

**Electronic Supplementary Information**  
**Polyesters derived from Bio-based Eugenol and 10-Undecenoic**  
**acid: Synthesis, Characterization, and Structure-Property**  
**Relationships**

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## 1. Experimental Section

### Preparation of precursor P1: 2-methoxy-4-[3-(2-methoxy-2-oxoethyl)]thiopropyl phenol

Eugenol (3.31 g, 20 mmol), methyl thioglycolate (2.57 g, 24 mmol), and benzoin dimethyl ether (DMPA, 0.0257 g, 0.1 mmol) as the photoinitiator, were transferred into a 10 mL quartz tube and adequately mixed into a homogeneous phase. Then the reaction system was irradiated with four 6W ultraviolet lamps ( $\lambda = 365$  nm), and detected by TLC (thin-layer chromatography) until eugenol completely disappearing. The crude product was immediately purified by column chromatography (petroleum ether/ethyl acetate, PE / EA = 5 : 1, v/v) to afford 5.12 g **P1** as a yellow oil. 95% yield; b.p.183-185°C (5 mmHg).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.85-1.93 (quint,  $J = 7.3$  Hz, 2H,  $-\text{SCH}_2-\text{CH}_2-\text{CH}_2-$ ), 2.61-2.66 (m, 4H,  $-\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ), 3.22 (s, 2H,  $-\text{S}-\text{CH}_2-\text{COOCH}_3$ ), 3.71 (s, 3H,  $-\text{COO}-\text{CH}_3$ ), 3.86 (s, 3H,  $\text{ArO}-\text{CH}_3$ ), 5.53 (s, 1H,  $\text{Ar}-\text{OH}$ ), 6.65–6.83 (m, 3H,  $\text{Ar}-\text{H}$ ) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  30.79 ( $-\text{SCH}_2-\text{CH}_2-\text{CH}_2-$ ), 32.05 ( $-\text{S}-\text{CH}_2-\text{CH}_2\text{CH}_2-$ ), 33.43 ( $-\text{SCH}_2\text{CH}_2-\text{CH}_2-$ ), 34.27 ( $-\text{S}-\text{CH}_2-\text{COOCH}_3$ ), 52.32 ( $-\text{COO}-\text{CH}_3$ ), 55.92 ( $\text{ArO}-\text{CH}_3$ ), 111.28 ( $\text{Ar}-\text{C}$ ), 114.46 ( $\text{Ar}-\text{C}$ ), 121.03 ( $\text{Ar}-\text{C}$ ), 133.20 ( $\text{Ar}-\text{C}$ ), 143.94 ( $\text{Ar}-\text{C}$ ), 146.61 ( $\text{Ar}-\text{C}$ ), 171.07 ( $-\text{CO}-\text{OCH}_3$ ) ppm; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{17}\text{O}_4\text{S}$  [ $\text{M}-\text{H}$ ] $^-$ : 269.0848, found 269.0852.

### Preparation of precursor P2: 2-methoxy-4-[3-(2-hydroxyethyl)]thiopropyl phenol

Eugenol (3.31 g, 20 mmol), 2-mercaptoethanol (1.91 g, 24 mmol), and benzoin dimethyl ether (DMPA, 0.0257 g, 0.1 mmol) as the photoinitiator, reacted as the same manner of **P1**. The crude product was washed three times by water from dichloromethane. The organic phase was dried over anhydrous magnesium sulphate, and then purified by column chromatography (PE : EA = 2 : 1) to afford 4.45 g **P2** as a yellow oil. 92% yield; b.p.218-220°C (5 mmHg).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.83-1.90 (quint,  $J = 7.2$  Hz, 2H,  $-\text{SCH}_2-\text{CH}_2-\text{CH}_2-$ ), 2.49-2.53 (t,  $J = 7.2$  Hz, 2H,  $-\text{S}-\text{CH}_2-\text{CH}_2\text{CH}_2-$ ), 2.61-2.65 (t,  $J = 7.4$  Hz, 2H,  $-\text{SCH}_2\text{CH}_2-\text{CH}_2-$ ), 2.68–2.71 (t,  $J = 6.2$  Hz, 2H,  $-\text{CH}_2-\text{CH}_2\text{OH}$ ), 3.68-3.71 (t,  $J = 6.0$  Hz, 2H,  $-\text{CH}_2-\text{OH}$ ), 3.84 (s, 3H,  $\text{ArO}-\text{CH}_3$ ), 6.64-6.832 (m, 3H,  $\text{Ar}-\text{H}$ ) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  31.19 ( $-\text{SCH}_2-\text{CH}_2-\text{CH}_2-$ ), 31.53 ( $-\text{S}-\text{CH}_2-\text{CH}_2\text{CH}_2-$ ), 34.38 ( $-\text{SCH}_2\text{CH}_2-\text{CH}_2-$ ), 34.88 ( $-\text{CH}_2-\text{CH}_2\text{OH}$ ), 55.98 ( $\text{ArO}-\text{CH}_3$ ), 60.83 ( $-\text{CH}_2-\text{OH}$ ), 111.48 ( $\text{Ar}-\text{C}$ ), 114.70 ( $\text{Ar}-\text{C}$ ), 121.02 ( $\text{Ar}-\text{C}$ ), 133.36 ( $\text{Ar}-\text{C}$ ), 143.91 ( $\text{Ar}-\text{C}$ ), 146.78 ( $\text{Ar}-\text{C}$ ) ppm; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{18}\text{O}_3\text{NaS}$  [ $\text{M}+\text{Na}$ ] $^+$ : 265.0874, found 265.0872.

**Preparation of monomer M1: methyl 2-{2-methoxy-4-[3-(2-methoxy-2-oxoethyl)]thiopropyl}phenoxy acetate**

Precursor **P1** (2.70 g, 10 mmol), methyl chloroacetate (2.16 g, 20 mmol), anhydrous  $K_2CO_3$  (2.76 g, 20 mmol), KI (0.083 g, 0.5 mmol), and 50 mL anhydrous  $CH_3CN$  were added into a 100 mL three-necked round bottom flask equipped with a magneton. Subsequently, the reaction mixture was refluxed at  $82^\circ C$  for 6 h in the protection of nitrogen. Then the suspension was cooled to room temperature, white solid was filtered off. The filtrate was concentrated under vacuum. Then the residue viscous oil was dissolved in 100 mL dichloromethane, and successively washed by water ( $2 \times 30$  mL), saturated NaCl solution ( $2 \times 30$  mL). The organic phase was dried over anhydrous magnesium sulphate, concentrated under vacuum. The resulting residue was purified by column chromatography (PE : EA = 3 : 1) to afford 2.96 g **M1** as a yellow viscous oil. 96% yield; b.p.  $196-197^\circ C$  (5 mmHg).

$^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.86–1.94 (quint,  $J = 7.4$  Hz, 2H,  $-SCH_2-CH_2-CH_2-$ ), 2.61–2.68 (m, 4H,  $-S-CH_2-CH_2-CH_2-$ ), 3.22 (s, 2H,  $-S-CH_2-COOCH_3$ ), 3.71 (s, 3H,  $-SCH_2COO-CH_3$ ), 3.78 (s, 3H,  $ArOCH_2COO-CH_3$ ), 3.87 (s, 3H,  $ArO-CH_3$ ), 4.66 (s, 2H,  $ArO-CH_2-COOCH_3$ ), 6.66–6.78 (m, 3H,  $Ar-H$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ , 100.6 MHz):  $\delta$  30.50 ( $-SCH_2-CH_2-CH_2-$ ), 31.97 ( $-S-CH_2-CH_2CH_2-$ ), 33.35 ( $-SCH_2CH_2-CH_2-$ ), 34.16 ( $-S-CH_2-COOCH_3$ ), 52.01 ( $-SCH_2COO-CH_3$ ), 52.23 ( $ArOCH_2COO-CH_3$ ), 55.85 ( $ArO-CH_3$ ), 66.67 ( $ArO-CH_2-COOCH_3$ ), 112.57 ( $Ar-C$ ), 114.74 ( $Ar-C$ ), 120.28 ( $Ar-C$ ), 135.82 ( $Ar-C$ ), 145.52 ( $Ar-C$ ), 149.58 ( $Ar-C$ ), 169.54 ( $ArOCH_2-CO-OCH_3$ ), 170.85 ( $-SCH_2-CO-OCH_3$ ) ppm; FTIR: 2949, 1739 (C=O), 1760 (C=O), 1514, 1277, 1150, 1008,  $767\text{ cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $C_{16}H_{23}O_6NaS$   $[M+Na]^+$ : 365.1035, found 365.1035.

