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Supporting Information

Hybrid Copolymerization of Acrylate and Thiirane monomers mediated by Trithiocarbonate

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EXPERIMENT SECTION

Synthesis of 2-(phenoxymethyl) thiirane (POMT). To a suspension of 2-(phenoxymethyl) oxirane (9.0 g, 60 mmol, 1 eq) in distilled water (30 mL), potassium thiocyanate (23.2 g, 240 mmol, 4 eq) was added and stirred for 24 h at 40 ℃. Afterwards, the organic phase was separated and the aqueous phase was extracted with diethyl ether (3 × 30 mL). The combined organic phases were dried over anhydrous sodium sulfate, further purification can be achieved by silica gel column chromatography using hexane/ethyl acetate (v/v = 9/1) to obtain the colorless viscous oil. Yield was 80%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.28 (dt, *J* = 9.0, 7.3 Hz, 2H), 6.97 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.94 – 6.87 (m, 2H), 4.22 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.90 (dd, *J* = 10.2, 7.1 Hz, 1H), 3.27 (dq, *J* = 6.9, 5.5 Hz, 1H), 2.61 (dt, *J* = 6.3, 1.1 Hz, 1H), 2.33 (dd, *J* = 5.3, 1.4 Hz, 1H).

Synthesis of 2-(butoxymethyl) thiirane (BOMT). To a solution of 2-(butoxymethyl)oxirane (32.5 g, 250 mmol, 1 eq) in distilled water (150 mL), potassium thiocyanate (72.75 g, 750 mmol, 3 eq) was added and stirred for 24 h at 40 °C. Subsequently, the organic phase was separated and dried over anhydrous sodium sulfate. The product 2-(butoxymethyl) thiirane as colorless viscous oil was obtained by reduced pressure distillation at around 100 °C. Yield was 70%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.64 (ddd, *J* = 10.7, 5.6, 1.3 Hz, 1H), 3.50 (td, *J* = 6.7, 1.4 Hz, 2H), 3.42 (ddd, *J* = 10.8, 6.8, 1.4 Hz, 1H), 3.08 (t, *J* = 6.1 Hz, 1H), 2.53 (d, *J* = 6.2 Hz, 1H), 2.22 (d, *J* = 5.4 Hz, 1H), 1.66 – 1.51 (m, 2H), 1.47 – 1.29 (m, 2H), 0.93 (td, *J* = 7.4, 1.4 Hz, 3H).

Synthesis of 2-((allyloxy)methyl)thiirane (AOMT). To a solution of allyl glycidyl ether (5.0 g, 43.9 mmol, 1 eq) in distilled water (30 mL), potassium thiocyanate (12.8 g, 131.6 mmol, 3 eq) was added and stirred for 24 h at 40 °C. Subsequently, the organic phase was separated and the aqueous phase was extracted with diethyl ether (2 × 30 mL). The combined organic phases were dried over anhydrous sodium sulfate, further purification can be achieved by silica gel column chromatography using hexane/ethyl acetate (v/v = 9/1) to obtain the colorless viscous oil. Yield was 84%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.99 – 5.72 (m, 1H), 5.37 – 5.03 (m, 2H), 3.99 (dd, *J* = 5.7, 1.4 Hz, 2H), 3.58 (dd, *J* = 10.6, 5.7 Hz, 1H), 3.48 – 3.30 (m, 1H), 3.02 (p, *J* = 6.0 Hz, 1H), 2.47 (d, *J* = 6.2 Hz, 1H), 2.16 (dd, *J* = 5.4, 1.3 Hz, 1H).

Synthesis of 2-methyl thiirane (MT). To a solution of 2-methyloxirane (29 g, 500 mmol, 1 eq) in distilled water (150 mL), potassium thiocyanate (194 g, 2 mol, 4 eq) was added and stirred at room temperature for 24 h. Afterwards, the organic phase was separated and dried over anhydrous sodium sulfate. The product 2-methyl thiirane as colorless liquid was obtained by distillation at about 95 °C. Yield was 75%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.93 (q, *J* = 5.9 Hz, 1H), 2.51 (dd, *J* = 6.3, 1.2 Hz, 1H), 2.20 – 2.04 (m, 1H), 1.55 – 1.47 (m, 3H).

