

# Copolymerization of tricyclopentadiene and ethylene catalyzed by thiophene-fused-heterocyclic cyclopentadienyl scandium complexes

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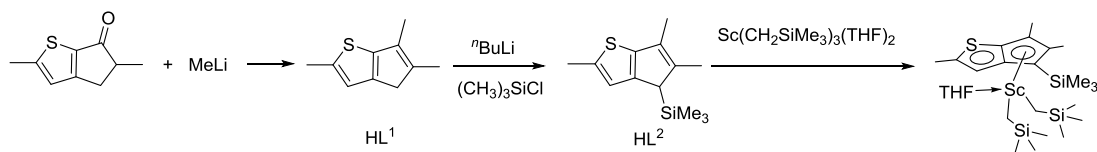
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### Synthetic route of complex 3



**Scheme S1.** Synthetic of complex 3.

Synthesis of similar ligand and complexes was described in literatures.<sup>1,2</sup>

HL<sup>1</sup>: MeLi (15.0 mL, 24.0 mmol, 1.6 M in diethyl ether) was added dropwise to a solution of 4,5-dihydro-2,5-dimethylcyclopenta[*b*]thiophen-6-one (3.01 g, 19.9 mmol) in diethyl ether 40.0 mL at  $-78^{\circ}\text{C}$ . Then the temperature increased to room temperature and the mixture was stirred overnight. Water (20.0 mL), ethyl acetate (40.0 mL), and aqueous HCl (2 N, 40.0 mL) were successively added. The mixture was stirred for 10 mins, the organic phase was collected and then aqueous saturated NaHCO<sub>3</sub> solution (100.0 mL) was added. The collected organic phase was dried with anhydrous MgSO<sub>4</sub> and solvent was removed under vacuum to give the residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The product was obtained as a yellowish oil (2.08 g, 64%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  6.66 (s, 1H, Cp'-H), 3.42 (s, 2H, Cp'-H), 2.03 (s, 3H, S-C-Me), 1.08 (s, 6H, Me<sub>2</sub>).

HL<sup>2</sup>: <sup>n</sup>BuLi (4.2 mL, 10.5 mmol, 2.5 M in diethyl ether) was added dropwise to a solution of HL<sup>1</sup> (2,5,6-trimethyl-4*H*-cyclopenta[*b*]thiophene) (1.64 g, 10.0 mmol) in diethyl ether 40.0 mL at  $-78^{\circ}\text{C}$ . The color of the reaction system changed to light yellow, and the reaction was carried out at  $-40^{\circ}\text{C}$  for 30 mins. Then the newly distilled (CH<sub>3</sub>)<sub>3</sub>SiCl (1.08 g, 10.00 mmol) was added to the lithium salt solution with a syringe and reacted at this temperature for 24 h. At the end of the reaction, the solvent was drained, add hexane extraction, filtered, and hexane was drained to obtain light brown pure HL<sup>2</sup> (2,5,6-Me<sub>3</sub>-4-SiMe<sub>3</sub>-cyclopenta[*b*]thiophene) (1.89 g, 81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  6.66 (s, 1H, Cp'-H), 3.23 (s, 1H, Cp'-H), 2.55 (s, 3H, S-C-Me), 2.07 (s, 6H, Me<sub>2</sub>), 0.02 (s, 9H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  151.3 (s, 1C, Cp'-C), 140.4 (s, 1C, Cp'-C), 138.8 (s, 1C, Cp'-C), 138.2 (s, 1C, Cp'-C), 129.1 (s, 1C, Cp'-C), 115.4 (s, 1C, Cp'-C), 48.3 (s, 1C, Cp'-C), 16.6 (s, 1C, S-C-Me), 15.4 (s, 1C,

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Me), 12.1 (s, 1C, Me), -2.4 (s, 3C, CH<sub>2</sub>SiMe<sub>3</sub>).

**Complex 3:** Under a nitrogen atmosphere, to a hexane solution (10 mL) of Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (0.90 g, 2.0 mmol) was added slowly 1 equiv of ligand HL<sup>2</sup> (0.44 g, 2.0 mmol) at room temperature. The mixture was stirred overnight to afford a yellow solution. Removal of solvent under vacuum to give the yellow solid, and the analytically pure compound was obtained through recrystallization in hexane at -30 °C (0.96 g, 91%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 6.31 (s, 1H, Cp-H), 3.59 (br, 4H, THF), 2.39 (s, 3H, S-C-Me), 2.21 (s, 3H, Me), 2.16 (s, 3H, Me), 1.20 (br, 4H, THF), 0.44 (s, 9H, SiMe<sub>3</sub>), 0.26 (s, 18H, CH<sub>2</sub>SiMe<sub>3</sub>), -0.06, -0.11 (AB, 2H, 11.6 Hz, ScCH<sub>2</sub>SiMe<sub>3</sub>), -0.18, -0.24 (AB, 2H, 11.6 Hz, ScCH<sub>2</sub>SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 139.9 (s, 1C, Cp'-C), 137.6 (s, 1C, Cp'-C), 134.5 (s, 1C, Cp'-C), 135.5 (s, 1C, Cp'-C), 116.0 (s, 1C, Cp'-C), 115.3 (s, 1C, Cp'-C), 107.3 (s, 1C, Cp'-C), 72.0 (s, 2C, THF), 43.4 (br, 1C, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), 41.8 (s, 1C, Sc-CH<sub>2</sub>SiMe<sub>3</sub>), 25.3 (s, 2C, THF), 16.7 (s, 1C, S-C-Me), 16.3 (s, 1C, Me), 13.2 (s, 1C, Me), 4.7 (s, 3C, ScCH<sub>2</sub>SiMe<sub>3</sub>), 4.6 (s, 3C, ScCH<sub>2</sub>SiMe<sub>3</sub>), 1.5 (s, 3C, SiMe<sub>3</sub>). Anal. Calcd. for C<sub>25</sub>H<sub>49</sub>OSScSi<sub>3</sub> (%): C, 59.99; H, 9.37. Found: C, 59.61; H, 9.55.

### Determination of TCPD incorporation

According to literature,<sup>3</sup> the assignment of NMR spectra of TCPD/E copolymer and the cycloolefin incorporation into the copolymers was calculated from the intensities of relative protons.

### Determination of ethylene concentrations

Ethylene concentrations in toluene can be calculated according to the Henry-Gesetz expression:<sup>4</sup>

$$[E] = P_E \cdot H_0 \cdot \exp\left(\frac{\Delta H_L}{RT}\right)$$

Where [E] is the ethylene concentration (mol/L), P<sub>E</sub> is the ethylene pressure (bar), H<sub>0</sub> is the Henry coefficient, ΔH<sub>L</sub> is the enthalpy of solvation for ethylene, R is the universal gas constant, and T is the solution temperature (K). For toluene, H<sub>0</sub> = 0.00175 mol/(L·bar) and ΔH<sub>L</sub> = 10742 W·s/mol.

### Determination of TCPD conversion

The TCPD conversion of the copolymer was calculated according to the formula:

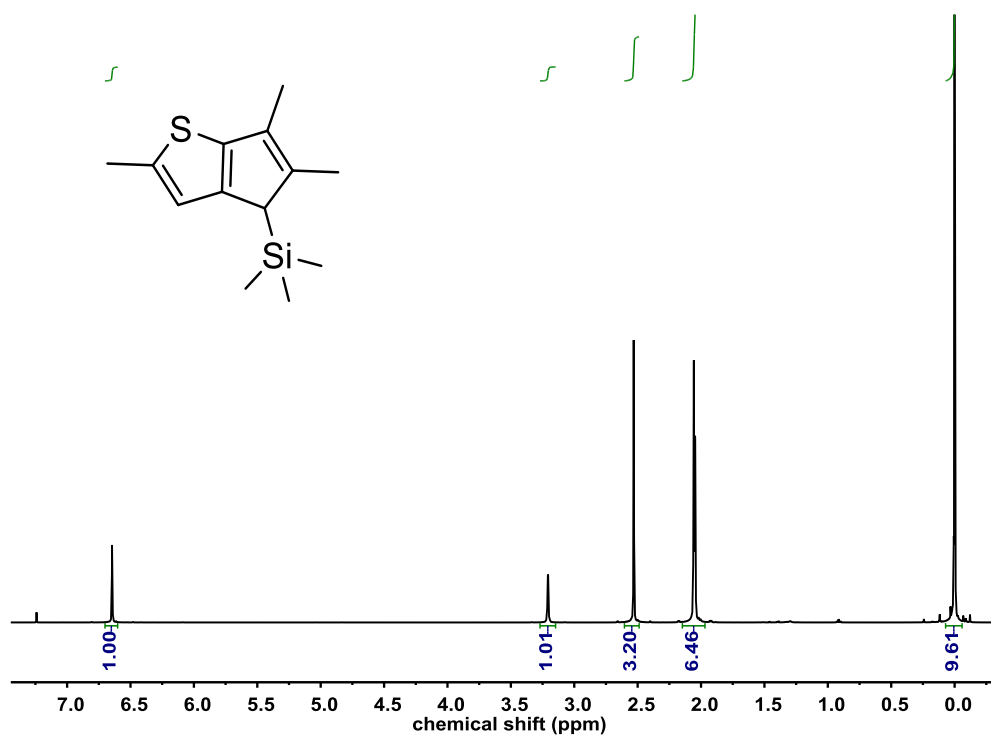
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$$\text{TCPD Conversion} = \frac{m_{\text{polymer}} \times \left( \frac{198 \times f_{\text{TCPD}}}{198 \times f_{\text{TCPD}} + 28 \times f_{\text{E}}} \right)}{m_{\text{TCPD}}} \times 100\%$$

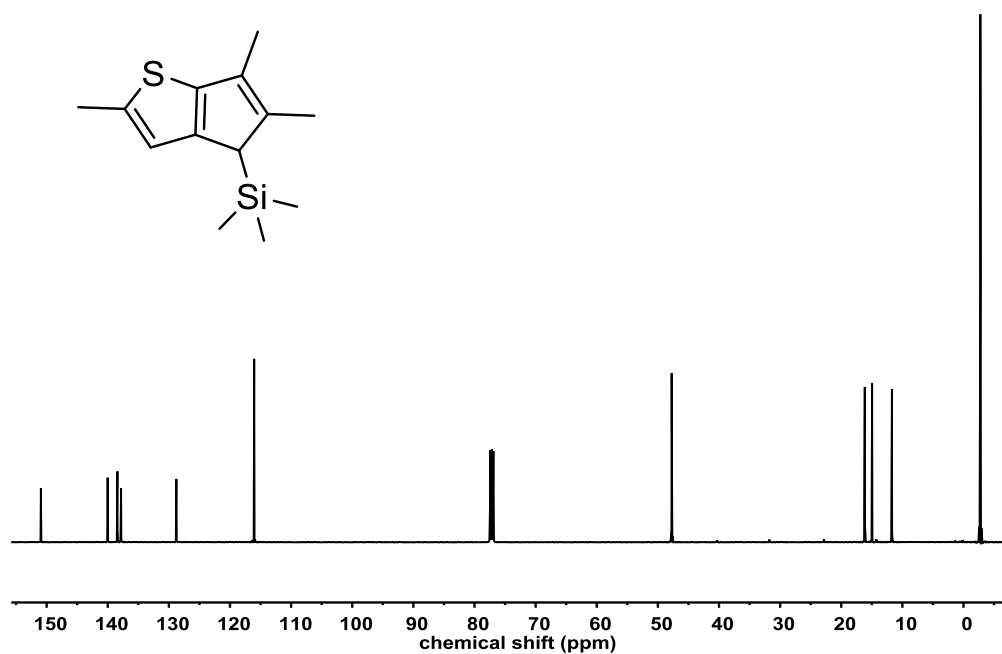
Where  $m_{\text{polymer}}$  is the mass of copolymer after drying,  $m_{\text{TCPD}}$  is the feeding mass of TCPD,  $f_{\text{TCPD}}$  is the TCPD incorporation,  $f_{\text{E}}$  is the ethylene incorporation.

## References

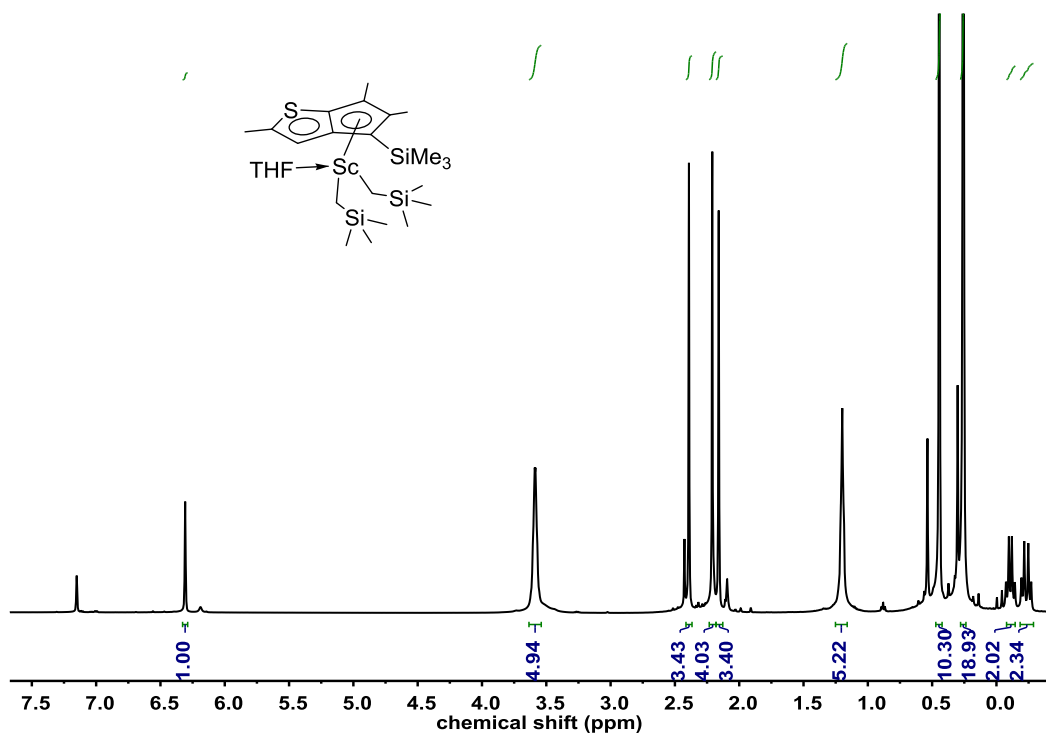
1. E. S. Park, J. H. Park, H. Yun and B. Y. Lee, *J. Organomet. Chem.*, 2011, **696**, 2451-2456.
2. C. J. Wu, B. Liu, F. Lin, M. Y. Wang and D. M. Cui, *Angew. Chem., Int. Ed.*, 2017, **56**, 6975-6979.
3. H. Park, A. Kim and B. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 938-944.
4. A. McKnight and R. Waymouth, *Macromolecules*, 1999, **32**, 2816-2825.