**Preparation of monomer M2: 1,4-bis{2-methoxy-4-[3-(2-methoxy-2-oxoethyl)]thiopropyl}-Phenoxy butane**

Precursor **P1** (5.67 g, 21 mmol), 1,4-dibromobutane (2.18 g, 10 mmol), anhydrous  $K_2CO_3$  (3.03 g, 22 mmol), KI (0.083 g, 0.5 mmol), and 80 mL anhydrous  $CH_3CN$ , were added into a 250 mL three-necked round bottom flask equipped with a magneton. Subsequently, the reaction mixture was refluxed at  $82^\circ C$  for 48 h in the protection of nitrogen. Then the suspension was cooled to room temperature, white solid was filtered off. The filtrate was concentrated under vacuum, then the residue viscous oil was dissolved in 200 mL dichloromethane, and successively washed by water ( $2 \times 80$  mL) and saturated NaCl solution ( $2 \times 80$  mL). The organic phase was dried over anhydrous magnesium sulphate, concentrated under vacuum. The resulting residue was

immediately purified by twice-recrystallization from methanol to afford 4.87 g **M2** as a white crystallization solid. 86% yield; m.p.78-79°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.87-1.94 (quint, *J* = 7.2 Hz, 4H, -SCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.01 (m, 4H, ArOCH<sub>2</sub>-CH<sub>2</sub>-), 2.62-2.67 (m, 8H, -S-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.22 (s, 4H, -S-CH<sub>2</sub>-COOCH<sub>3</sub>), 3.72 (s, 6H, -SCH<sub>2</sub>COO-CH<sub>3</sub>), 3.84 (s, 6H, ArO-CH<sub>3</sub>), 4.06 (m, 4H, ArO-CH<sub>2</sub>-CH<sub>2</sub>-), 6.67-6.82 (m, 3H, Ar-*H*) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 26.10 (ArOCH<sub>2</sub>-CH<sub>2</sub>-), 30.68 (-SCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 32.10 (-S-CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>-), 33.48 (-SCH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-), 34.23 (-S-CH<sub>2</sub>-COOCH<sub>3</sub>), 52.33 (-SCH<sub>2</sub>COO-CH<sub>3</sub>), 56.00 (ArO-CH<sub>3</sub>), 68.88 (ArO-CH<sub>2</sub>-CH<sub>2</sub>-), 112.45 (Ar-C), 113.48 (Ar-C), 120.41 (Ar-C), 134.14 (Ar-C), 146.83 (Ar-C), 149.47 (Ar-C), 170.96 (-SCH<sub>2</sub>-CO-OCH<sub>3</sub>) ppm; FTIR: 2956, 1730 (C=O), 1514, 1225, 1139, 1006, 781 cm<sup>-1</sup>; HRMS (ESI) m/z calcd for C<sub>30</sub>H<sub>42</sub>O<sub>8</sub>NaS<sub>2</sub> [M+Na]<sup>+</sup>: 617.2219, found 617.2218.

### **Preparation of monomer M3: 2-{2-methoxy-4-[3-(2-hydroxyethyl)]thiopropyl}phenoxy alcohol**

Precursor **P2** (4.84 g, 20 mmol), ethylene carbonate (3.59 g, 40 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (5.52 g, 40 mmol) and 60 mL anhydrous DMF, were added into a 100 mL three-necked round bottom flask equipped with a magneton. Subsequently, the reaction mixture was reacted at 80°C for 24 h in the protection of nitrogen. Then the suspension was cooled to room temperature, white solid was filtered off. The filtrate was dissolved into 200 mL dichloromethane, and successively washed by water (2 × 50 mL) and saturated NaCl solution (2 × 50 mL). The organic phase was dried over anhydrous magnesium sulfate, concentrated under vacuum. The resulting residue was purified by column chromatography (PE : EA = 1 : 2) to afford 4.86 g **M3** as a white solid. 85% yield; m.p.32-33°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.85-1.93 (quint, *J* = 7.1 Hz, 2H, -SCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.51-2.55 (t, *J* = 7.2 Hz, 2H, -S-CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>-), 2.64-2.69 (t, *J* = 7.2 Hz, 2H, -SCH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-), 2.70-2.73 (t, *J* = 5.8 Hz, 2H, -S-CH<sub>2</sub>-CH<sub>2</sub>OH), 2.78 (s, 2H, -OH alcohol), 3.69-3.73 (t, *J* = 5.8 Hz, 2H, -SCH<sub>2</sub>-CH<sub>2</sub>-OH), 3.85 (s, 3H, ArO-CH<sub>3</sub>), 3.89-3.91 (t, *J* = 5.8 Hz, 2H, ArOCH<sub>2</sub>-CH<sub>2</sub>-OH), 3.90-4.11 (t, *J* = 5.8 Hz, 2H, ArO-CH<sub>2</sub>-CH<sub>2</sub>OH), 6.69-6.86 (m, 3H, Ar-*H*) ppm; <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ 31.04 (-SCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 31.35 (-S-CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>-), 34.37 (-SCH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-), 35.19 (-S-CH<sub>2</sub>-CH<sub>2</sub>OH), 55.92 (ArO-CH<sub>3</sub>), 60.49 (-SCH<sub>2</sub>-CH<sub>2</sub>-OH), 61.30 (ArOCH<sub>2</sub>-CH<sub>2</sub>-OH), 71.73 (ArO-CH<sub>2</sub>-CH<sub>2</sub>OH), 112.30 (Ar-C), 115.20 (Ar-C), 120.67 (Ar-C), 135.36 (Ar-C), 146.31 (Ar-C), 149.78 (Ar-C) ppm; FTIR: 3454, 3262, 2926, 1517, 1262, 1235, 1141, 1031, 797 cm<sup>-1</sup>; HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>NaS [M+Na]<sup>+</sup>: 309.1136, found 309.1134.

### Preparation of monomer **M4**: 1,4-bis{2-methoxy-4-[3-(2-hydroxyethyl)]thiopropyl}phenoxy butane

Precursor **P2** (5.08 g, 21 mmol), 1,4-dibromobutane (2.18 g, 10 mmol), anhydrous  $K_2CO_3$  (3.03 g, 22 mmol), KI (0.083 g, 0.5 mmol), and 80 mL anhydrous  $CH_3CN$ , were added into a 250 mL three-necked round bottom flask equipped with a magneton. Subsequently, the reaction mixture was refluxed at  $82^\circ C$  for 48 h in the protection of nitrogen. Then the suspension was cooled to room temperature, white solid was filtered off. The filtrate was concentrated under vacuum. Then the residue viscous oil was redissolved in 200 mL dichloromethane, and successively washed by water ( $2 \times 50$  mL) and saturated NaCl solution ( $2 \times 50$  mL), the organic phase was dried over anhydrous magnesium sulphate, concentrated under vacuum. The resulting residue was immediately purified by twice-recrystallization from acetone / diethyl ether ( $V_{\text{acetone}} / V_{\text{ether}} = 3:1$ ) to afford 4.57 g **M4** as a white solid. 85% yield; m.p.  $56-57^\circ C$ .

$^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.86-1.93 (quint,  $J = 7.3$  Hz, 4H,  $-SCH_2-CH_2-CH_2-$ ), 2.01 (m, 4H,  $ArOCH_2-CH_2-$ ), 2.07 (s, 2H,  $-OH$  alcohol), 2.51-2.54 (t,  $J = 7.2$  Hz, 4H,  $-S-CH_2-CH_2CH_2-$ ), 2.64-2.68 (t,  $J = 7.4$  Hz, 4H,  $-SCH_2CH_2-CH_2-$ ), 2.71-2.74 (t,  $J = 6.0$  Hz, 4H,  $-S-CH_2-CH_2OH$ ), 3.69-3.72 (t, 4H,  $J = 5.8$  Hz,  $-SCH_2-CH_2-OH$ ), 3.84 (s, 6H,  $ArO-CH_3$ ), 4.07 (m, 4H,  $ArO-CH_2-CH_2-$ ), 6.68-6.82 (m, 3H,  $Ar-H$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ , 100.6 MHz):  $\delta$  26.09 ( $ArOCH_2-CH_2-$ ), 31.11 ( $-SCH_2-CH_2-CH_2-$ ), 31.42 ( $-S-CH_2-CH_2CH_2-$ ), 34.34 ( $-SCH_2CH_2-CH_2-$ ), 35.16 ( $-S-CH_2-CH_2OH$ ), 56.05 ( $ArO-CH_3$ ), 60.57 ( $-SCH_2-CH_2-OH$ ), 68.91 ( $ArO-CH_2-CH_2-$ ), 112.48 ( $Ar-C$ ), 113.53 ( $Ar-C$ ), 120.44 ( $Ar-C$ ), 134.23 ( $Ar-C$ ), 146.82 ( $Ar-C$ ), 149.46 ( $Ar-C$ ) ppm; FTIR: 3320, 2928, 1470, 1265, 1235, 1141, 1037, 808  $cm^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $C_{28}H_{42}O_6NaS_2$   $[M+Na]^+$ : 561.2321, found 561.2318.