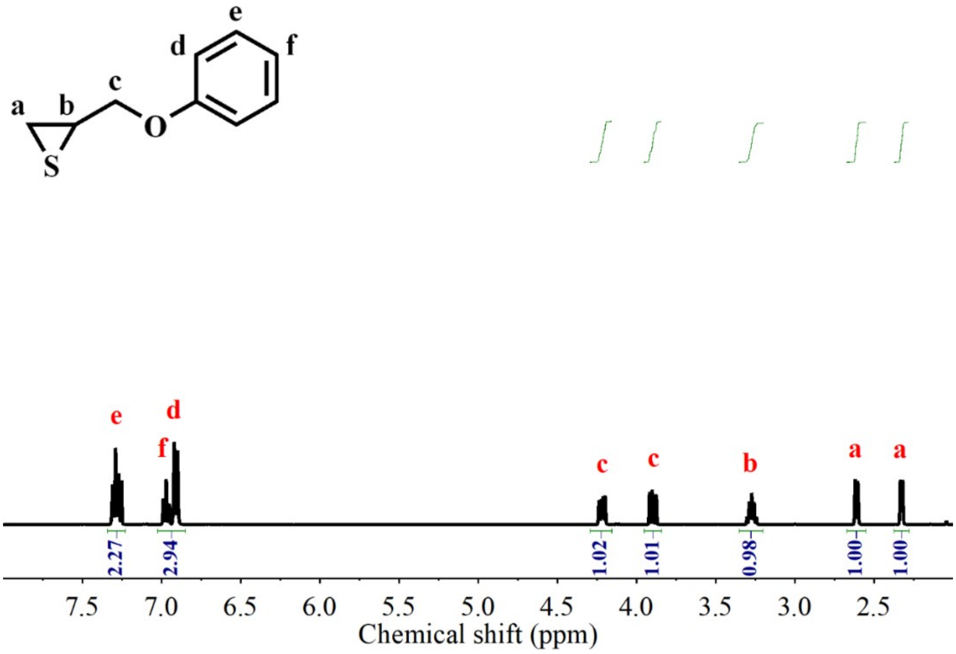


Figure S1. ^{1}H NMR spectrum of 2-(phenoxymethyl) thiirane (POMT).

