

## Supporting Information

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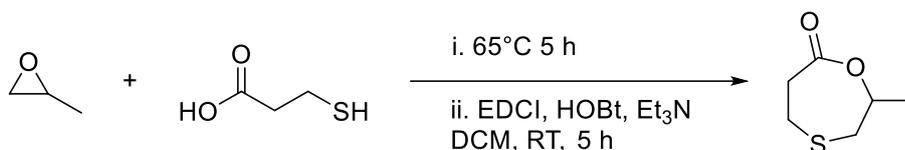
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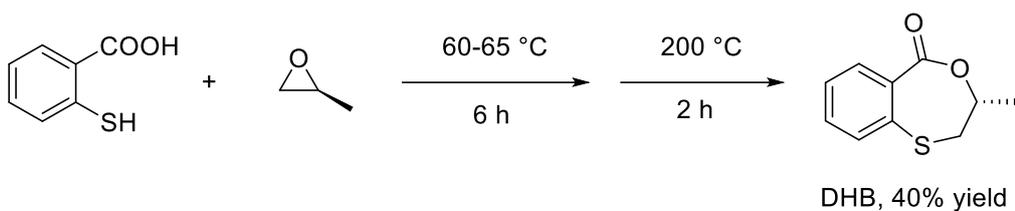
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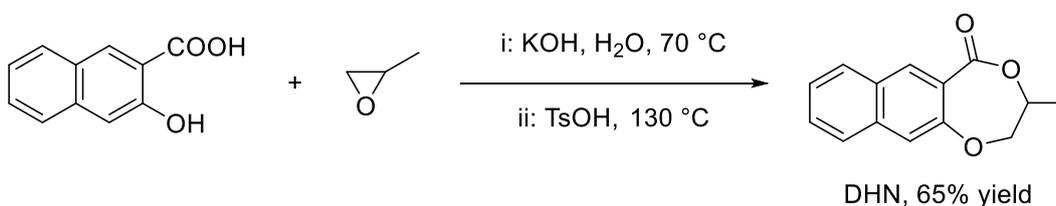
## General Monomer Preparations



### Scheme S1. Synthesis of *rac*-MTO.

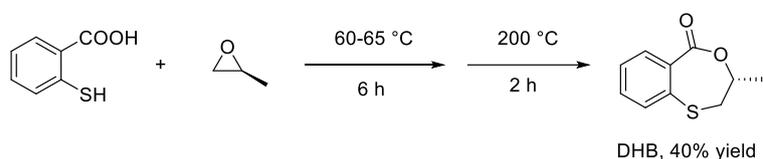


### Scheme S2. Synthesis of DHB.



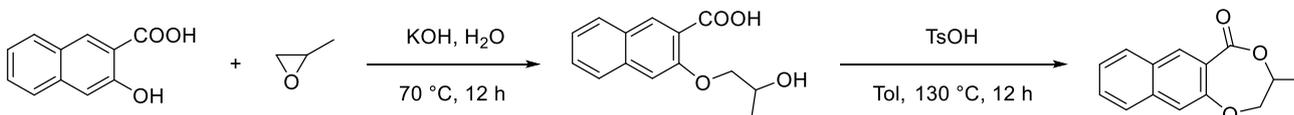
### Scheme S3. Synthesis of DHN.

#### Synthesis of DHB



Literature procedure was modified for the synthesis of DHB.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.68 – 7.64 (m, 1H), 7.52 – 7.48 (m, 1H), 7.48 – 7.41 (m, 2H), 4.38 – 4.30 (m, 1H), 3.22 (dd, *J* = 12.3, 3.3 Hz, 1H), 2.96 (dd, *J* = 12.3, 11.5 Hz, 1H), 1.48 (d, *J* = 6.2 Hz, 3H).

#### Synthesis of DHN



Literature procedure was modified for the synthesis of DHN.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 4.70 – 4.62 (m, 1H), 4.33 – 4.17 (m, 2H), 1.37 (d, *J* = 6.4 Hz, 3H).

# NMR spectra of Monomer

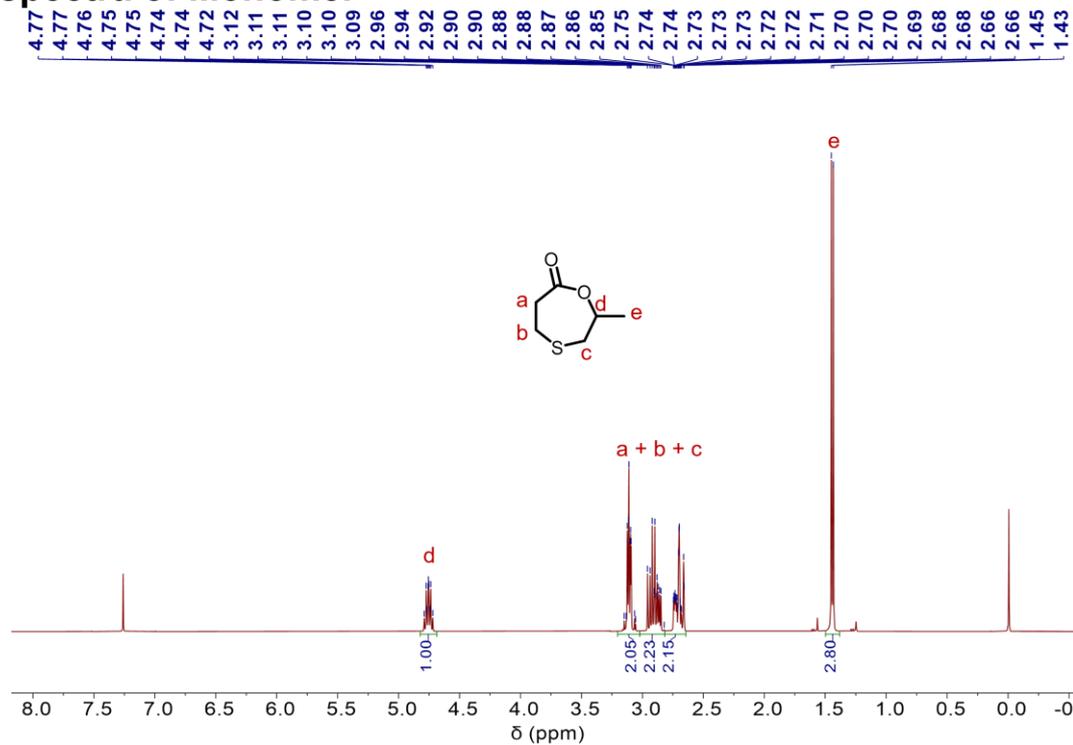


Fig. S1  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of MTO. Residual solvent peak at 7.26 ppm for  $\text{CHCl}_3$

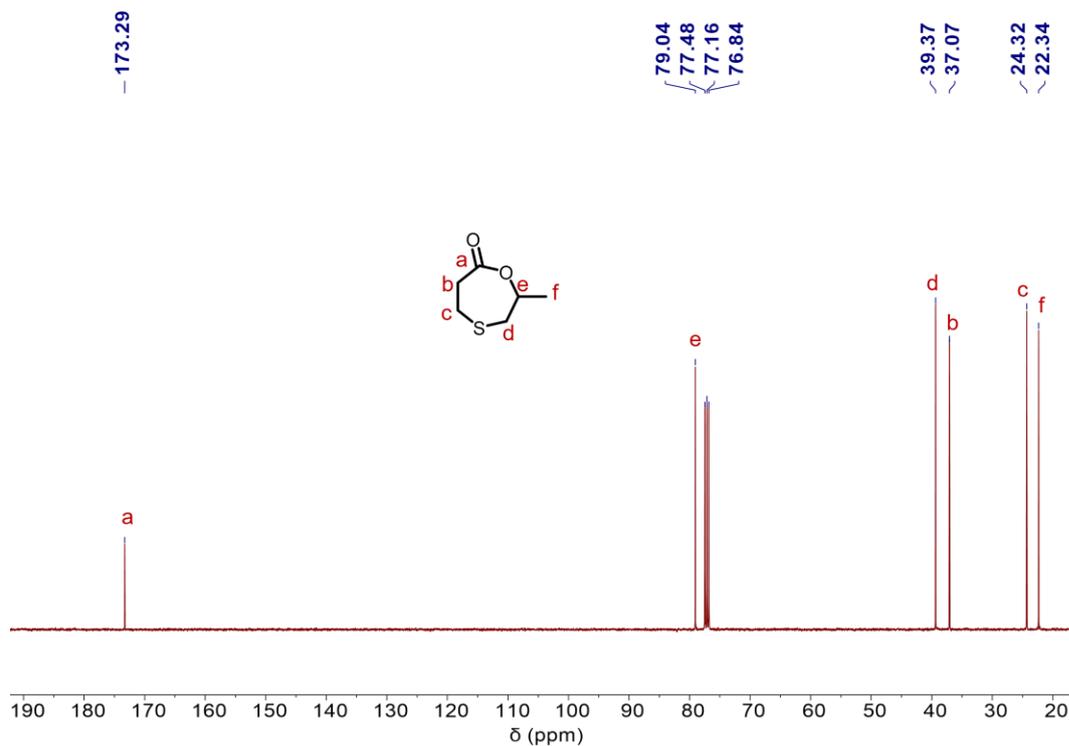
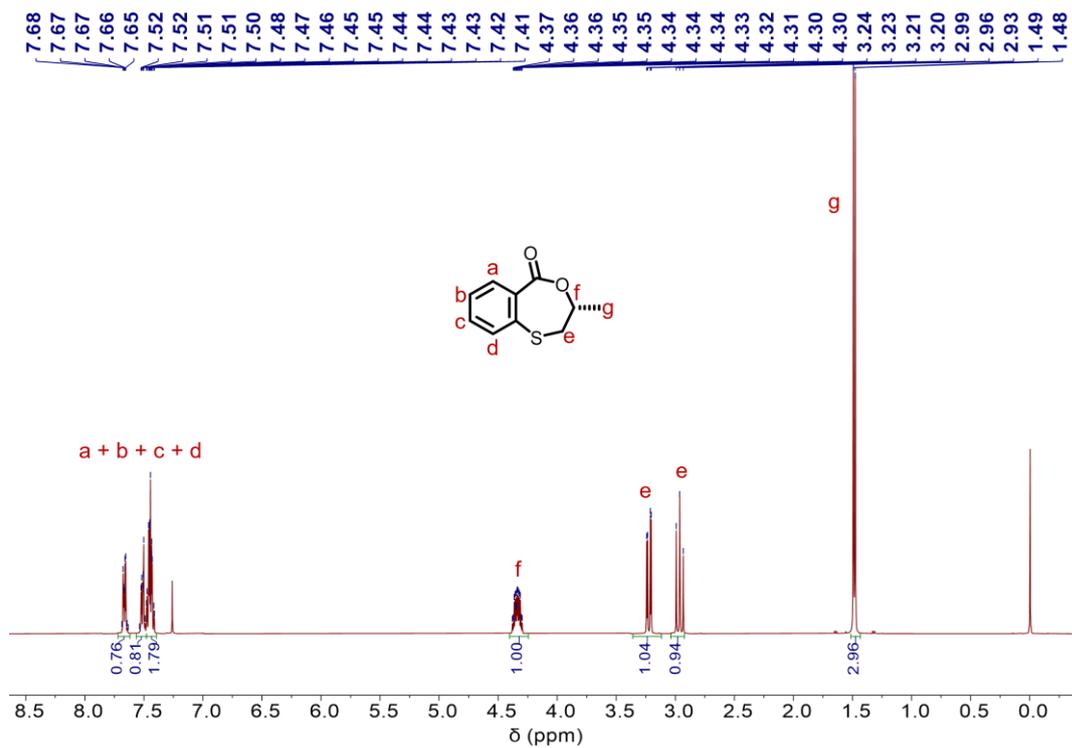
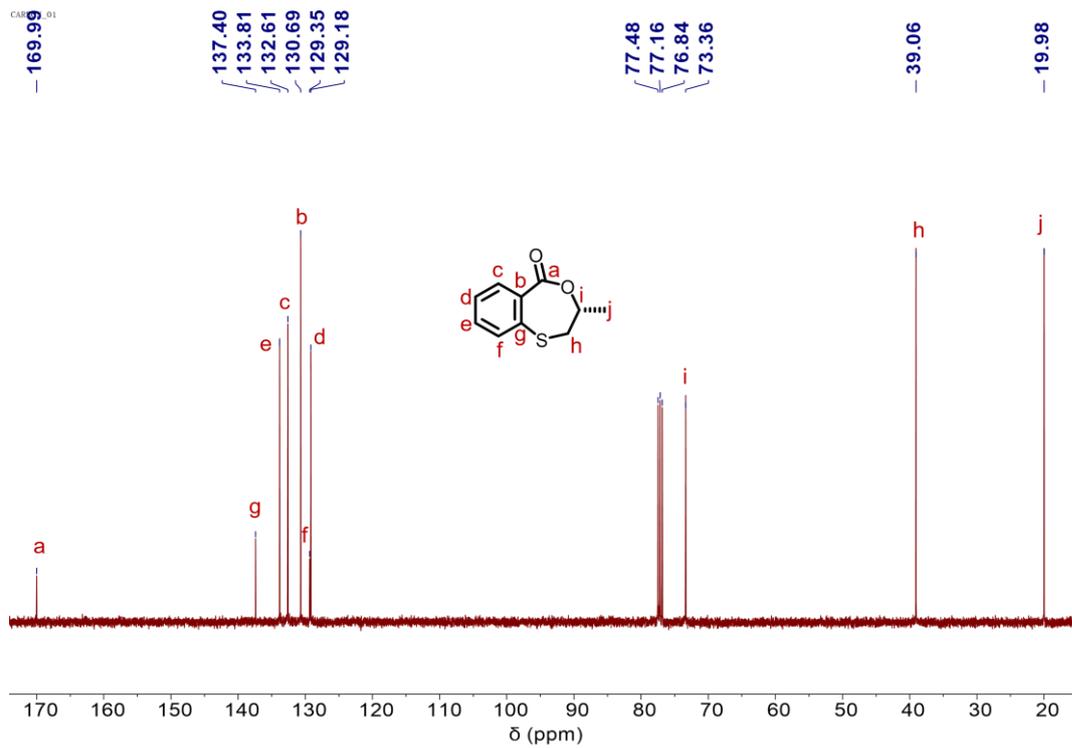


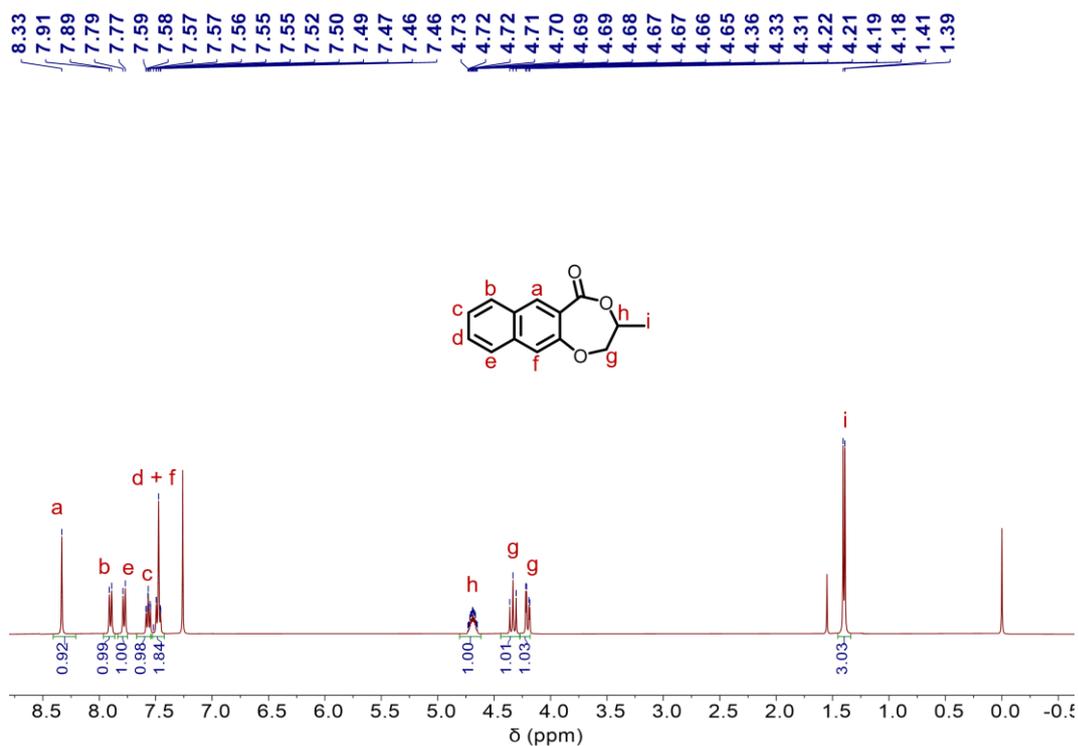
Fig. S2  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of MTO.



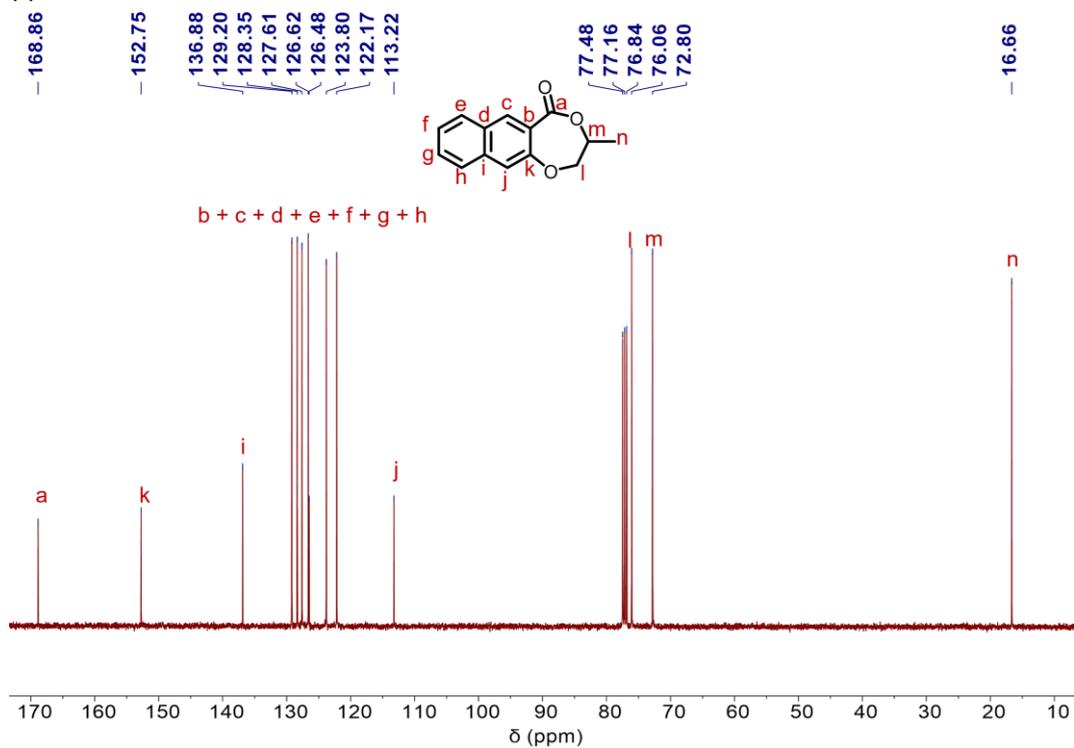
**Fig. S3**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C) spectrum of DHB. Residual solvent peak at 7.26 ppm for  $\text{CHCl}_3$ .



**Fig. S4**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 25 °C) spectrum of DHB.



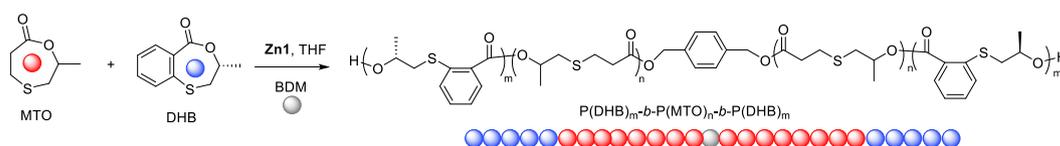
**Fig. S5** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of DHN. Residual solvent peak at 7.26 ppm for CHCl<sub>3</sub>, 1.55 ppm for H<sub>2</sub>O.



**Fig. S6** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C) spectrum of DHN.

## General Polymerization Procedures

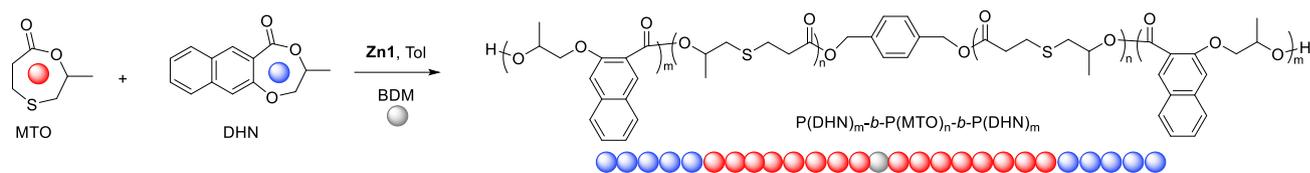
Polymerization was performed in 20 mL oven-dried glass reactors inside the glovebox under ambient conditions. The MTO and DHB/DHN were simply dissolved with THF (Tol if the second monomer was DHN), then the BDM relative to the MTO 1/1000 equivalent was added. After BDM was completely dissolved, a certain amount of solvent and **Zn1** were added to perform the polymerization. After a desired time period, the polymerization was immediately quenched by addition of a certain amount of benzoic acid/CDCl<sub>3</sub> (10 mg/mL) and were later analyzed by <sup>1</sup>H NMR to obtain the percent monomer conversion data. The quenched mixture was then precipitated into cold methanol while stirring, filtered, washed with cold methanol to remove any unreacted monomer and dried in a vacuum oven at 60 °C overnight to a constant weight.



**Table S1** Zn1 catalyzed copolymerization of MTO and DHB.<sup>a</sup>

Entry	Monomer	[MTO]/[DHB]/[Cat.]/[I]	Time (h)	Conv. <sup>b</sup> (%) (MTO/DHB)	<i>M<sub>n</sub></i> <sup>c</sup> (kDa)	<i>Đ</i> <sup>c</sup>
1	MTO	500/0/2/1	5 min	99	72	1.06
2	MTO	1000/0/2/1	20 min	99	143	1.08
3	DHB	0/1000/2/1	10	40	n.d.	n.d.
4	MTO/DHB	500/400/2/1	18	99/45	n.d.	n.d.
5	MTO/DHB	500/400/2/1	34	99/48	n.d.	n.d.
6	MTO/DHB	500/300/2/1	18	99/45	n.d.	n.d.
7	MTO/DHB	1000/800/2/1	18	99/44	n.d.	n.d.
8	MTO/DHB	1000/600/2/1	18	99/40	n.d.	n.d.
9	MTO/DHB	1000/400/2/1	18	99/40	n.d.	n.d.

<sup>a</sup>Conditions: n(MTO) = 0.5 mmol, BDM as an initiator, room temperature, n.d. = not determined, [M] = 2 M or [MTO + DHB]<sub>0</sub> = 2 M in tetrahydrofuran. <sup>b</sup>Monomer conversion was measured by <sup>1</sup>H NMR of the quenched solution. <sup>c</sup>Number-average molecular weight (*M<sub>n</sub>*) and dispersity index (*Đ* = *M<sub>w</sub>*/*M<sub>n</sub>*) were determined by size exclusion chromatography (SEC) at 40 °C in tetrahydrofuran.



**Table S2** Zn1 catalyzed copolymerization of MTO and DHN.<sup>a</sup>

Entry	Monomer	[MTO]/[DHN]/[Cat.]/[I]	Time (h)	Conv. <sup>b</sup> (%) (MTO/DHN)	$M_n^c$ (kDa)	$\mathcal{D}^c$
1	MTO	500/0/2/1	5 min	99	72	1.06
2	MTO	1000/0/2/1	20 min	99	143	1.08
3	DHN	0/1000/2/1	10	66	n.d.	n.d.
4	MTO/DHN	500/400/2/1	24	99/66	121	1.31
5	MTO/DHN	500/300/2/1	24	99/65	n.d.	n.d.
6	MTO/DHN	500/200/2/1	24	99/60	n.d.	n.d.
7	MTO/DHN	1000/800/2/1	24	99/67	n.d.	n.d.
8	MTO/DHN	1000/600/2/1	24	99/65	n.d.	n.d.
9	MTO/DHN	1000/400/2/1	24	99/59	n.d.	n.d.
10	MTO/DHN	1500/1200/2/1	24	99/70	316	1.26
11	MTO/DHN	1500/765/2/1	24	99/64	278	1.29
12	MTO/DHN	2000/1200/2/1	20	99/54	272	1.28

<sup>a</sup>Conditions: n(MTO) = 0.5 mmol, BDM as an initiator, room temperature, n.d. = not determined, [M] = 2 M or [MTO + DHN]<sub>0</sub> = 2 M in toluene. <sup>b</sup>Monomer conversion was measured by <sup>1</sup>H NMR of the quenched solution. <sup>c</sup>Number-average molecular weight ( $M_n$ ) and dispersity index ( $\mathcal{D} = M_w/M_n$ ) were determined by size exclusion chromatography (SEC) at 40 °C in tetrahydrofuran.

