

## Supporting Information

### **A Straightforward and Rapid Synthesis of Polydithioacetals in the Presence of Chlorodimethylsilane**

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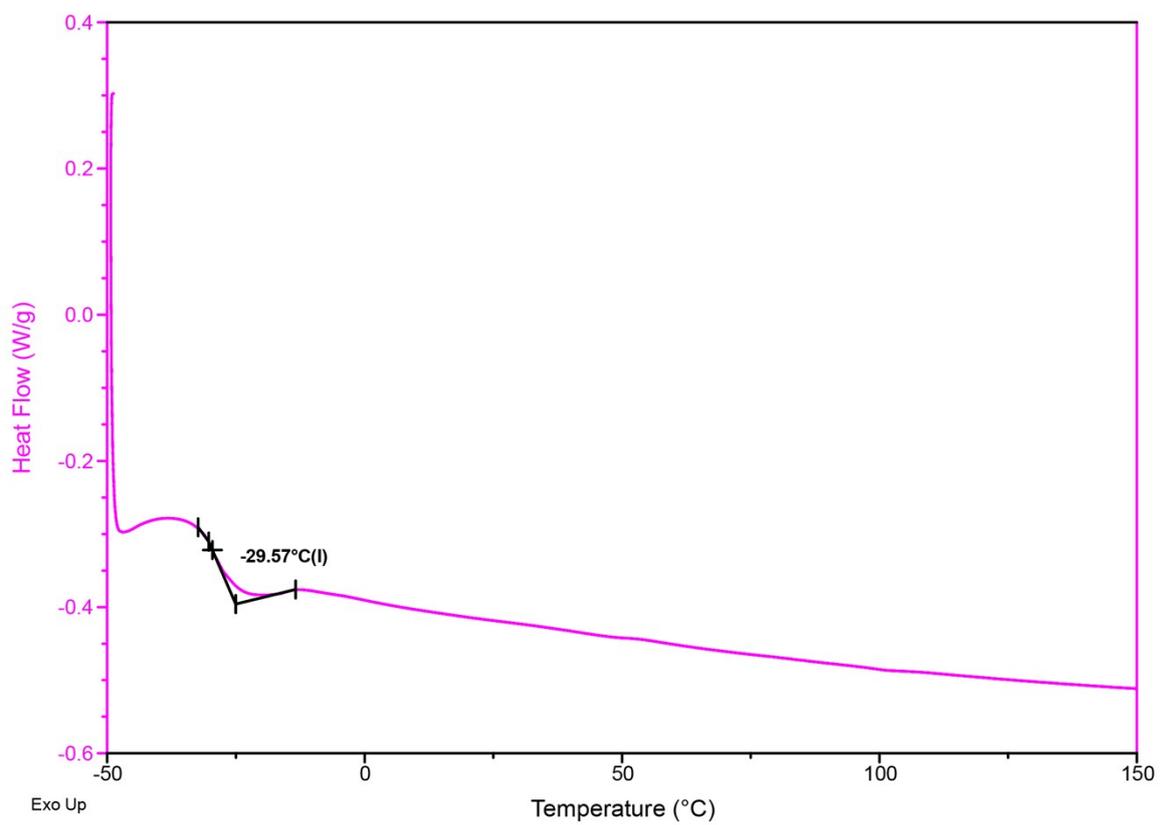
## Materials

Benzaldehyde (BA, purified by redistillation,  $\geq 99.5\%$ , Sigma-Aldrich), 3-nitrobenzaldehyde (99%, Sigma-Aldrich), 4-cyanobenzaldehyde (95%, Sigma-Aldrich), 4-formylbenzoic acid (97%, Sigma-Aldrich), *p*-anisaldehyde (98%, Sigma-Aldrich), 4-hydroxybenzaldehyde (98%, Sigma-Aldrich), 4-chlorobenzaldehyde (98%, Sigma-Aldrich), 2-thiophenecarboxaldehyde (98%, Sigma-Aldrich), 4-hydroxy-3-methoxybenzaldehyde (vanillin, 99%, Sigma-Aldrich), 1-pyrenecarboxaldehyde (99%, Sigma-Aldrich), 4-(1,2,2-triphenylethenyl)benzaldehyde (Sigma-Aldrich), ferrocenecarboxaldehyde (98%, Sigma-Aldrich), 1,4-butanedithiol (98%, Sigma-Aldrich), 1,6-hexanedithiol (HDT, 96%, Sigma-Aldrich), 1,8-octanedithiol (97%, Sigma-Aldrich), ethylene glycol bismercaptoacetate ( $\geq 95.0\%$ , Sigma-Aldrich), 2,2'-(ethylenedioxy) diethanethiol (95%, Sigma-Aldrich), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 99.99%, Sigma-Aldrich), *p*-toluenesulfonic acid monohydrate (PTSA, ACS reagent,  $\geq 98.5\%$ , Sigma-Aldrich), methanesulfonic acid (MSA,  $\geq 99.0\%$ , Sigma-Aldrich) and chlorodimethylsilane (CDMS, 98%, Aldrich),  $\text{H}_2\text{O}_2$  35% (Sigma-Aldrich), and trimethylsilyl chloride ( $\geq 98.0\%$ , Sigma-Aldrich) were used as received. Tetrahydrofuran (THF, 99%, Sigma-Aldrich), chloroform ( $\text{CHCl}_3$ , 99%, Sigma-Aldrich), 1,2-dichloroethane (DCE, 99.8%, Aldrich), 1,4-dioxane (for liquid chromatography LiChrosolv®, Supleco), 2-methyltetrahydrofuran (2-MeTHF,  $\geq 99\%$ , Sigma-Aldrich), *N,N*-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), 1-methyl-2-pyrrolidinone (NMP, for liquid chromatography LiChrosolv®, Supleco) and *N,N*-dimethylacetamide (DMAc, 99.8%, Aldrich) were anhydrous and were of HPLC quality and used without further purification. Methanol (MeOH) was of reagent grade and used as received.

## Instrumentation

$^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra were recorded using an Agilent VNMRS 500 instrument in  $\text{CDCl}_3$ . Gel permeation chromatography (GPC) measurements were carried out with Agilent Instrument (series 1100), using a refractive index detector loaded

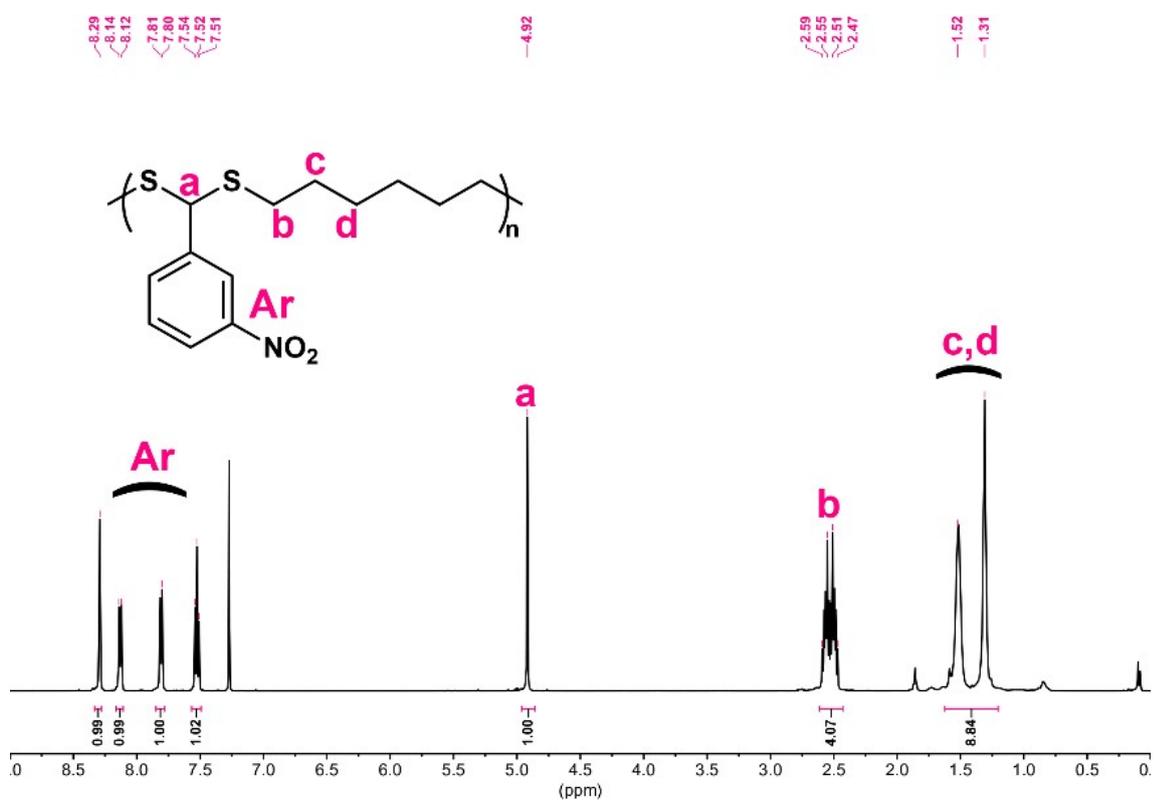
with Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2, 4.6 mm internal diameter, 300 mm length, packed with 5  $\mu\text{m}$  particles). The effective molecular weight ranges of the columns are 2000–4,000,000, 50–100,000, 500–30,000, and 500–20,000 g/mol, respectively. THF was used as an eluent at a flow rate of 0.3 mL/min at 30  $^{\circ}\text{C}$ , and 2,6-di-*tert*-butyl-4-methylphenol was used as an internal standard. The number-average molecular weight ( $M_n$ ) and dispersity ( $D$ ) of the polymers were calculated based on narrow linear polystyrene (PS) standards (Polymer Laboratories) ranging between 2300 and 3,050,000 g/mol. FT-IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR instrument over the range of 4000–400  $\text{cm}^{-1}$ . Differential scanning calorimetry (DSC) measurements were carried out on a TA DSC Q10 instrument under a nitrogen atmosphere in the temperature range from -50  $^{\circ}\text{C}$  to 150  $^{\circ}\text{C}$  at a scanning rate of 20  $^{\circ}\text{C}/\text{min}$ . All data were collected from a second heating cycle, and the glass transition temperatures ( $T_g$ ) were determined from the midpoint of calculated onset and endset temperatures of the glass transition region of the related DSC trace.



**Figure S1.** DSC thermogram of P1.

## Synthesis of P2

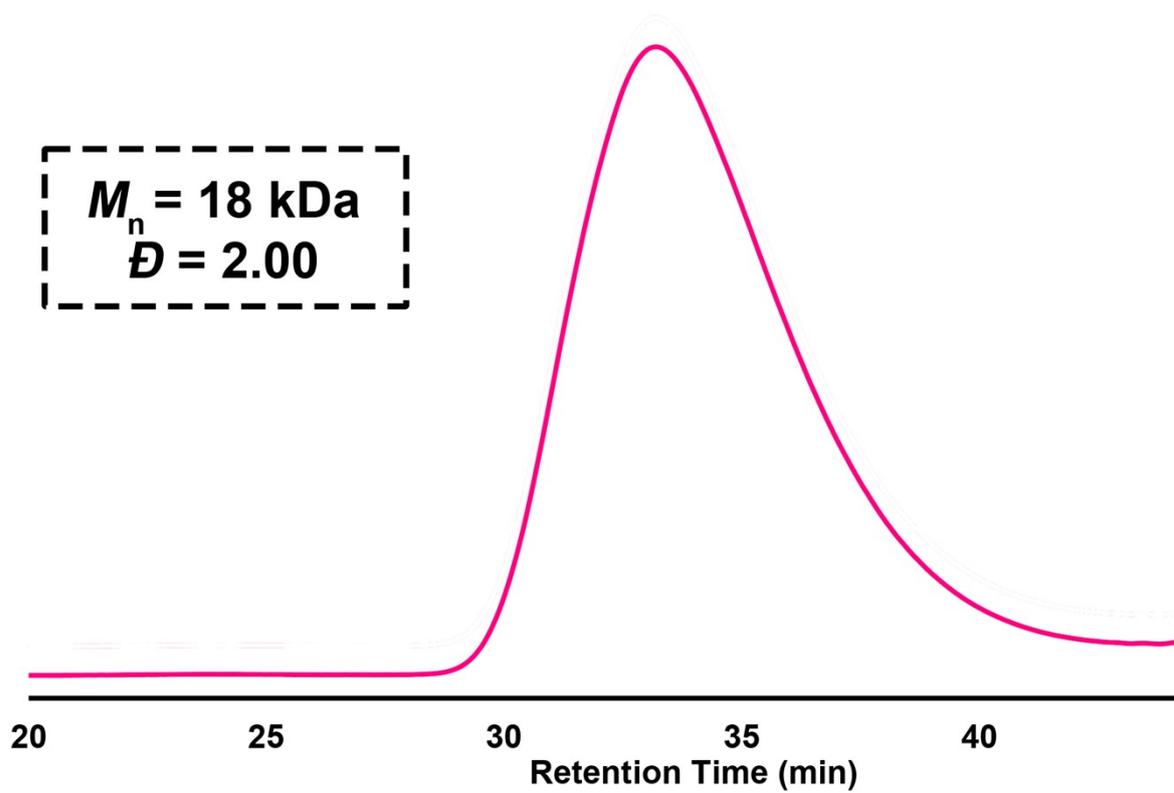
General procedure was followed: 3-Nitrobenzaldehyde (332 mg, 2.20 mmol), HDT (306  $\mu$ L, 2.00 mmol), and CDMS (111  $\mu$ L, 1.00 mmol) were reacted in 500  $\mu$ L of THF. P2 was obtained as a white sticky solid (yield = 478 mg, 84%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.29-7.51 (4H, ArH), 4.92 (1H, ArCHS), 2.59-2.47 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.52-1.31 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.30, 142.77, 133.99, 129.63, 122.97, 122.82, 50.90, 31.84, 28.64, 28.02.



**Figure S2.**  $^1\text{H}$  NMR spectrum of P2 ( $\text{CDCl}_3$ , 500 MHz).



**Figure S3.** <sup>13</sup>C NMR spectrum of P2 (CDCl<sub>3</sub>, 125 MHz).



**Figure S4.** GPC chromatogram of P2.

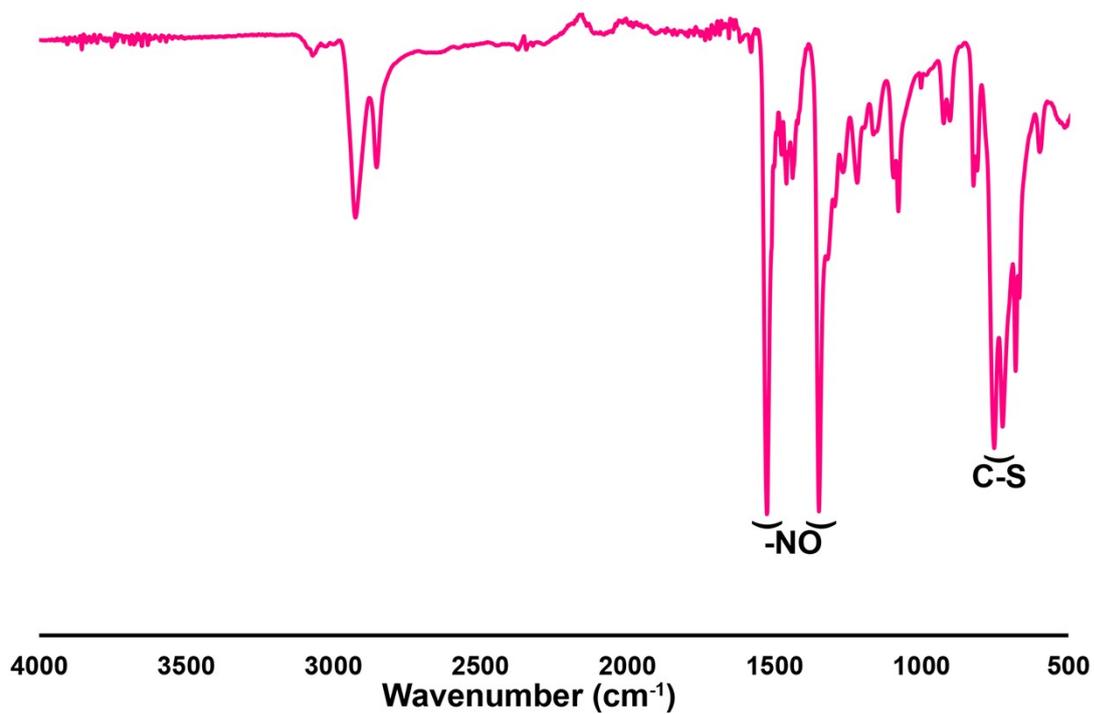


Figure S5. FT-IR spectrum of P2.

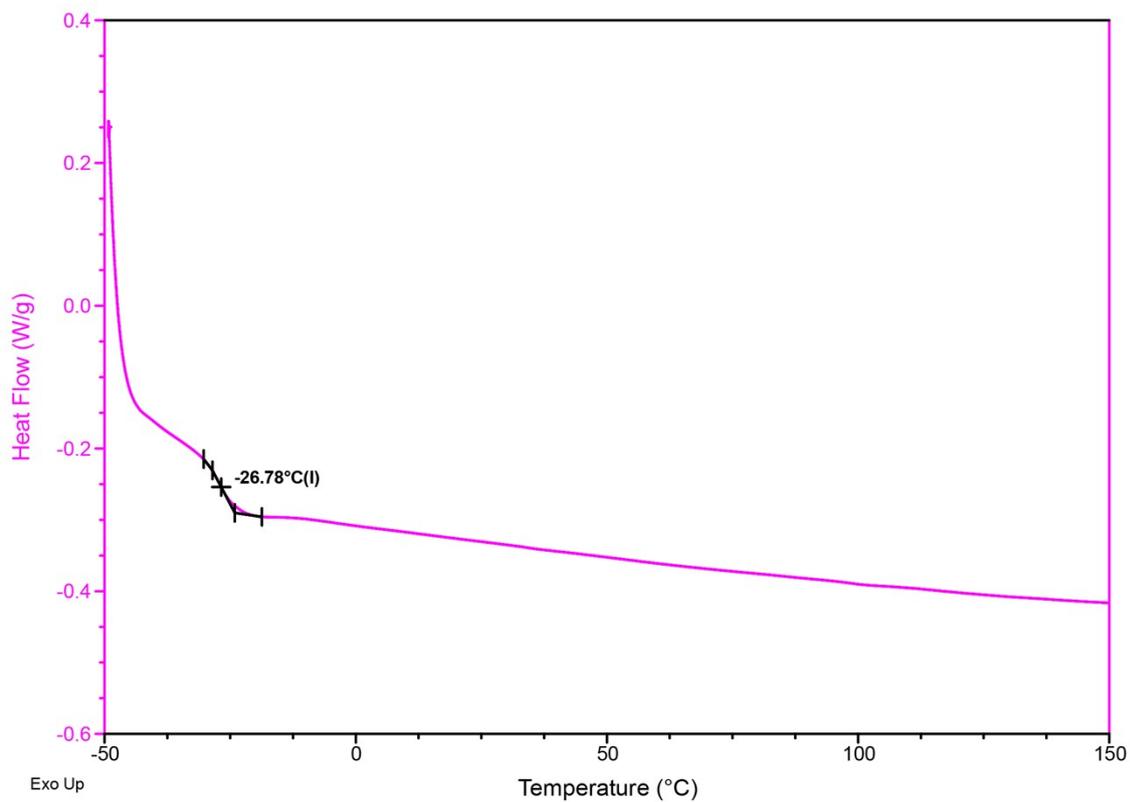
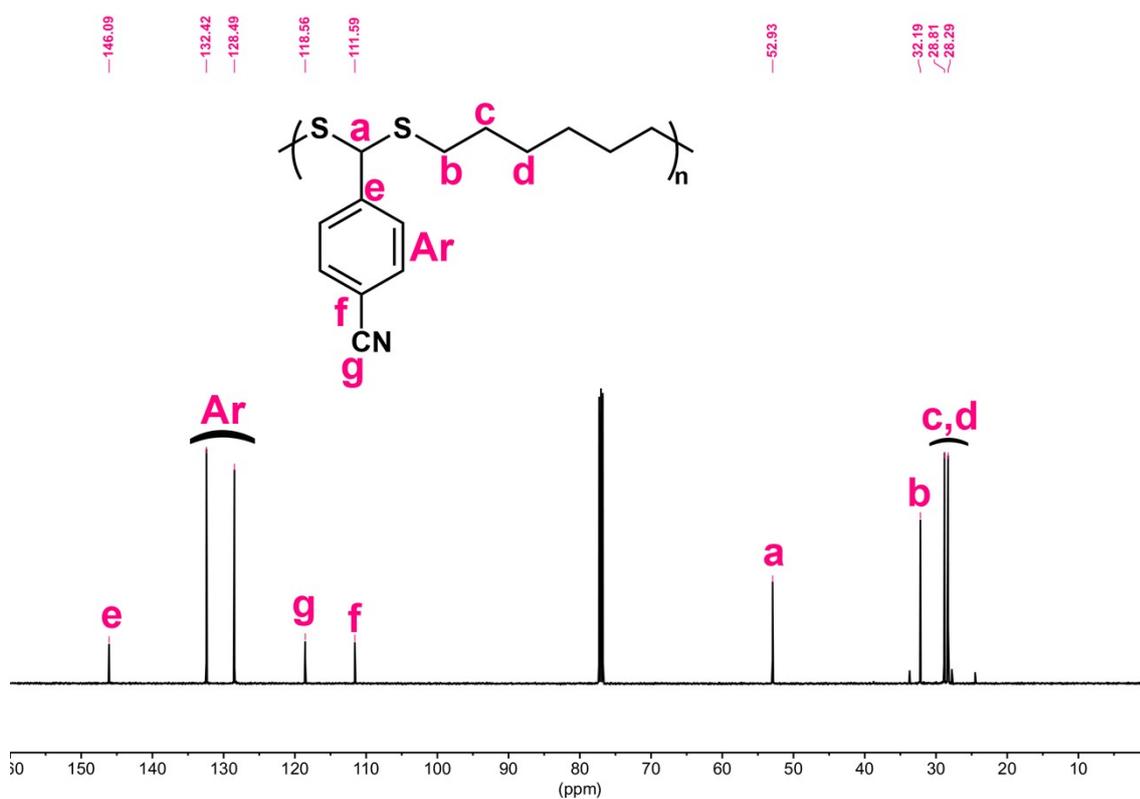


Figure S6. DSC thermogram of P2.

## Synthesis of P3

General procedure was followed: 4-Cyanobenzaldehyde (288 mg, 2.20 mmol), HDT (306  $\mu$ L, 2.00 mmol), and CDMS (111  $\mu$ L, 1.00 mmol) were reacted in 500  $\mu$ L of THF. P3 was obtained as a white sticky solid (yield = 400 mg, 76%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62-7.55 (4H, ArH), 4.84 (1H, ArCHS), 2.49 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.49-1.29 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.09, 132.42, 128.49, 118.56, 111.59, 52.93, 32.19, 28.81, 28.29.



**Figure S7.**  $^{13}\text{C}$  NMR spectrum of P3 ( $\text{CDCl}_3$ , 125 MHz).

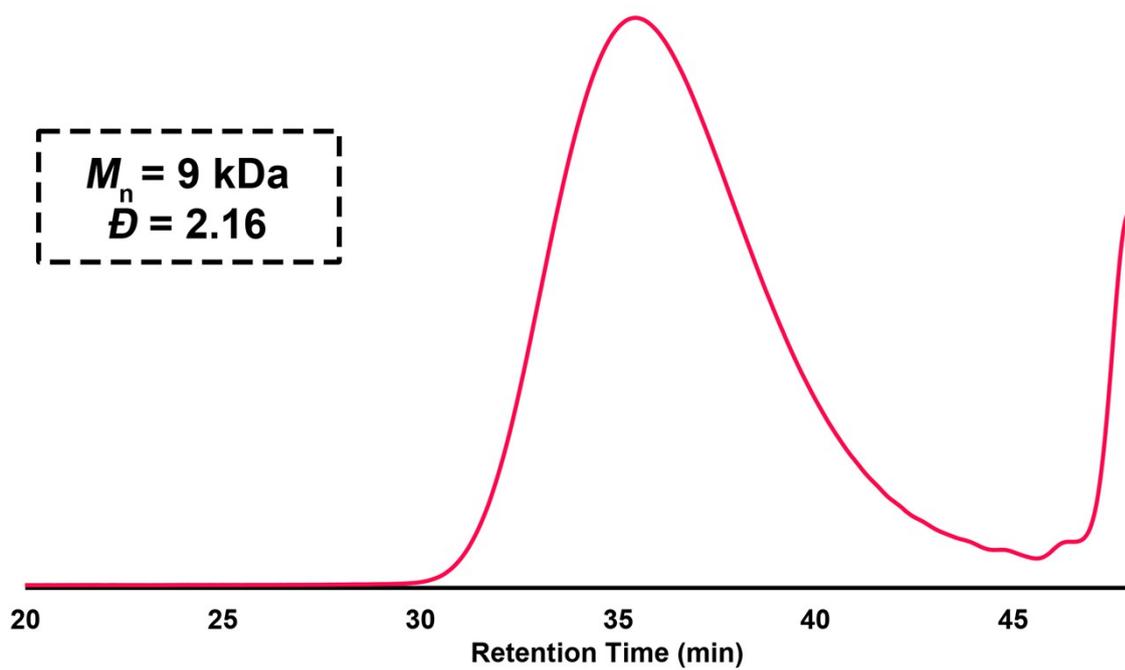


Figure S8. GPC chromatogram of P3.