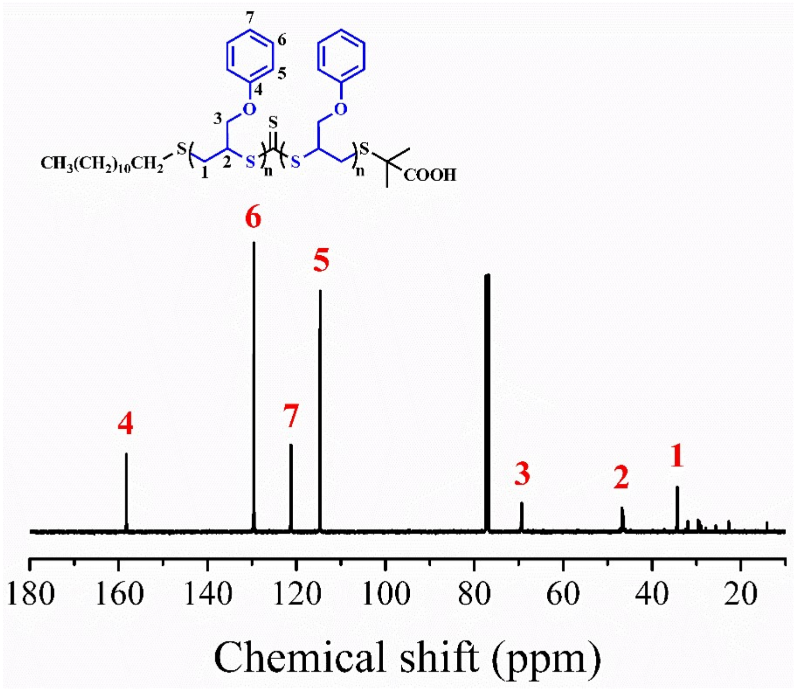
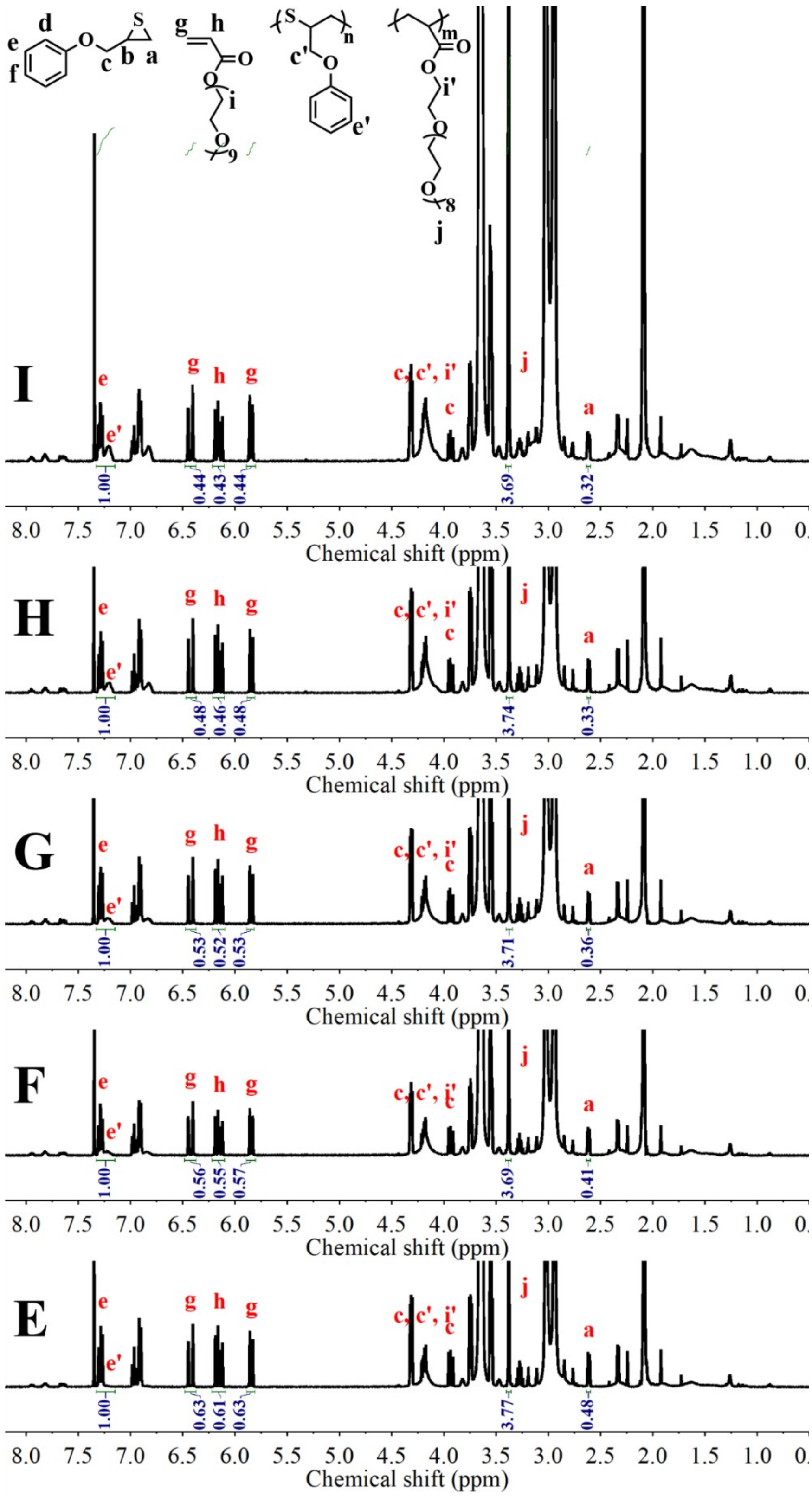


Figure S2. ^{13}C NMR spectrum of PPOMT$_{20}$.



