks marked as asterisk were dimethyl sulfoxide-d_6.

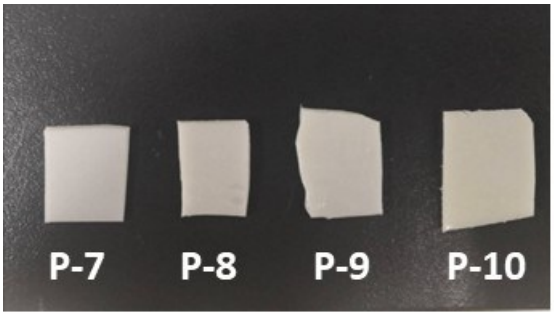


Figure S10. The pictures of copolymers P-7~P-10.

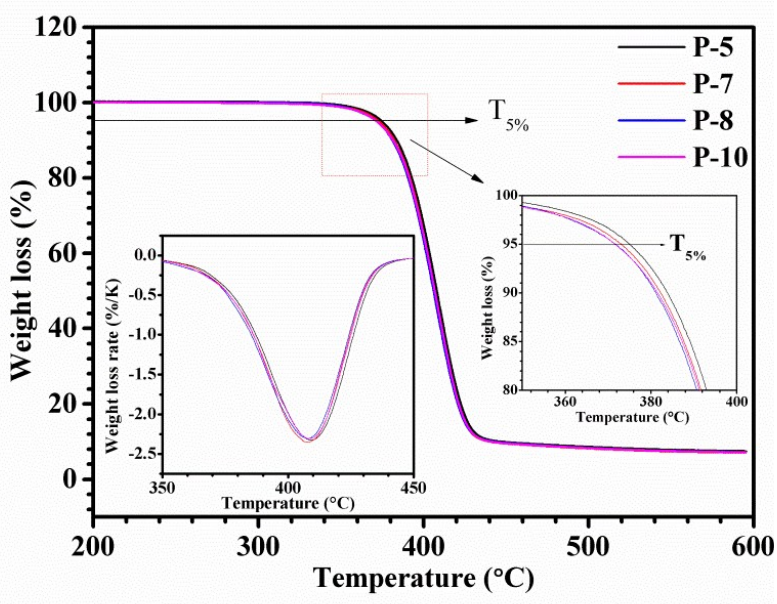
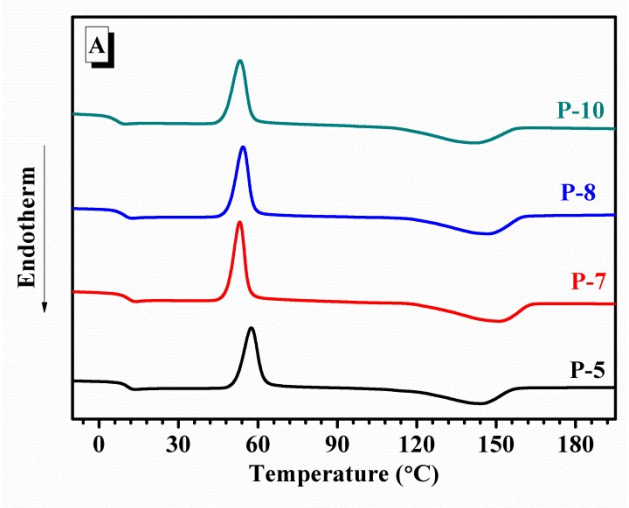


Figure S11. TGA and DTG curves of PTT-*co*-PDPT-*co*-PTrMOT copolymers obtained via different sulfonic acid. Inlet is the corresponding DTG curves and partial magnification of the TGA.