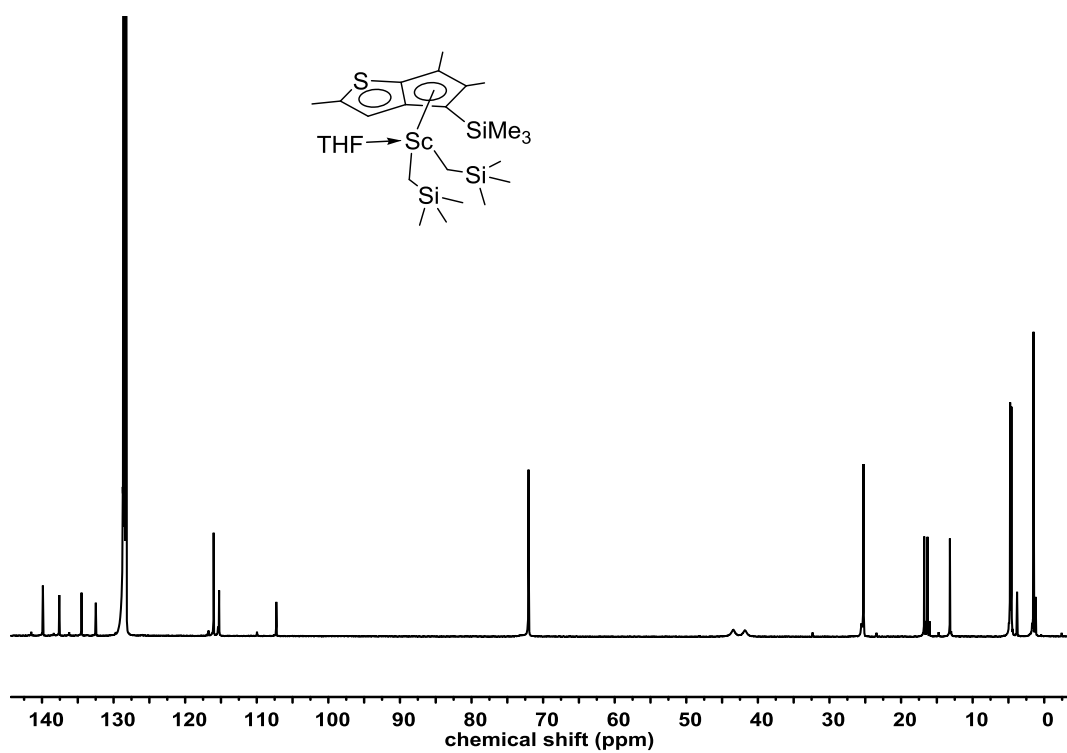
**Fig. S1**  $^1\text{H}$  NMR spectrum of 2,5,6-Me<sub>3</sub>-4-SiMe<sub>3</sub>-cyclopenta[*b*]thiophene (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C).



**Fig. S2**  $^{13}\text{C}$  NMR spectrum of 2,5,6-Me<sub>3</sub>-4-SiMe<sub>3</sub>-cyclopenta[*b*]thiophene (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C).

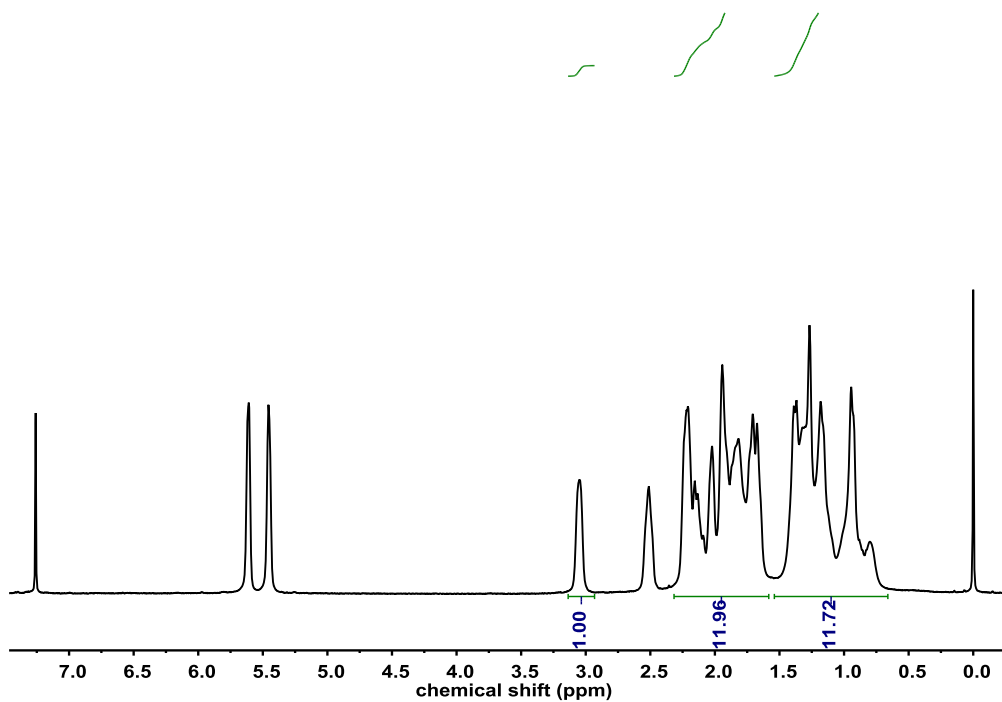


**Fig. S3**  $^1\text{H}$  NMR spectrum of complex 3 (500 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).

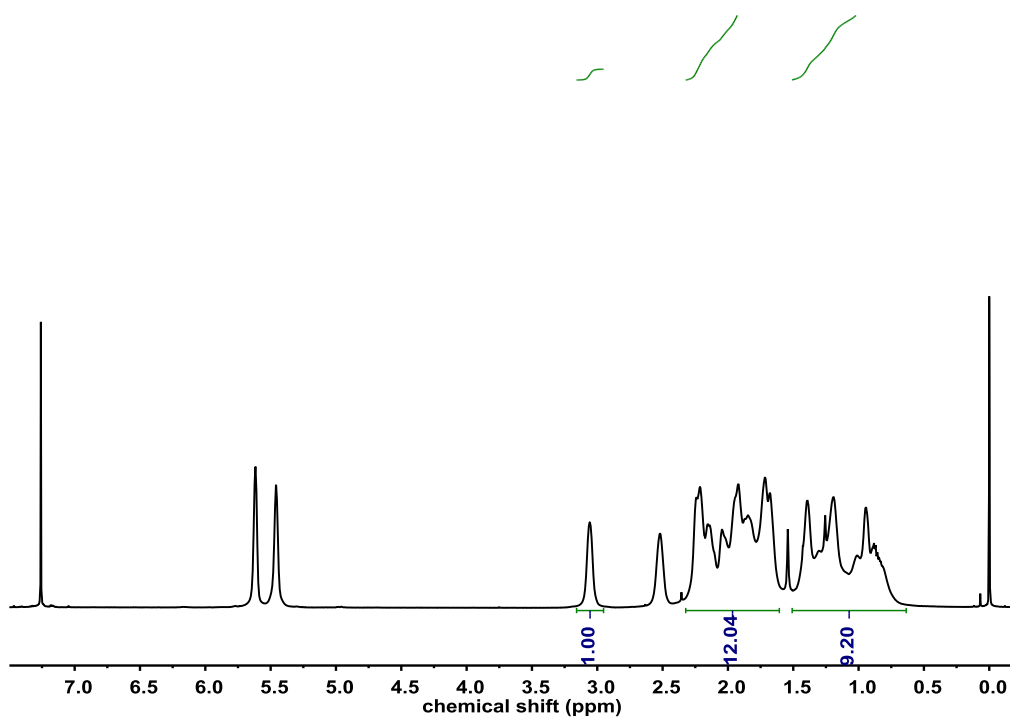


**Fig. S4**  $^{13}\text{C}$  NMR spectrum of complex 3 (500 MHz,  $\text{C}_6\text{D}_6$ , 25 °C).

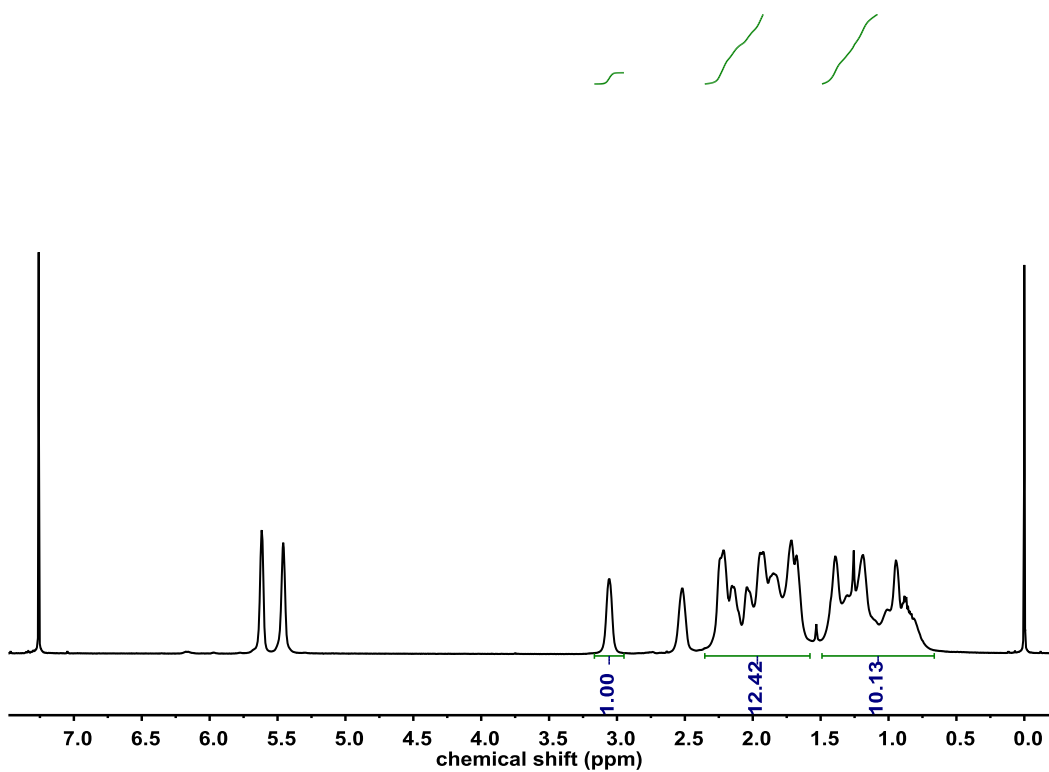




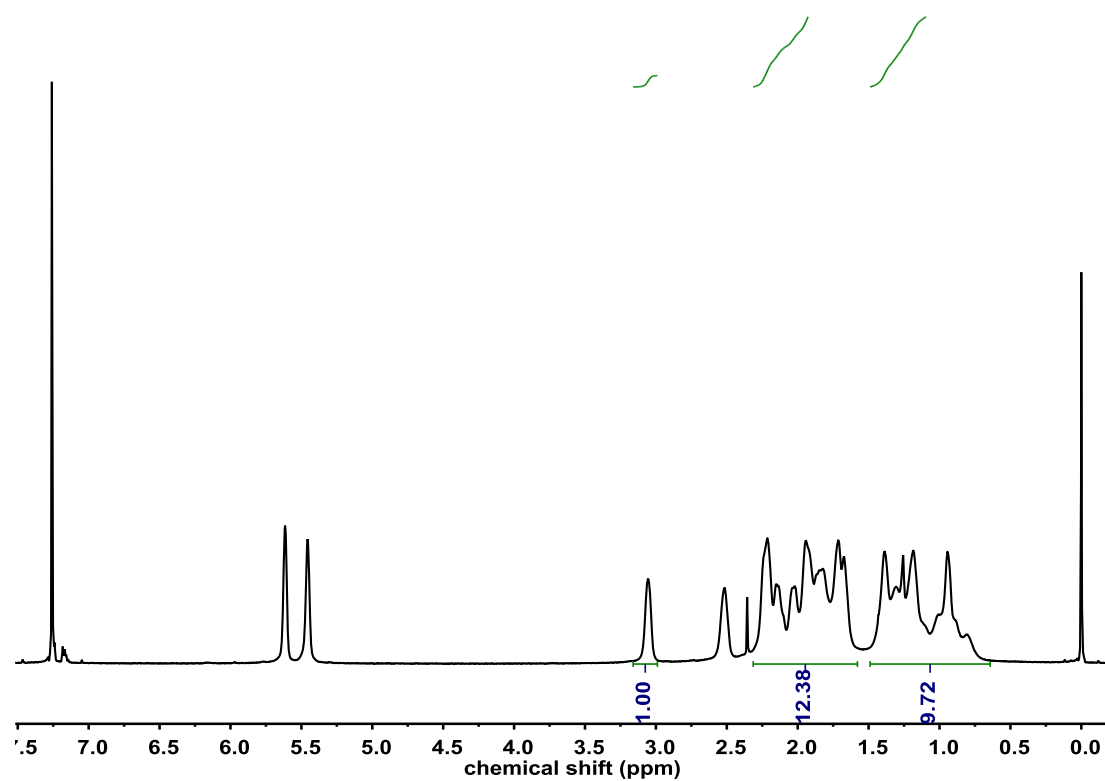
**Fig. S5** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 1).



