Electronic Supplementary Information

Catalyst-free， atom-economical and regioselective multicomponent polymerizations of diamines, CS_2 and diepoxides toward functional polydithiourethanes

Xu Zhao, [a] Linlin Wang, [a] Guodong Zhou, [b] Shengyu Feng, [a] Lei Li*[a]

a. Key Laboratory of Special Functional Aggregated Materials of Ministry of Education, Shandong Key Laboratory of Advanced Silicone Materials and Technology, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China.
b. Jinan Shengquan Group Share Holding Co., Ltd., Jinan 250204, China.

*Corresponding author's e-mail: lei.li@sdu.edu.cn

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Materials and Characterizations

Materials

1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, 1,3-diaminopropane, *N*,*N'*-dimethyl- 1,3-propanediamine, 1,3-bis(aminomethyl)benzene, 1,4-butanediol diglycidyl ether and 1,2,7,8-diepoxyoctane were purchased from Heowns reagent company. 1,1,3,3-Tetramethyl-1,3-bis[3-(epoxyethylmethoxy)propyl]disiloxane was purchased from Bide Pharmatech Ltd. 1,6-Hexanediamine was purchased from TCI (Shanghai) Chemical Industry Development Co., Ltd. All the above diamines and diepoxides were used without purification. Carbon disulfide was provided by Shanghai Aladdin Biochemical Technology Co. Ltd (China) and distilled over CaH_2.

Characterizations

Nuclear magnetic resonance (NMR). ^1H and ^{13}C NMR spectra were measured at room temperature with a Bruker Advance 300 (500) spectrometer. Deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) was used as solvent.

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR was tested on a Bruker Tensor 27 infrared spectrophotometer using KBr compression technique with a frequency collection range from 4000 cm^{-1} to 400 cm^{-1} at room temperature.

Thermogravimetric analysis (TGA). 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.

Differential scanning calorimetry (DSC). 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 -80 °C to 100 °C at a rate of 10 °C/min, then cooled to -80 °C at a rate of -10 °C/min, finally heated from -80 °C to 100 °C at a rate of 10 °C/min. T_g was determined from the third run.

Fluorescence spectroscopy. Fluorescence spectroscopy tests were performed on a Hitachi F-7000 fluorescence spectrophotometer using a monochromatic Xe lamp as the excitation source.

Gel permeation chromatography (GPC). The number (M_n) and weight-average (M_w) molecular weights and polydispersity indices (M_w/M_n) of the polymers were estimated on Agilent PL-GPC 50 & Agilent PL-GPC 220 instruments (USA). Polystyrene standards were utilized, and DMF was used as the eluent at a flow rate of 1.0 mL/min at room temperature.

Inductively coupled plasma mass spectrometry (ICP-MS). The concentration of Hg^{2+} was determined on an ICP-MS Agilent 7800.

General Procedure for synthesis of polymers P1-P11

A typical synthetic procedure for the preparation of polymer **P1** is given below as an example.

1,1,3,3 -Tetramethyl- 1,3-bis[3-(epoxyethylmethoxy)propyl]disiloxane (**3a**, 362 mg, 1 mmol) , CS_2 (**2**, 240 μl, 4 mmol) and THF (2mL) were added into a round flask with a magnetic stirring bar inside. Then, 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (**1a**, 248 mg, 1 mmol) was added slowly to the mixture by using an ice-water bath and the reaction was stirred at room temperature for 24 hours. The solution was precipitated in THF/methyl tert-butyl ether three times (3 × 30 mL), and the precipitate was dried in a vacuum oven at 40 ^{o}C for 12 h, yielding polymer **P1** in the form of a yellow viscous solid in a yield of 97%.

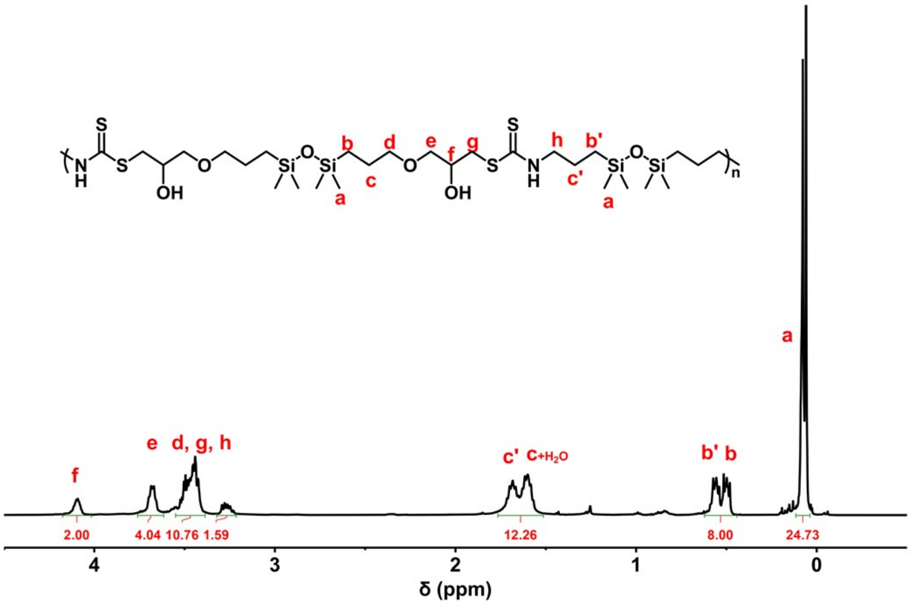


Fig. S1 ^1H NMR spectrum of polymer **P1** in $CDCl_3$.

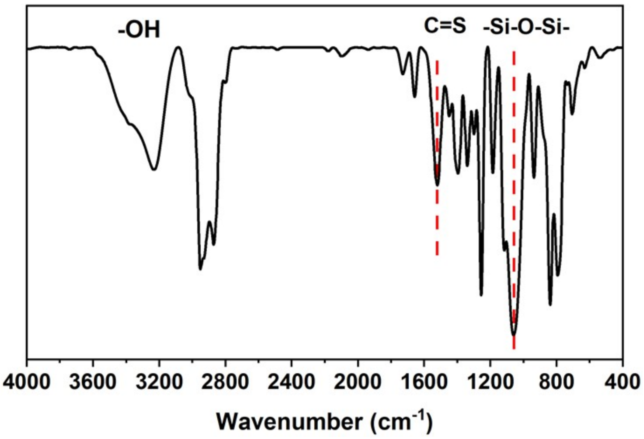


Fig. S2 FT-IR spectrum of polymer **P1**.