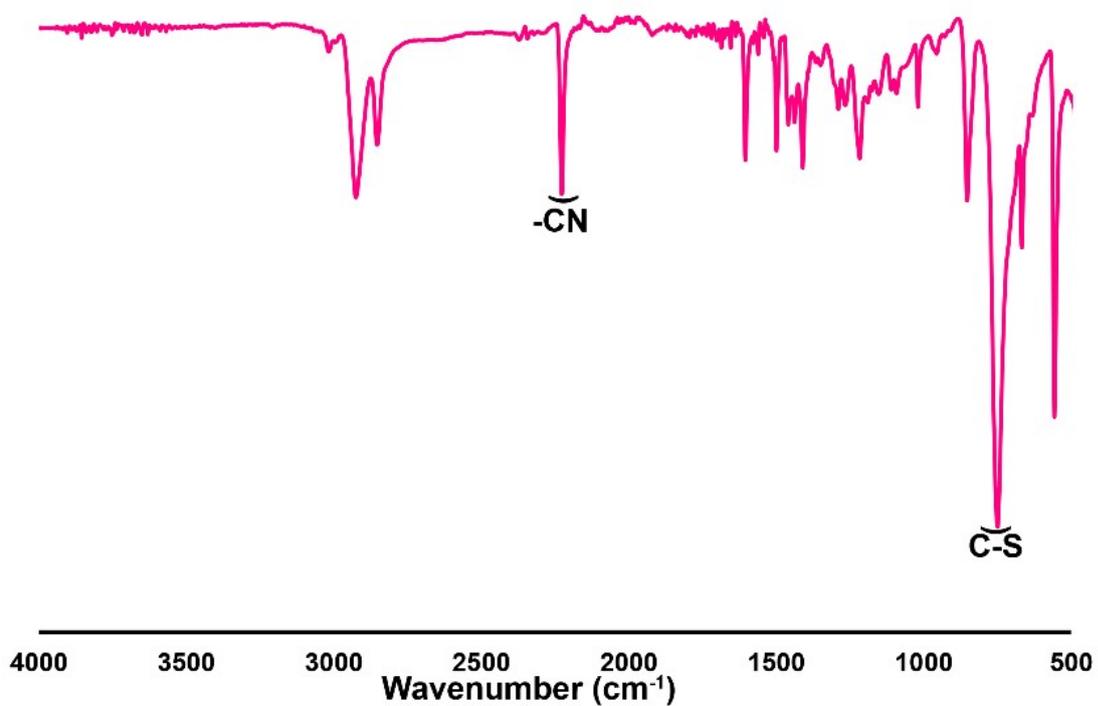
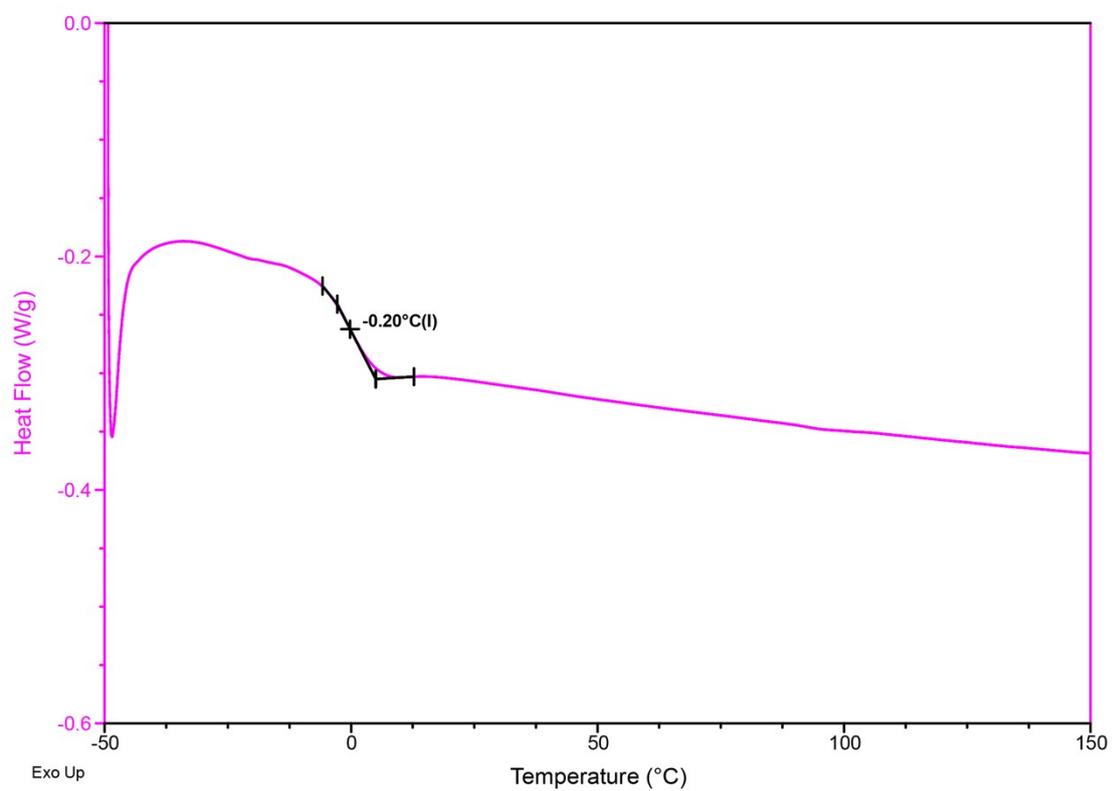


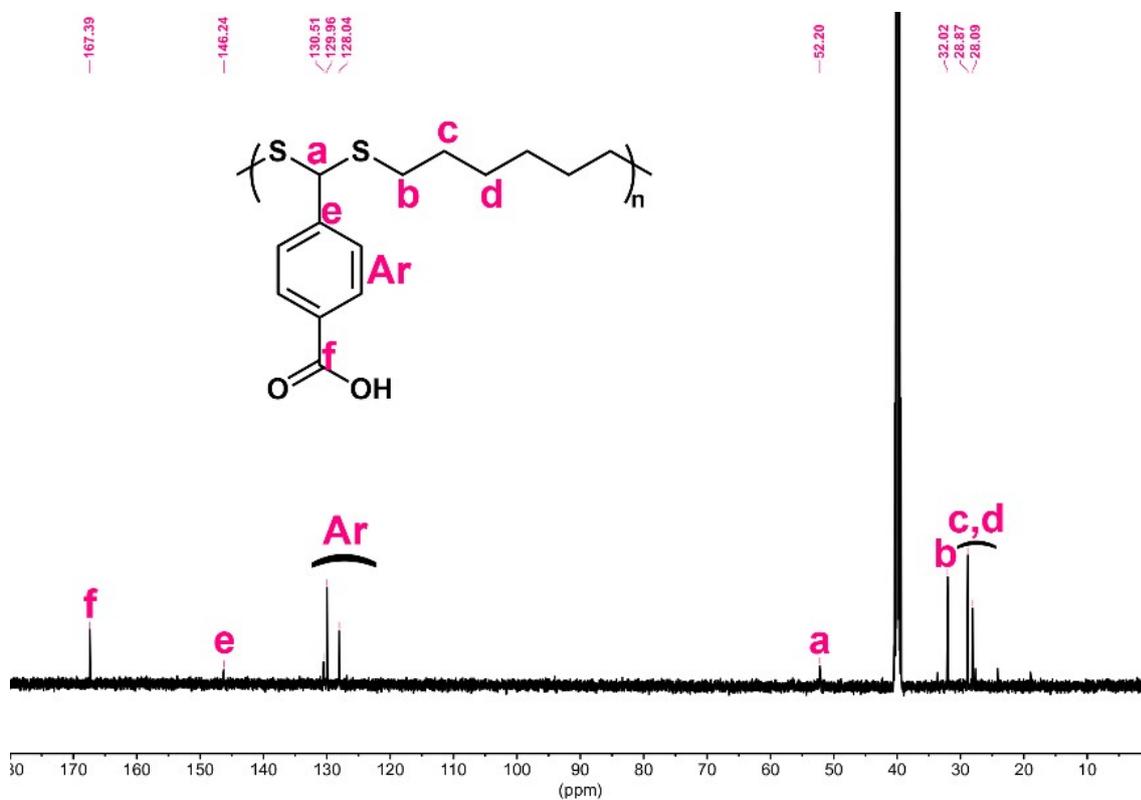
Figure S9. FT-IR spectrum of P3.



**Figure S10.** DSC thermogram of P3.

## Synthesis of P4

General procedure was followed: 4-Formylbenzoic acid (330 mg, 2.20 mmol), HDT (306  $\mu$ L, 2.00 mmol), and CDMS (111  $\mu$ L, 1.00 mmol) were reacted in 500  $\mu$ L of THF. (Caution! The mixture was a solid mass in the reaction medium and became slurry within 2 min after adding CDMS to the reaction medium). P4 was obtained as a white solid (yield = 457 mg, 81%).  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO):  $\delta$  7.88-7.49 (4H, ArH), 5.08 (1H, ArCHS), 2.42 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.42-1.20 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO):  $\delta$  167.39, 146.24, 130.51, 129.96, 128.04, 52.20, 32.02, 28.87, 28.09.



**Figure S11.**  $^{13}\text{C}$  NMR spectrum of P4 ( $\text{CDCl}_3$ , 125 MHz).

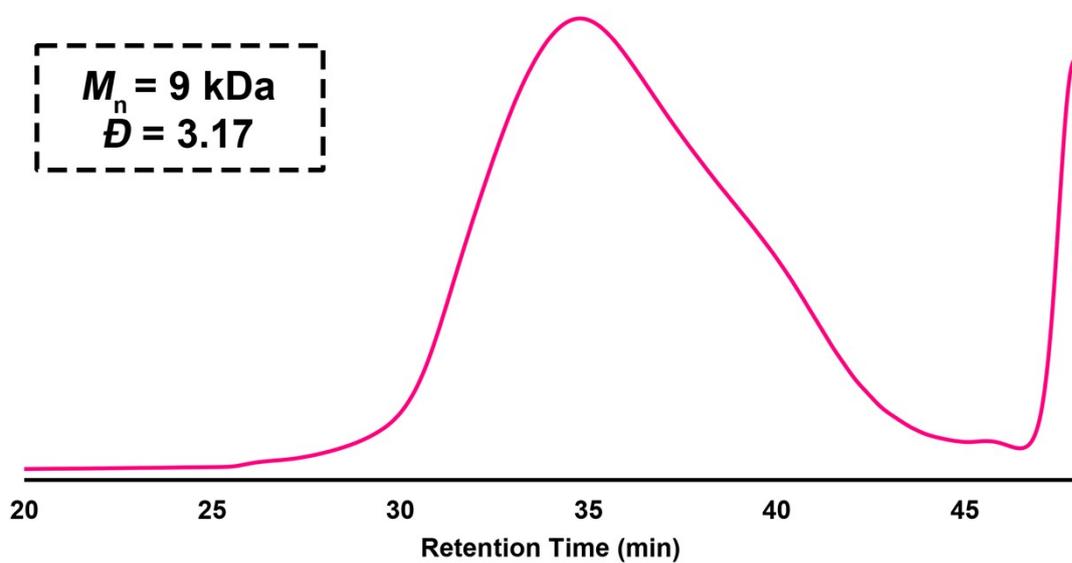


Figure S12. GPC chromatogram of P4.

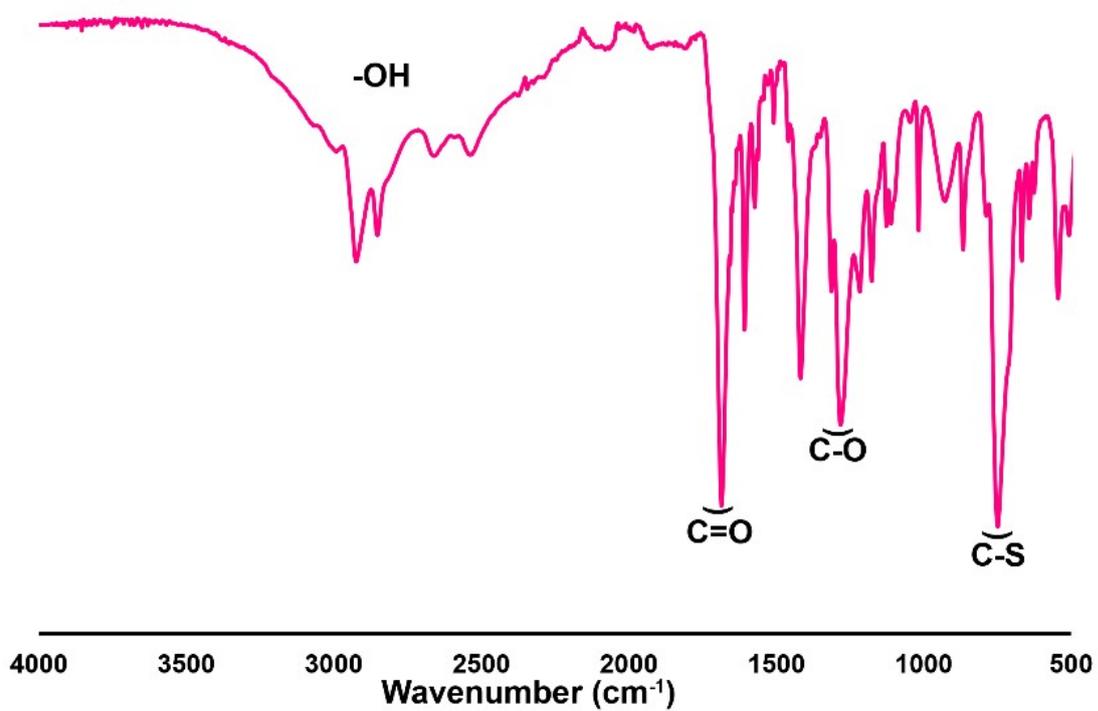
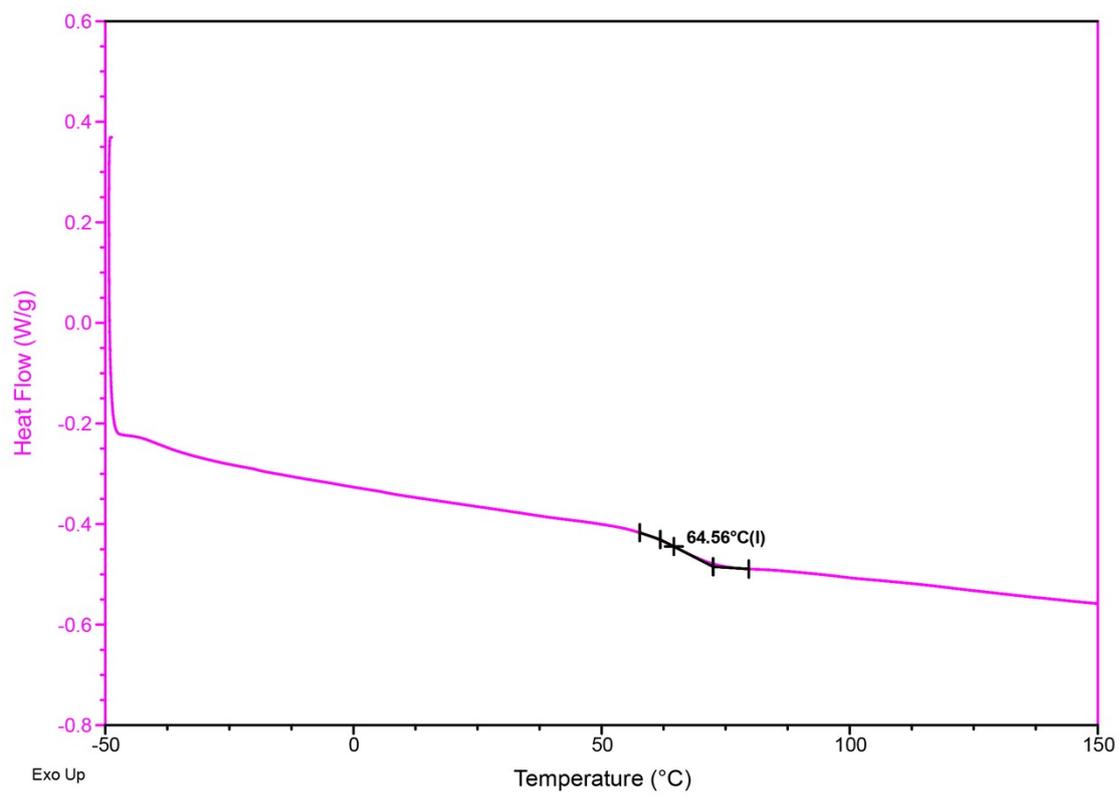


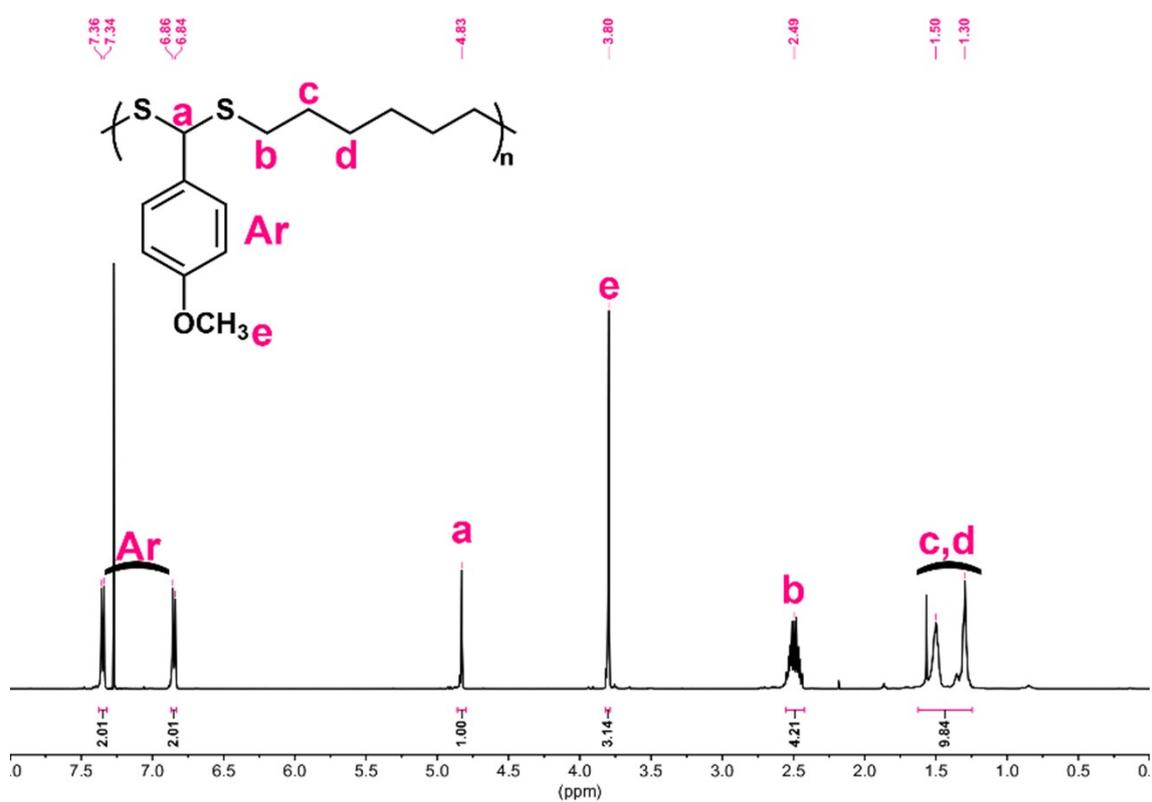
Figure S13. FT-IR spectrum of P4.



**Figure S14.** DSC thermogram of P4.

## Synthesis of P5

General procedure was followed: *p*-Anisaldehyde (268  $\mu$ L, 2.20 mmol), HDT (306  $\mu$ L, 2.00 mmol), and CDMS (111  $\mu$ L, 1.00 mmol) were reacted in 500  $\mu$ L of THF. P5 was obtained as a white sticky solid (yield = 439 mg, 82%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36-6.84 (4H, ArH), 4.83 (1H, ArCHS), 3.80 (3H, ArOCH<sub>3</sub>), 2.49 (4H, SCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>S), 1.50-1.30 (8H, SCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>S);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.10, 132.48, 128.83, 113.84, 55.31, 52.68, 32.18, 29.00, 28.43.



**Figure S15.**  $^1\text{H}$  NMR spectrum of P5 ( $\text{CDCl}_3$ , 500 MHz).

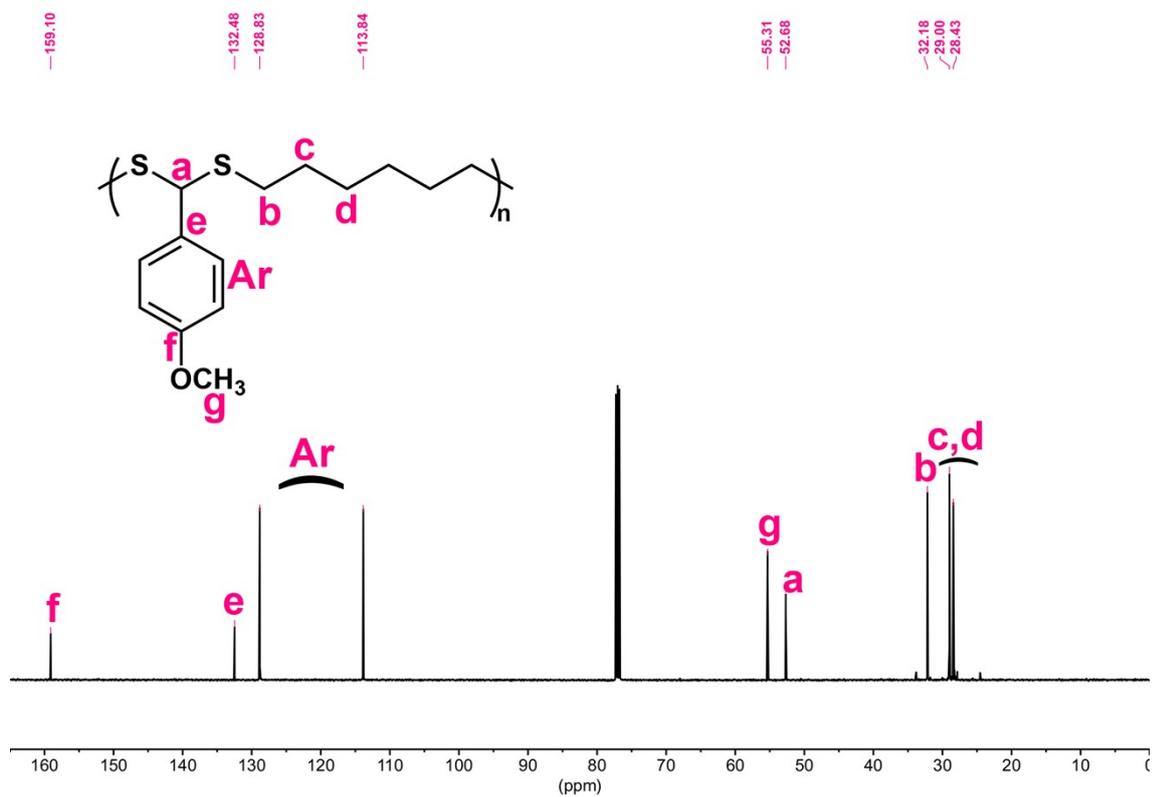


Figure S16. <sup>13</sup>C NMR spectrum of P5 (CDCl<sub>3</sub>, 125 MHz).

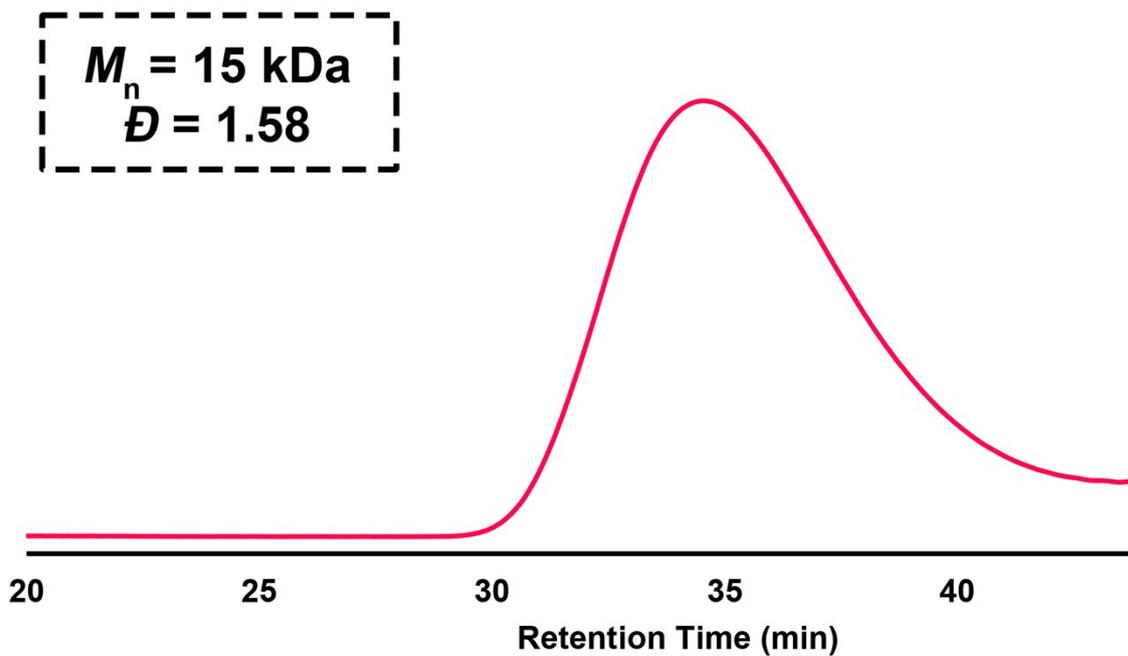
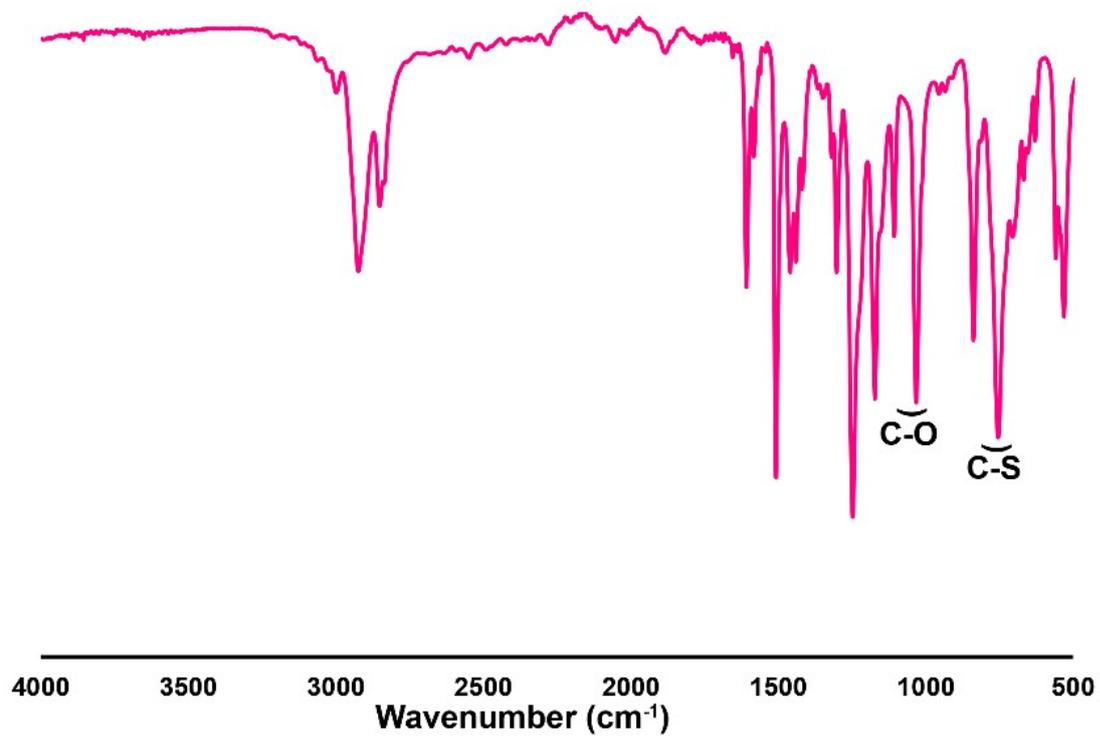
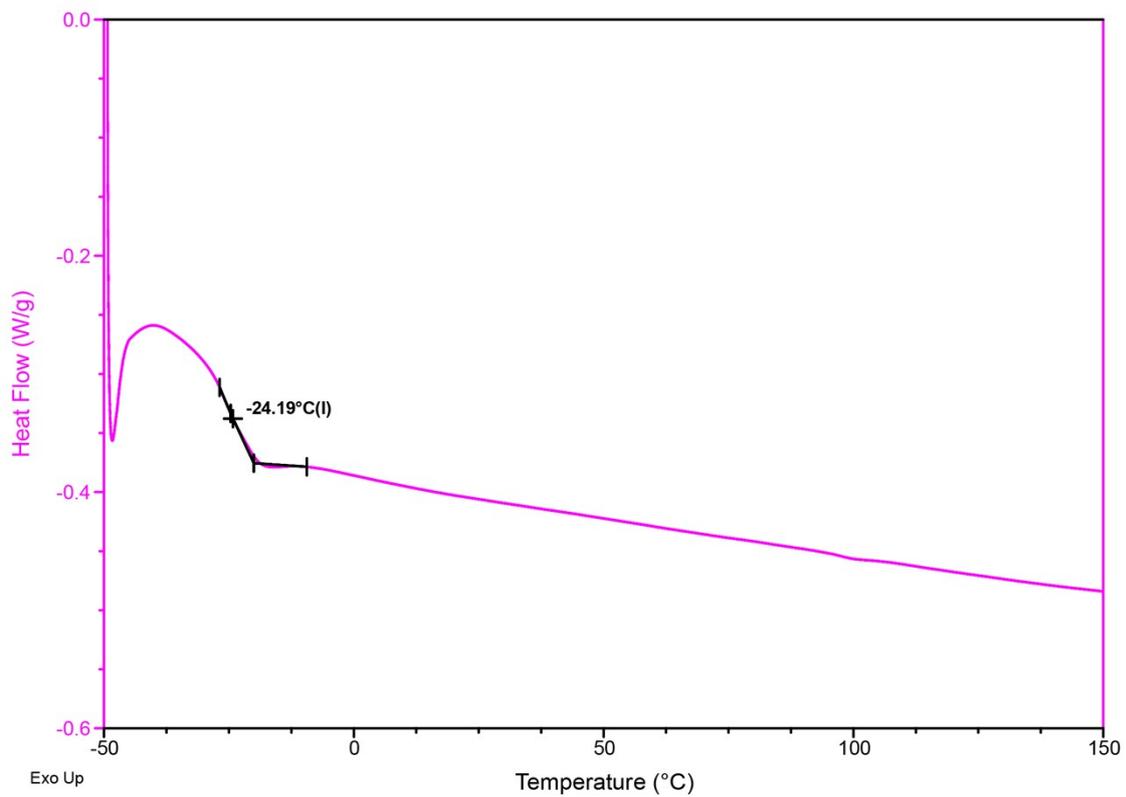


Figure S17. GPC chromatogram of P5.