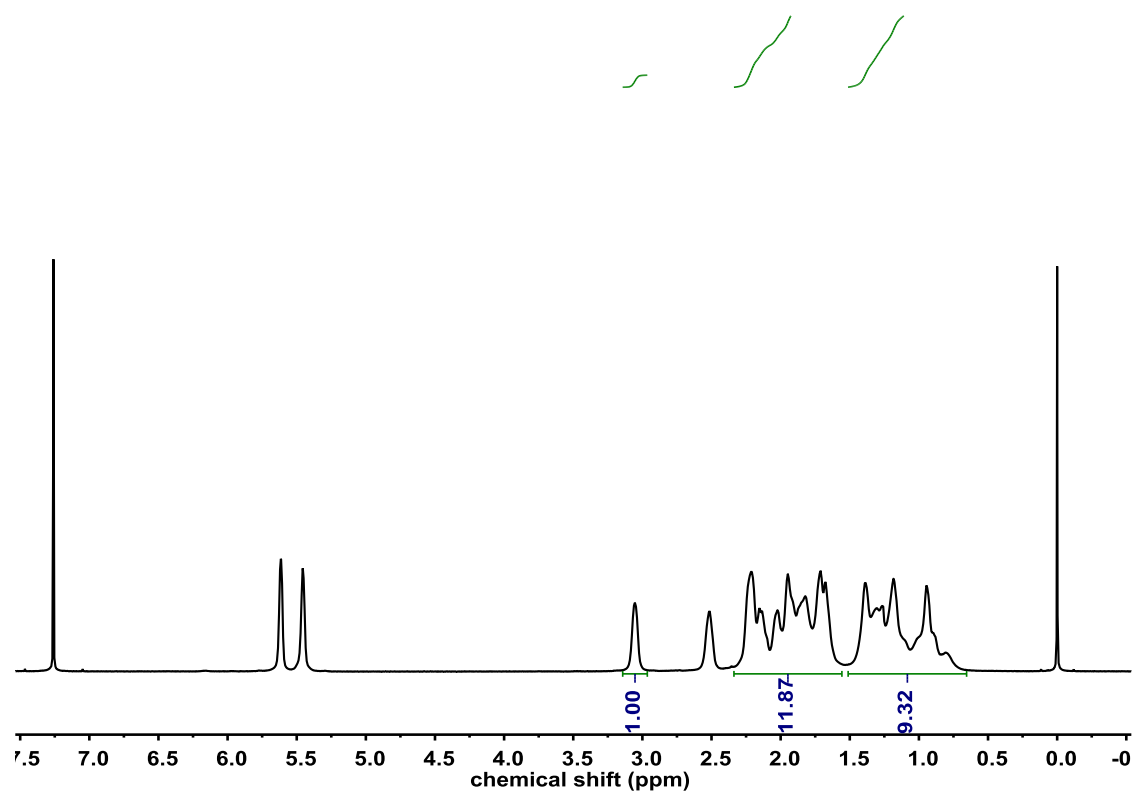
**Fig. S6** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 2).



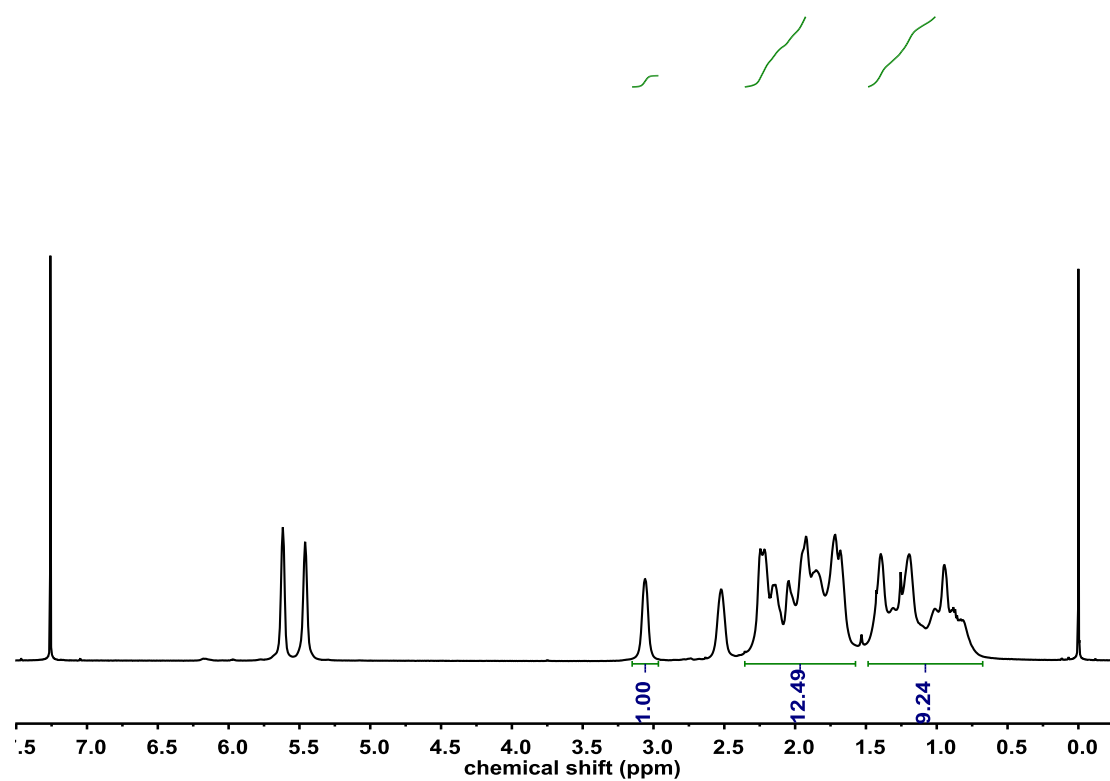
**Fig. S7** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 3).



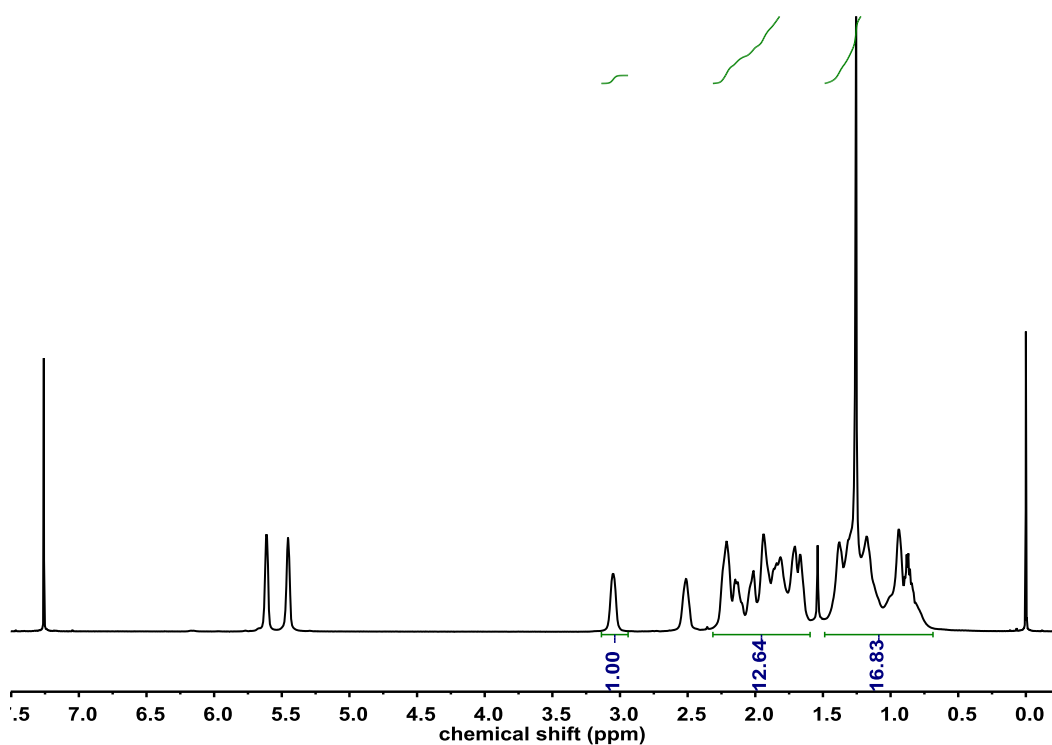
**Fig. S8** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 4).



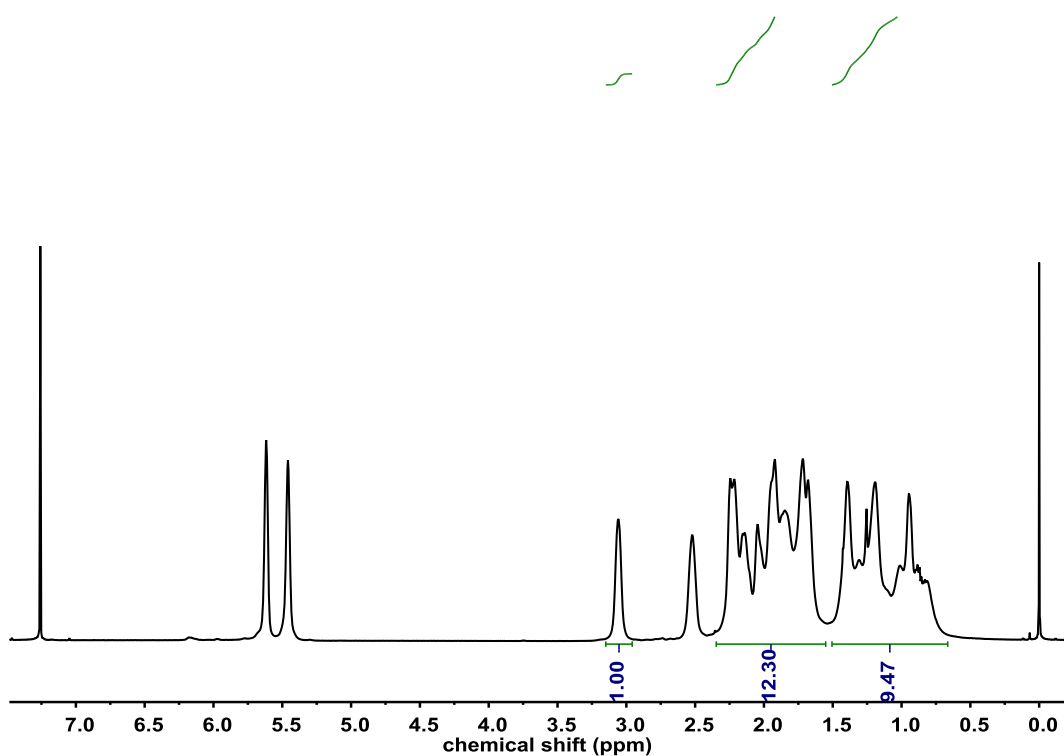
**Fig. S9** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 5).



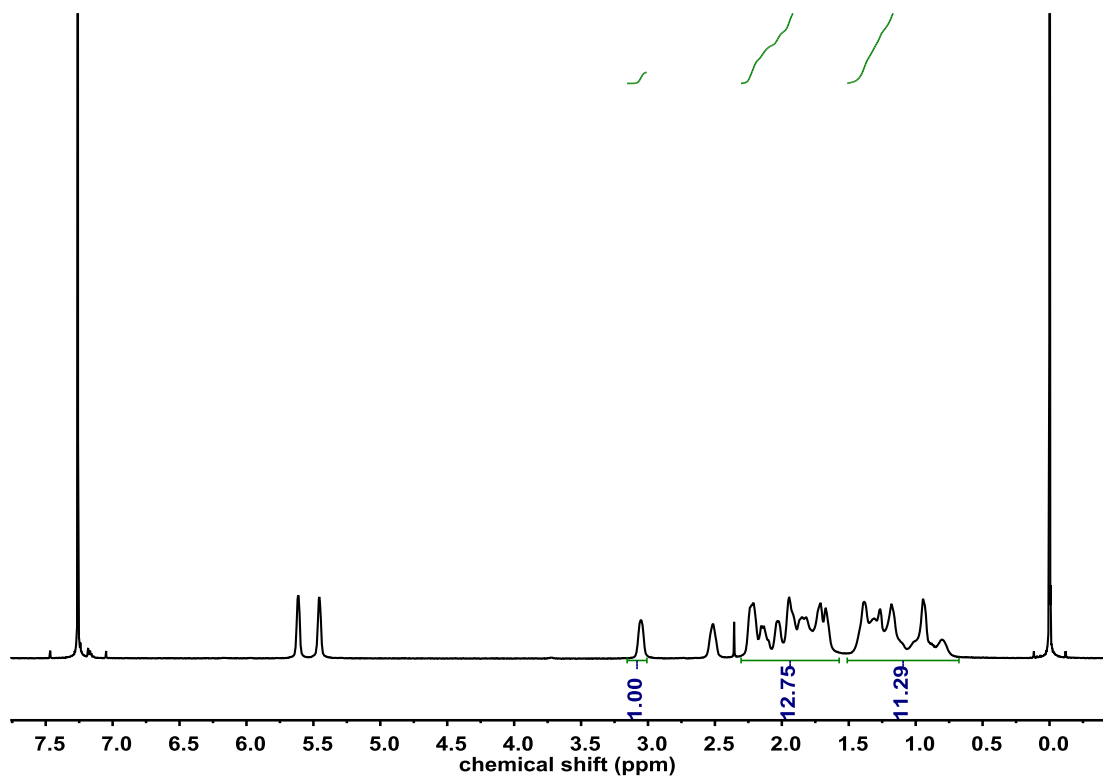
**Fig. S10** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 6).



