Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supporting Information

# Cu-Catalyzed Four-Component Polymerization of Alkynes, Sulfonyl Azides, Nucleophiles and Electrophiles

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**Table of Contents**

**1. Experimtal Section**

**Synthesis of the diyne 1b**

Bis(4-bromophenyl) ether (3.0 mmol, 984.2 mg), trimethylsilylacetylene (7.5 mmol, 1100 μL), $PdCl_2(PPh_3)_2$ (0.3 mmol, 210.3 mg), $PPh_3$ (0.6 mmol ,158.4 mg) and CuI (0.3 mmol, 57.1 mg) were dissolved in the mixture solvent of THF (15 mL) and TEA (5 mL). The reaction mixture was stirred at 70 ℃ overnight. After the reaction was completed, the mixture was cooled to room temperature and filtered by a short pad of Celite. The solvent was removed in vacuo. The residue was purified by column chromatography, giving the pure product ((oxybis(4,1-phenylene))bis(ethyne-2,1-diyl))bis(trimethylsilane) as a white powder in 67% yield (728.9 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 5.6 Hz, 4H), 6.93 (d, *J* = 5.6 Hz, 4H), 0.28-0.17 (m, 18H). (**Figure S1**)
((Oxybis(4,1-phenylene))bis(ethyne-2,1-diyl))bis(trimethylsilane) (0.82 mmol, 288.2 mg) and $K_2CO_3$ (2.44 mmol, 337.2 mg) were added in the mixture solvent of methanol (1 mL) and THF (3 mL) in a 15 mL vial. The reaction mixture was stirred at room temperature for 12 h. After the reaction was completed, the mixture was filtered to remove $K_2CO_3$ and the residue was extracted with DCM (3 × 20 mL). The organic layer was collected and dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The target product 4,4'-oxybis(ethynylbenzene) (**1b**) was obtained as a yellow powder in 89% yield (159.1 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.7 Hz, 5H), 6.98 (d, *J* = 8.7 Hz, 4H), 3.07 (s, 2H). (**Figure S2**)

**Synthesis of the diyne 1c**

4,4'-Diiodo-1,1'-biphenyl (1.0 mmol, 40.6 mg), trimethylsilylacetylene (2.5 mmol, 350 μL), $PdCl_2(PPh_3)_2$ (0.05 mmol, 35.1 mg) and CuI (0.05 mmol, 9.5 mg) were dissolved in 30 mL mixture solvent of THF (20 mL) and TEA (10 mL). The reaction mixture was stirred at 60 ℃ overnight. After the reaction was completed, the mixture was cooled to room temperature and filtered by a short pad of Celite. The solvent was removed in vacuo and the residue was purified by column chromatography, giving the pure product as a white powder 4,4'-bis((trimethylsilyl)ethynyl)-1,1'-biphenyl in 68% yield (235.7 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 8H), 0.44-0.19 (m, 18H). (**Figure S3**)
4,4'-Bis((trimethylsilyl)ethynyl)-1,1'-biphenyl (0.5 mmol, 173.2 mg) and $K_2CO_3$ (1.5 mmol, 207.3 mg) were added in the mixture solvent of methyl alcohol (1 mL) and THF (3 mL). The reaction mixture was stirred at room temperature for 12 h. After the reaction was completed, the mixture was filtered to remove $K_2CO_3$ and the residue was extracted with DCM (3 × 15 mL). The organic layer was collected and dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The target product 4,4'-diethynyl-1,1'-biphenyl (**1c**) was obtained as a white powder in 93% yield (94.1 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.67-7.52 (m, 8H), 3.16 (s, 2H). (**Figure S4**)

**Synthesis of sulfonyl azide 2b**

4-Methoxybenzenesulfonyl chloride (5.0 mmol, 1.03 g) was dissolved in the mixture of acetone (10 mL) and water (10 mL). $NaN_3$ (6.5 mmol, 423 mg) was added into the mixture in an ice bath. The reaction was recovered to room temperature and the mixture was stirred for 12 h. After the reaction was completed, the acetone was removed in vacuo. The residual solution was extracted by EtOAc (3 × 50 mL). The organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The 4-methoxybenzenesulfonyl azide (**2b**) was obtained as a white powder in 91% yield (969.2 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 3.94 (s, 3H). (**Figure S5**)

**Synthesis of sulfonyl azide 2c**

Using the same synthesis method as that for sulfonyl azide **2b**, the 4-nitrobenzenesulfonyl azide (**2c**) was obtained as a yellow powder in 86% yield (1.02 g). $^1$H NMR (500 MHz, $CDCl_3$): δ7.93 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 17.1 Hz, 2H). (**Figure S6**)

**Synthesis of sulfonyl azide 2d**

Using the same synthesis method as that for sulfonyl azide **2b**, 4-bromobenzenesulfonyl azide (**2d**) was obtained as a white powder in 90% yield (1.17 g). $^1$H NMR (500 MHz, $d_6$-DMSO): δ 8.10-7.87 (m, 4H). (**Figure S7**)

**Synthesis of diol 3b**

3-Mercaptopropionic acid (55.0 mmol, 4.8 mL), acetone (25.0 mmol, 1.9 mL) and a catalytic amount of trifluoroacetic acid (TFA) were added into a 20 mL vial under nitrogen atmosphere at room temperature for 4 h. The reaction mixture was quenched in an ice bath. Then, the solution was filtered and washed three times with

cold water and hexane. 3,3'-(propane-2,2'-diylbis(sulfanediyl))dipropionic acid (TK-COOH) was obtained in vacuo as a white powder in 80% yield. Then, TK-COOH (1.5 mmol, 378.5 mg) was dissolved in 10 mL anhydrous THF solution, followed by the dropwise addition of the solution which was prepared using $LiAlH_4$ (19.5 mmol, 740.0 mg) dissolved in 10 mL anhydrous THF. Then the mixture was stirred at 70 ℃ for 1 h. After the reaction was completed, NaOH solution (10%) was slowly added into the mixture until no gas was produced. The solution was filtered and the combined organic layers were washed with brine (3 × 15 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The pure product of **3b** was obtained as a yellow oil in 91% yield (305.8 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 3.94-3.68 (m, 4H), 2.86-2.71 (m, 4H), 2.63 (s, 2H), 1.94-1.79 (m, 4H), 1.62 (s, 6H). (**Figure S8**)

**Synthesis of the trans-4-nitro-β-nitrostyrene 4e**

4-Nitrobenzaldehyde (5.0 mmol, 755.6 mg), $NH_4OAc$ (34.5 mmol 2105.8 mg) and nitromethane (12.0 mmol, 925.0 mg) were dissolved in 9 mL acetic acid in 25 mL round-bottom flask. The mixture was stirred at reflux temperature for 6 h. After the reaction was completed, the reaction solution was gradually cooled to room temperature and dropped into a large amount of water to quench the reaction. Then, the solution was neutralized with a 2 M sodium hydroxide solution. The mixture was extracted with EtOAc (3 × 50 mL) and the organic layer was collected. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography, giving the pure product **4e** as a yellow powder in 65% yield (631.9 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 13.8 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 13.8 Hz, 1H). (**Figure S9**)

**Synthesis of methyl 2-(hydroxymethyl)acrylate**

Methyl acrylate (10.0 mmol, 860.0 mg) and 30% formaldehyde solution (13.0 mmol, 1300 μL) were dissolved in the mixture solvent of dioxane (15 mL) and water (15 mL) in a 50 mL bottom flask. Then, DABCO (10.0 mmol, 112.1 mg) was added into the mixture and stirred at the room temperature for 6 h. After the reaction was completed, the mixture solution was extracted with EtOAc (3×50 mL) and collected the organic layer. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography, giving the pure product methyl 2-(hydroxymethyl)acrylate as a colorless oil in 48% (557.4 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 6.36-6.20 (m, 1H), 5.86 (d, *J* = 1.2 Hz, 1H), 4.34 (t, *J* = 5.4 Hz, 2H), 3.94-3.68 (m, 3H), 2.73-2.18 (m, 1H). (**Figure S10**)

**Synthesis of ethyl 2-(((tert-butoxycarbonyl)oxy)methyl)acrylate 4h**

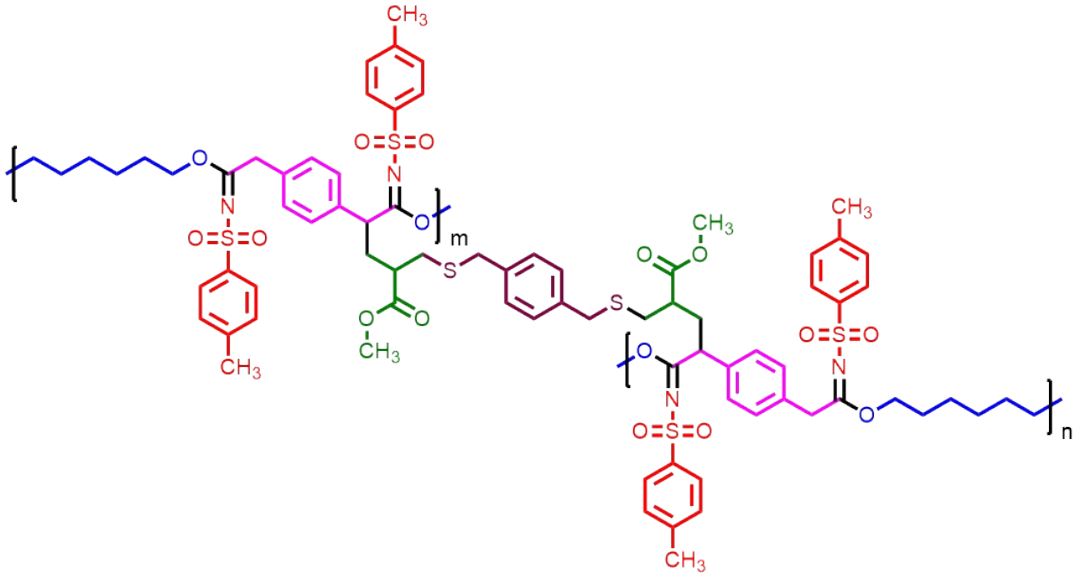
Ethyl 2-(hydroxymethyl)acrylate (6.0 mmol, 780.0 mg) and $Boc_2O$ (6.6 mmol, 1600 μL) were dissolved in 1 mL DCM in a 20 mL vial. The solution was cooled to 0 ℃. Then, DMAP (0.6 mmol, 73.2 mg) was slowly added into the reaction solution at 0 ℃. The mixture was cooled to room temperature and stirred for 12 h. After the reaction was completed, the reaction solution was diluted with DCM. The organic layer was washed with 4 N HCl solution, saturated $NaHCO_3$ solution and brine. The organic layer was collected and dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography, giving the pure product **4h** as a colorless oil in 89% yield (1.2 g). $^1$H NMR (500 MHz, $CDCl_3$): δ 6.38 (s, 1H), 5.88 (s, 1H), 4.82 (s, 2H), 4.13-4.54 (m, 2H), 1.51 (s, 9H), 1.38-1.29 (m, 3H). (**Figure S11)**

**Synthesis of methyl 2-(((tert-butoxycarbonyl)oxy)methyl)acrylate 4i**

Using the same procedure of **4h** for the synthesis of **4i**, the product **4i** was obtained as colorless oil in 84% yield (1.8 g). $^1$H NMR (500 MHz, $CDCl_3$): δ 6.40 (s, 1H), 5.92 (s, 1H), 4.81 (s, 2H), 3.79 (s, 3H), 1.51 (s, 9H). (**Figure S12**)

**Synthesis of P1a/2a/3a/4i/6**

**P1a/2a/3a/4i** (40.5 mg) and TEA (0.03 mmol, 5 μL) was dissolved in DMF (1 mL). Then 1,4-benzenedimethanethiol **6** (0.18 mmol, 30.6 mg) was slowly added into the solution. The mixture was stirred at room temperature for 4 h. The solution was precipitated in methanol. The product was washed with methanol for three times and collected by centrifugation. The pure product **P1a/2a/3a/4i/6** was obtained as a brown solid in 90 % yield.



P1a/2a/3a/4i/6

**Scheme S1.** The structure of P1a/2a/3a/4i/6.

**2. Reaction Conditions Screening for 4-CP**

**Table S1**. Effect of Catalyst on the 4-CP of 1a, 2a, 3a and 4a[a]

| Entry | Catalysts | Yield (%) | $M_n$[b] | $M_w$[b] | $Đ$[b] |
|---|---|---|---|---|---|
| 1 | CuI | 64 | 11000 | 15000 | 1.37 |
| 2 | CuCl | 51 | 9800 | 12300 | 1.25 |
| 3 | CuBr | 65 | 13400 | 19700 | 1.37 |
| 4 | $Cu(CH_3CN)_4PF_6$ | 62 | 9500 | 15600 | 1.64 |
| 5 | $(CuOTf)_2Tol$ | 48 | 8600 | 13700 | 1.59 |

[a] Conditions: experiments were carried out at room temperature in the glove box for 12 h in THF. [1a] = [3a] = [4a] = 0.2 M, [2a] = 0.6 M, [TEA] = 1.0 M, [Cu(I)] = 0.04 M. [b] $M_n$, $M_w$ and $Đ$ were determined by GPC in DMF with PMMA standards.

**Table S2.** Effect of Solvent on the 4-CP of 1a, 2a, 3a and 4a[a]

| Entry | Solvent | Yield (%) | $M_n$[b] | $M_w$[b] | $Đ$[b] |
|---|---|---|---|---|---|
| 1 | DMF | 53 | 8600 | 12000 | 1.31 |
| 2 | DCM | 54 | 6900 | 8500 | 1.23 |
| 3 | THF | 65 | 13000 | 20000 | 1.47 |
| 4 | $CHCl_3$ | 48 | 7300 | 9100 | 1.28 |
| 5 | DMSO | 34 | 7300 | 8600 | 1.18 |
| 6 | Toluene | -[c] | - | - | - |

[a] Conditions: experiments were carried out at room temperature in the glove box for 12 h. [1a] = [3a] = [4a] = 0.2 M, [2a] = 0.6 M, [TEA] = 1.0 M, [CuBr] = 0.04 M. [b] $M_n$, $M_w$ and $Đ$ were determined by GPC in DMF with PMMA standards. [c] No polymers were detected.