### Preparation of monomer **M5**: 11-[(2-hydroxyethyl)thio]undecan-1-ol

10-Undecen-1-ol (2.61 g, 15 mmol), 2-mercaptoethanol (1.43 g, 18 mmol) and DMPA (0.0192 g, 0.075 mmol) reacted following the similar protocol as **P1**. The crude product was purified by crystallization from methanol to afford 3.65 g **M5** as a white solid. 98% yield; m.p.  $62-63^\circ C$ .

$^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.28-1.44 (m, 14H,  $-CH_2-$  aliphatic), 1.53-1.62 (m, 4H,  $-SCH_2-CH_2-CH_2-$  and  $-CH_2-CH_2OH$ ), 1.88 (s, 2H,  $-OH$  alcohol), 2.50-2.54 (t,  $J = 7.4$  Hz, 2H,  $-S-CH_2-CH_2CH_2-$ ), 2.71-2.74 (t,  $J = 7.4$  Hz, 2H,  $-S-CH_2-CH_2OH$ ), 3.62-3.65 (t,  $J = 6.6$  Hz, 2H,  $-CH_2-OH$ ), 3.70-3.73 (t,  $J = 6.0$  Hz, 2H,  $-SCH_2-CH_2-OH$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ , 100.6 MHz):  $\delta$  25.75 ( $-CH_2-$  aliphatic), 28.82 ( $-CH_2-$  aliphatic), 29.17 ( $-CH_2-$  aliphatic), 29.41 ( $-CH_2-$  aliphatic), 29.45 ( $-CH_2-$  aliphatic), 29.46 ( $-CH_2-$  aliphatic), 29.54 ( $-CH_2-$  aliphatic), 29.77 ( $-CH_2-$  aliphatic),

31.83 (-CH<sub>2</sub>-CH<sub>2</sub>OH), 32.74 (-S-CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>-), 35.14 (-CH<sub>2</sub>-CH<sub>2</sub>OH), 60.51 (-CH<sub>2</sub>-OH), 62.85 (-SCH<sub>2</sub>-CH<sub>2</sub>-OH) ppm; FTIR: 3280, 2921, 2850, 1466, 1270, 1242, 1149, 1055, 724 cm<sup>-1</sup>; HRMS (ESI) m/z calcd for C<sub>13</sub>H<sub>27</sub>O<sub>2</sub>S [M-H]<sup>-</sup>: 247.1732, found 247.1740.

#### **Preparation of monomer M6: 11-[(2-methoxy-2-oxoethyl)thio]undecan-1-ol**

10-Undecen-1-ol (2.61 g, 15 mmol), methyl thioglycolate (1.93 g, 18 mmol) and DMPA (0.0192 g, 0.075 mmol) reacted following the similar protocol as **P1**. The crude product was purified by crystallization from methanol to afford 3.97 g **M6** as a white solid. 96% yield; m.p.39-40°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.28-1.44 (m, 14H, -CH<sub>2</sub>- aliphatic), 1.50 (s, 1H, -OH alcohol), 1.50-1.63 (m, 4H, -SCH<sub>2</sub>-CH<sub>2</sub>- and -CH<sub>2</sub>-CH<sub>2</sub>OH), 2.61-2.64 (t, *J* = 7.2 Hz, 2H, -S-CH<sub>2</sub>-CH<sub>2</sub>-), 3.22 (s, 2H, -S-CH<sub>2</sub>-CO-), 3.62-3.65 (t, *J* = 6.4 Hz, 2H, -CH<sub>2</sub>-OH), 3.74 (s, 3H, -COO-CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 25.75 (-CH<sub>2</sub>- aliphatic), 28.70 (-CH<sub>2</sub>- aliphatic), 28.97 (-CH<sub>2</sub>- aliphatic), 29.14 (-CH<sub>2</sub>- aliphatic), 29.41 (-CH<sub>2</sub>- aliphatic), 29.44(-CH<sub>2</sub>- aliphatic), 29.47 (-CH<sub>2</sub>- aliphatic), 29.55 (-CH<sub>2</sub>- aliphatic), 32.75 (-CH<sub>2</sub>-CH<sub>2</sub>OH), 32.76 (-S-CH<sub>2</sub>-CH<sub>2</sub>-), 33.48 (-CO-CH<sub>2</sub>-), 52.30 (-COO-CH<sub>3</sub>), 62.85 (-CH<sub>2</sub>-OH), 171.10 (-CO-) ppm; FTIR: 3325, 2921, 2851, 1736 (C=O), 1464, 1301, 1269, 1163, 1063, 898 cm<sup>-1</sup>; HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>28</sub>O<sub>3</sub>NaS [M+Na]<sup>+</sup>: 299.1657, found 299.1651.

#### **Preparation of monomer M7: methyl 11-[(2-methoxy-2-oxoethyl)thio]undecanoate**

Methyl 10-undecenoate (3.03 g, 15 mmol), methyl thioglycolate (1.93 g, 18 mmol) and DMPA (0.0192 g, 0.075 mmol) as the photoinitiator, were reacted following the similar protocol as **P1**. The crude product was purified by crystallization from methanol to afford 4.38 g **M7** as a white solid. 96% yield; m.p.32-33°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.28-1.39 (m, 12H, -CH<sub>2</sub>- aliphatic), 1.55-1.63 (m, 4H, -SCH<sub>2</sub>-CH<sub>2</sub>- and -CH<sub>2</sub>-CH<sub>2</sub>CO-), 2.28-2.32 (t, *J* = 7.4 Hz, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-CO-), 2.61-2.64 (t, *J* = 7.2 Hz, 2H, -S-CH<sub>2</sub>-CH<sub>2</sub>-), 3.22 (s, 2H, -S-CH<sub>2</sub>-CO-), 3.68 (s, 3H, -CH<sub>2</sub>CH<sub>2</sub>COO-CH<sub>3</sub>), 3.74 (s, 3H, -SCH<sub>2</sub>COO-CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 24.84 (-CH<sub>2</sub>- aliphatic), 28.61 (-CH<sub>2</sub>- aliphatic), 28.90 (-CH<sub>2</sub>- aliphatic), 29.03 (-CH<sub>2</sub>- aliphatic), 29.12 (-CH<sub>2</sub>- aliphatic), 29.25 (-CH<sub>2</sub>- aliphatic), 29.30 (-CH<sub>2</sub>- aliphatic), 32.62 (-S-CH<sub>2</sub>-CH<sub>2</sub>-), 33.34 (-CH<sub>2</sub>-CH<sub>2</sub>-CO-), 33.94 (-S-CH<sub>2</sub>-CO-), 51.23 (-SCH<sub>2</sub>COO-CH<sub>3</sub>), 52.11 (-CH<sub>2</sub>CH<sub>2</sub>COO-CH<sub>3</sub>), 170.85 (-SCH<sub>2</sub>-CO-), 173.98 (-CH<sub>2</sub>CH<sub>2</sub>-CO-) ppm; FTIR: 2926, 2853, 1739 (C=O), 1436, 1278, 1169, 1011, 880, 723 cm<sup>-1</sup>; HRMS (ESI) m/z calcd for C<sub>15</sub>H<sub>28</sub>O<sub>4</sub>NaS [M+Na]<sup>+</sup>: 327.1606, found 327.1605.