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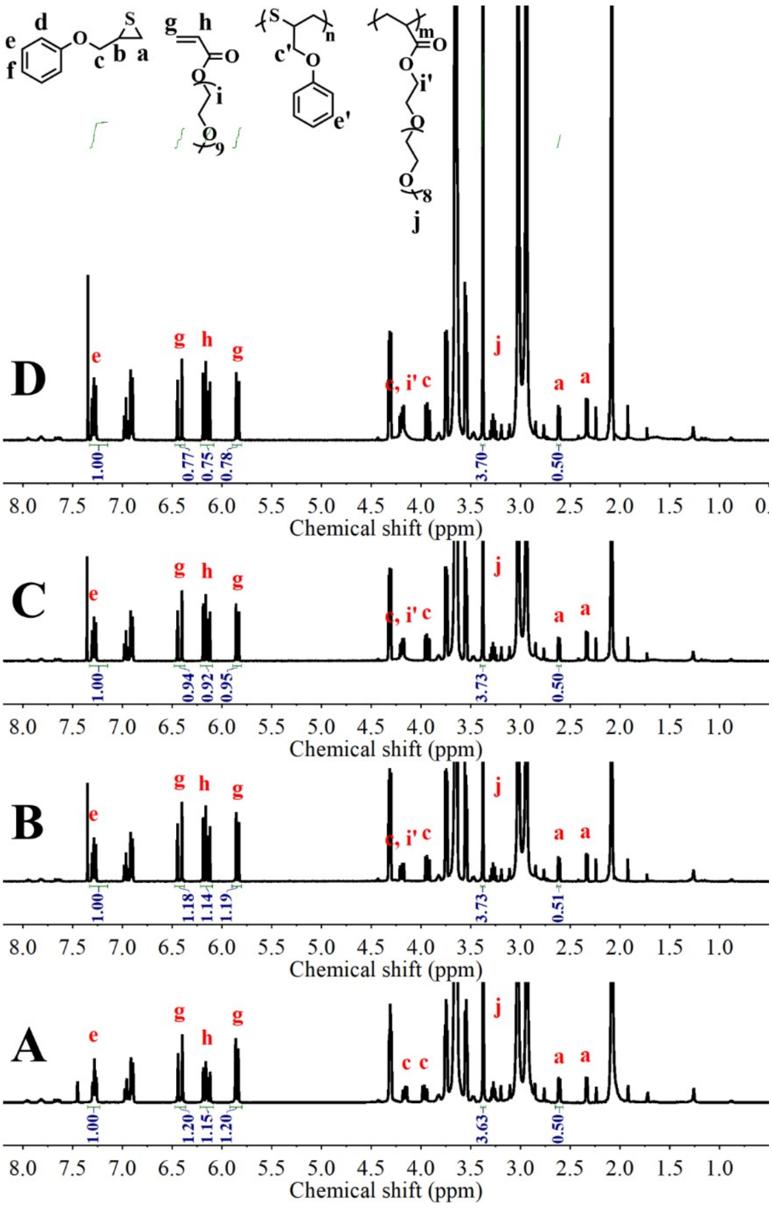

Figure S3. ^{1}H NMR spectra of the reaction mixture after polymerization of (A) 0 h, (B) 0.5 h, (C) 1 h, (D) 1.5 h, (E) 2.5 h, (F) 3.5 h, (G) 4 h, (H) 4.5 h and (I) 5 h. A portion (50 μL) of reaction mixture was taken out and dissolved into CDCl$_3$ for ^{1}H NMR analysis to calculate the monomer conversion at scheduled time interval.

The conversion of POMT and OEGA were calculated according to the following equations:

$$\text{Conversion (\%)}_{\text{POMT}} = \left(1 - \frac{2a_t}{e + e'}\right) \times 100\%$$

$$\text{Conversion (\%)}_{\text{OEGA}} = \left(1 - \frac{g_t + h_t + g_t}{j}\right) \times 100\%$$

