

## Supplementary information

### **In Situ Reductive Polymerization of Bio-Based $\alpha$ -Lipoamides toward Functional Poly( $\beta$ -Hydroxy Thioether)s**

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## Experimental Section:

### Materials

$\alpha$ -Lipoic acid and *N,N'*-disuccinimidyl carbonate were purchased from Shanghai Dibai Biotechnology Co., Ltd. Phenyl glycidyl ether and 1,4-butanediol diglycidyl ether were purchased from Heowns reagent company. Sodium borohydride was purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents and solvents, unless otherwise specified, were purchased from commercial sources and were used without further purification.

### Instruments

Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) NMR spectra were recorded on a Bruker AV-300 spectrometer operating at 300 MHz for proton and 75 MHz for carbon nuclei using  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  as solvent, respectively.

Thermogravimetric analysis (TGA) was measured through ADTQ 600 of TA Instrument from 30 °C to 600 °C with a heating rate of 10 °C /min under a nitrogen atmosphere.

The glass transition temperatures ( $T_g$ ) of the resultant polymers were determined by using a Mettler Toledo differential scanning calorimetry under a nitrogen atmosphere. All polymers were heated from -60 °C to 100 °C at a rate of 10 °C/min, then cooled to -60 °C at a rate of -10 °C /min, finally heated from -60 °C to 100 °C at a rate of 10 °C /min.  $T_g$  was determined from the third run.

The number ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights and polydispersity indices ( $D$  values) of the polymers were measured on Waters 1515 equipped with a refractive index (RI) detector. Polystyrene standards were utilized, and THF was used as the eluent at a flow rate of 1.0 mL/min at room temperature.

### **In situ reductive polymerization of $\alpha$ -lipoamide with diepoxides**

A typical polymerization procedure for the synthesis of **P1** was given as an example. Into a 5 mL round-bottom flask equipped with a magnetic stirrer was placed with *N*-butyl  $\alpha$ -lipoamide (261 mg, 1 mmol) and 1,4-butanediol diglycidyl ether (184  $\mu$ L, 1 mmol) in 1 mL of THF at room temperature. After stirring to dissolution, NaBH<sub>4</sub> (37.8 mg, 1 mmol dissolved in 284  $\mu$ L of water) was added dropwise to the mixture in an ice-water bath. Subsequently, the reaction mixture became biphasic. The formation of the oil phase in the THF-water biphasic system is due to the salting-out effect caused by the high ionic strength of the aqueous NaBH<sub>4</sub> solution (and the inorganic salts generated during the reaction). This significantly reduces the miscibility of THF with the aqueous phase. The reaction was purged with N<sub>2</sub> for 5 min, sealed, and stirred at room temperature for 48 h. After the reaction was completed, the mixture separated into two phases. The upper oil phase was directly removed using a pipette and then poured into methyl *tert*-butyl ether to precipitate the polymer P1. (yield: 77%) All polymerizations were performed following the same general procedure with no exceptions.

### **Synthesis of model compound 3**

Into a 5 mL round-bottom flask equipped with a magnetic stirrer was placed with *N*-allyl  $\alpha$ -lipoamide (245 mg, 1 mmol) and phenyl glycidyl ether (270  $\mu$ L, 2 mmol) in 1 mL of THF at room temperature. After stirring to dissolution, NaBH<sub>4</sub> (37.8 mg, 1 mmol dissolved in 284  $\mu$ L of water) was added dropwise to the mixture in an

ice-water bath. The reaction was purged with N<sub>2</sub> for 5 min, sealed, and stirred at room temperature for 48 h. After the reaction was completed, the oil phase was separated. After solvent removal, the product was obtained without further purification. (yield: 85%).

### **Synthesis of $\alpha$ -Lipoic acid-*N*-hydroxysuccinimide ester (LA-NHS)**

$\alpha$ -Lipoic acid (4.8 g, 23 mmol, 1.0 equiv) was dissolved in acetonitrile (200 mL). To this solution were added *N,N'*-disuccinimidyl carbonate (7.2 g, 28 mmol, 1.2 equiv) and triethylamine (10 mL, 71 mmol). The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure at 35 °C. The residue was dissolved in dichloromethane, washed with saturated aqueous NaHCO<sub>3</sub> solution (3 × 50 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give LA-NHS ester as a yellow solid. (yield: 81%).

### **Syntheses of $\alpha$ -lipoamide monomers**

Detailed experimental procedures for the synthesis of *N*-butyl  $\alpha$ -lipoamide (**1a**) are given below as an example.

LA-NHS (6.0 g, 20 mmol) was dissolved in dichloromethane (80 mL). *n*-Butylamine (2.2 g, 30 mmol) was added dropwise to the solution. The resulting mixture was stirred at room temperature for 5 h. After completion of the reaction, the organic

layer was washed with saturated brine ( $3 \times 60$  mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give *N*-butyl  $\alpha$ -lipoamide as a yellow solid. (yield: 79%). For monomer **1b**, since allylamine hydrochloride was used, it was first neutralized with triethylamine in DCM to liberate the free amine, followed by the addition of LA-NHS.

### **Oxidative conversion of the polymer**

Polymer **P1** (463 mg, 1 mmol) was dissolved in THF (4 mL) with stirring. *m*-chloroperoxybenzoic acid (*m*-CPBA) ( 517 mg, 3 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was then poured into anhydrous methyl *tert*-butyl ether (50 mL) to precipitate the modified polymer **P1'**. (yield: 86%).

### **Post-modification of the polymer**

Polymer **P1** (463 mg, 1 mmol) was dissolved in THF (2 mL) with stirring. 4-Dimethylaminopyridine (24 mg, 0.2 mmol) and triethylamine (28  $\mu$ L, 0.2 mmol) were added, followed by diketene (340  $\mu$ L, 4.4 mmol). The mixture was stirred at room temperature overnight. The reaction mixture was precipitated into methyl *tert*-butyl ether three times to afford polymer **P1''**. (yield: 91%).

Polymer **P1''** (648 mg, 1 mmol) was dissolved in THF (2 mL) with stirring. Benzylamine (218  $\mu$ L, 2 mmol) was added, and the mixture was stirred at room

temperature overnight. The resulting solution was precipitated into methyl *tert*-butyl ether three times to give the final modified polymer **P1'''**. (yield: 82%).

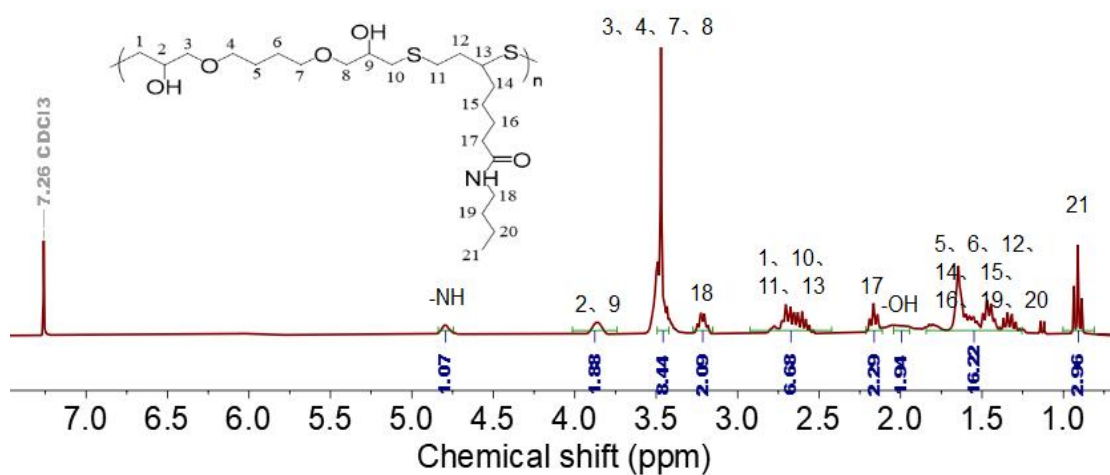


Figure S1.  $^1\text{H}$  NMR spectrum of **P1** in  $\text{CDCl}_3$ .

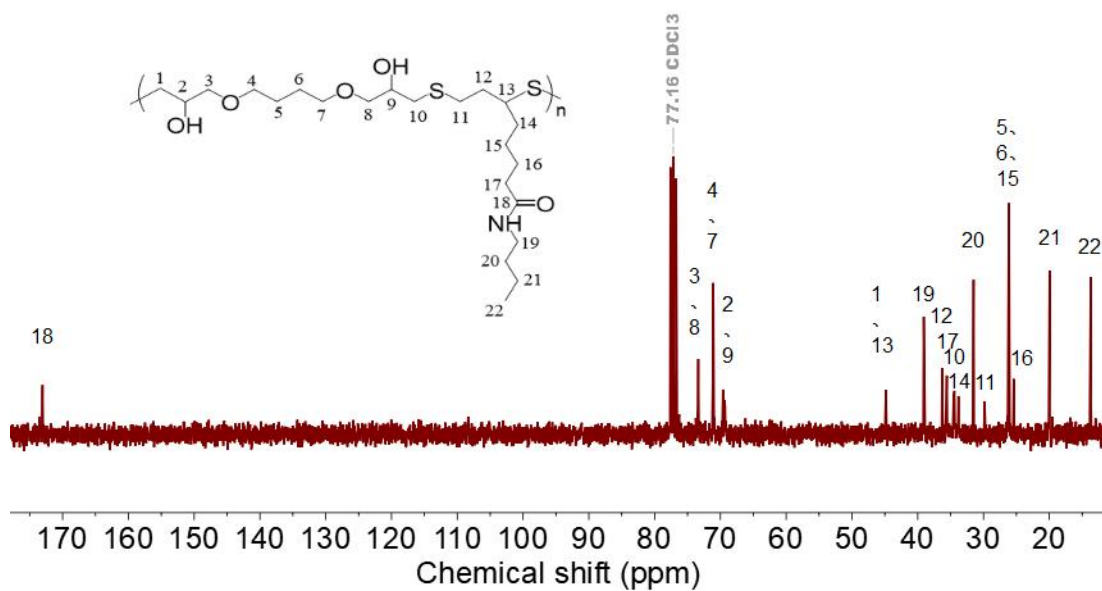
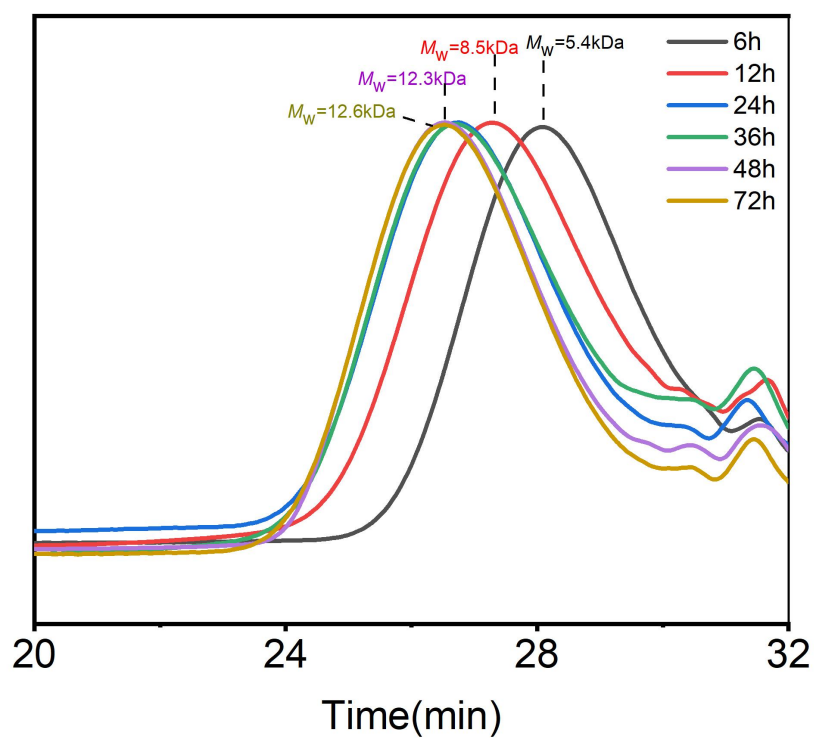
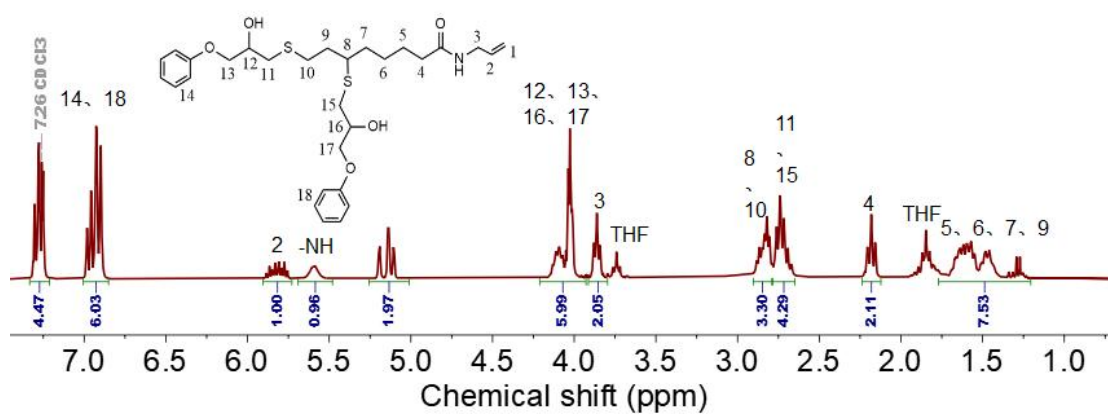