**Table S3.** Effect of Temperature on the 4-CP of 1a, 2a, 3a and 4a[a]

| Entry | Temperature (℃) | Yield (%) | $M_n$[b] | $M_w$[b] | $Đ$[b] |
|---|---|---|---|---|---|
| 1 | rt | 65 | 13500 | 19900 | 1.47 |
| 2 | 40 | 53 | 8400 | 10600 | 1.27 |
| 3 | 50 | 50 | 7900 | 10500 | 1.30 |
| 4 | 60 | -[c] | - | - | - |

[a] Conditions: experiments were carried out under different temperature in the glove box for 12 h in THF. [1a] = [3a] = [4a] = 0.2 M, [2a] = 0.6 M, [TEA]= 1.0 M, [CuBr] = 0.04 M. [b] $M_n$, $M_w$ and $Đ$ were determined by GPC in DMF with PMMA standards. [c] Insoluble gel was observed.

**Table S4.** Effect of Monomer Concentration on the 4-CP of 1a, 2a, 3a and 4a[a]

| Entry | [1a] (M) | Yield (%) | $M_n$[b] | $M_w$[b] | $Đ$[b] |
|---|---|---|---|---|---|
| 1 | 0.05 | trace | - | - | - |
| 2 | 0.1 | 15 | 10800 | 13200 | 1.22 |
| 3 | 0.2 | 62 | 16000 | 24900 | 1.50 |
| 4 | 0.3 | 64 | 12900 | 19300 | 1.49 |
| 5 | 0.4 | -[c] | - | - | - |

[a] Conditions: experiments were carried out at room temperature in the glove box for 12 h in THF. [1a] = [3a] = [4a], [2a] = 3 [1a], [TEA] = 5 [1a], [CuBr] = 0.2 [1a]. [b] $M_n$, $M_w$ and $Đ$ were determined by GPC in DMF with PMMA standards. [c] Insoluble gel was observed.

**Table S5.** Effect of Time on the 4-CP of 1a, 2a, 3a and 4a[a]

| Entry | Time (h) | Yield (%) | $M_n$[b] | $M_w$[b] | $Đ$[b] |
|---|---|---|---|---|---|
| 1 | 0.1 | 36 | 3600 | 4200 | 1.18 |
| 2 | 0.5 | 43 | 4500 | 5600 | 1.25 |
| 3 | 1 | 43 | 7900 | 10800 | 1.22 |
| 4 | 2 | 52 | 9800 | 12500 | 1.27 |
| 5 | 4 | 50 | 9900 | 13900 | 1.40 |
| 6 | 6 | 59 | 10000 | 15000 | 1.50 |
| 7 | 12 | 60 | 15100 | 20800 | 1.38 |
| 8 | 24 | 64 | 13600 | 20200 | 1.48 |
| 9 | 36 | 58 | 13400 | 18700 | 1.39 |
| 10 | 48 | 48 | 12100 | 18500 | 1.53 |
| 11 | 60 | -[c] | - | - | - |

[a] Conditions: experiments were carried out at room temperature in the glove box in THF. [1a] = [3a] = [4a] = 0.2 M, [2a] = 0.6 M, [TEA] = 1.0 M, [CuBr] = 0.04 M. [b] $M_n$, $M_w$ and $Đ$ were determined by GPC in DMF with PMMA standards. [c] Insoluble gel was observed.