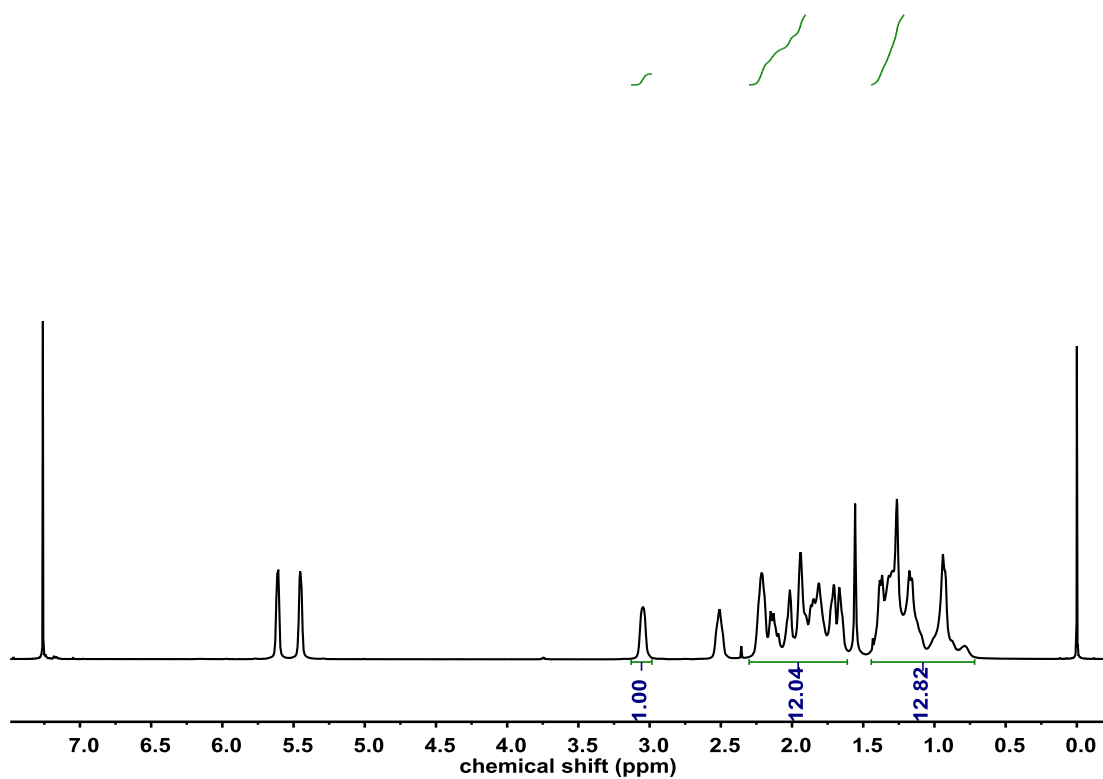
**Fig. S11** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 7).



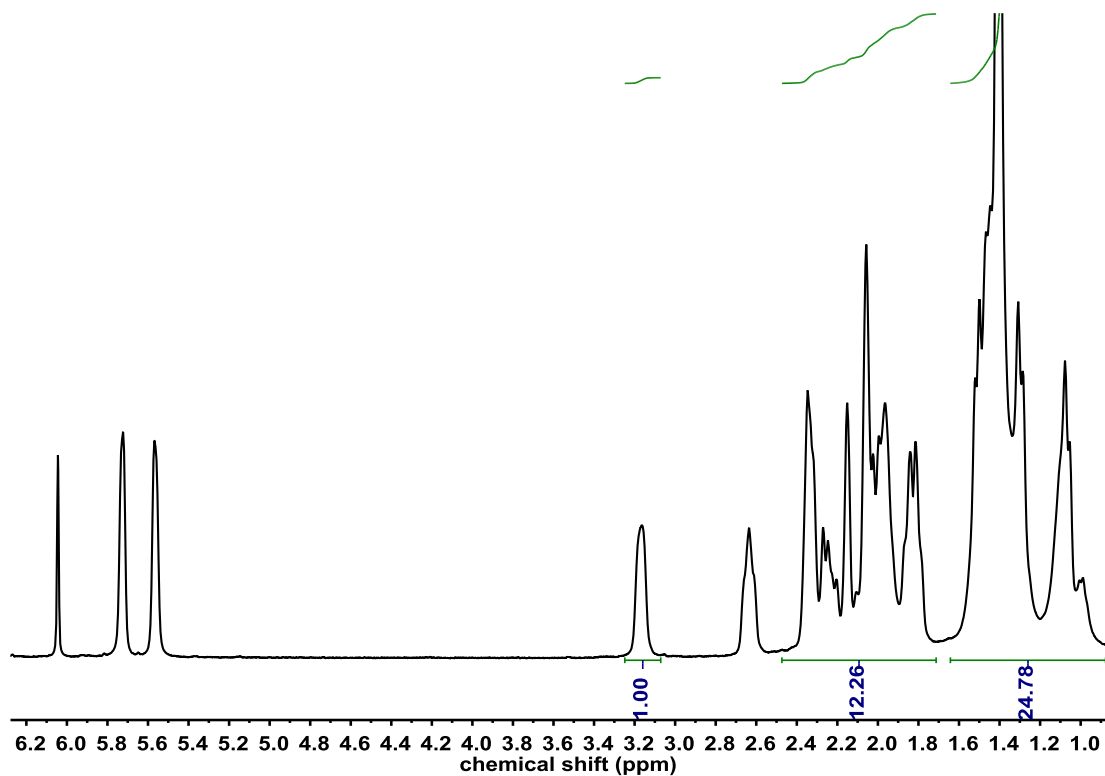
**Fig. S12** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 8).



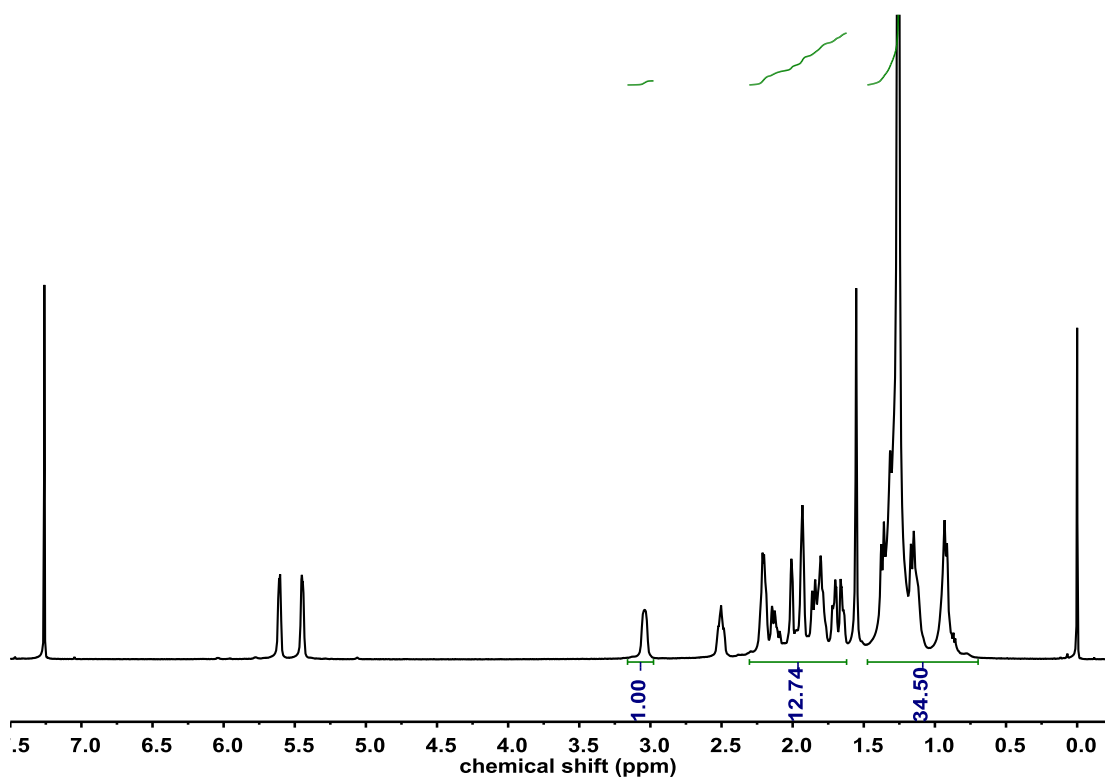
**Fig. S13** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 9).



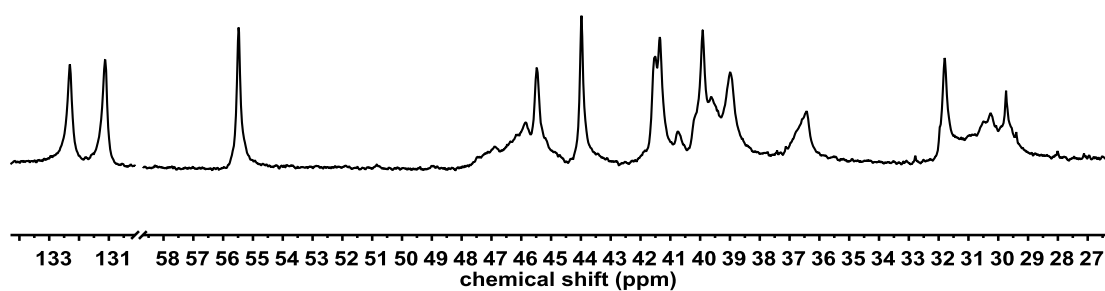
**Fig. S14** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 10).



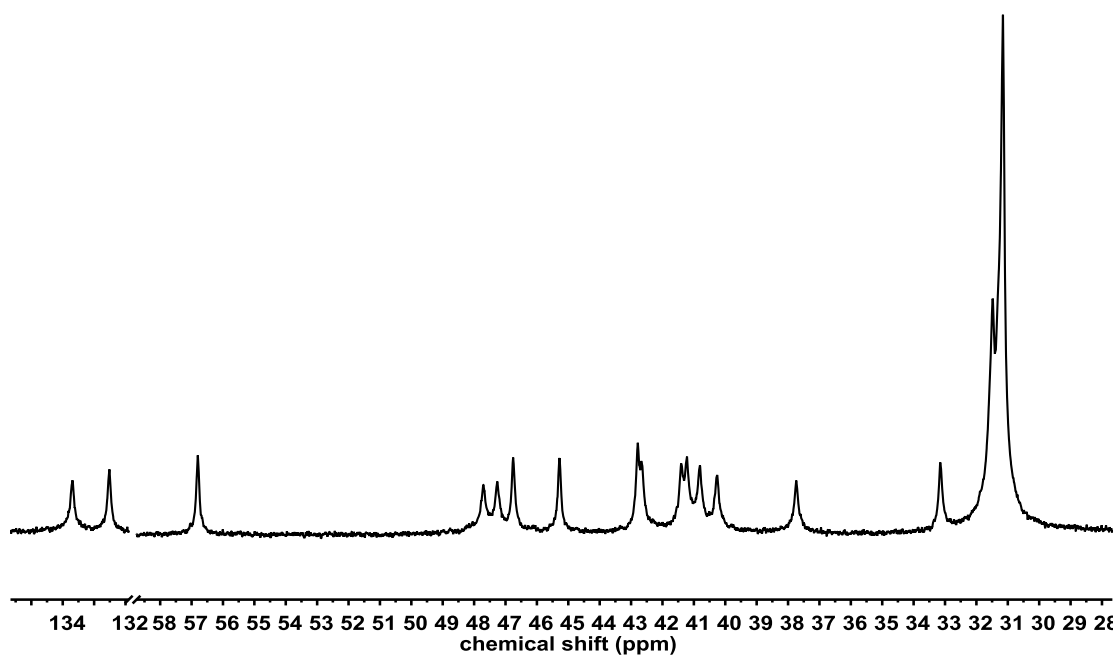
**Fig. S15** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 25 °C, Table 1, entry 11).



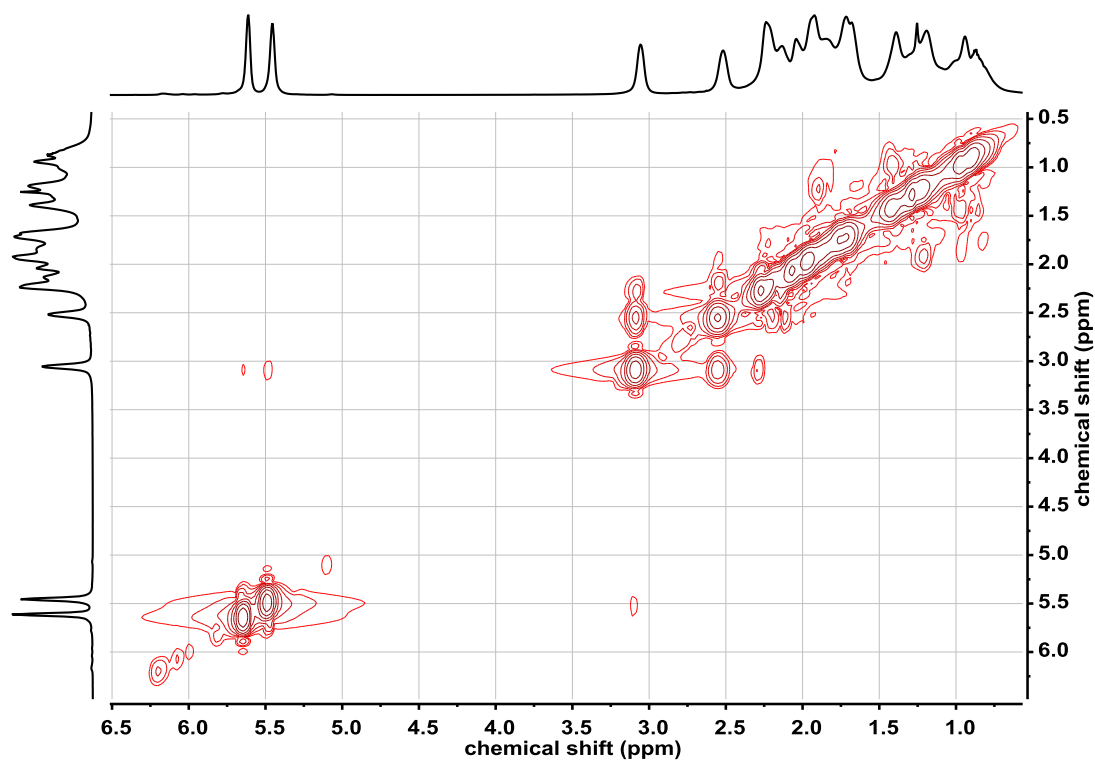
**Fig. S16** <sup>1</sup>H NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 12).