## 2. Characterization Section

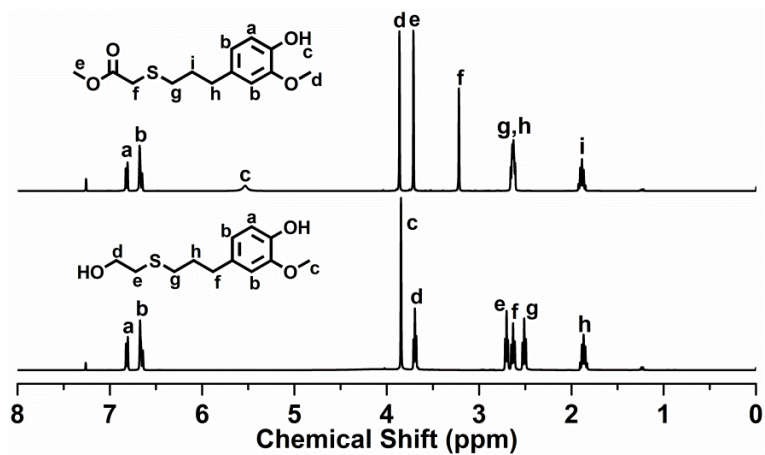


Figure S1.  $^1\text{H}$  NMR spectra of P1 and P2

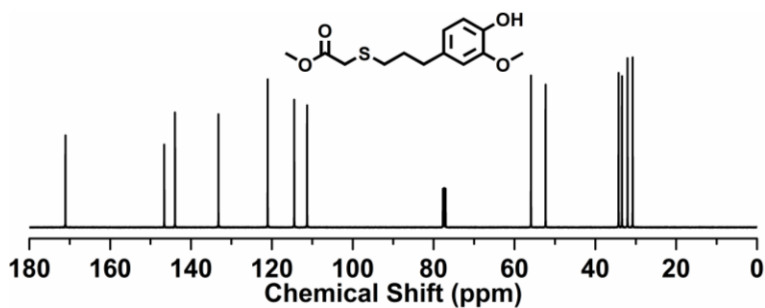


Figure S2.  $^{13}\text{C}$  NMR spectrum of P1

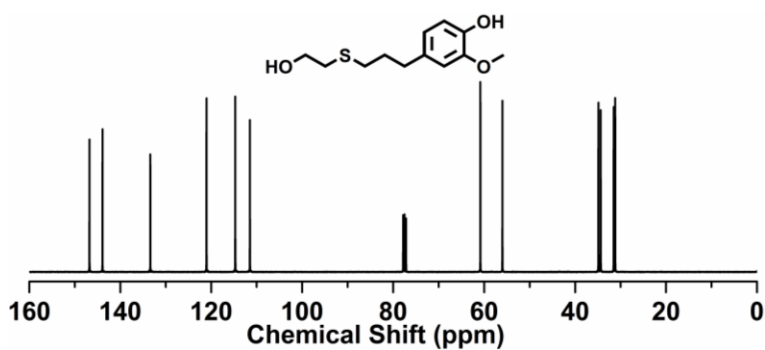


Figure S3.  $^{13}\text{C}$  NMR spectrum of P2

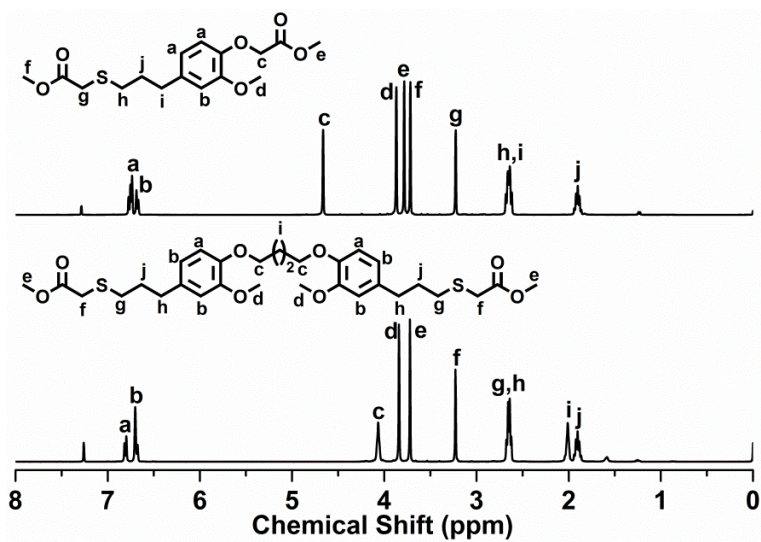


Figure S4.  $^1\text{H}$  NMR spectra of M1 and M2

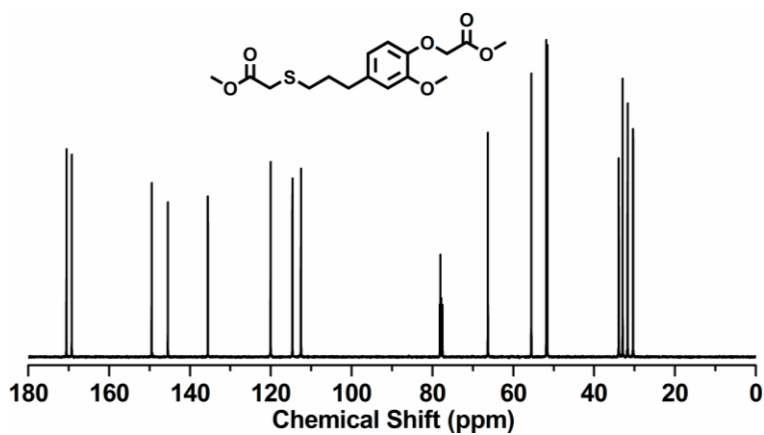


Figure S5.  $^{13}\text{C}$  NMR spectrum of M1

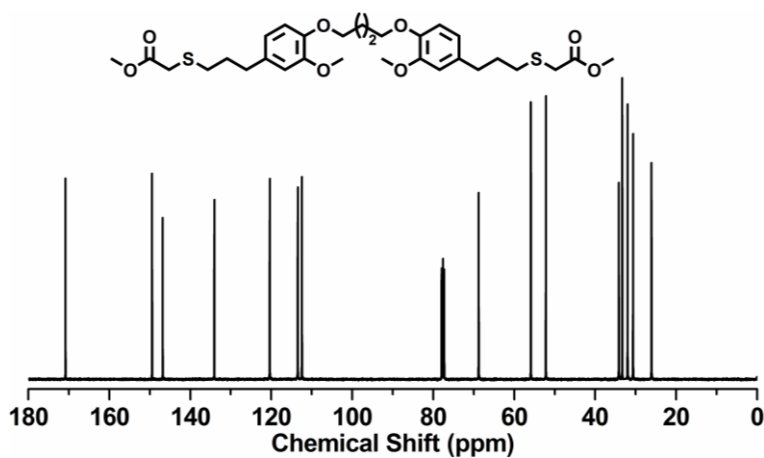
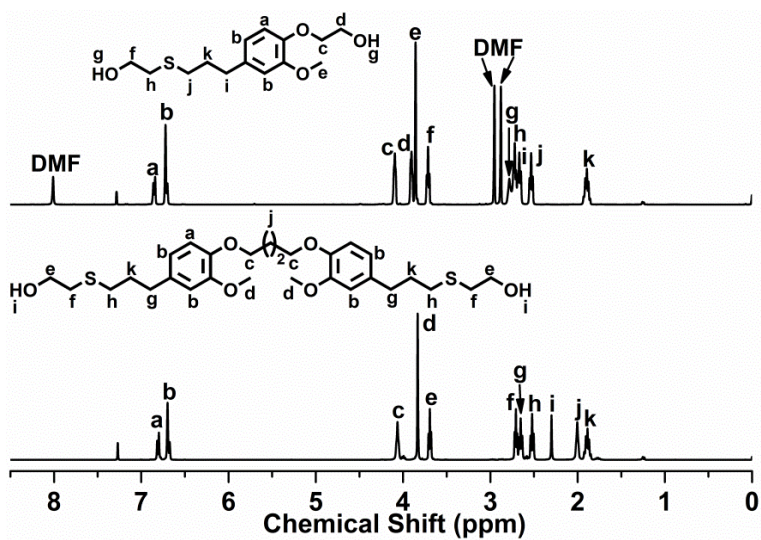
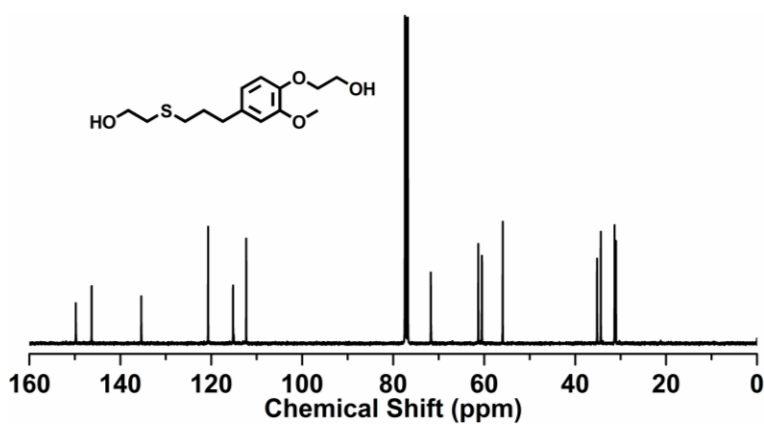