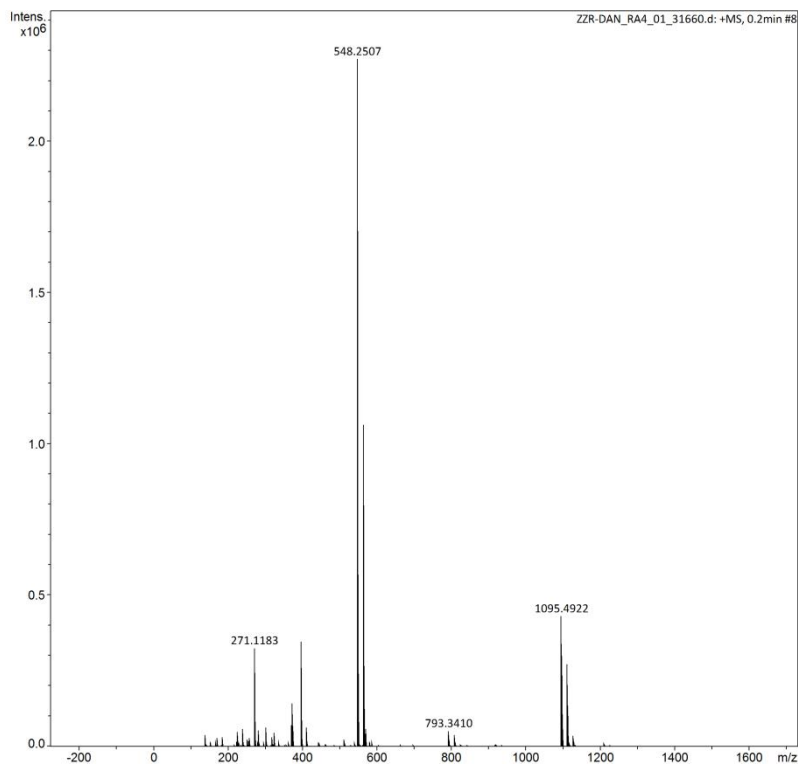
Figure S2.  $^{13}\text{C}$  NMR spectrum of **P1** in  $\text{CDCl}_3$ .



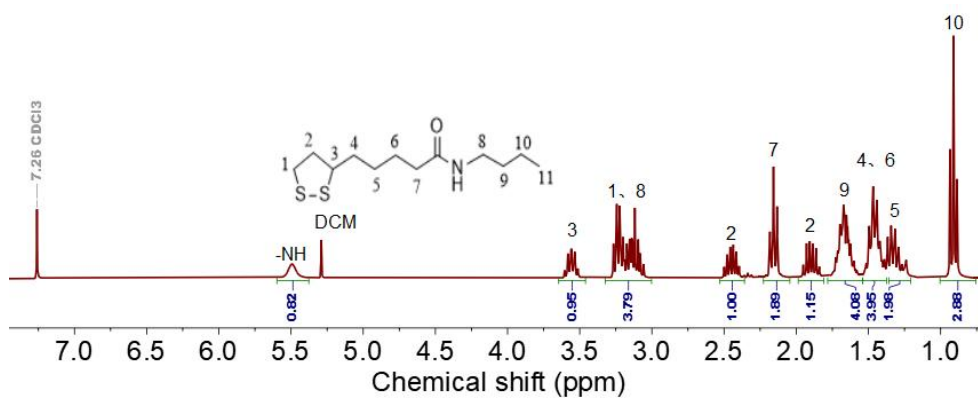
**Figure S3.** GPC monitoring the polymerization process of **P1**



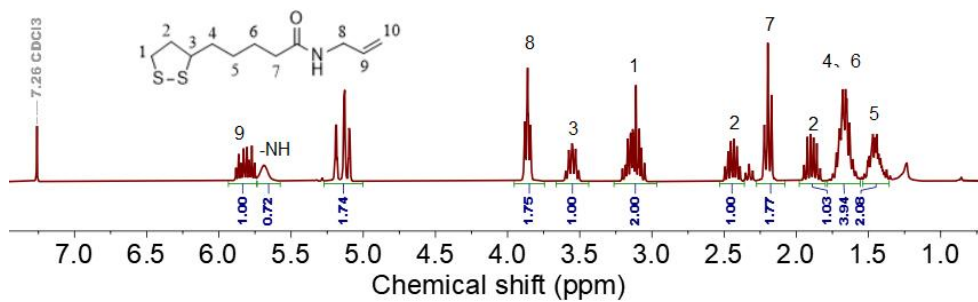
**Figure S4.**  $^1\text{H}$  NMR spectrum of model compound **3** in  $\text{CDCl}_3$ .



**Figure S5.** Mass spectrum of model compound **3**.



**Figure S6.**  $^1\text{H}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ .



**Figure S7.**  $^1\text{H}$  NMR spectrum of **1b** in  $\text{CDCl}_3$ .

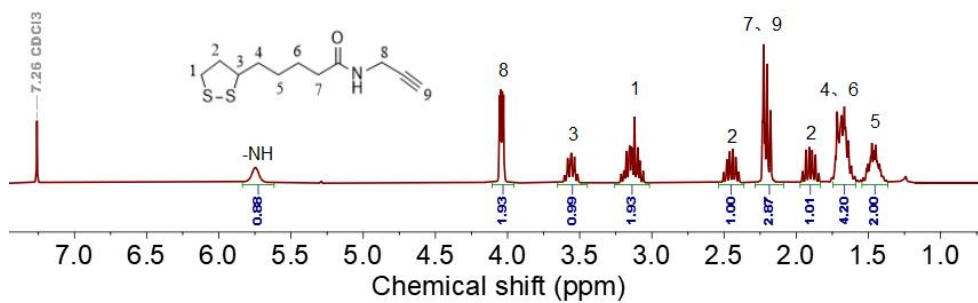


Figure S8. <sup>1</sup>H NMR spectrum of **1c** in CDCl<sub>3</sub>

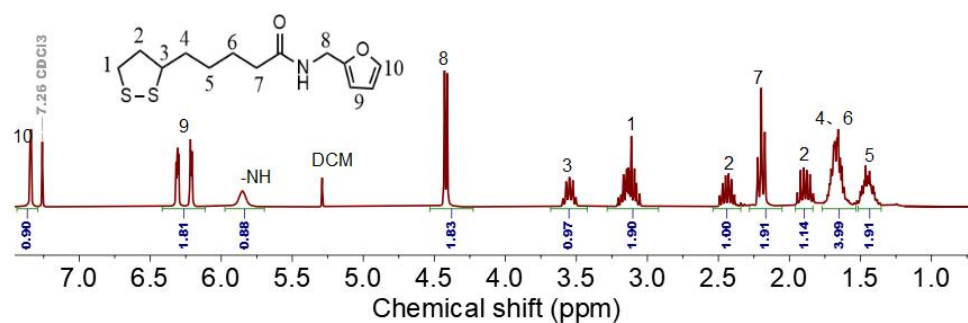


Figure S9. <sup>1</sup>H NMR spectrum of **1d** in CDCl<sub>3</sub>.

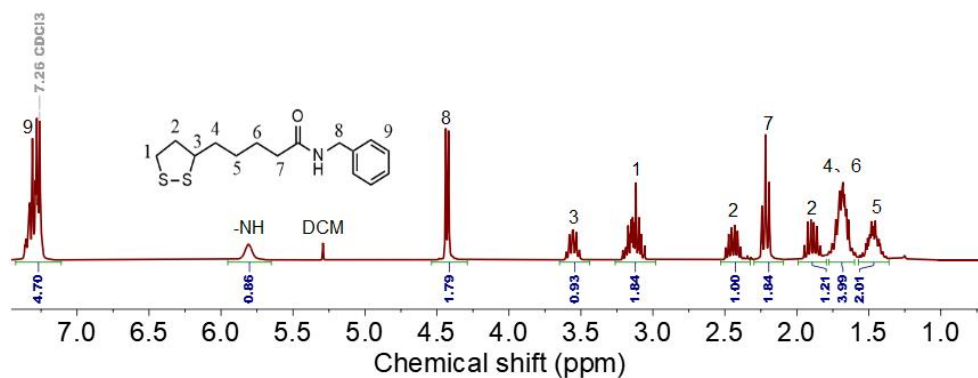


Figure S10. <sup>1</sup>H NMR spectrum of **1e** in CDCl<sub>3</sub>.