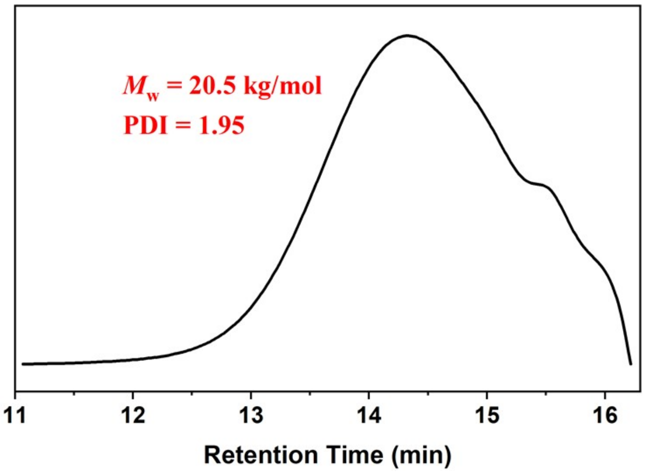


Fig. S3 GPC curve of polymer **P1**.

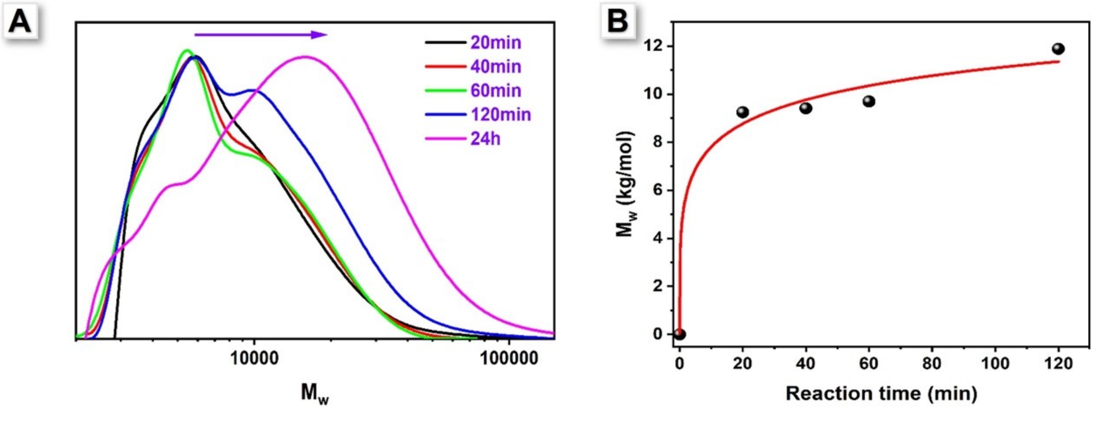
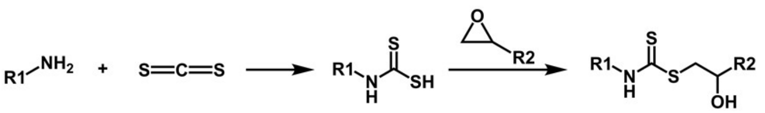


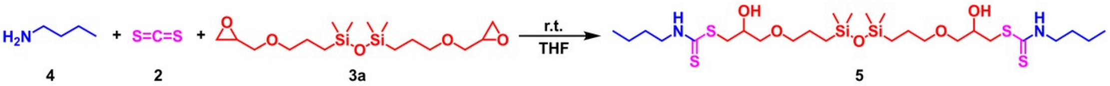
Fig. S4 GPC curves (A) and molecular weight changes (B) of MCP at different reaction times.



Scheme S1 Proposed mechanism of amine-CS_2-epoxy three-component reaction.

Synthesis of model compound by amine-CS_2-epoxy reaction

1,1,3,3 -Tetramethyl- 1,3-bis[3-(epoxyethylmethoxy)propyl]disiloxane (**3a**, 362 mg, 1 mmol) , CS_2 (**2**, 240 µl, 4 mmol) and THF (2 mL) were added into a round flask with a magnetic stirring bar inside. Then, n-butylamine (**4**, 146 mg, 2 mmol) was added slowly to the mixture by using an ice-water bath and the reaction was stirred at room temperature for 24 hours. The solvent was removed on the rotary evaporator to obtain model compound **5**.



Scheme S2 The synthetic route of model compound **5**.

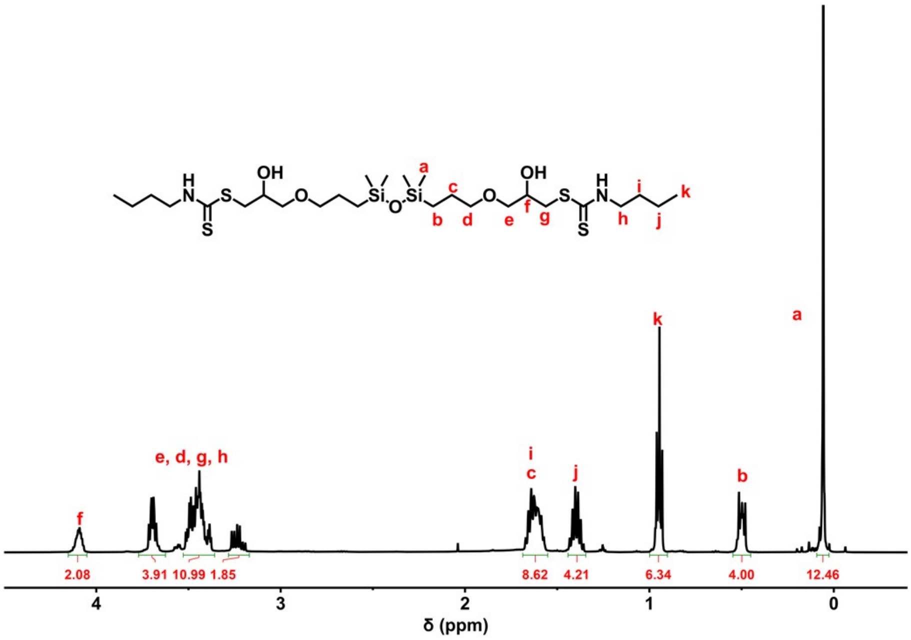


Fig. S5 ^{1}H NMR spectrum of model compound **5** in $CDCl_3$.

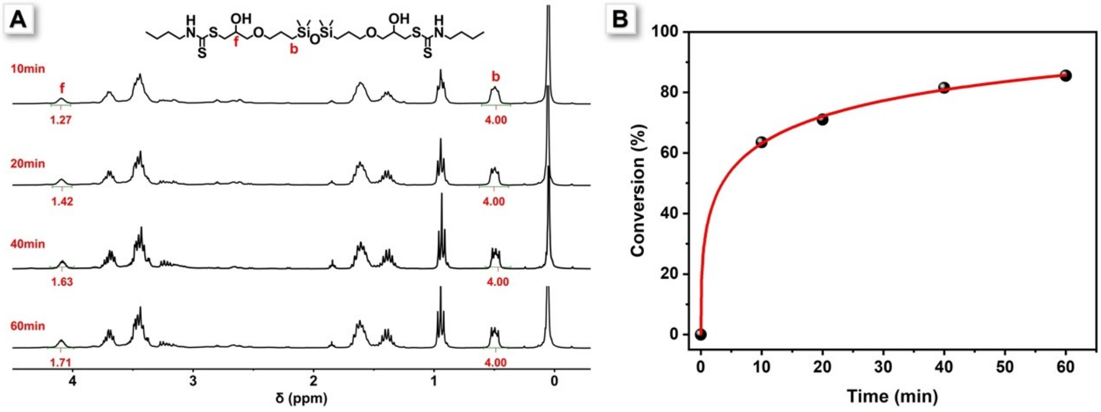


Fig. S6 ^{1}H NMR spectra (A) and conversion efficiency (B) of multicomponent reaction at different reaction times.