**Table S3** One-pot ring-opening copolymerization to prepare triblock TPEs (TPE1, TPE2, TPE3).<sup>a</sup>

Entry	Monomer	[MTO]/[DHB]/[Cat.]/[I]	Conv. (%) <sup>b</sup>	Time (h)	Polymer	<sup>c</sup> F <sub>DHB</sub>	M <sub>n</sub> <sup>d</sup> (kDa)	Đ <sup>d</sup>
1	MTO/DHB	1000/600/2/1	99/40	18	TPE1	0.19	119	1.57
2	MTO/DHB	1000/600/2/1	99/50	26	TPE2	0.25	120	1.61
3	MTO/DHB	1000/800/2/1	99/51	26	TPE3	0.30	141	1.43

<sup>a</sup>Conditions: The polymerizations were conducted at r.t. with an initial monomer concentration of [MTO + DHB]<sub>0</sub> = 2 M in tetrahydrofuran. <sup>b</sup>Monomer conversion was measured by <sup>1</sup>H NMR of the quenched solution. <sup>c</sup>F<sub>DHB</sub> was determined by <sup>1</sup>H NMR. <sup>d</sup>Number-average molecular weight (M<sub>n</sub>) and dispersity index (Đ = M<sub>w</sub>/M<sub>n</sub>) were determined by size exclusion chromatography (SEC) at 40 °C in chloroform.

**Table S4** One-pot ring-opening copolymerization to prepare triblock TPEs (TPE4, TPE5, TPE6, TPE7).<sup>a</sup>

Entry	Monomer	[MTO]/[DHN]/[Cat.]/[I]	Conv. (%) <sup>b</sup>	Time (h)	Polymer	<sup>c</sup> F <sub>DHN</sub>	M <sub>n</sub> <sup>d</sup> (kDa)	Đ <sup>d</sup>
1	MTO/DHN	1500/765/2/1	99/51	18	TPE4	0.21	260	1.27
2	MTO/DHN	1500/900/2/1	99/50	18	TPE5	0.22	212	1.26
3	MTO/DHN	1500/1200/2/1	99/50	22	TPE6	0.33	273	1.31
4	MTO/DHN	1500/1200/2/1	99/80	36	TPE7	0.39	231	1.26

<sup>a</sup>Conditions: The polymerizations were conducted at r.t. with an initial monomer concentration of [MTO + DHN]<sub>0</sub> = 2 M in toluene. <sup>b</sup>Monomer conversion was measured by <sup>1</sup>H NMR of the quenched solution. <sup>c</sup>F<sub>DHN</sub> was determined by <sup>1</sup>H NMR. <sup>d</sup>Number-average molecular weight (M<sub>n</sub>) and dispersity index (Đ = M<sub>w</sub>/M<sub>n</sub>) were determined by size exclusion chromatography (SEC) at 40 °C in tetrahydrofuran.

## Polymer Characterization

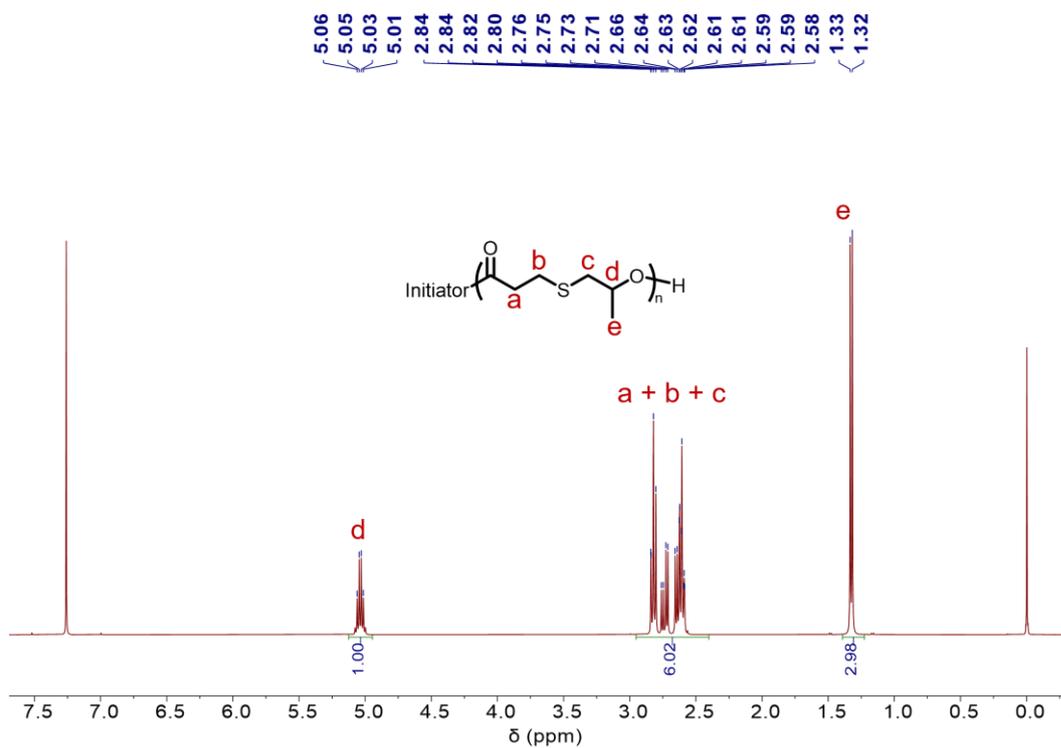


Fig. S7  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of PMTO obtained by  $[\text{MTO}]/[\text{Zn1}]/[\text{I}] = 100/2/1$ .

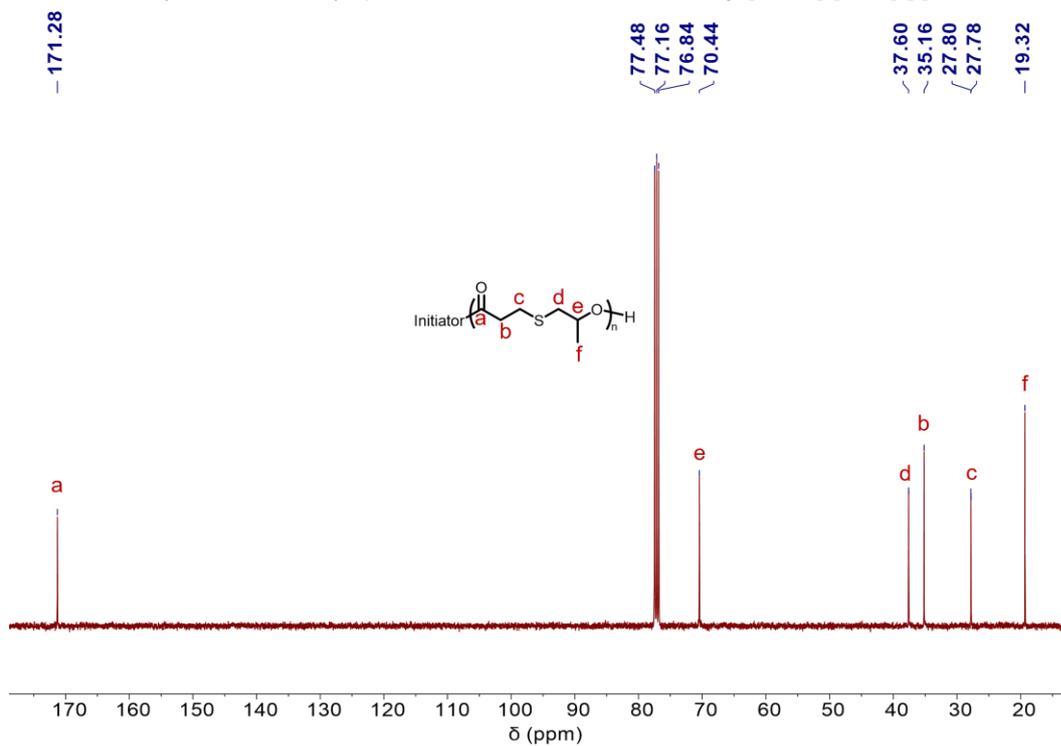
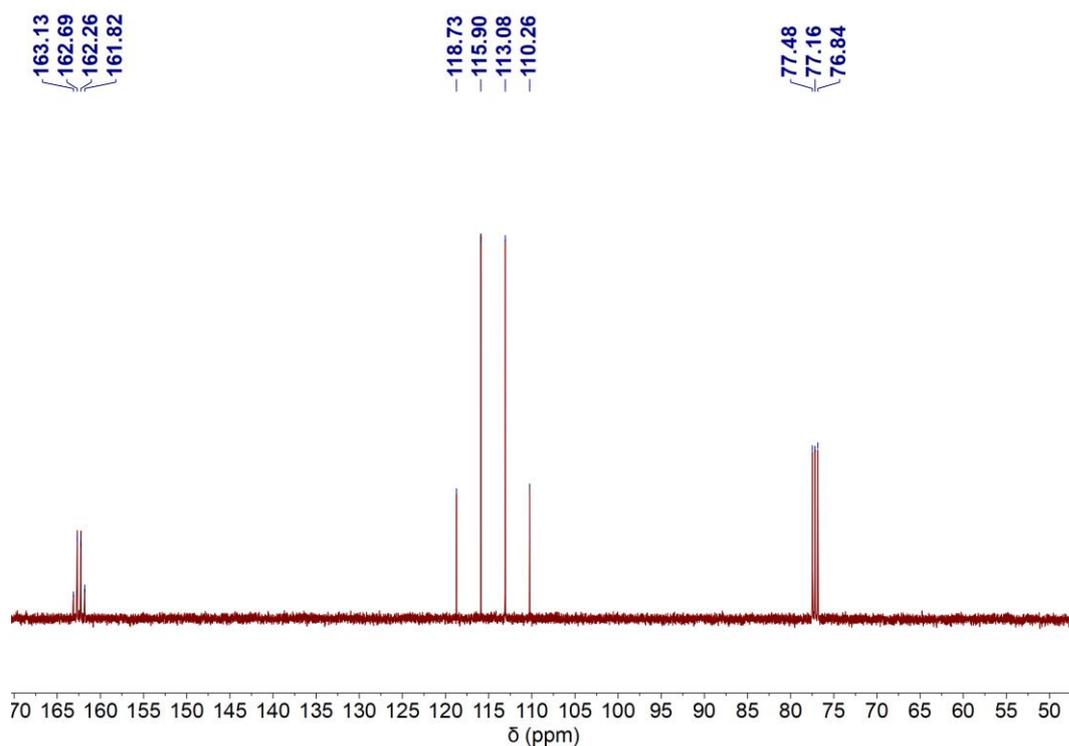
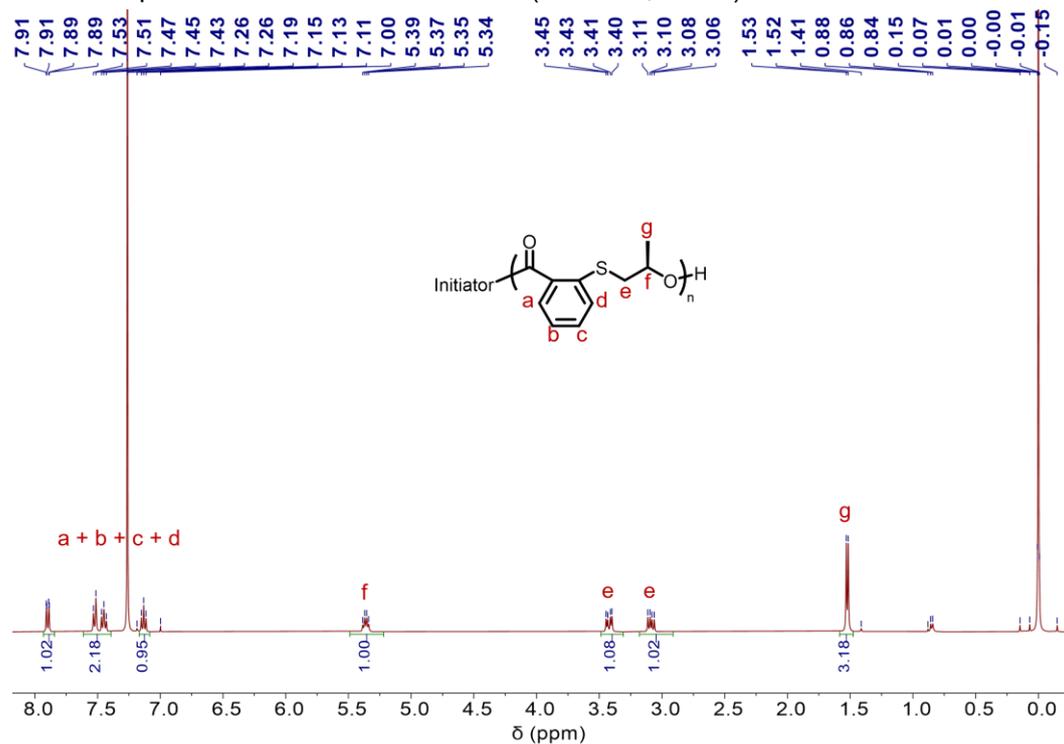


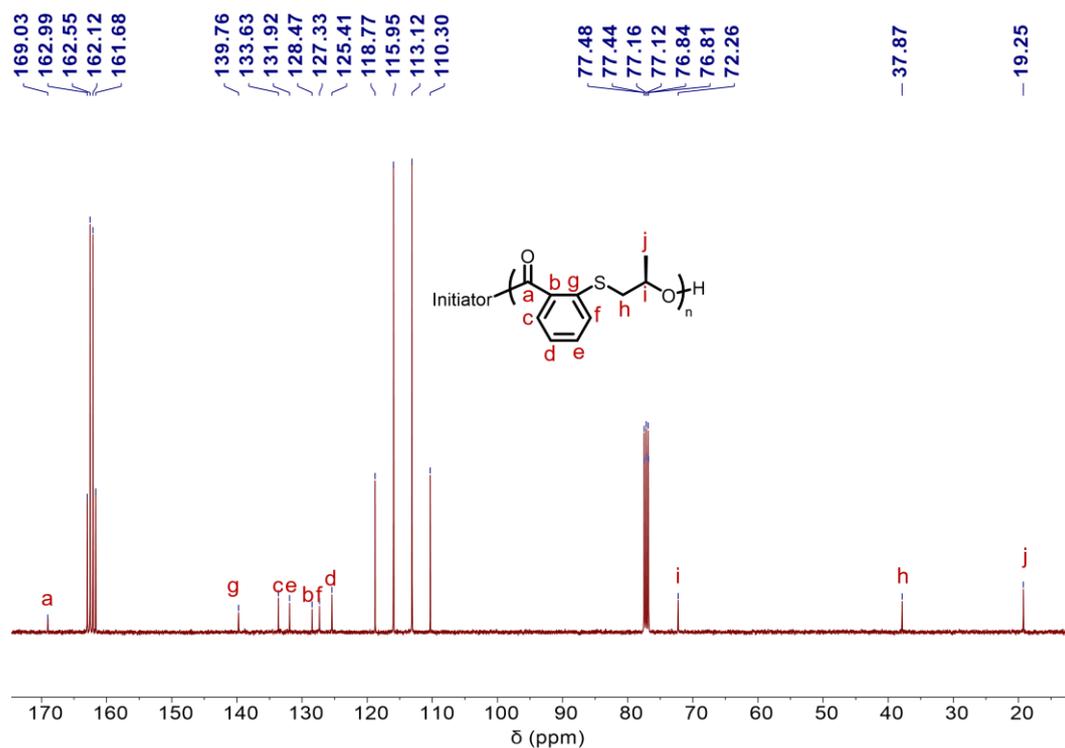
Fig. S8  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of PMTO



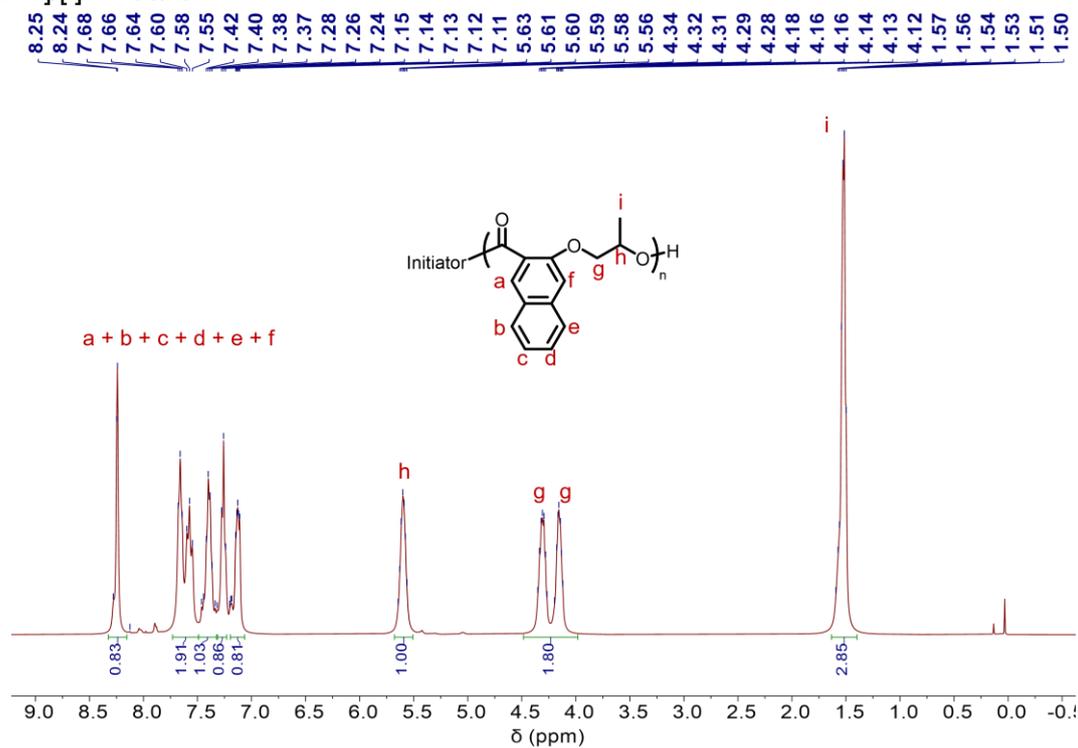
**Fig. S9**  $^{13}\text{C}$  NMR spectrum of  $\text{CDCl}_3 + \text{CF}_3\text{COOD}$  (v/v = 3:1, 25 °C) as reference.



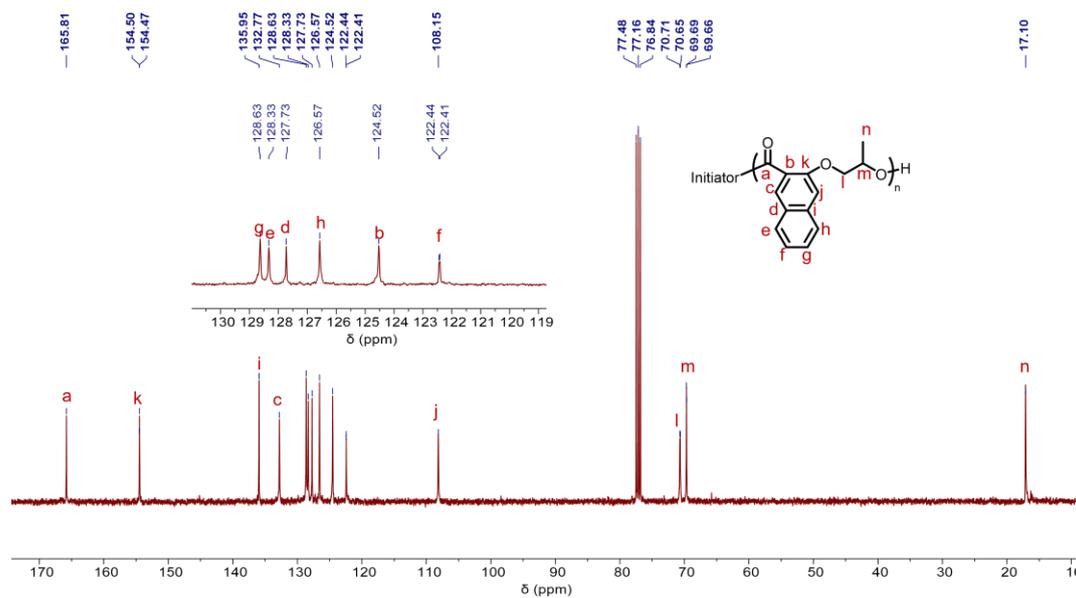
**Fig. S10**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C) spectrum of P(DHB) obtained by  $[\text{DHB}]/[\text{Zn1}]/[\text{I}] = 100/2/1$ .



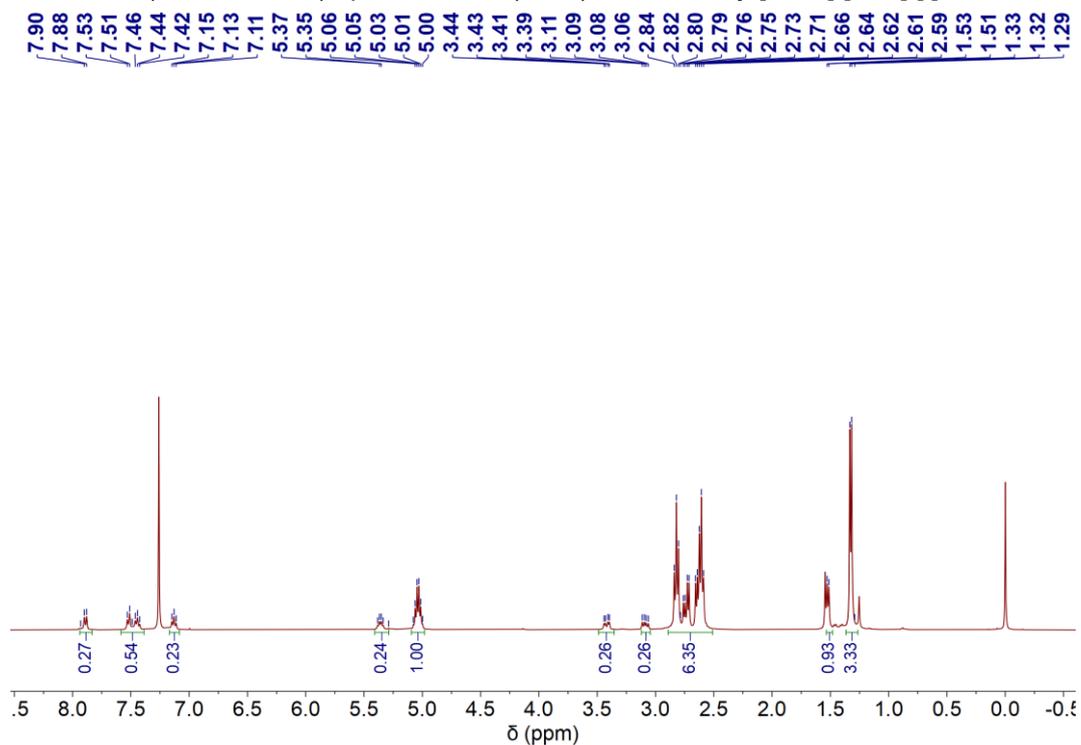
**Fig. S11** <sup>13</sup>C NMR (CDCl<sub>3</sub> : CF<sub>3</sub>COOD = 3 : 1 (v/v), 25 °C) spectrum of P(DHB) obtained by [DHB]/[Zn1]/[I] = 100/2/1.



**Fig. S12** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of P(DHN) obtained by [DHN]/[Zn1]/[I] = 100/2/1.



**Fig. S13** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C) spectrum of P(DHN) obtained by [DHN]/[Zn1]/[I] = 100/2/1.



**Fig. S14** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) of TPE1 ( $F_{\text{DHB}} = 0.19$ ), 1.55 ppm for H<sub>2</sub>O.