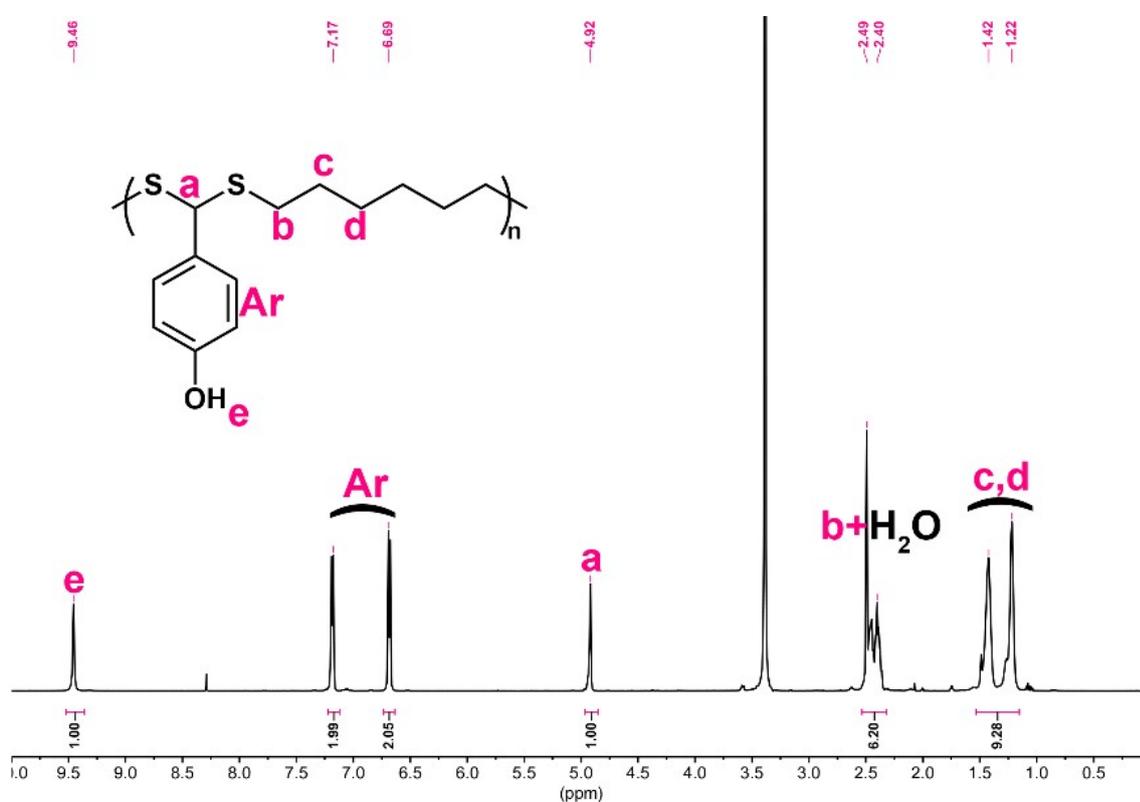
**Figure S18.** FT-IR spectrum of P5.



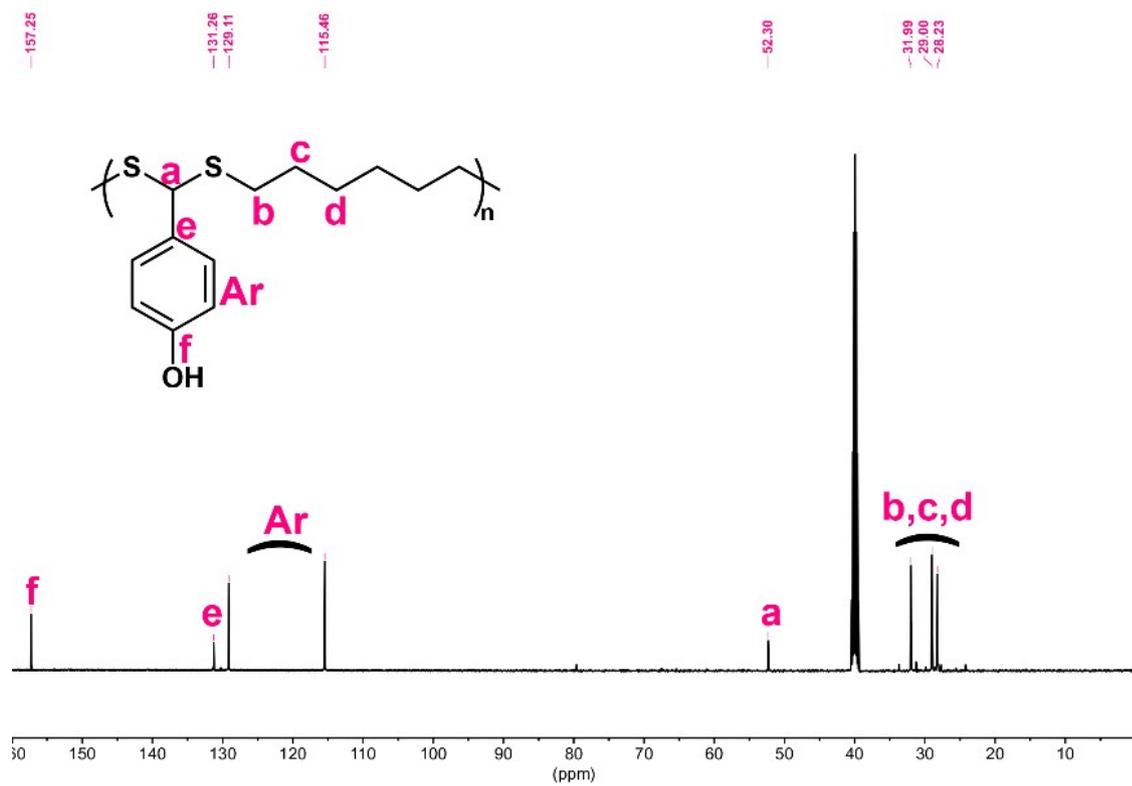
**Figure S19.** DSC thermogram of P5.

## Synthesis of P6

General procedure was followed: *p*-Hydroxybenzaldehyde (269 mg, 2.20 mmol), HDT (306  $\mu$ L, 2.00 mmol), and CDMS (111  $\mu$ L, 1.00 mmol) were reacted in 500  $\mu$ L of THF. P6 was obtained as a white sticky solid (yield = 406 mg, 80%).  $^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO):  $\delta$  9.46 (1H, ArOH) 7.17-6.69 (4H, ArH), 4.92 (1H, ArCHS), 2.49-2.40 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.42-1.22 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO):  $\delta$  157.25, 131.26, 129.11, 115.46, 52.30, 31.99, 29.00, 28.23.



**Figure S20.**  $^1\text{H}$  NMR spectrum of P6 ( $d_6$ -DMSO, 500 MHz).



Figure

e S21. <sup>13</sup>C NMR spectrum of P6 (*d*<sub>6</sub>-DMSO, 125 MHz).

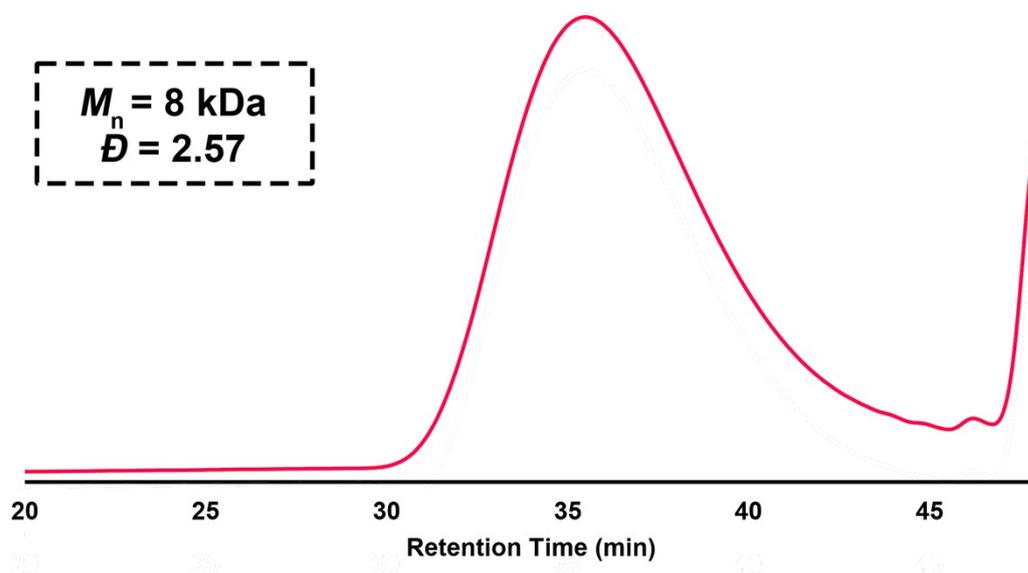


Figure S22. GPC chromatogram of P6.

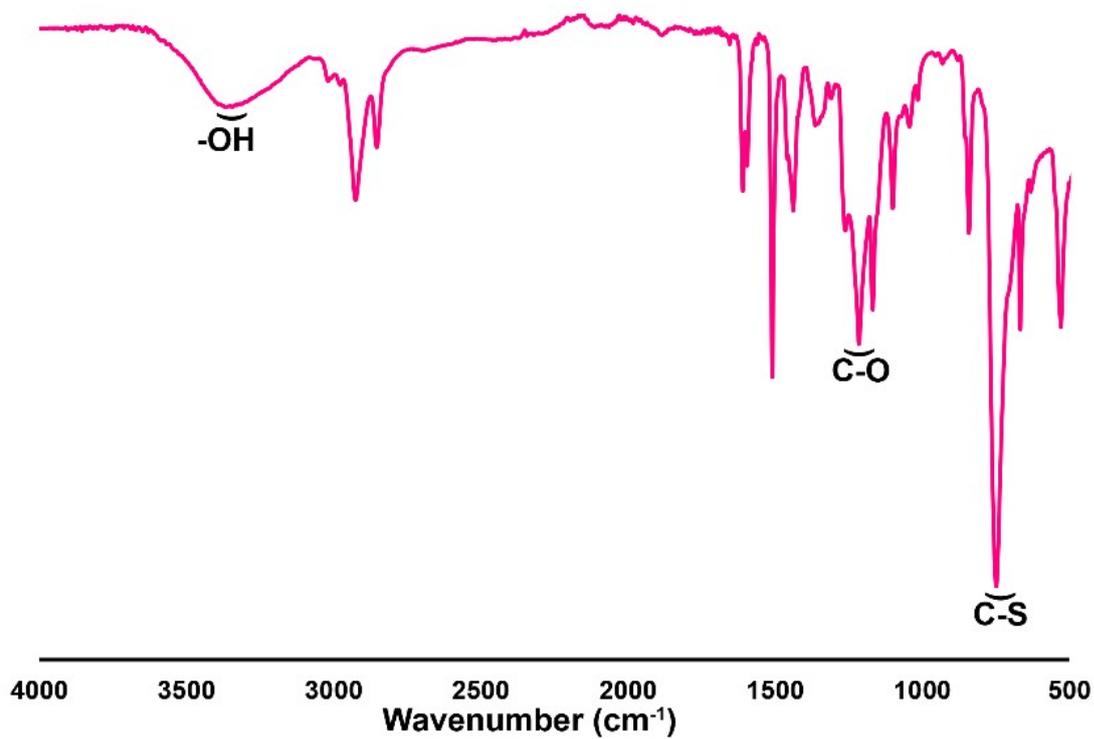


Figure S23. FT-IR spectrum of P6.

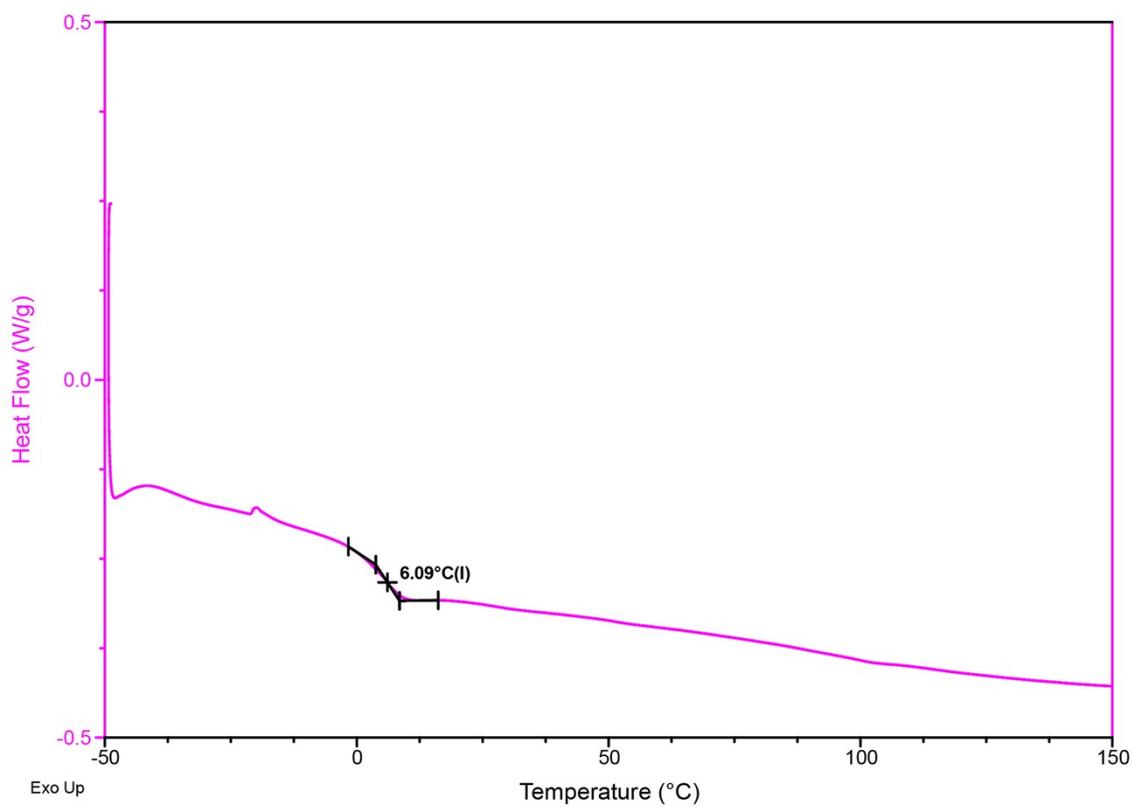
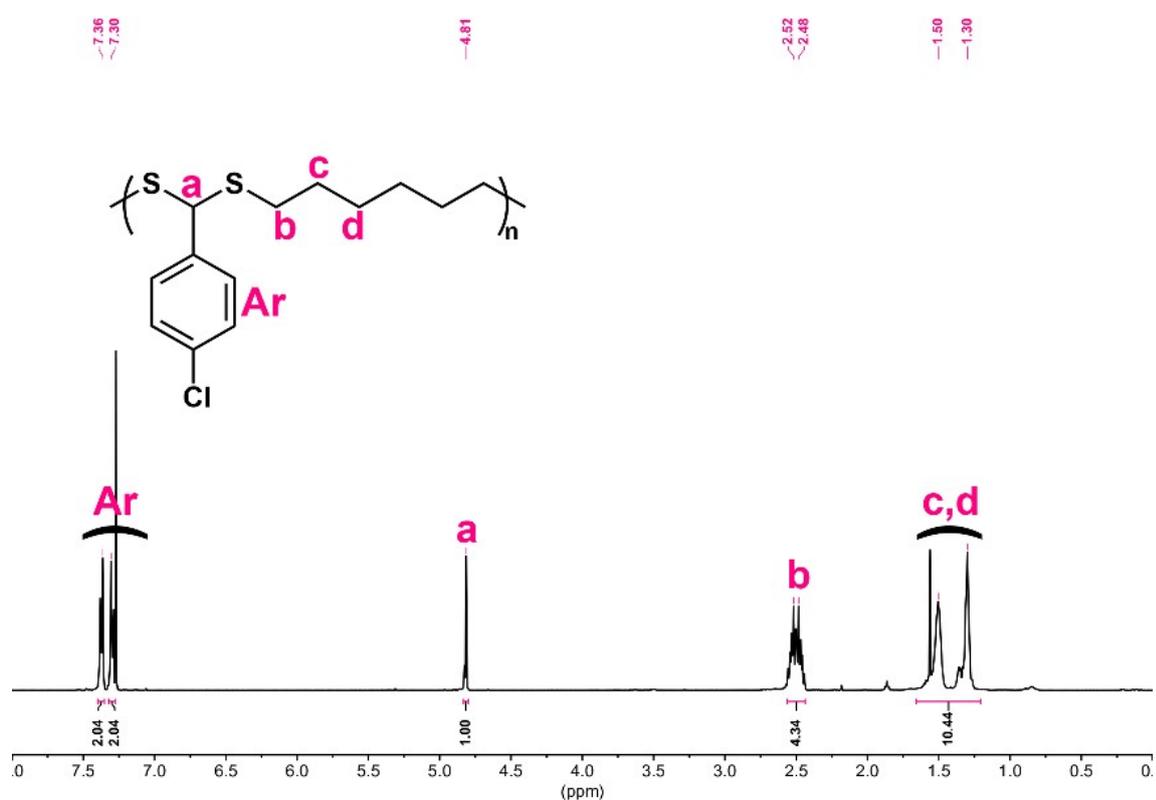


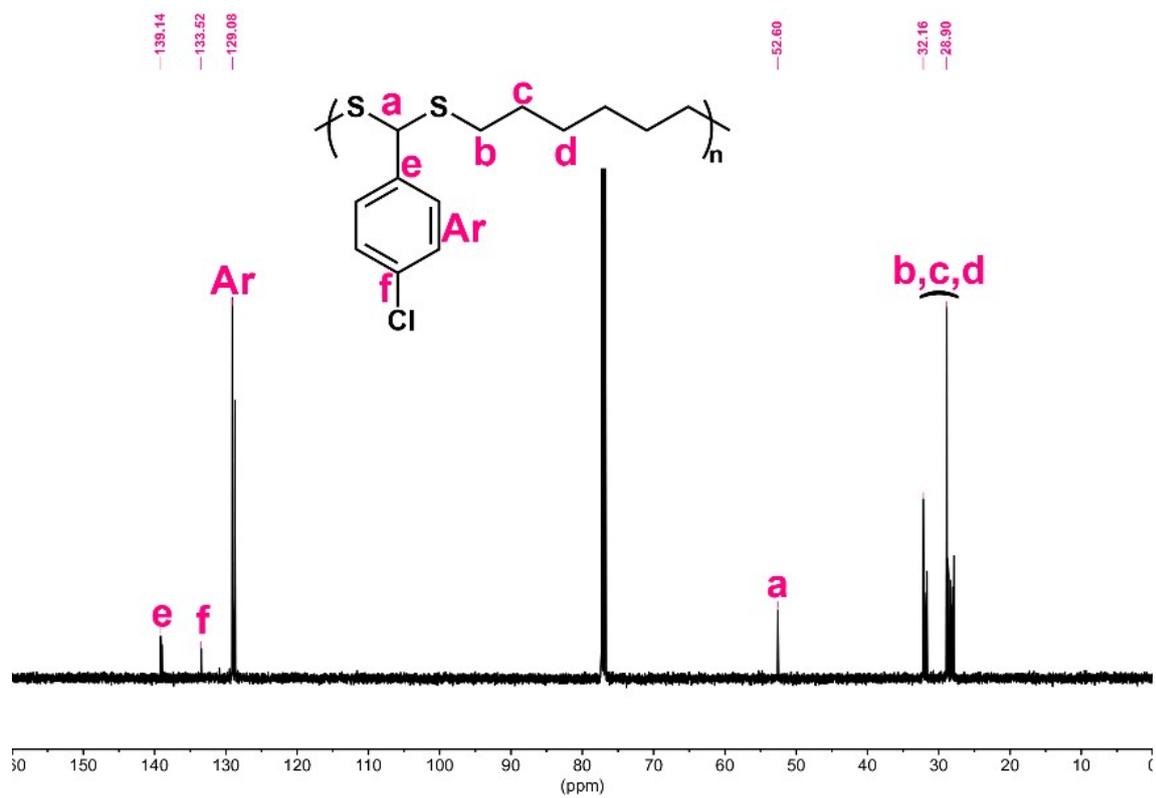
Figure S24. DSC thermogram of P6.

## Synthesis of P7

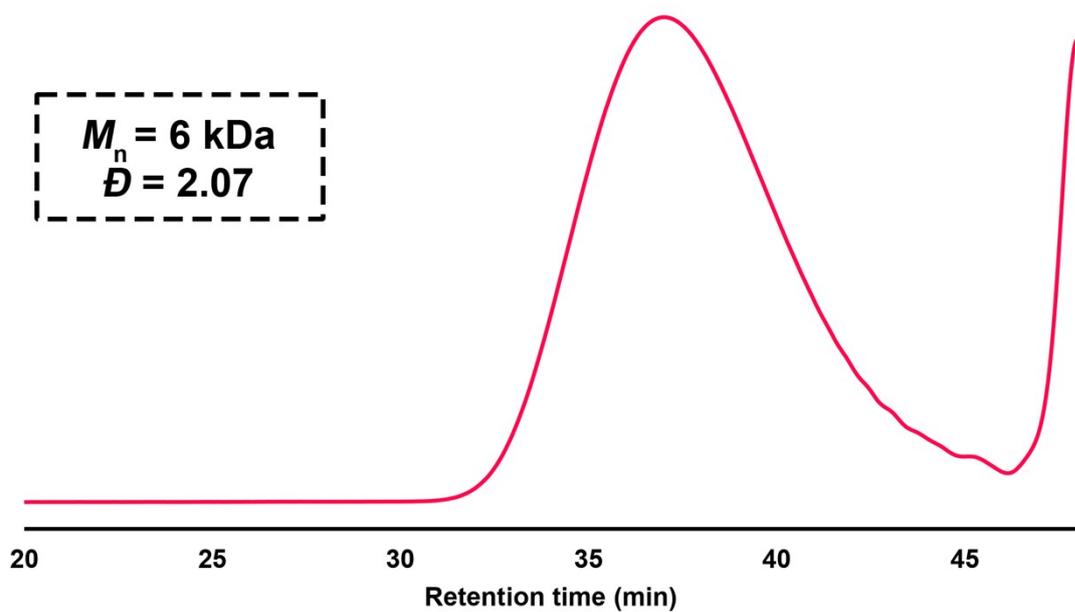
General procedure was followed: 4-Chlorobenzaldehyde (309 mg, 2.20 mmol), HDT (306  $\mu$ L, 2.00 mmol), and CDMS (111  $\mu$ L, 1.00 mmol) were reacted in 500  $\mu$ L of THF. P7 was obtained as a pale yellow sticky solid (yield = 408 mg, 75%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36-7.30 (4H, ArH), 4.81 (1H, ArCHS), 2.57-2.48 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.50-1.30 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.14, 133.52, 129.08, 52.60, 32.16, 28.90.



**Figure S25.**  $^1\text{H}$  NMR spectrum of P7 ( $\text{CDCl}_3$ , 500 MHz).



**Figure S26.**  $^{13}\text{C}$  NMR spectrum of P7 ( $\text{CDCl}_3$ , 500 MHz).



Figure

re S27. GPC chromatogram of P7.