Comparison between amine-epoxy and amine-CS_2-expoy reactions based on model compound experiments

(1) Model compound experiment of amine-epoxy reaction

1,1,3,3-Tetramethyl-1,3-bis[3-(epoxyethylmethoxy)propyl]disiloxane (**3a**, 362 mg, 1 mmol) , n-butylamine (**4**, 146 mg, 2 mmol) and THF (2 mL) were added into a round flask with a magnetic stirring bar inside. Then, the reaction was stirred at room temperature for 24 hours. The solvent was removed on the rotary evaporator to obtain a crude residue. The residue was characterized by ^1H NMR spectrum. The unreacted n-butylamine was also removed on the rotary evaporator.

(2) Model compound experiment of amine-CS_2-epoxy reaction

According to the above procedure, the amine-CS_2-epoxy reaction was performed with the exception that CS_2 (**2**, 240 μl, 4 mmol) was added to the reaction mixture.

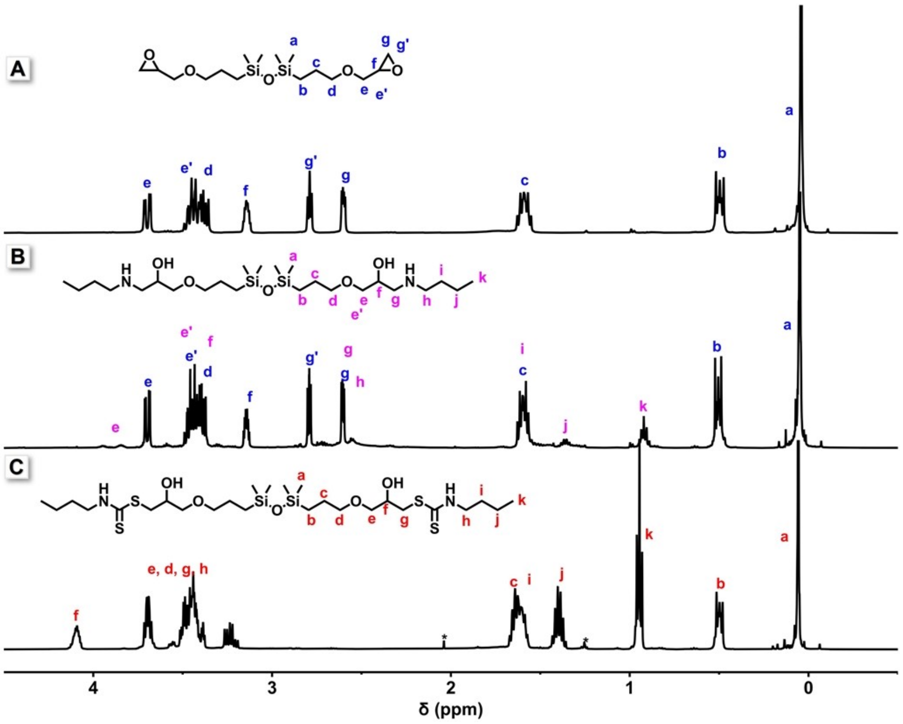


Fig. S7 ^1H NMR spectra of compound **3a** (A), crude products for amine-epoxy (B) and amine-CS_2-epoxy (C) reactions after 24 h.

Comparison between amine-epoxy and amine-CS_2-expoy reactions based on polymerization experiments

(1) Polymerization experiment of amine-epoxy reaction

1,1,3,3-Tetramethyl-1,3-bis[3-(epoxyethylmethoxy)propyl]disiloxane (**3a**, 362 mg, 1 mmol) , 1,3-

bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (**1a**, 248 mg, 1 mmol) and THF (2 mL) were added into a round flask with a magnetic stirring bar inside. Then, the reaction was stirred at room temperature for 24 hours. The solvent was removed on the rotary evaporator to obtain a crude residue. The residue was characterized by ^{1}H NMR spectrum.

(2) Polymerization experiment of amine-CS_2-expoy reaction

According to the above procedure, the amine-CS_2-epoxy polymerization was performed with the exception that CS_2 (**2**, 240 μl, 4 mmol) was added to the reaction mixture.

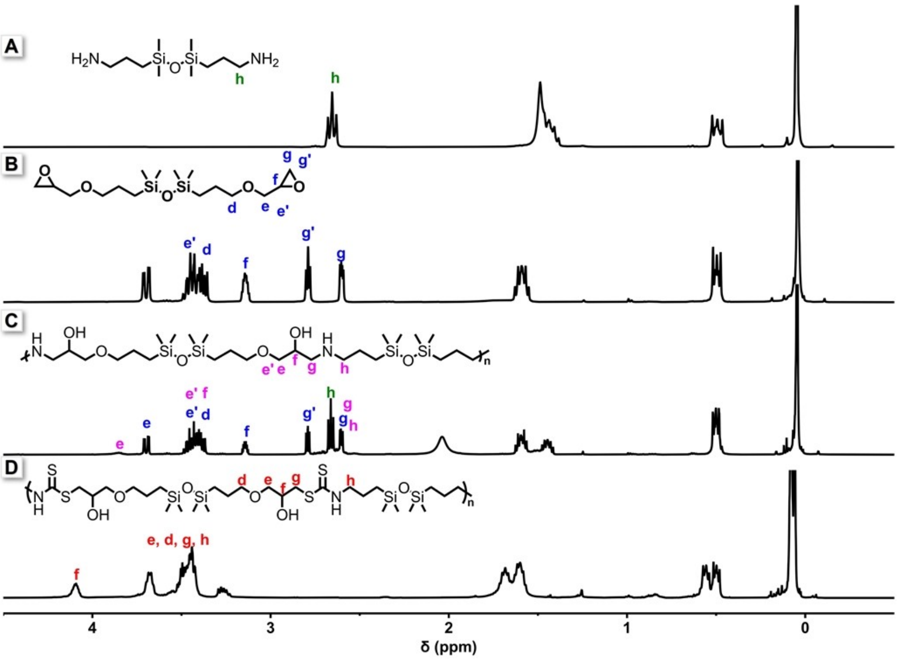


Fig. S8 ^{1}H NMR spectra of compounds **1a** (A) and **3a** (B), and crude products for amine-epoxy (C) and amine-CS_2-epoxy (D) polymerizations after 24 h.