**3. $^1$H NMR Spectra of Monomers**

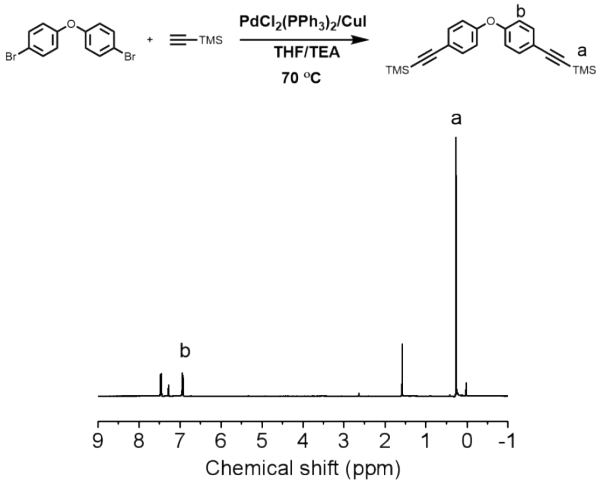



**Figure S1.** $^1$H NMR spectrum of ((oxybis(4,1-phenylene))bis(ethyne-2,1-diyl))bis(trimethylsilane) in $CDCl_3$.

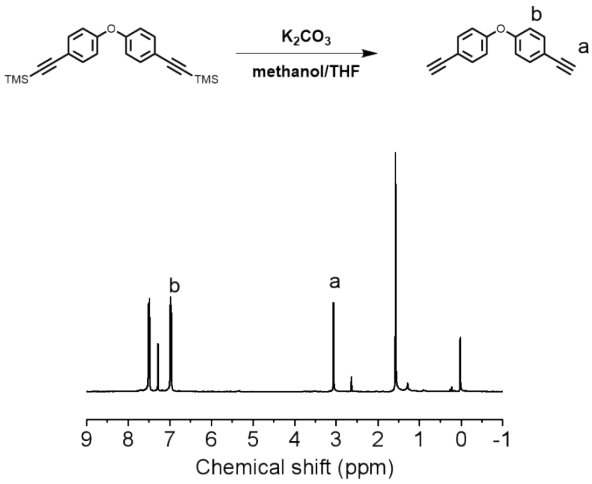



**Figure S2.** $^1$H NMR spectrum of 1b in $CDCl_3$

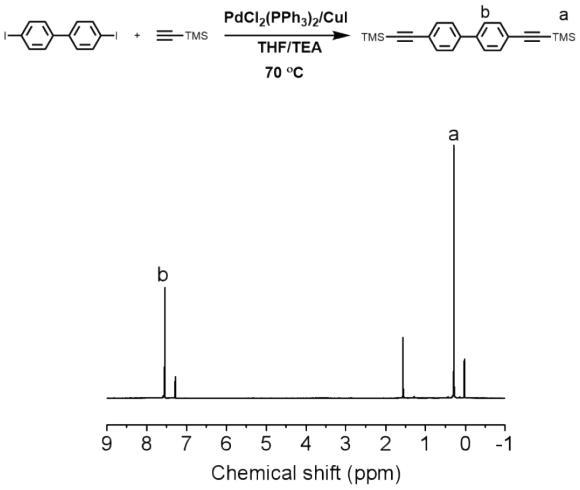



**Figure S3.** $^{1}$H NMR spectrum of 4,4'-bis((trimethylsilyl)ethynyl)-1,1'-biphenyl in $CDCl_3$.

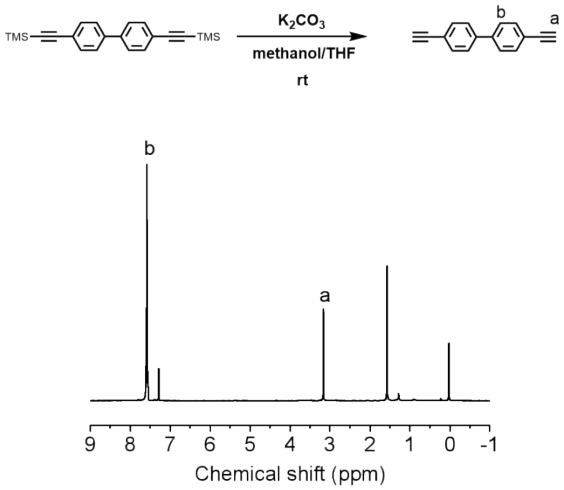



**Figure S4.** $^{1}$H NMR spectrum of 1c in $CDCl_3$.

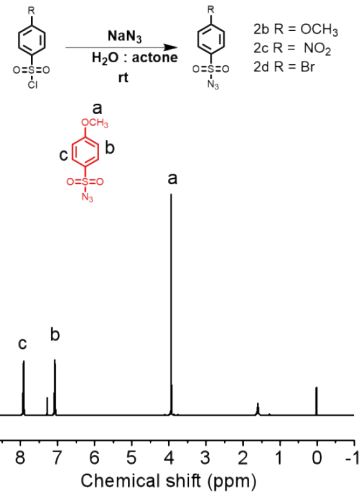



**Figure S5.** $^{1}$H NMR spectrum of 2b in $CDCl_3$.

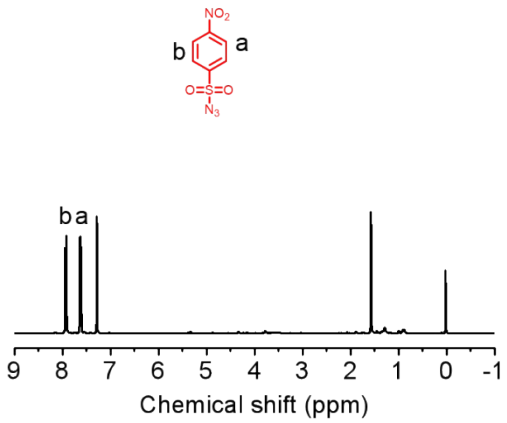



**Figure S6.** $^{1}H$ NMR spectrum of 2c in $CDCl_3$.

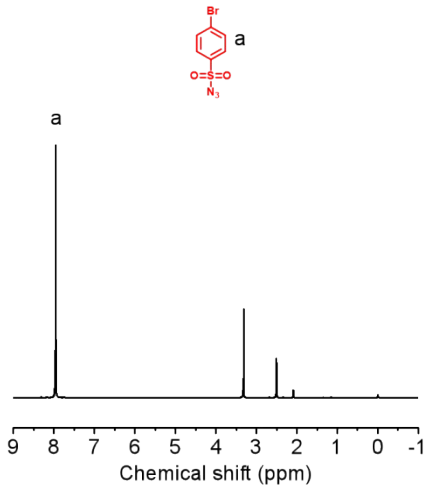



**Figure S7.** $^{1}H$ NMR spectrum of 2d in $d_6$-DMSO.

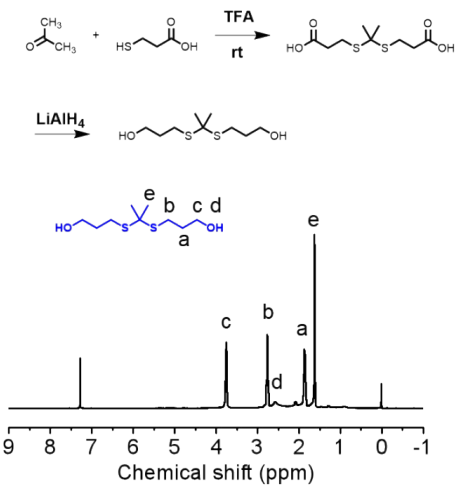



**Figure S8.** $^{1}$H NMR spectrum of 3b in $CDCl_3$.

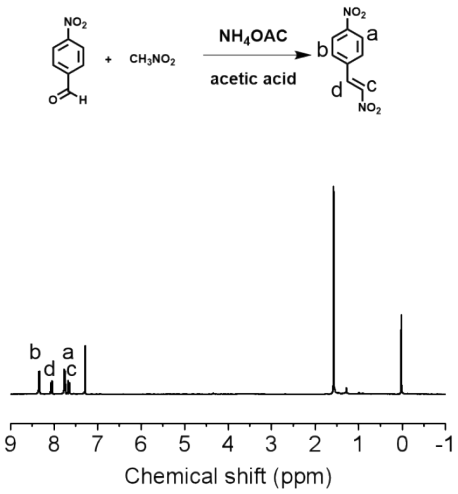