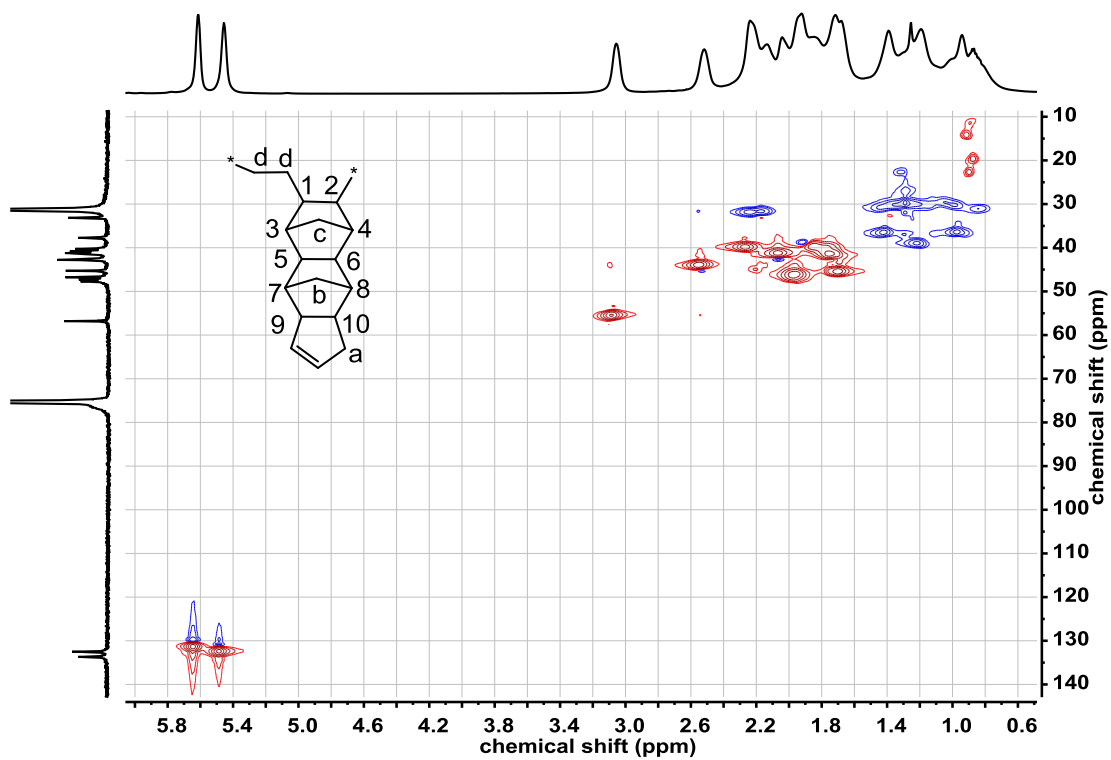
**Fig. S17** <sup>13</sup>C NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 6).



**Fig. S18** <sup>13</sup>C NMR spectrum of TCPD/E copolymer (500 MHz, CDCl<sub>3</sub>, 25 °C, Table 1, entry 12).



**Fig. S19**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of TCPD/E copolymer (500 MHz,  $\text{CDCl}_3$ , 25 °C, Table 1, entry 6).



**Fig. S20**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of TCPD/E copolymer (500 MHz,  $\text{CDCl}_3$ , 25 °C, Table 1, entry 6).



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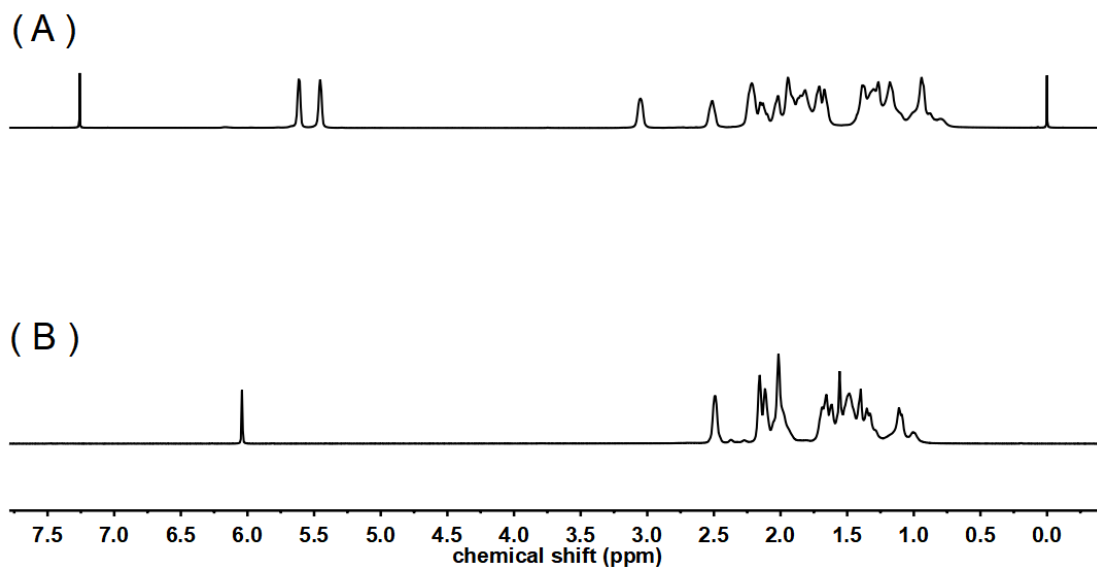
## Microstructure of Ethylene and TCPD Copolymers

**Table S1.** Chemical shift assignment of TCPD/E copolymers

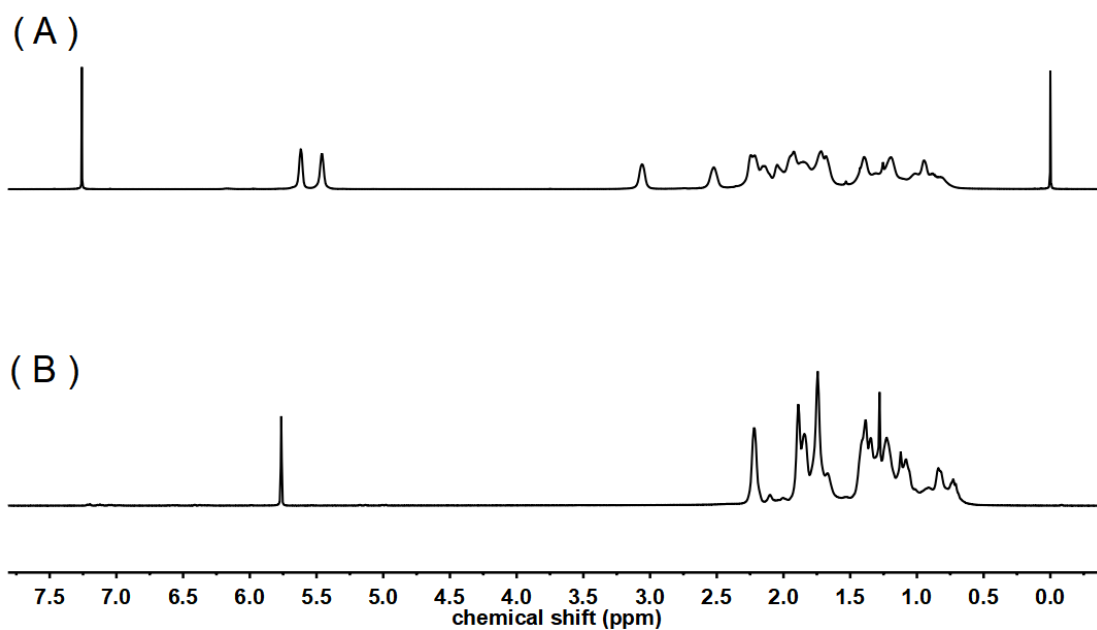
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Assignment (Carbon number)	<sup>1</sup> H NMR Chemical shift (ppm)	<sup>13</sup> C NMR Chemical shift (ppm)
CH (1)	1.98	46.3, 47.4
CH (2)	1.98	46.8, 45.9
CH (3,4)	1.70	45.4
CH (5,6)	1.85	39.2-40.3
CH (7,8)	2.05	41.1-41.8
CH (9)	3.04	55.4
CH (10)	2.51	43.9
CH (11)	5.48	132.2
CH (12)	5.65	131.3
CH <sub>2</sub> (a)	2.10-2.30	32.0
CH <sub>2</sub> (b)	1.10-1.20,1.75-1.85	32.0
CH <sub>2</sub> (c)	0.94, 1.38	36.6
CH <sub>2</sub> (d)	0.70-1.50	30.0

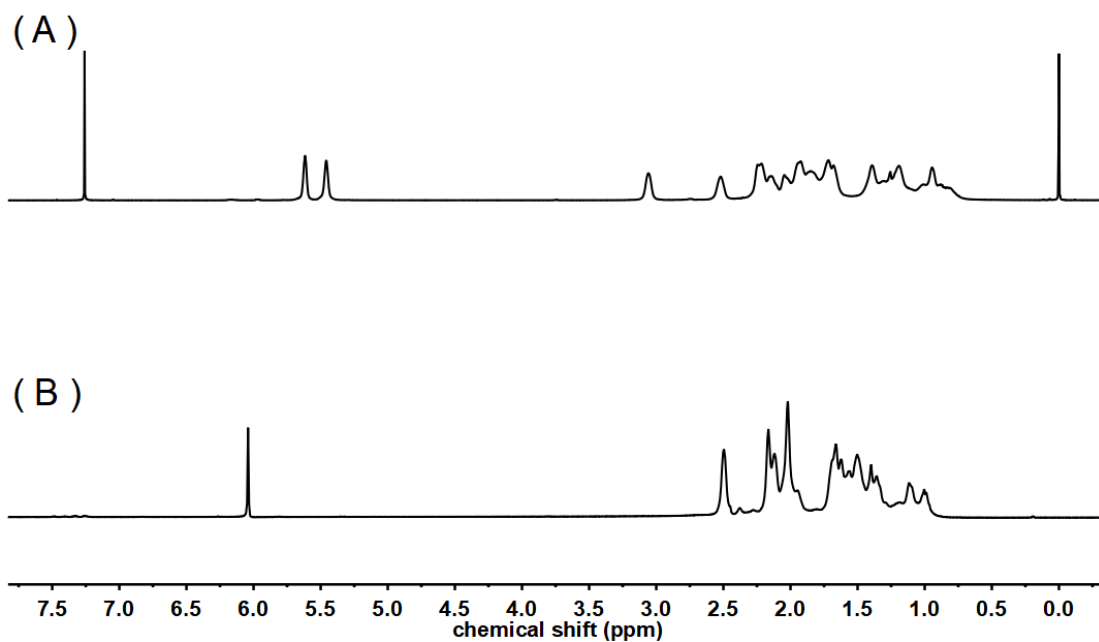
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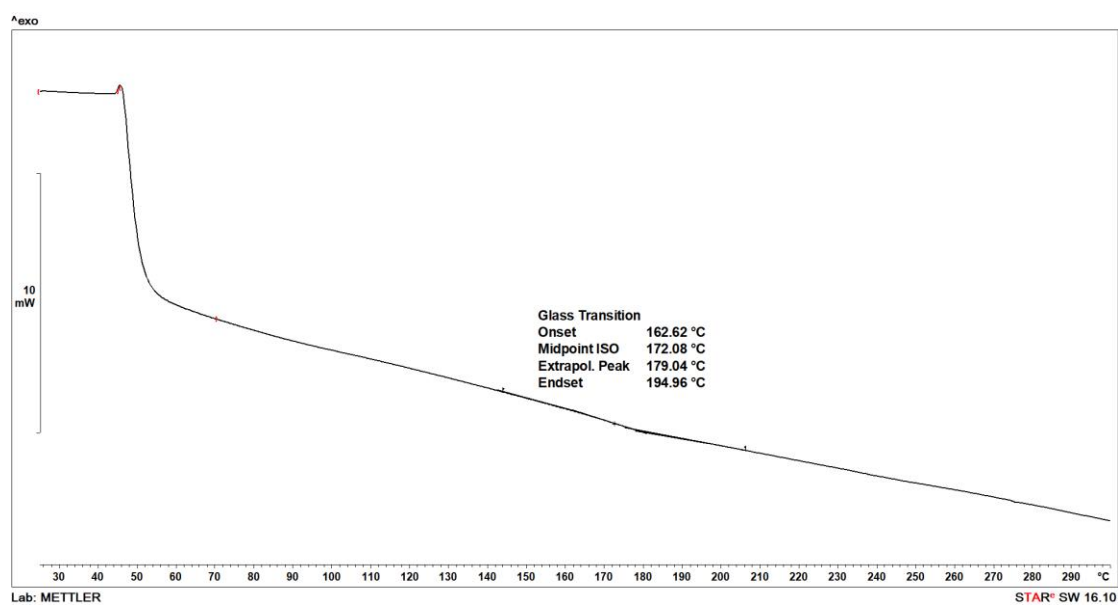
**Fig. S21**  $^1\text{H}$  NMR spectrum of TCPD/E copolymers before hydrogenation (**A**, 500 MHz,  $\text{CDCl}_3$ , 25 °C, Table 1, entry 1) and after hydrogenation (**B**, 500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25 °C, Table 2, entry 1).