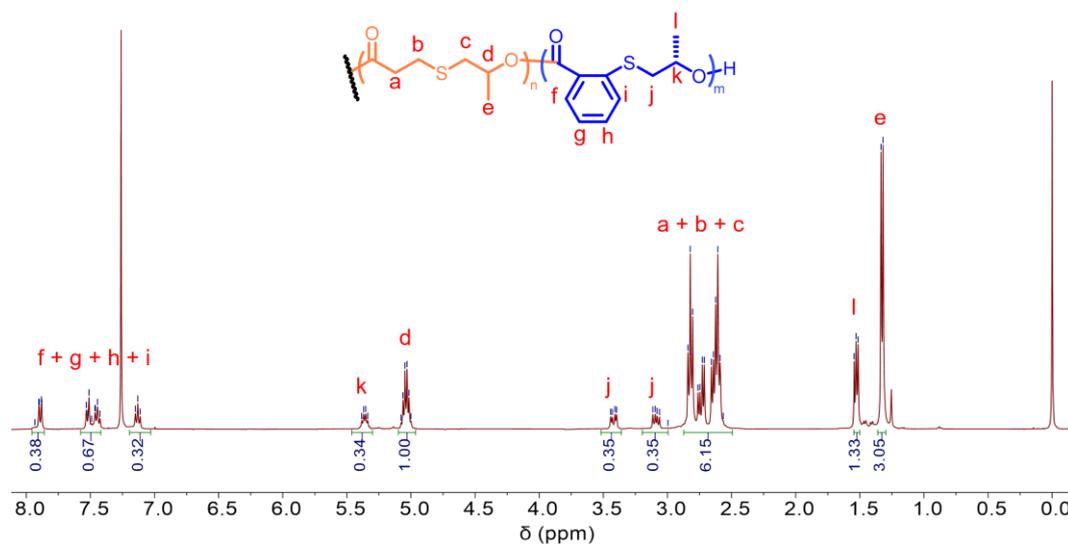
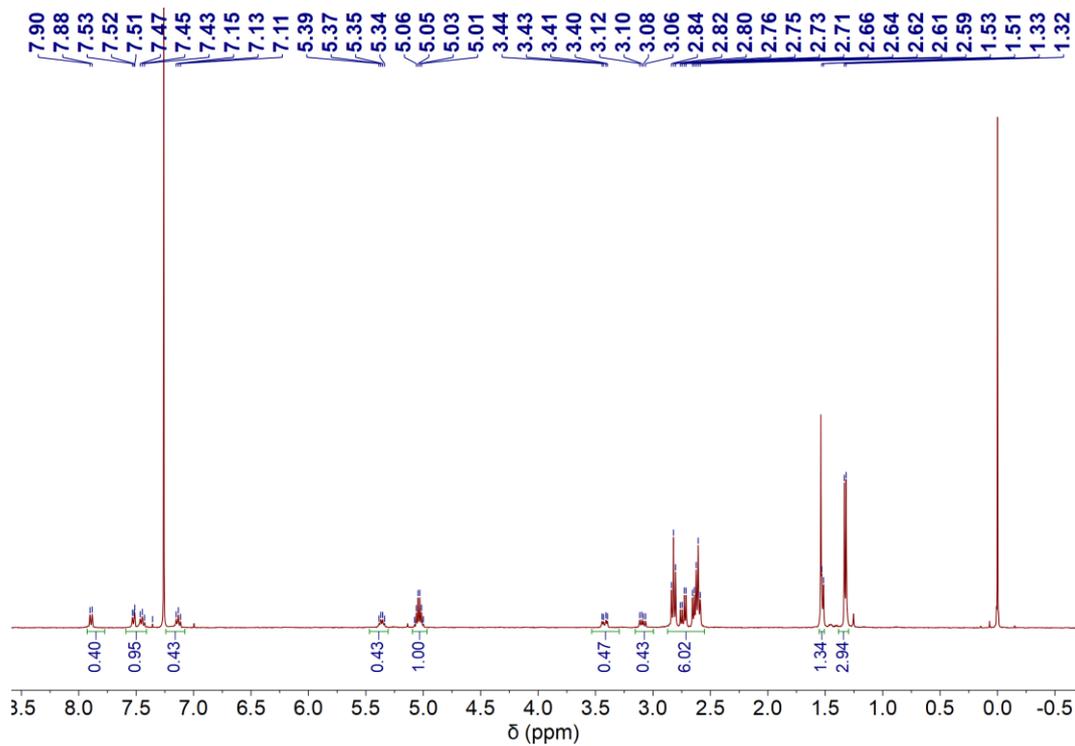


Fig. S15 <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) of TPE2 ( $F_{\text{DHB}} = 0.25$ ), 1.55 ppm for H<sub>2</sub>O.



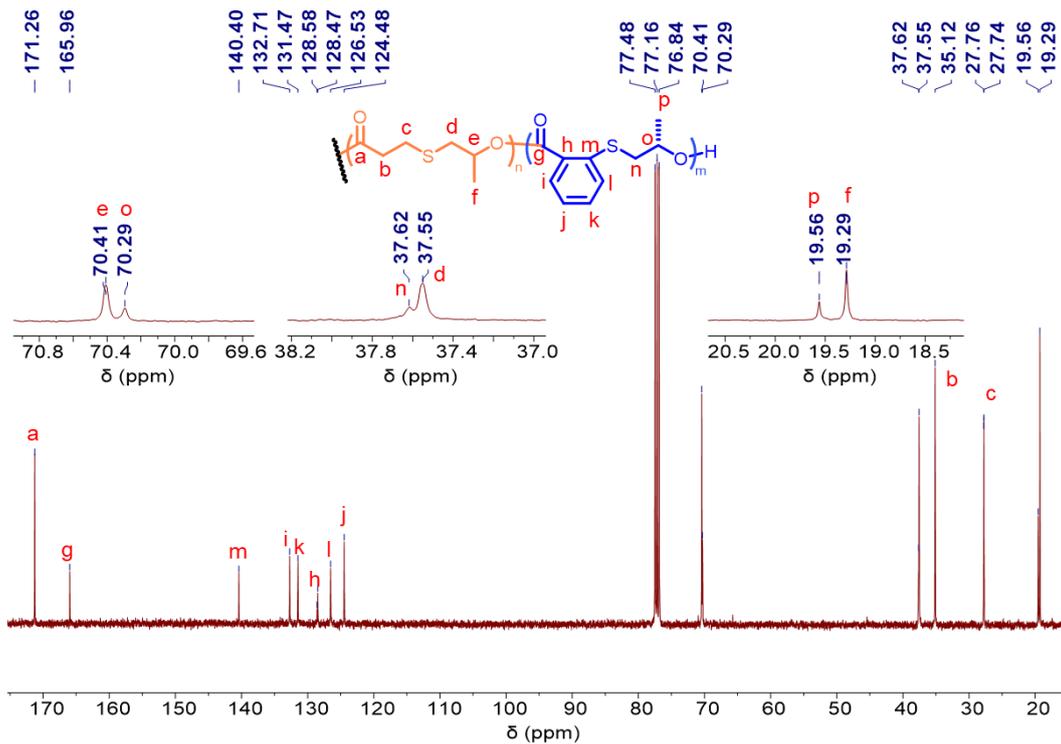


Fig. S17  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 25 °C) of TPE1.

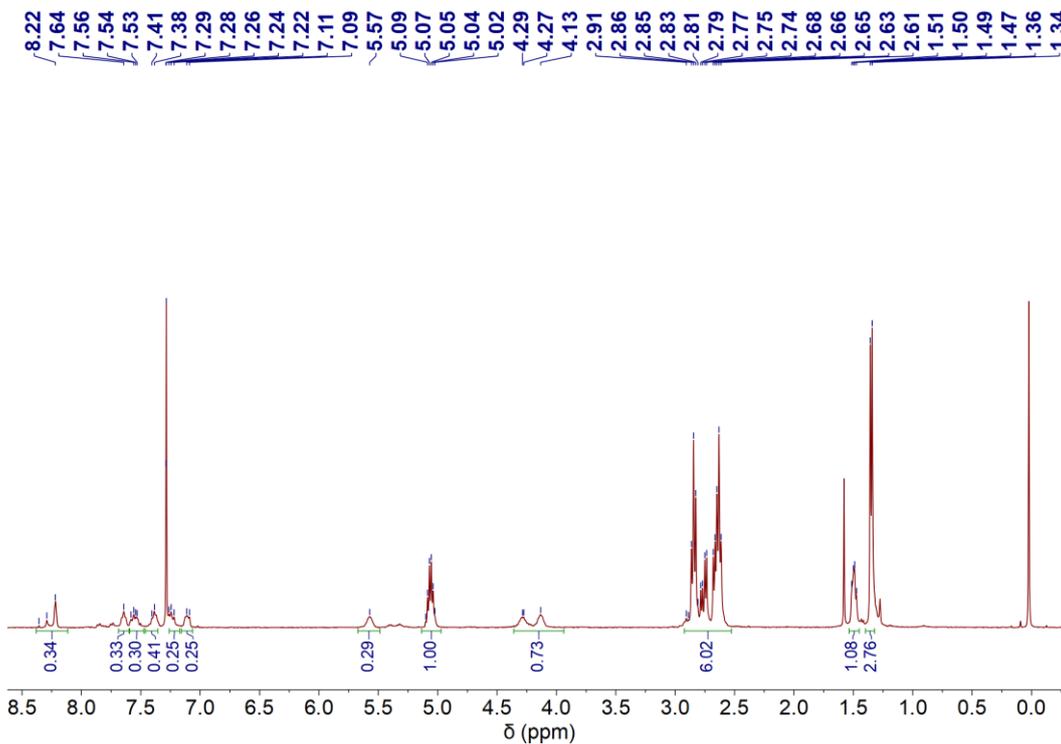
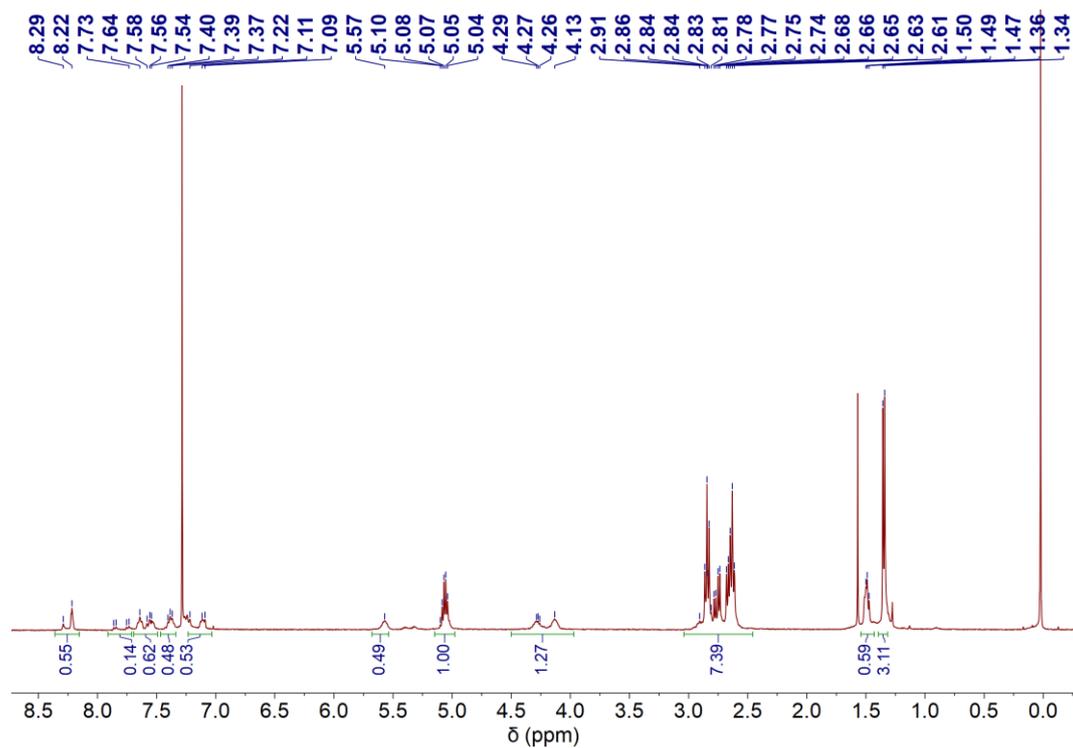
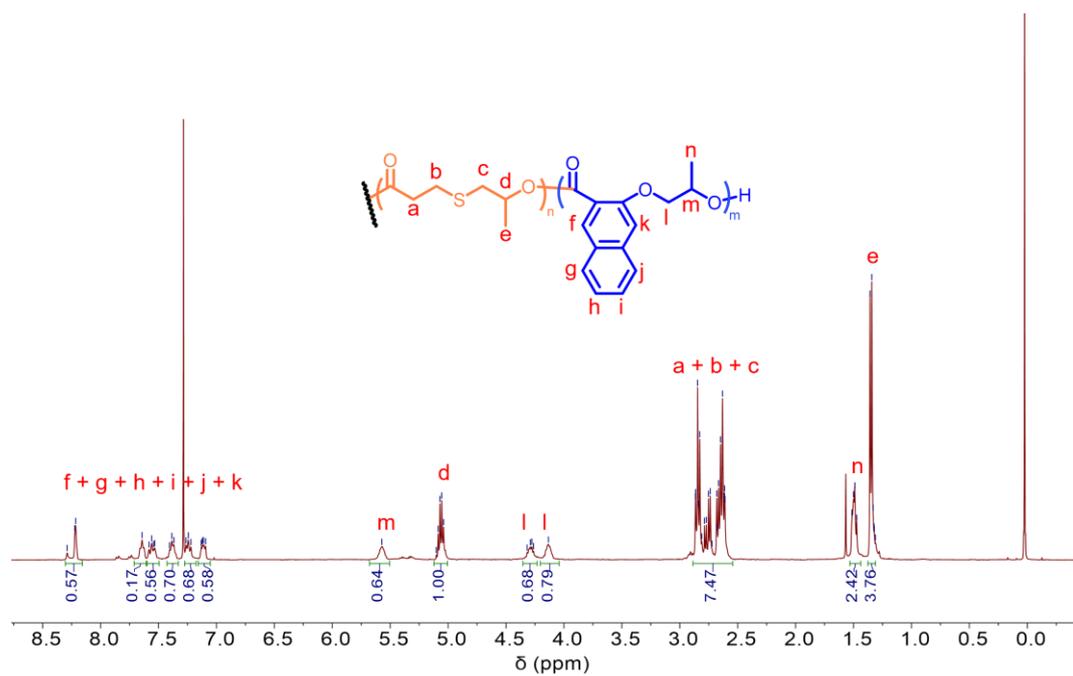


Fig. S18  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C) of TPE5 ( $F_{\text{DHN}} = 0.22$ ), 1.55 ppm for  $\text{H}_2\text{O}$ .



**Fig. S19**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25\text{ }^\circ\text{C}$ ) of TPE6 ( $F_{\text{DHN}} = 0.33$ ), 1.55 ppm for  $\text{H}_2\text{O}$ .



**Fig. S20**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25\text{ }^\circ\text{C}$ ) of TPE7 ( $F_{\text{DHN}} = 0.39$ ), 1.55 ppm for  $\text{H}_2\text{O}$ .

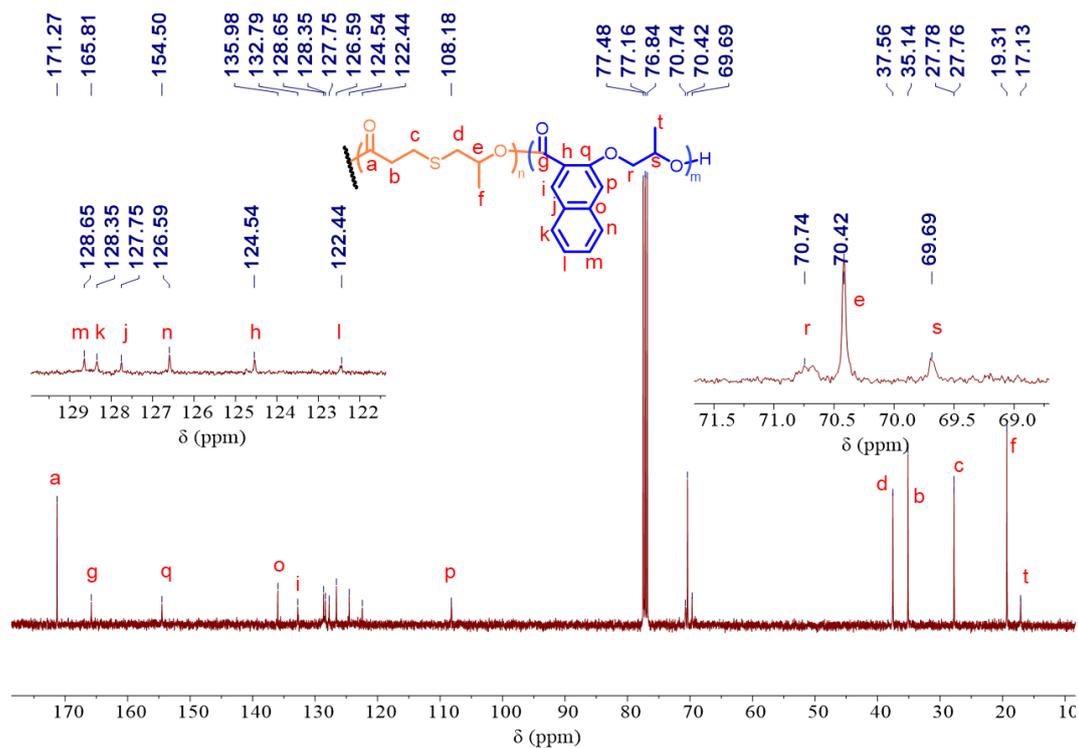


Fig. S21  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 25 °C) of TPE4.

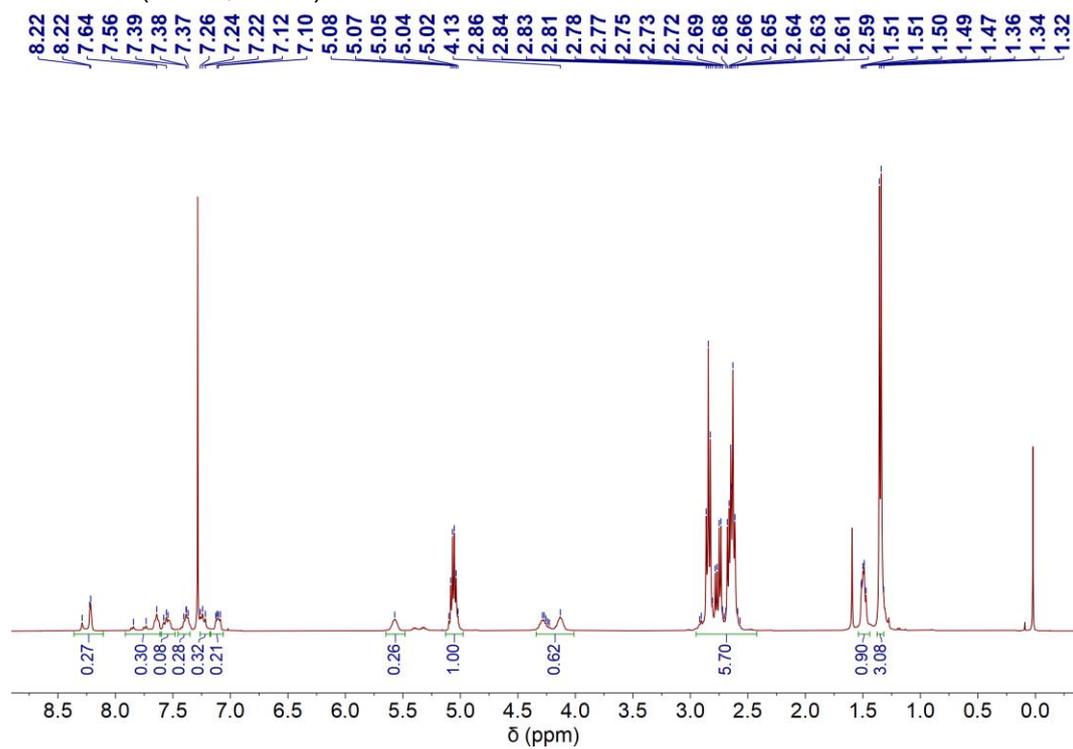
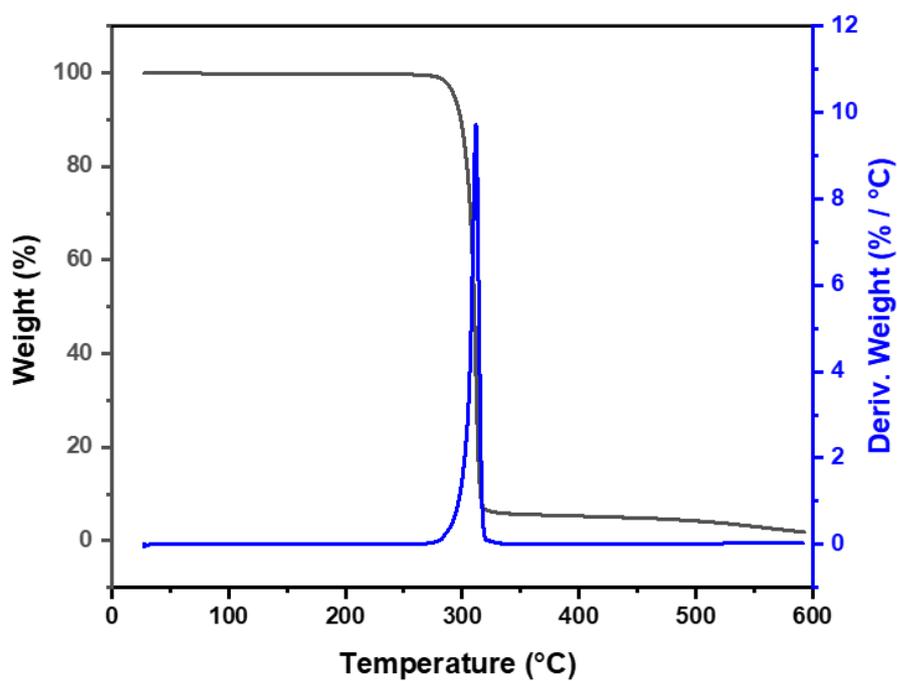


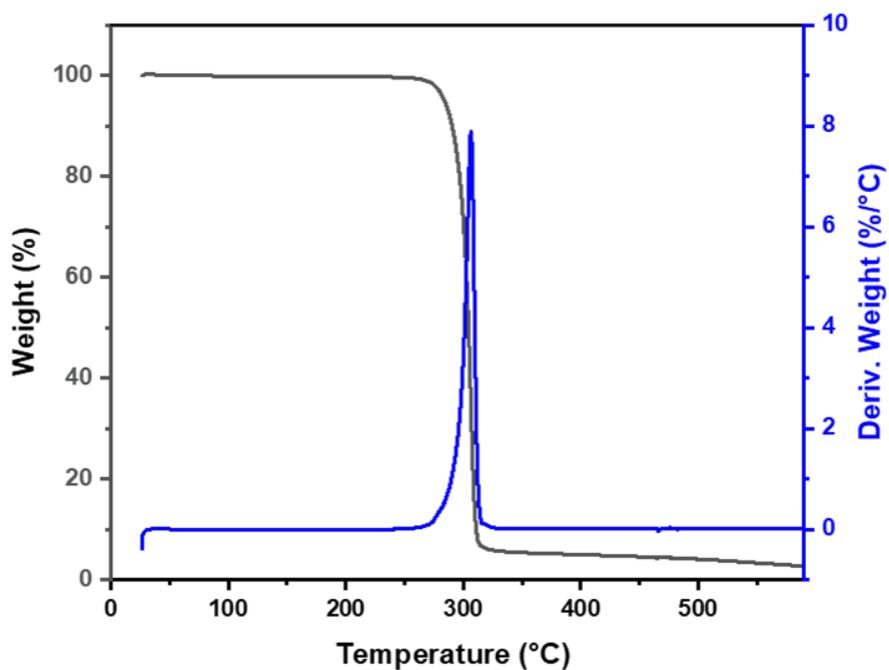
Fig. S22  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C) of TPE4 ( $F_{\text{DHN}} = 0.21$ ), 1.55 ppm for  $\text{H}_2\text{O}$ .