General Procedure for post-modifications of polymer P1

A typical synthetic procedure of polymer **P1’** is given below as an example.

Polymer **P1** (100 mg) was added in THF (1 mL) and dissolved at room temperature with stirring. Then, triethylamine (0.39 mmol, 40 mg), a catalytic amount of DMAP and acetyl chloride (0.33 mmol, 23 μl) were added. The resulting reaction mixture was stirred at room temperature for 24 hours, after which the contents were poured into water and extracted with CH_2Cl_2. The resulting solution was dried to obtain modified polymer **P1’**.

Polymerization Results of polymers P1-P11

Table S1. Polymerization results of MCPs of diamines, CS_2 and diepoxides

polymer	yield (%)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	T_g(°C)	$T_{d,5\%}$(°C)
P1	97	10.5	20.5	1.95	-24	216
P2	95	4.2	8.7	2.06	-16	195
P3	94	6.6	9.3	1.40	1	203
P4	88	9.3	13.7	1.48	-23	210
P5	87	10.1	16.1	1.59	-23	213
P6	88	10.4	16.8	1.61	-14	186
P7	90	9.3	17.3	1.85	-15	218
P8	90	12.1	22.1	1.83	-33	216
P9	90	11.3	25.1	2.21	-20	182
P10	89	8.5	14.2	1.66	-17	207
P11	95	29.2	53.1	1.82	-17	250

^{1}H NMR Spectra of polymers P2-P11

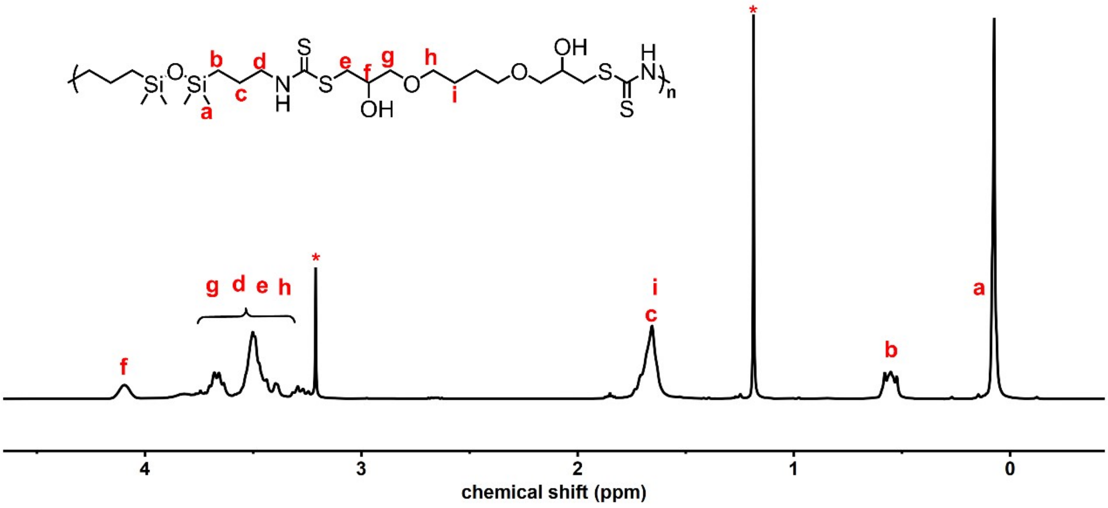


Fig. S9 ^{1}H NMR spectrum of polymer P2 in $CDCl_3$. The solvent peaks are marked with asterisks.

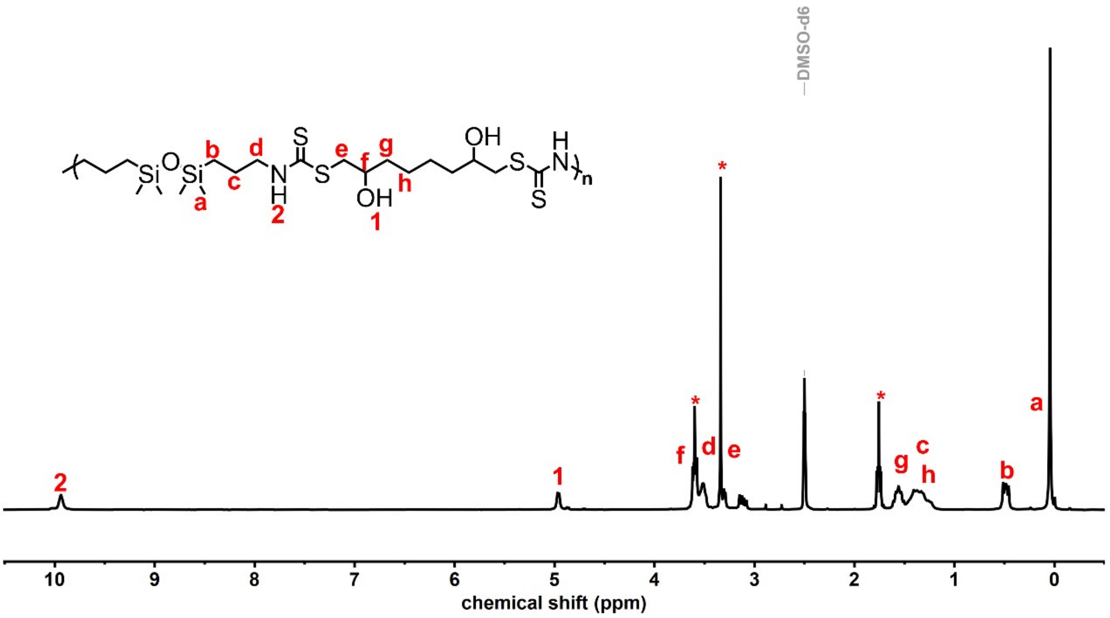


Fig. S10 ^{1}H NMR spectrum of polymer P3 in DMSO-d_6. The solvent peaks are marked with asterisks.