**Figure S9.** $^{1}$H NMR spectrum of 4e in $CDCl_3$.

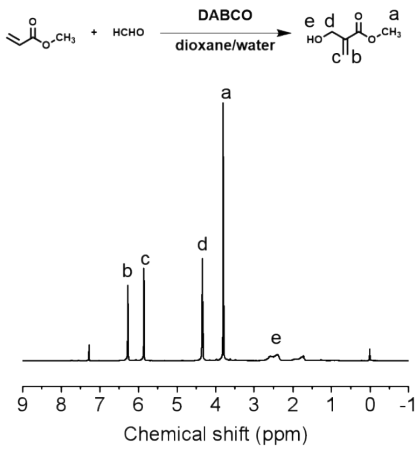



**Figure S10.** $^{1}$H NMR spectrum of methyl 2-(hydroxymethyl)acrylate in $CDCl_3$.

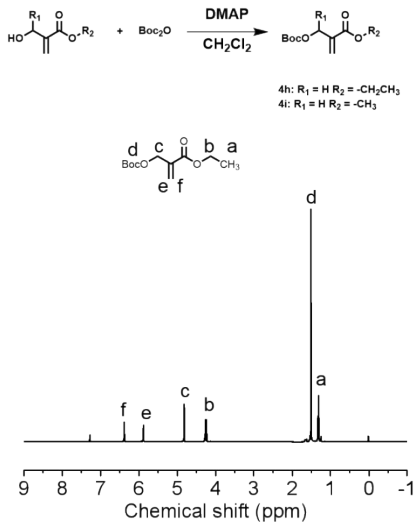



**Figure S11.** $^1$H NMR spectrum of 4h in $CDCl_3$.

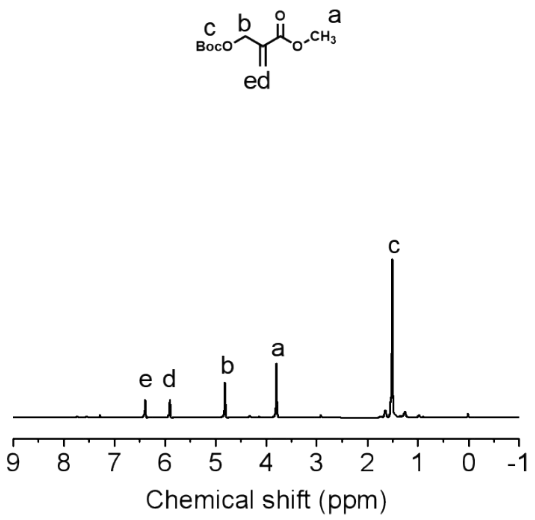



**Figure S12.** $^1$H NMR spectrum of 4i in $CDCl_3$.

**4. $^1$H NMR Spectra of Synthetic Polymers**

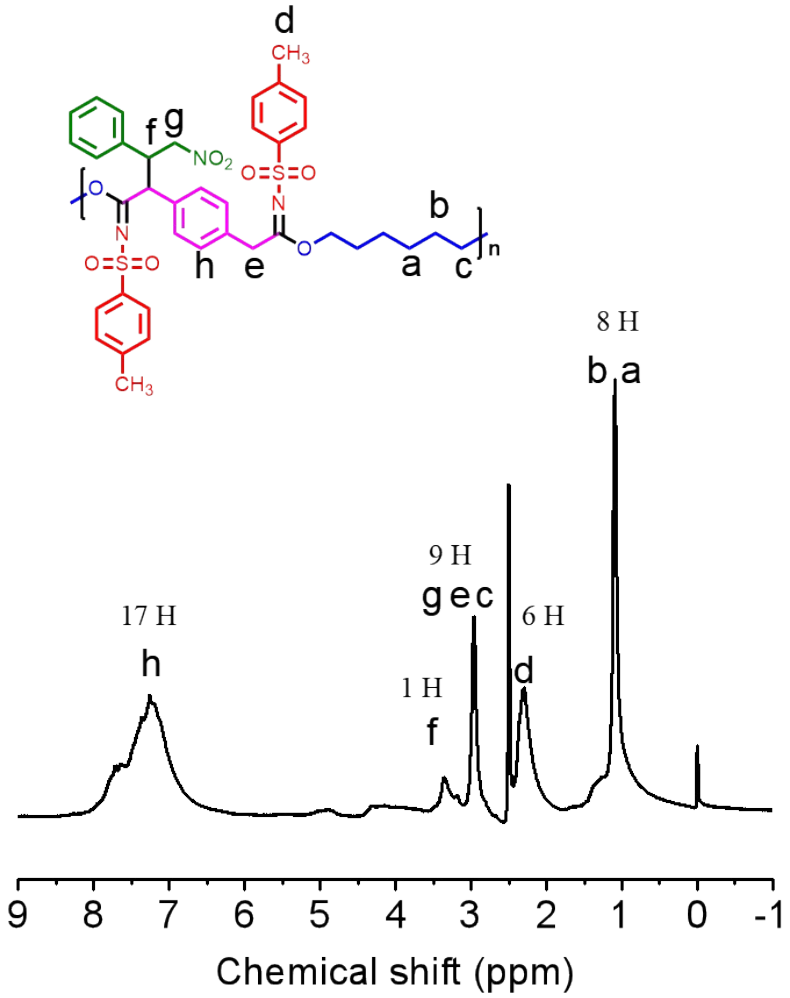



**Figure S13.** $^1$H NMR spectrum of P1a/2a/3a/4a in $d_6$-DMSO.

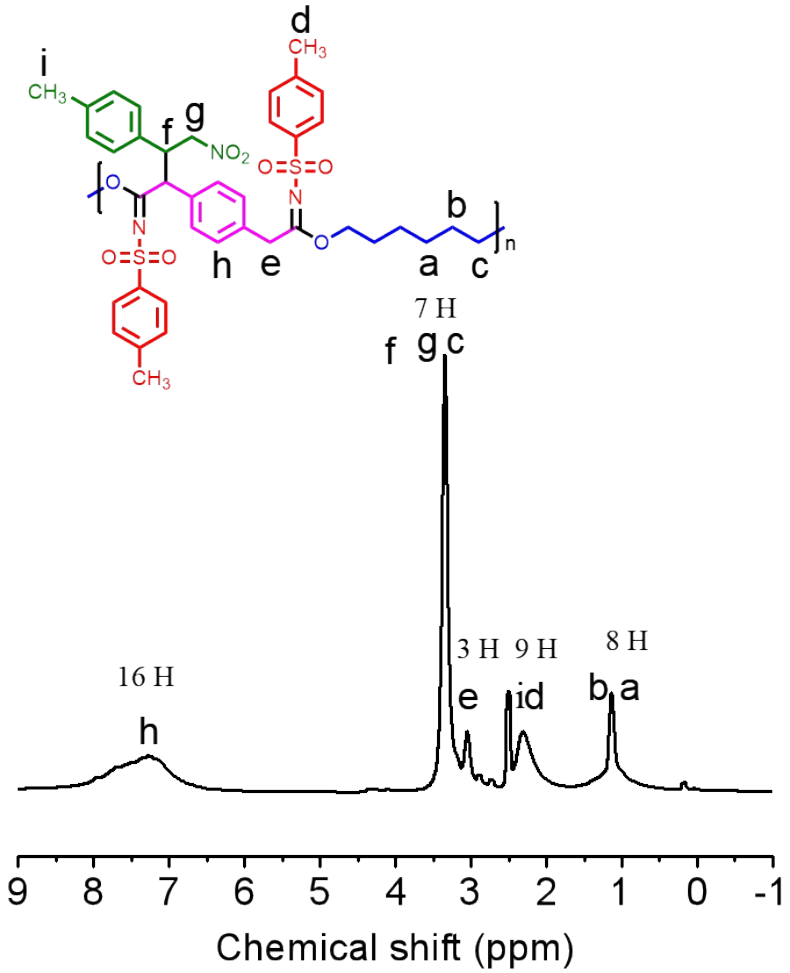



**Figure S14.** $^{1}$H NMR spectrum of P1a/2a/3a/4b in $d_6$-DMSO.

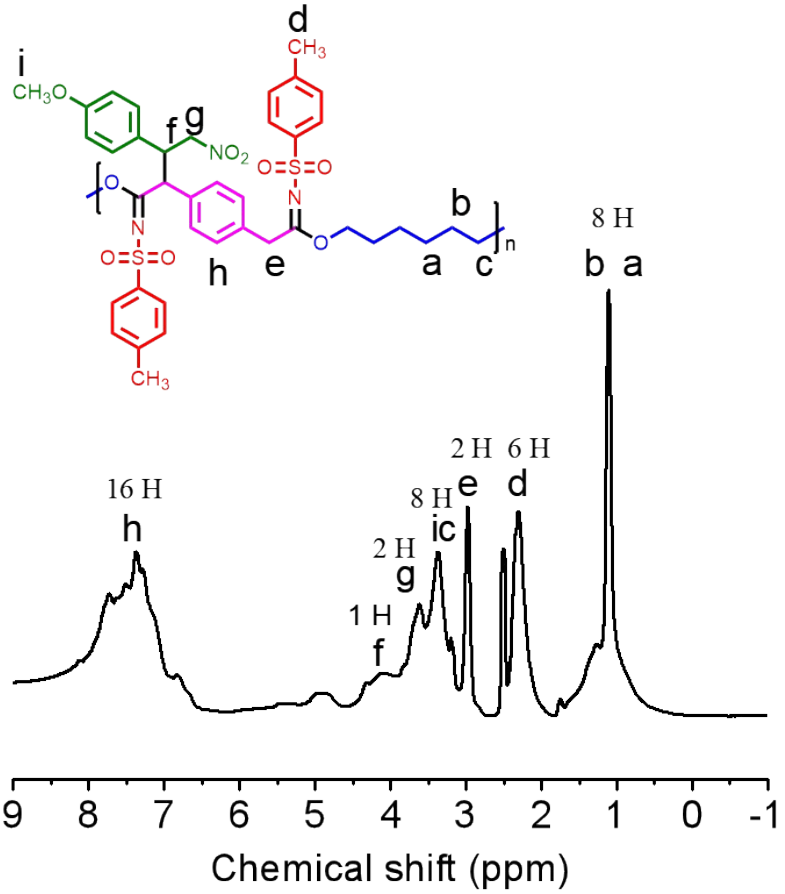



**Figure S15.** $^{1}$H NMR spectrum of P1a/2a/3a/4c in $d_6$-DMSO.

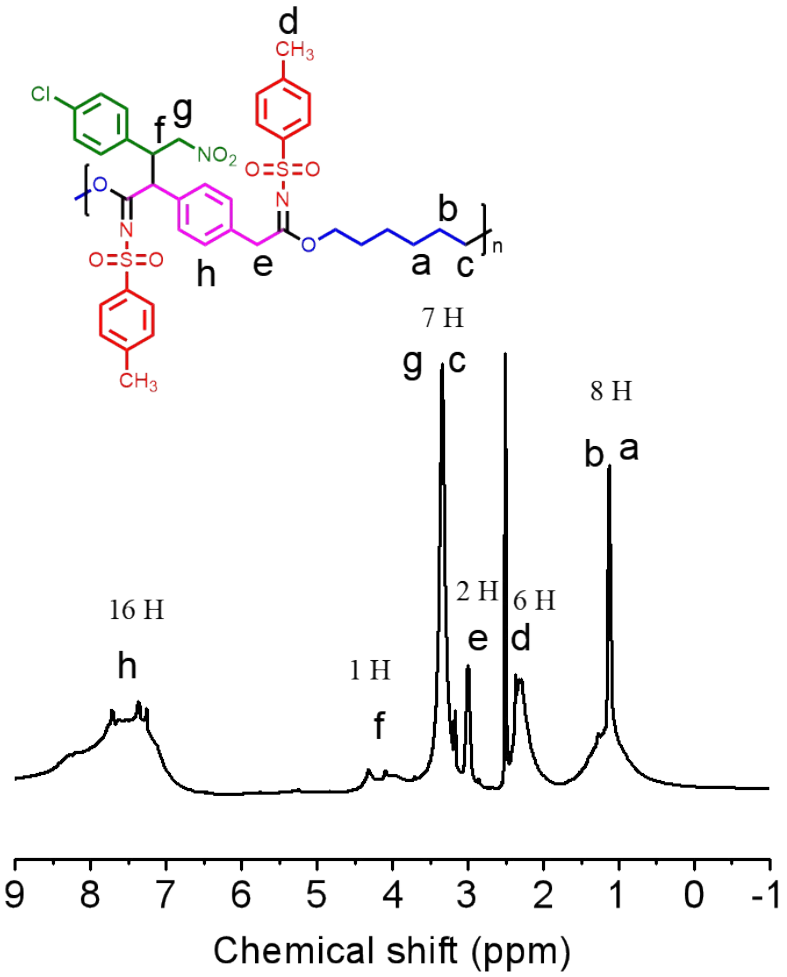



**Figure S16.** $^{1}$H NMR spectrum of P1a/2a/3a/4d in $d_6$-DMSO.

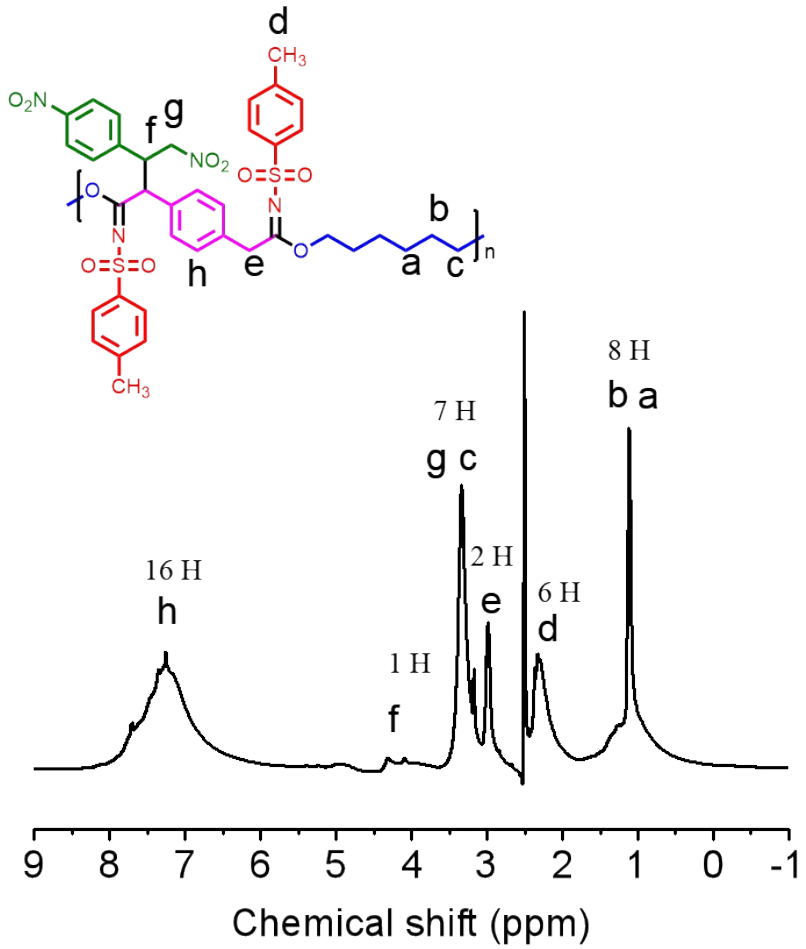



**Figure S17.** $^{1}$H NMR spectrum of P1a/2a/3a/4e in $d_6$-DMSO.

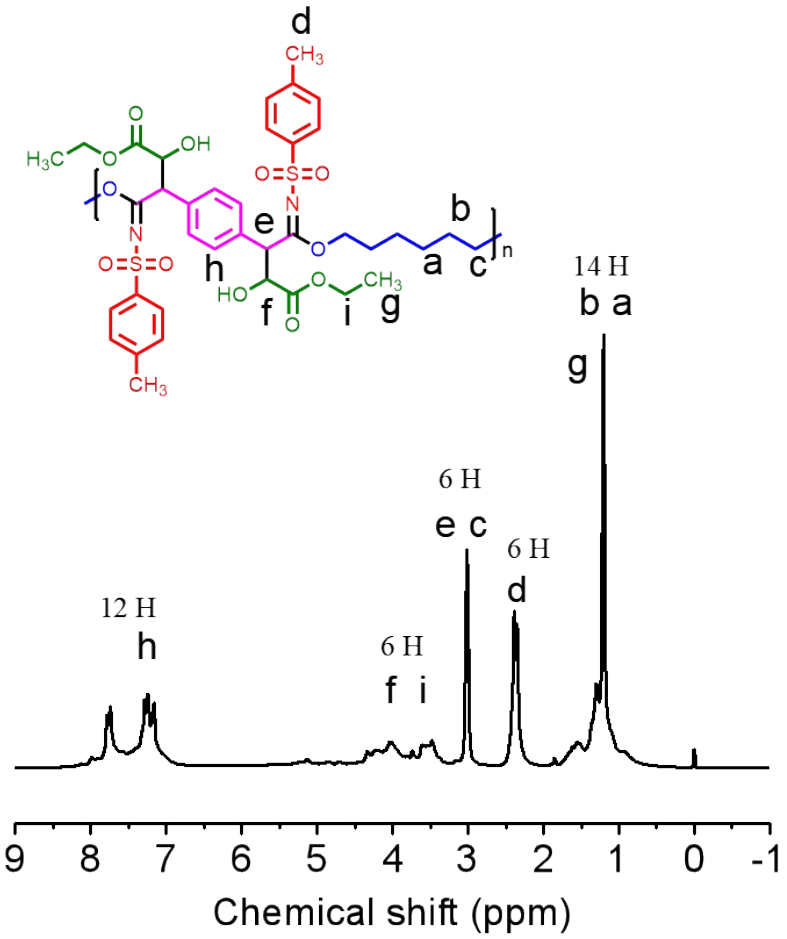