**Table S5** Summary of  $T_g$ ,  $T_m$  and  $T_d$  for TPE1 ~ TPE7

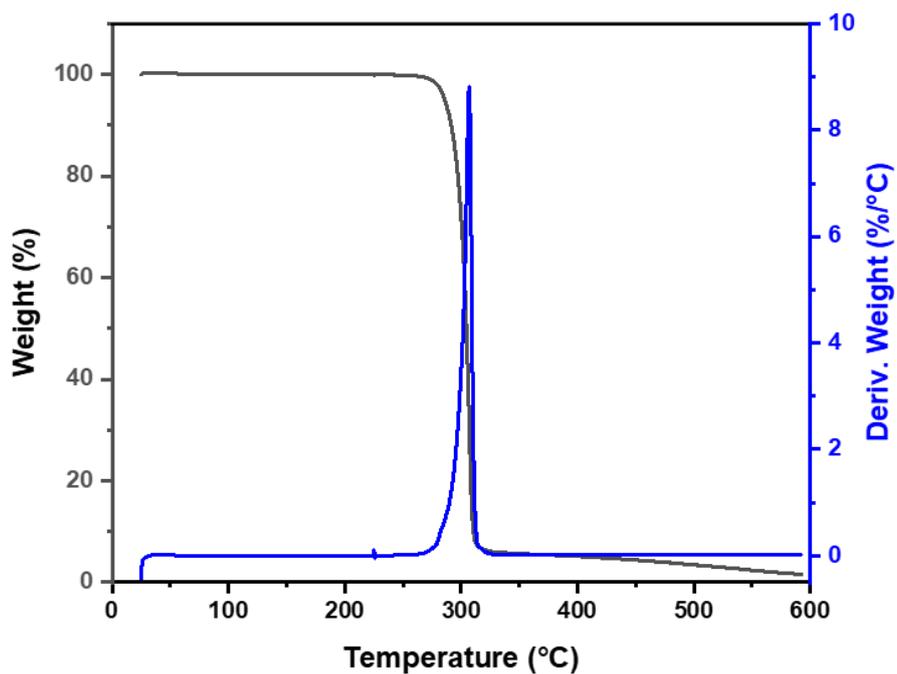
Sample	$T_d$ (°C)	$T_m$ or $T_g$ (°C)
TPE1	293	167
TPE2	284	172
TPE3	286	180
TPE4	297	99
TPE5	297	95
TPE6	295	92
TPE7	296	95



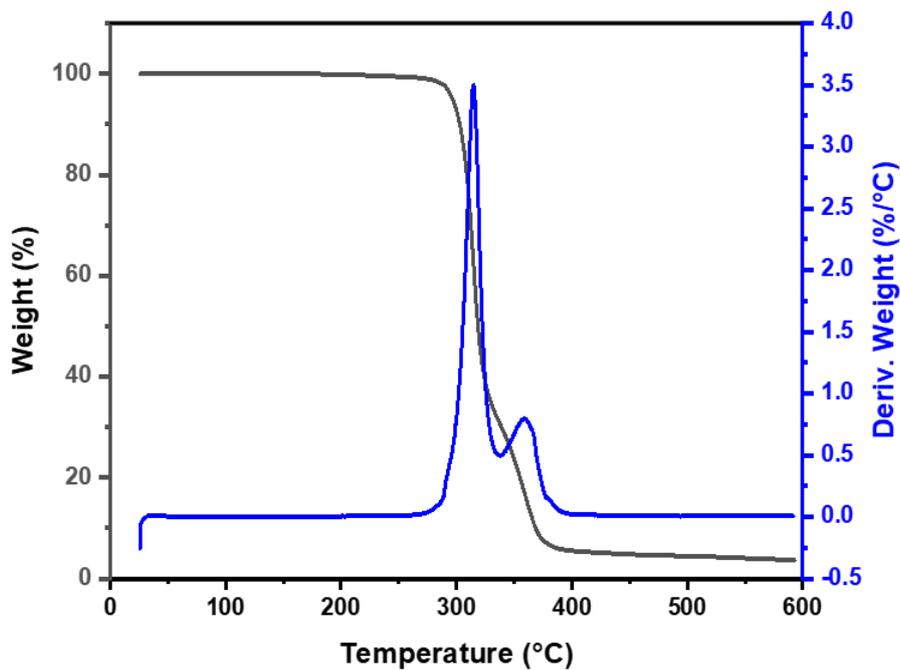
**Fig. S23** TGA and DTG curves for TPE1 ( $F_{DHB} = 0.19$ ),  $T_d = 293$  °C,  $T_{max} = 312$  °C.



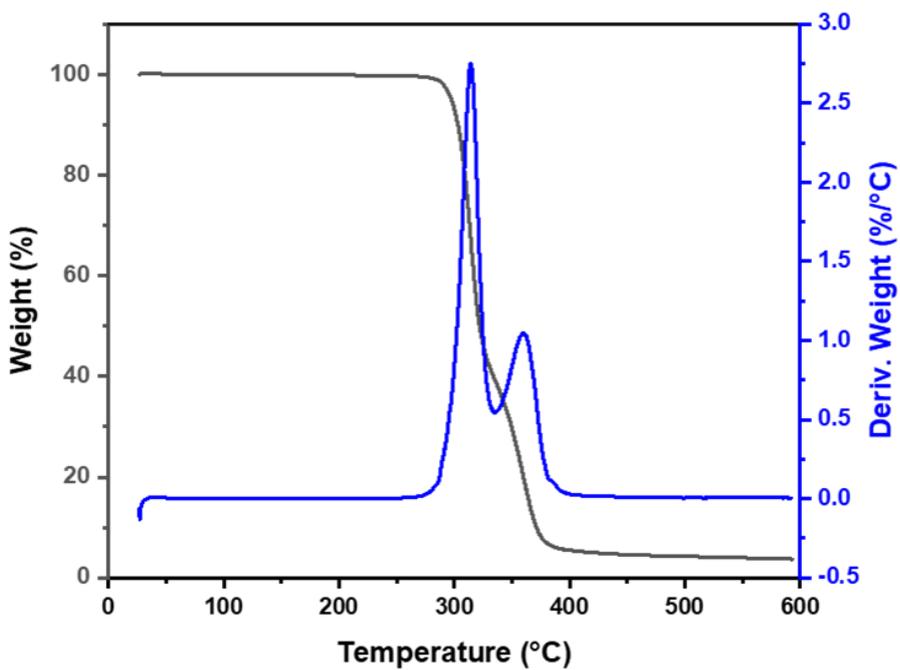
**Fig. S24** TGA and DTG curves for TPE2 ( $F_{\text{DHB}} = 0.25$ ),  $T_d = 284$  °C,  $T_{\text{max}} = 306$  °C.



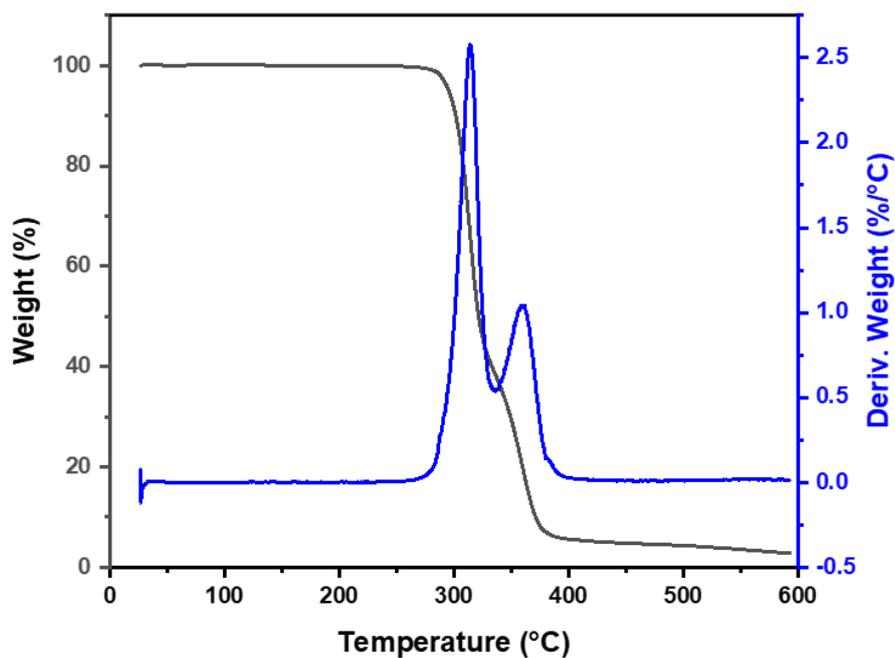
**Fig. S25** TGA and DTG curves for TPE3 ( $F_{\text{DHB}} = 0.30$ ),  $T_d = 286$  °C,  $T_{\text{max}} = 307$  °C.



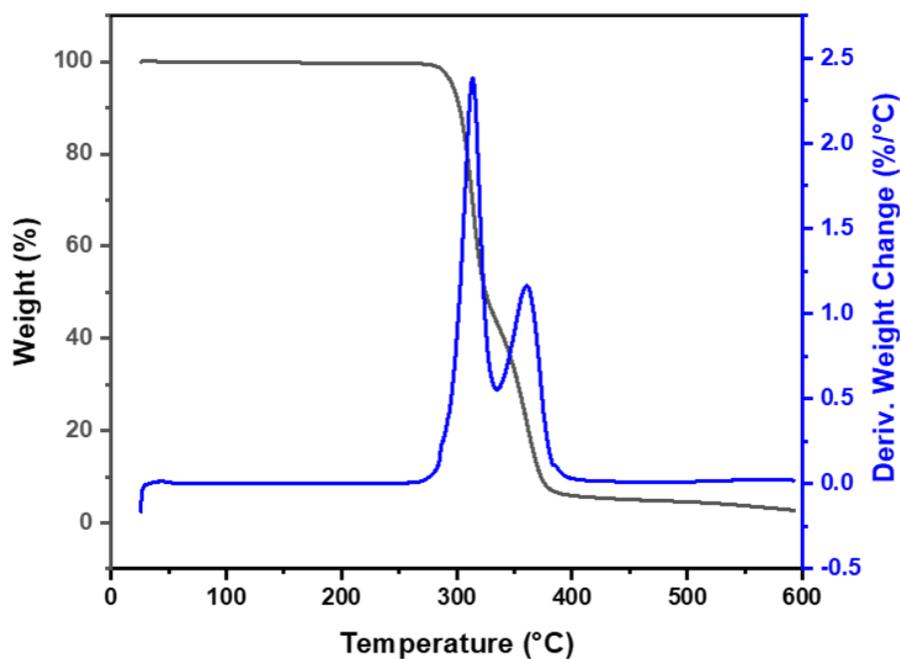
**Fig. S26** TGA and DTG curves for TPE4 ( $F_{\text{DHN}} = 0.21$ ),  $T_d = 297$  °C,  $T_{\text{max}1} = 315$  °C,  $T_{\text{max}2} = 358$  °C.



**Fig. S27** TGA and DTG curves for TPE5 ( $F_{\text{DHN}} = 0.22$ ),  $T_d = 297$  °C,  $T_{\text{max}1} = 314$  °C,  $T_{\text{max}2} = 361$  °C.



**Fig. S28** TGA and DTG curves for TPE6 ( $F_{\text{DHN}} = 0.33$ ),  $T_d = 295$  °C,  $T_{\text{max}1} = 314$  °C,  $T_{\text{max}2} = 361$  °C.



**Fig. S29** TGA and DTG curves for TPE7 ( $F_{\text{DHN}} = 0.39$ ),  $T_d = 296$  °C,  $T_{\text{max}1} = 313$  °C,  $T_{\text{max}2} = 361$  °C.

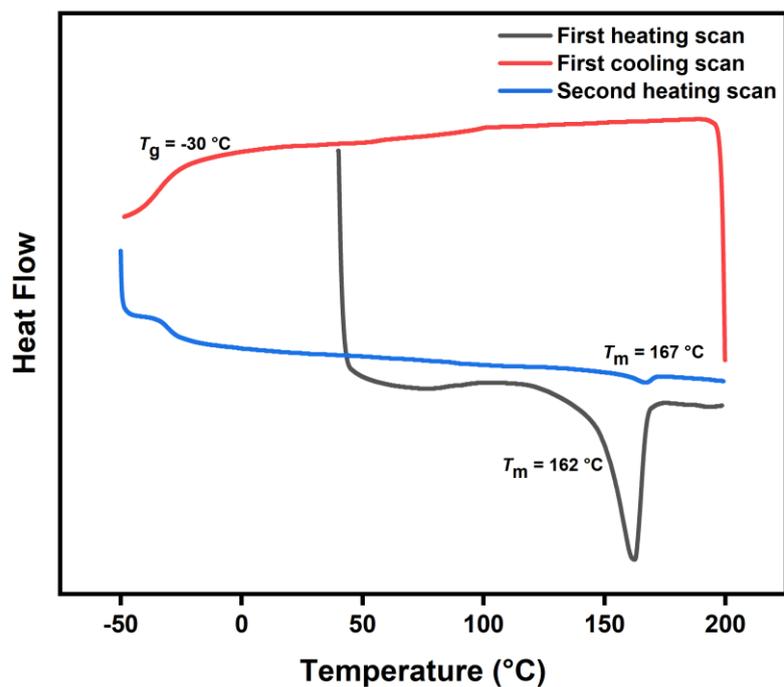


Fig. S30 DSC curves for TPE1 ( $F_{\text{DHB}} = 0.19$ ),  $T_g = -30\text{ }^{\circ}\text{C}$ ,  $T_m = 167\text{ }^{\circ}\text{C}$ .

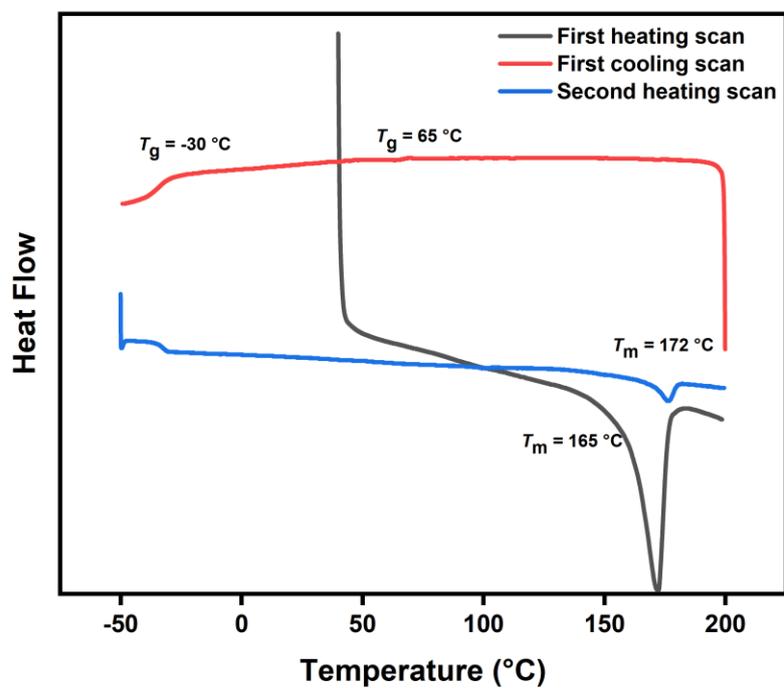


Fig. S31 DSC curves for TPE2 ( $F_{\text{DHB}} = 0.25$ ),  $T_{g1} = -30\text{ }^{\circ}\text{C}$ ,  $T_{g2} = 65\text{ }^{\circ}\text{C}$ ,  $T_m = 172\text{ }^{\circ}\text{C}$ .

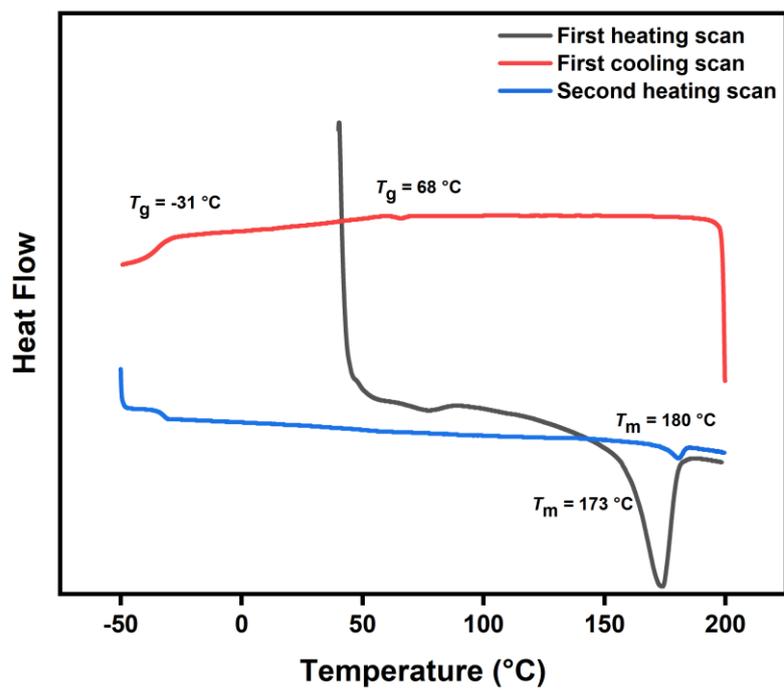


Fig. S32 DSC curves for TPE3 ( $F_{\text{DHB}} = 0.30$ ),  $T_{g1} = -31\text{ }^\circ\text{C}$ ,  $T_{g2} = 68\text{ }^\circ\text{C}$ ,  $T_m = 180\text{ }^\circ\text{C}$ .

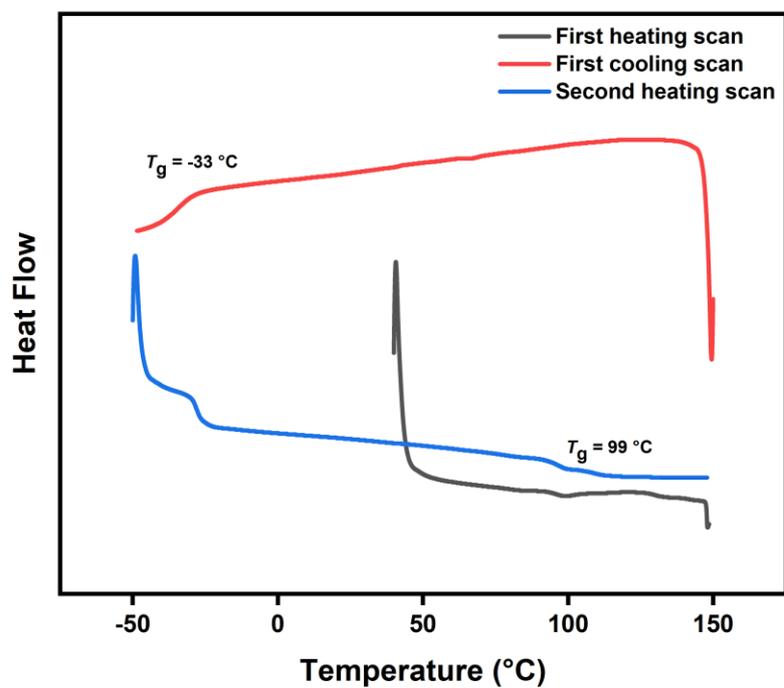


Fig. S33 DSC curves for TPE4 ( $F_{\text{DHN}} = 0.21$ ),  $T_{g1} = -33\text{ }^\circ\text{C}$ ,  $T_{g2} = 99\text{ }^\circ\text{C}$ .

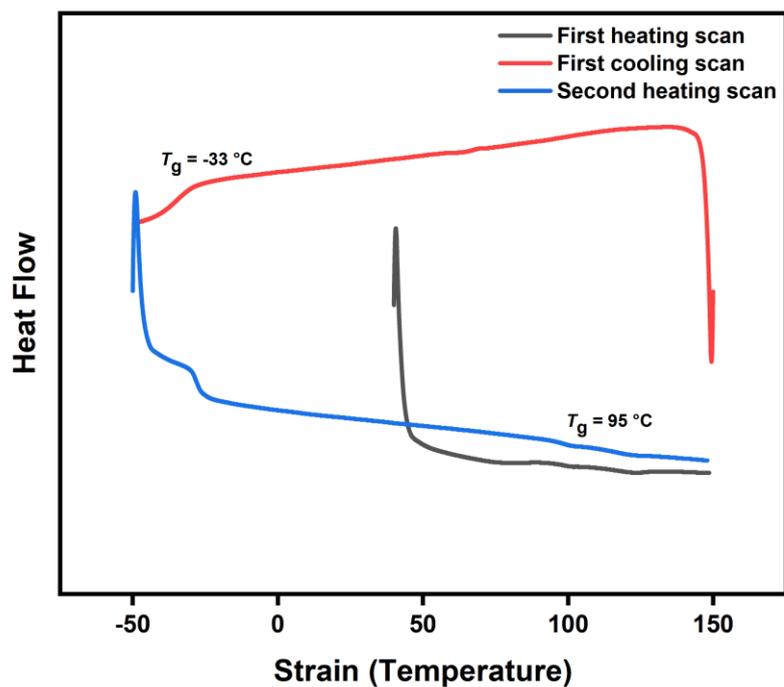


Fig. S34 DSC curves for TPE5 ( $F_{\text{DHN}} = 0.22$ ),  $T_{g1} = -33\text{ }^\circ\text{C}$ ,  $T_{g2} = 95\text{ }^\circ\text{C}$ .

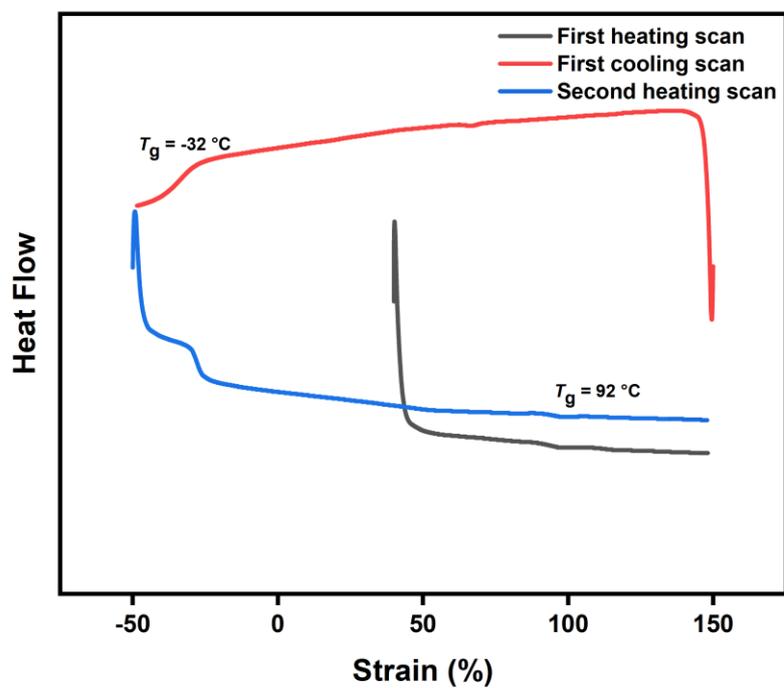
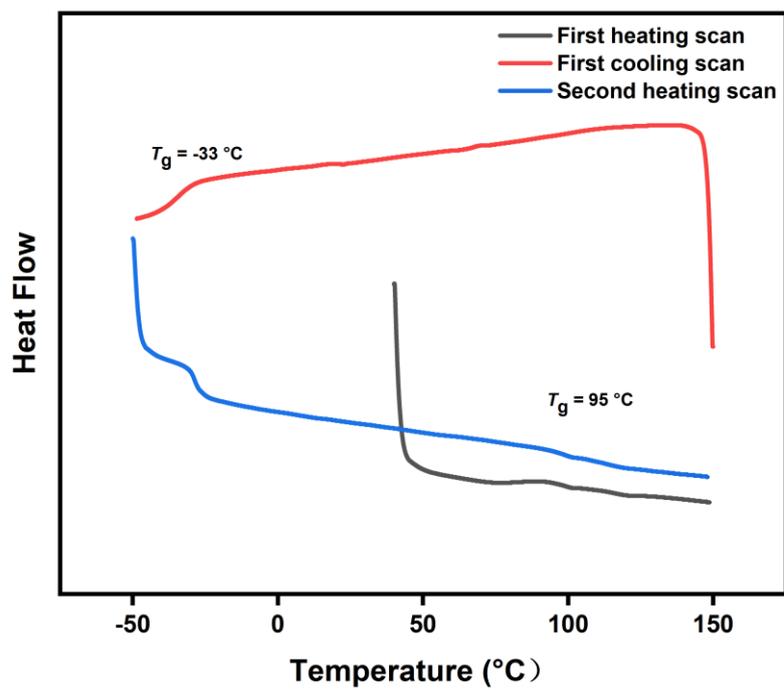
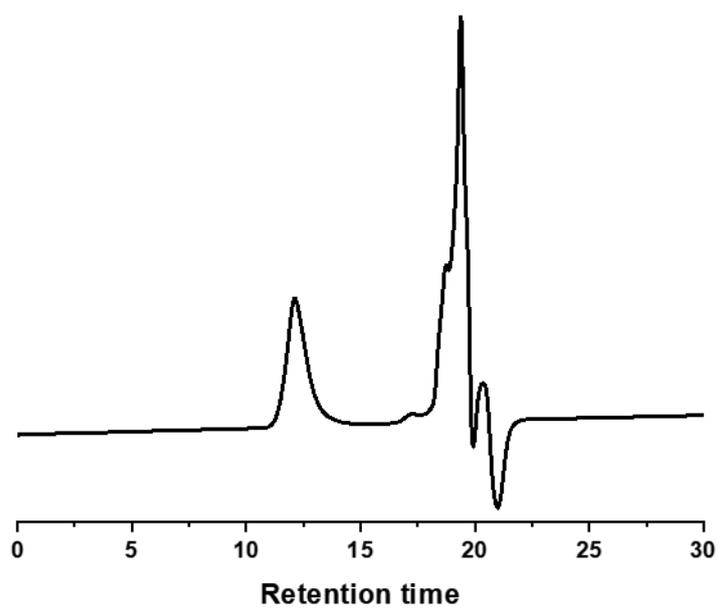


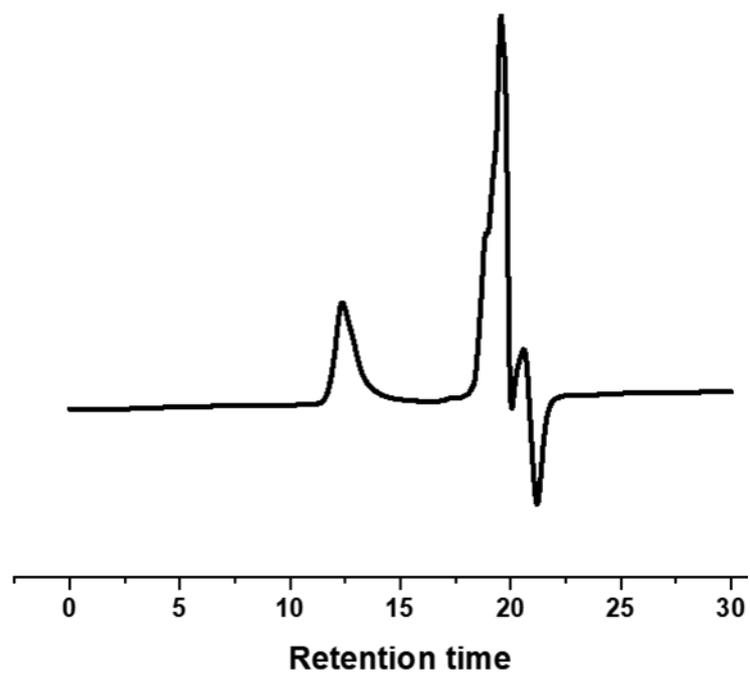
Fig. S35 DSC curves for TPE6 ( $F_{\text{DHN}} = 0.33$ ),  $T_{g1} = -32\text{ }^\circ\text{C}$ ,  $T_{g2} = 92\text{ }^\circ\text{C}$ .