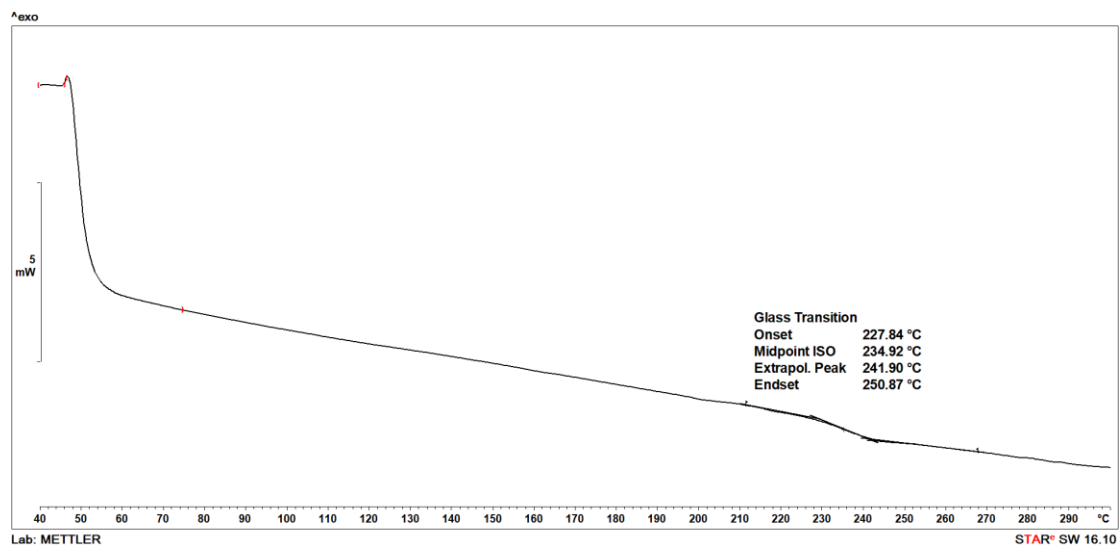
**Fig. S22**  $^1\text{H}$  NMR spectrum of TCPD/E copolymers before hydrogenation (**A**, 500 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ , Table 1, entry 6) and after hydrogenation (**B**, 500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25  $^\circ\text{C}$ , Table 2, entry 2).



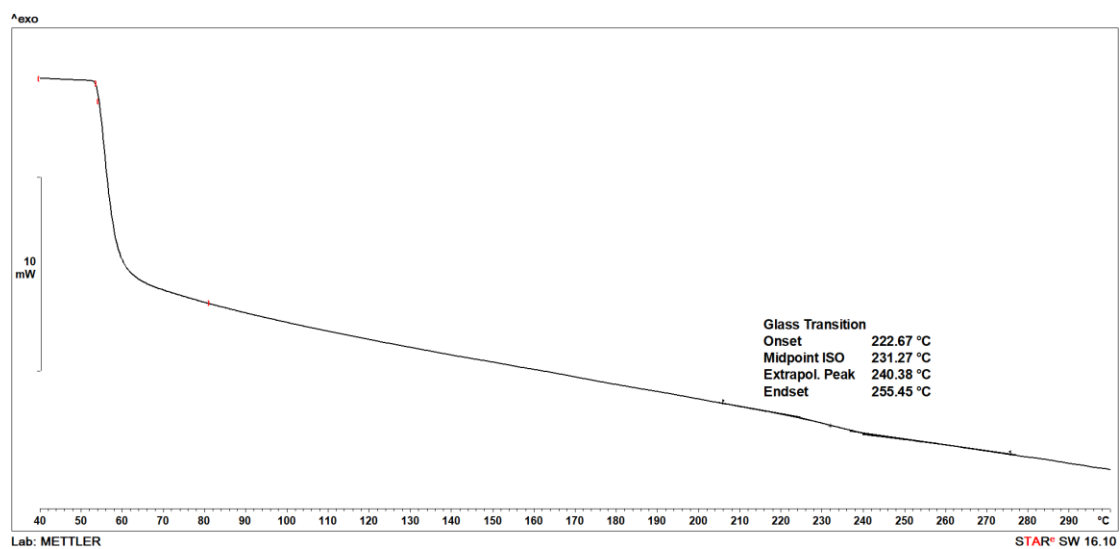
**Fig. S23**  $^1\text{H}$  NMR spectrum of TCPD/E copolymers before hydrogenation (**A**, 500 MHz,  $\text{CDCl}_3$ , 25 °C, Table 1, entry 9) and after hydrogenation (**B**, 500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25 °C, Table 2, entry 3).



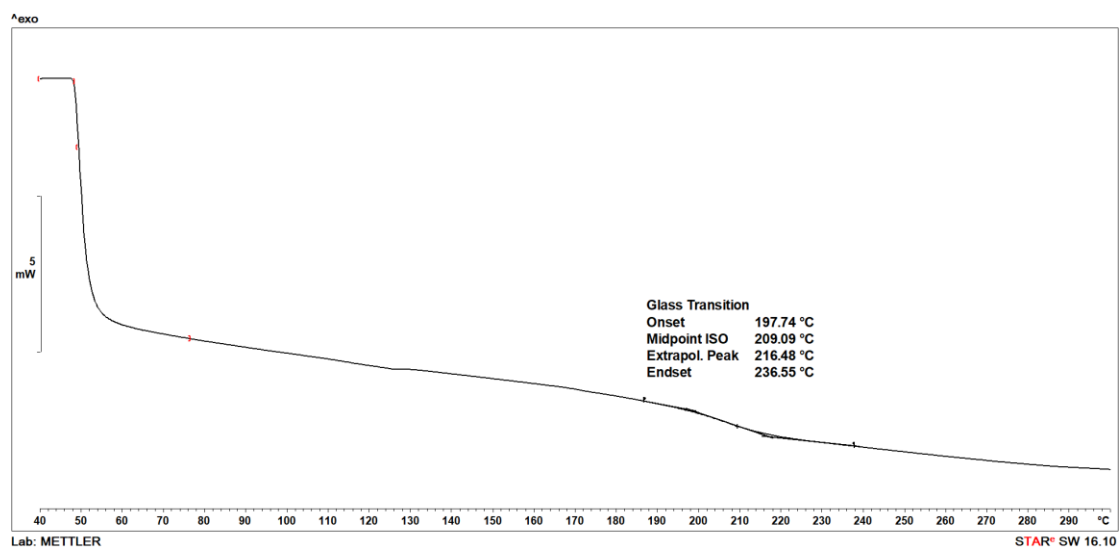
**Fig. S24** DSC curve of the TCPD/E copolymer (Table 1, entry 1).



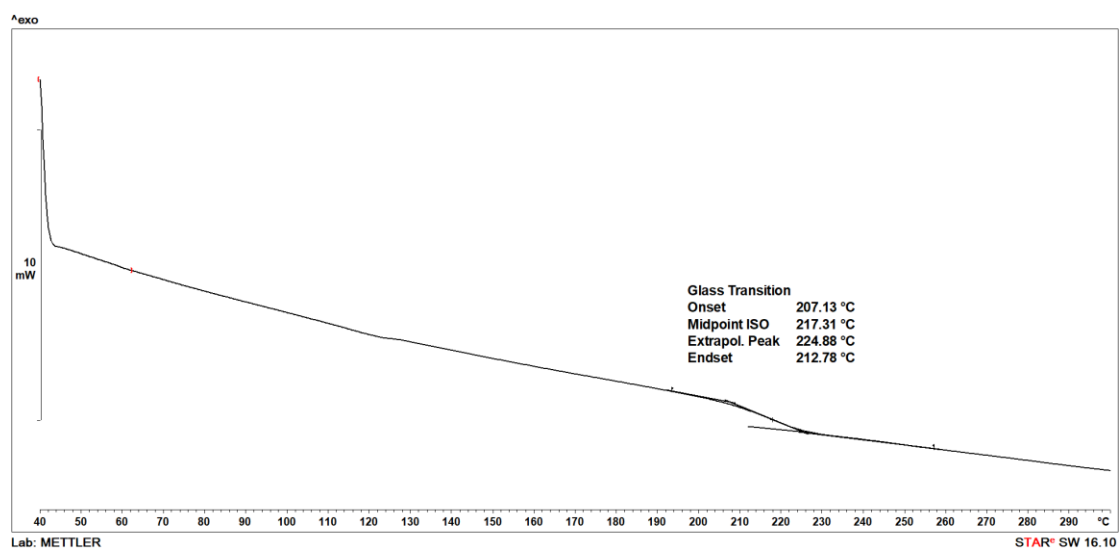
**Fig. S25** DSC curve of the TCPD/E copolymer (Table 1, entry 2).



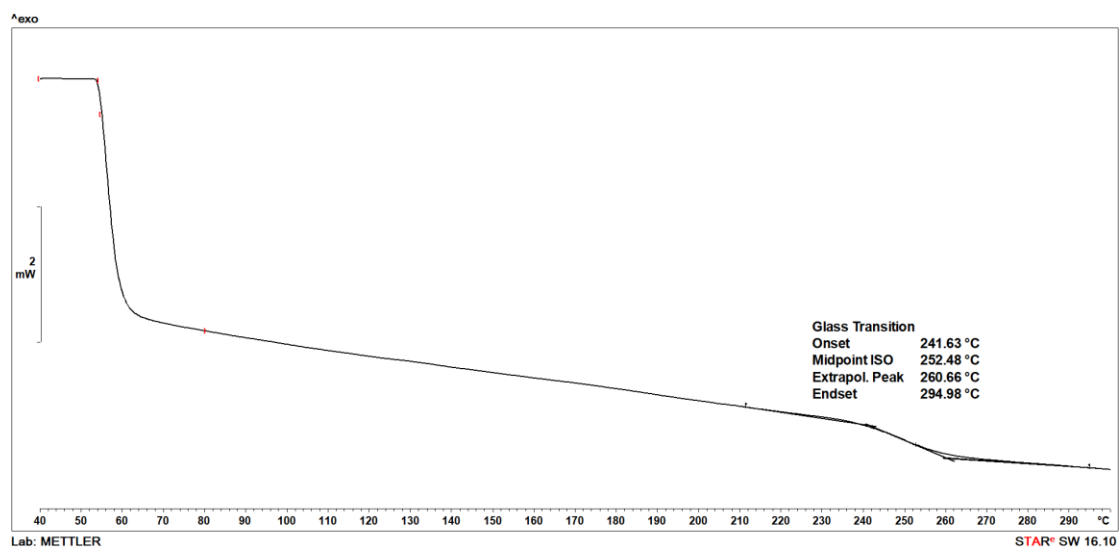
**Fig. S26** DSC curve of the TCPD/E copolymer (Table 1, entry 3).



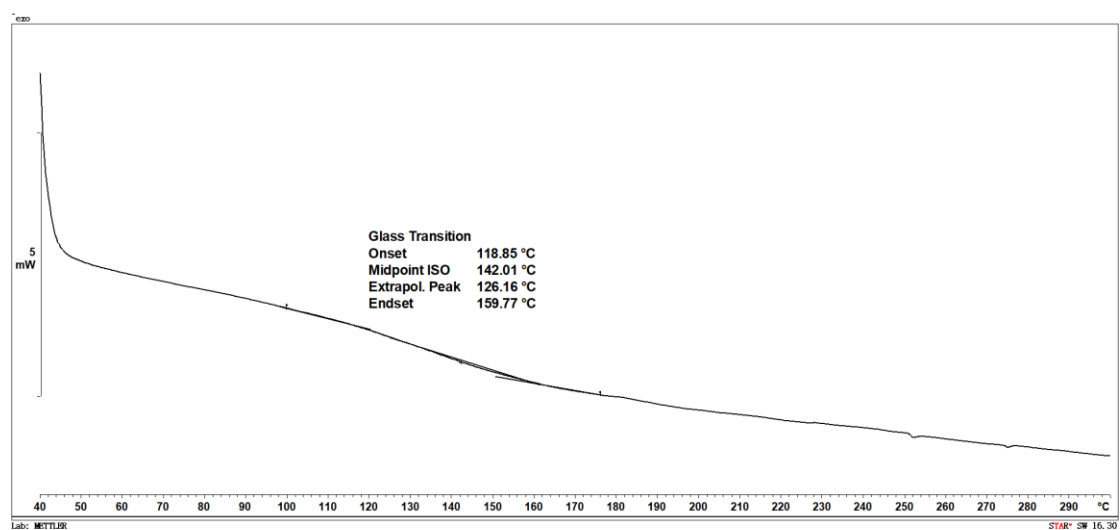
**Fig. S27** DSC curve of the TCPD/E copolymer (Table 1, entry 4).



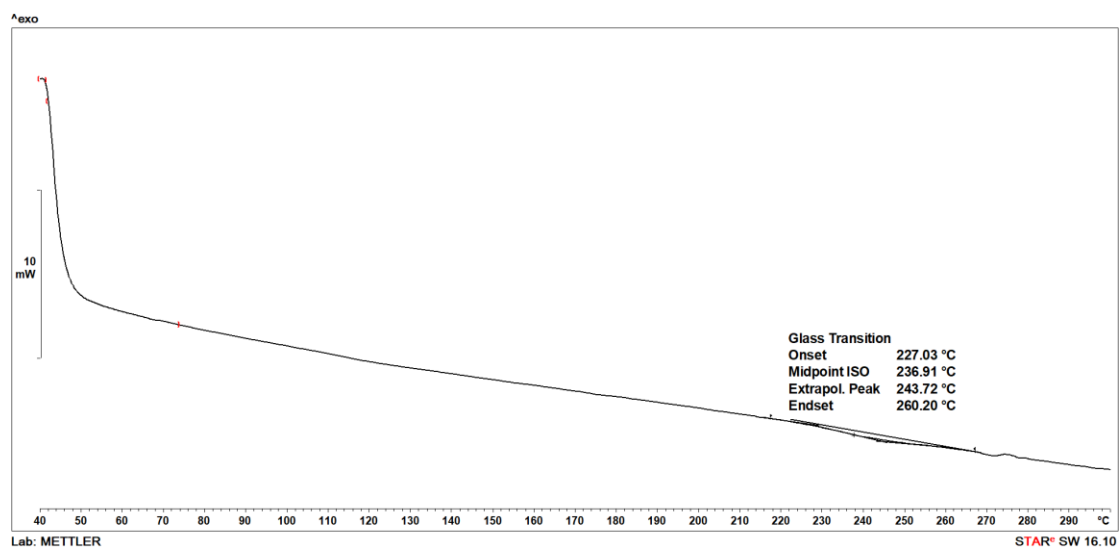
**Fig. S28** DSC curve of the TCPD/E copolymer (Table 1, entry 5).