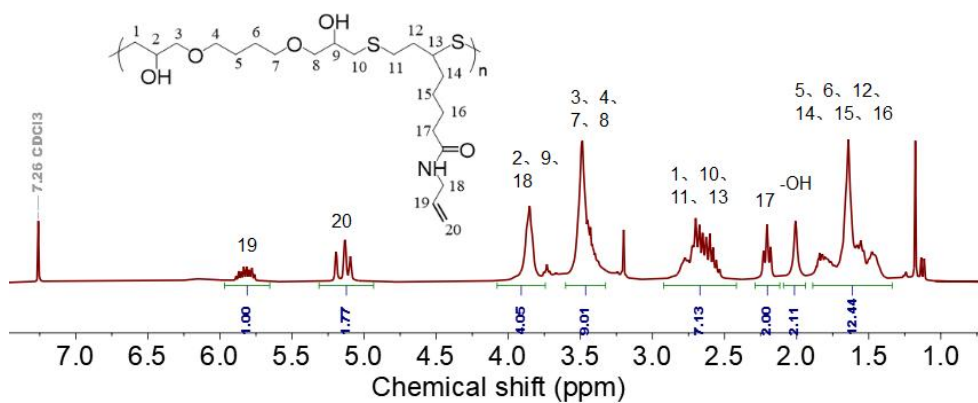
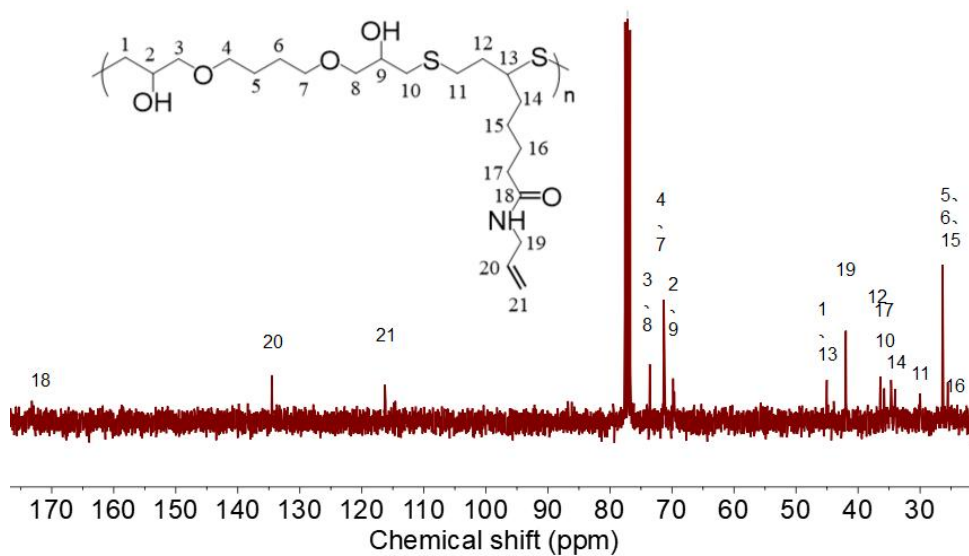
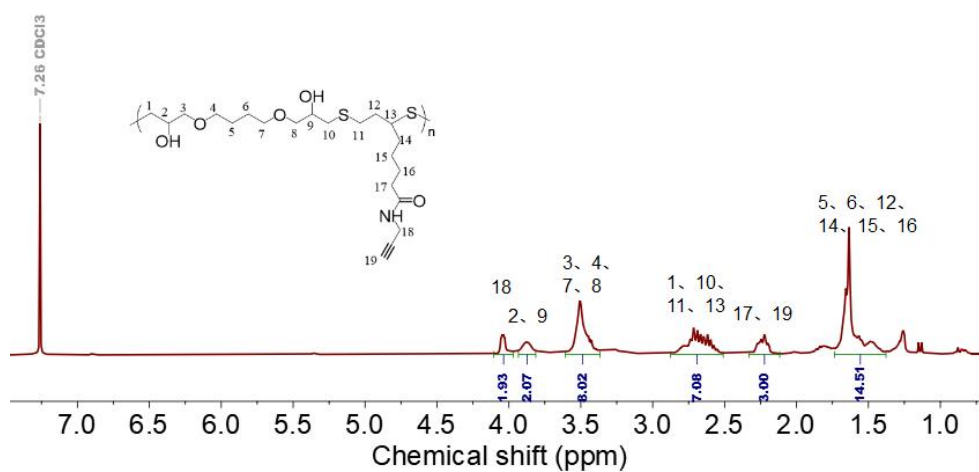


Figure S11. <sup>1</sup>H NMR spectrum of **P2** in CDCl<sub>3</sub>.



**Figure S12.**  $^{13}\text{C}$  NMR spectrum of P2 in  $\text{CDCl}_3$ .



**Figure S13.**  $^1\text{H}$  NMR spectrum of P3 in  $\text{CDCl}_3$ .

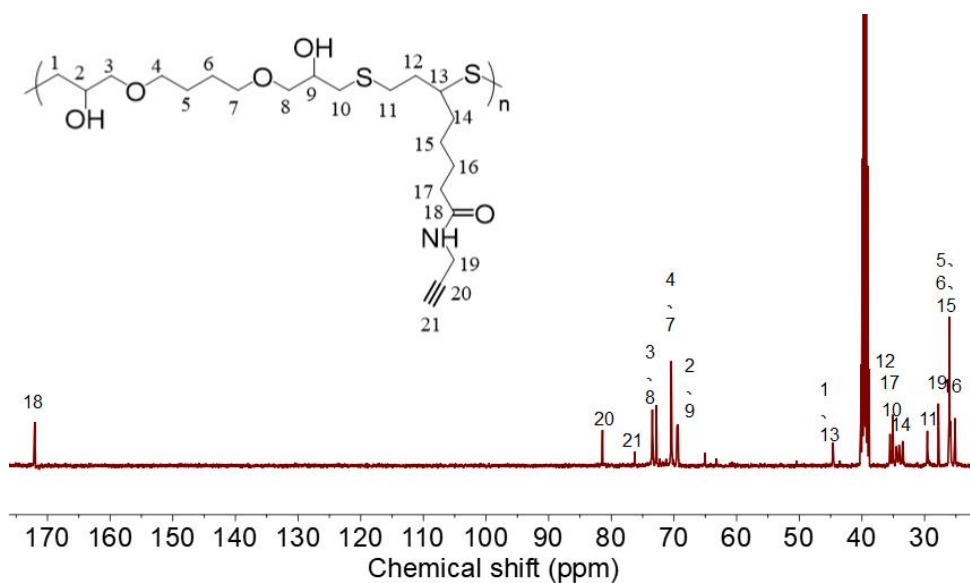


Figure S14.  $^{13}\text{C}$  NMR spectrum of P3 in  $\text{DMSO-}d_6$ .

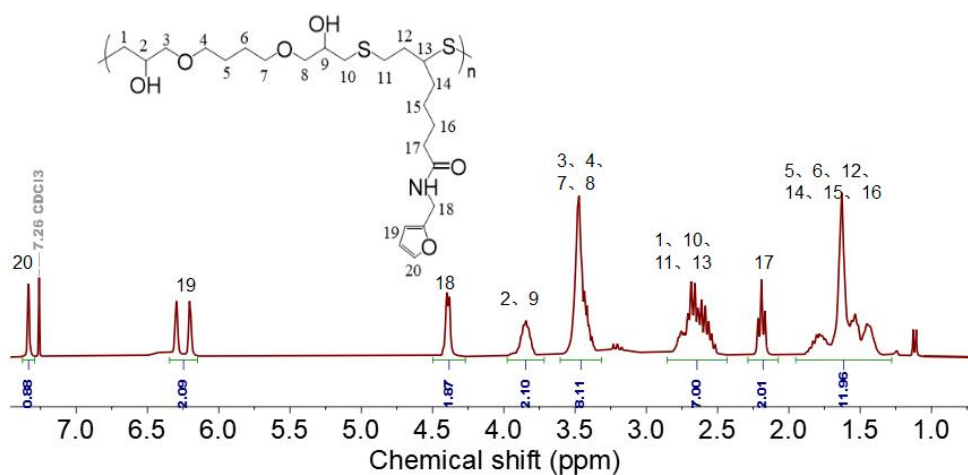


Figure S15.  $^1\text{H}$  NMR spectrum of P4 in  $\text{CDCl}_3$ .

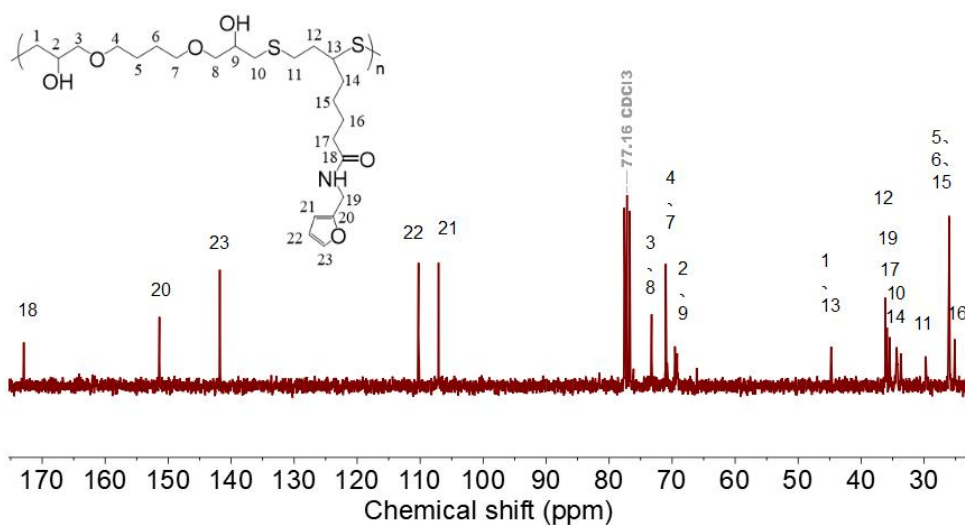


Figure S16.  $^{13}\text{C}$  NMR spectrum of P4 in  $\text{CDCl}_3$ .

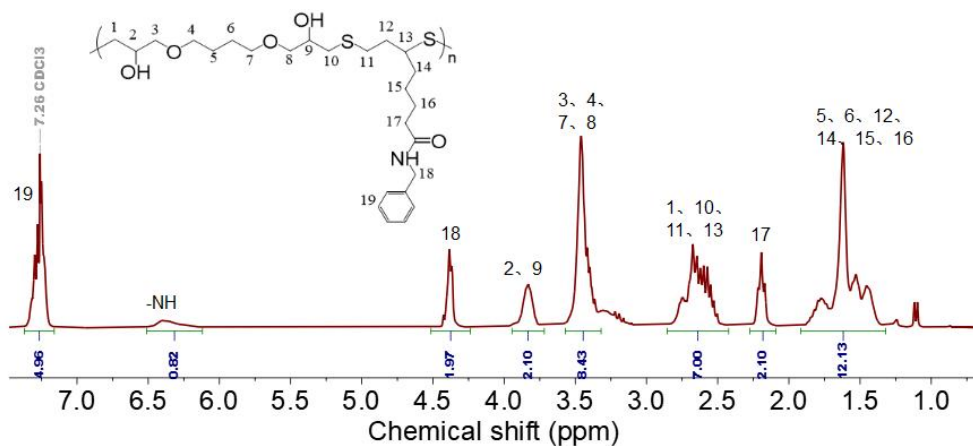


Figure S17. <sup>1</sup>H NMR spectrum of **P5** in CDCl<sub>3</sub>.