Figure S6.  $^{13}\text{C}$  NMR spectrum of M2

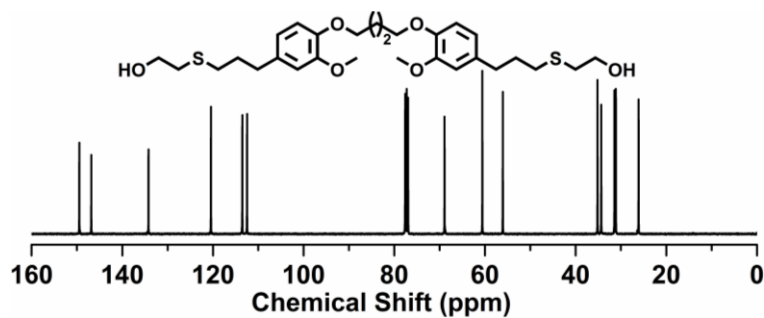




**Figure S7.**  $^1\text{H}$  NMR spectra of M3 and M4



**Figure S8.**  $^{13}\text{C}$  NMR spectrum of M3



**Figure S9.**  $^{13}\text{C}$  NMR spectrum of M4

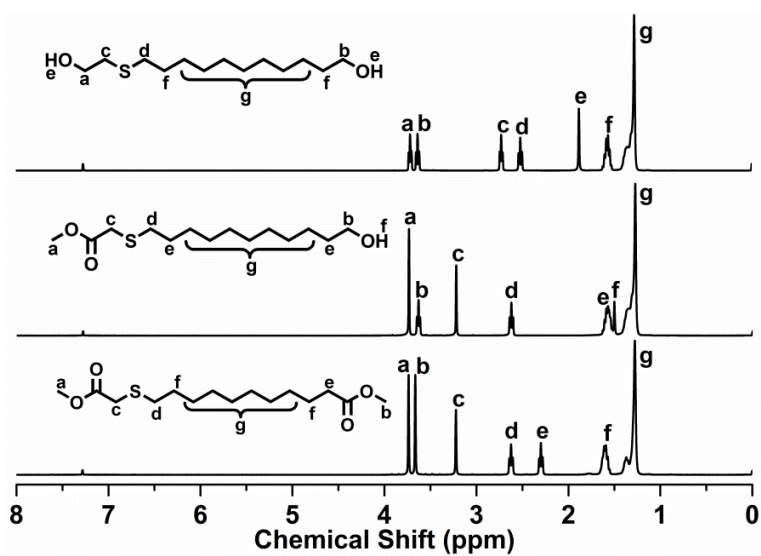


Figure S10.  $^1\text{H}$  NMR spectra of M5, M6 and M7

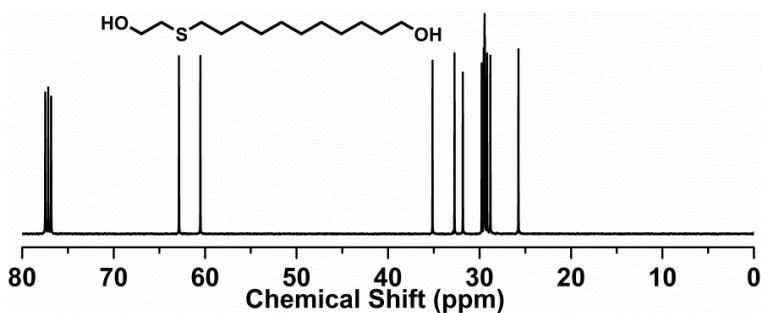


Figure S11.  $^{13}\text{C}$  NMR spectrum of M5

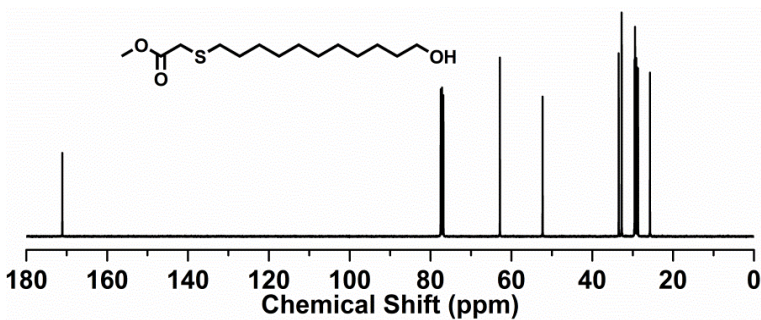


Figure S12.  $^{13}\text{C}$  NMR spectrum of M6

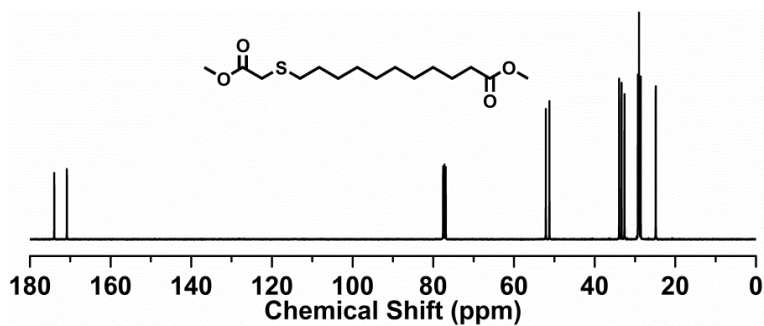


Figure S13. <sup>13</sup>C NMR spectrum of M7

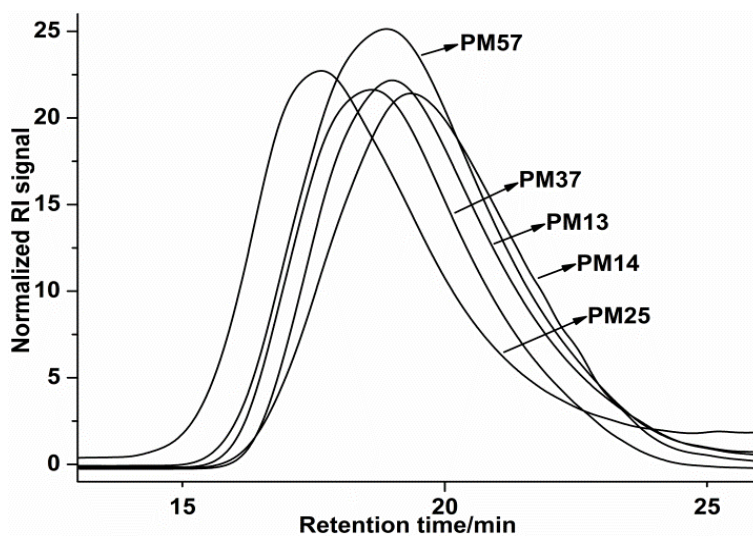


Figure S14. SEC traces of PM13, PM14, PM25, PM37 and PM57

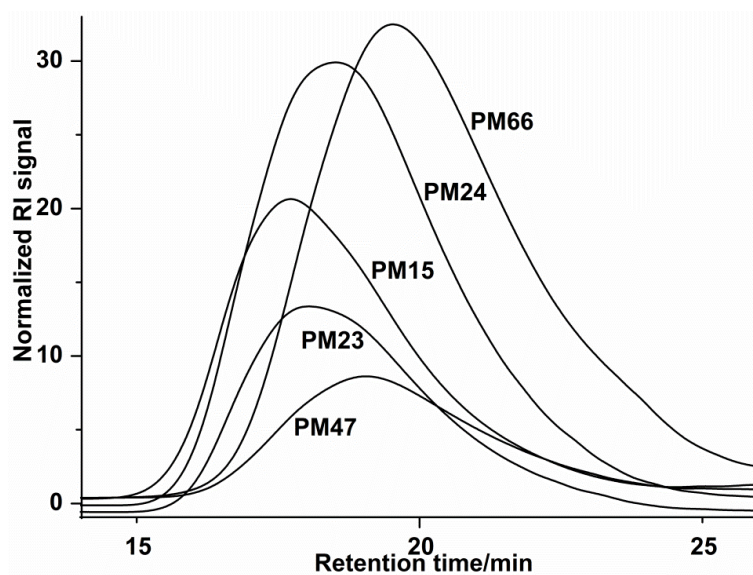
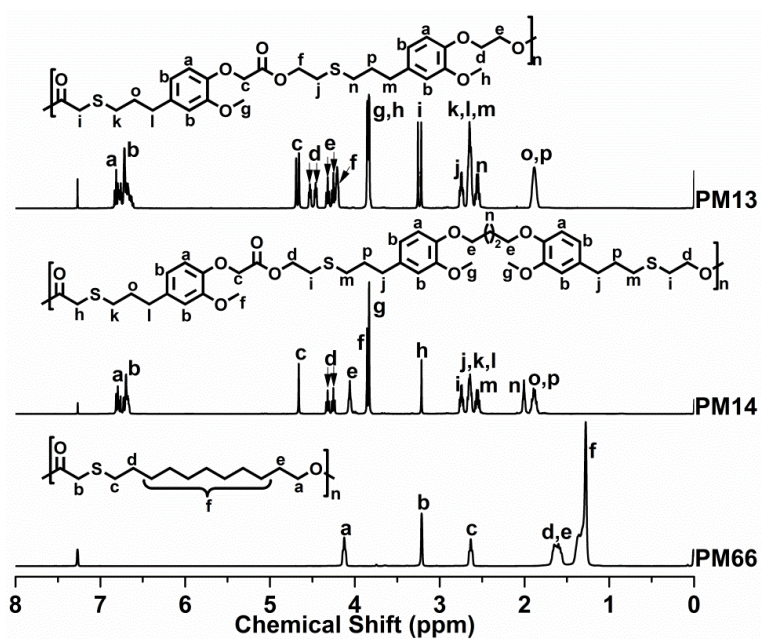
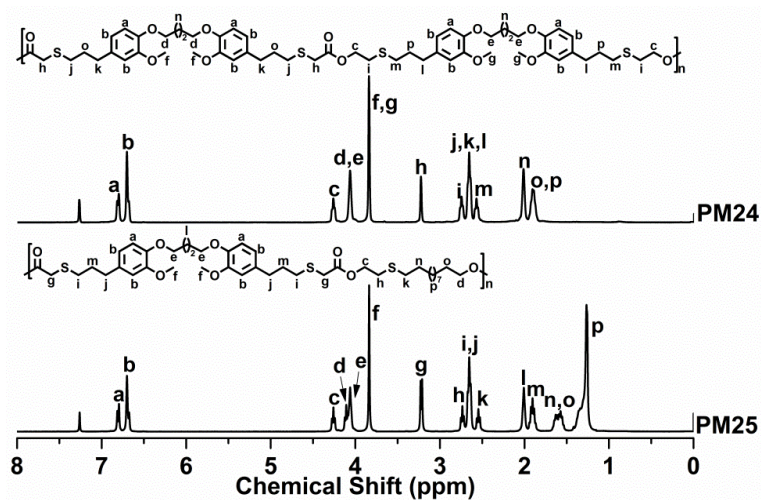