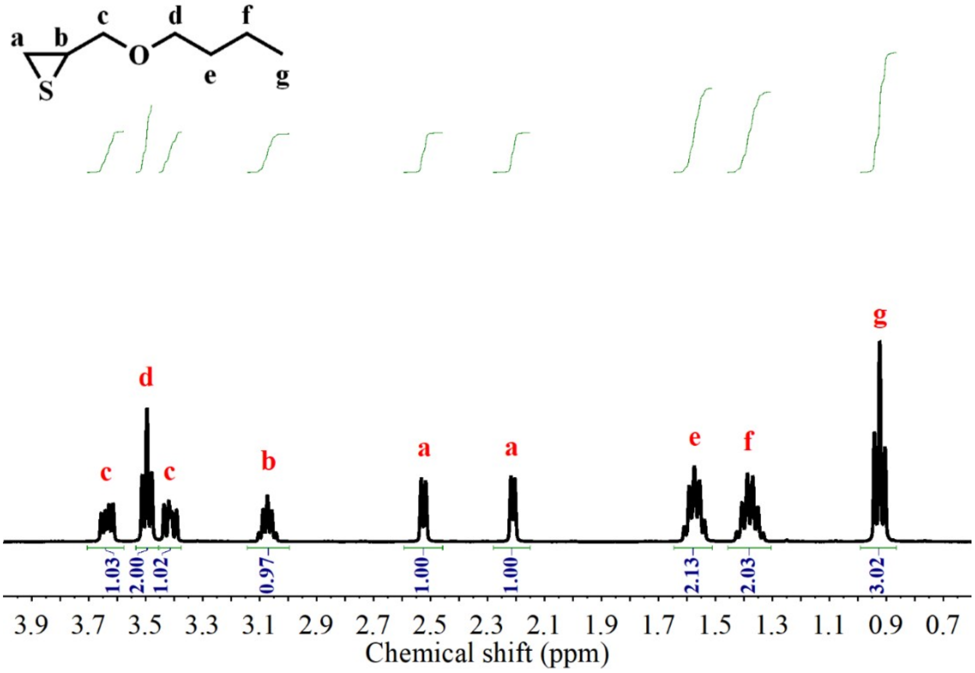

Figure S4. ^{1}H NMR spectrum of 2-(butoxymethyl) thiirane (BOMT).

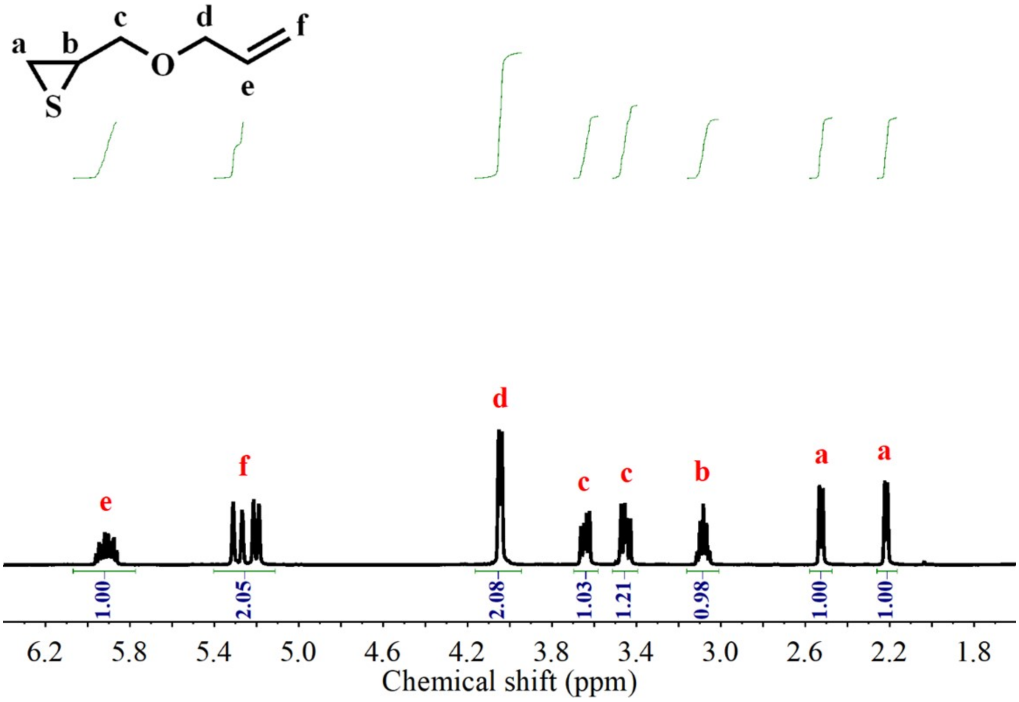

Figure S5. ^{1}H NMR spectrum of 2-((allyloxy)methyl) thiirane (AOMT).