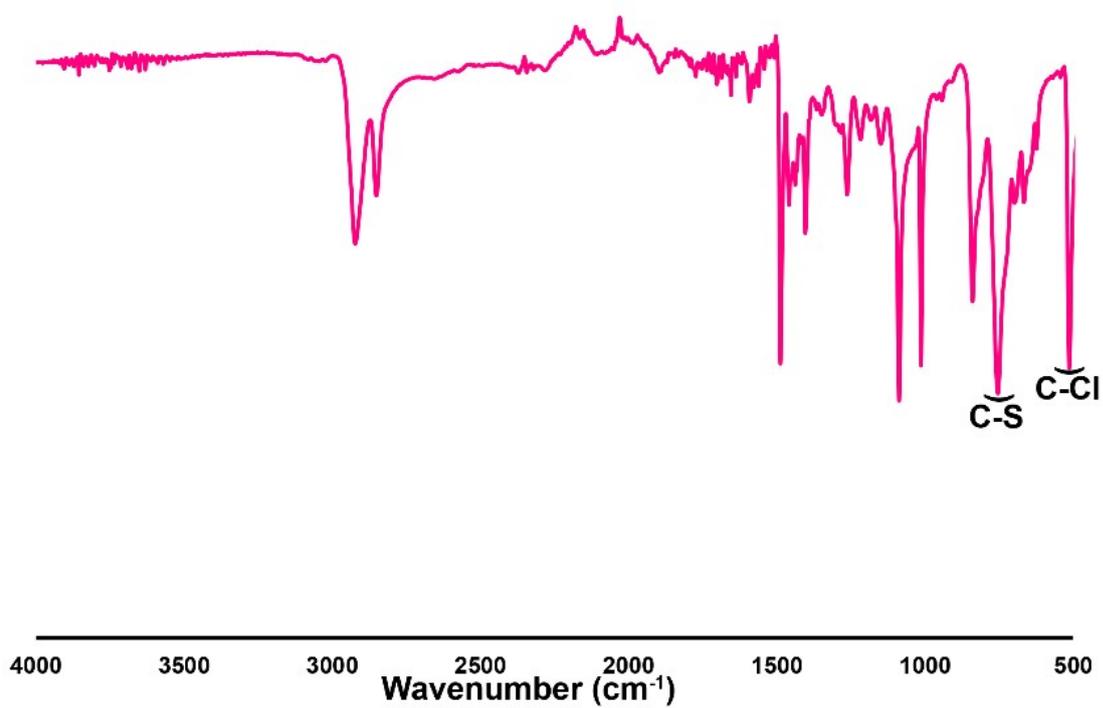
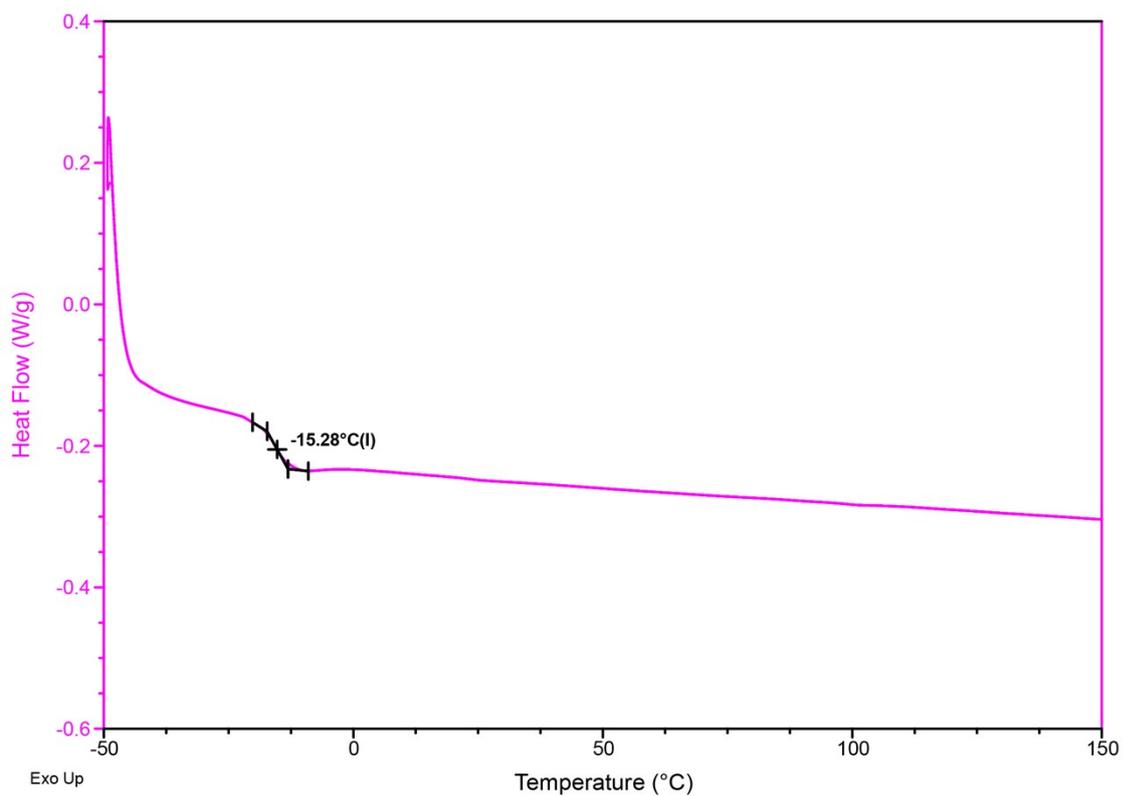


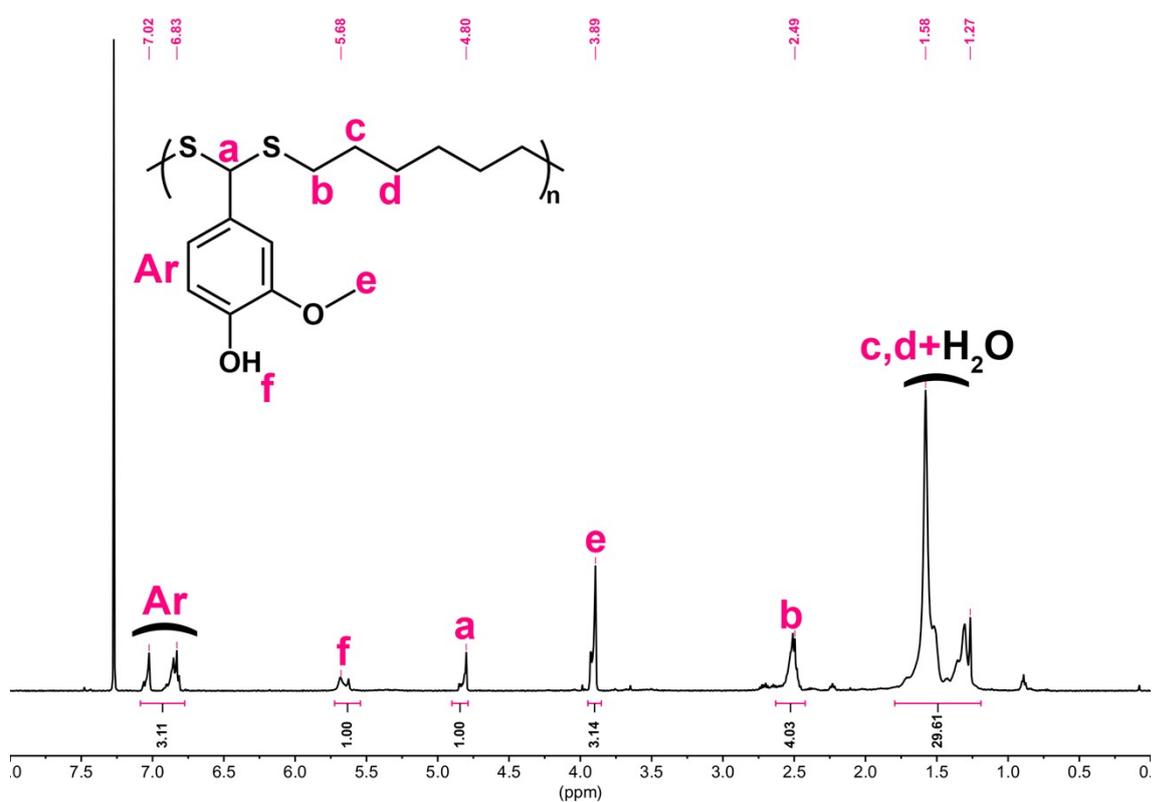
Figure S28. FT-IR spectrum of P7.



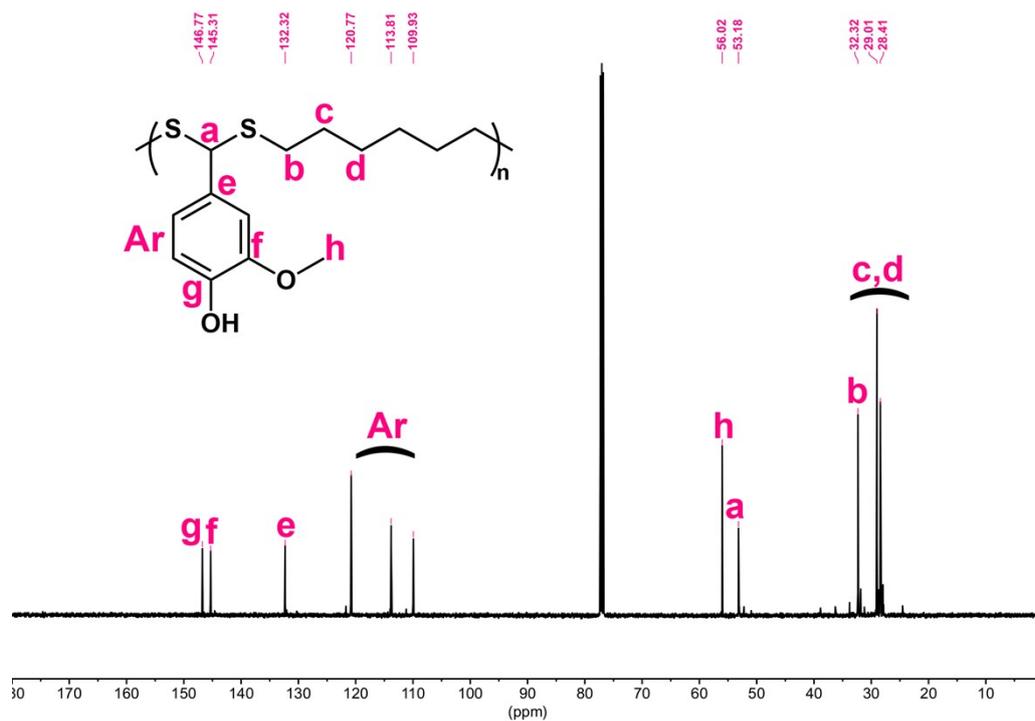
**Figure S29.** DSC thermogram of P7.

## Synthesis of P8

General procedure was followed: Vanillin (335 mg, 2.20 mmol), HDT (306  $\mu$ L, 2.00 mmol), and CDMS (111  $\mu$ L, 1.00 mmol) were reacted in 500  $\mu$ L of THF. P8 was obtained as a white sticky solid (yield = 494 mg, 87%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.02-6.83 (3H, ArH), 5.68 (1H, OH), 4.80 (1H, ArCHS), 3.89 (3H, ArOCH<sub>3</sub>), 2.49 (4H, SCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>S), 1.58-1.27 (8H, SCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>S);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.77 145.31, 132.32, 120.77, 113.81, 109.93, 56.02, 53.18, 32.32, 29.01, 28.41.



**Figure S30.**  $^1\text{H}$  NMR spectrum of P8 ( $\text{CDCl}_3$ , 500 MHz).



**Figure S31.** <sup>13</sup>C NMR spectrum of P8 (CDCl<sub>3</sub>, 125 MHz).

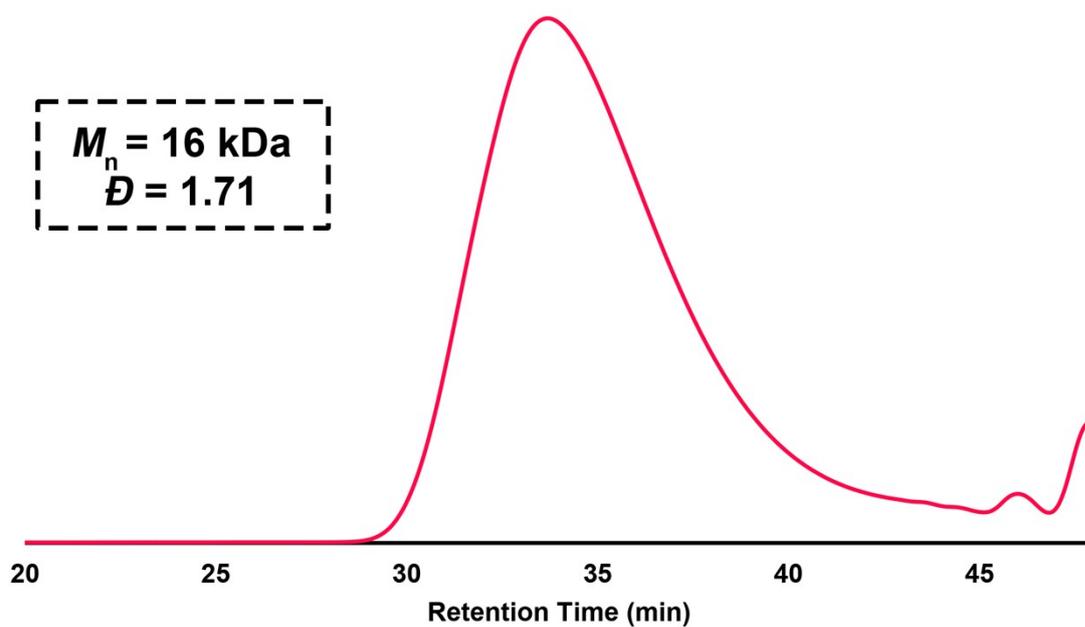


Figure S32. GPC chromatogram of P8.

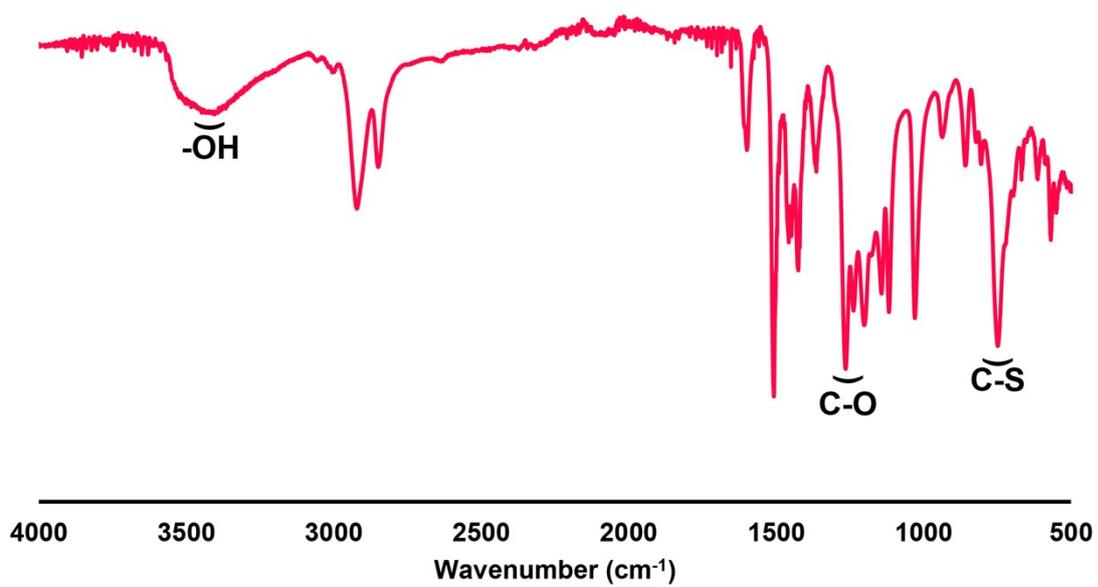
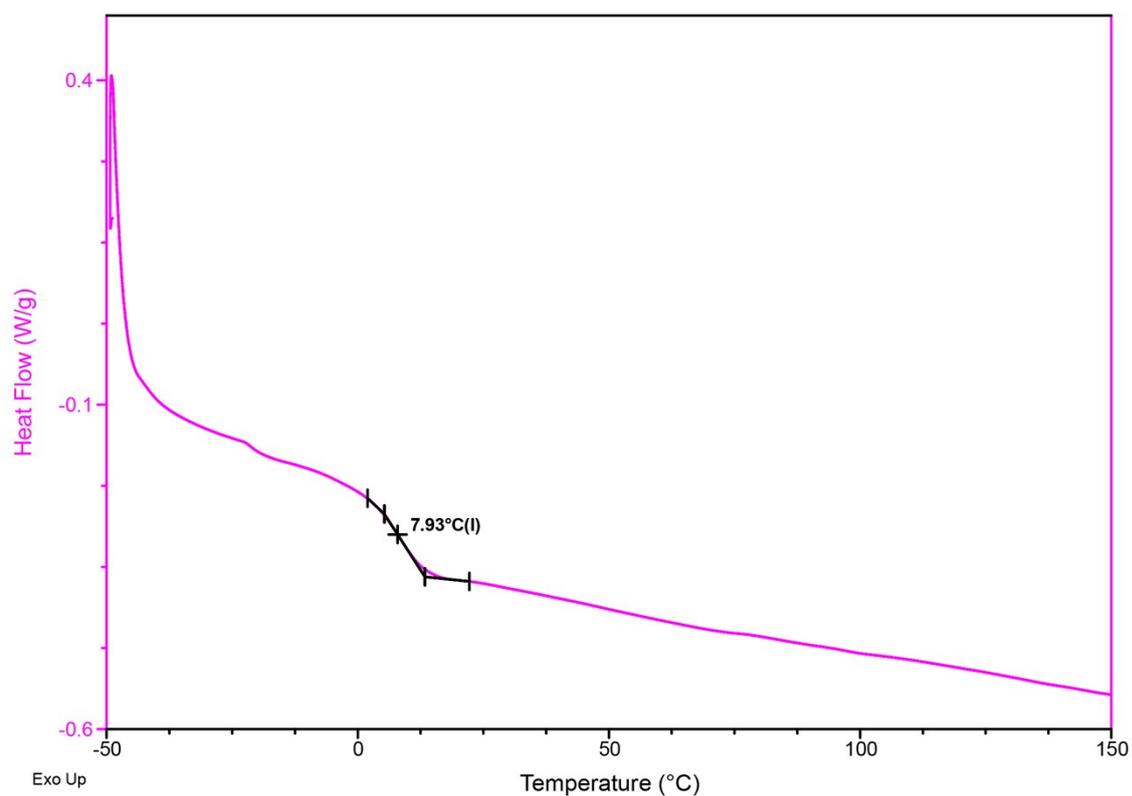


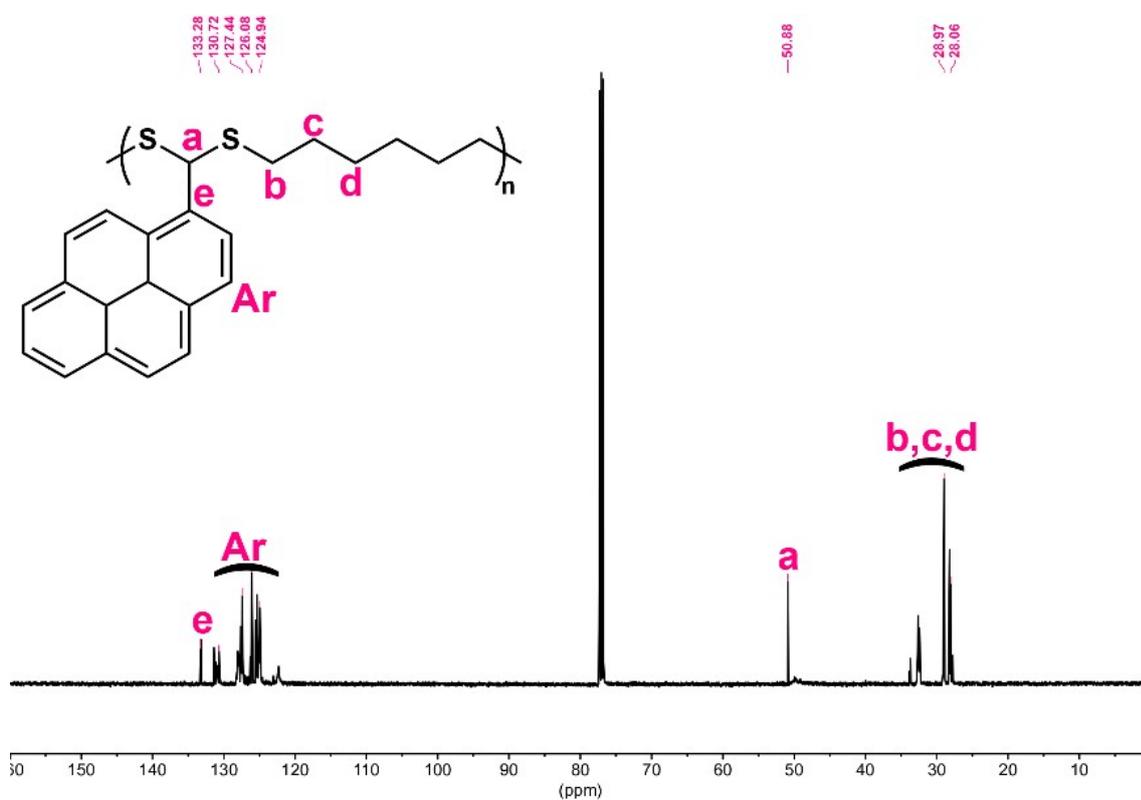
Figure S33. FT-IR spectrum of P8.



**Figure S34.** DSC thermogram of P8.

## Synthesis of P9

General procedure was followed: 1-Pyrenecarboxaldehyde (507 mg, 2.20 mmol), HDT (306  $\mu\text{L}$ , 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P9 was obtained as a yellow solid (yield = 651 mg, 90%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.32-7.91 (9H, *ArH*), 5.85 (1H, *ArCHS*), 2.45-2.39 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.37-1.10 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.29, 130.72, 127.44, 126.08, 124.94, 50.08, 28.97, 28.06.



**Figure S35.**  $^{13}\text{C}$  NMR spectrum of P9 ( $\text{CDCl}_3$ , 125 MHz).

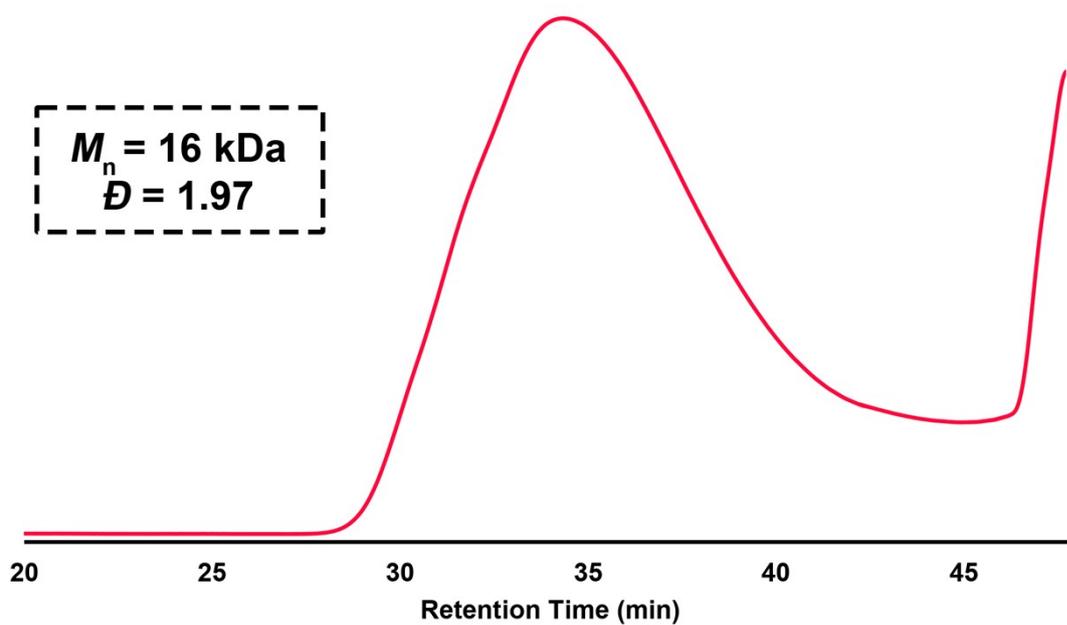


Figure S36. GPC chromatogram of P9.

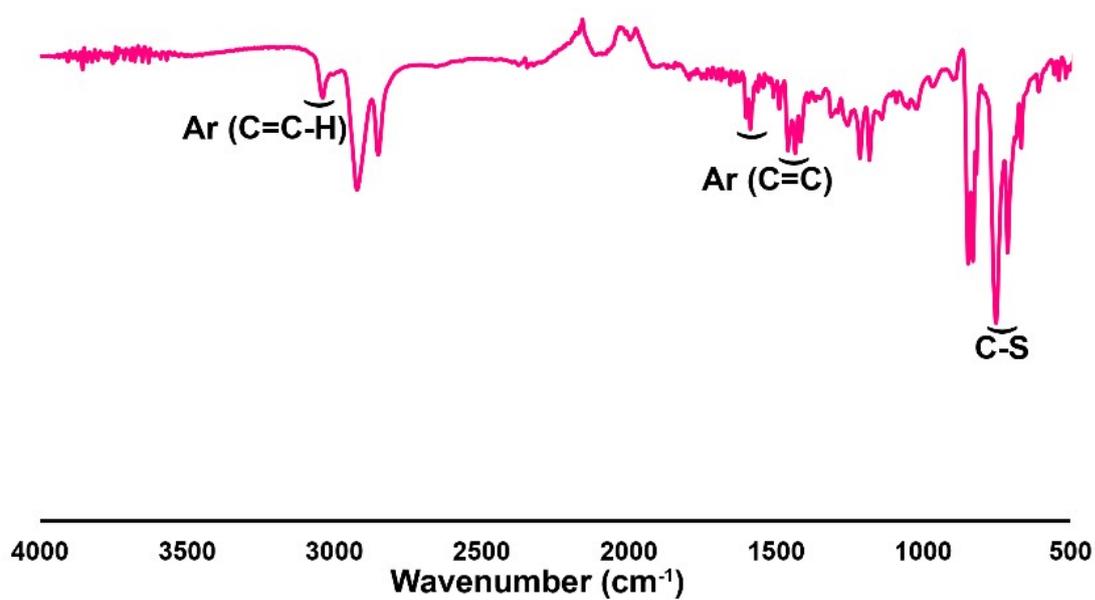
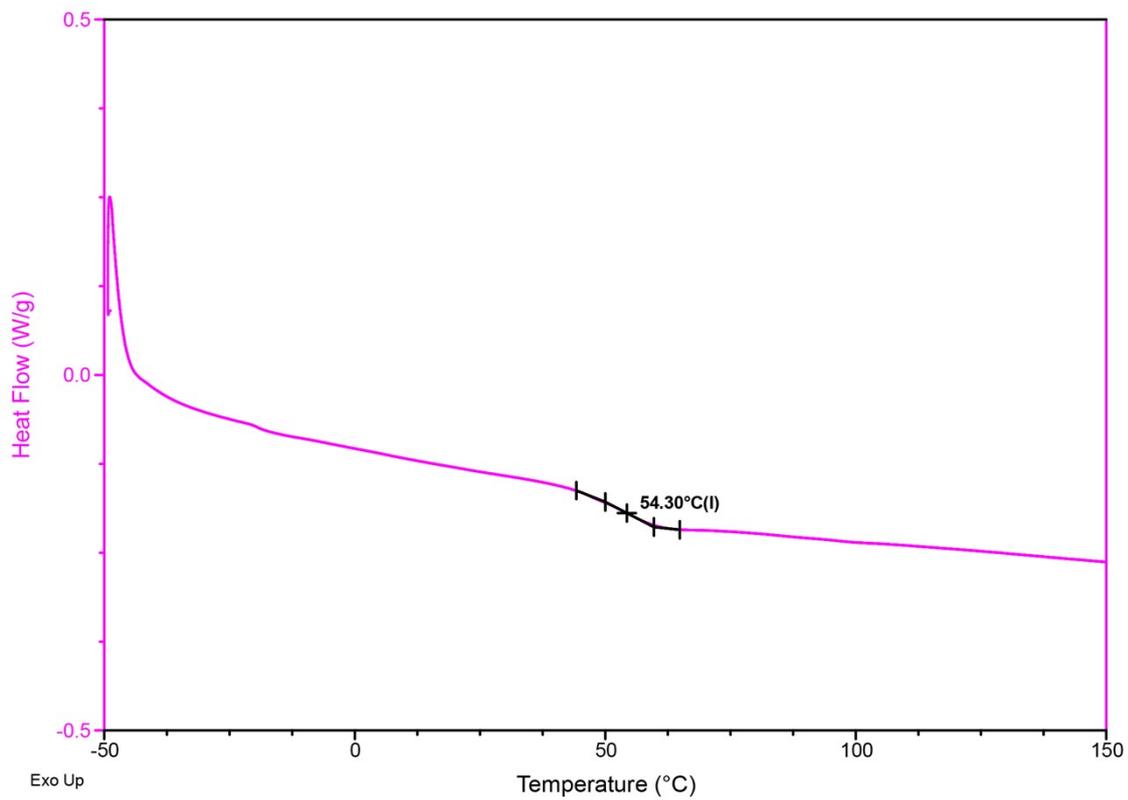


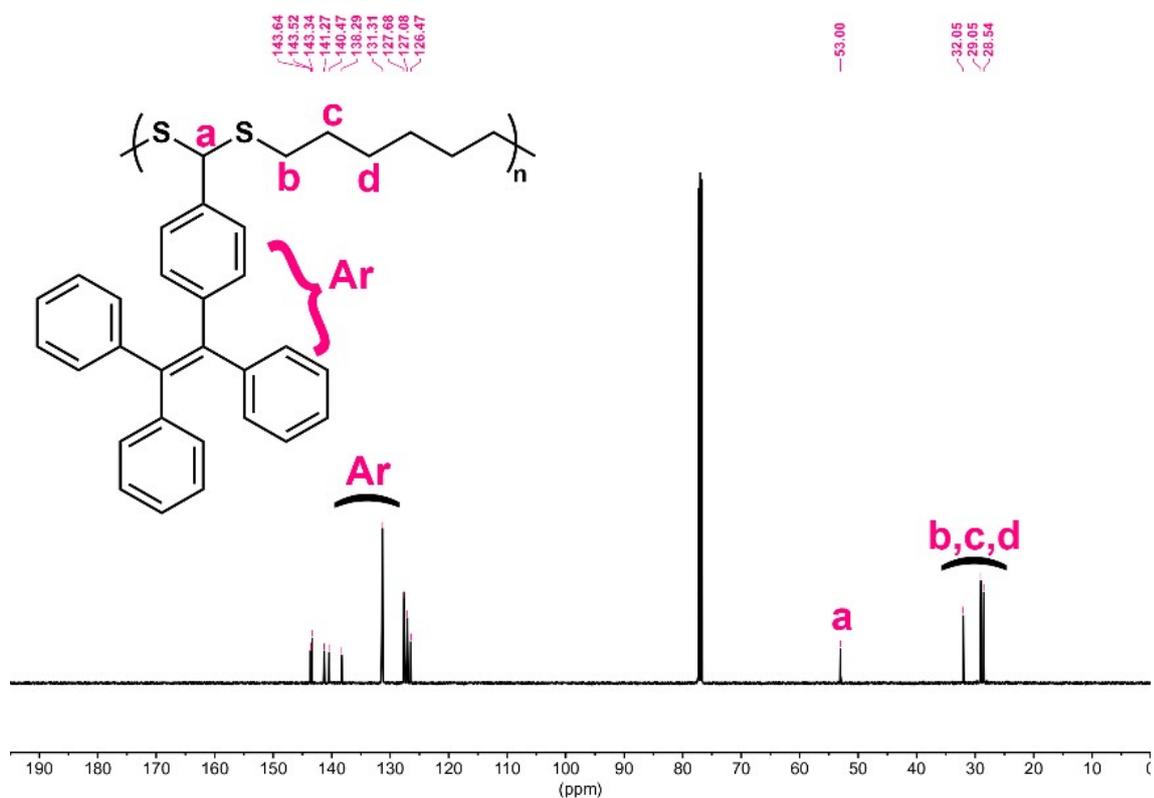
Figure S37. FT-IR spectrum of P9.