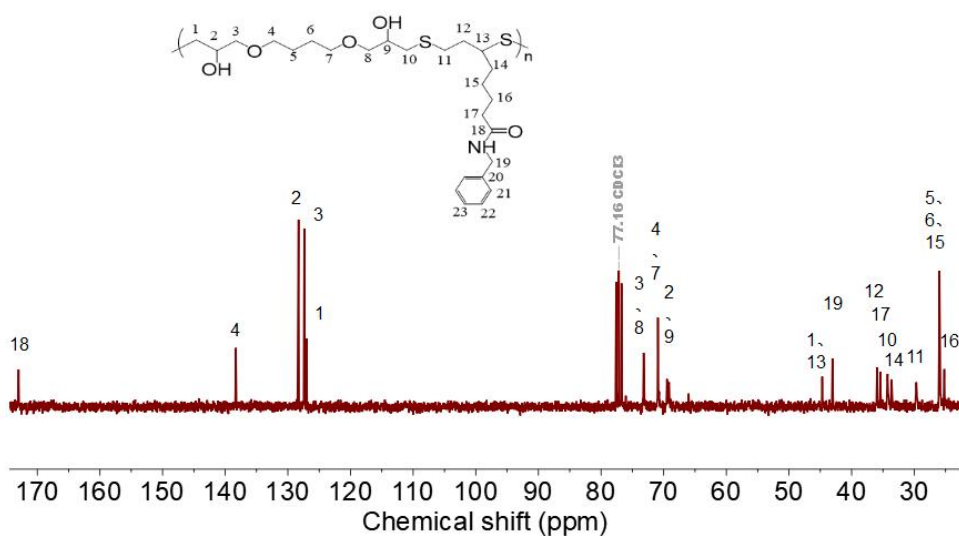


Figure S18. <sup>13</sup>C NMR spectrum of **P5** in CDCl<sub>3</sub>.

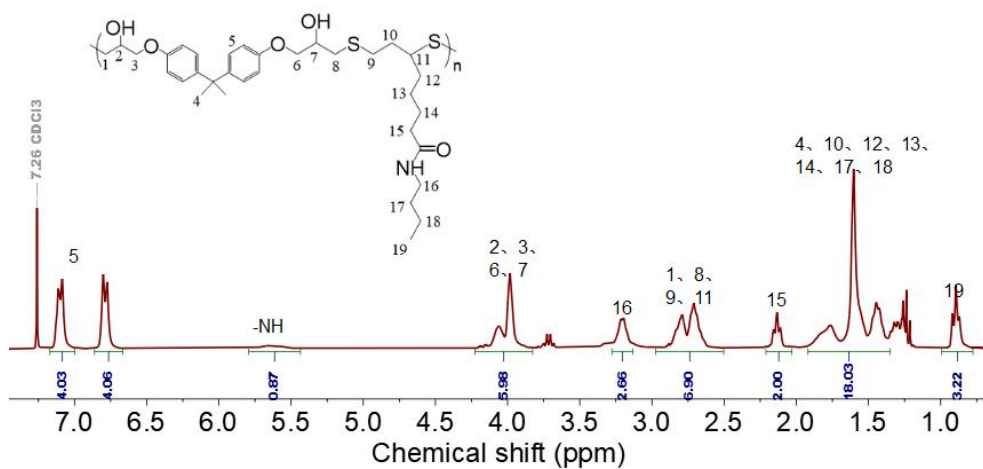
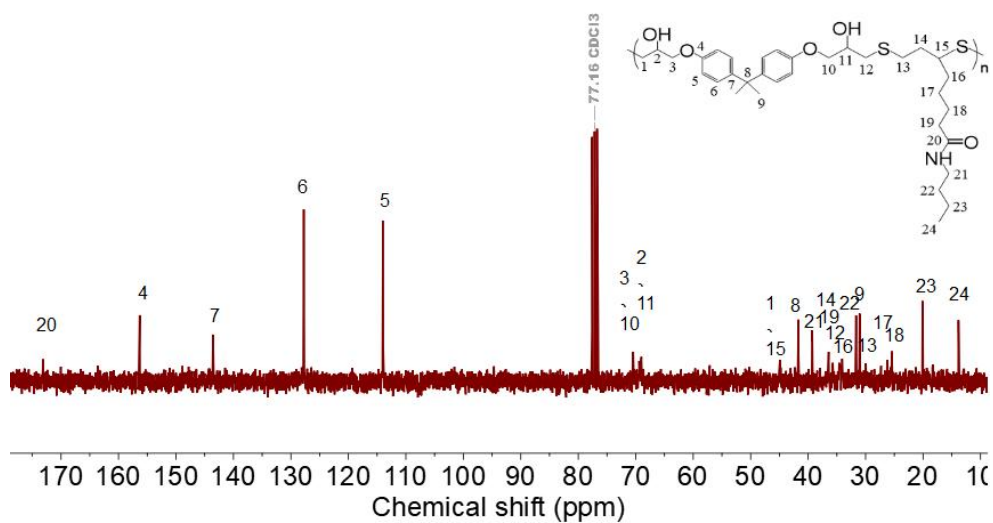
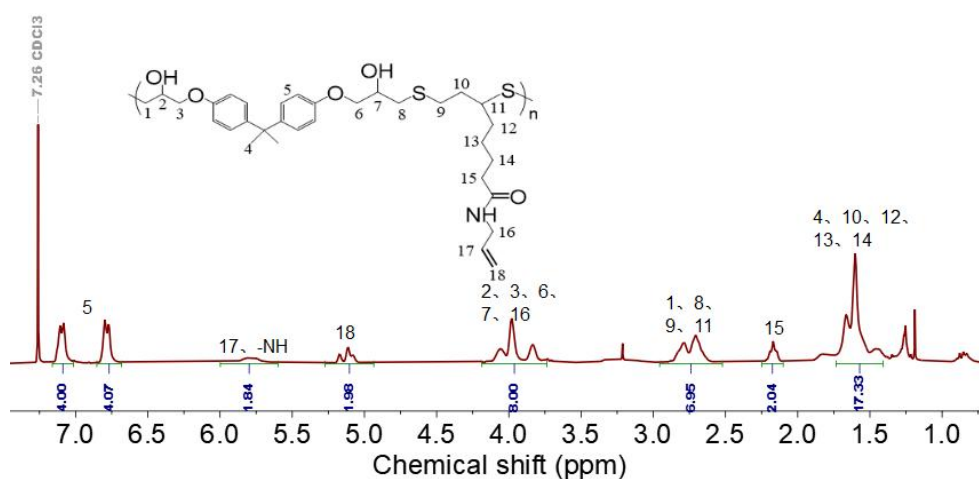


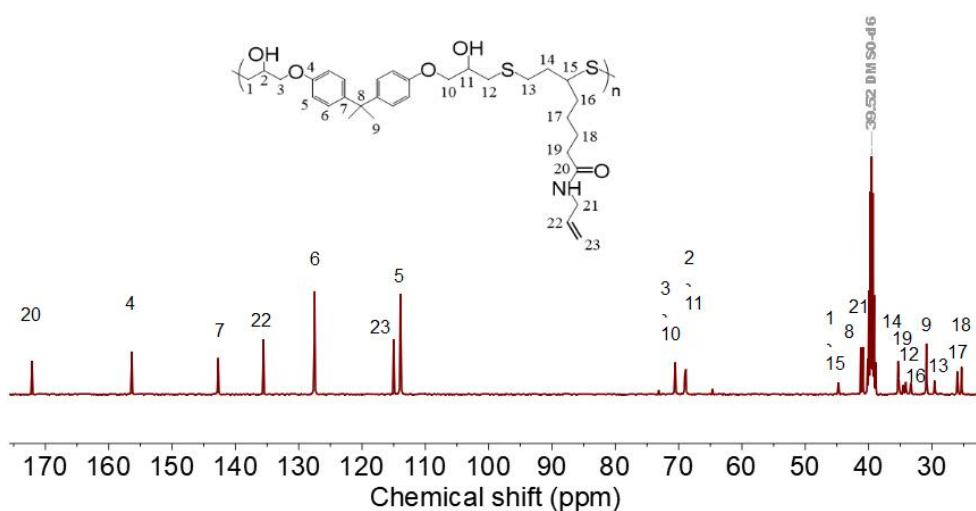
Figure S19. <sup>1</sup>H NMR spectrum of **P6** in CDCl<sub>3</sub>.



**Figure S20.**  $^{13}\text{C}$  NMR spectrum of **P6** in  $\text{CDCl}_3$ .



**Figure S21.**  $^1\text{H}$  NMR spectrum of **P7** in  $\text{CDCl}_3$ .



**Figure S22.**  $^{13}\text{C}$  NMR spectrum of **P7** in  $\text{DMSO}-d_6$ .

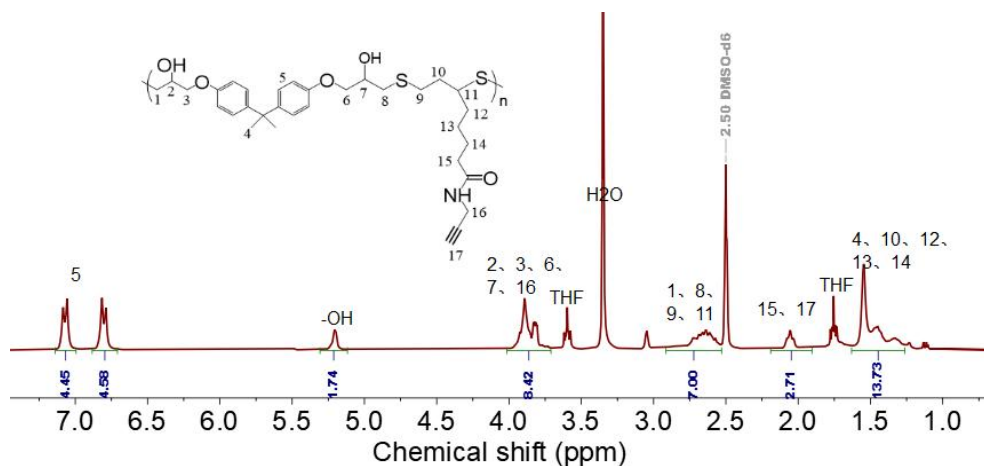


Figure S23.  $^1\text{H}$  NMR spectrum of P8 in  $\text{DMSO-}d_6$ .

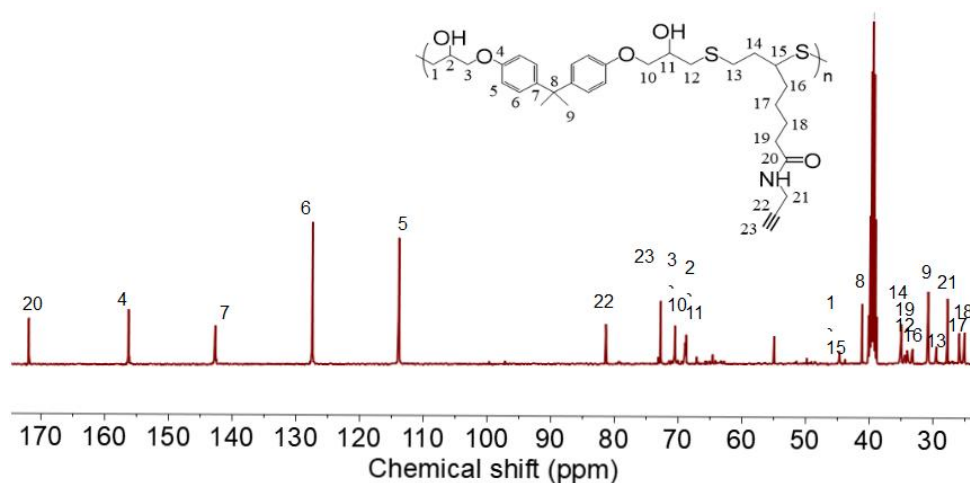


Figure S24.  $^{13}\text{C}$  NMR spectrum of P8 in  $\text{DMSO-}d_6$ .