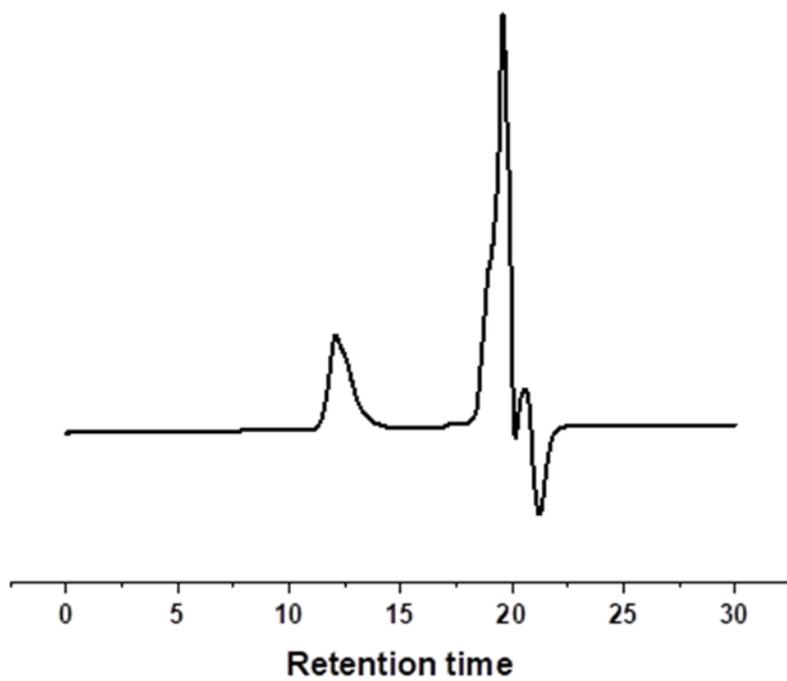
**Fig. S36** DSC curves for TPE7 ( $F_{\text{DHN}} = 0.39$ ),  $T_{g1} = -33\text{ °C}$ ,  $T_{g2} = 95\text{ °C}$ .



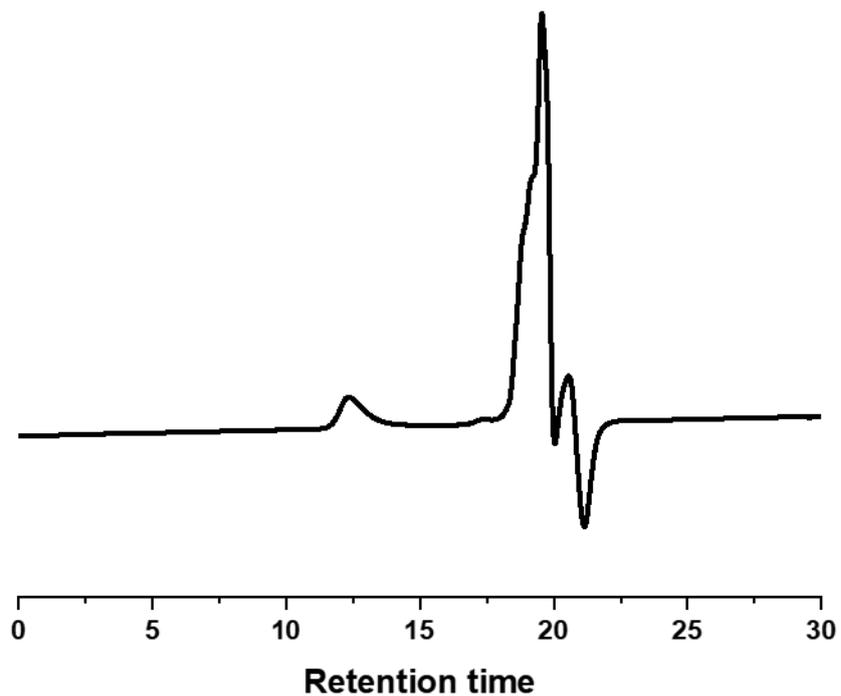
**Fig. S37** SEC trace of TPE4 ( $F_{\text{DHN}} = 0.21$ ) (Table S4, entry 1,  $M_n = 260\text{ kDa}$ ,  $\bar{D} = 1.27$ ).



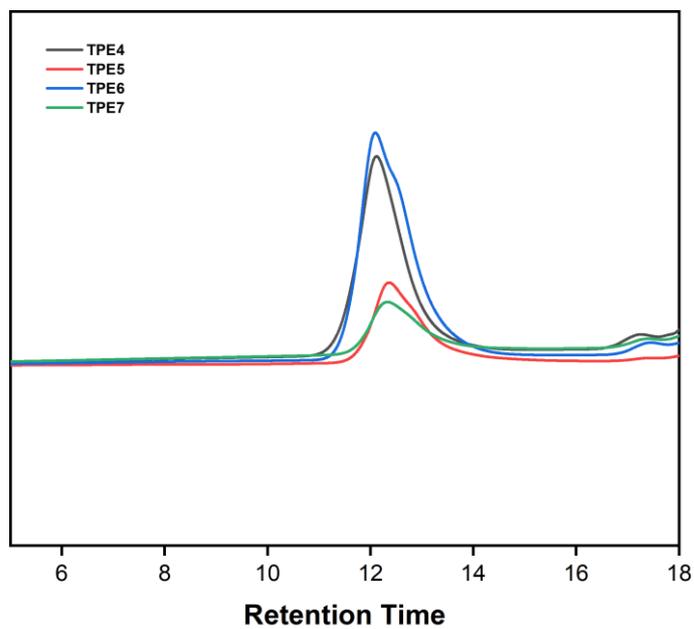
**Fig. S38** SEC trace of TPE5 ( $F_{\text{DHN}} = 0.22$ ) (Table S4, entry 2,  $M_n = 212$  kDa,  $\bar{D} = 1.26$ ).



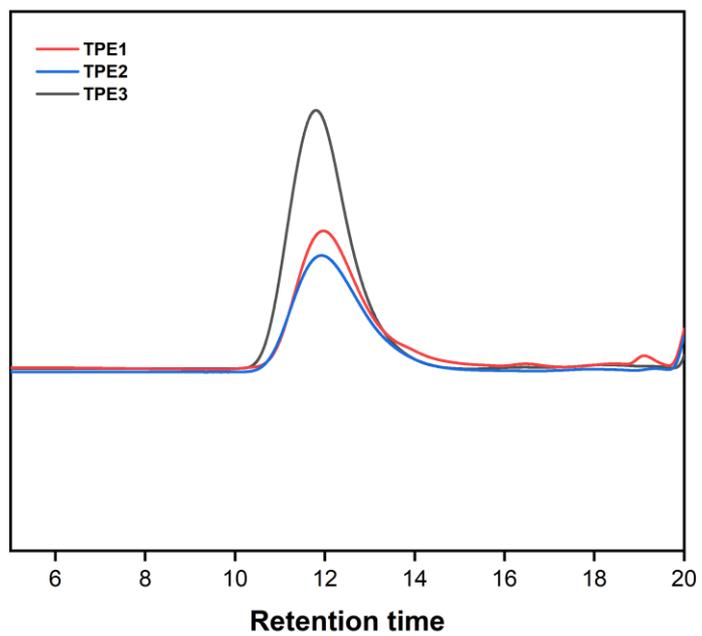
**Fig. S39** SEC trace of TPE6 ( $F_{\text{DHN}} = 0.33$ ) (Table S4, entry 3,  $M_n = 273$  kDa,  $\bar{D} = 1.31$ ).



**Fig. S40** SEC trace of TPE7 ( $F_{\text{DHN}} = 0.39$ , TPE7) (Table S4, entry 4,  $M_n = 231\text{kDa}$ ,  $\bar{D} = 1.26$ ).



**Fig. S41** Overlay Plot of SEC Curves for TPE4 ~ TPE7



**Fig. S42** Overlay Plot of SEC Curves for TPE1 ~ TPE3

## General Mechanical Property

As for MTO-co-DHB, the polymer (approximately 2 g) was dissolved in 50 mL of chloroform, and the resulting polymer solution was then poured into a polytetrafluoroethylene (PTFE) mold. Subsequently, the solution was allowed to dry naturally at room temperature to form a solid film. As for MTO-co-DHN, the polymer (approximately 2 g) was dissolved in 20 mL of dichloromethane, the following steps were identical to those described above.

The obtained polymer film was cut into dog-bone-shaped specimens ( $50 \times 4 \times 0.2 \text{ mm}^3$ ) for tensile testing.

**Table S6** Stress, strain, and Young's modulus values for five replicates of tensile tests at 10 mm/min for TPE1 ( $F_{\text{DHB}} = 0.19$ ).

Sample Number	$\sigma_{\text{B}}$ (MPa)*	$\epsilon_{\text{B}}$ (%)†	$E'$ (MPa)‡	$U_{\text{T}}$ (MJ m <sup>-3</sup> )#
1	16.6	1101	1.7	87.8
2	16.1	1104	1.7	87.1
3	16.3	1105	2.2	89.0
4	17.9	1265	1.8	112.7
5	17.7	1062	2.5	88.4
Average	$16.9 \pm 0.8$	$1127 \pm 79$	$2.0 \pm 0.4$	$93.0 \pm 11.0$

\*Stress at break ( $\sigma_{\text{B}}$ ); †Strain at break ( $\epsilon_{\text{B}}$ ); ‡Young's modulus ( $E'$ ) calculated as the slope from 0 to 3% strain; #Toughness ( $U_{\text{T}}$ ).

**Table S7** Stress, strain, and Young's modulus values for four replicates of tensile tests at 10 mm/min for TPE2 ( $F_{\text{DHB}} = 0.25$ ).

Sample Number	$\sigma_{\text{B}}$ (MPa)*	$\epsilon_{\text{B}}$ (%)†	$E'$ (MPa)‡	$U_{\text{T}}$ (MJ m <sup>-3</sup> )#
1	16.9	1590	23.7	122.9
2	18.1	1275	24.0	105.9
3	17.7	1464	19.0	122.9
4	19.5	1737	20.0	162.9
Average	$18.1 \pm 1.0$	$1516 \pm 196$	$21.7 \pm 2.2$	$128.7 \pm 24.0$

\*Stress at break ( $\sigma_{\text{B}}$ ); †Strain at break ( $\epsilon_{\text{B}}$ ); ‡Young's modulus ( $E'$ ) calculated as the slope from 0 to 3% strain; #Toughness ( $U_{\text{T}}$ ).

**Table S8** Stress, strain, and Young's modulus values for six replicates of tensile tests at 10 mm/min for TPE3 ( $F_{DHB} = 0.30$ ).

Sample Number	$\sigma_B$ (MPa)*	$\epsilon_B$ (%) <sup>†</sup>	$E'$ (MPa) <sup>‡</sup>	$U_T$ (MJ m <sup>-3</sup> ) <sup>#</sup>
1	20.8	1261	40.0	117.1
2	20.1	1247	36.5	107.8
3	18.2	1288	34.2	106.2
4	19.4	1277	36.1	110.9
5	17.3	1215	35.6	97.9
6	18.8	1584	31.3	136.6
Average	19.1 ± 1.3	1312 ± 136	35.6 ± 2.6	112.8 ± 13.3

\*Stress at break ( $\sigma_B$ ); <sup>†</sup>Strain at break ( $\epsilon_B$ ); <sup>‡</sup>Young's modulus ( $E'$ ) calculated as the slope from 0 to 3% strain; <sup>#</sup>Toughness ( $U_T$ ).

**Table S9** Stress, strain, and Young's modulus values for five replicates of tensile tests at 10 mm/min for TPE4 ( $F_{DHN} = 0.21$ ).

Sample Number	$\sigma_B$ (MPa)*	$\epsilon_B$ (%) <sup>†</sup>	$E'$ (MPa) <sup>‡</sup>	$U_T$ (MJ m <sup>-3</sup> ) <sup>#</sup>
1	25.8	1250	3.8	121.5
2	25.9	1337	3.7	125.7
3	26.0	1601	3.3	157.8
4	24.2	1441	3.4	130.0
5	23.9	1457	3.2	132.0
Average	25.2 ± 1.0	1417 ± 133	3.5 ± 0.3	133.0 ± 14.2

\*Stress at break ( $\sigma_B$ ); <sup>†</sup>Strain at break ( $\epsilon_B$ ); <sup>‡</sup>Young's modulus ( $E'$ ) calculated as the slope from 0 to 3% strain; <sup>#</sup>Toughness ( $U_T$ ).

**Table S10** Stress, strain, and Young's modulus values for five replicates of tensile tests at 10 mm/min for TPE5 ( $F_{DHN} = 0.22$ ).

Sample Number	$\sigma_B$ (MPa)*	$\epsilon_B$ (%) <sup>†</sup>	$E'$ (MPa) <sup>‡</sup>	$U_T$ (MJ m <sup>-3</sup> ) <sup>#</sup>
1	26.0	1218	4.2	116.6
2	27.2	1194	4.4	120.2
3	24.1	1093	4.8	125.4
4	25.4	1132	4.5	102.2
5	25.0	1112	4.5	104.1
Average	25.5 ± 1.2	1149 ± 54	4.5 ± 0.2	113.7 ± 10.1

\*Stress at break ( $\sigma_B$ ); †Strain at break ( $\epsilon_B$ ); ‡Young's modulus ( $E'$ ) calculated as the slope from 0 to 3% strain; #Toughness ( $U_T$ ).

**Table S11** Stress, strain, and Young's modulus values for five replicates of tensile tests at 10 mm/min for TPE6 ( $F_{DHN} = 0.33$ )

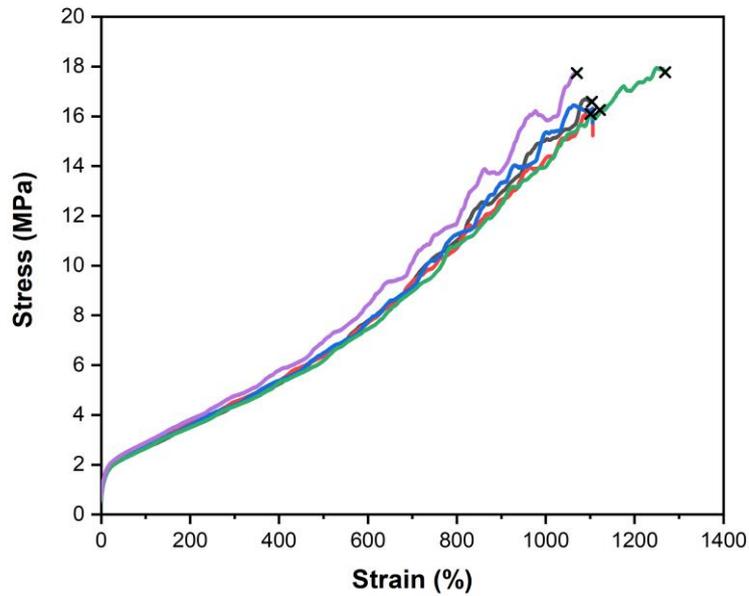
Sample Number	$\sigma_B$ (MPa)*	$\epsilon_B$ (%)†	$E'$ (MPa)‡	$U_T$ (MJ m <sup>-3</sup> )#
1	25.1	1042	3.9	103.6
2	27.5	1173	4.4	118.7
3	24.2	1104	3.5	111.5
4	24.8	1318	4.5	127.5
5	26.4	1092	4.2	117.4
Average	25.6 ± 1.3	1146 ± 107	4.1 ± 0.4	115.7 ± 8.9

\*Stress at break ( $\sigma_B$ ); †Strain at break ( $\epsilon_B$ ); ‡Young's modulus ( $E'$ ) calculated as the slope from 0 to 3% strain; #Toughness ( $U_T$ ).

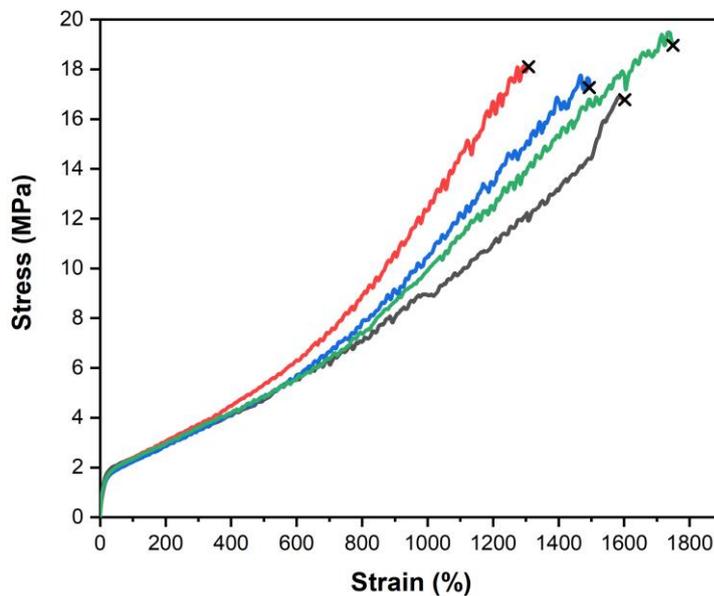
**Table S12** Stress, strain, and Young's modulus values for six replicates of tensile tests at 10 mm/min for TPE7 ( $F_{DHN} = 0.39$ )

Sample Number	$\sigma_B$ (MPa)*	$\epsilon_B$ (%)†	$E'$ (MPa)‡	$U_T$ (MJ m <sup>-3</sup> )#
1	28.9	992	149.1	116.8
2	31.4	925	241.6	112.5
3	29.0	1200	178.5	147.8
4	29.4	1055	141.4	131.4
5	30.0	1074	158.0	139.9
6	30.3	973	190.6	119.4
Average	29.8 ± 0.9	1037 ± 97	176.5 ± 36.8	128.0 ± 14.0

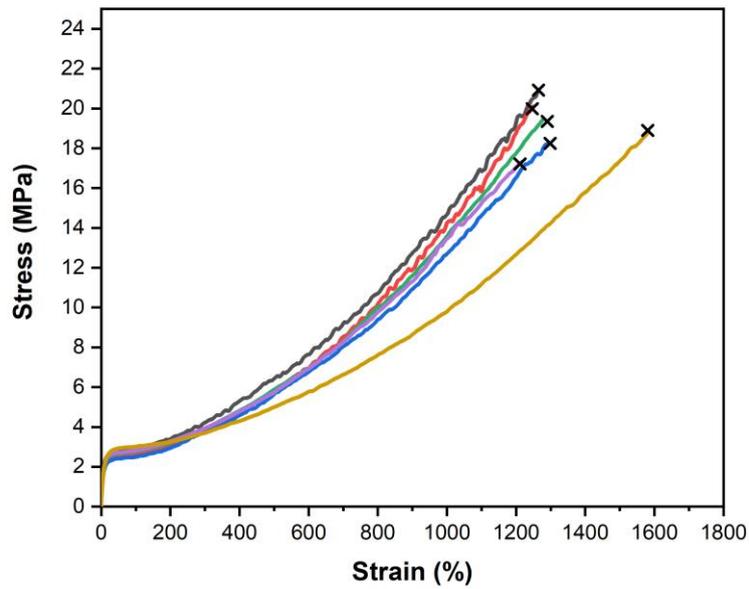
\*Stress at break ( $\sigma_B$ ); †Strain at break ( $\epsilon_B$ ); ‡Young's modulus ( $E'$ ) calculated as the slope from 0 to 3% strain; #Toughness ( $U_T$ ).



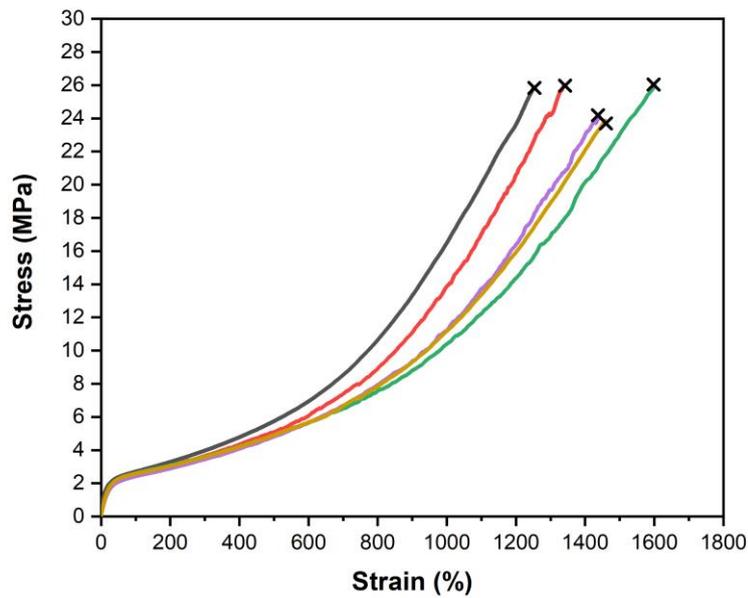
**Fig. S43** Uniaxial tensile testing of TPE1 ( $F_{DHB} = 0.19$ ) with five replicates at a strain rate of 10 mm/min. Stress, strain, and Young's modulus values for each of the five replicates are tabulated in **Table S6**.



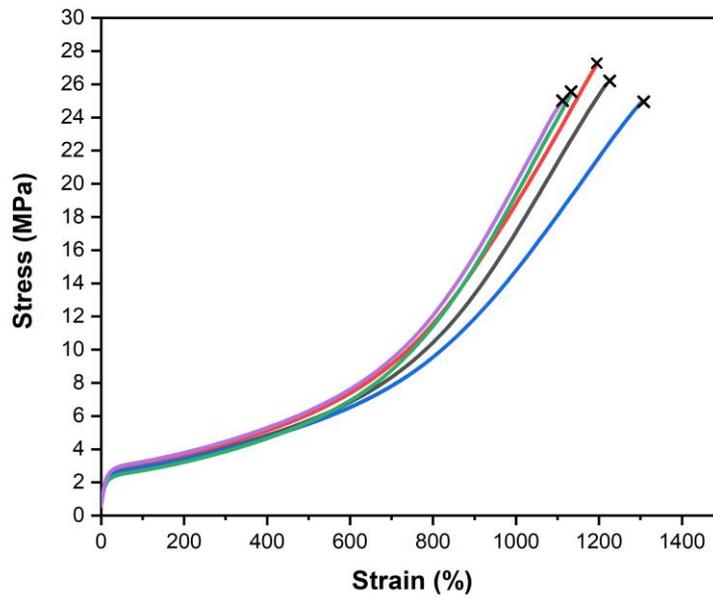
**Fig. S44** Uniaxial tensile testing of TPE2 ( $F_{DHB} = 0.25$ ) with four replicates at a strain rate of 10 mm/min. Stress, strain, and Young's modulus values for each of the four replicates are tabulated in **Table S7**.