**Figure S38.** DSC thermogram of P9.

## Synthesis of P10

General procedure was followed: 4-(1,2,2-Triphenylethenyl)benzaldehyde (397 mg, 1.10 mmol), HDT (153  $\mu$ L, 1.00 mmol), and CDMS (56  $\mu$ L, 0.50 mmol) were reacted in 250  $\mu$ L of THF. P10 was obtained as a greenish solid (yield = 462 mg, 94%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14-6.97 (19H, ArH), 4.79 (1H, ArCHS), 2.44 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.49-1.29 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.64, 143.52, 143.34, 141.27, 140.47, 138.29, 131.31, 127.68, 127.08, 126.47, 53.00, 32.05, 29.05, 28.54.



**Figure S39.**  $^{13}\text{C}$  NMR spectrum of P10 ( $\text{CDCl}_3$ , 125 MHz).

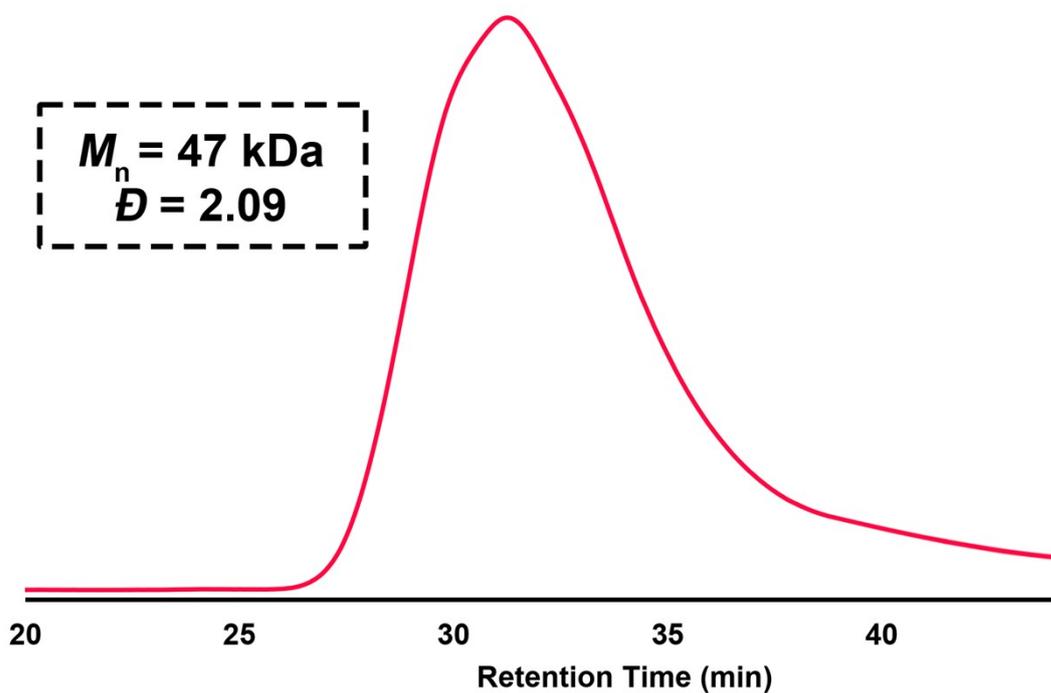


Figure S40. GPC chromatogram of P10.

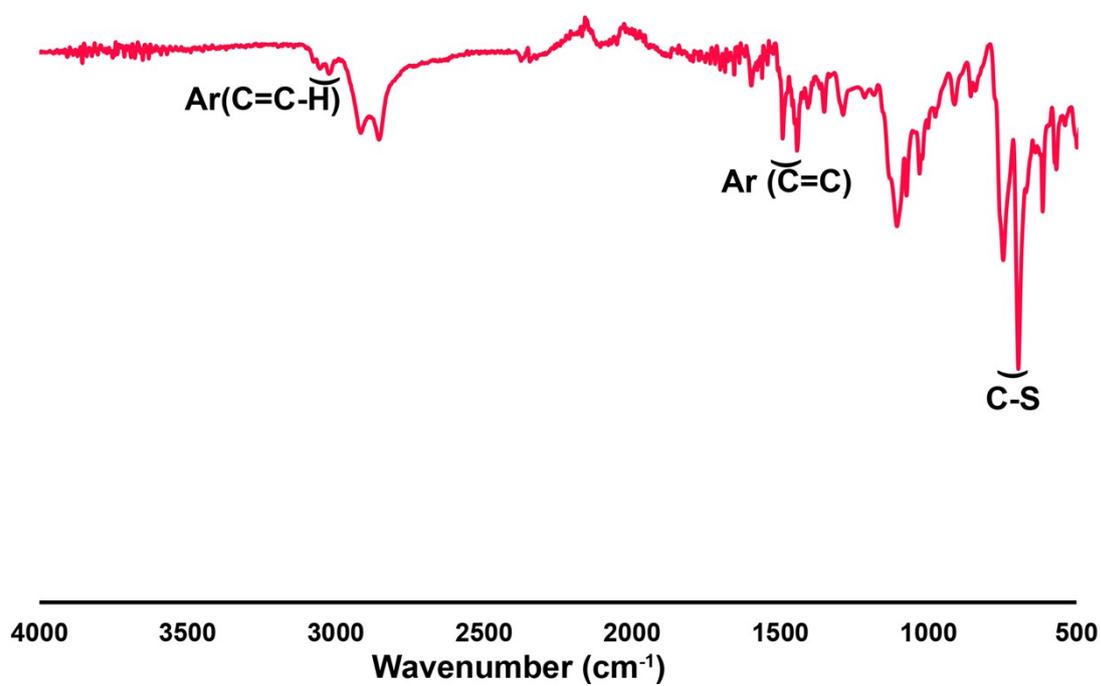
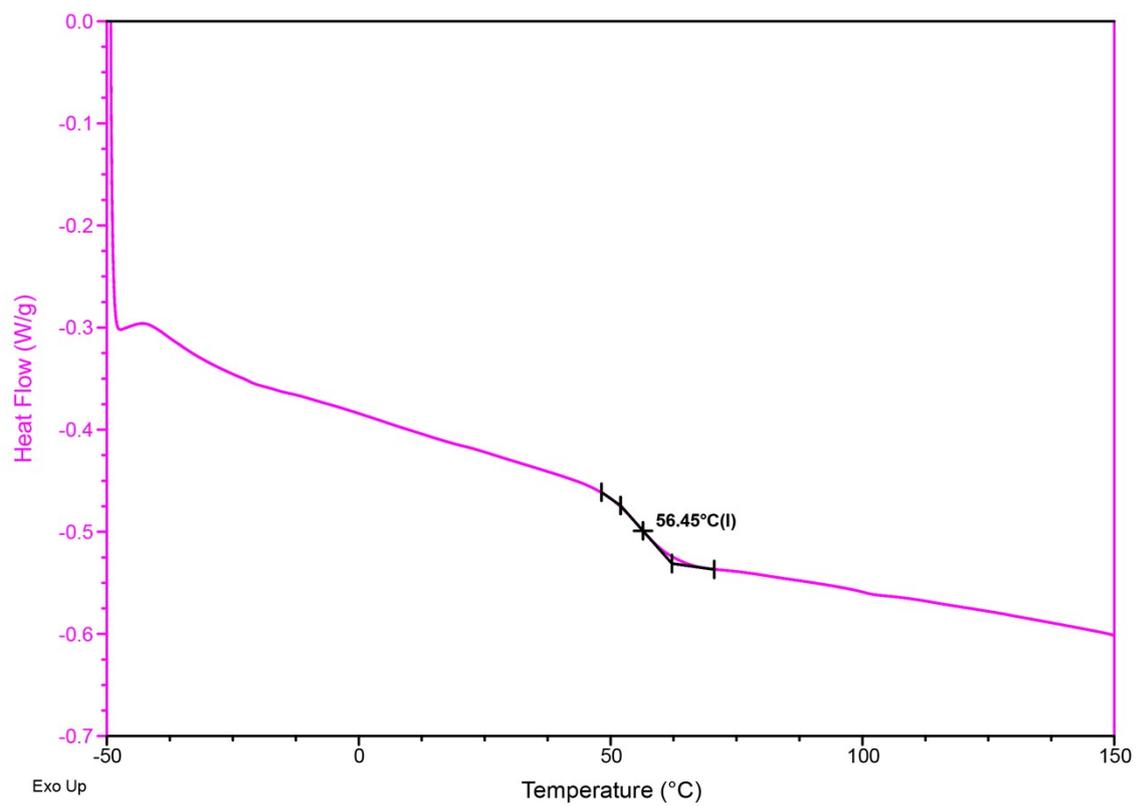


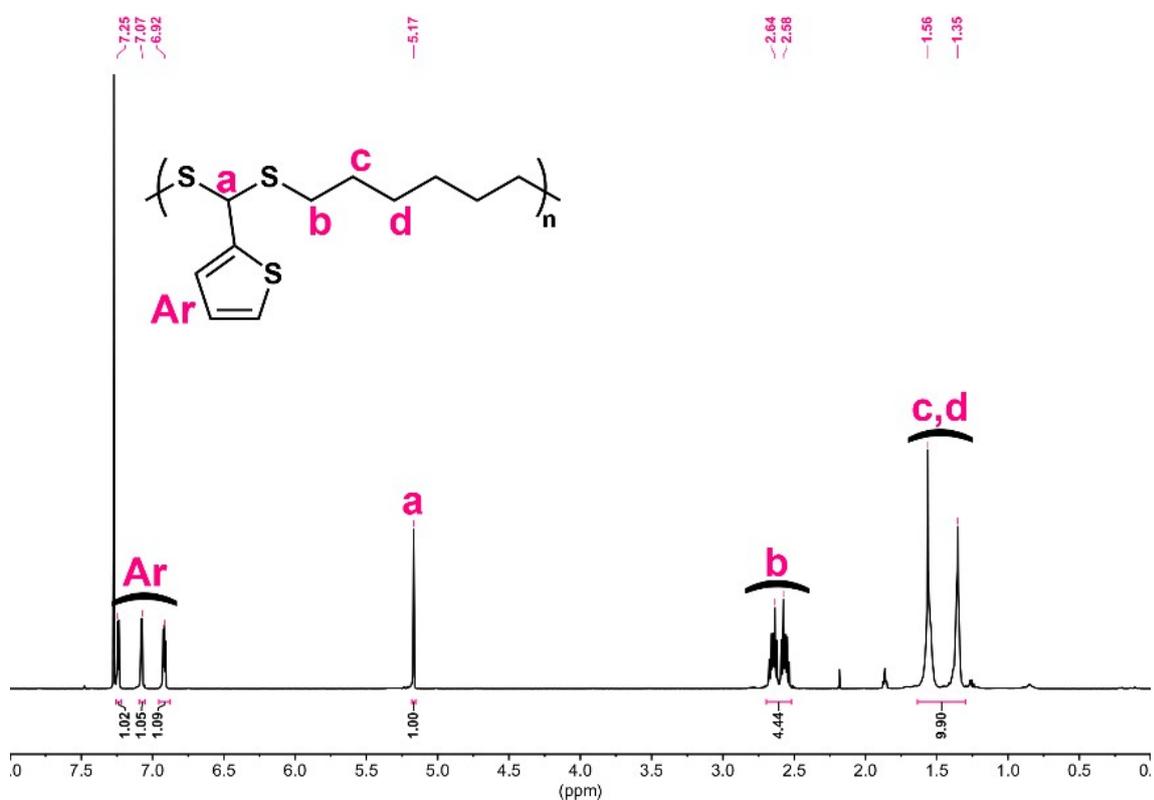
Figure S41. FT-IR spectrum of P10.



**Figure S42.** DSC thermogram of P10.

## Synthesis of P11

General procedure was followed: 2-Thiophenecarboxaldehyde (206  $\mu\text{L}$ , 2.20 mmol), HDT (306  $\mu\text{L}$ , 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P11 was obtained as a white sticky solid (yield = 433 mg, 89%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.25-6.92 (3H, ArH), 5.17 (1H, ArCHS), 2.64-2.58 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.56-1.35 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.15, 126.44, 125.76, 125.45, 48.41, 32.01, 28.90, 28.45.



**Figure S43.**  $^1\text{H}$  NMR spectrum of P11 ( $\text{CDCl}_3$ , 500 MHz).

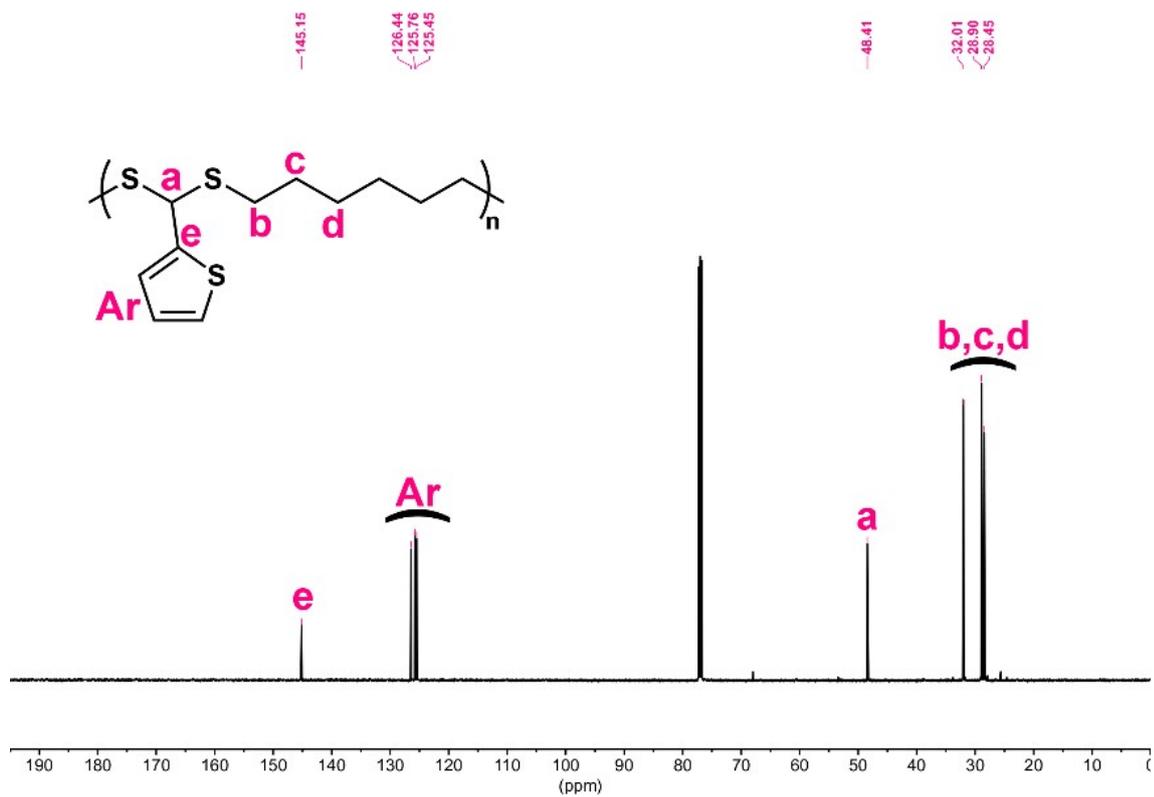


Figure S44. <sup>13</sup>C NMR spectrum of P11 (CDCl<sub>3</sub>, 125 MHz).

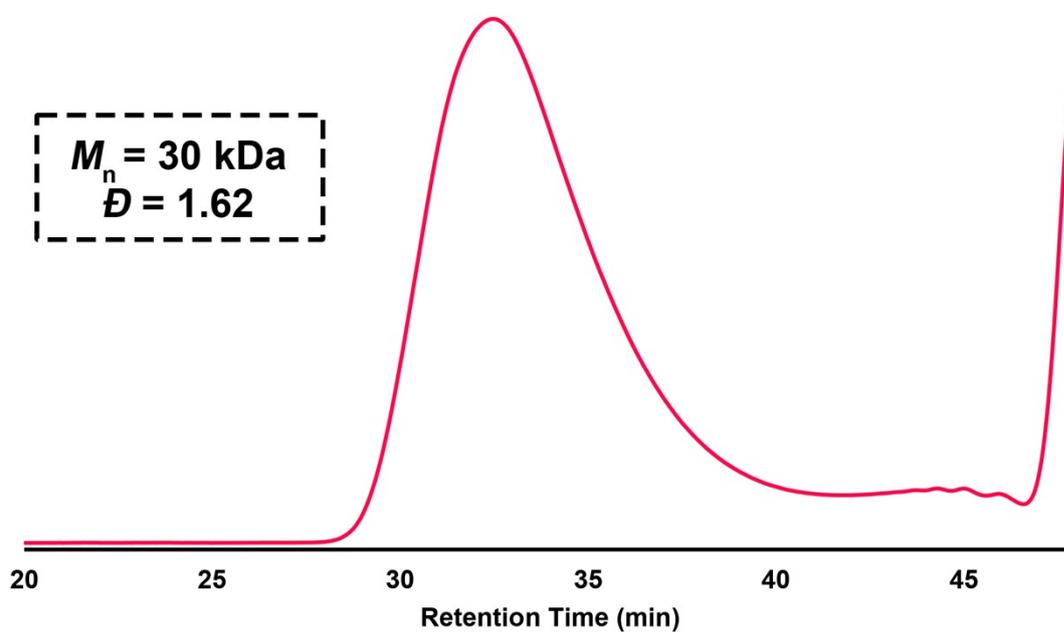
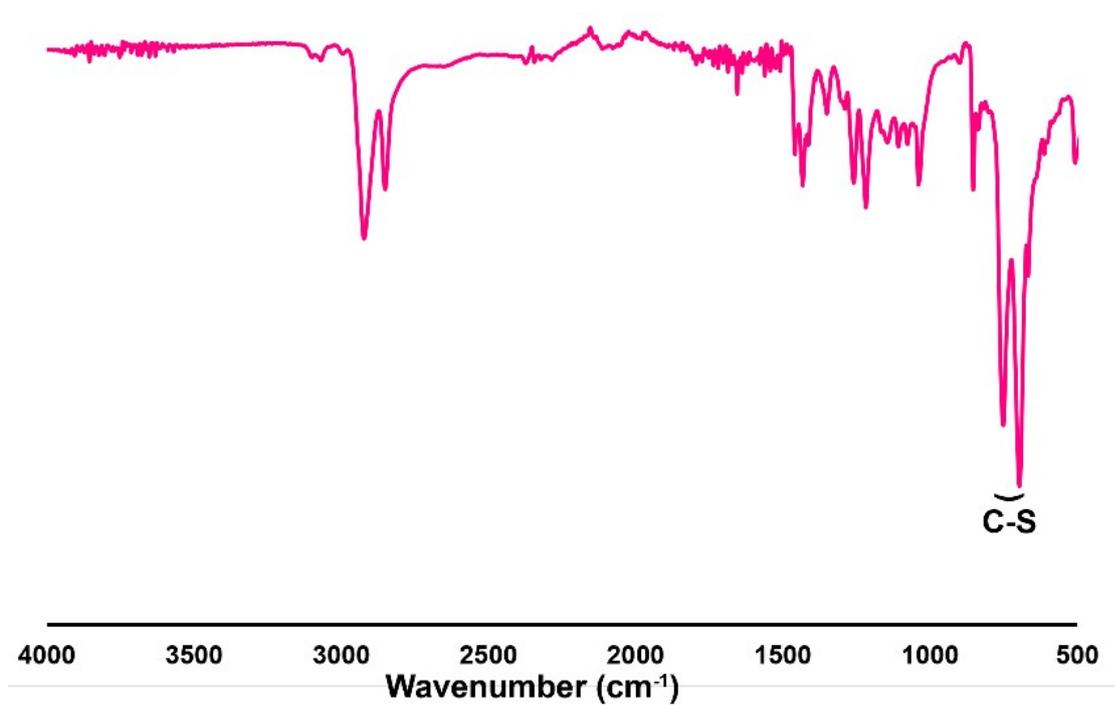


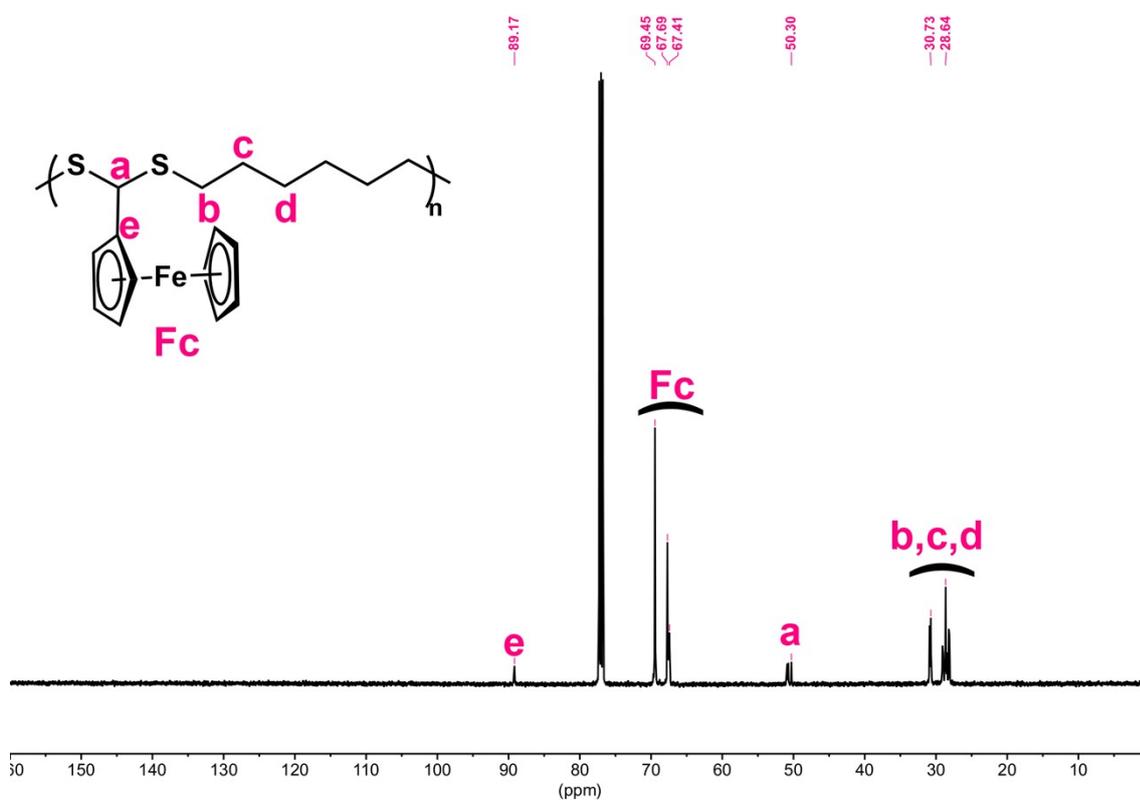
Figure S45. GPC chromatogram of P11.



**Figure S46.** FT-IR spectrum of P11.

## Synthesis of P12

General procedure was followed: Ferrocenecarboxaldehyde (471 mg, 2.20 mmol), HDT (306  $\mu\text{L}$ , 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P12 was obtained as a reddish sticky solid (yield = 636 mg, 92%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.77 (1H, ArCHS), 4.27-4.15 (9H, FcH), 2.70-2.53 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.68-1.40 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  89.17, 69.45, 67.69, 67.41, 50.30, 30.73, 28.64.