**Figure S18.** $^{1}H$ NMR spectrum of P1a/2a/3a/4f in $CDCl_3$.

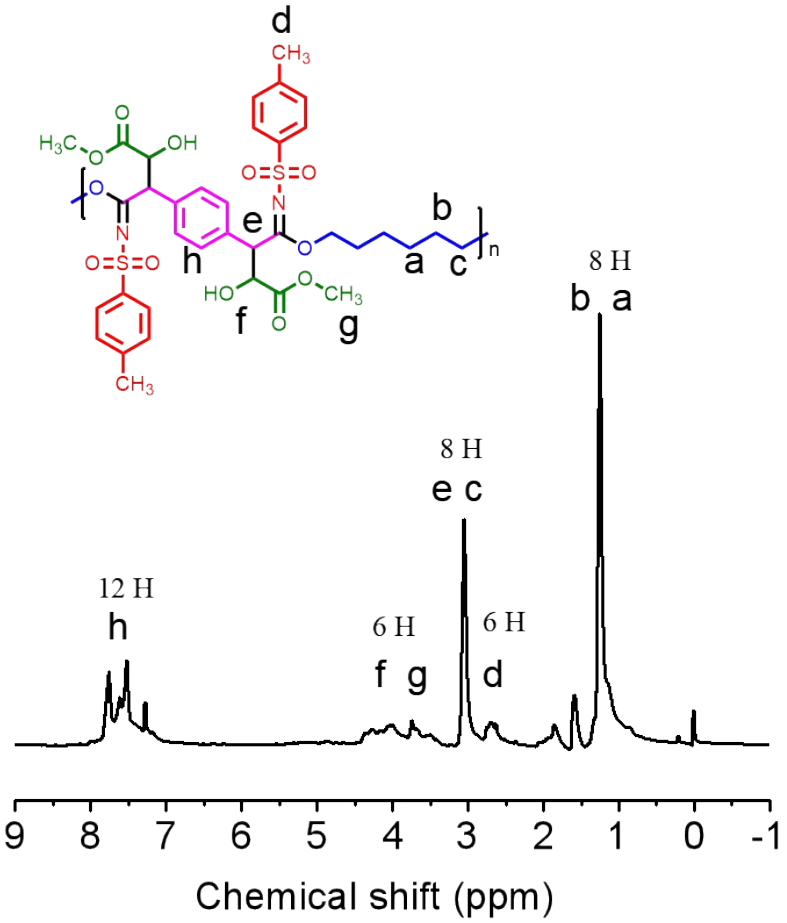



**Figure S19.** $^{1}H$ NMR spectrum of P1a/2a/3a/4g in $CDCl_3$.

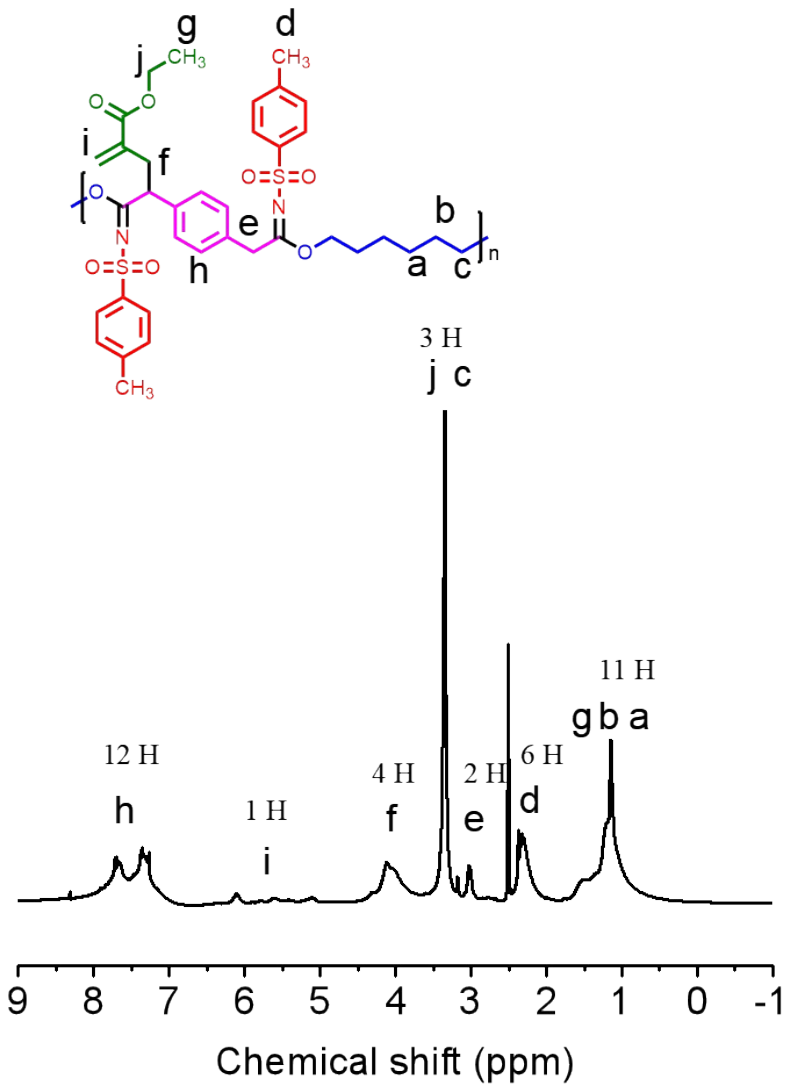



**Figure S20.** $^{1}$H NMR spectrum of P1a/2a/3a/4h in $d_6$-DSMO.

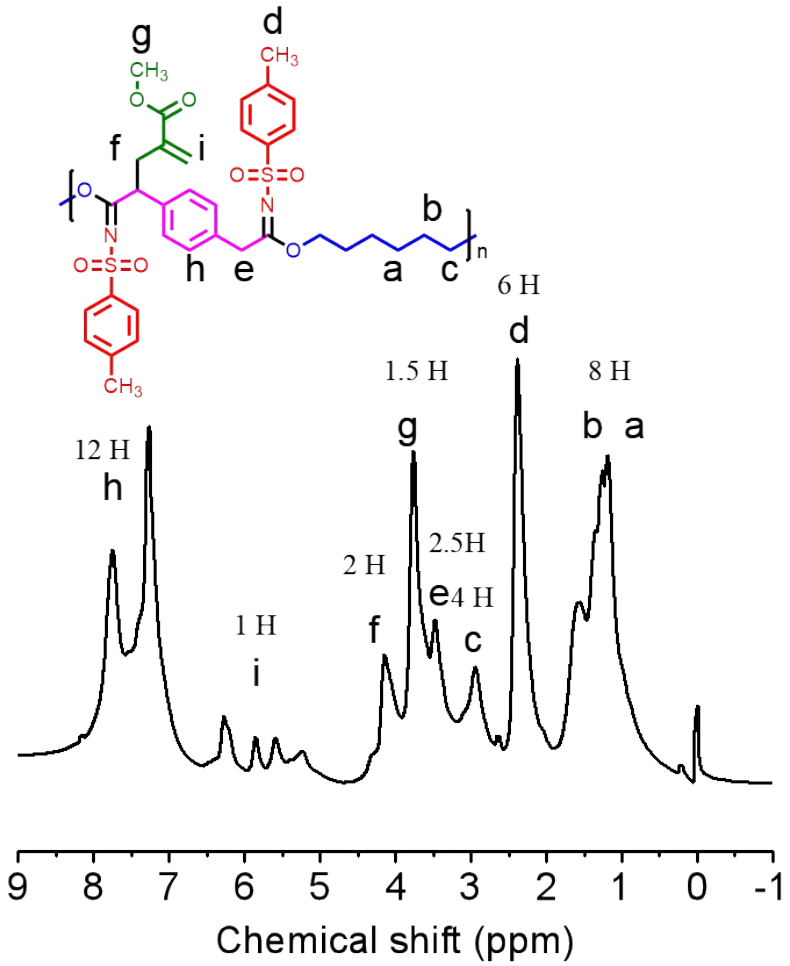



**Figure S21.** $^{1}$H NMR spectrum of P1a/2a/3a/4i in $d_6$-DSMO.

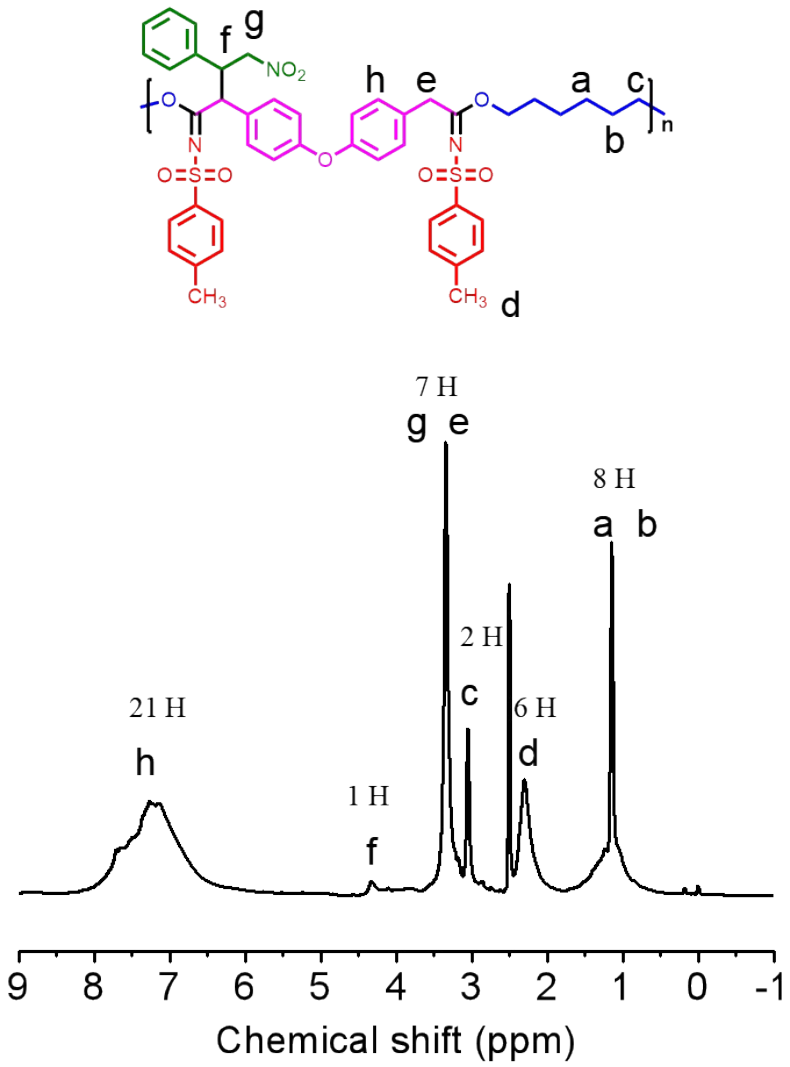



**Figure S22.** $^{1}$H NMR spectrum of P1b/2a/3a/4a in $d_6$-DSMO.

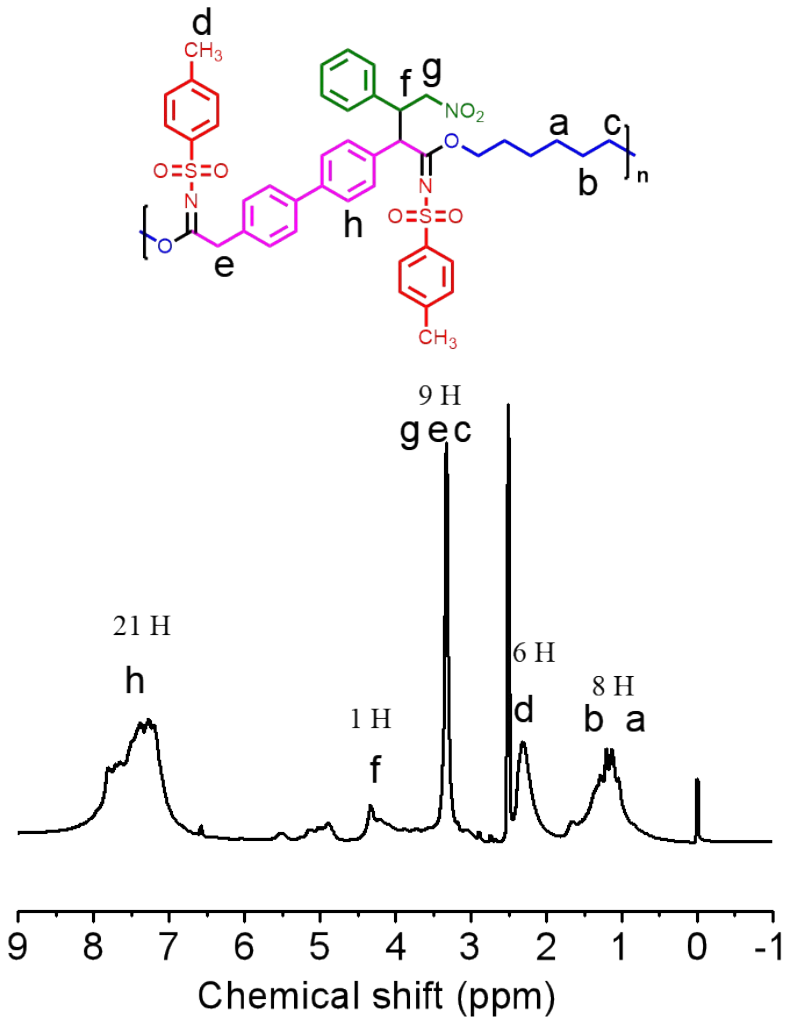



**Figure S23.** $^{1}$H NMR spectrum of P1c/2a/3a/4a in $d_6$-DSMO.

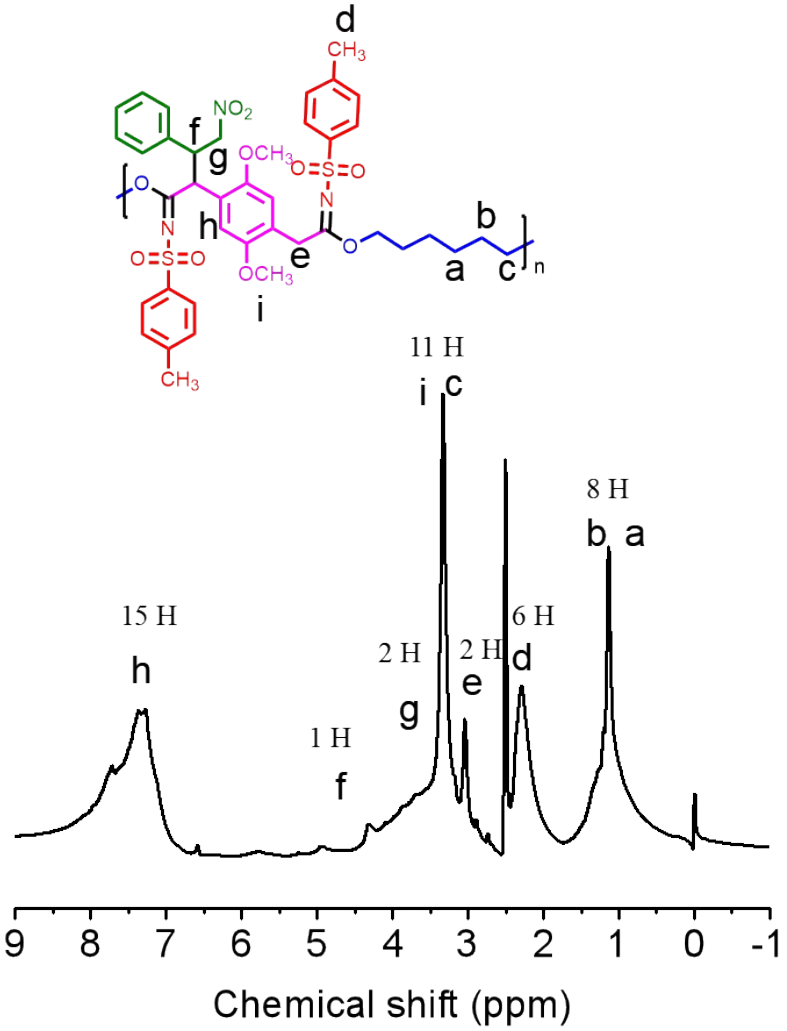



**Figure S24.** $^{1}$H NMR spectrum of P1d/2a/3a/4a in $d_6$-DSMO.

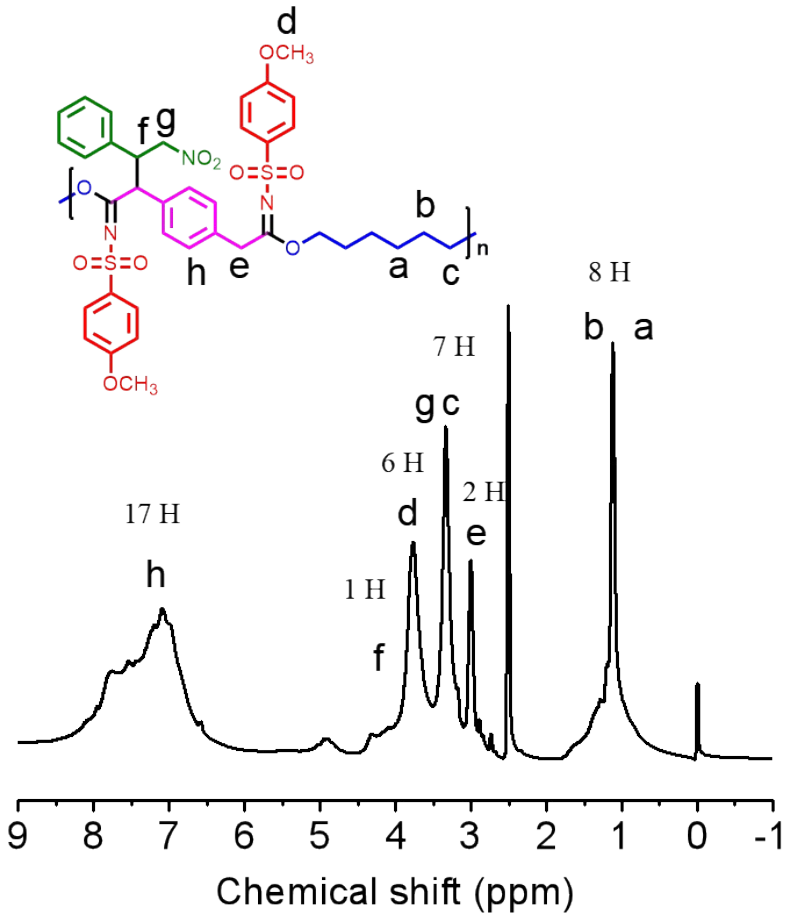



**Figure S25.** $^{1}$H NMR spectrum of P1a/2c/3a/4a in $d_6$-DSMO.

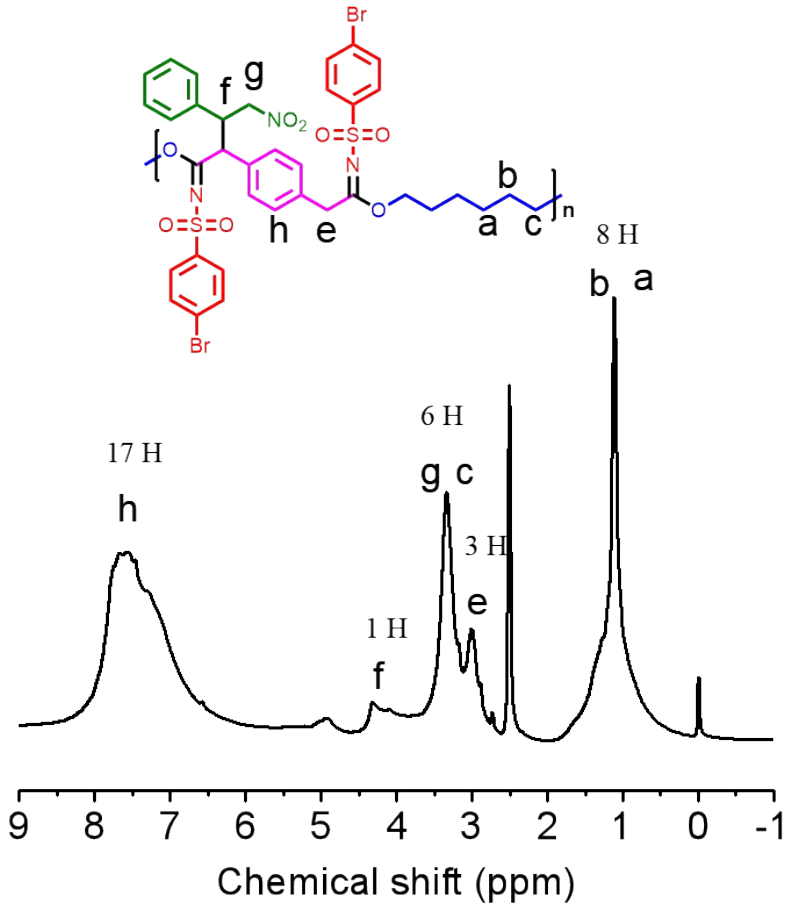



**Figure S26.** $^{1}$H NMR spectrum of P1a/2d/3a/4a in $d_6$-DSMO.

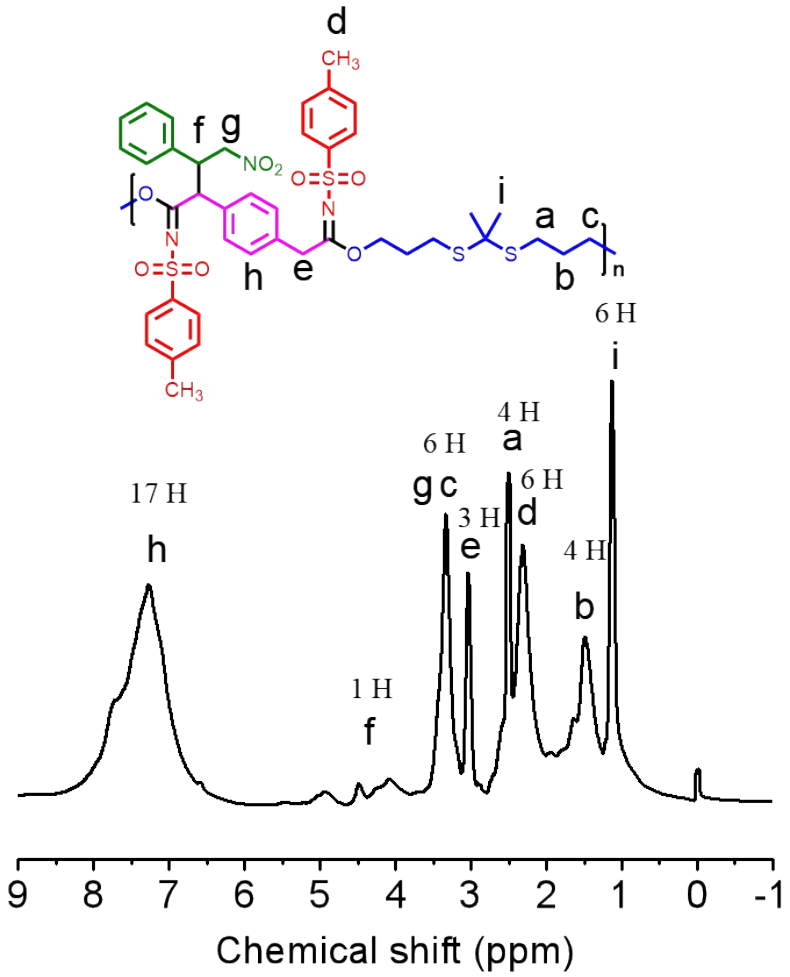