Figure S15. SEC traces of PM15, PM23, PM24, PM47 and PM66



**Figure S16.**  $^1\text{H}$  NMR spectra of **PM13**, **PM14** and **PM66**



**Figure S17.**  $^1\text{H}$  NMR spectra of **PM24** and **PM25**

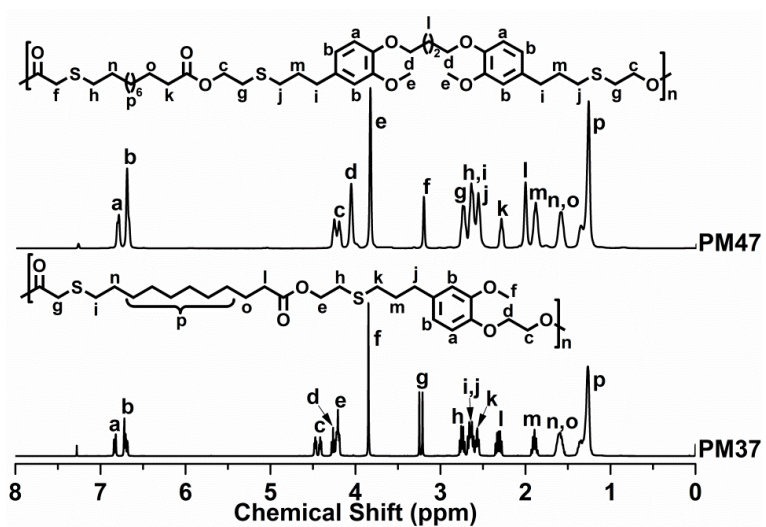


Figure S18.  $^1\text{H}$  NMR spectra of **PM37** and **PM47**

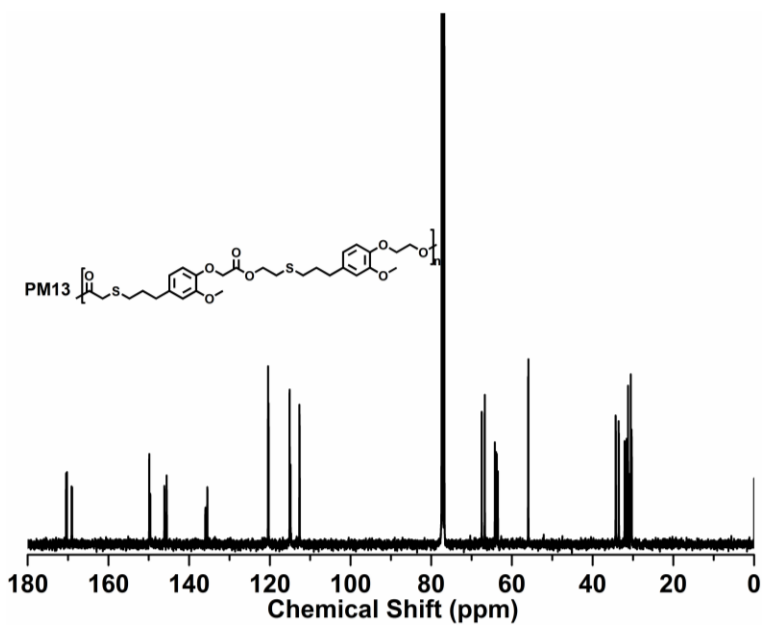


Figure S19.  $^{13}\text{C}$  NMR spectrum of **PM13**

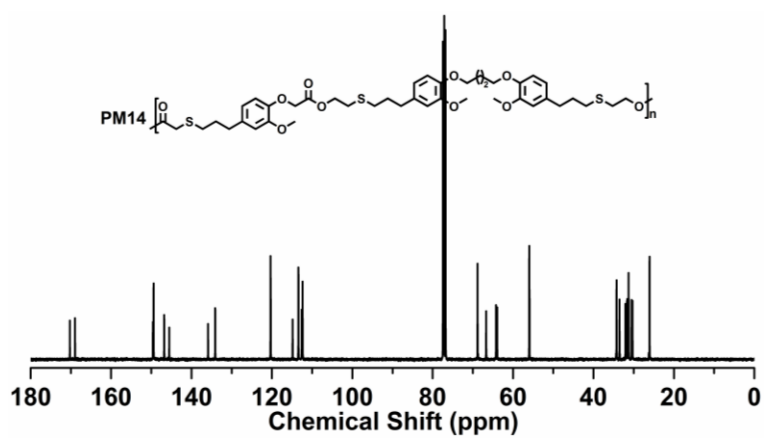


Figure S20.  $^{13}\text{C}$  NMR spectrum of PM14

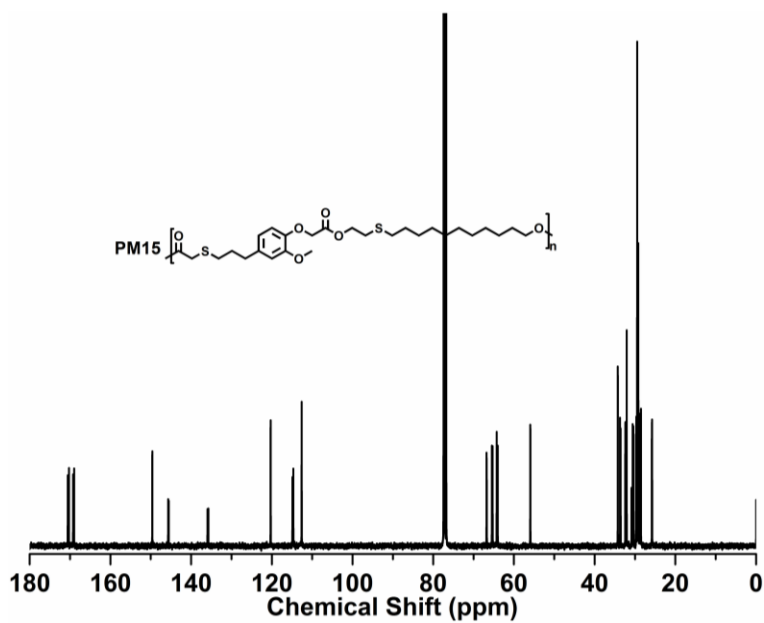


Figure S21.  $^{13}\text{C}$  NMR spectrum of PM15