**Figure S47.**  $^{13}\text{C}$  NMR spectrum of P12 ( $\text{CDCl}_3$ , 125 MHz).

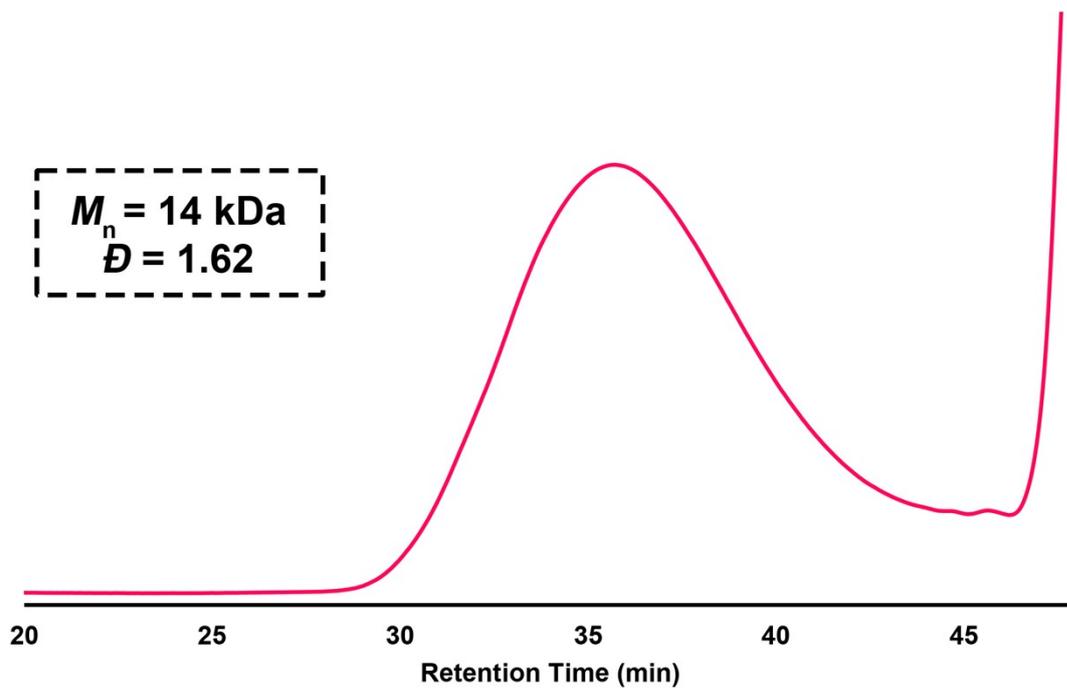


Figure S48. GPC chromatogram of P12.

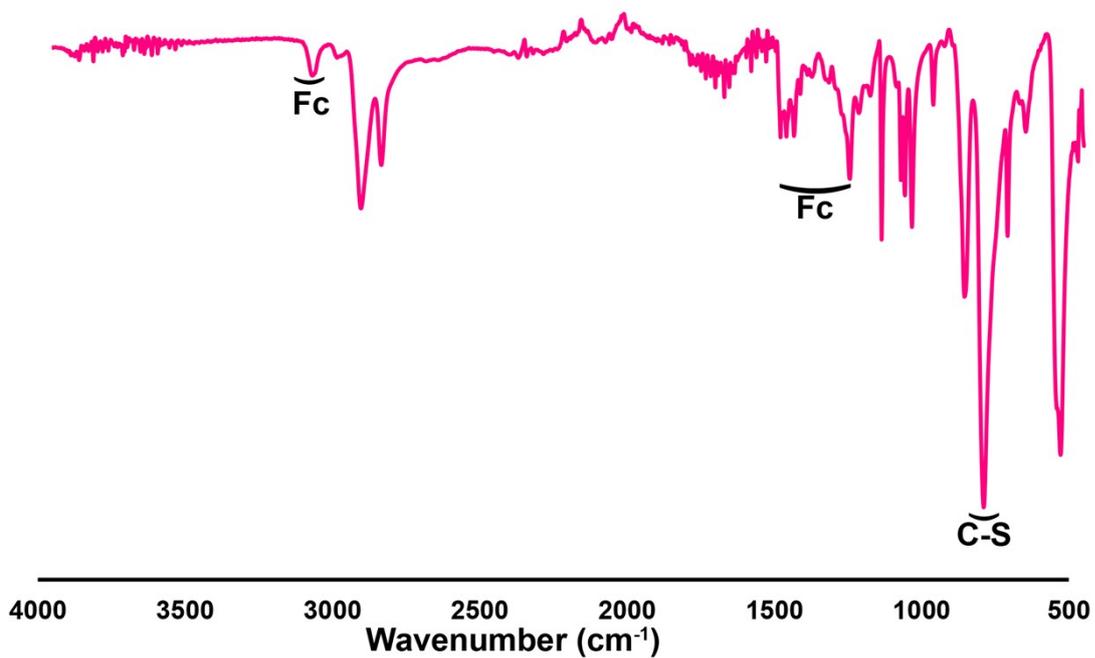
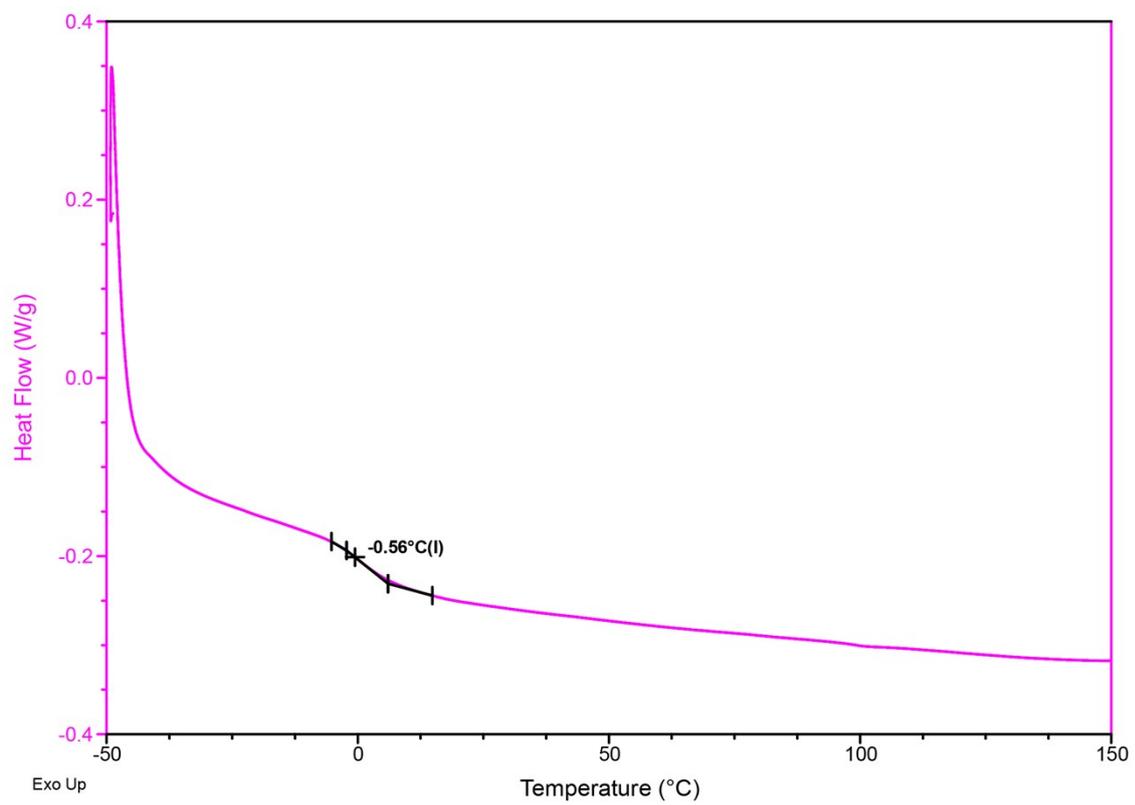


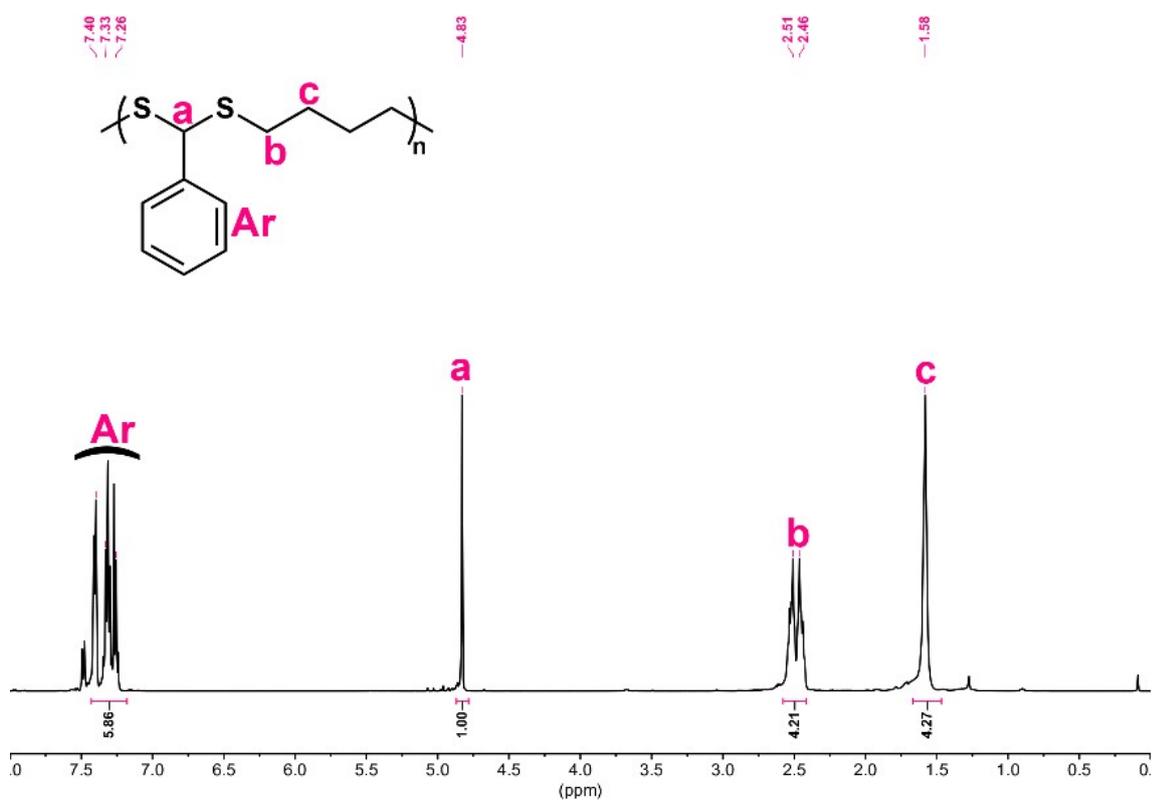
Figure S49. FT-IR spectrum of P12.



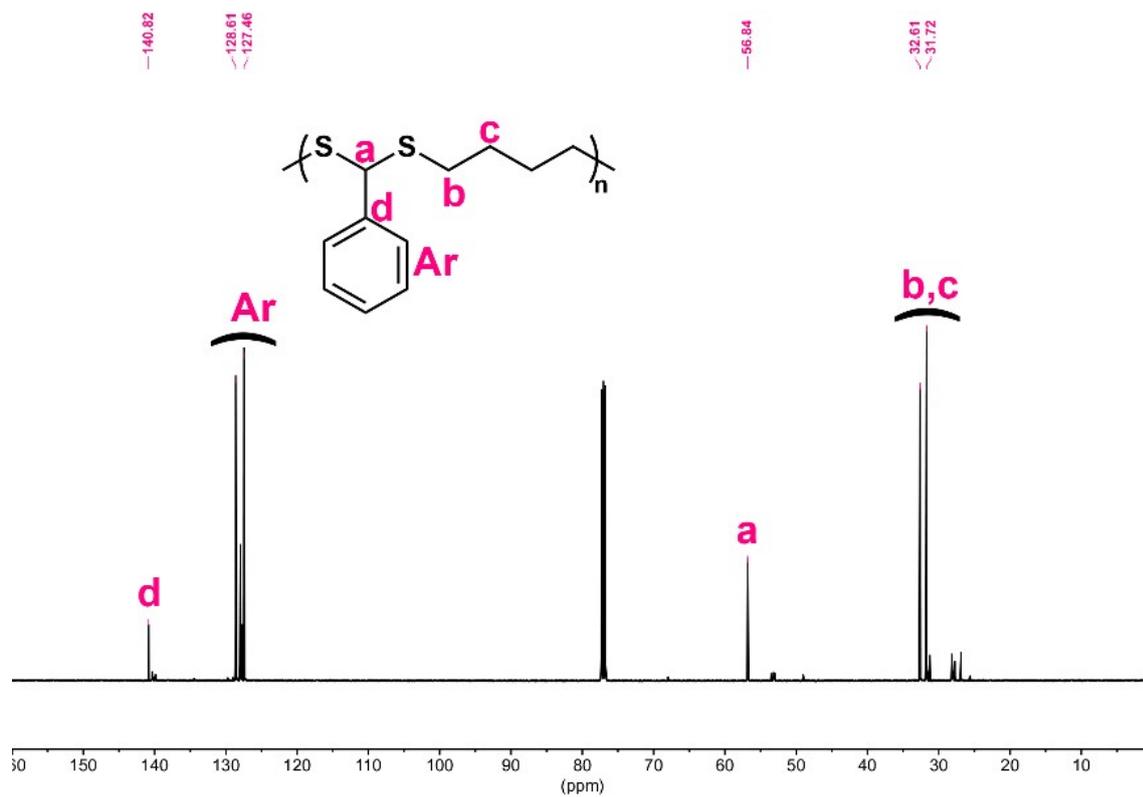
**Figure S50.** DSC thermogram of P12.

## Synthesis of P13

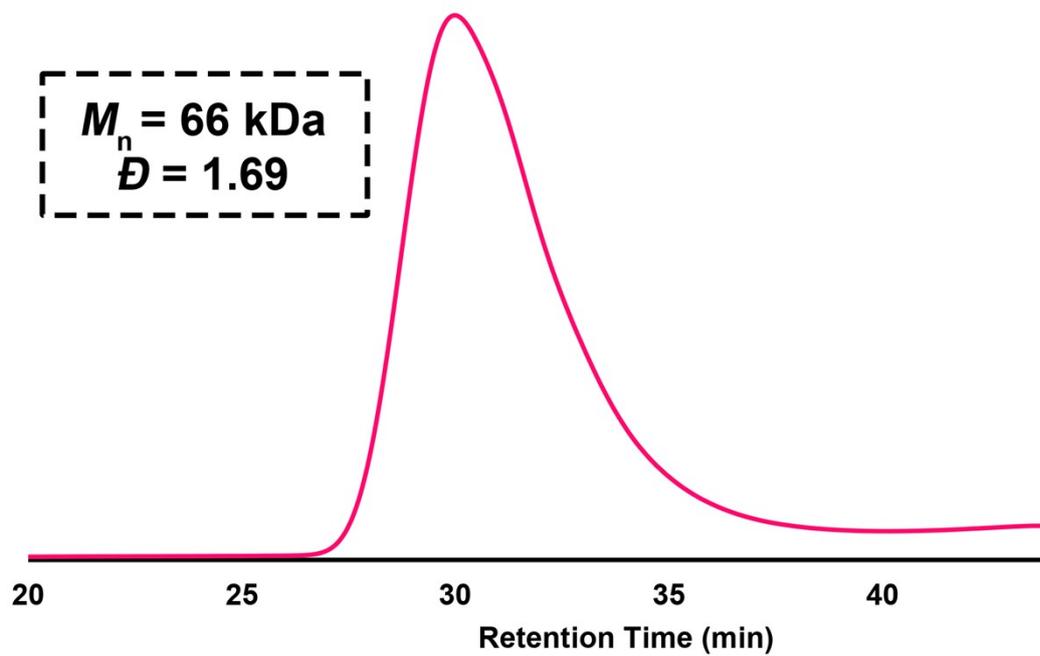
General procedure was followed: BA (224  $\mu\text{L}$ , 2.20 mmol), 1,4-butanedithiol (235  $\mu\text{L}$ , 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P13 was obtained as a white sticky solid (yield = 411 mg, 98%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40-7.26 (5H, ArH), 4.83 (1H, ArCHS), 2.51-2.46 (4H,  $\text{SCH}_2(\text{CH}_2)_2\text{CH}_2\text{S}$ ), 1.58 (4H,  $\text{SCH}_2(\text{CH}_2)_2\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.82, 128.61, 127.46, 56.84, 32.61, 31.72.



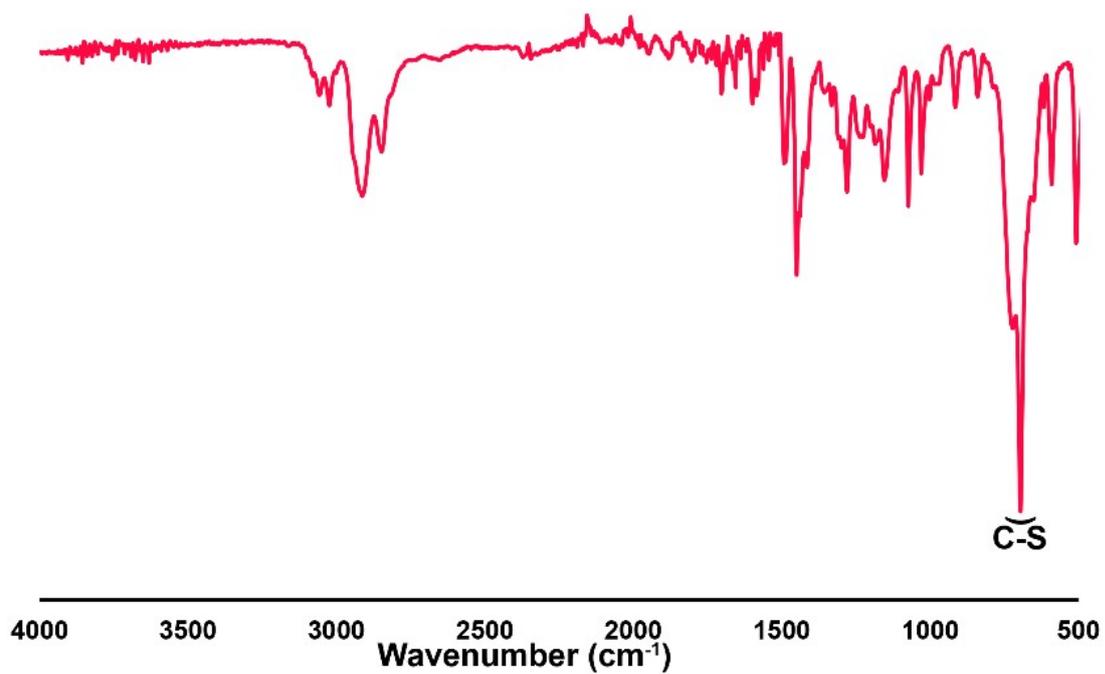
**Figure S51.**  $^1\text{H}$  NMR spectrum of P13 ( $\text{CDCl}_3$ , 500 MHz).



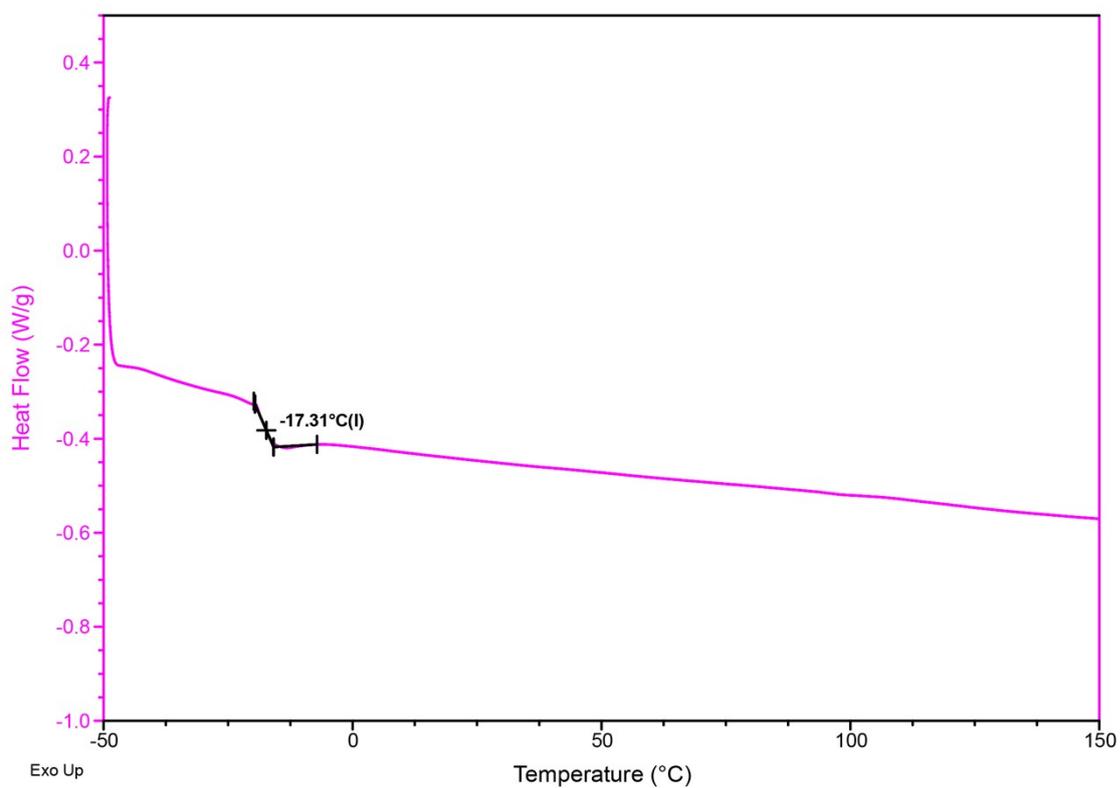
**Figure S52.**  $^{13}\text{C}$  NMR spectrum of P13 ( $\text{CDCl}_3$ , 125 MHz).



**Figure S53.** GPC chromatogram of P13.



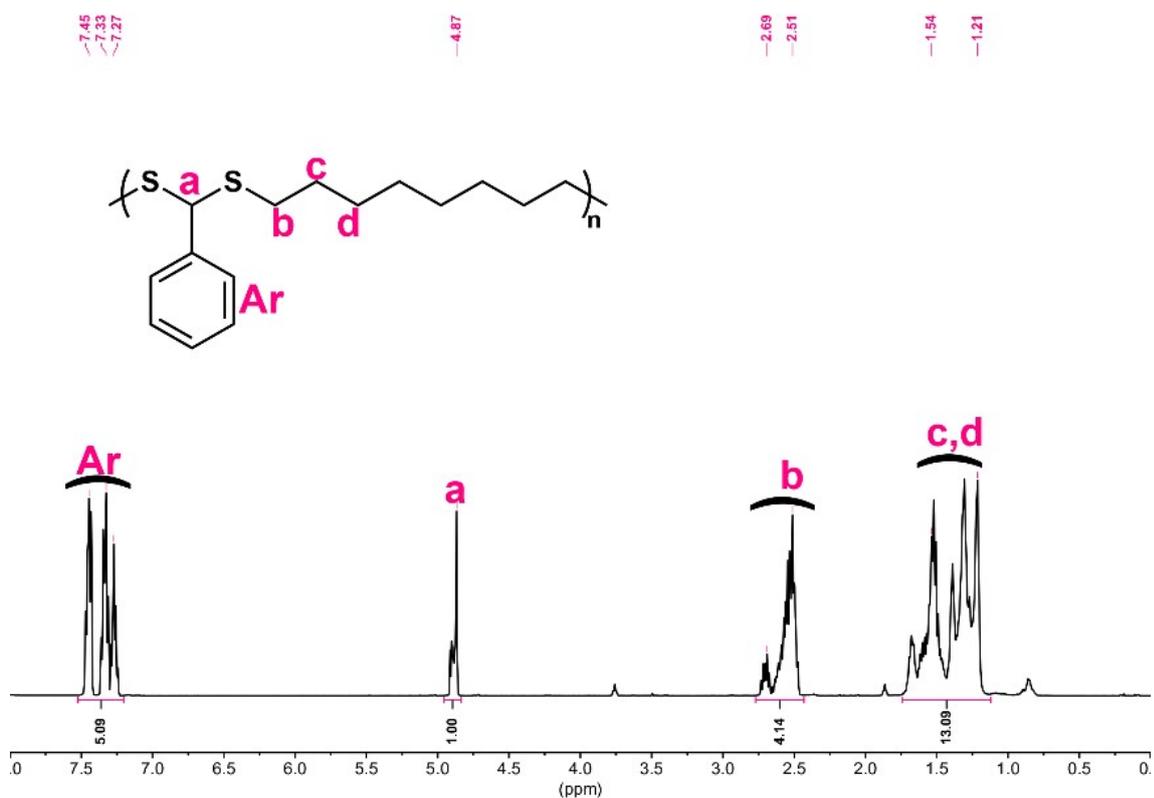
**Figure S54.** FT-IR spectrum of P13.



**Figure S55.** DSC thermogram of P13.

## Synthesis of P14

General procedure was followed. BA (224  $\mu\text{L}$ , 2.20 mmol), 1,8-octanedithiol (368  $\mu\text{L}$ , 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P14 was obtained as a white sticky solid (yield = 516 mg, 97%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45-7.27 (5H, ArH), 4.87 (1H, ArCHS), 2.69-2.51 (4H,  $\text{SCH}_2(\text{CH}_2)_6\text{CH}_2\text{S}$ ), 1.54-1.21 (12H,  $\text{SCH}_2(\text{CH}_2)_6\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.62, 128.49, 127.69, 53.30, 32.26, 29.11, 28.79.



**Figure S56.**  $^1\text{H}$  NMR spectrum of P14 ( $\text{CDCl}_3$ , 500 MHz).

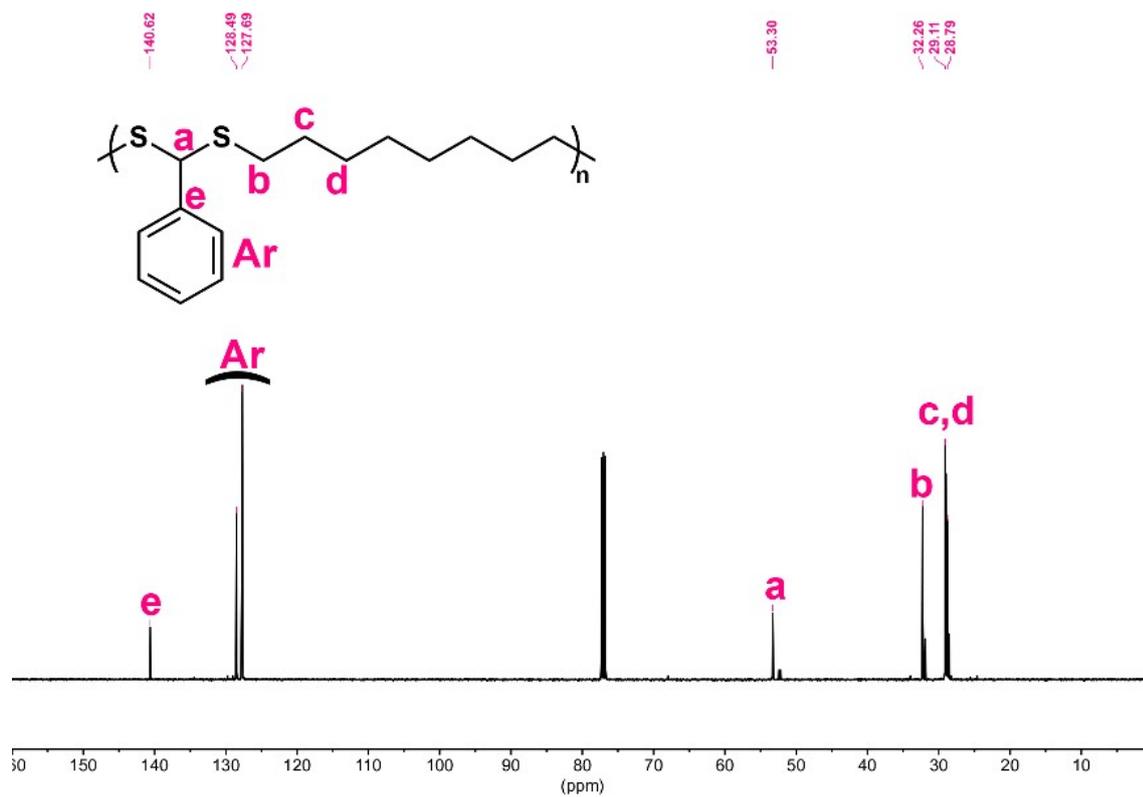


Figure S57.  $^{13}\text{C}$  NMR spectrum of P14 ( $\text{CDCl}_3$ , 125 MHz).