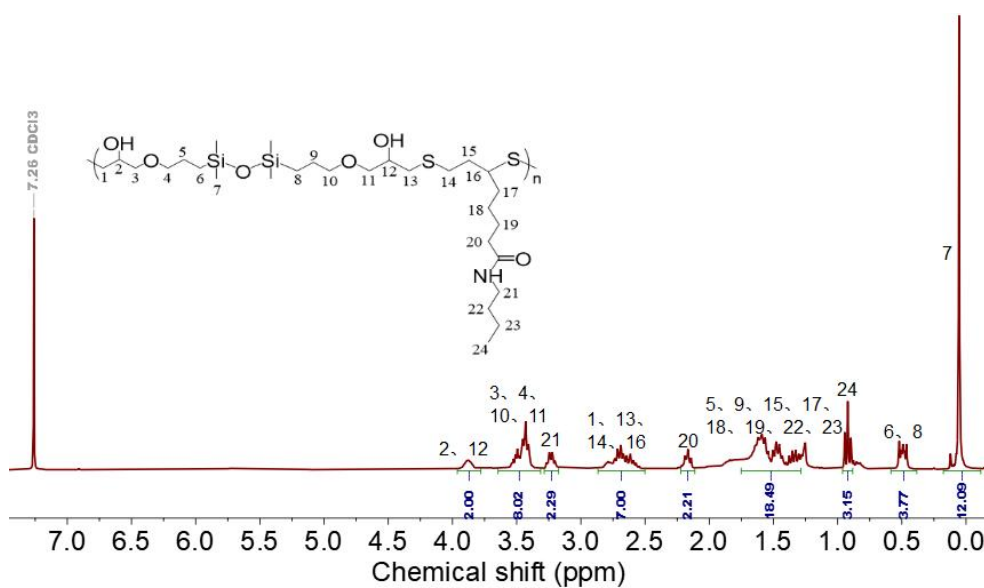


Figure S25.  $^1\text{H}$  NMR spectrum of P9 in  $\text{CDCl}_3$ .

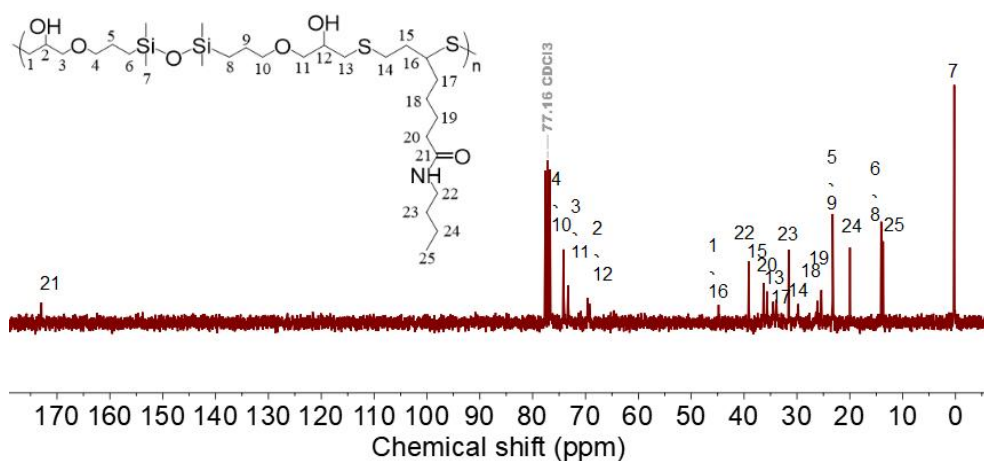


Figure S26.  $^{13}\text{C}$  NMR spectrum of P9 in  $\text{CDCl}_3$ .

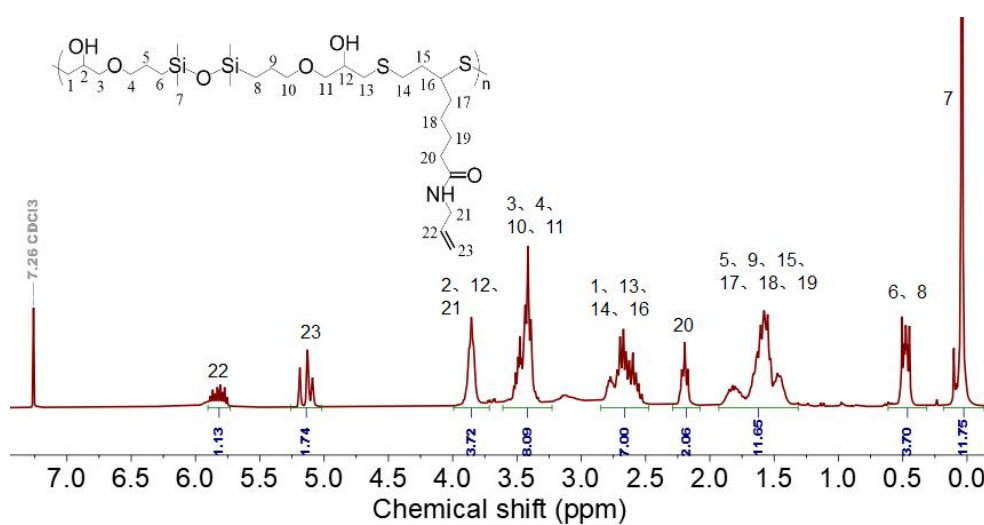


Figure S27.  $^1\text{H}$  NMR spectrum of P10 in  $\text{CDCl}_3$ .

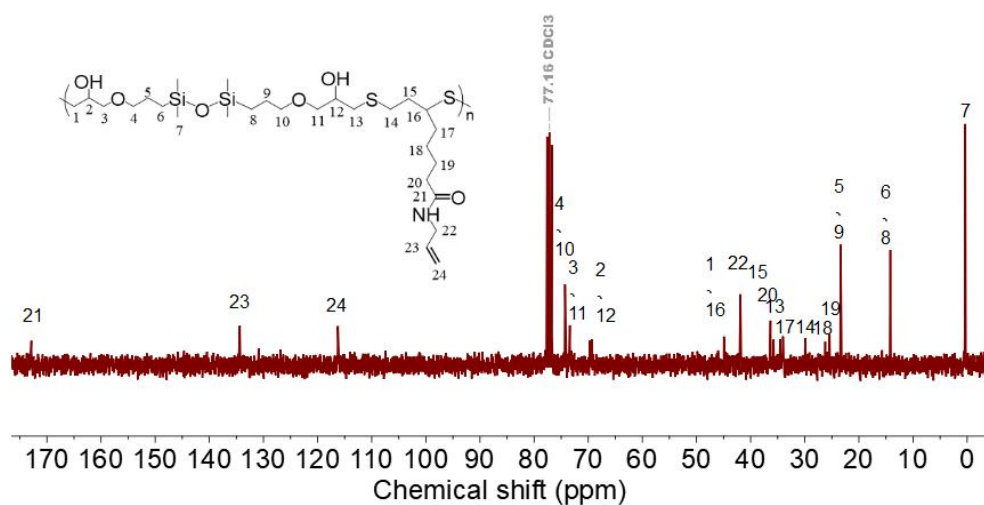
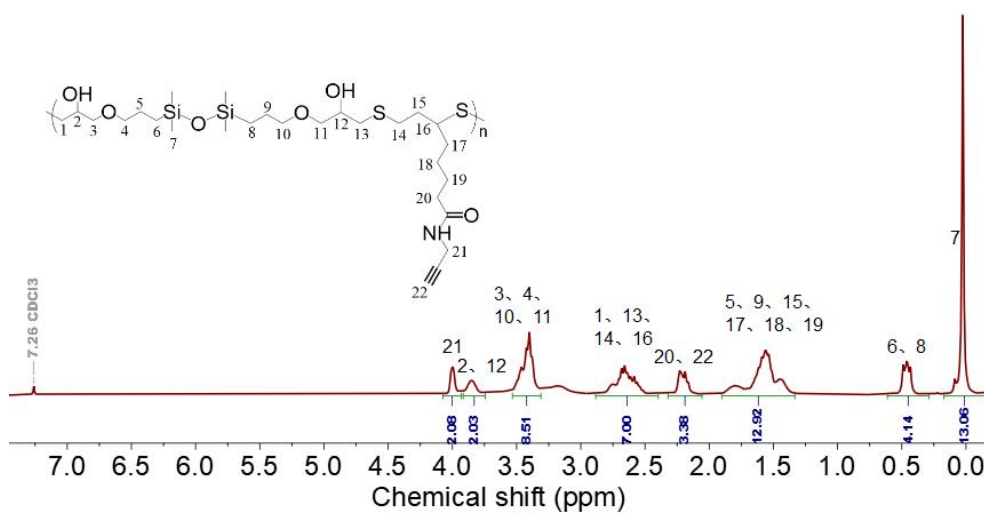
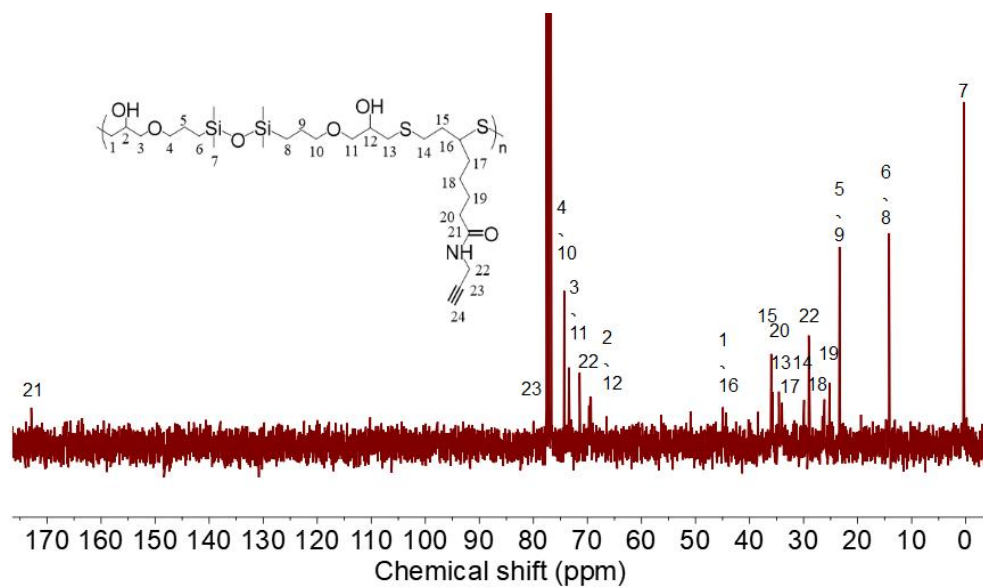


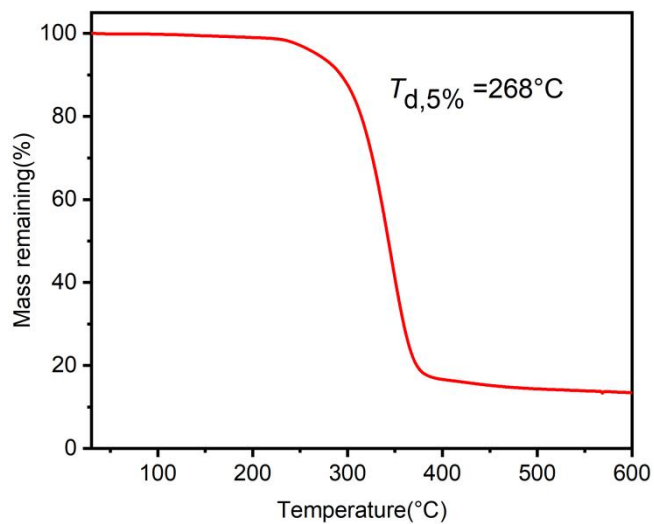
Figure S28.  $^{13}\text{C}$  NMR spectrum of P10 in  $\text{CDCl}_3$ .