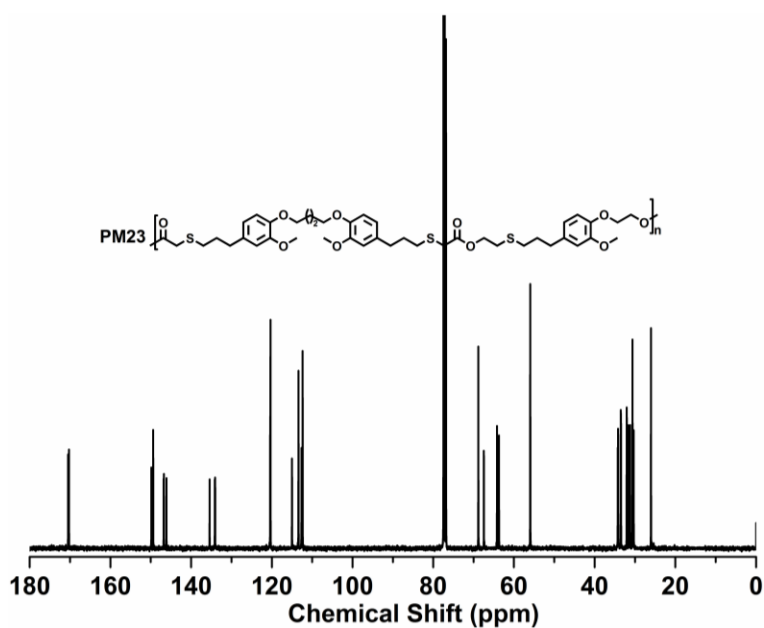


Figure S22.  $^{13}\text{C}$  NMR spectrum of PM23

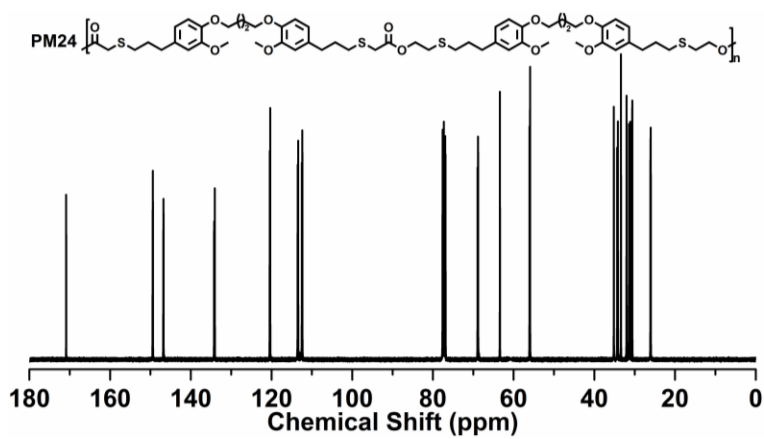
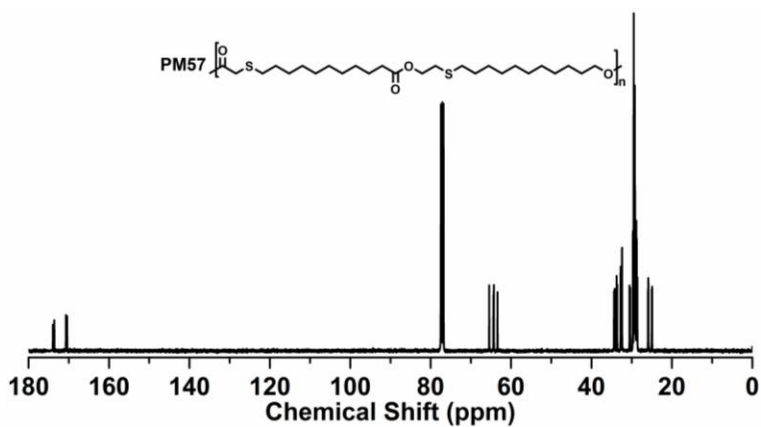


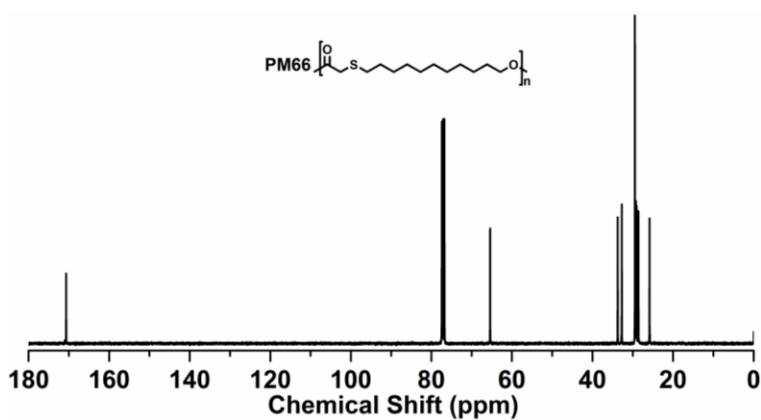
Figure S23.  $^{13}\text{C}$  NMR spectrum of PM24



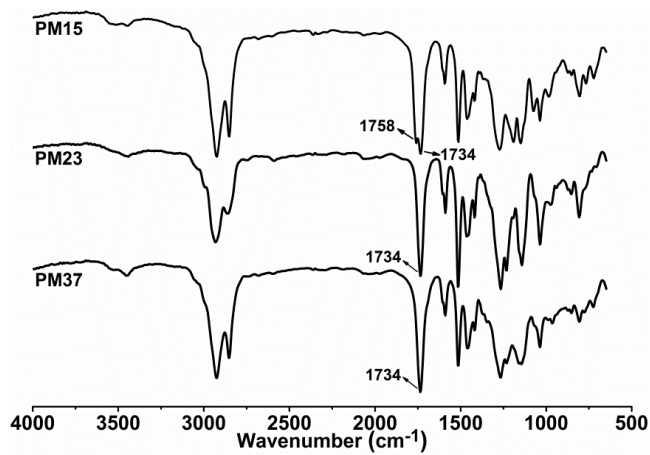




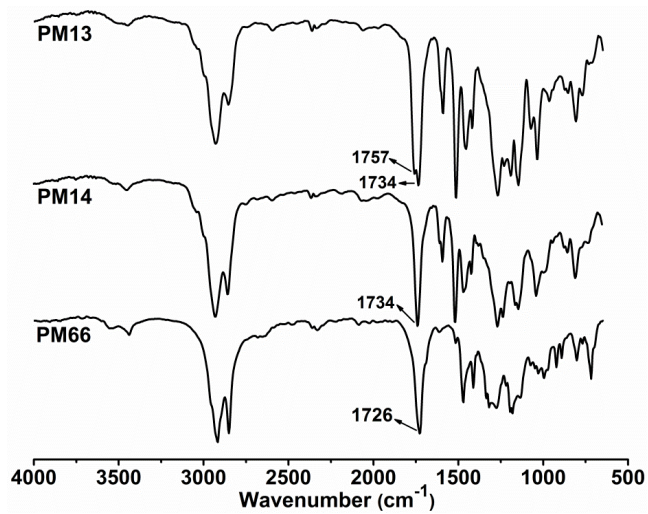
**Figure S27.**  $^{13}\text{C}$  NMR spectrum of PM57



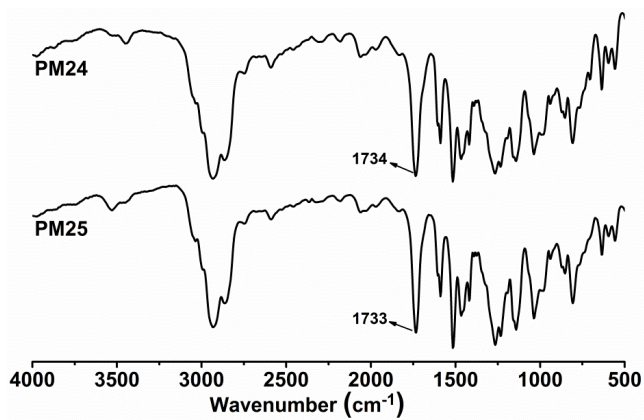
**Figure S28.**  $^{13}\text{C}$  NMR spectrum of PM66



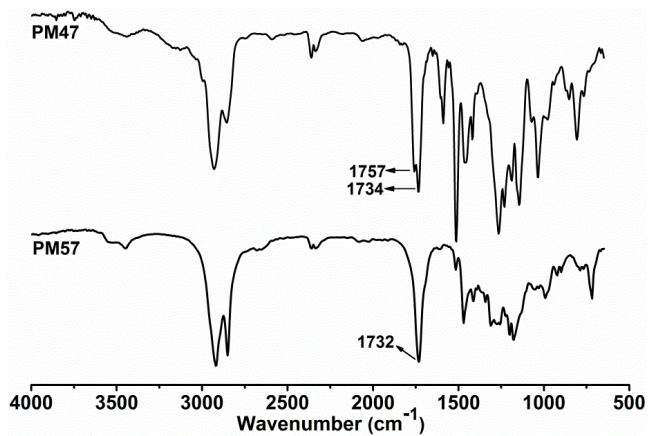
**Figure S29.** FTIR spectra of PM15, PM23 and PM37