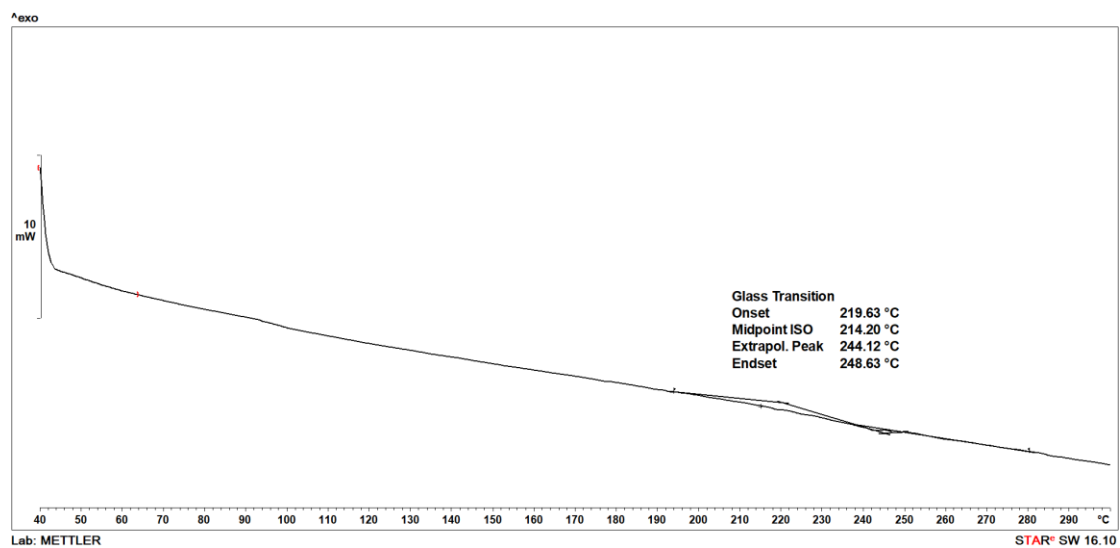
**Fig. S29** DSC curve of the TCPD/E copolymer (Table 1, entry 6).



**Fig. S30** DSC curve of the TCPD/E copolymer (Table 1, entry 7).

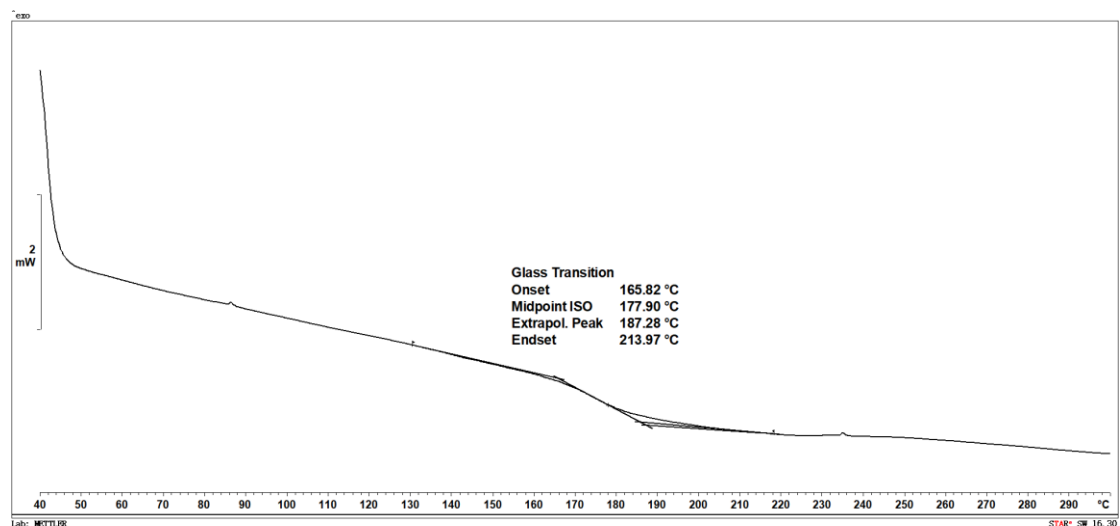


**Fig. S31** DSC curve of the TCPD/E copolymer (Table 1, entry 8).

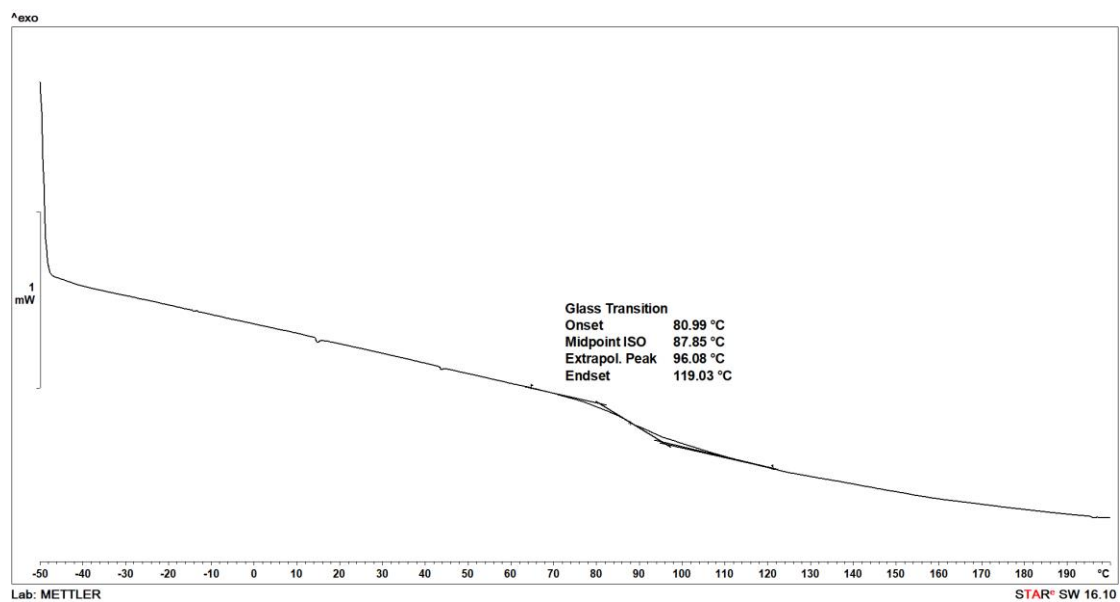


**Fig. S32** DSC curve of the TCPD/E copolymer (Table 1, entry 9).

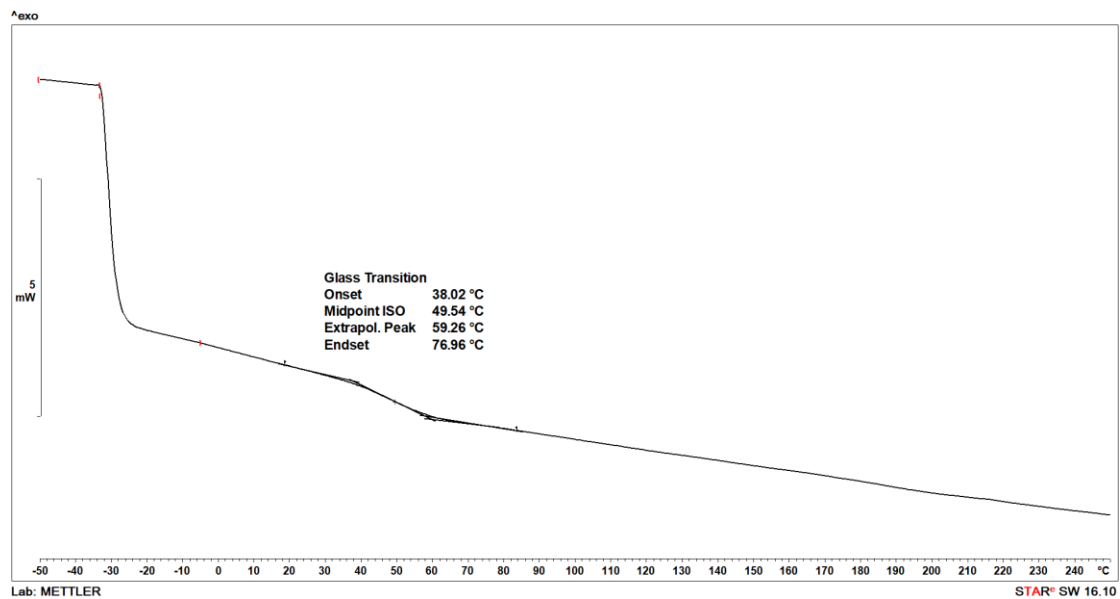




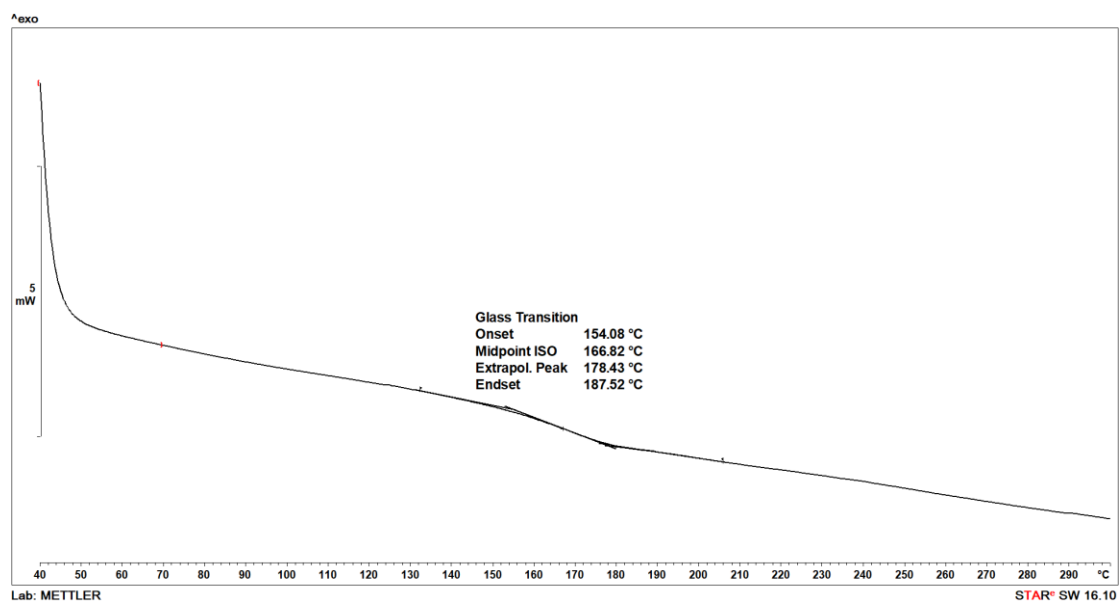
**Fig. S33** DSC curve of the TCPD/E copolymer (Table 1, entry 10).



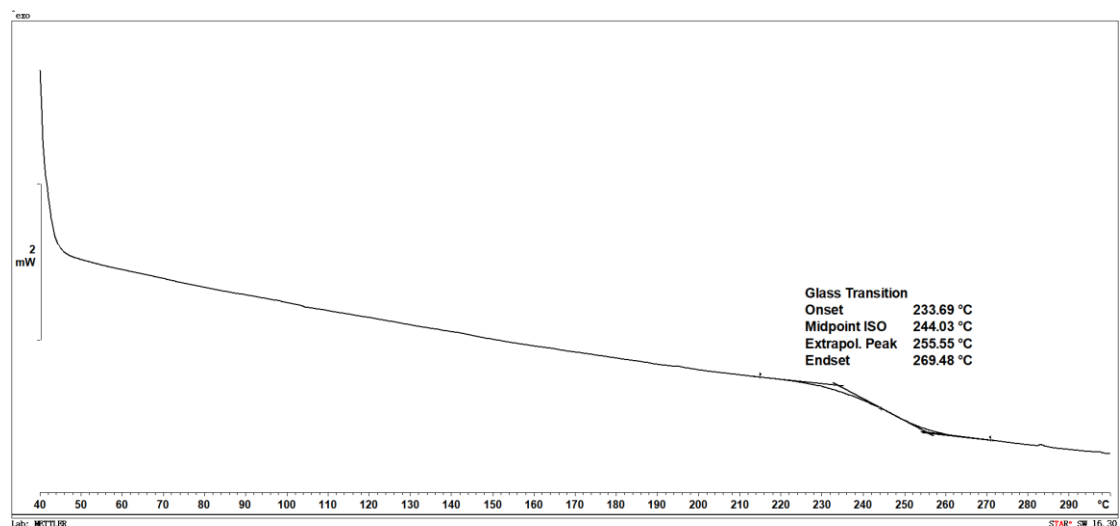
**Fig. S34** DSC curve of the TCPD/E copolymer (Table 1, entry 11).



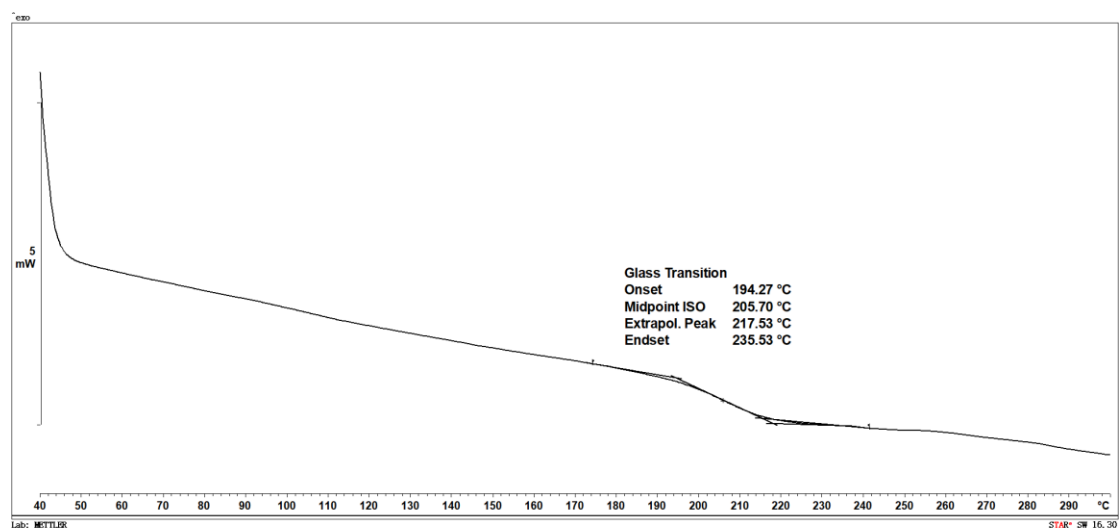
**Fig. S35** DSC curve of the TCPD/E copolymer (Table 1, entry 12).