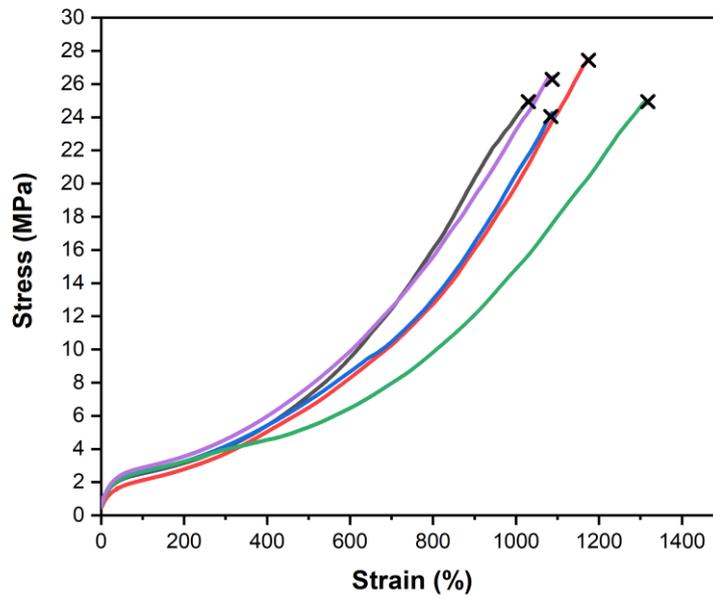
**Fig. S45** Uniaxial tensile testing of TPE3 ( $F_{DHB} = 0.30$ ) with six replicates at a strain rate of 10 mm/min. Stress, strain, and Young's modulus values for each of the six replicates are tabulated in **Table S8**.



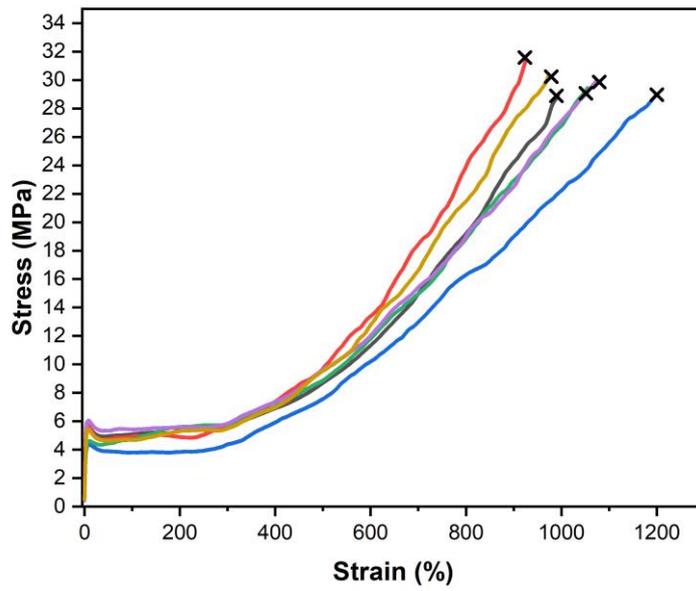
**Fig. S46** Uniaxial tensile testing of TPE4 ( $F_{DHN} = 0.21$ ) with five replicates at a strain rate of 10 mm/min. Stress, strain, and Young's modulus values for each of the five replicates are tabulated in **Table S9**.



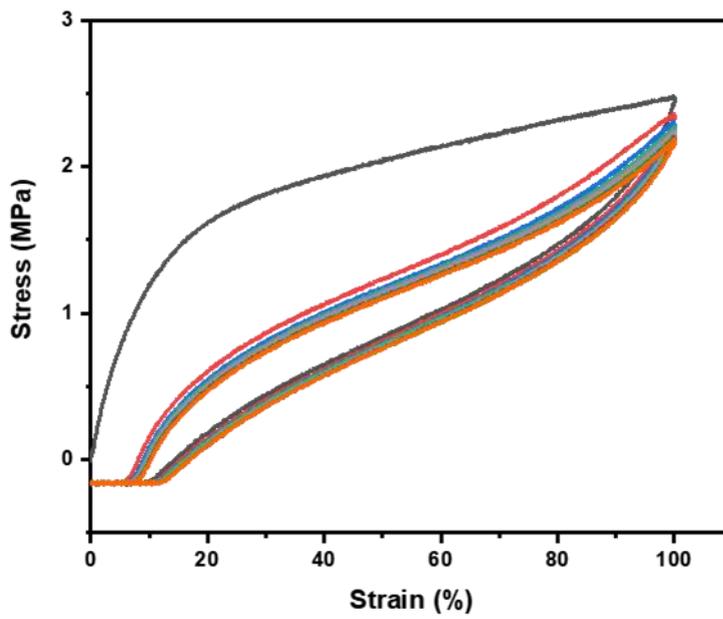
**Fig. S47** Uniaxial tensile testing of TPE5 ( $F_{DHN} = 0.22$ ) with five replicates at a strain rate of 10 mm/min. Stress, strain, and Young's modulus values for each of the five replicates are tabulated in **Table S10**.



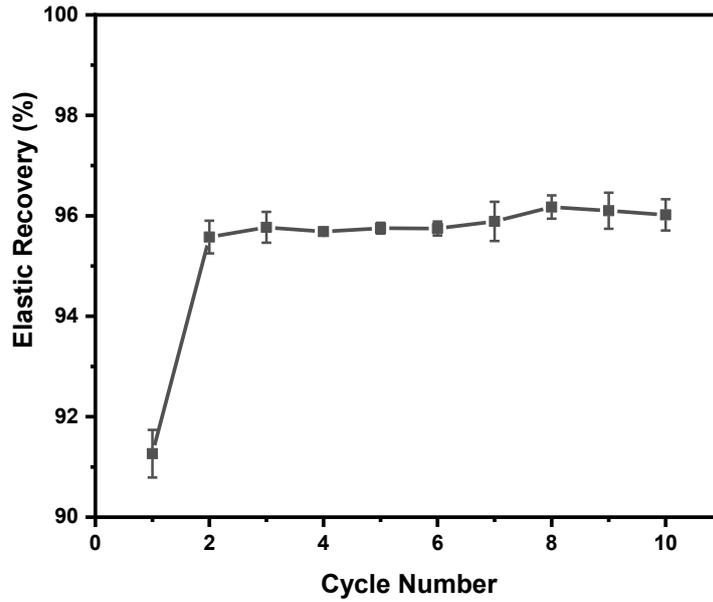
**Fig. S48** Uniaxial tensile testing of TPE6 ( $F_{DHN} = 0.33$ ) with five replicates at a strain rate of 10 mm/min. Stress, strain, and Young's modulus values for each of the five replicates are tabulated in **Table S11**.



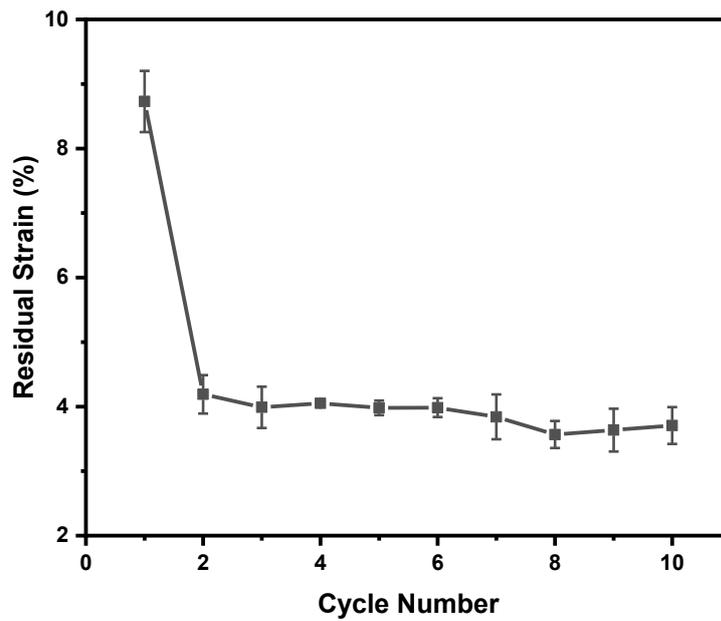
**Fig. S49** Uniaxial tensile testing of TPE7 ( $F_{DHN} = 0.39$ ) with six replicates at a strain rate of 10 mm/min. Stress, strain, and Young's modulus values for each of the five replicates are tabulated in **Table S12**.



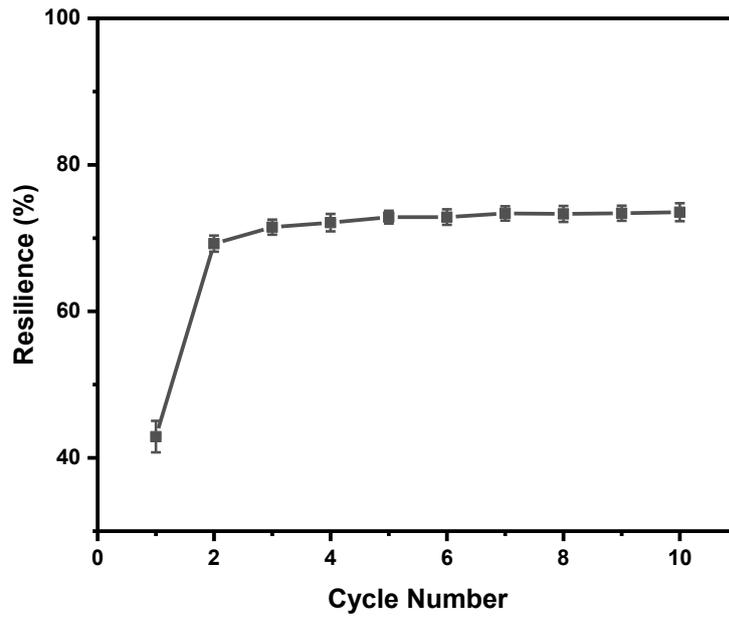
**Fig. S50** Cyclic tensile testing of TPE1 ( $F_{DHB} = 0.19$ ) at a rate of 50 mm/min (10 cycles).



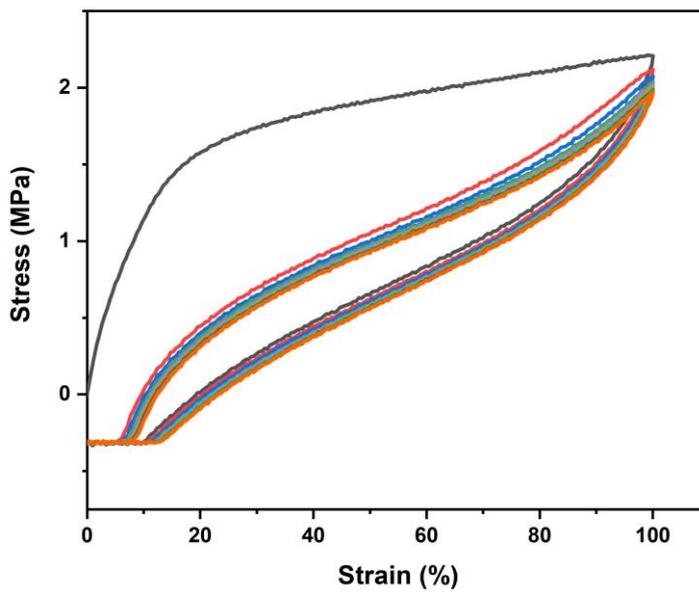
**Fig. S51** Elastic recovery of TPE1 ( $F_{DHB} = 0.19$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



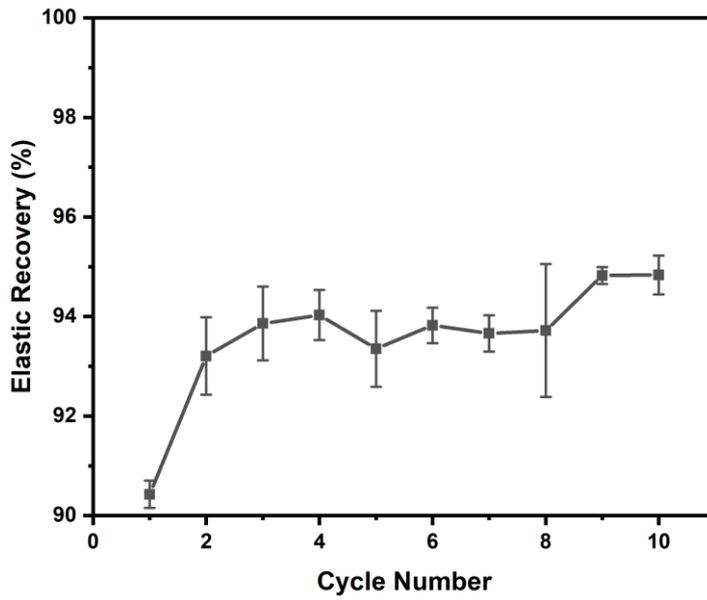
**Fig. S52** Residual strain of TPE1 ( $F_{DHB} = 0.19$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



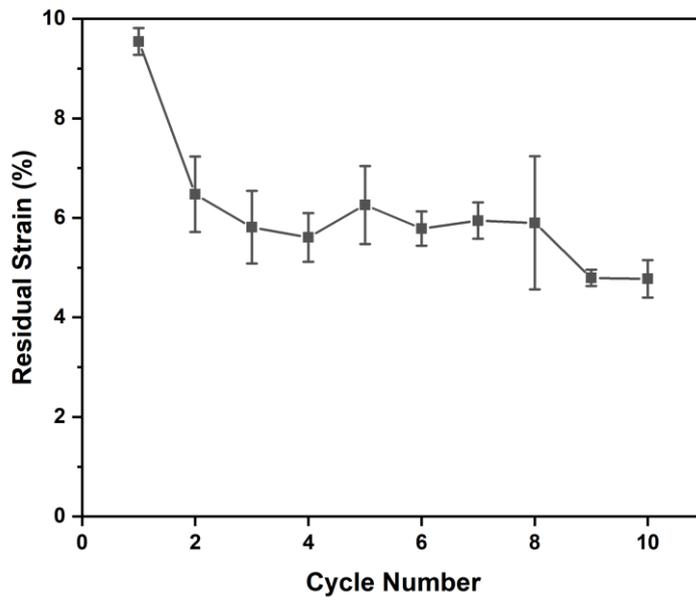
**Fig. S53** Resilience of TPE1 ( $F_{DHB} = 0.19$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



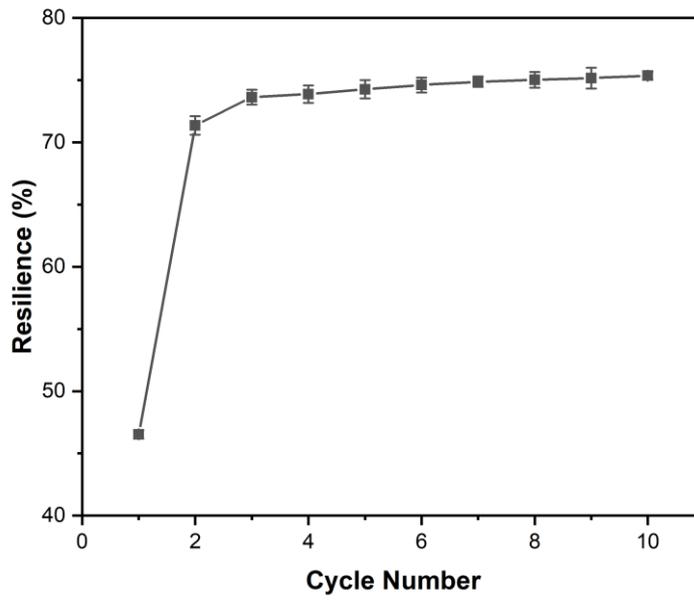
**Fig. S54** Cyclic tensile testing of TPE2 ( $F_{DHB} = 0.25$ ) at a rate of 50 mm/min (10 cycles).



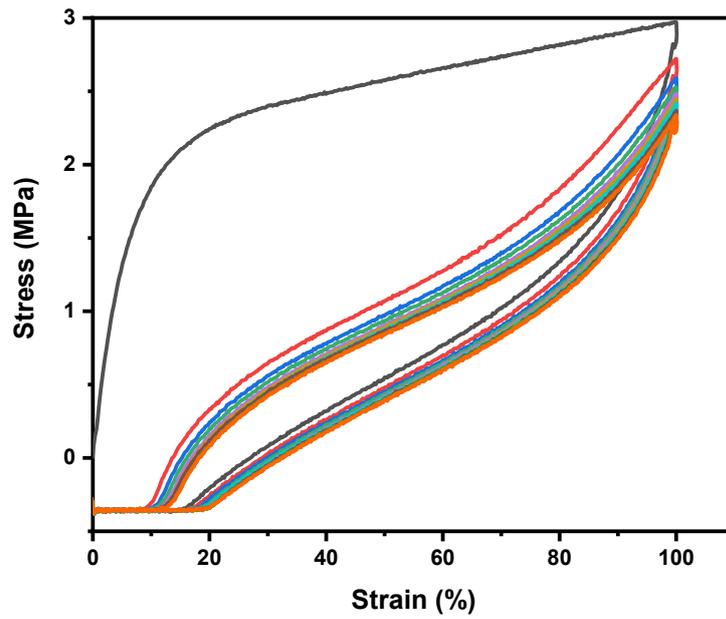
**Fig. S55** Elastic recovery of TPE2 ( $F_{DHB} = 0.25$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



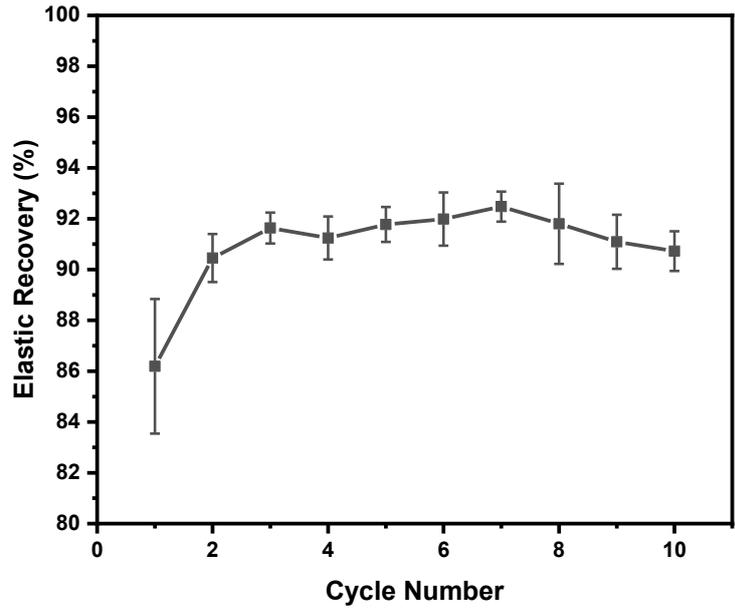
**Fig. S56** Residual strain of TPE2 ( $F_{DHB} = 0.25$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



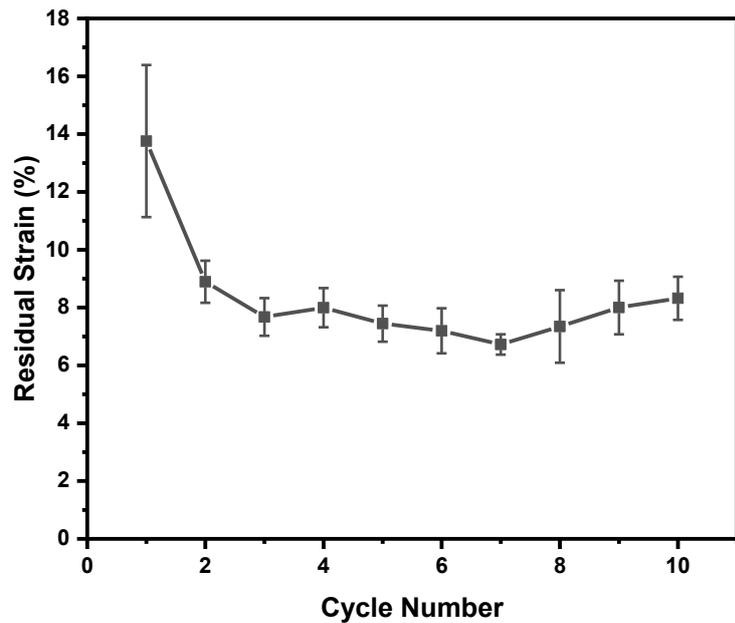
**Fig. S57** Resilience of TPE2 ( $F_{DHB} = 0.25$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



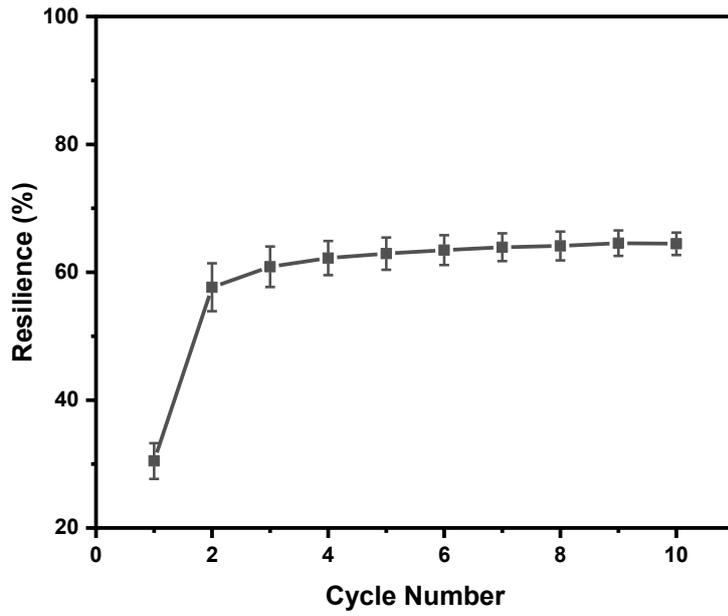
**Fig. S58** Cyclic tensile testing of TPE3 ( $F_{DHB} = 0.30$ ) at a rate of 50 mm/min (10 cycles).



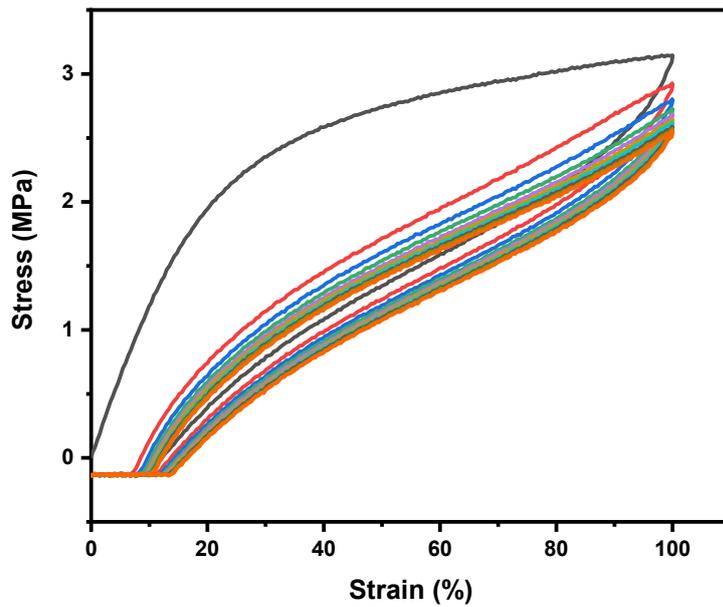
**Fig. S59** Elastic recovery of TPE3 ( $F_{DHB} = 0.30$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



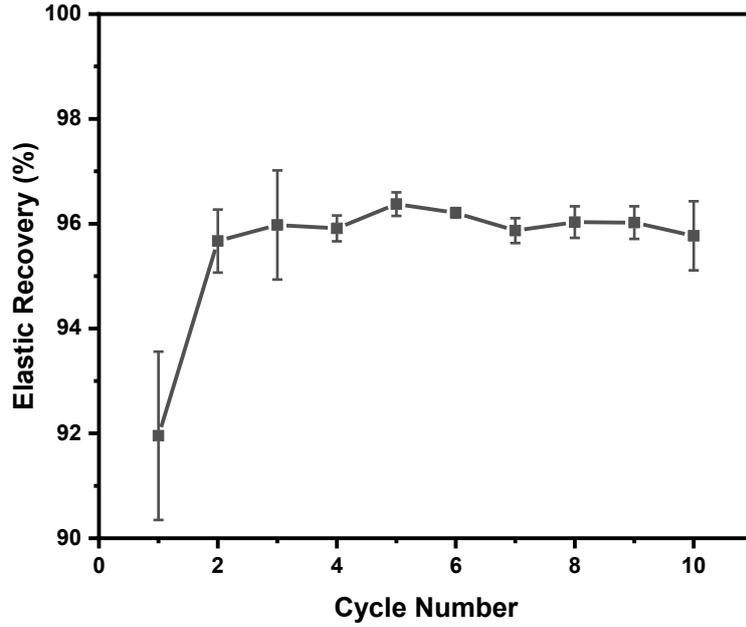
**Fig. S60** Residual strain of TPE3 ( $F_{DHB} = 0.30$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



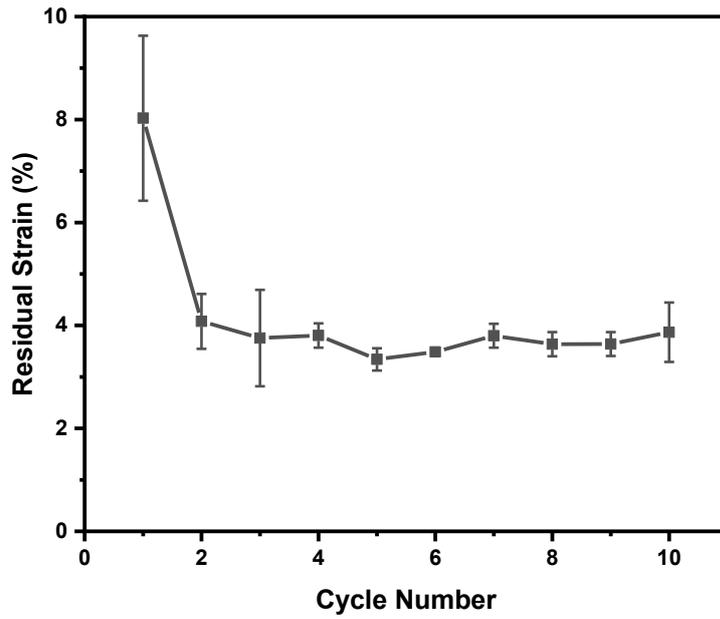
**Fig. S61** Resilience of TPE3 ( $F_{DHB} = 0.30$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



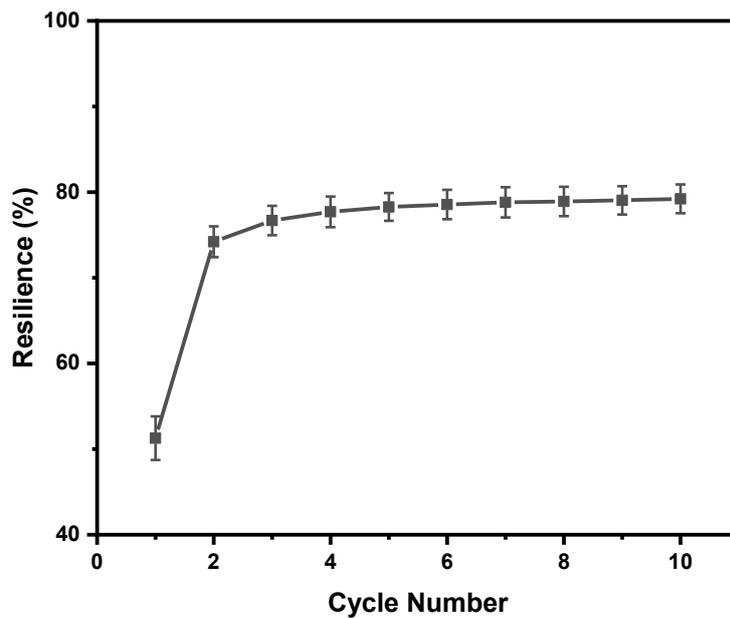
**Fig. S62** Cyclic tensile testing of TPE4 ( $F_{DHN} = 0.21$ ) at a rate of 50 mm/min (10 cycles).