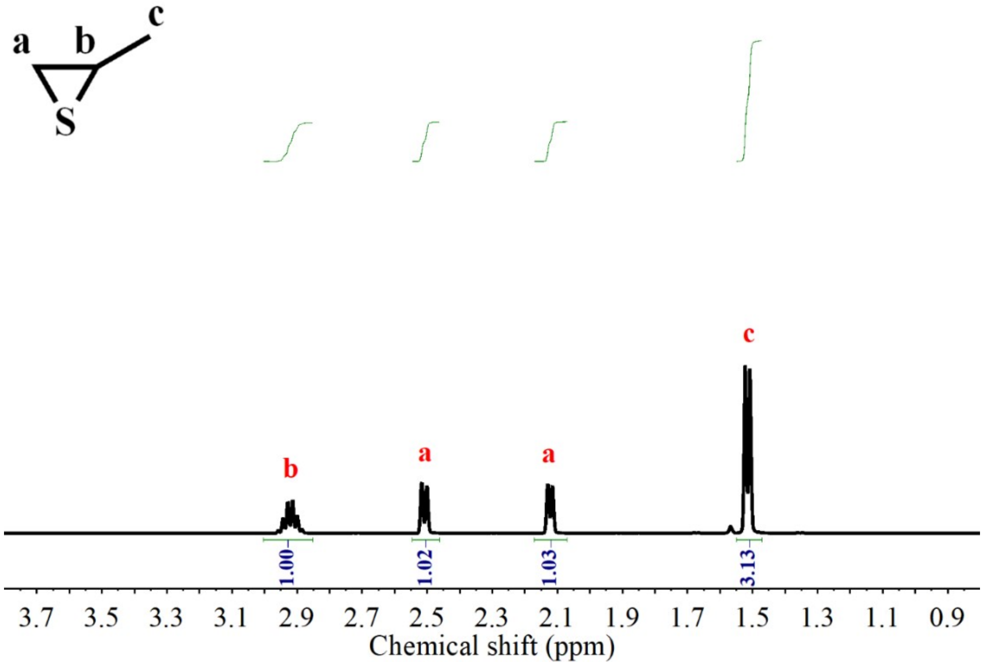

Figure S6. ^1H NMR spectrum of 2-methyl thiirane (MT).

Table S1. Anionic ring-opening polymerization of thiirane

Entry[a]	**Thiiranes**	**$[DTMPA]_0/[TPPCl]_0/[thiiranes]_0$**	**Conversion(%)**[b]	**M_n (g/mol)**[c]	**M_w/M_n**[c]
1	BOMT	5:1:500	100	8300	1.47
2	AOMT	1:3:100	98	13200	1.52
3	MT	5:1:500	95	9600	1.59

[a]AROP of thiirane was performed at 65 °C for 24 h in DMAc. [b]The monomer conversion was determined by ^1H NMR spectrum. [c]The molecular weight (M_n) and M_w/M_n were determined by GPC.