**Fig. S36** DSC curve of the hydrogenated TCPD/E copolymer (Table 2, entry 1).



**Fig. S37** DSC curve of the hydrogenated TCPD/E copolymer (Table 2, entry 2).



**Fig. S38** DSC curve of the hydrogenated TCPD/E copolymer (Table 2, entry 3).

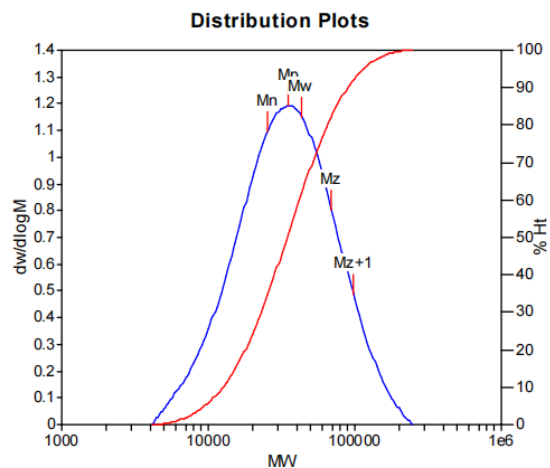


Fig. S39 GPC curve of the TCPD/E copolymer (Table 1, entry 1).

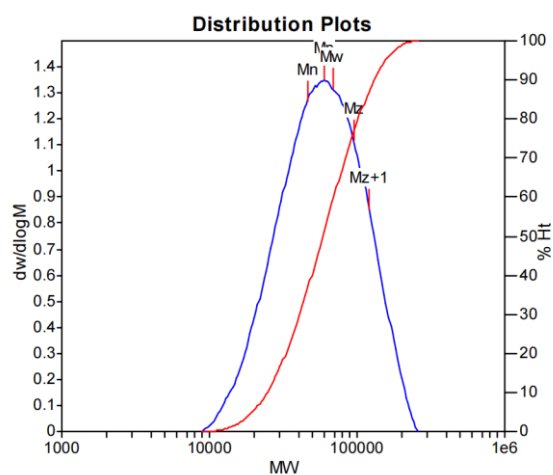


Fig. S40 GPC curve of the TCPD/E copolymer (Table 1, entry 2).

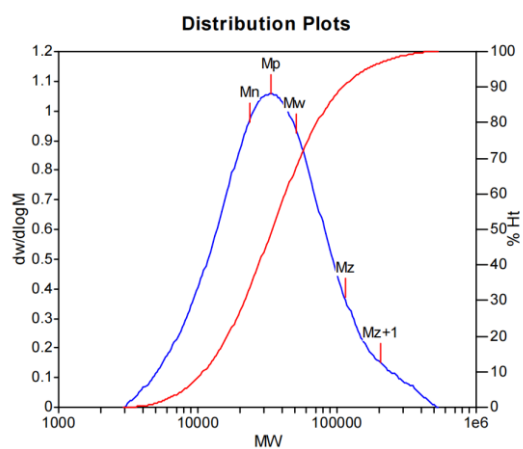
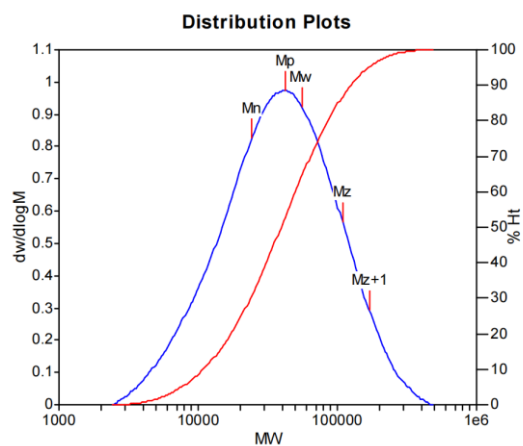
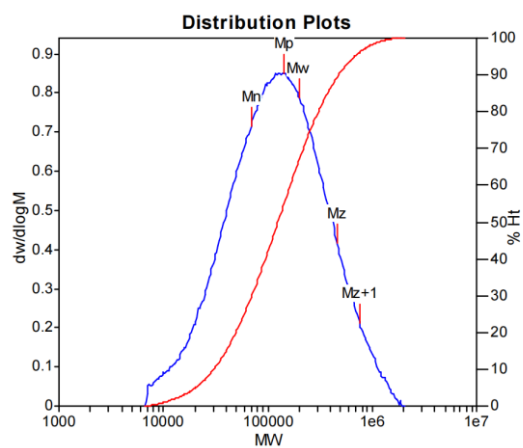


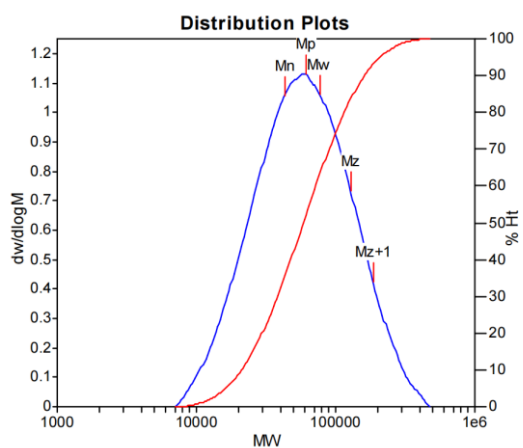
Fig. S41 GPC curve of the TCPD/E copolymer (Table 1, entry 3).



**Fig. S42** GPC curve of the TCPD/E copolymer (Table 1, entry 4).



**Fig. S43** GPC curve of the TCPD/E copolymer (Table 1, entry 5).



**Fig. S44** GPC curve of the TCPD/E copolymer (Table 1, entry 6).

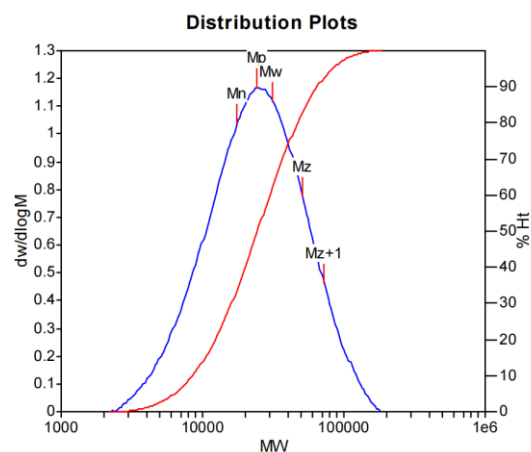


Fig. S45 GPC curve of the TCPD/E copolymer (Table 1, entry 7).

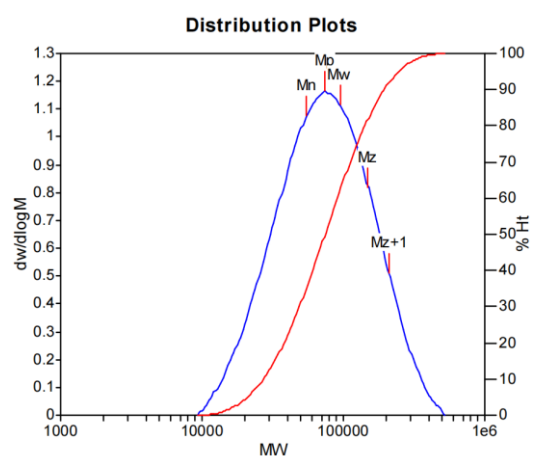


Fig. S46 GPC curve of the TCPD/E copolymer (Table 1, entry 8).

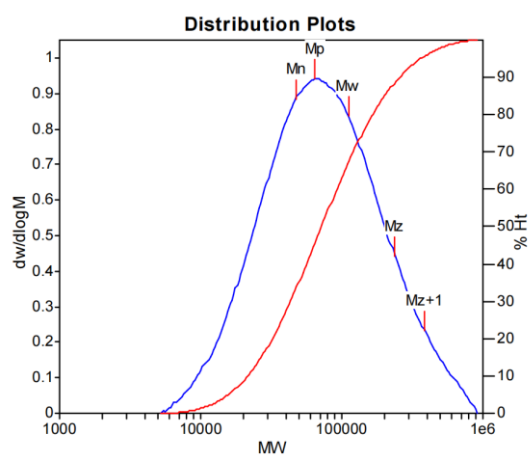


Fig. S47 GPC curve of the TCPD/E copolymer (Table 1, entry 9).

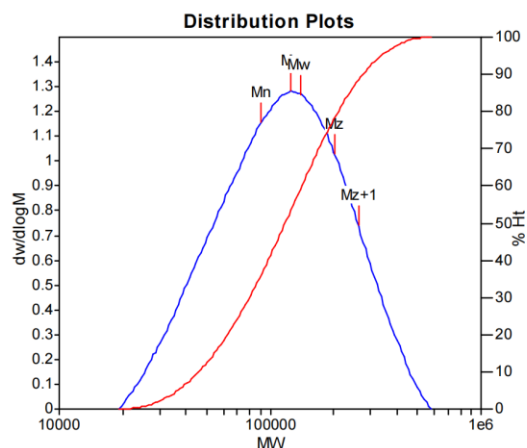


Fig. S48 GPC curve of the TCPD/E copolymer (Table 1, entry 10).

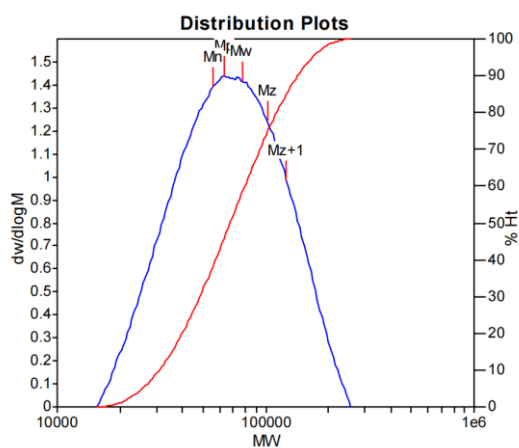


Fig. S49 GPC curve of the TCPD/E copolymer (Table 1, entry 11).

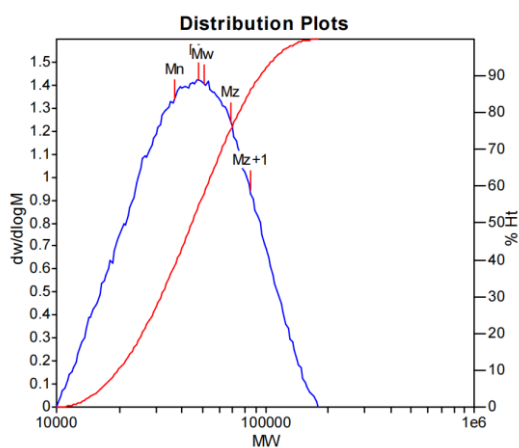
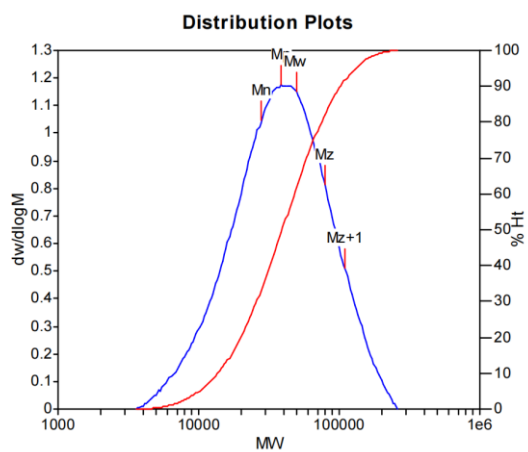
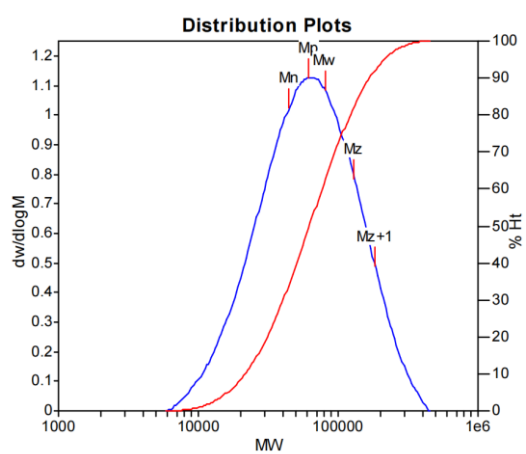


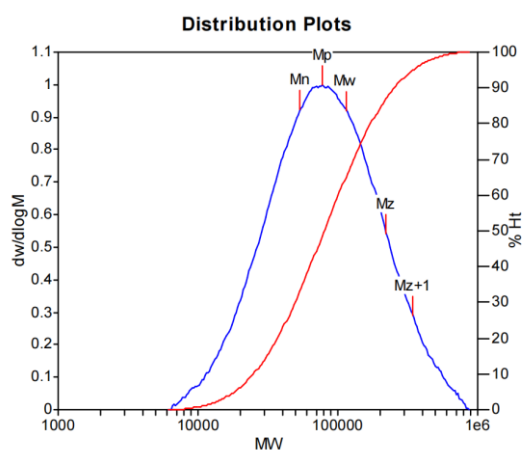
Fig. S50 GPC curve of the TCPD/E copolymer (Table 1, entry 12).



**Fig. S51** GPC curve of the hydrogenated TCPD/E copolymer (Table 2, entry 1).



**Fig. S52** GPC curve of the hydrogenated TCPD/E copolymer (Table 2, entry 2).



**Fig. S53** GPC curve of the hydrogenated TCPD/E copolymer (Table 2, entry 3).