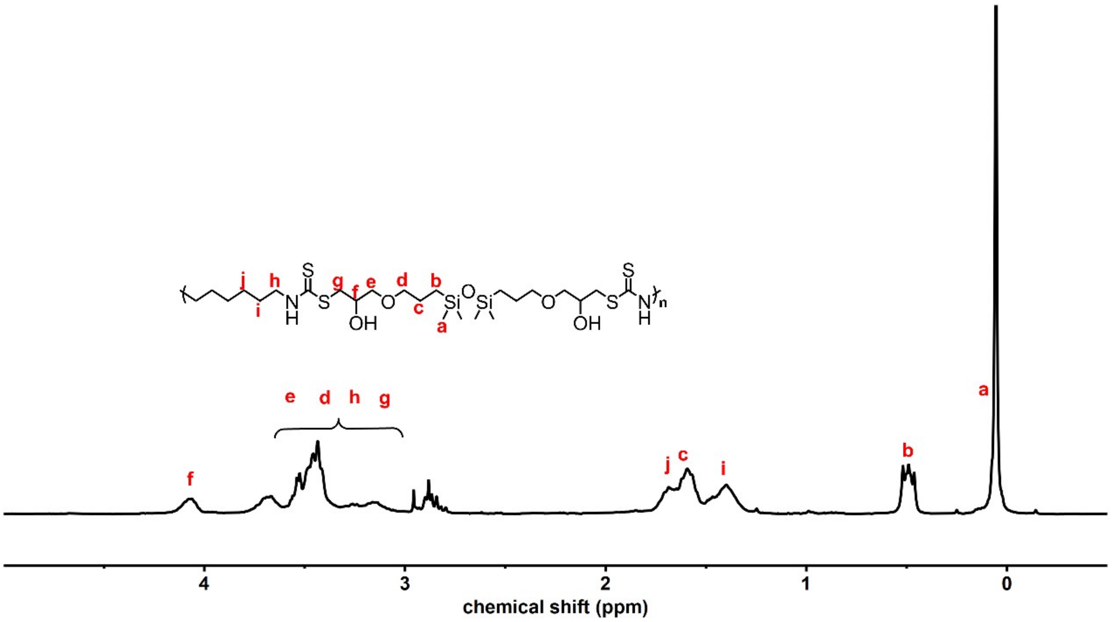


Fig. S11 ^{1}H NMR spectrum of polymer P4 in $CDCl_3$.

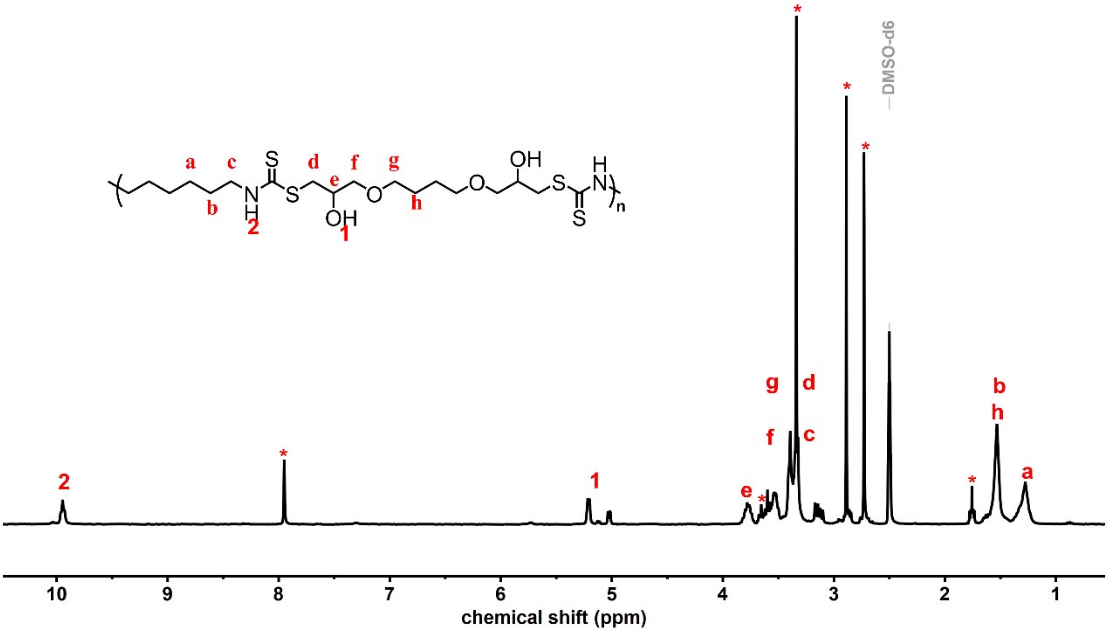


Fig. S12 ^{1}H NMR spectrum of polymer P5 in DMSO-d$_6$. The solvent peaks are marked with asterisks.

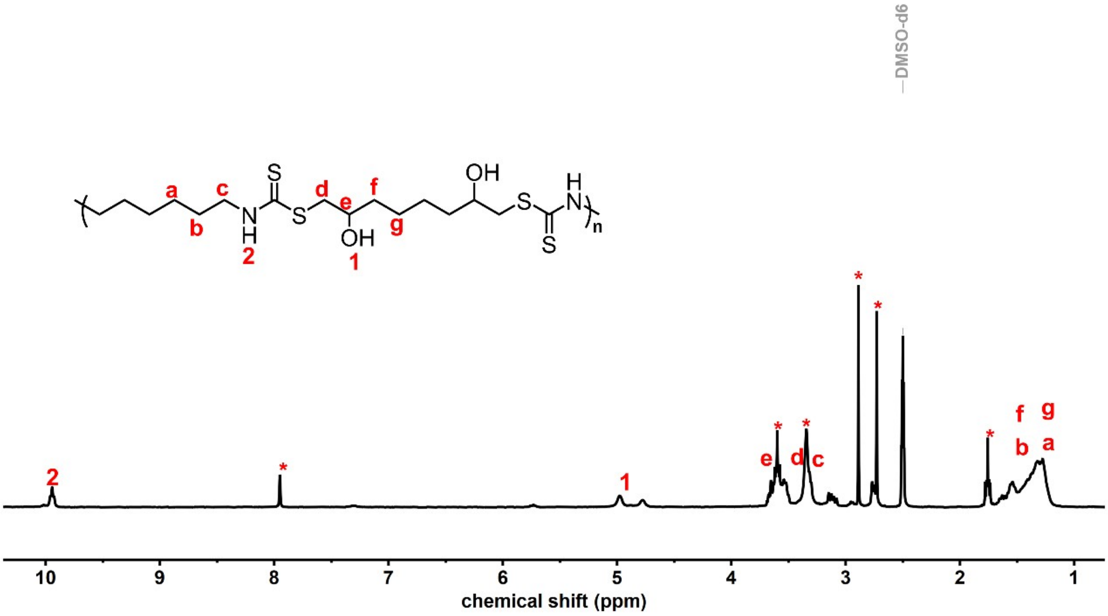


Fig. S13 ^{1}H NMR spectrum of polymer P6 in DMSO-d$_6$. The solvent peaks are marked with asterisks.