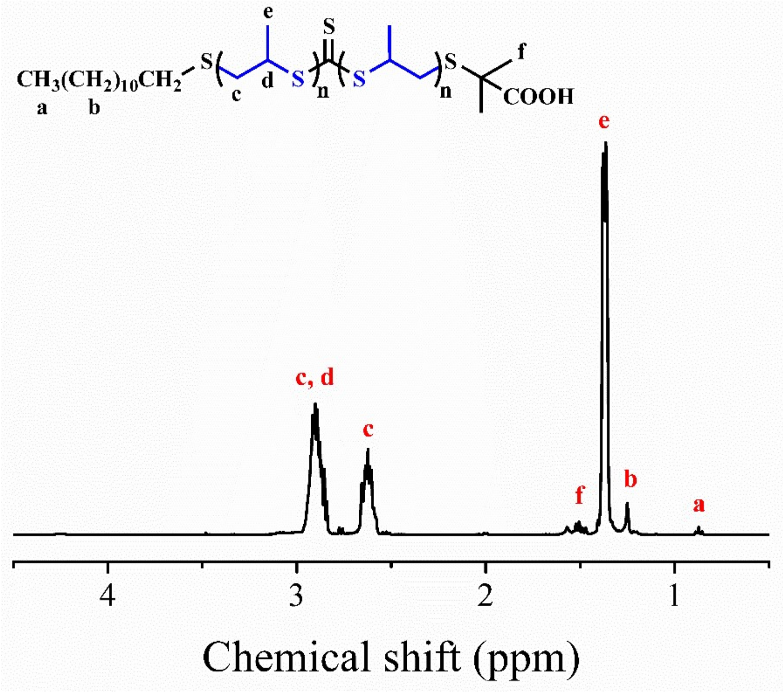

Figure S7. ^{1}H NMR spectrum of poly(2-methyl thiirane) (PMT).

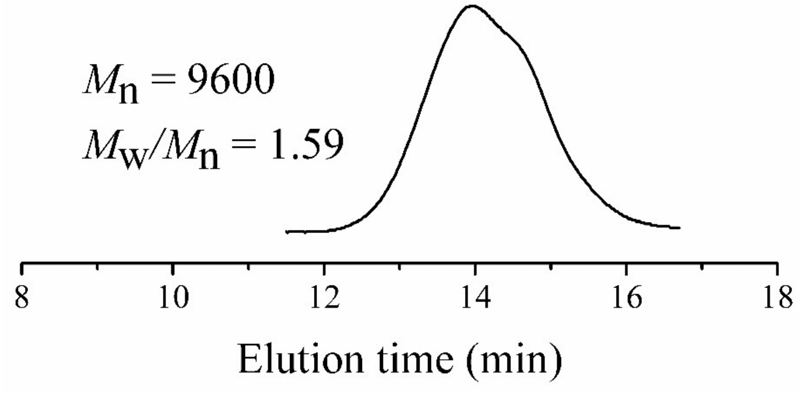

Figure S8. GPC curve of poly(2-methyl thiirane) (PMT).

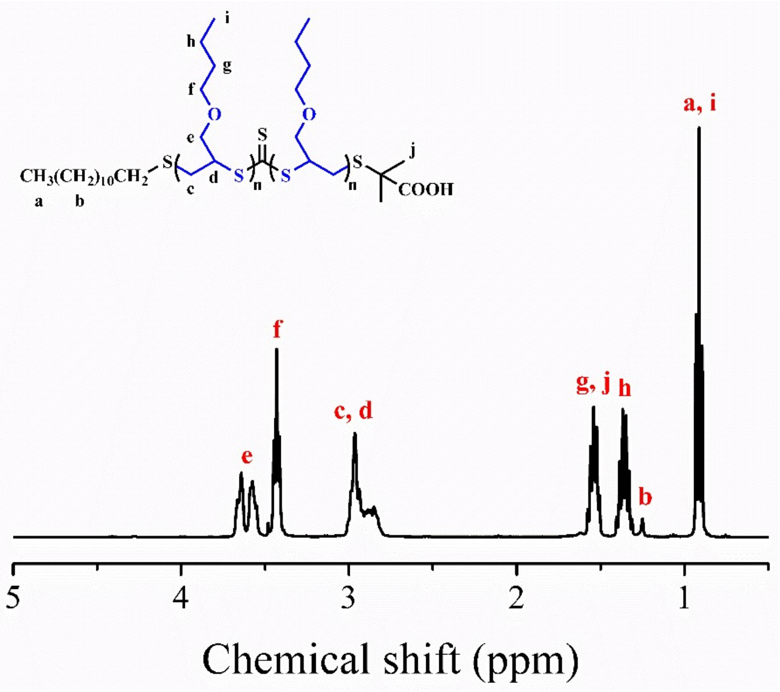

Figure S9. ^{1}H NMR spectrum of poly(2-(butoxymethyl) thiirane) (PBOMT).