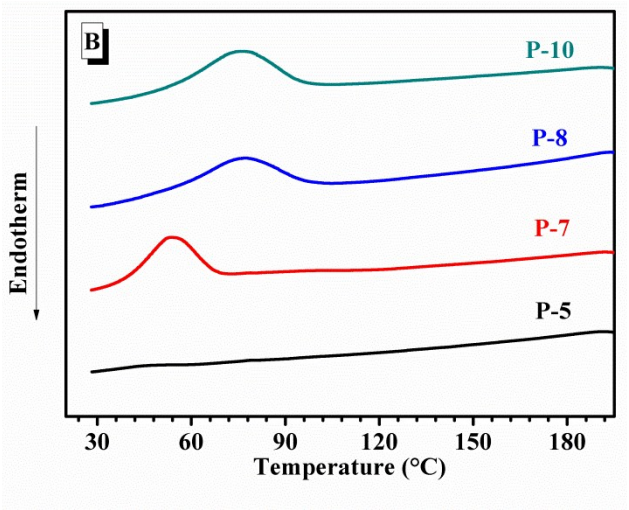
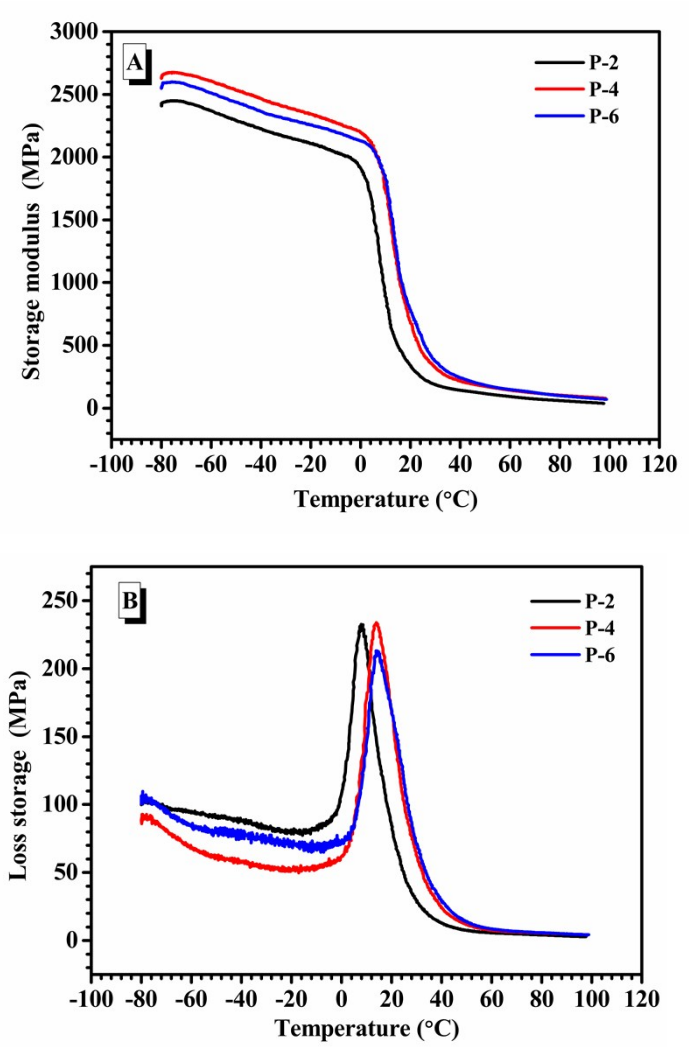


Figure S12. (A) second heating curves of PTT-*co*-PDPT-*co*-PTrMOT copolymers obtained via different sulfonic acids. (B) cooling curves of PTT-*co*-PDPT-*co*-PTrMOT copolymers obtained via different sulfonic acids.



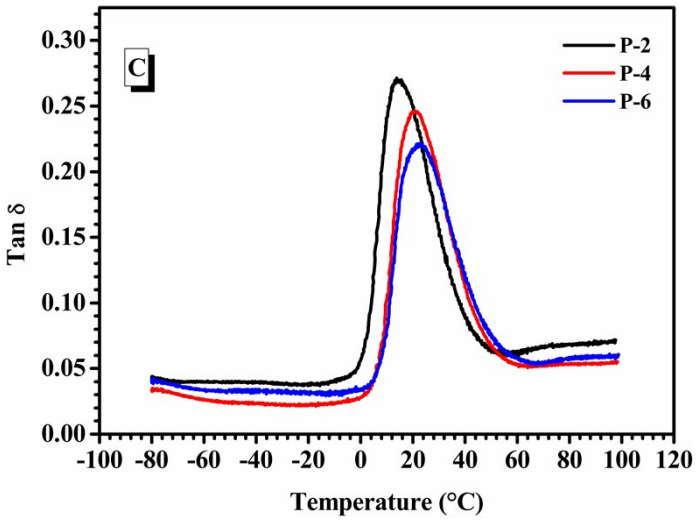


Figure S13. DMA curves of the copolymers. (A)Storage modulus curves. (B) Loss modulus. (C) Tan δ as a function of temperature.

Table S1. Glass transition temperature of PTT-*co*-PDPT-*co*-PTrMOT copolymers

Sample	PTT:PDPT:PTrMOT (wt%)	[η] (dL/g)	$T_{g,DSC}$ (°C)	$T_{g,DMA}$
P-1	100:0:0	0.57	---	79.7
P-2	39:50:11	0.60	5.8	14.2
P-3	55:40:5	0.75	14.3	38.1
P-4	47:46:7	0.82	10.4	20.7
P-5	46:46:8	1.06	10.3	30.3
P-6	45:48:7	0.88	10.4	22.6