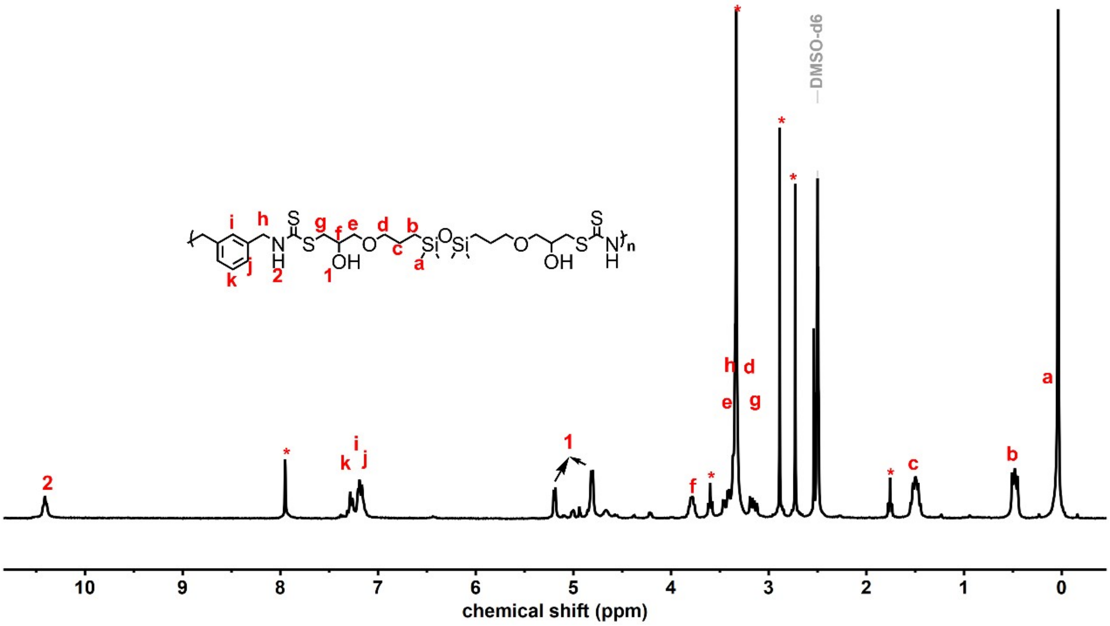


Fig. S14 ^{1}H NMR spectrum of polymer P7 in DMSO-d$_6$. The solvent peaks are marked with asterisks.

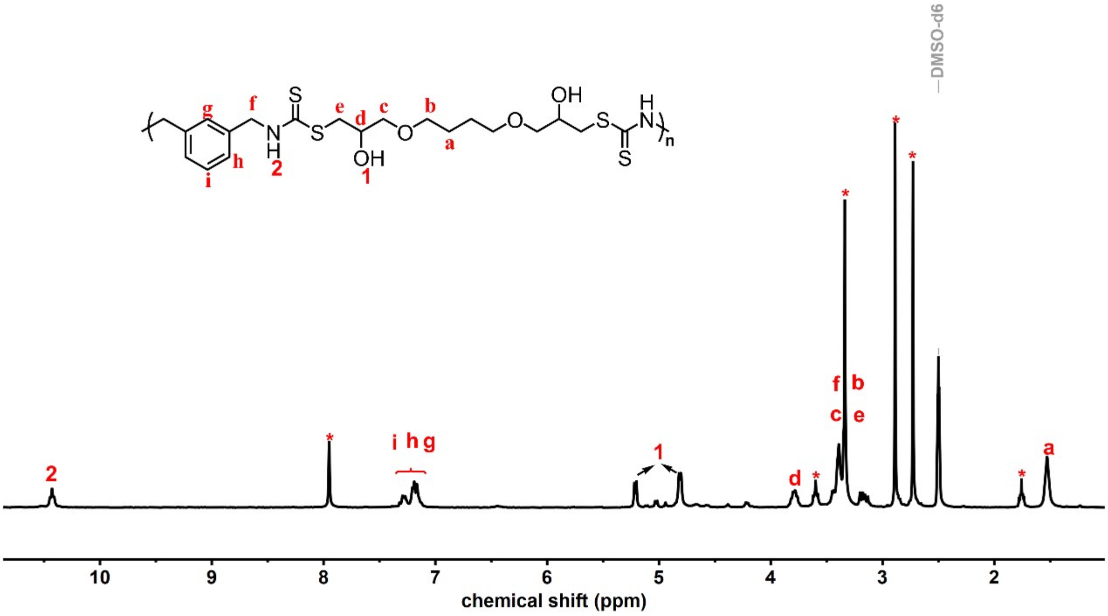


Fig. S15 ^{1}H NMR spectrum of polymer P8 in DMSO-d$_6$. The solvent peaks are marked with asterisks.

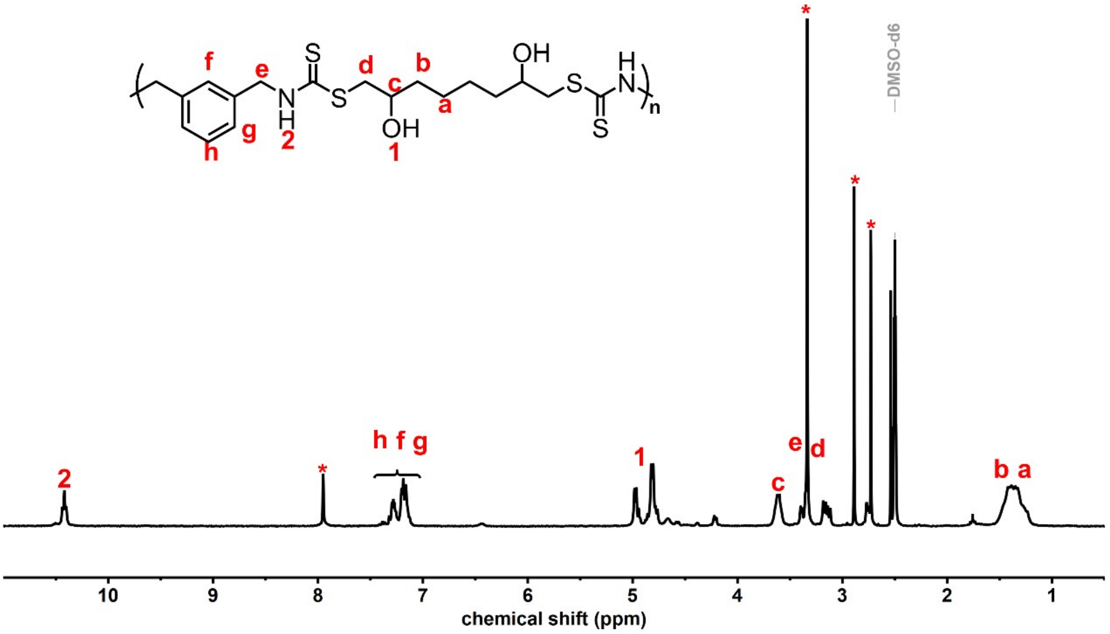


Fig. S16 ^{1}H NMR spectrum of polymer P9 in DMSO-d$_6$. The solvent peaks are marked with asterisks.