**Figure S27.** $^{1}$H NMR spectrum of P1a/2a/3b/4a in $d_6$-DSMO.

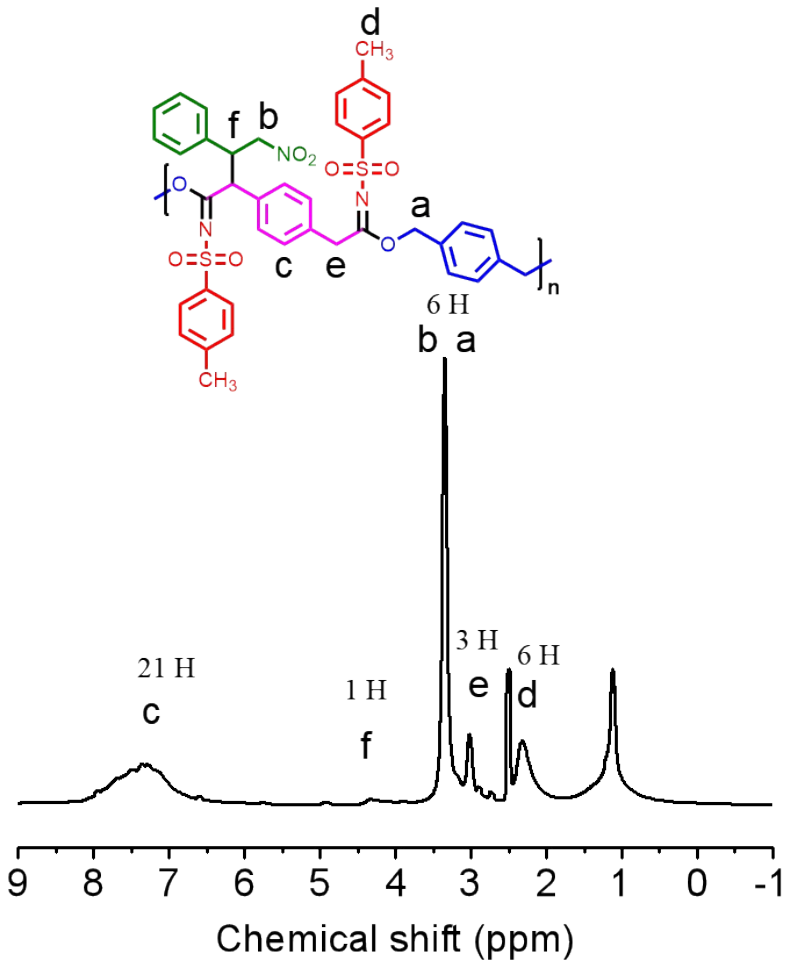



**Figure S28.** $^{1}$H NMR spectrum of P1a/2a/3c/4a in $d_6$-DSMO.

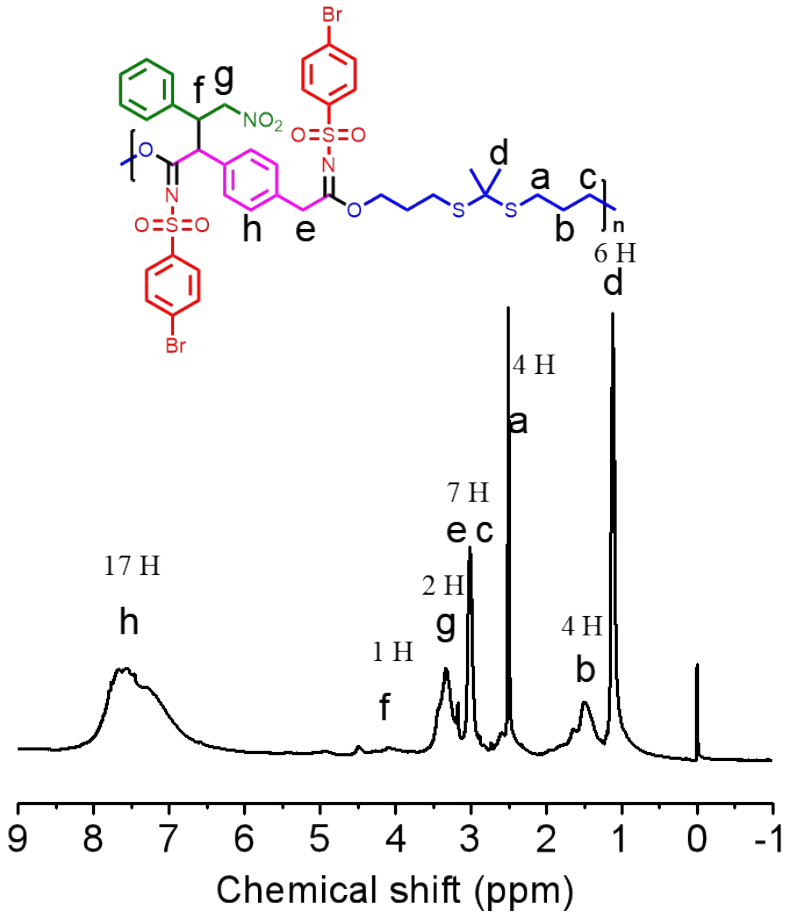



**Figure S29.** $^{1}$H NMR spectrum of P1a/2d/3b/4a in $d_6$-DSMO.

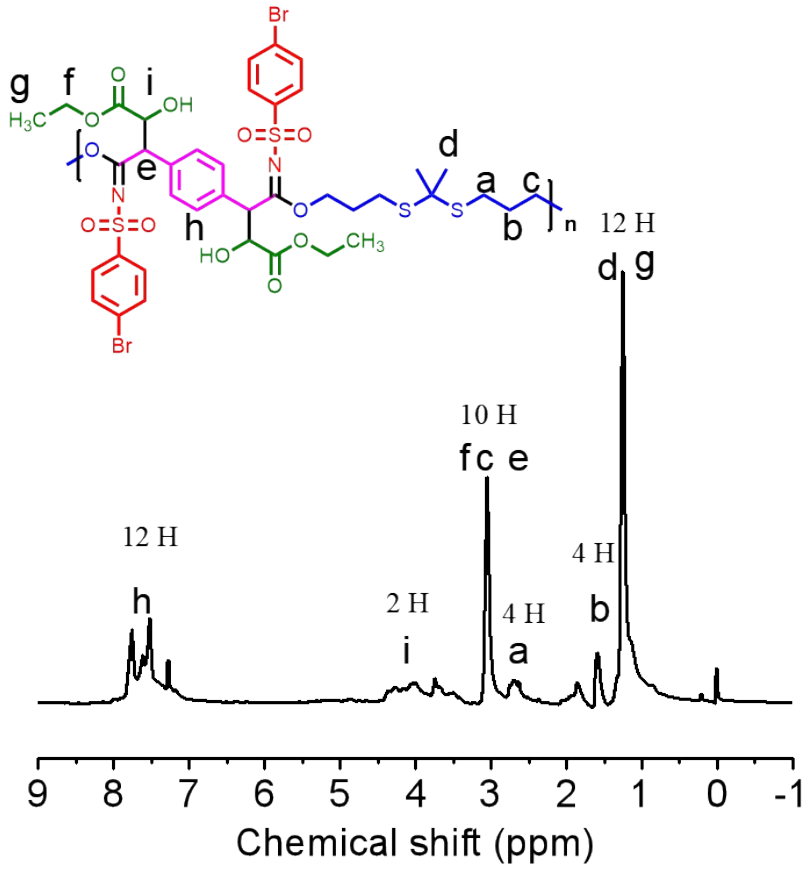



**Figure S30.** $^{1}H$ NMR spectrum of P1a/2d/3b/4f in $CDCl_3$.

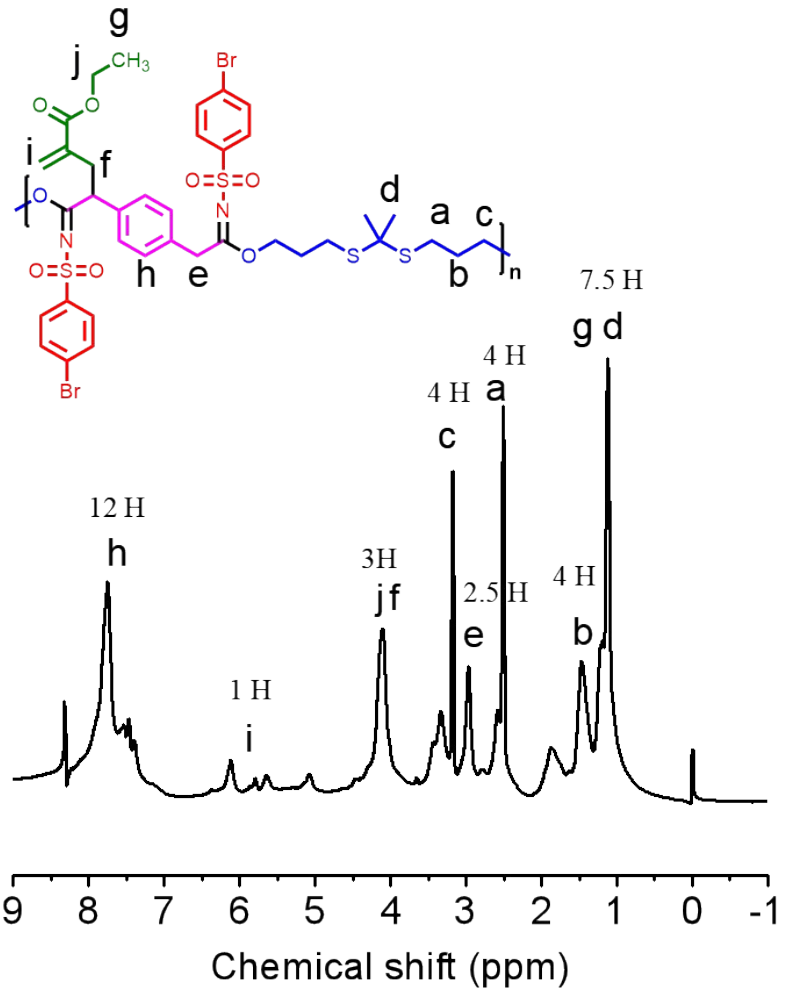



**Figure S31.** $^{1}$H NMR spectrum of P1a/2d/3b/4h in $d_6$-DSMO.

**5. Structural Characterization of P1a/2a/3a/4f**

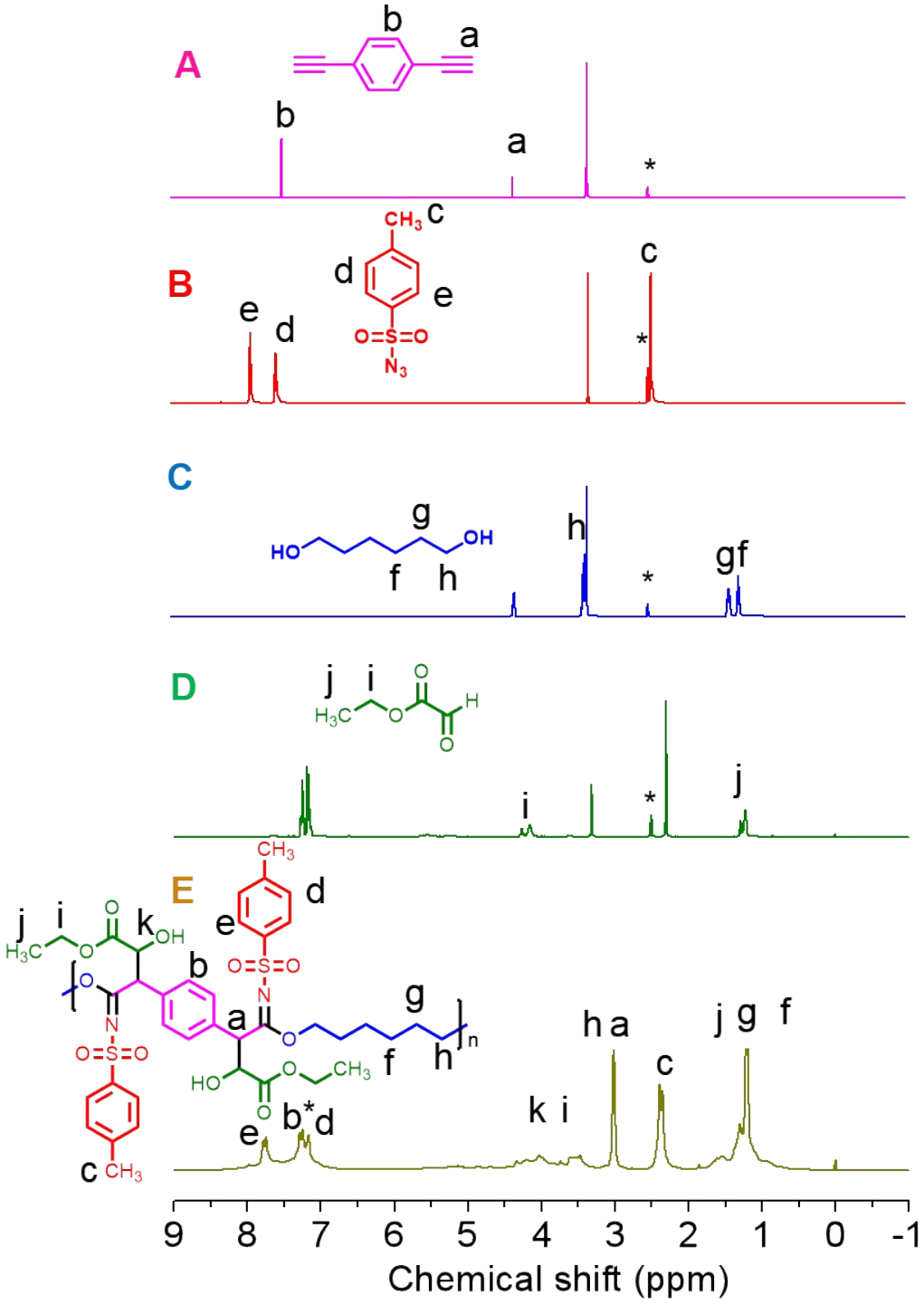



**Figure S32.** $^{1}$H NMR spectra of 1a, 2a, 3a, 4f and P1a/2a/3a/4f in $d_6$-DMSO or $CDCl_3$. The peaks of related solvents are marked with asterisks.

**6. Structural Characterization of P1a/2a/3a/4h**

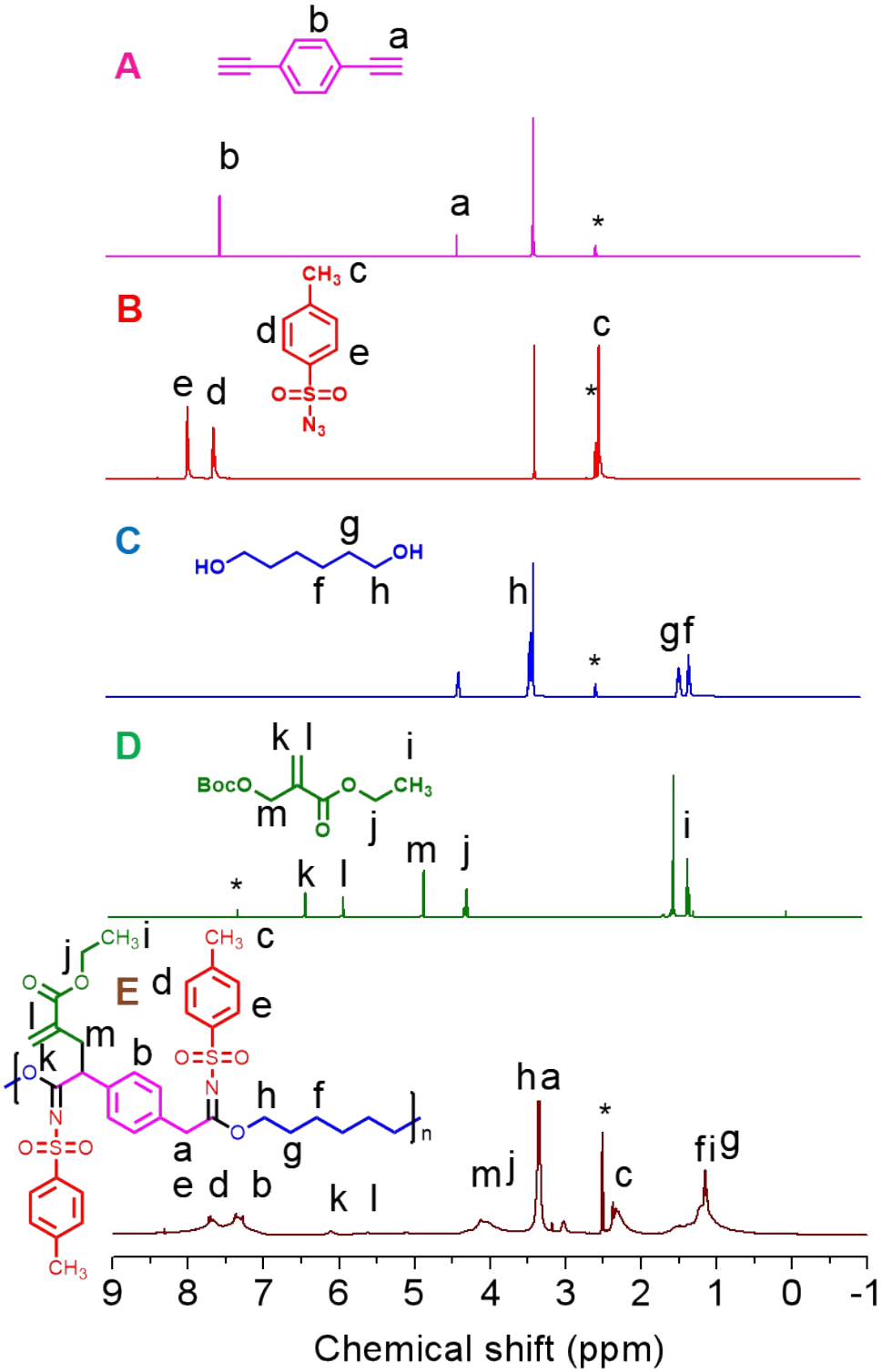



**Figure S33.** $^{1}$H NMR spectra of 1a, 2a, 3a, 4h and P1a/2a/3a/4h in $d_6$-DMSO or $CDCl_3$. The peaks of related solvents are marked with asterisks.