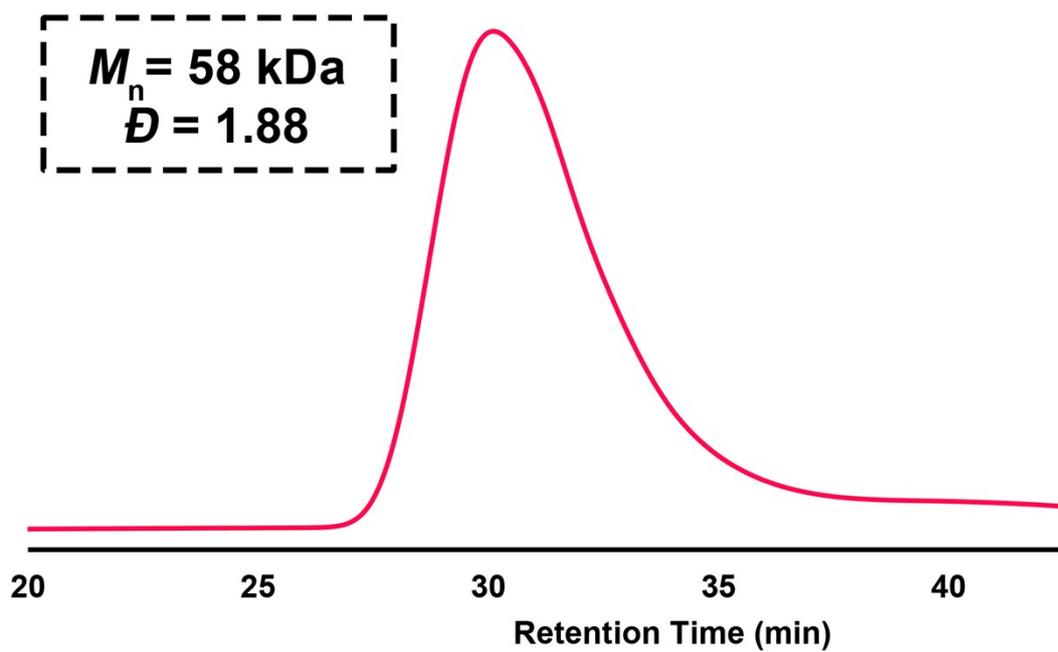
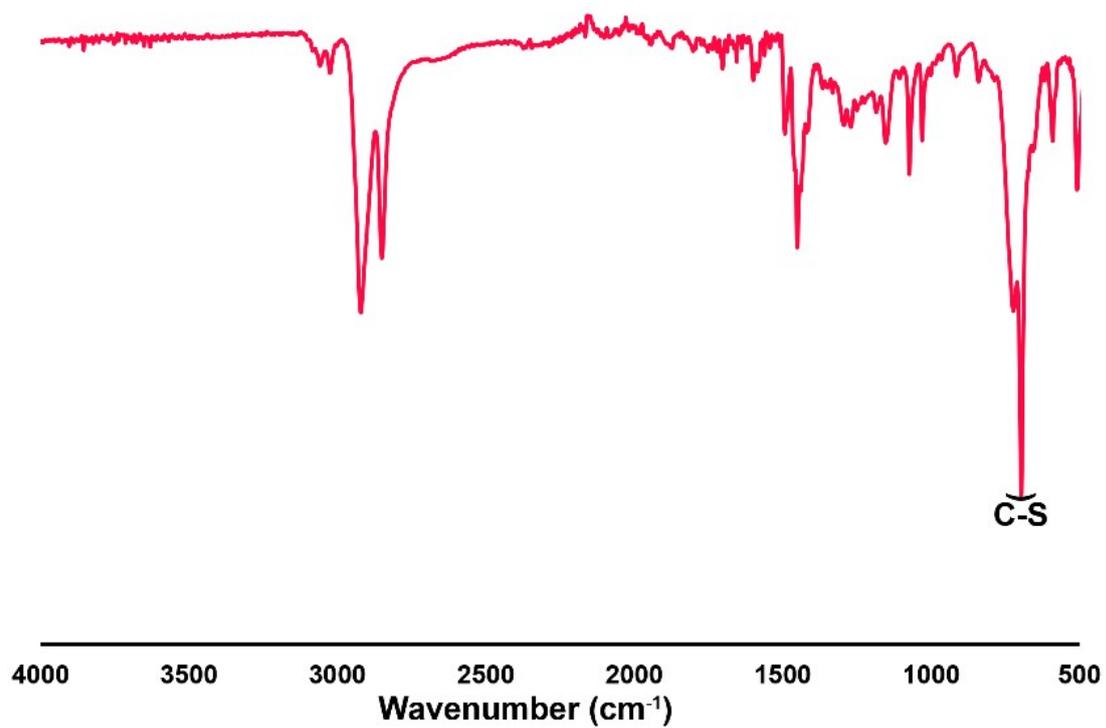
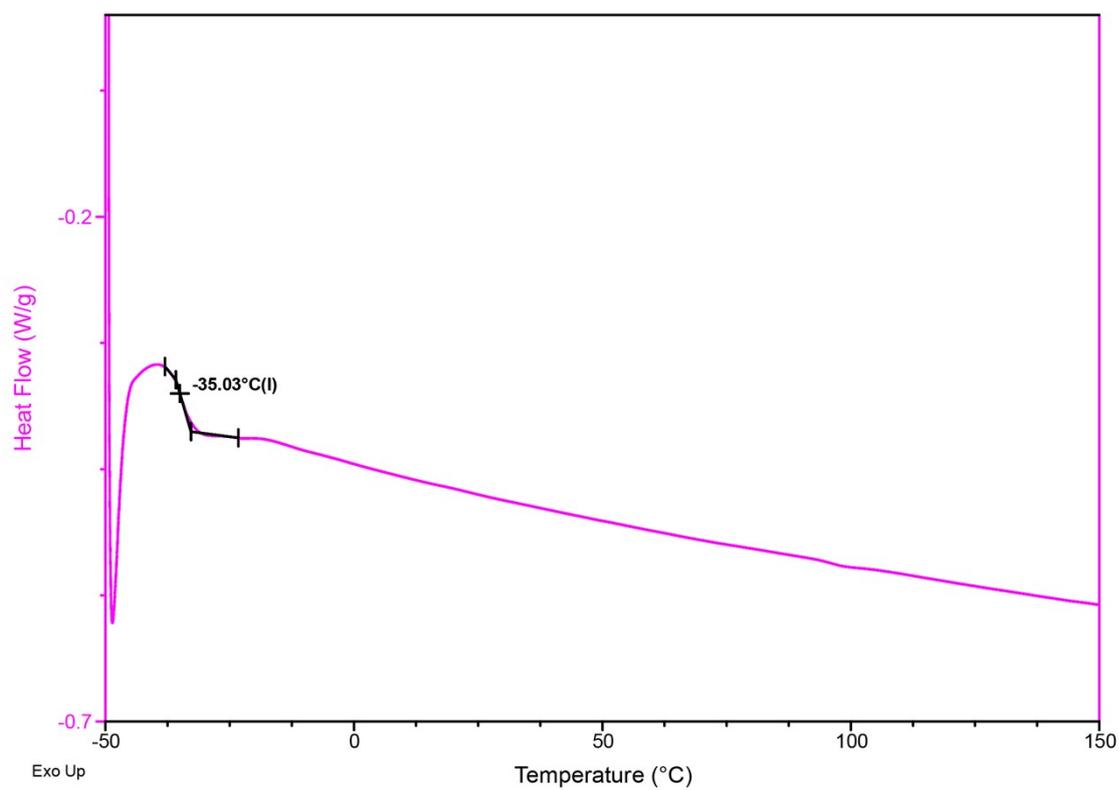


Figure S58. GPC chromatogram of P14.



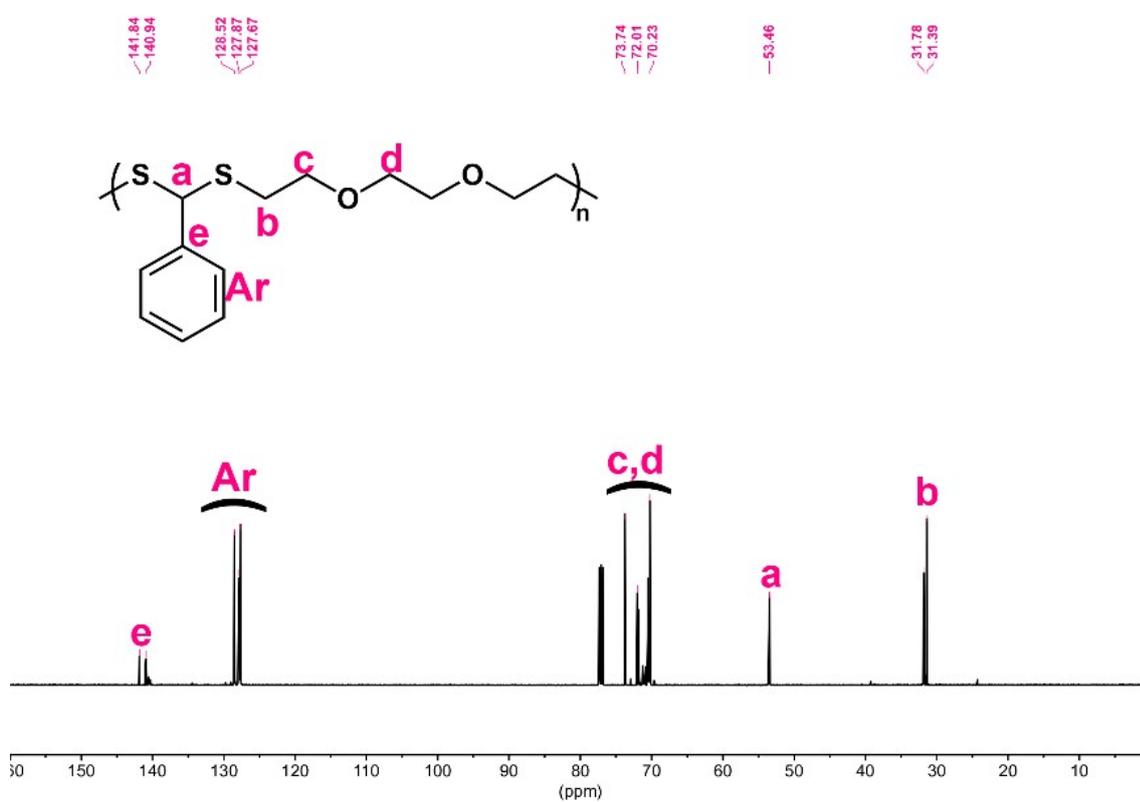
**Figure S59.** FT-IR spectrum of P14.



**Figure S60.** DSC thermogram of P14.

## Synthesis of P15

General procedure was followed: BA (224  $\mu\text{L}$ , 2.20 mmol), 2,2'-(ethylenedioxy)diethanethiol (326  $\mu\text{L}$ , 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P15 was obtained as a white sticky solid (yield = 513 mg, 95%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42-7.25 (5H, ArH), 5.09 (1H, ArCHS), 3.58-3.52 (8H,  $\text{SCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{S}$ ), 2.78-2.69 (4H,  $\text{SCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.84, 140.94, 128.52, 127.87, 127.67, 73.74, 72.01, 70.23, 53.46, 31.78, 31.39.



**Figure S61.**  $^{13}\text{C}$  NMR spectrum of P15 ( $\text{CDCl}_3$ , 125 MHz).

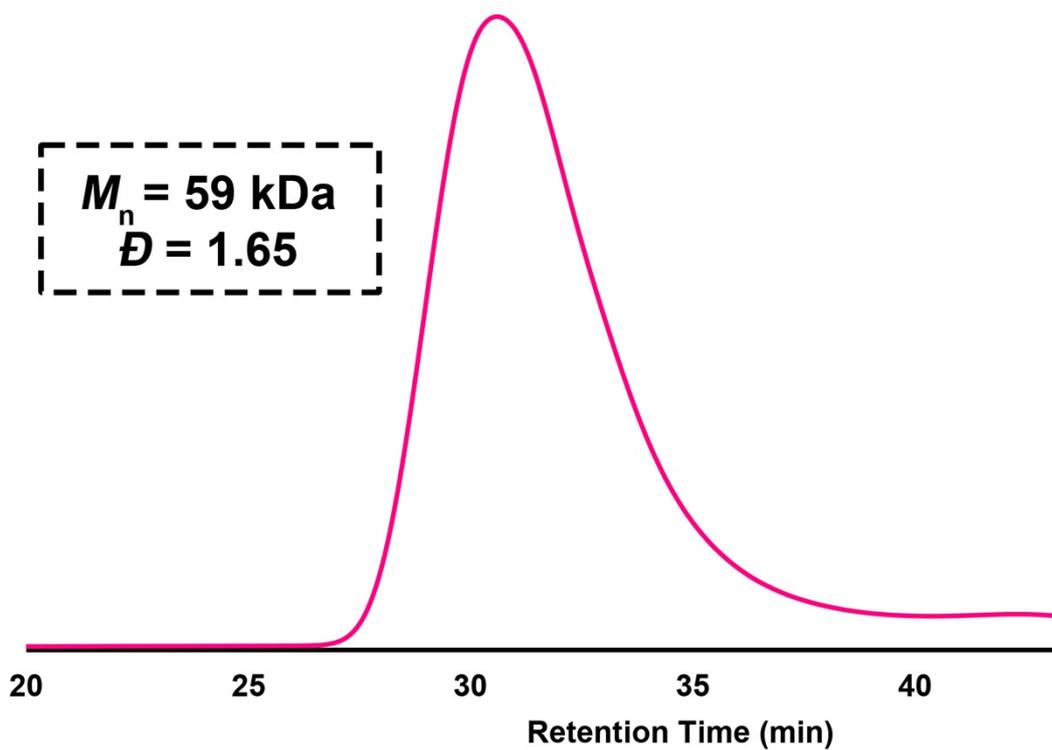


Figure S62. GPC chromatogram of P15.

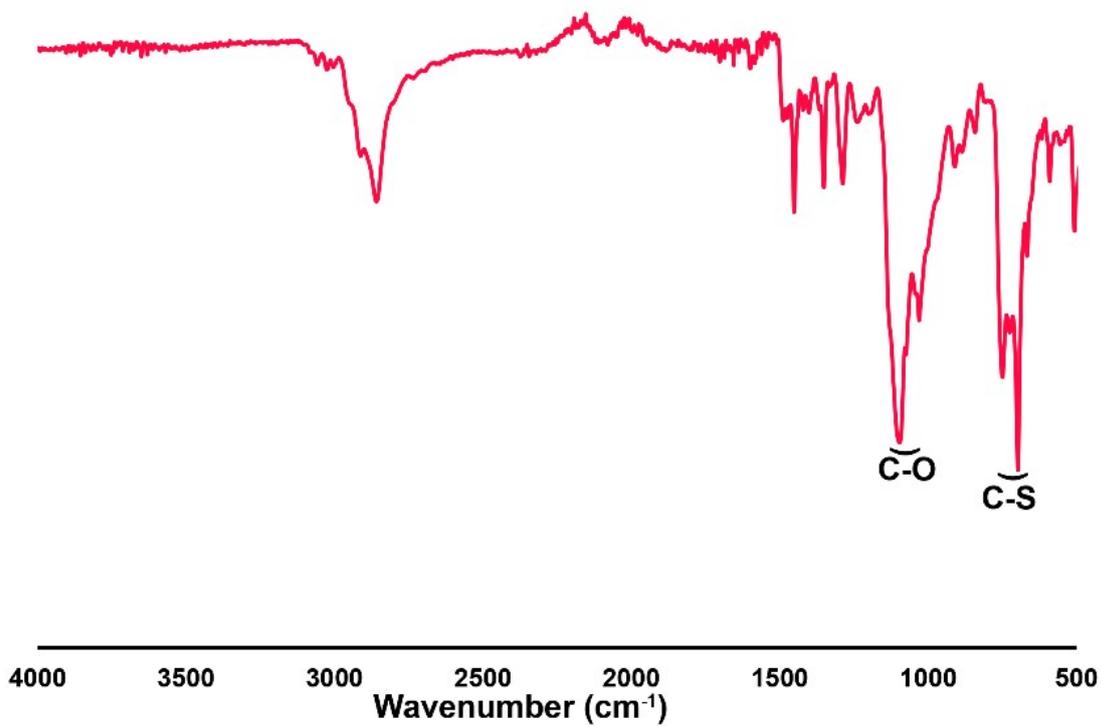
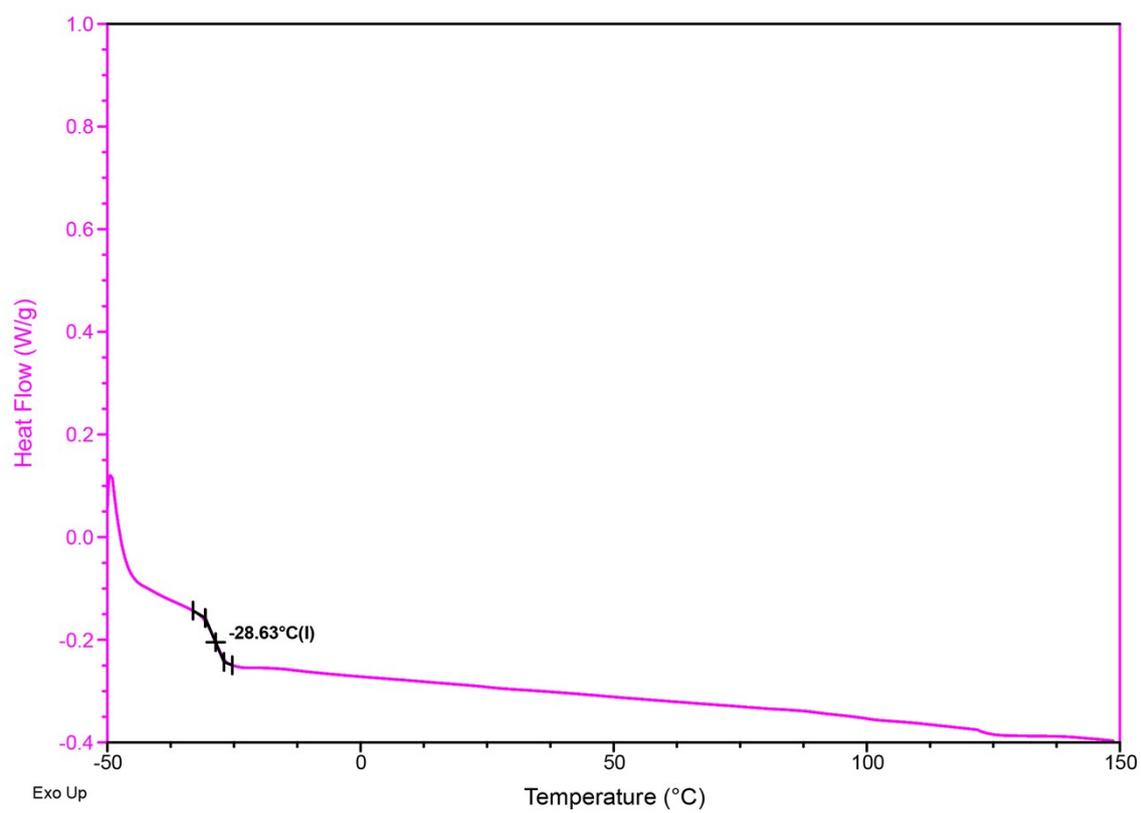


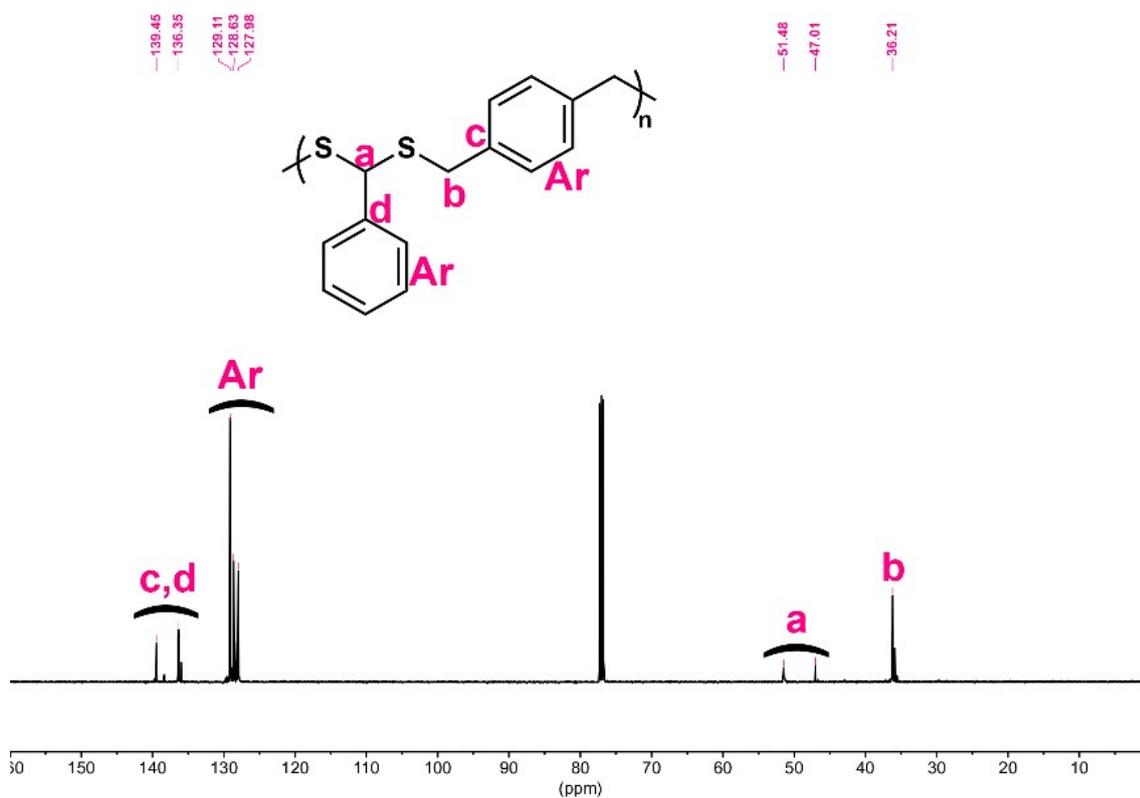
Figure S63. FT-IR spectrum of P15.



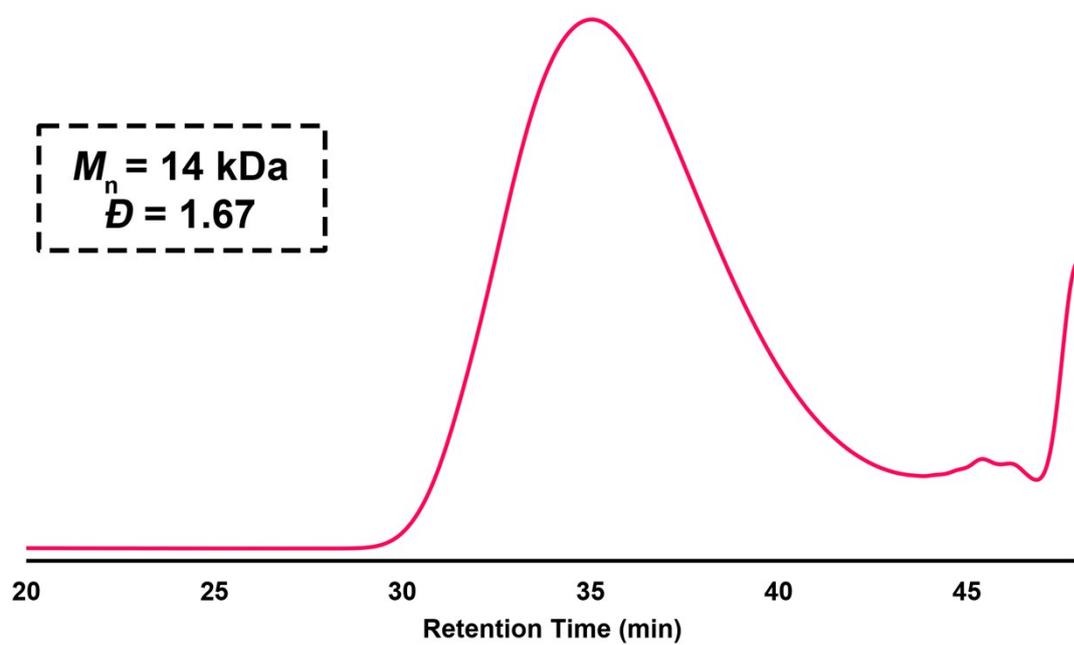
**Figure S64.** DSC thermogram of P15.

## Synthesis of P16

General procedure was followed: BA (224  $\mu\text{L}$ , 2.20 mmol), 1,4-benzenedimethanethiol (341 mg, 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P16 was obtained as a white solid (yield = 454 mg, 88%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.31-7.03 (9H, ArH), 4.47 (1H, ArCHS), 3.71-3.54 (4H,  $\text{CH}_2\text{Ar}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.45, 136.35, 129.11, 128.63, 127.98, 51.48, 47.01, 36.21.



**Figure S65.**  $^{13}\text{C}$  NMR spectrum of P16 ( $\text{CDCl}_3$ , 500 MHz).



**Figure S66.** GPC chromatogram of P16.

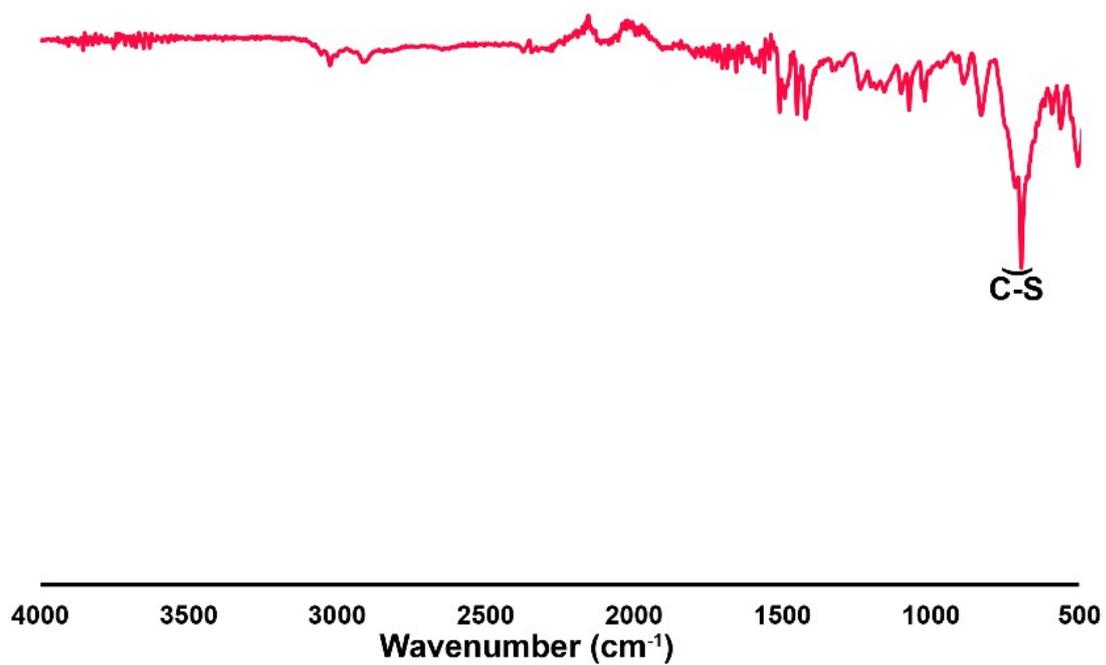


Figure S67. FT-IR spectrum of P16.