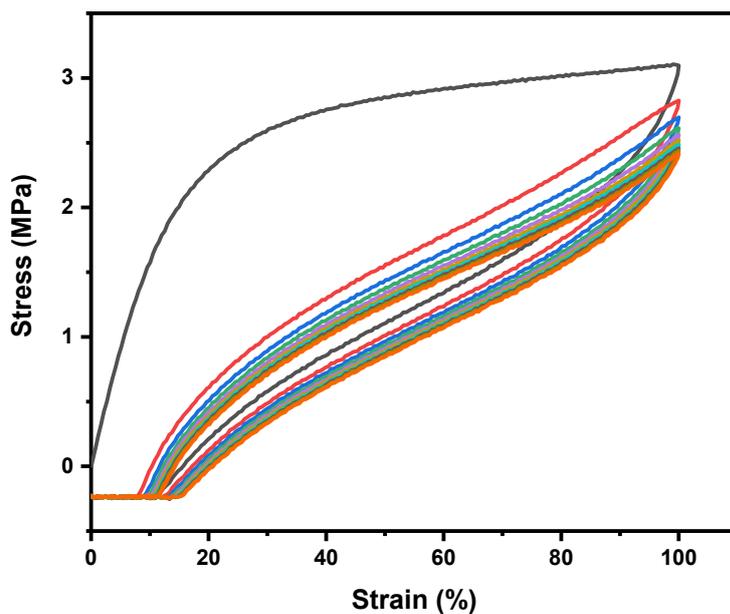
**Fig. S63** Elastic recovery of TPE4 ( $F_{DHN} = 0.21$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



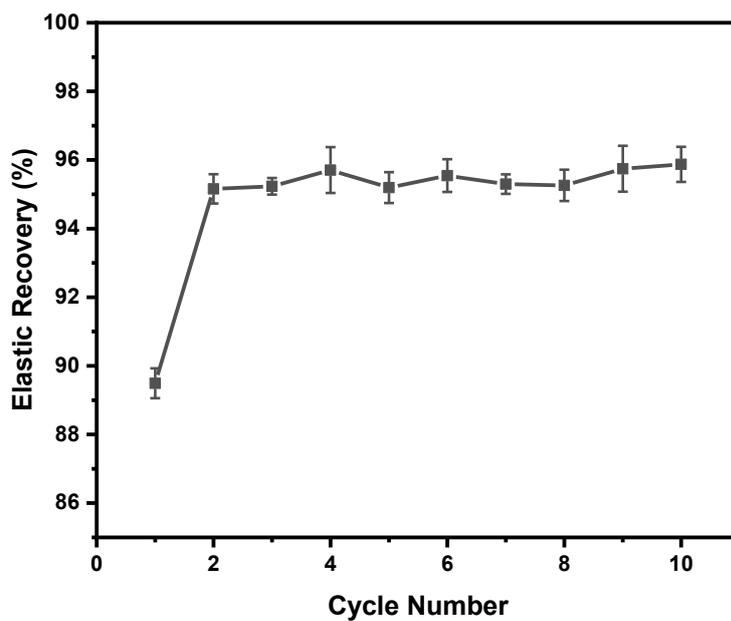
**Fig. S64** Residual strain of TPE4 ( $F_{DHN} = 0.21$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



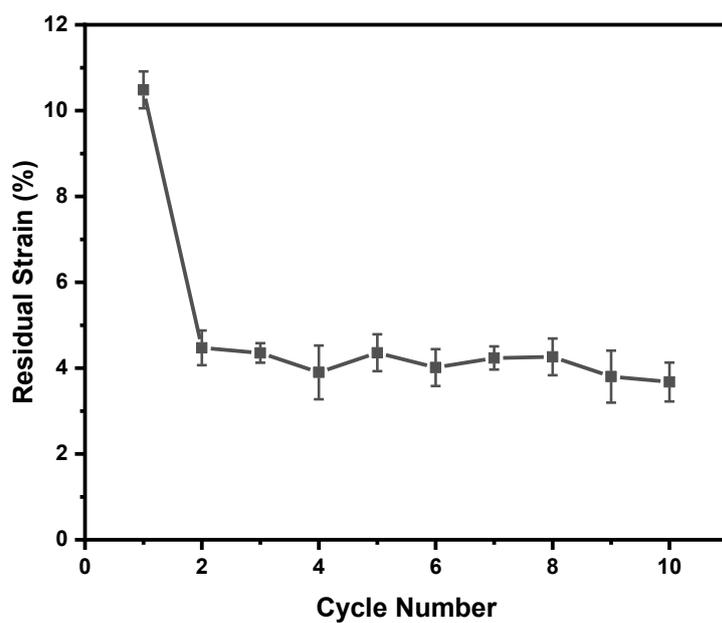
**Fig. S65** Resilience of TPE4 ( $F_{DHN} = 0.21$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



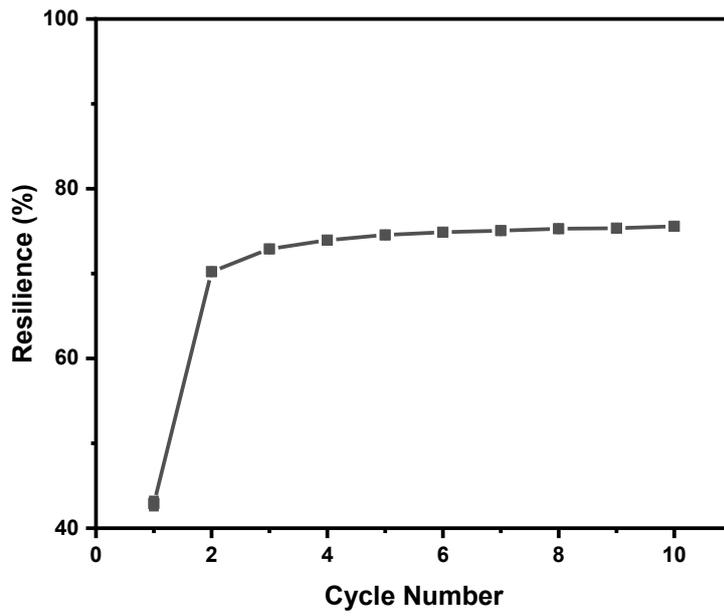
**Fig. S66** Cyclic tensile testing of TPE5 ( $F_{DHN} = 0.22$ ) at a rate of 50 mm/min (10 cycles).



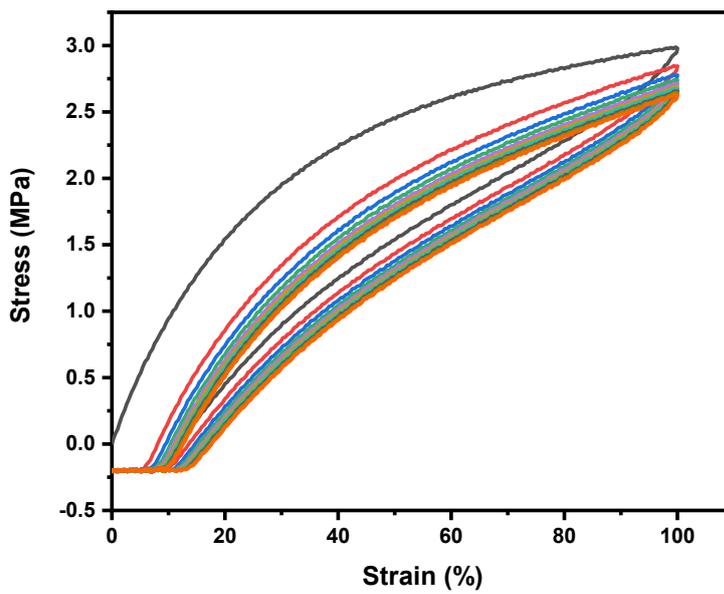
**Fig. S67** Elastic recovery of TPE5 ( $F_{DHN} = 0.22$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 4 specimens.



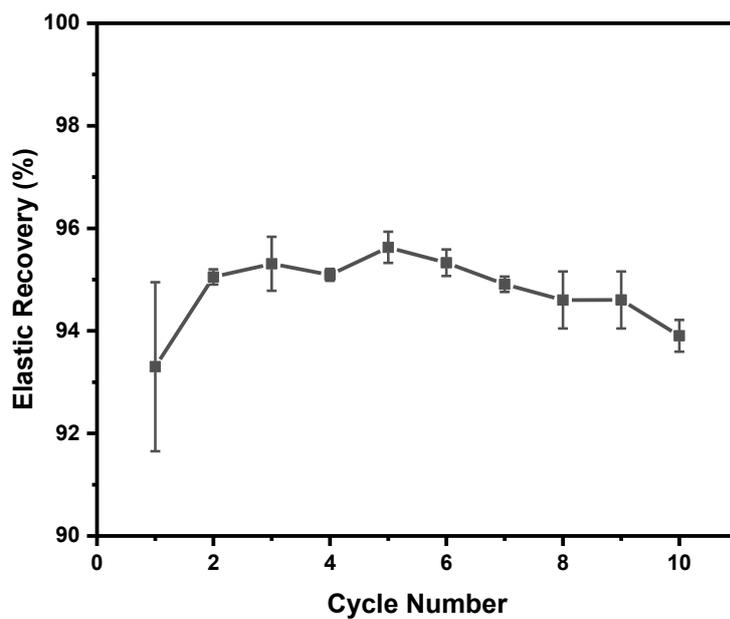
**Fig. S68** Residual strain of TPE5 ( $F_{DHN} = 0.22$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 4 specimens.



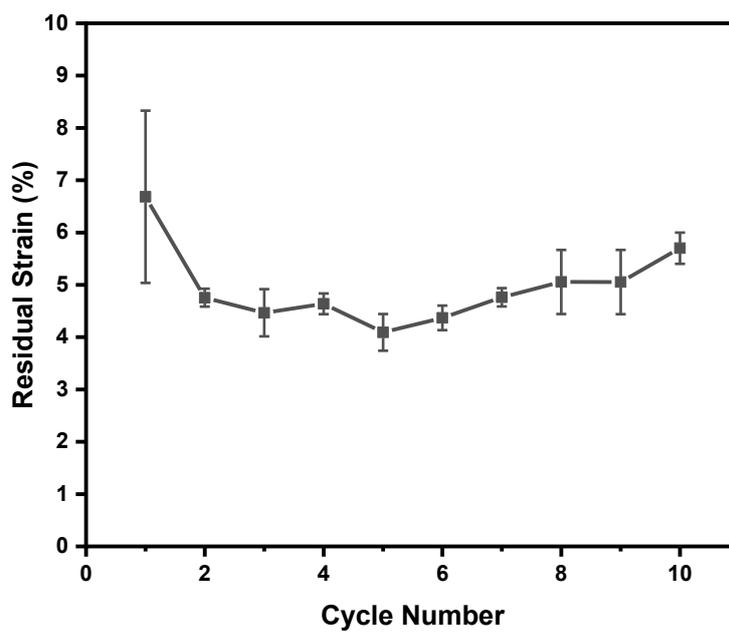
**Fig. S69** Resilience of TPE5 ( $F_{DHN} = 0.22$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 4 specimens.



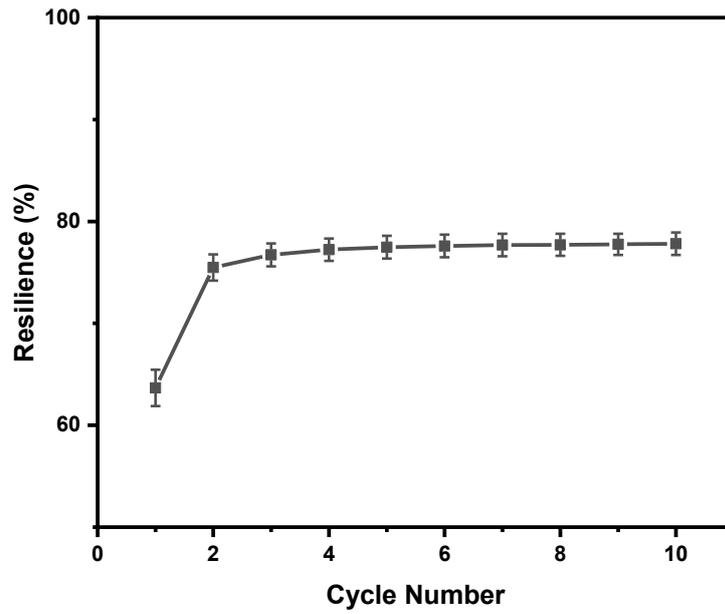
**Fig. S70** Cyclic tensile testing of TPE6 ( $F_{DHN} = 0.33$ ) at a rate of 50 mm/min (10 cycles).



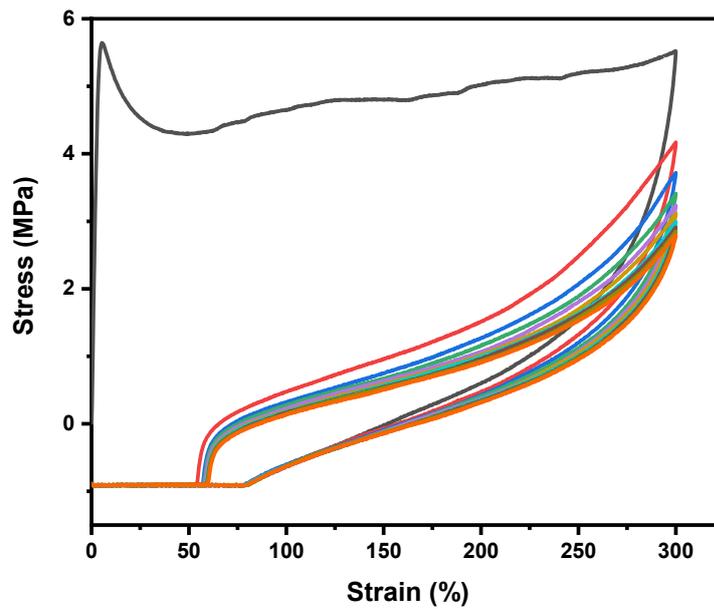
**Fig. S71** Elastic recovery of TPE6 ( $F_{DHN} = 0.33$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



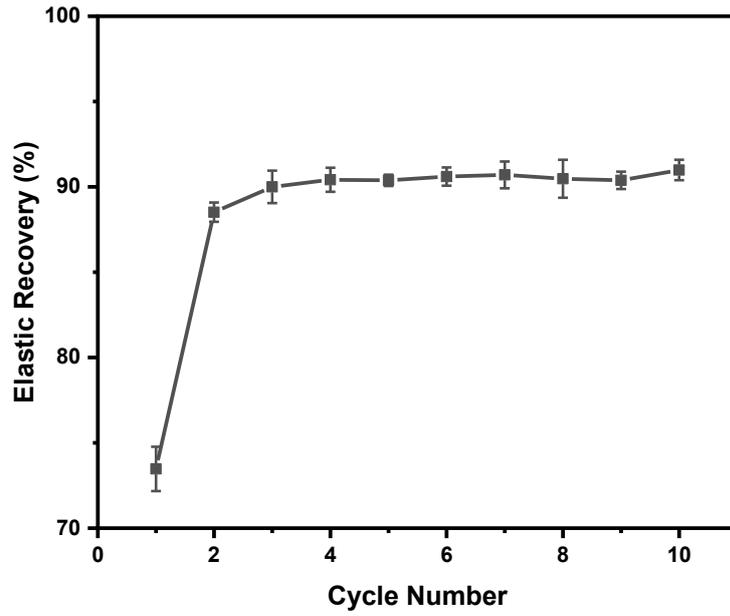
**Fig. S72** Residual strain of TPE6 ( $F_{DHN} = 0.33$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



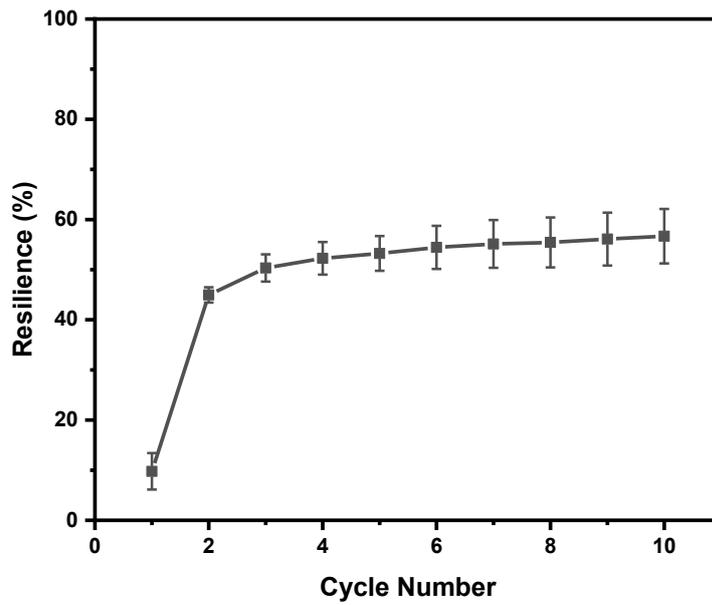
**Fig. S73** Resilience of TPE6 ( $F_{DHN} = 0.33$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



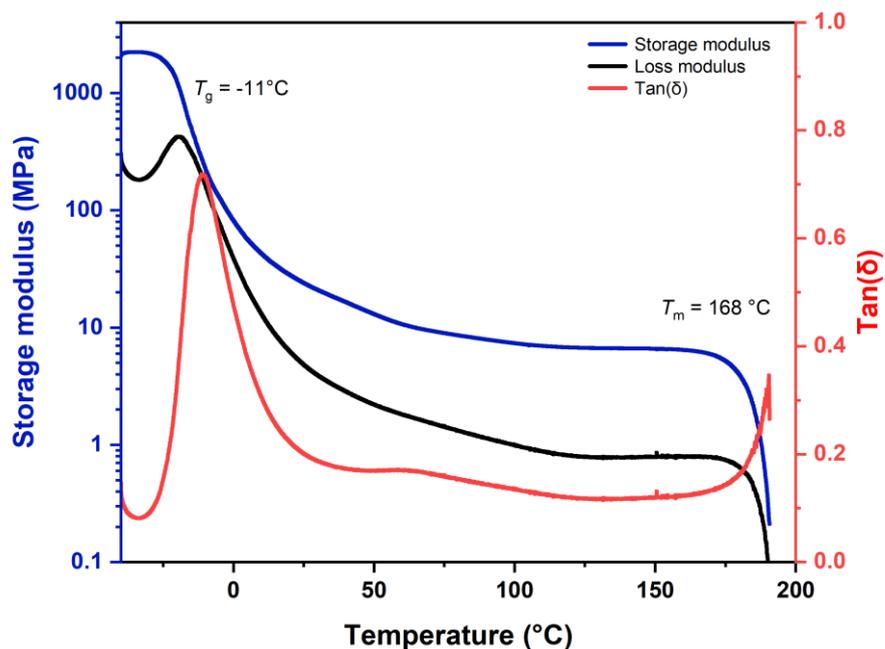
**Fig. S74** Cyclic tensile testing of TPE7 ( $F_{DHN} = 0.39$ ) at a rate of 50 mm/min (10 cycles).



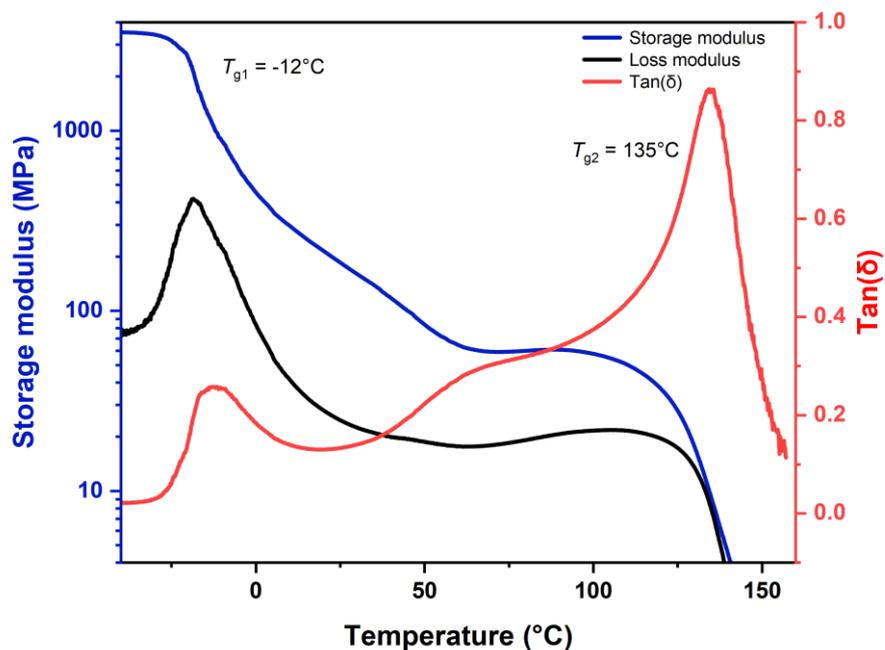
**Fig. S75** Elastic recovery of TPE7 ( $F_{DHN} = 0.39$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



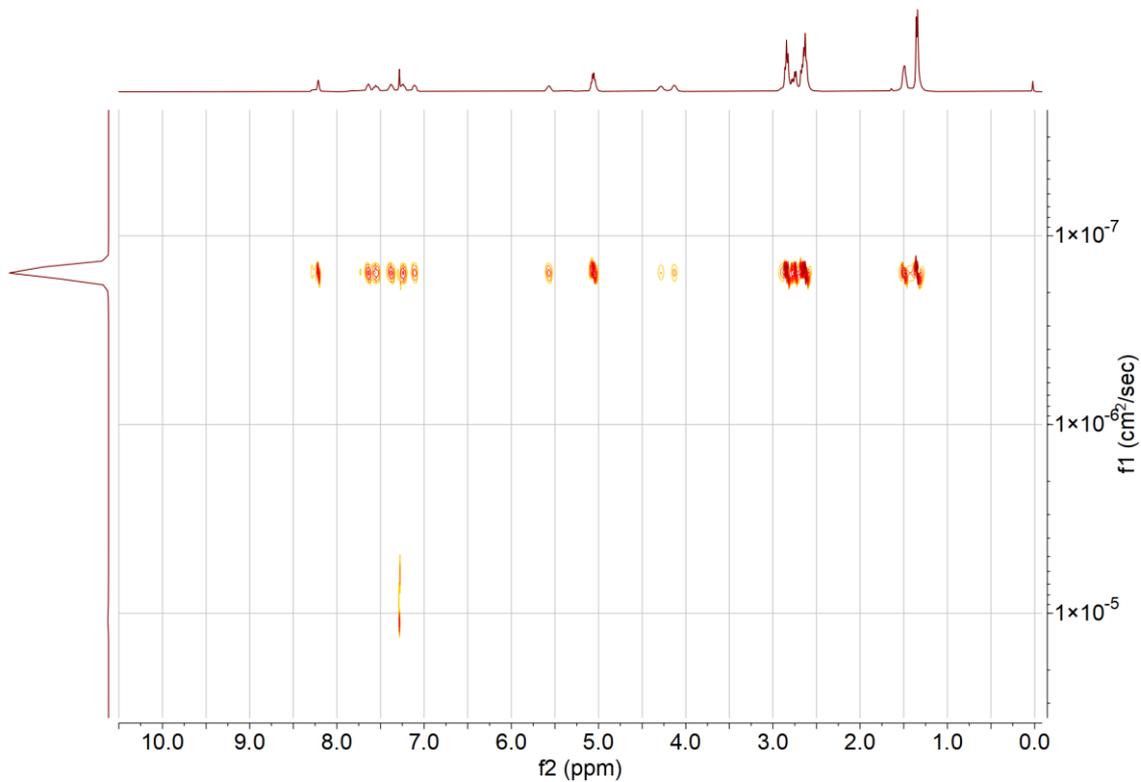
**Fig. S76** Resilience of TPE7 ( $F_{DHN} = 0.39$ ) determined from cyclic tensile tests. Error bars represent a standard deviation of 3 specimens.