**7. TGA curves of polymers**

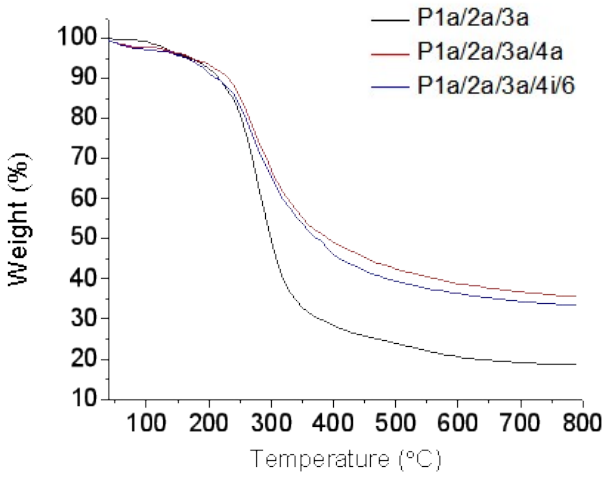



**Figure S34.** TGA curves of P1a/2a/3a, P1a/2a/3a/4a and P1a/2a/3a/4i/6.

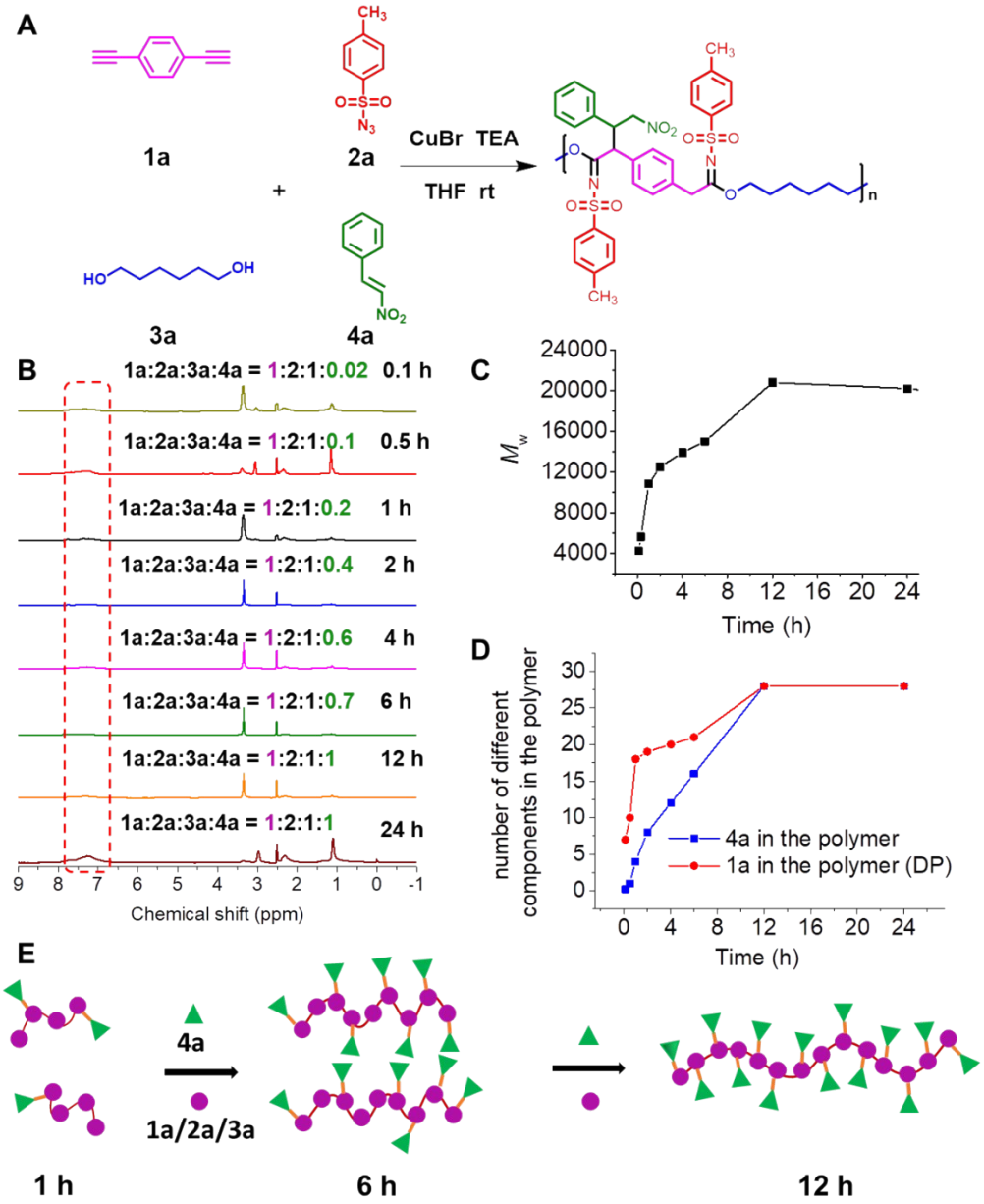



**Figure S35.** (A) The synthetic route of P1a/2a/3a/4a. (B) $^1$H-NMR spectra of P1a/2a/3a/4a at different time intervals (0.1 h, 0.5 h, 1 h, 2 h, 4 h, 6 h, 12 h, and 24 h) in $d_6$-DMSO . (C) The change of $M_w$ (P1a/2a/3a/4a) versus polymerization time. (D) The relative number change of 1a and 4a in the polymers versus polymerization time. (E) The process of polymerization together with functionalization indicated by cartoon.

**8. Structural Characterization of P1, P2, P3 and P4**

**Table S6.** One Pot Four-component Tandem Polyertizations of Different Monomers[a]

| Entry | Polymers | Monomers 4 | Yield (%) | $M_n$[b] | $M_w$[b] | $Đ$[b] |
|---|---|---|---|---|---|---|
| 1 | P1[c] | - | 71 | 4800 | 7200 | 1.5 |
| 2 | P2 | 4a | 63 | 11900 | 14800 | 1.24 |
| 3 | P3 | 4f | 85 | 8900 | 13800 | 1.55 |
| 4 | P4 | 4h | 69 | 15100 | 25100 | 1.67 |

[a] Conditions: experiments were carried out at room temperature in the glove box in DMF for 18 h. [1a] = [3a] = [4a] = 0.2 M, [2a] = 0.6 M, [4f] = [4h] = 0.6 M, [CuBr] = 0.04 M, [TEA] = 1.0 M. [b] $M_n$, $M_w$ and $Đ$ were determined by GPC in DMF with PMMA standards. [c] The polymer was synthesized at room temperature in DMF for 6 h.