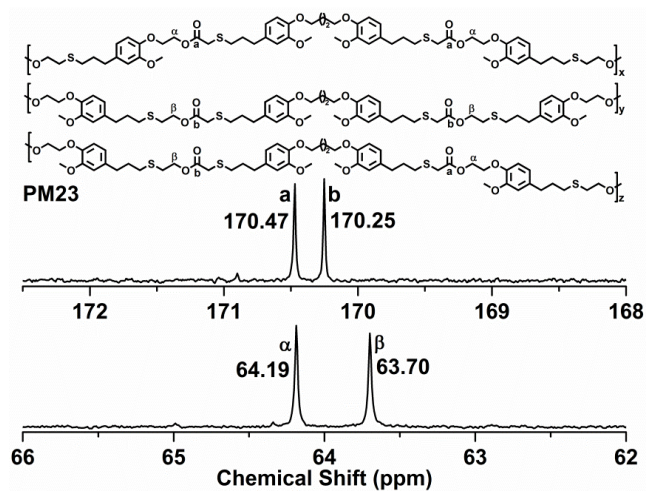
**Figure S30.** FTIR spectra of PM13, PM14 and PM66



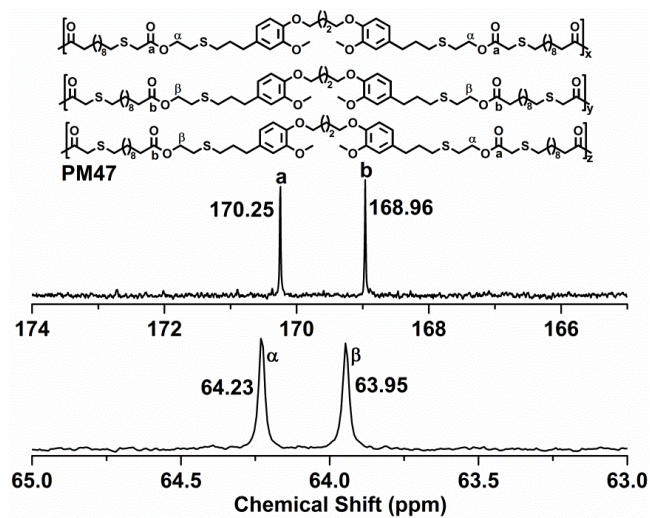
**Figure S31.** FTIR spectra of PM24 and PM25



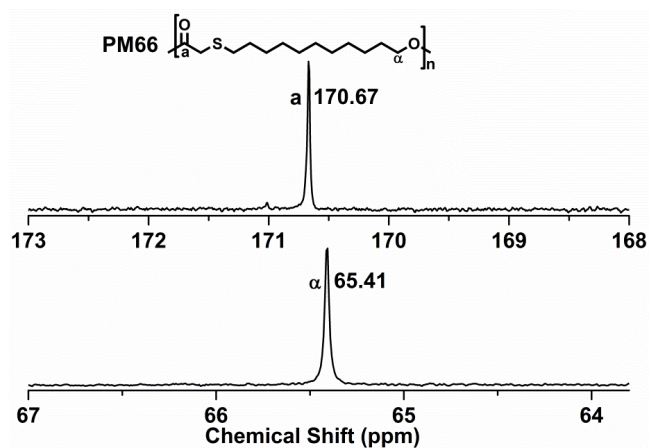
**Figure S32.** FTIR spectra of PM47 and PM57



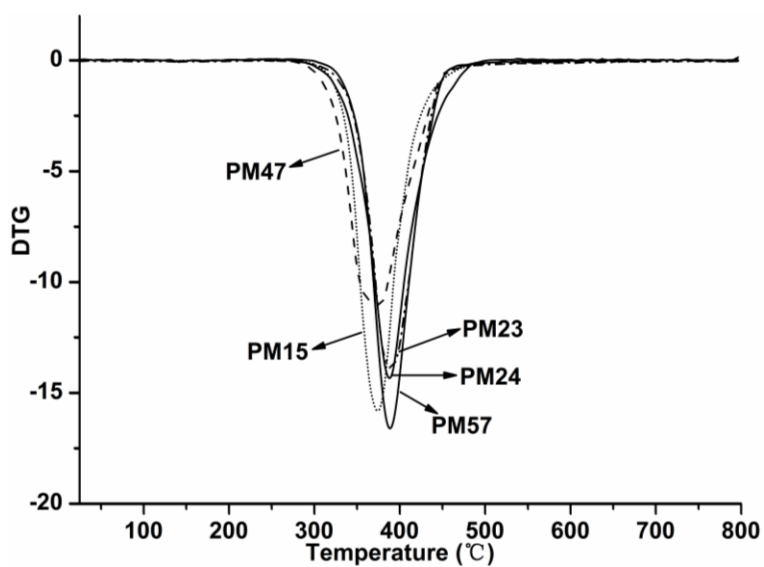
**Figure S33.**  $^{13}\text{C}$ -NMR signals used for the microstructure analysis of **PM23** with indication of the dyads to which they are assigned



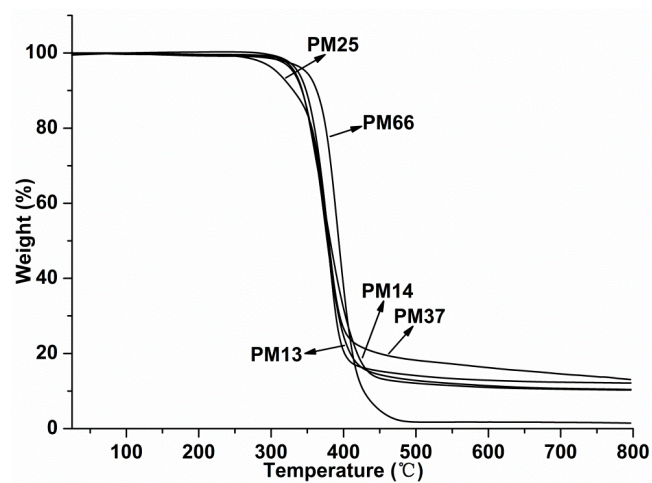
**Figure S34.**  $^{13}\text{C}$ -NMR signals used for the microstructure analysis of **PM47** with indication of the dyads to which they are assigned



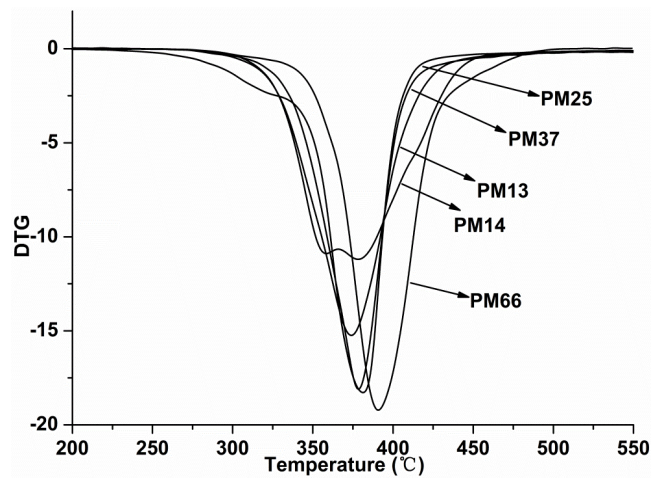
**Figure S35.**  $^{13}\text{C}$ -NMR signals used for the microstructure analysis of **PM66** with indication of the dyads to which they are assigned



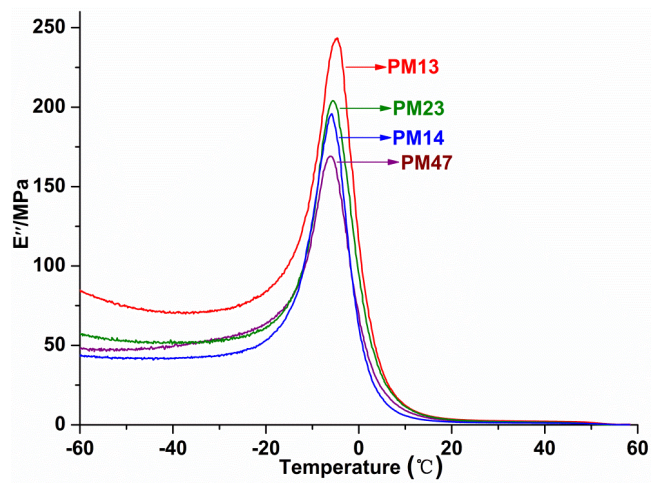
**Figure S36.** TGA derivative curves of **PM15**, **PM23**, **PM24**, **PM47** and **PM57** at a heating rate of  $10^{\circ}\text{C min}^{-1}$



**Figure S37.** TGA curves of **PM13**, **PM14**, **PM25**, **PM37** and **PM66** at a heating rate of  $10^{\circ}\text{C min}^{-1}$



**Figure S38.** TGA derivative curves of **PM13**, **PM14**, **PM25**, **PM37** and **PM66** at a heating rate of  $10^{\circ}\text{C min}^{-1}$



**Figure S39.** Loss modulus as a function of temperature for **PM13**, **PM14**, **PM23** and **PM47**