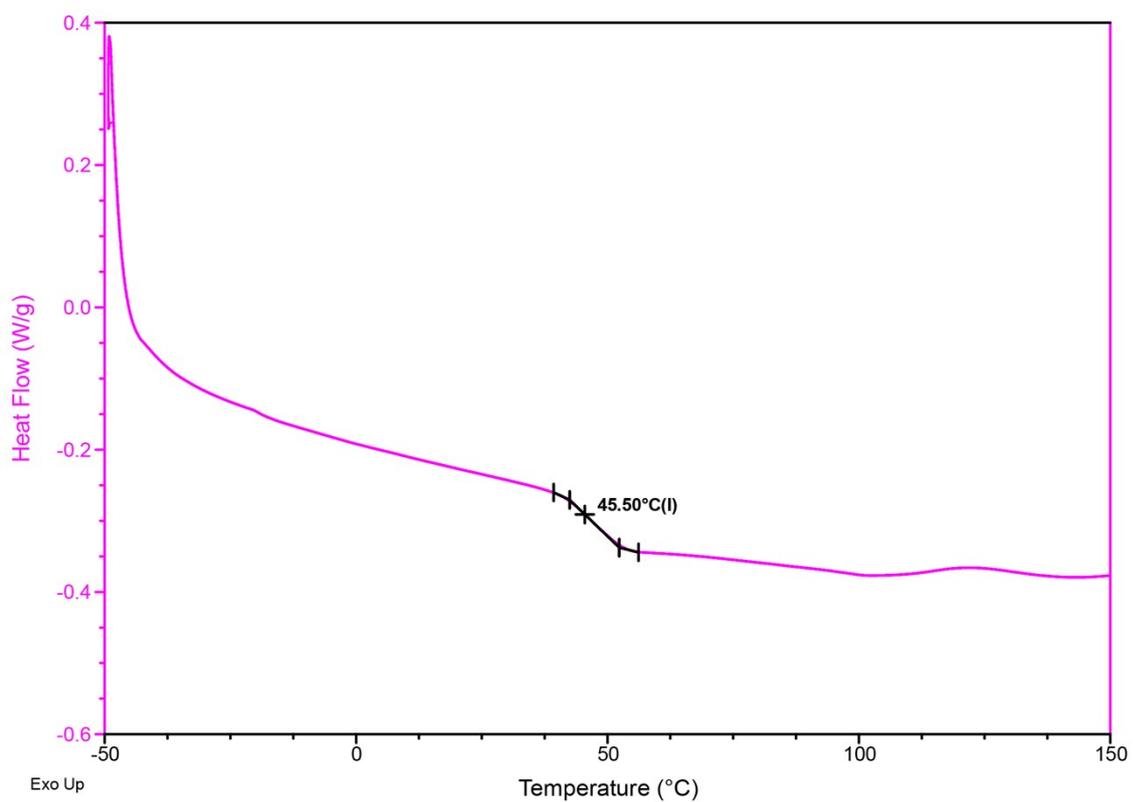
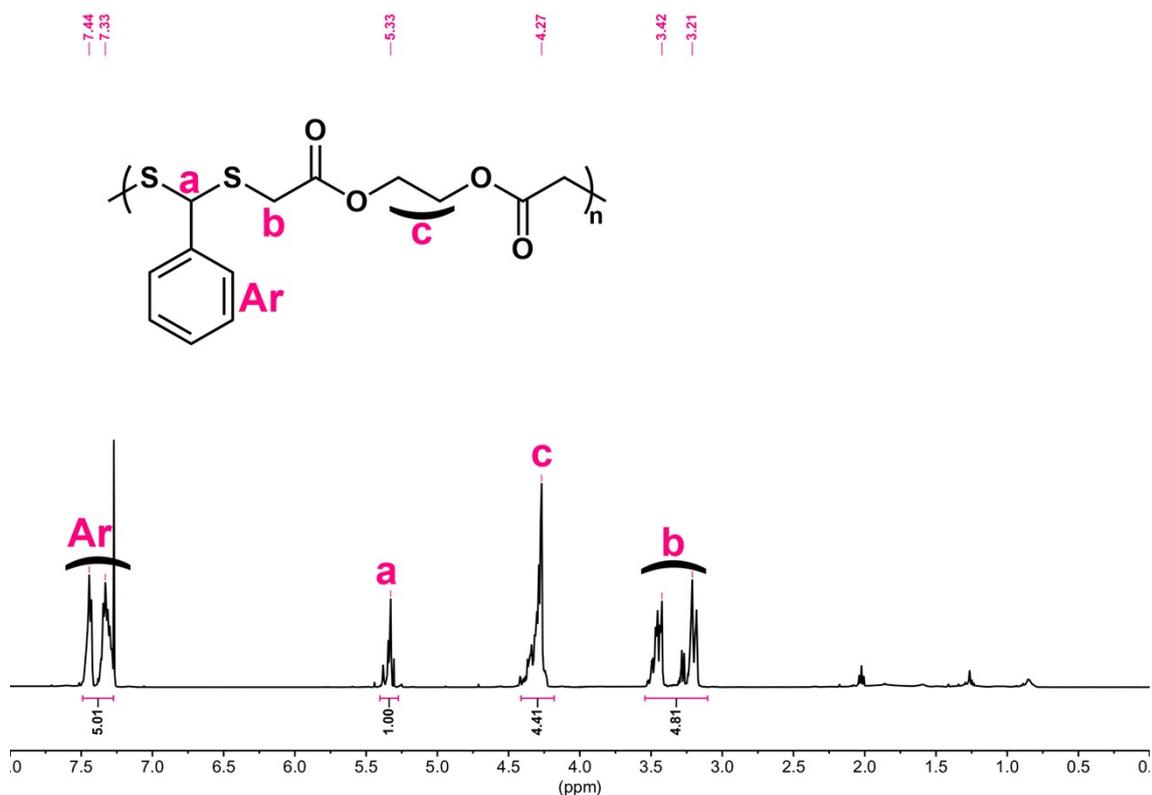


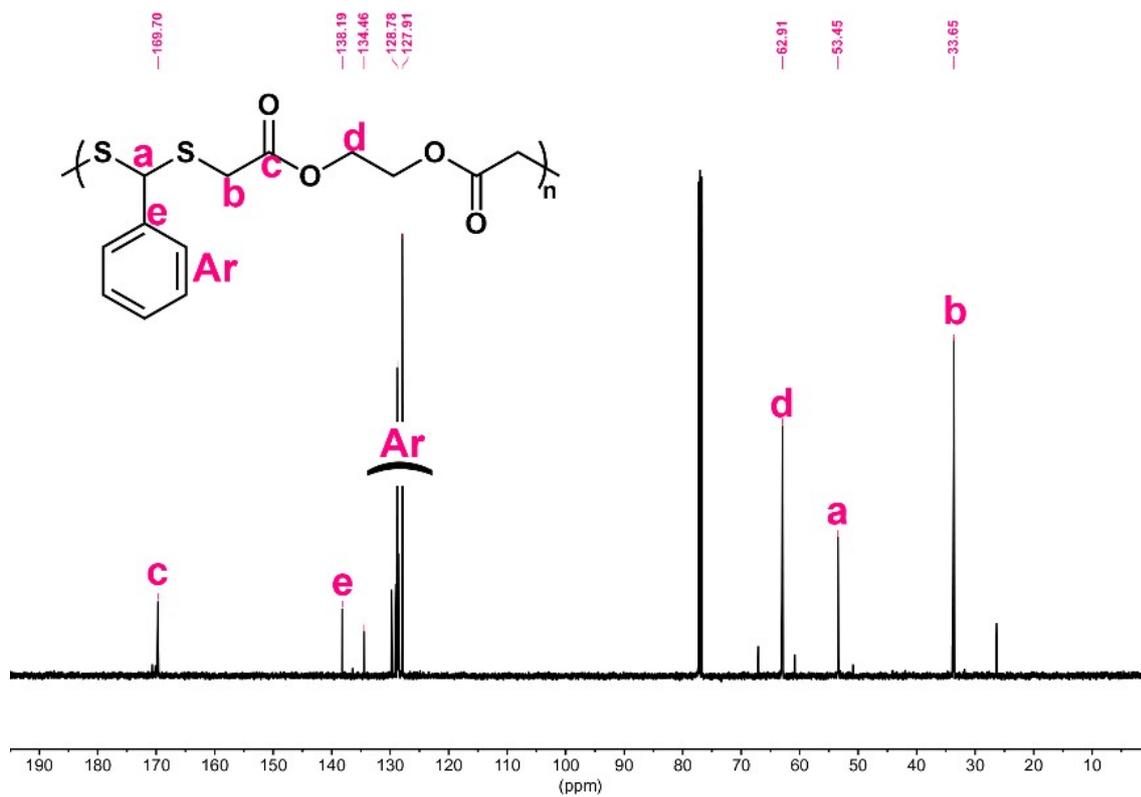
Figure S68. DSC thermogram of P16.

## Synthesis of P17

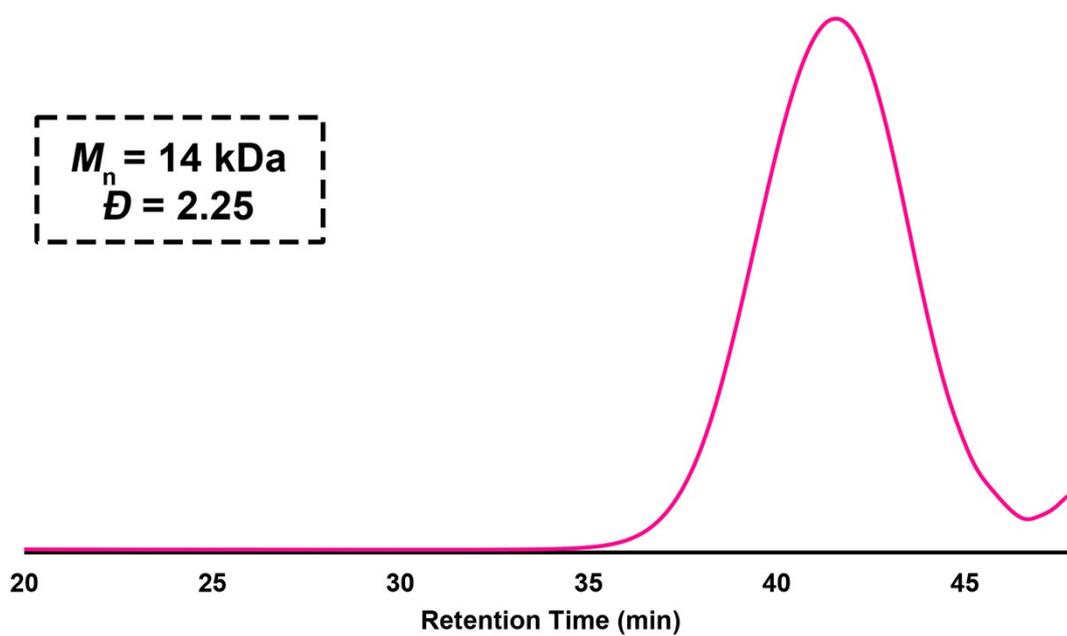
General procedure was followed: BA (224  $\mu\text{L}$ , 2.20 mmol), ethylene glycol bis-mercaptopacetate (319  $\mu\text{L}$ , 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P17 was obtained as a white sticky solid (yield = 530 mg, 89%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41-7.33 (5H, ArH), 5.33 (1H, ArCHS), 4.27 (4H,  $\text{SCH}_2(\text{C}=\text{O})\text{OCH}_2\text{CH}_2\text{O}(\text{C}=\text{O})\text{CH}_2\text{S}$ ), 3.42-3.21 (4H,  $\text{SCH}_2(\text{C}=\text{O})\text{OCH}_2\text{CH}_2\text{O}(\text{C}=\text{O})\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.70, 138.19, 134.46, 128.78, 127.91, 62.91, 53.45, 33.65.



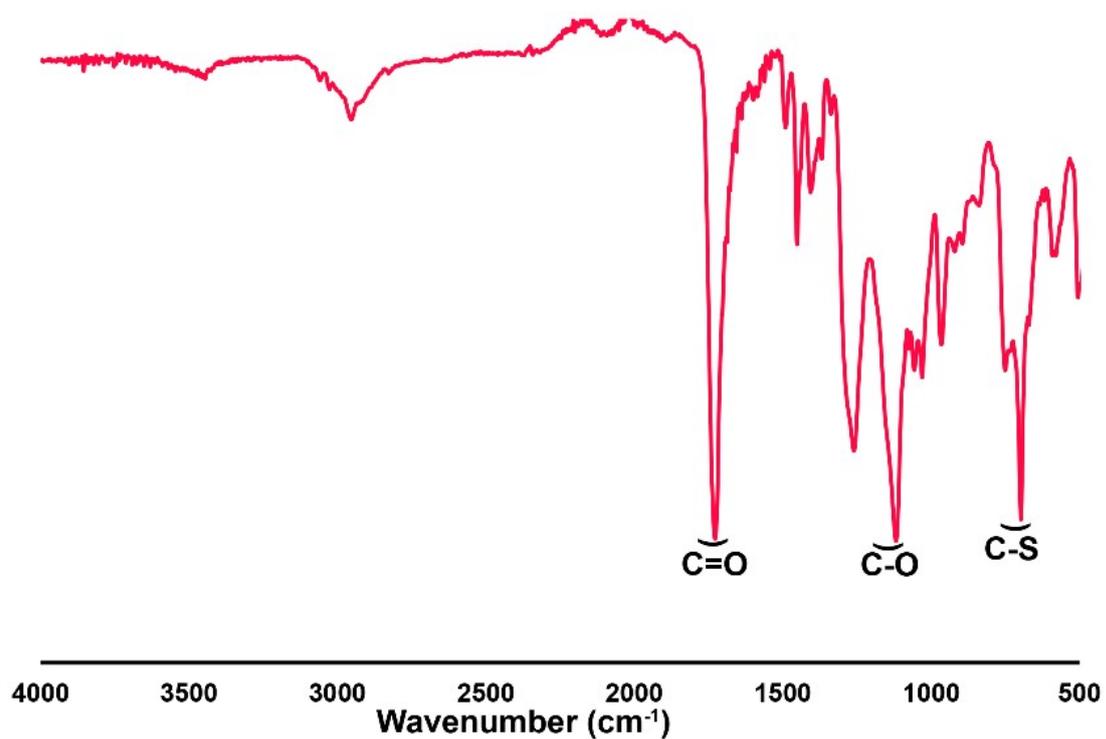
**Figure S69.**  $^1\text{H}$  NMR spectrum of P17 ( $\text{CDCl}_3$ , 500 MHz).



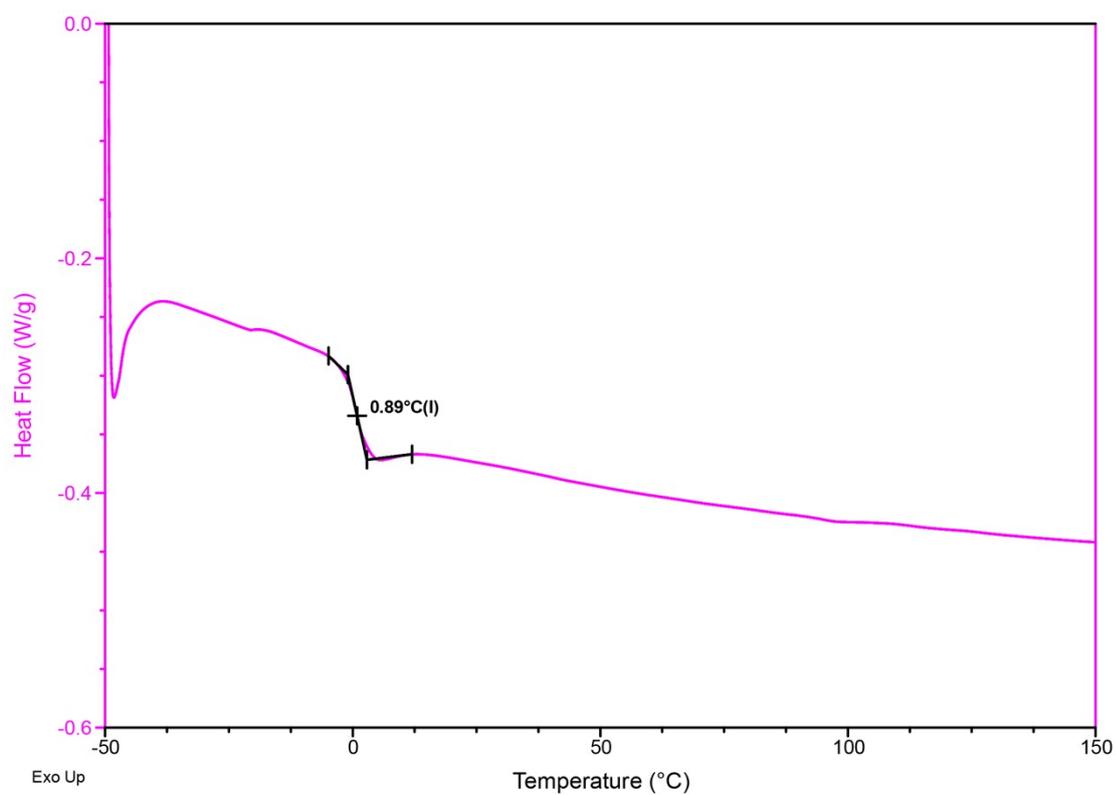
**Figure S70.** <sup>13</sup>C NMR spectrum of P17 (CDCl<sub>3</sub>, 500 MHz).



**Figure S71.** GPC chromatogram of P17.



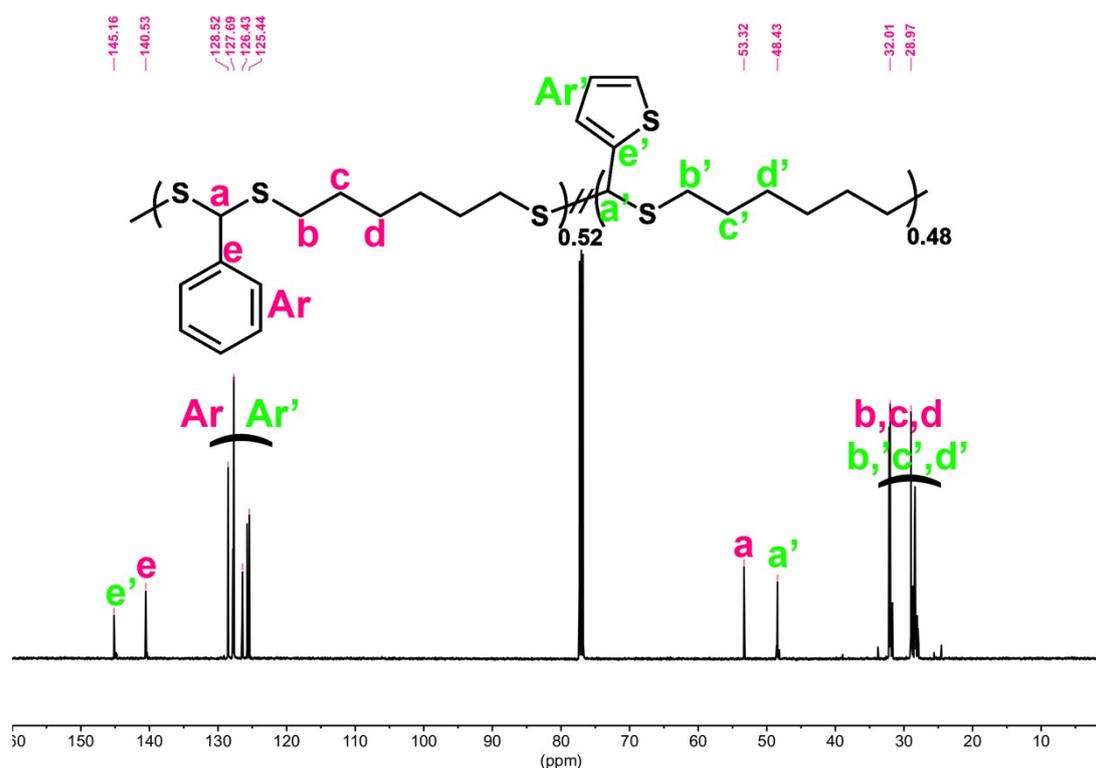
**Figure S72.** FT-IR spectrum of P17.



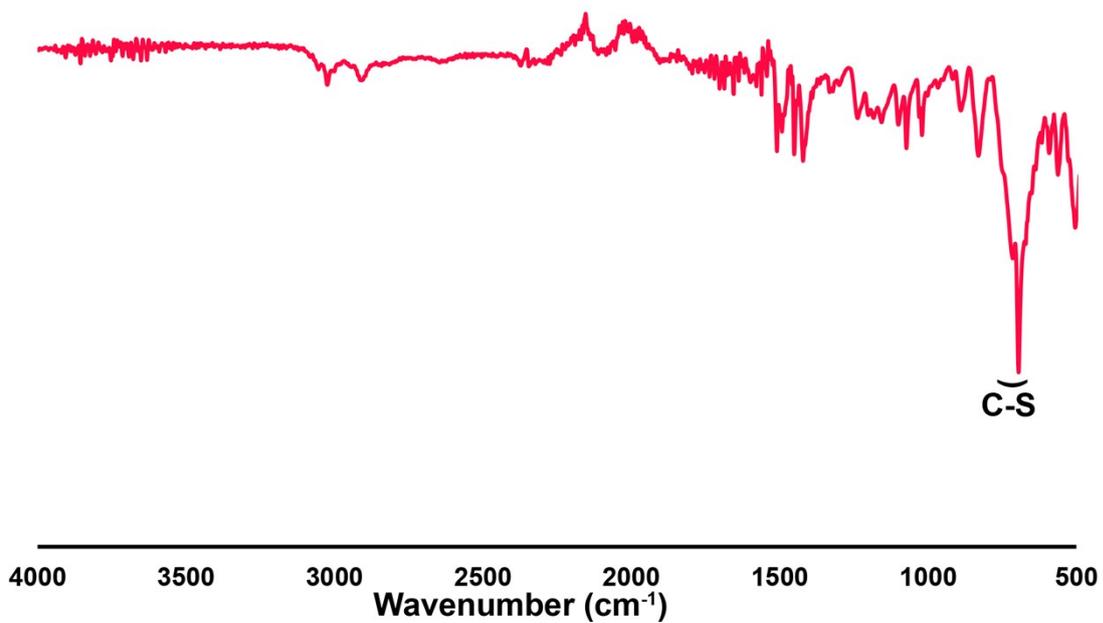
**Figure S73.** DSC thermogram of P17.

## Synthesis of P18

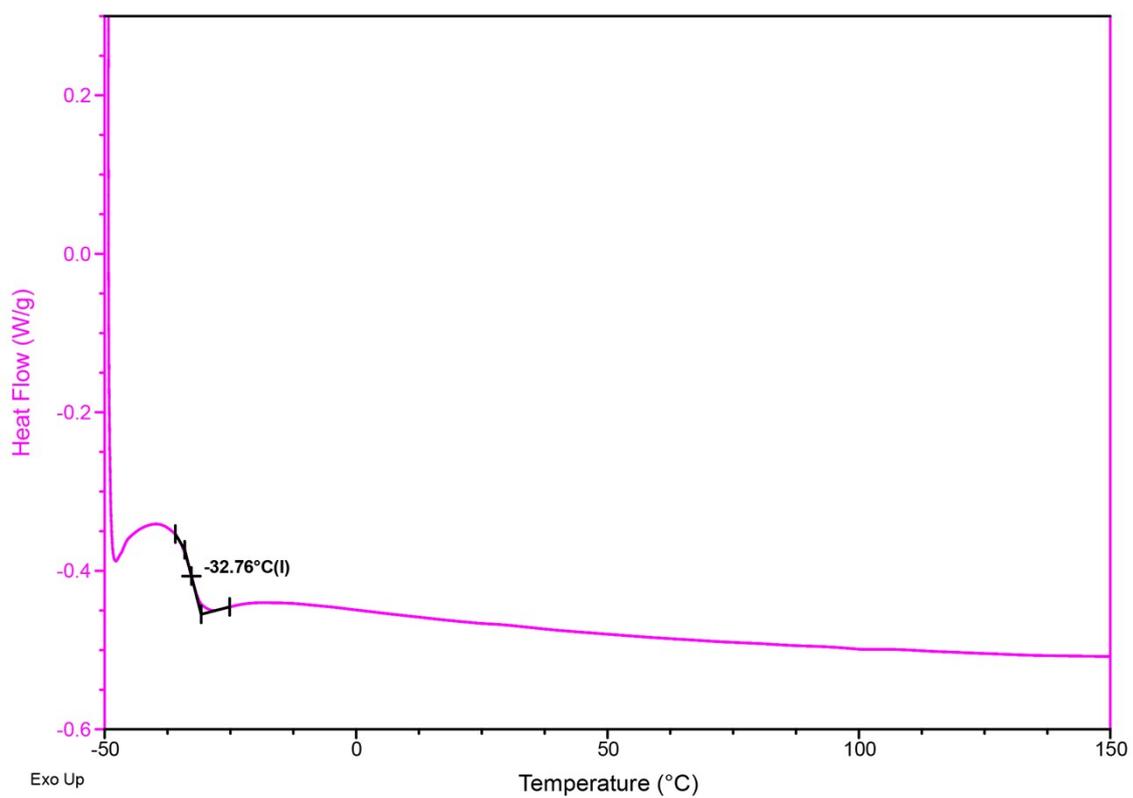
General procedure was followed: BA (112  $\mu\text{L}$ , 1.10 mmol), 2-thiophenecarboxyaldehyde (103  $\mu\text{L}$ , 1.10 mmol), HDT (306  $\mu\text{L}$ , 2.00 mmol), and CDMS (111  $\mu\text{L}$ , 1.00 mmol) were reacted in 500  $\mu\text{L}$  of THF. P18 was obtained as a white sticky solid (yield = 442 mg, 92%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44, 6.92 (8H, ArH), 5.17 (1H, ArCHS), 4.85 (1H, ArCHS), 2.62-2.51 (4H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ ), 1.53-1.33 (8H,  $\text{SCH}_2(\text{CH}_2)_4\text{CH}_2\text{S}$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.16, 140.53, 128.52, 127.69, 126.43, 125.44, 53.32, 48.43, 32.01, 28.97.



**Figure S74.**  $^{13}\text{C}$  NMR spectrum of P18 ( $\text{CDCl}_3$ , 125 MHz).



**Figure S75.** FT-IR spectrum of P18.



**Figure S76.** DSC thermogram of P18.