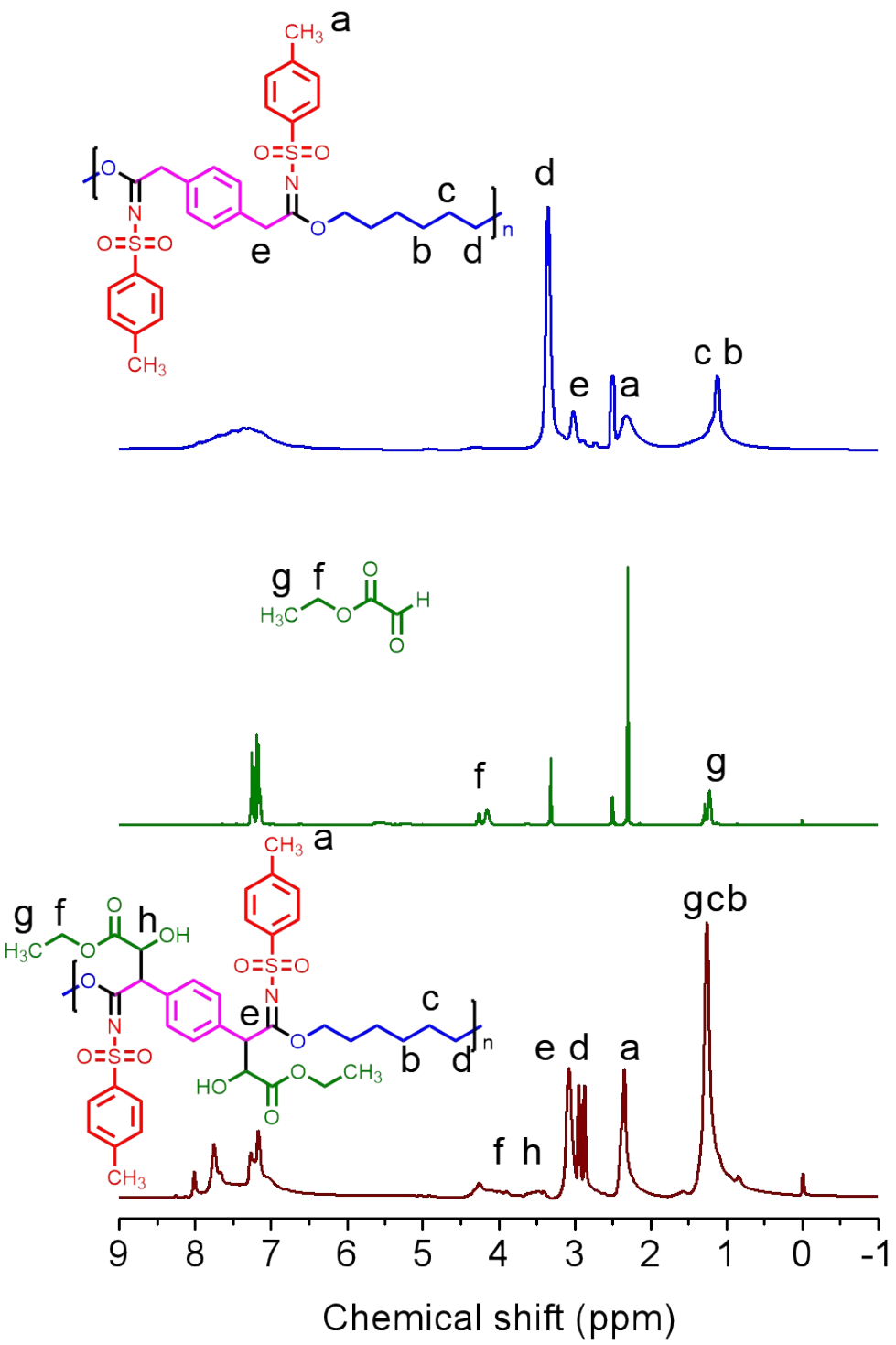



**Figure S36.** $^{1}$H NMR spectra of P1(A), 4f (B) and P3 (C) in $d_6$-DMSO.

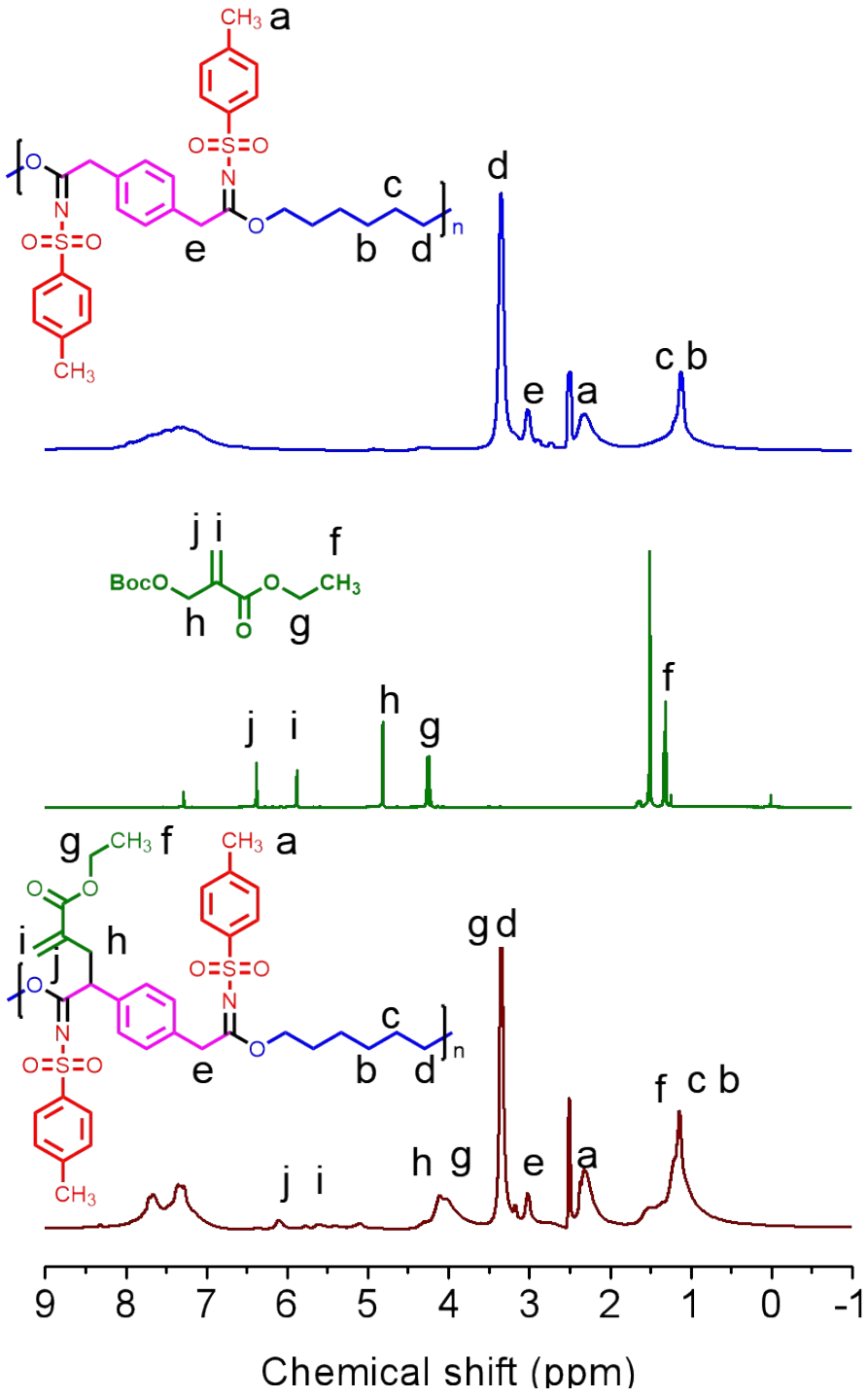



**Figure S37.** $^{1}$H NMR spectra of P1 (A), 4h (B) and P4 (C) in $d_6$-DMSO.

**9. $^1$H NMR Spectra of the Mixture of 3a and 4h**

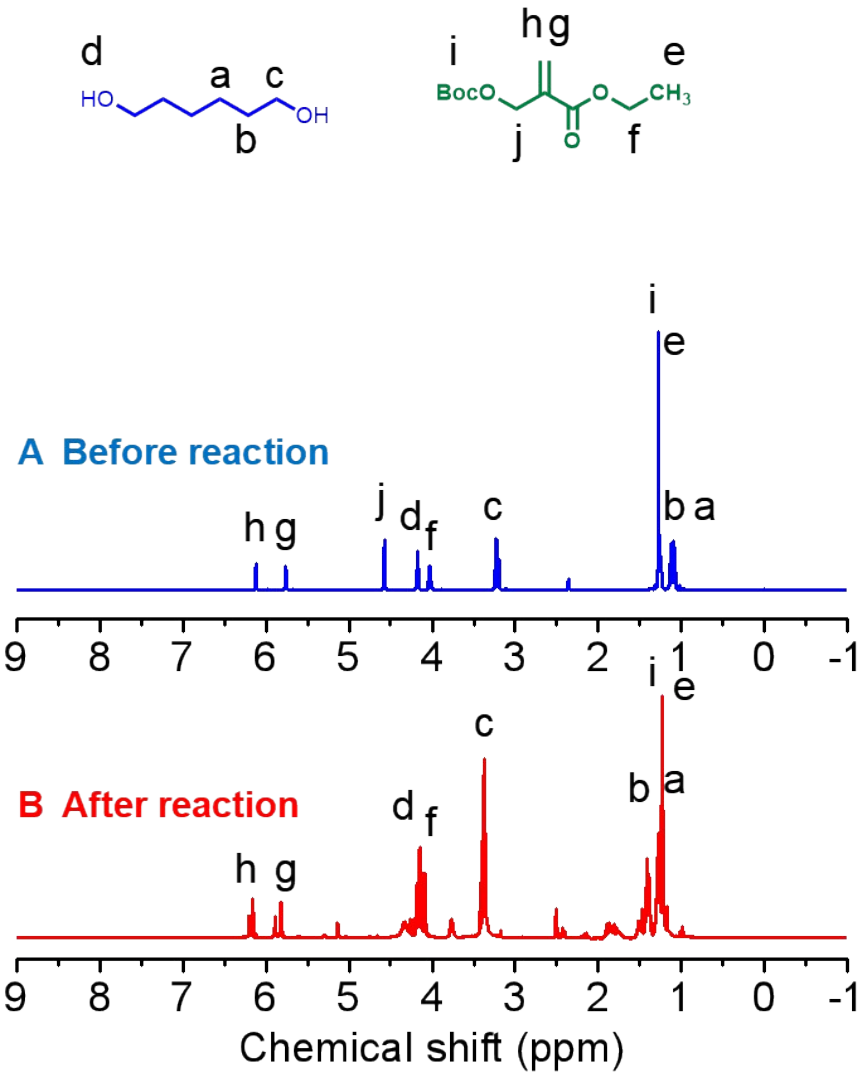



**Figure S38.** $^1$H NMR spectra of the mixture of 3a and 4h in $d_6$-DMSO before and after reaction.

**10. GPC curves of polymers**

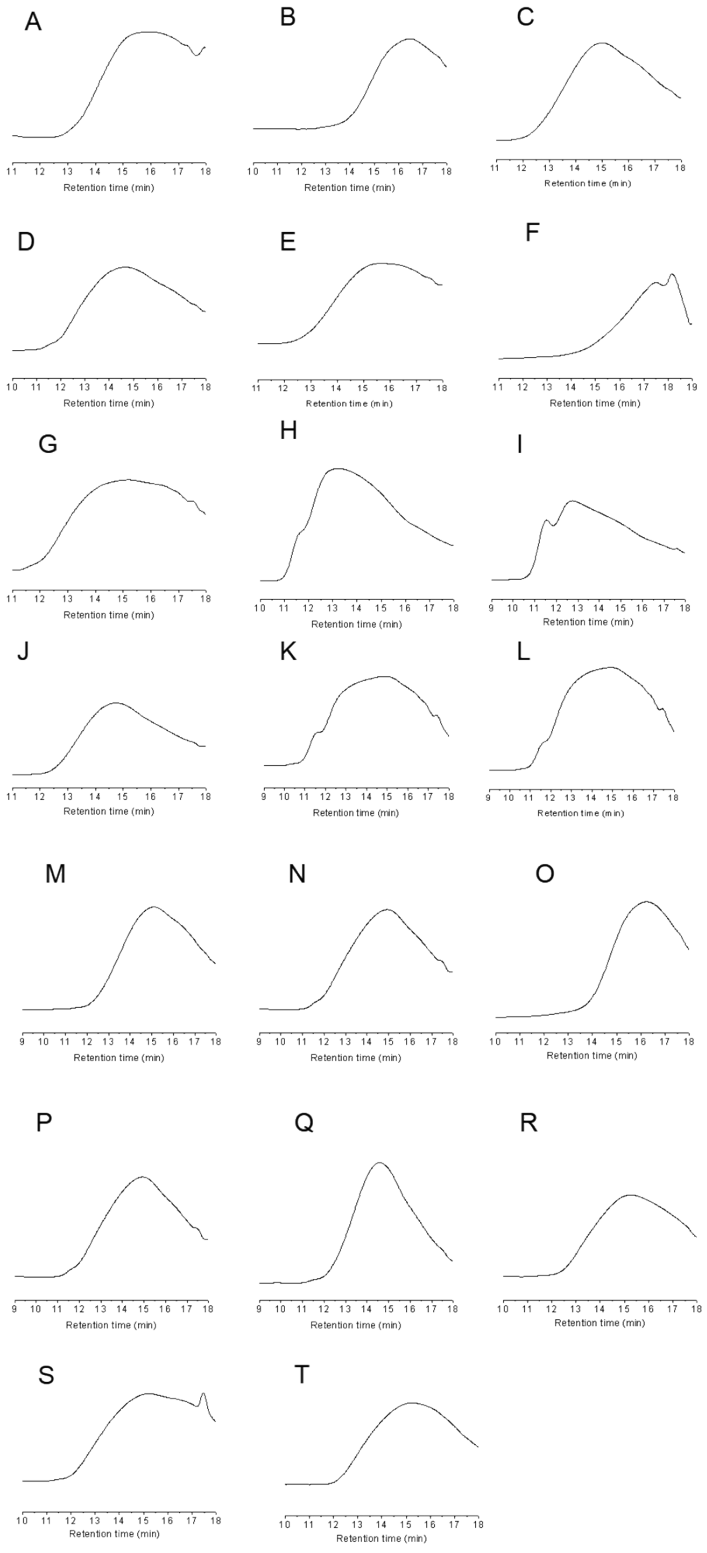



**Figure S39.** GPC curve of (A) P1a/2a/3a/4a, (B) P1a/2a/3a/4b, (C) P1a/2a/3a/4c, (D) P1a/2a/3a/4d, (E) P1a/2a/3a/4e, (F) P1a/2a/3a/4f, (G) P1a/2a/3a/4g, (H) P1a/2a/3a/4h, (I) P1a/2a/3a/4i, (J) P1b/2a/3a/4a, (K) P1c/2a/3a/4a, (L) P1d/2a/3a/4a, (M) P1a/2b/3a/4a, (N) P1a/2d/3a/4a, (O) P1a/2a/3b/4a, (P) P1a/2a/3c/4a, (Q) P1a/2d/3b/4a, (R) P1a/2d/3b/4f, (S) P1a/2d/3b/4h, (T) P1a/2d/3a/4b.

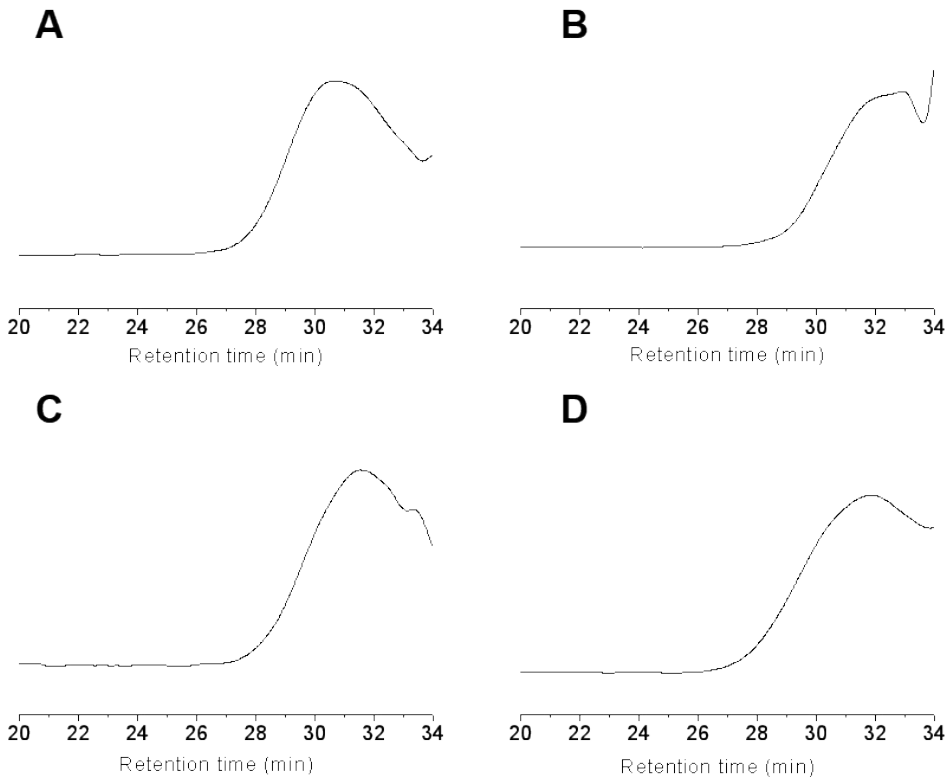



**Figure S40.** GPC curve of (A) P1a/2a/3a/4a, (B) P1a/2a/3a/4f, (C) P1a/2a/3a/4h, (D) P1c/2a/3a/4a (Absolute molecular weights were determined by DMF SEC using a MALLS detector).

**11. $^1$H NMR Spectrum of P1a/2a/3a/4i/5**

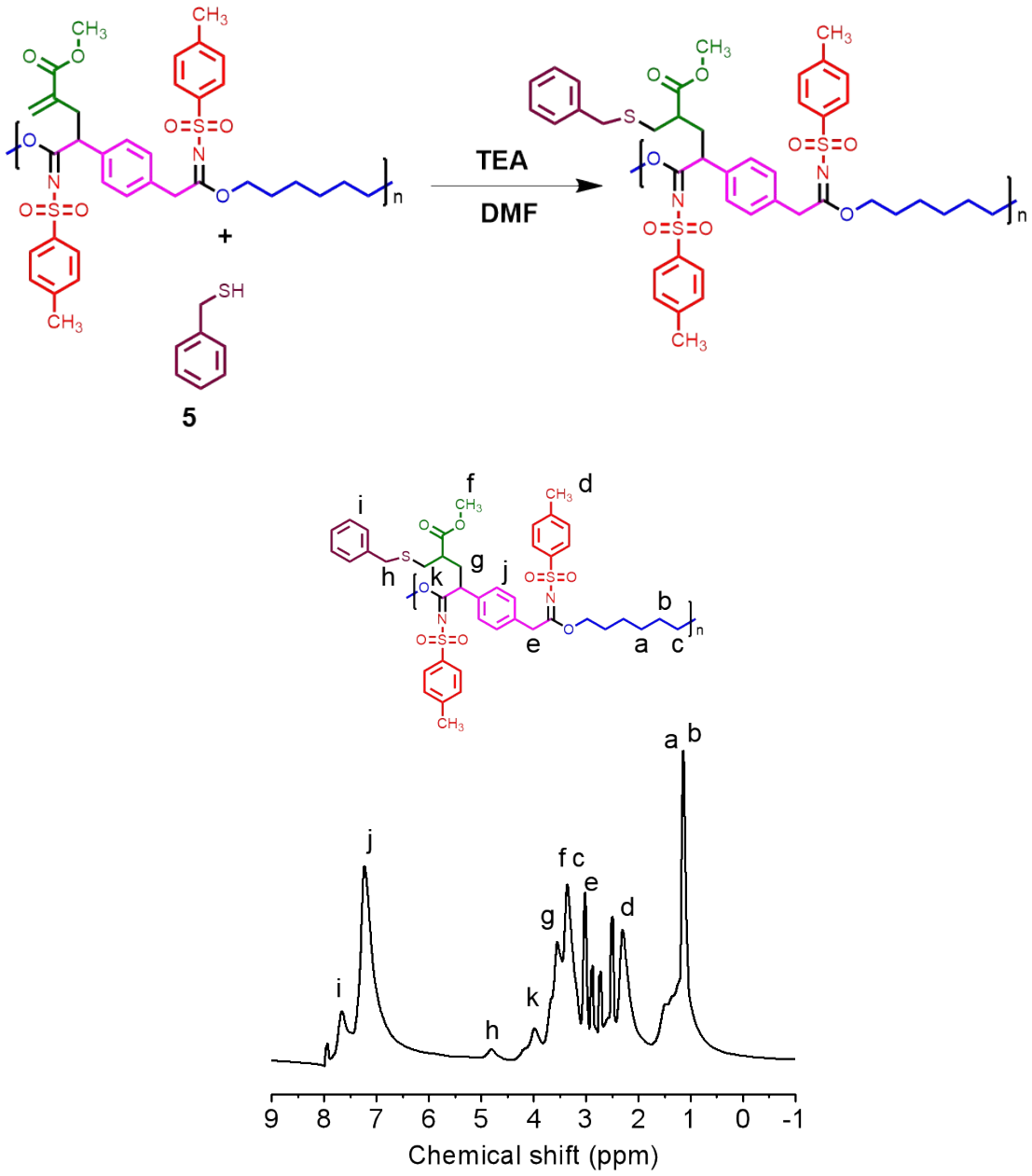



**Figure S41.** $^1$H NMR spectrum of P1a/2a/3a/4i/5 in $d_6$-DMSO.