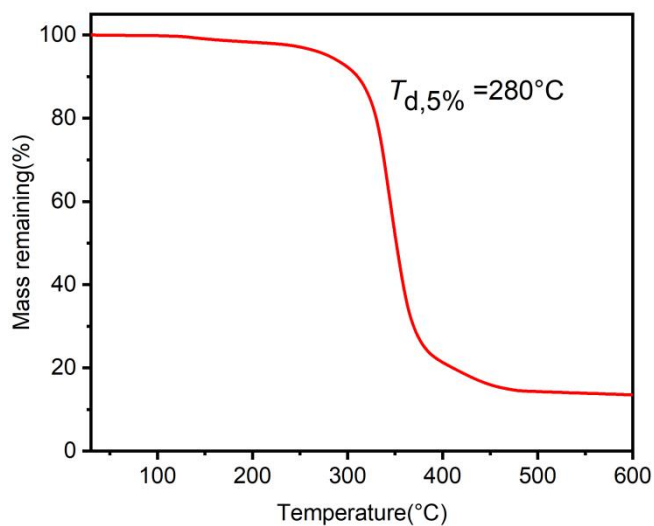
**Figure S29.**  $^1\text{H}$  NMR spectrum of **P11** in  $\text{CDCl}_3$ .



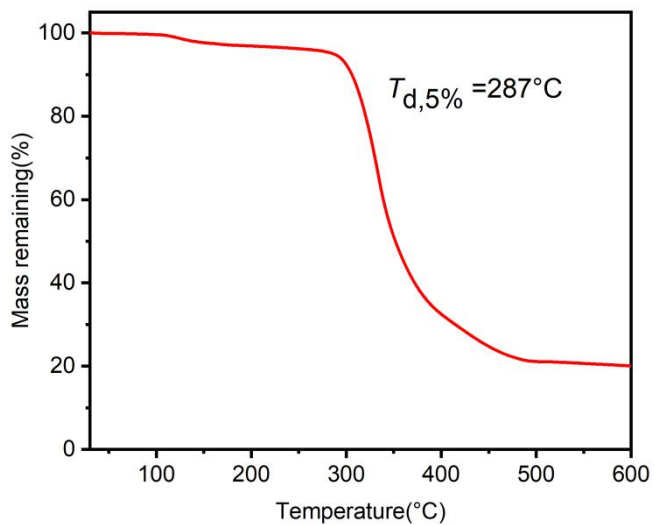
**Figure S30.**  $^{13}\text{C}$  NMR spectrum of **P11** in  $\text{CDCl}_3$ .