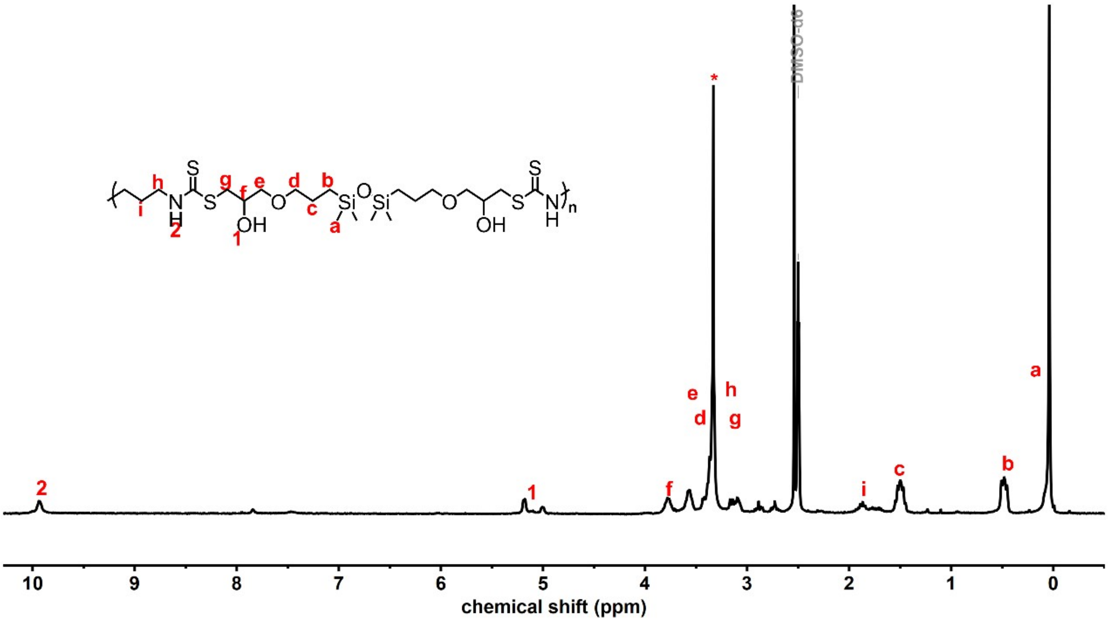


Fig. S17 ^{1}H NMR spectrum of polymer P10 in DMSO-d$_6$. The solvent peaks are marked with asterisks.

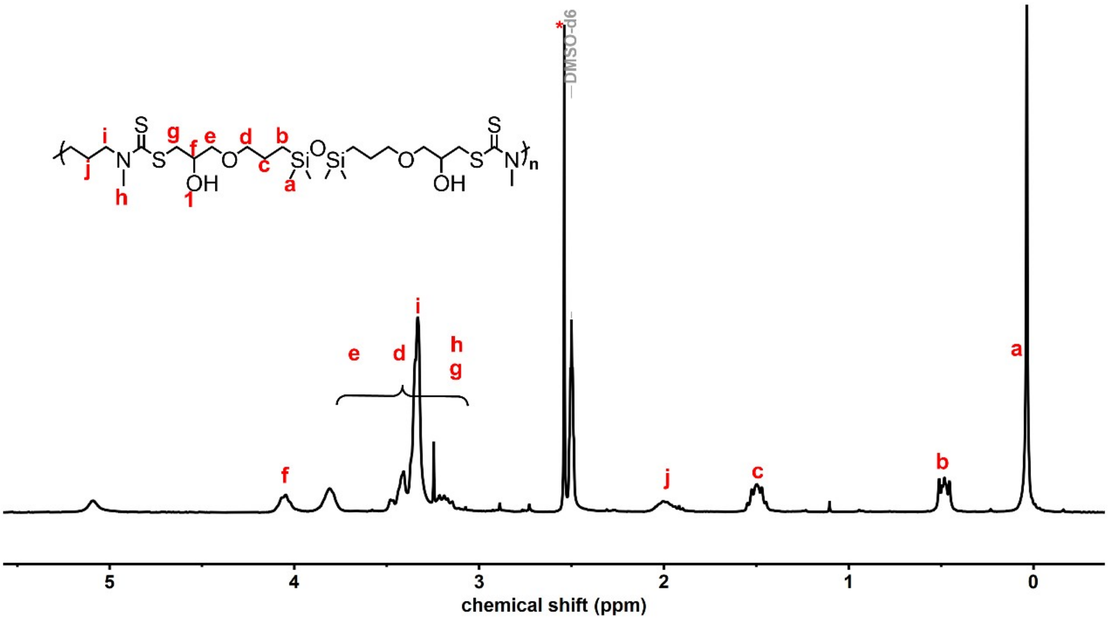


Fig. S18 ^{1}H NMR spectrum of polymer P11 in DMSO-d$_6$. The solvent peaks are marked with asterisks.

FT-IR Spectra of polymers P2-P11

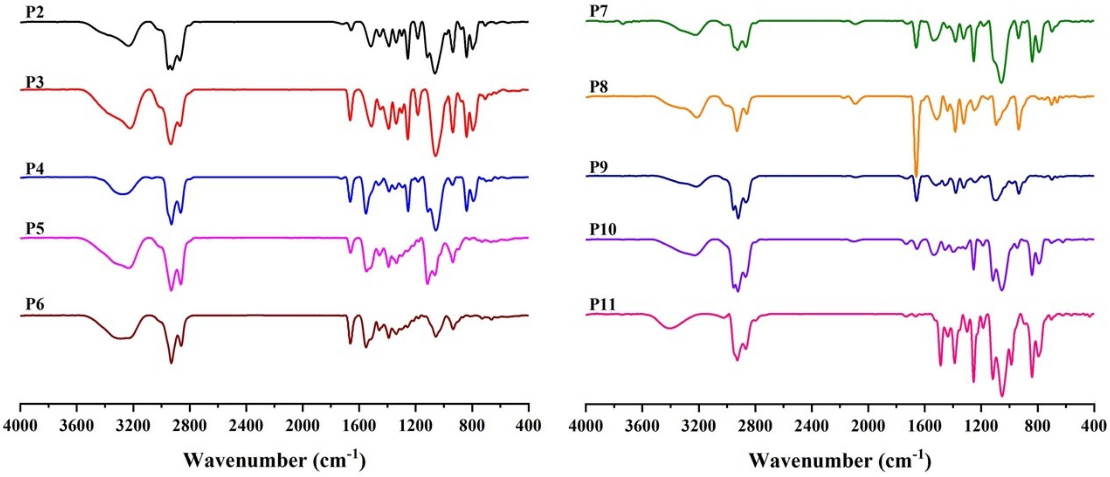


Fig. S19 FT-IR spectra of polymers P2-P11.