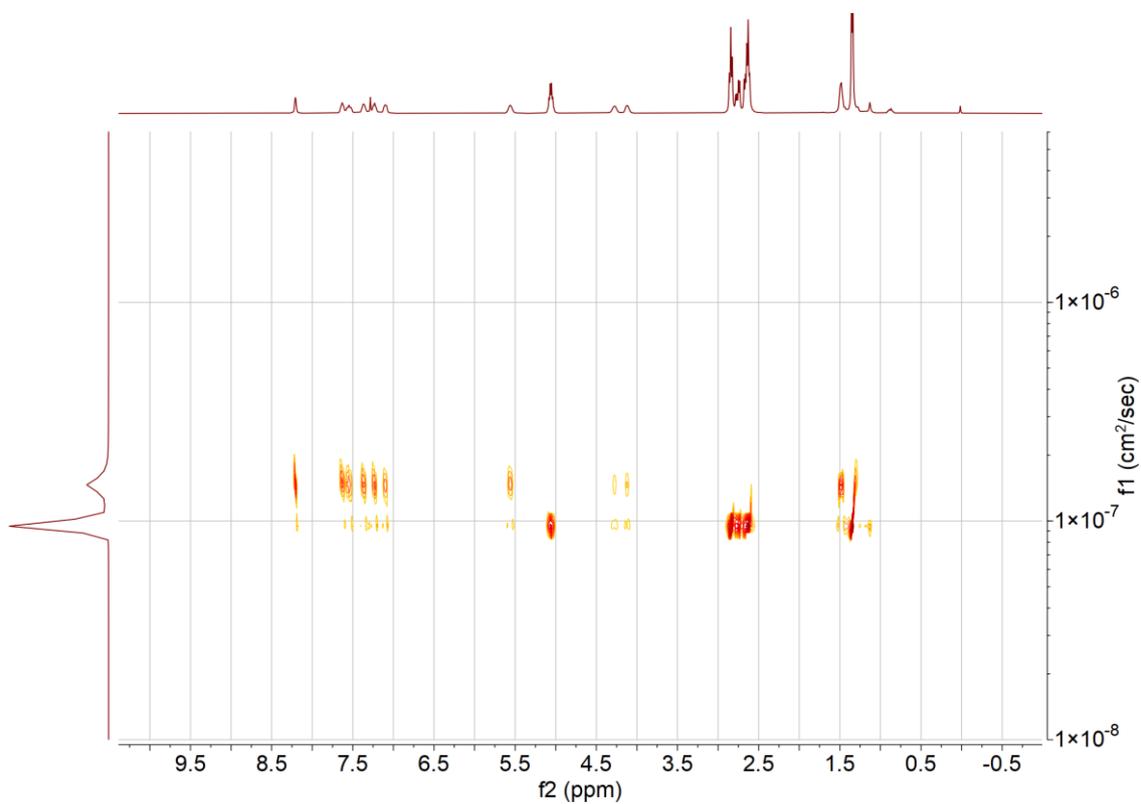
**Fig. S77** Overlay plots of storage modulus  $E'$ , loss modulus  $E''$  and  $\tan\delta$  ( $E''/E'$ ) for TPE1 measured by DMA (tension film mode, 0.1% stain, 1 Hz,  $3^\circ\text{C min}^{-1}$ ).



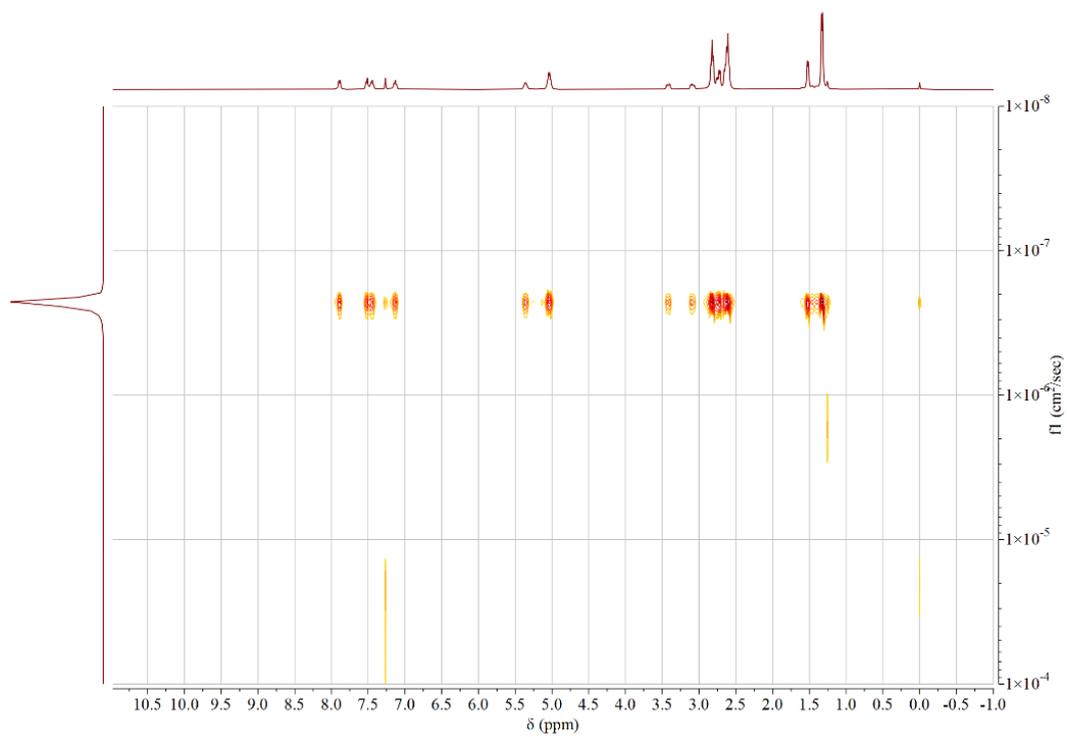
**Fig. S78** Overlay plots of storage modulus  $E'$ , loss modulus  $E''$  and  $\tan\delta$  ( $E''/E'$ ) for TPE4 measured by DMA (tension film mode, 0.1% stain, 1 Hz,  $3^\circ\text{C min}^{-1}$ ).



**Fig. S79** The DOSY spectrum of TPE4.



**Fig. S80** The DOSY spectrum of PMTO and P(DHN) homopolymers.

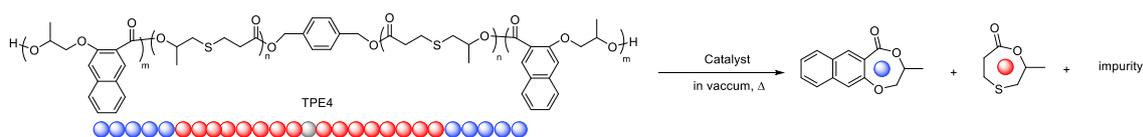


**Fig. S81** The DOSY spectrum of TPE2

## General procedure for the depolymerization of polymers in Bulk

In the glovebox, stock solutions of Sn(Oct)<sub>2</sub> (0.05 mg/μL, 10 mg Sn(Oct)<sub>2</sub> in 2 ml THF) and PEG-6000 (dried solid) were prepared. The Sn(Oct)<sub>2</sub> (100 μL, 5 wt%) and PEG (200-300 mg, 200-300 wt%) stock solutions were mixed in a Schlenk before copolymer was added as a solid (200 mg). The copolymer, Sn(Oct)<sub>2</sub> and PEG mixture was dissolved in a minimum amount of Tol (approx. 2 mL) before the solvent was removed in vacuum. A water-cooled cold-finger condenser was connected to the Schlenk and the reaction mixture was heated to 160-200 °C with magnetic stirring under vacuum (0.1–1 mbar). After 6 h, a pale yellow or white oily solid was collected which was determined to be mixed monomer (approx. 158 mg, 78% yield MTO, 74% yield DHB or DHN as determined by <sup>1</sup>H NMR spectroscopy)

## Recycling of tri-BCP PMTO-*b*-P(DHN)

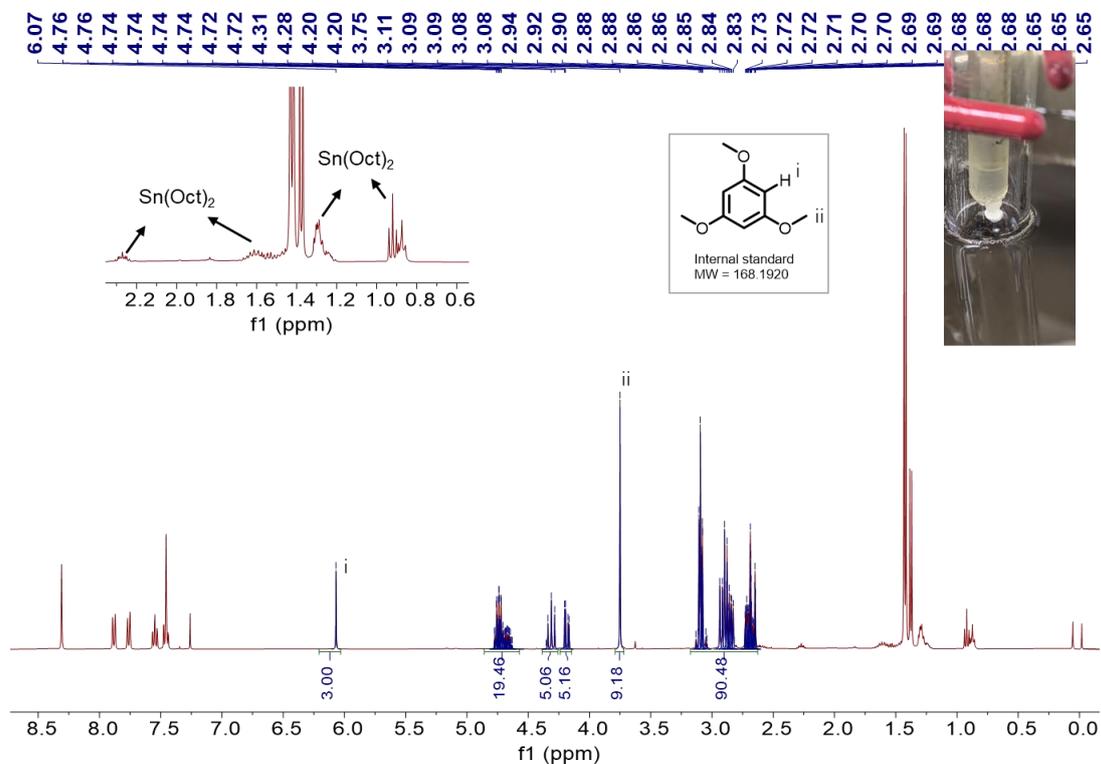


**Table S13** Chemical recycling of TPE4.<sup>a</sup>

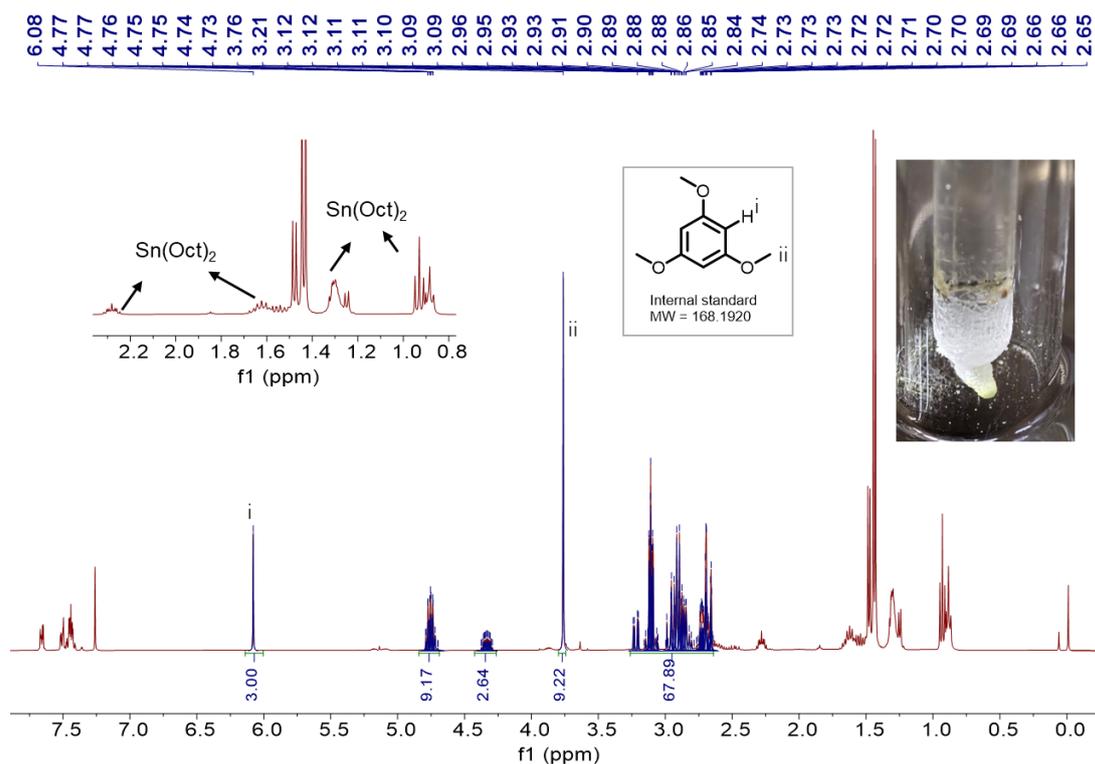
Entry	Catalyst	Temp. (°C)	Time (h)	Conv. (%) <sup>b</sup>	
				MTO	DHN
1	ZnCl <sub>2</sub> (2 wt%)	160	5	-	-
2	SnCl <sub>2</sub> (2 wt%)	160	5	-	-
3	<sup>t</sup> BuOK (2 wt%)	140	5	-	-
4	<sup>t</sup> BuOK (2 wt%)	160	5	-	-
5	<sup>t</sup> BuOK (2 wt%)	180	5	-	-
6	TBD (2 wt%)	160	5	-	-
7	TBD (2 wt%)	180	5	-	-
8	<b>Zn1</b> (5 wt%)	170	5	44	40
9	<b>Zn1</b> (10 wt%)	170	5	51	71
10	Zn(acac) <sub>2</sub> (10 wt%)	170	5	40	30
11	Al(acac) <sub>3</sub> (10 wt%)	170	5	60	53
12	Al(acac) <sub>3</sub> (10 wt%)	180	5	67	60
13	Sn(Oct) <sub>2</sub> (5 wt%)	170	5	77	75
14	Sn(Oct) <sub>2</sub> (5 wt%)	170	6	86	75
15 <sup>c</sup>	Sn(Oct) <sub>2</sub> (5 wt%)	170	5	78	74
16 <sup>d</sup>	Sn(Oct) <sub>2</sub> (5 wt%)	200	8	72	70
17 <sup>e</sup>	Sn(Oct) <sub>2</sub> (5 wt%)	160	6	82	70
18 <sup>e, f</sup>	Sn(Oct) <sub>2</sub> (5 wt%)	180	6	75	68
19 <sup>e, g</sup>	Sn(Oct) <sub>2</sub> (5 wt%)	200	6	65	62

<sup>a</sup>Copolymer and catalyst were premixed in Tol and the volatiles were removed under vacuum, then 200 wt% of PEG-6000 was added. <sup>b</sup>Conversion of monomers was measured by <sup>1</sup>H NMR of a solution (CDCl<sub>3</sub>) of the internal standard (1,3,5-trimethoxybenzene) and the resulting product on the

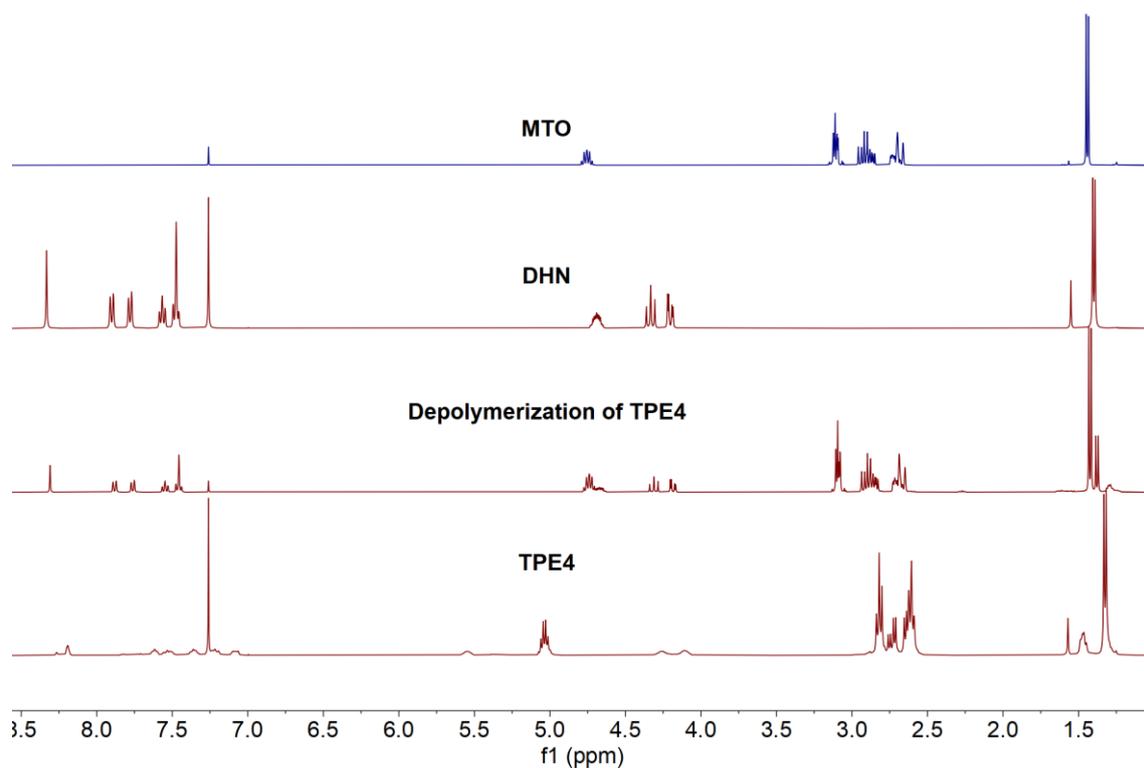
condenser. <sup>c</sup>The mass of the copolymer was 200 mg. <sup>d</sup>The mass of the copolymer was 1 g, and the conversion of monomers was determined by weighing. <sup>e</sup>The hard-segments was P(DHB). <sup>f</sup>The mass of the copolymer was 200 mg. <sup>g</sup>The copolymer was 1 g in mass, and the monomer yield was determined by weighing.



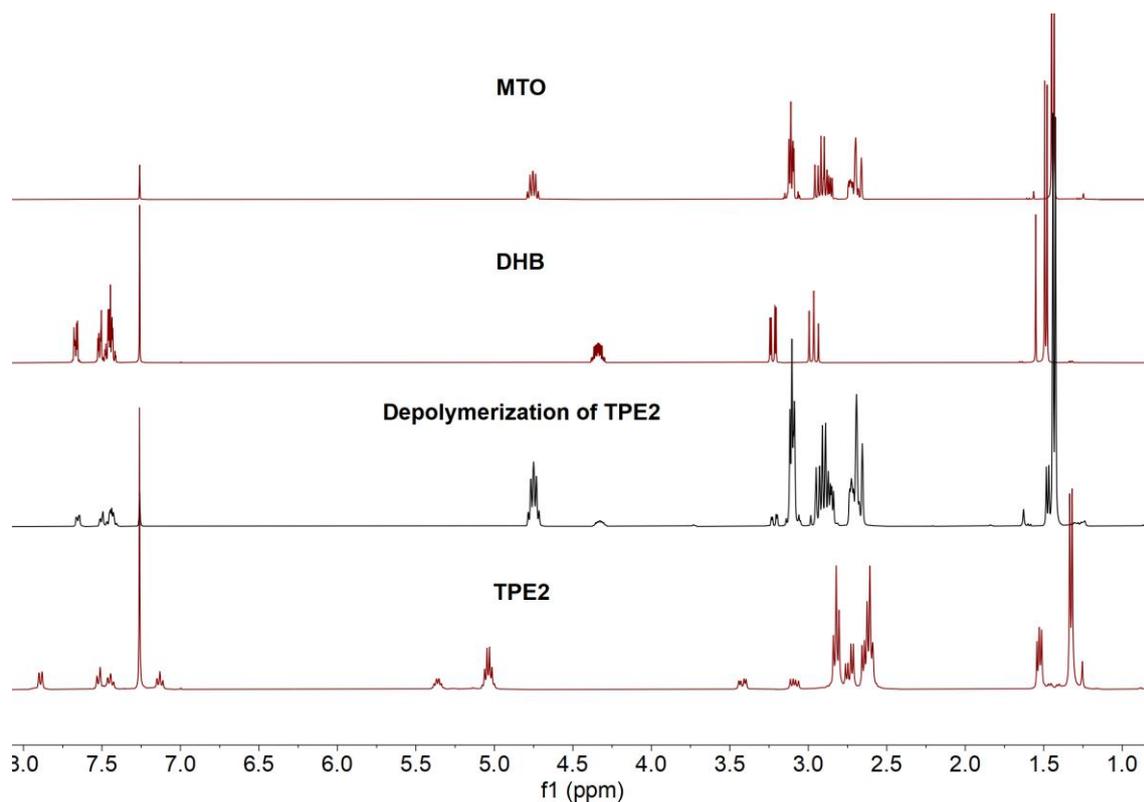
**Fig. S82** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of the mixture of internal standard (3 mg) and chemical recycled mixed monomer from TPE4 (38 mg) (**Table S13**, entry 14).



**Fig. S83**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25\text{ }^\circ\text{C}$ ) spectrum of the mixture of internal standard (3 mg) and chemical recycled mixed monomer from TPE2 (25 mg) (Table S13, entry 17).



**Fig. S84** Chemical recyclability of TPE4 ( $F_{\text{DHN}} = 0.21$ ) as shown by  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ). Top and second from top, starting MTO and DHN. Third from top, the mixed monomers obtained using 5 wt%  $\text{Sn}(\text{Oct})_2$  after degradation at  $170\text{ }^\circ\text{C}$  for 5 h (After purification). Bottom, TPE4 ( $F_{\text{DHN}} = 0.21$ ).



**Fig. S85** Chemical recyclability of TPE2 ( $F_{\text{DHB}} = 0.25$ ) as shown by  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ). Top and second from top, starting MTO and DHB. Third from top, the mixed monomers obtained using 5 wt%  $\text{Sn}(\text{Oct})_2$  after degradation at 170 °C for 5 h (After purification). Bottom, TPE2 ( $F_{\text{DHB}} = 0.25$ ).

## Reference

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