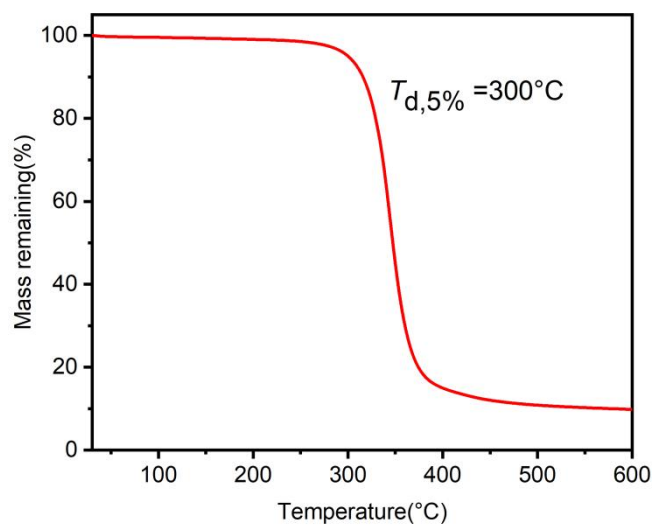
**Figure S31.** TGA curve of P1



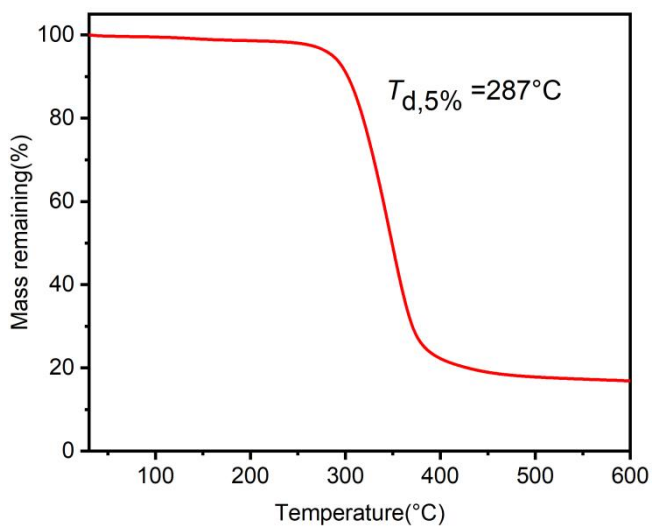
**Figure S32.** TGA curve of P2



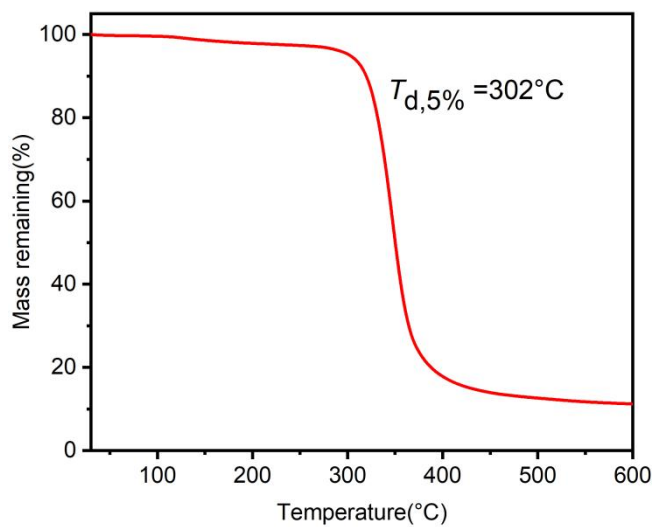
**Figure S33.** TGA curve of P3



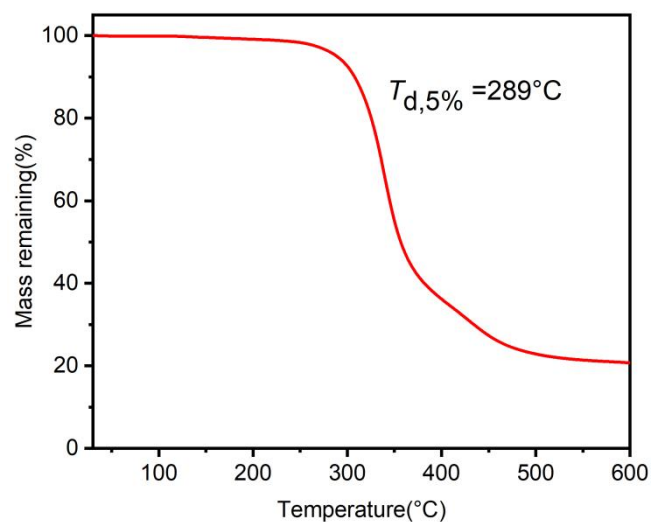
**Figure S34.** TGA curve of P4



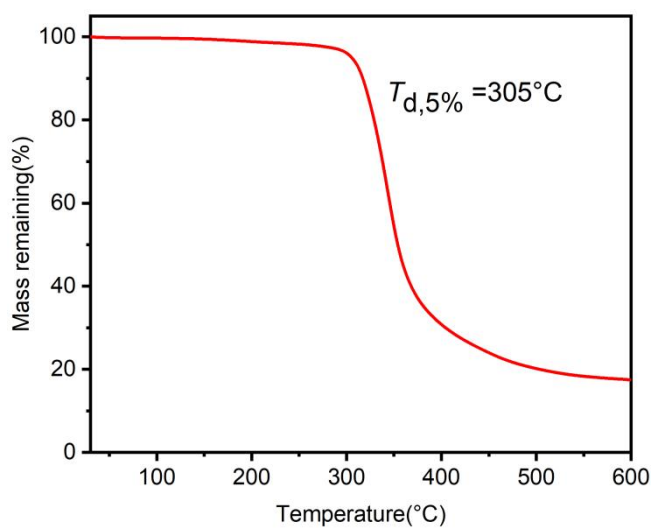
**Figure S35.** TGA curve of P5



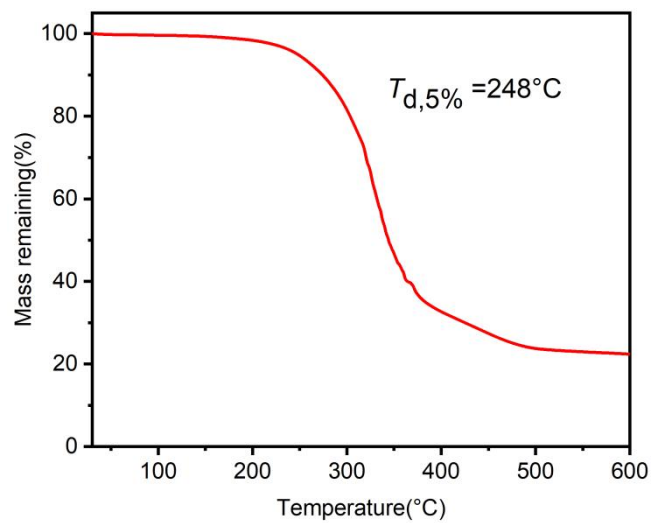
**Figure S36.** TGA curve of P6



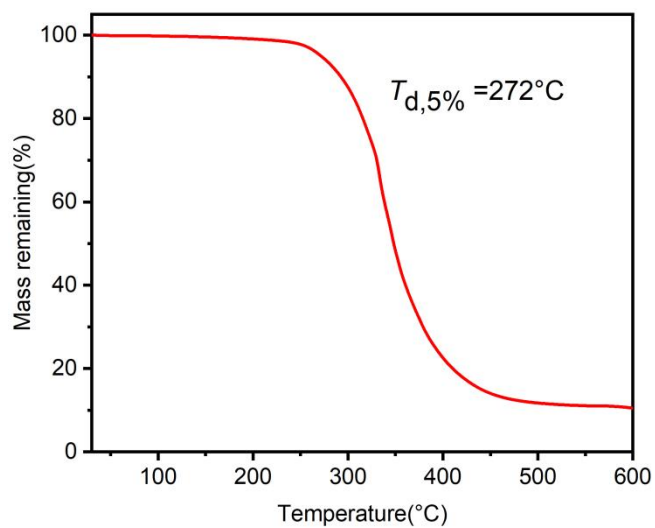
**Figure S37.** TGA curve of P7



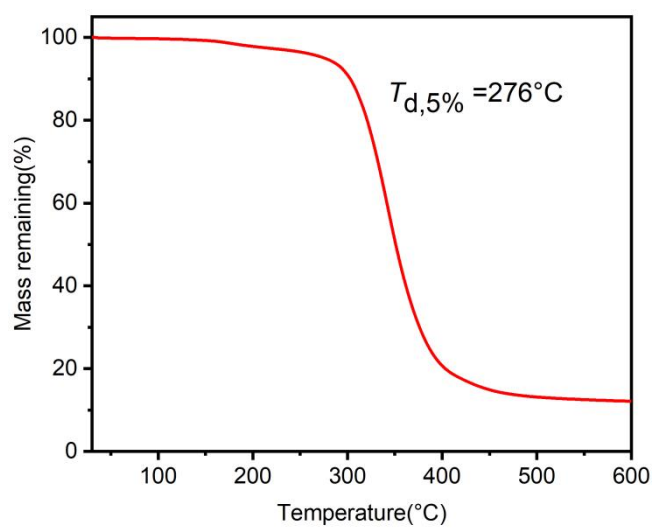
**Figure S38.** TGA curve of P8



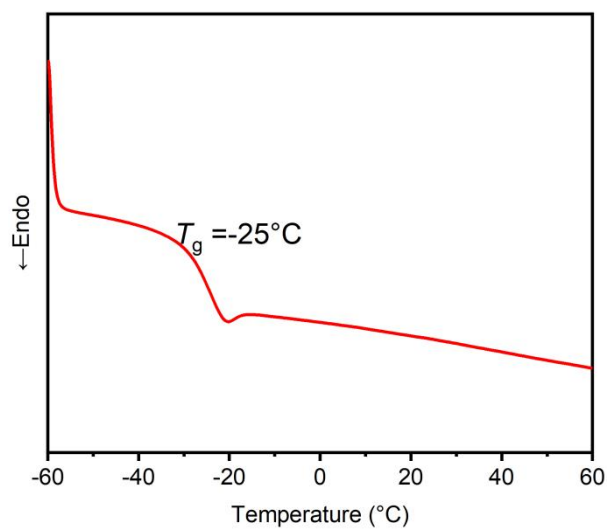
**Figure S39.** TGA curve of P9



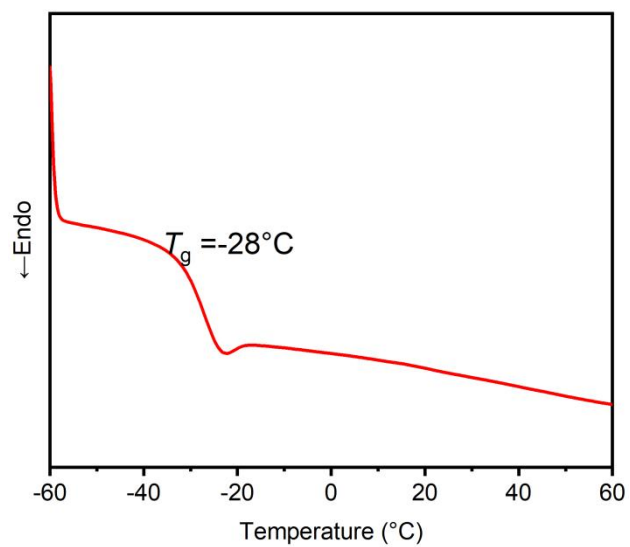
**Figure S40.** TGA curve of P10



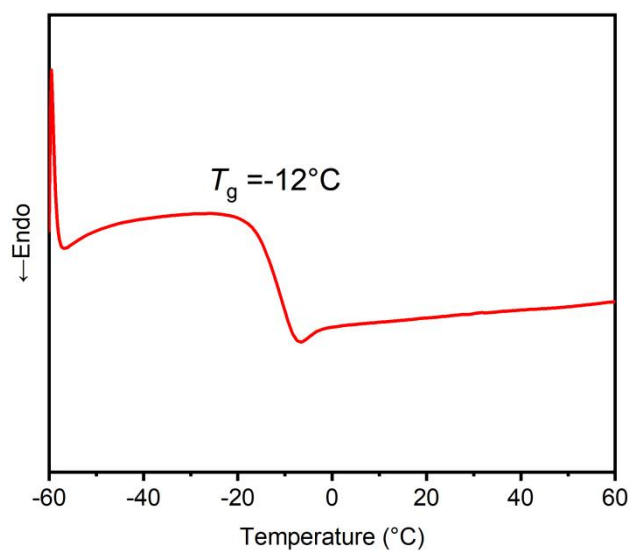
**Figure S41.** TGA curve of P11



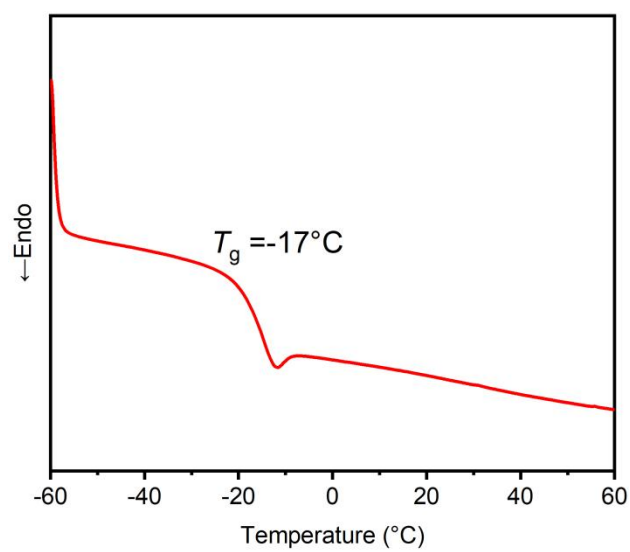
**Figure S42.** DSC curve of P1



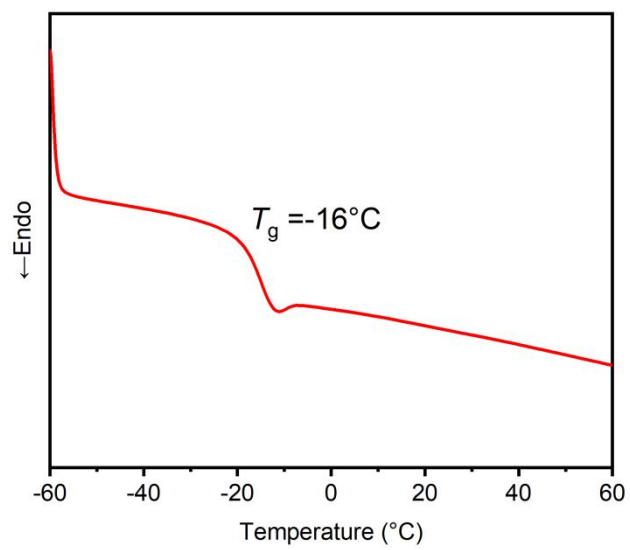
**Figure S43.** DSC curve of P2



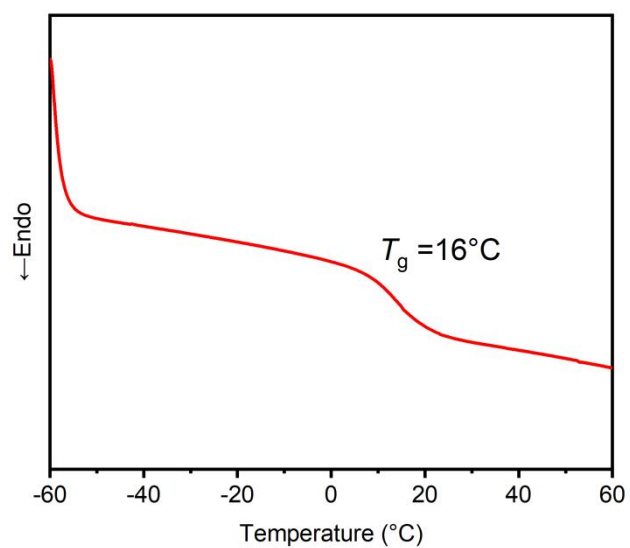