GPC Curves of polymers P2-P11

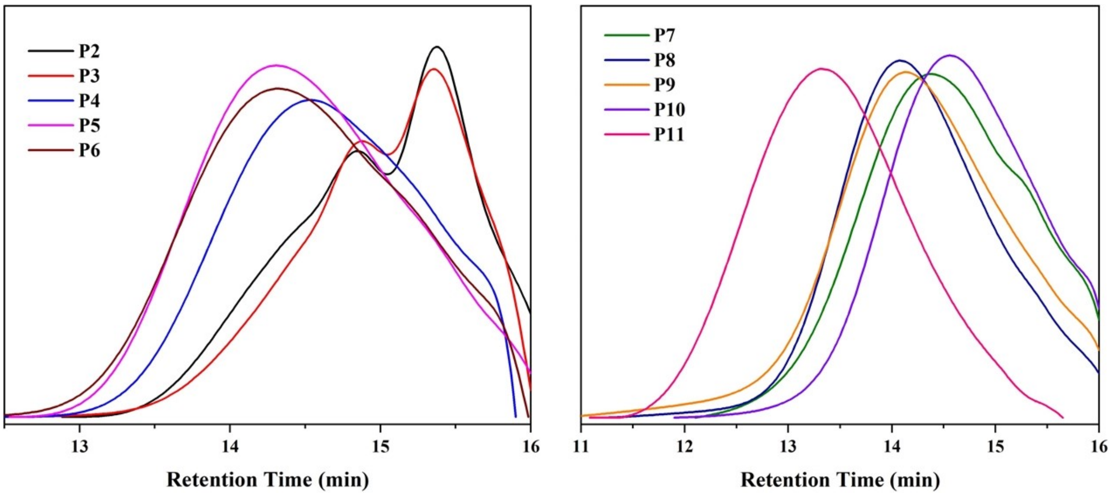


Fig. S20 GPC curves of polymers P2-P11.

Fluorescence Spectra of polymers P1-P11

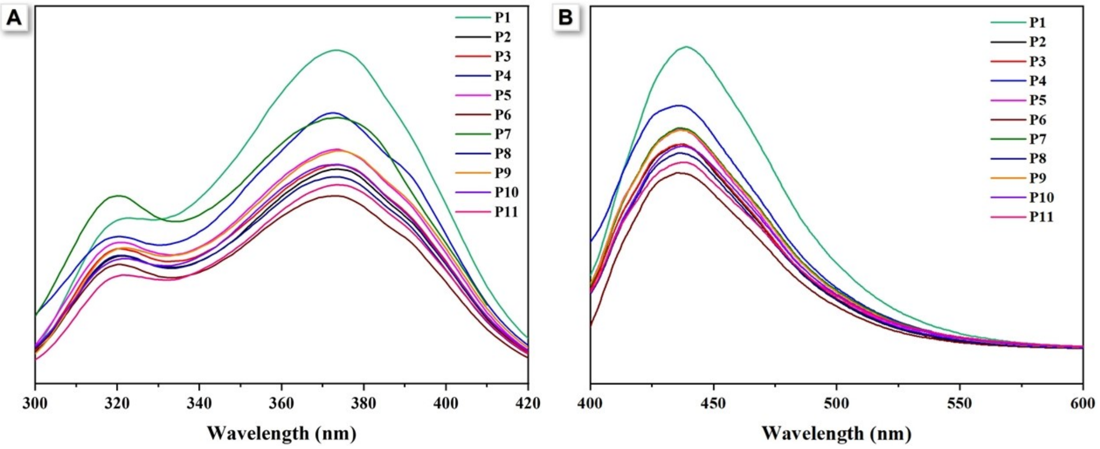


Fig. S21 Fluorescence excitation spectra (A) and emission spectra (B) of polymers P1-P11. Polymers P1-P11 were all dissolved in DMF at a concentration of 0.1mg/mL.

TGA Curves of polymers P1-P11

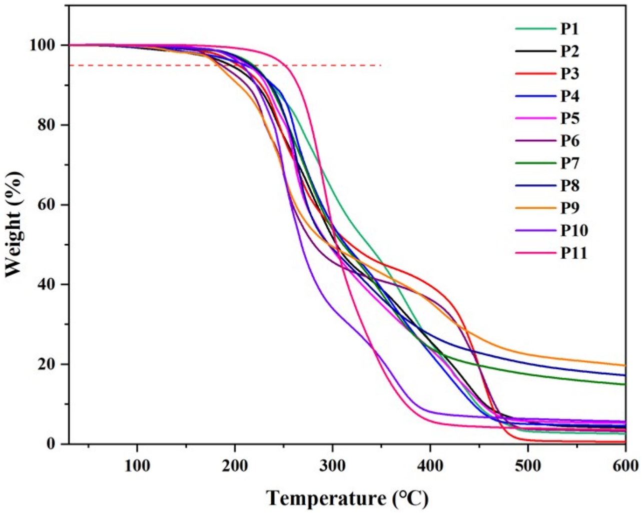


Fig. S22 TGA curves of polymers P1-P11.

DSC Curves of polymers P1-P11

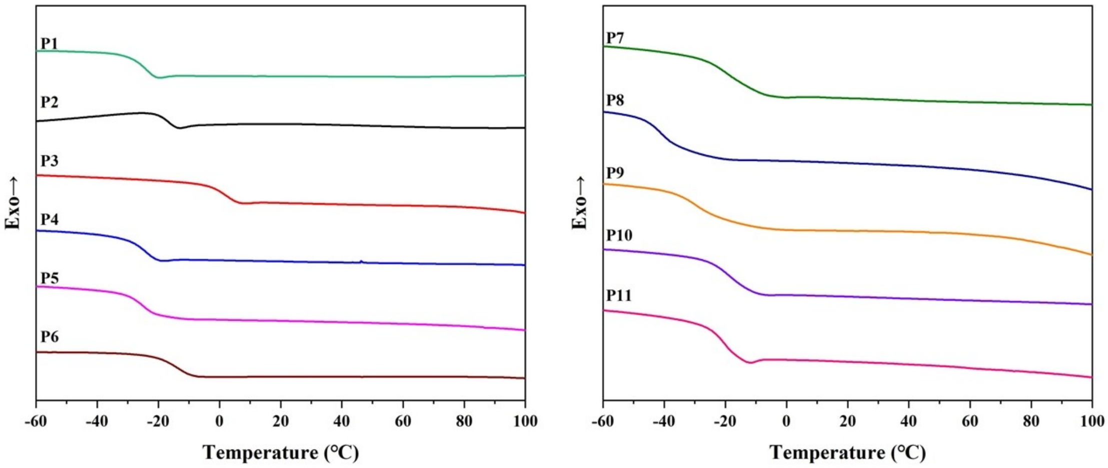


Fig. S23 DSC curves of polymers P1-P11.