**Figure S44.** DSC curve of P3



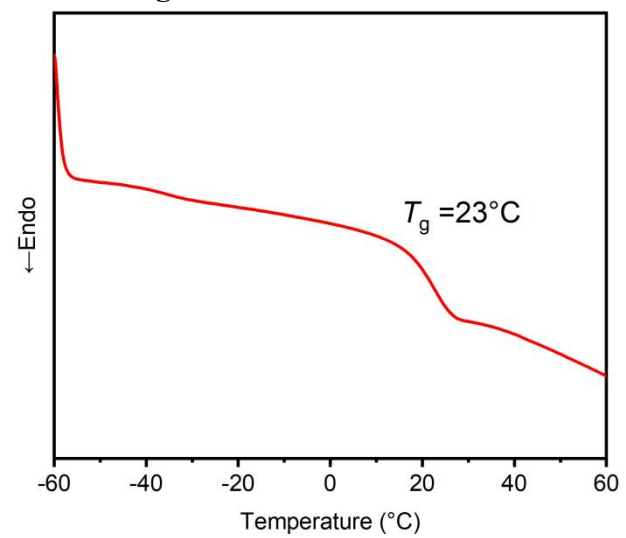
**Figure S45.** DSC curve of P4



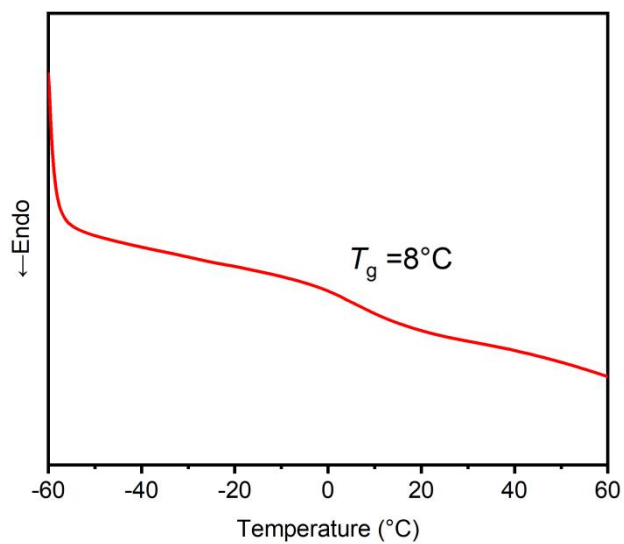
**Figure S46.** DSC curve of P5



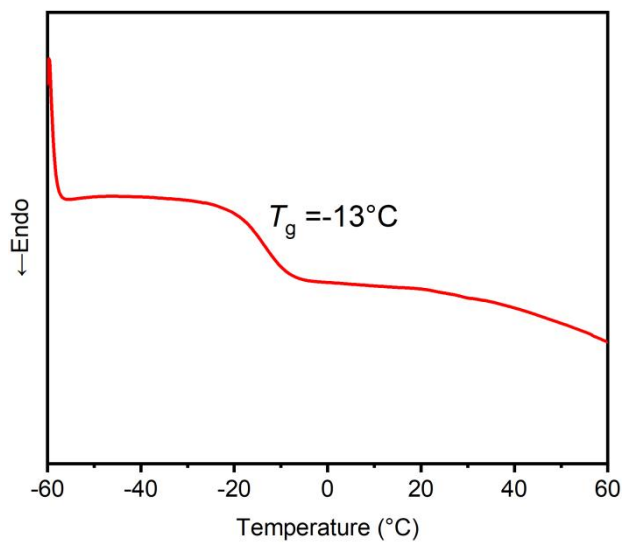
**Figure S47.** DSC curve of P6



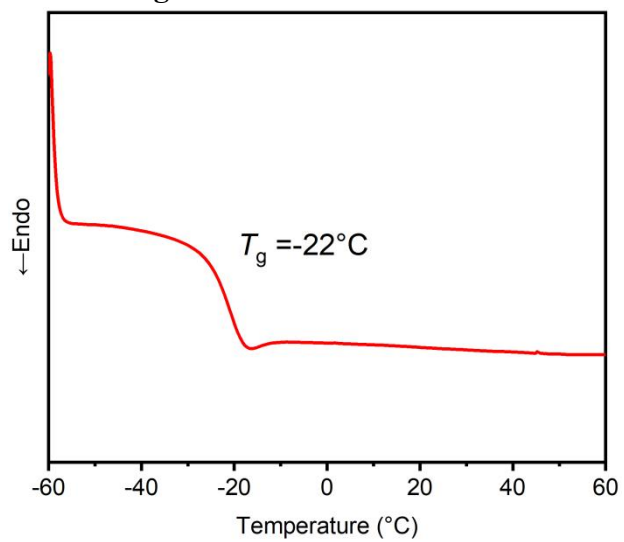
**Figure S48.** DSC curve of P7



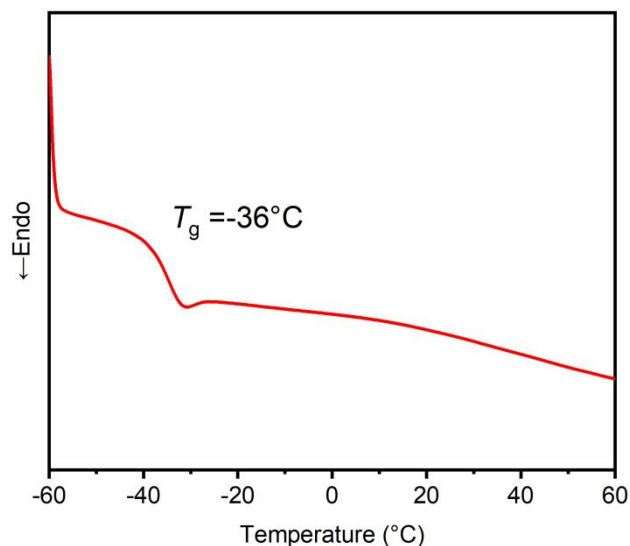
**Figure S49.** DSC curve of **P8**



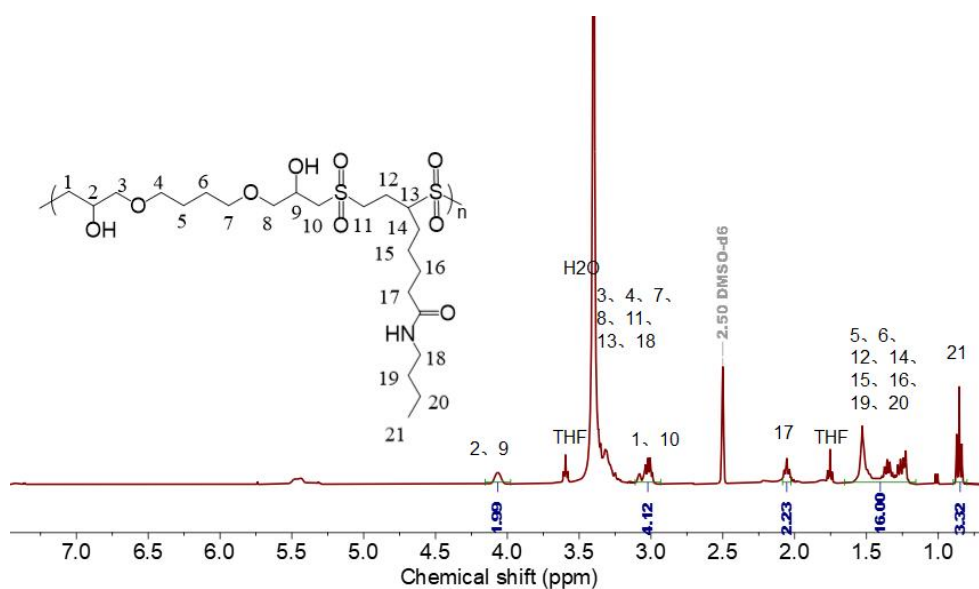
**Figure S50.** DSC curve of **P9**



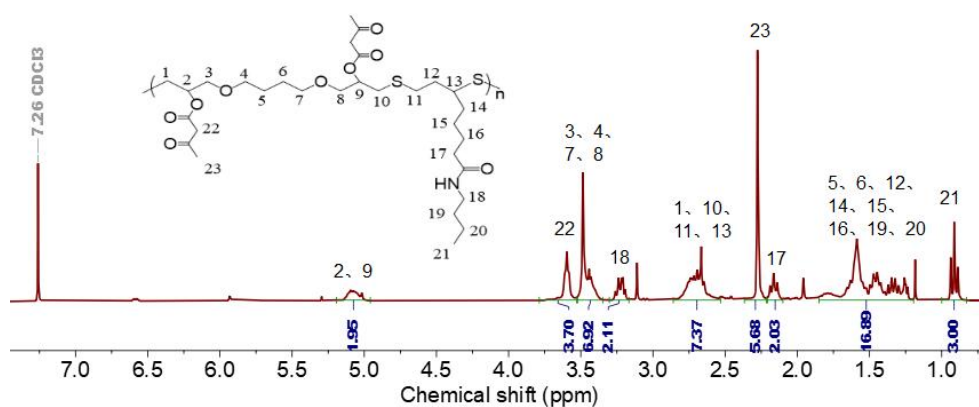
**Figure S51.** DSC curve of **P10**



**Figure S52.** DSC curve of P11



**Figure S53.**  $^1\text{H}$  NMR spectrum of P1' in  $\text{DMSO-}d_6$ .



**Figure S54.**  $^1\text{H}$  NMR spectrum of P1'' in  $\text{CDCl}_3$ .

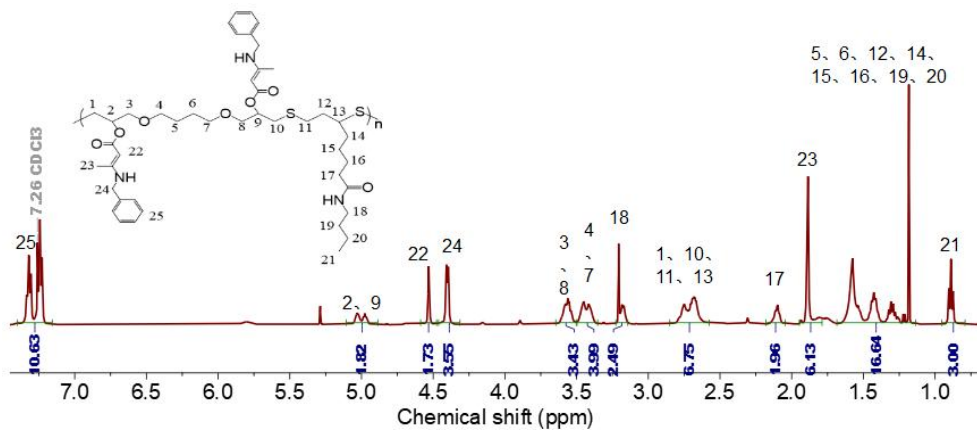


Figure S55. <sup>1</sup>H NMR spectrum of P1''' in CDCl<sub>3</sub>.

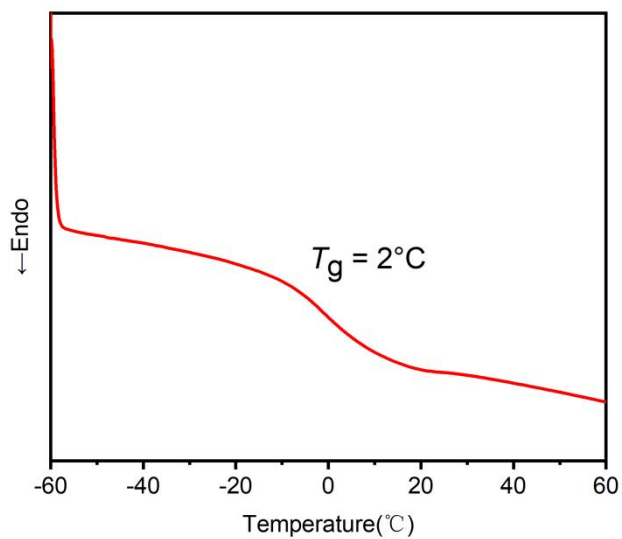


Figure S56. DSC curve of P1'

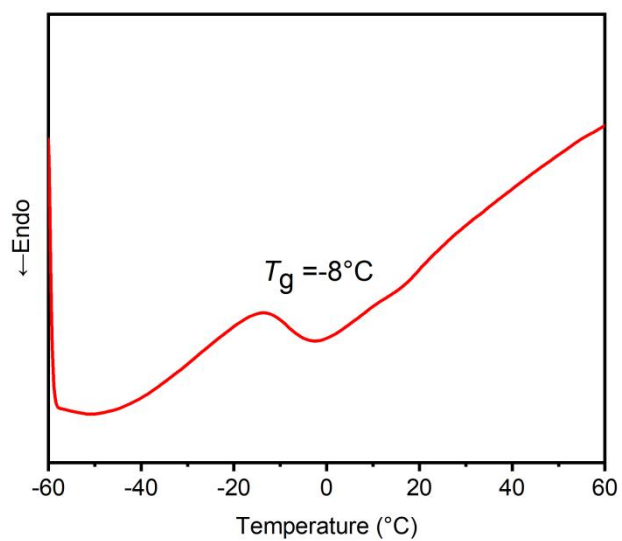


Figure S57. DSC curve of P1'''