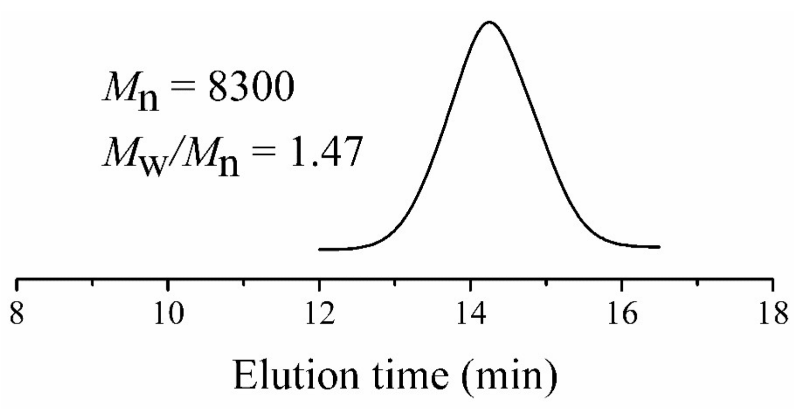

Figure S10. GPC curve of poly(2-(butoxymethyl) thiirane) (PBOMT).

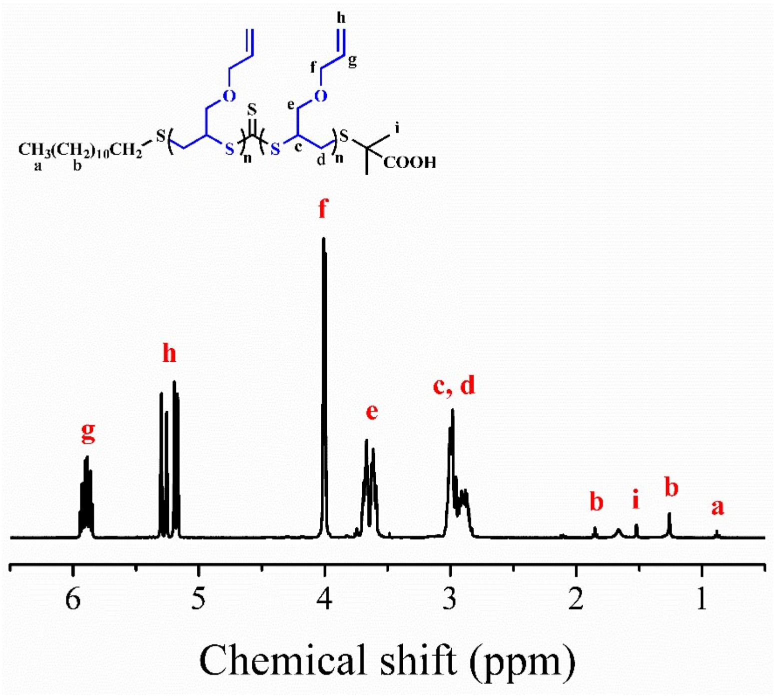

Figure S11. ^{1}H NMR spectrum of poly(2-((allyloxy)methyl) thiirane) (PAOMT).

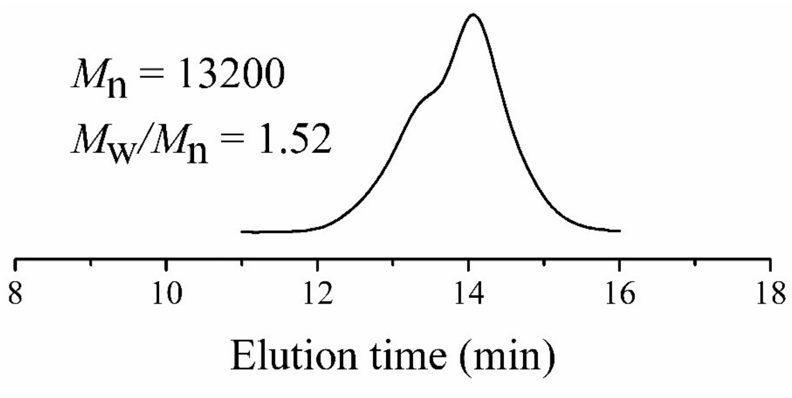

Figure S12. GPC curve of poly(2-((allyloxy)methyl) thiirane) (PAOMT).

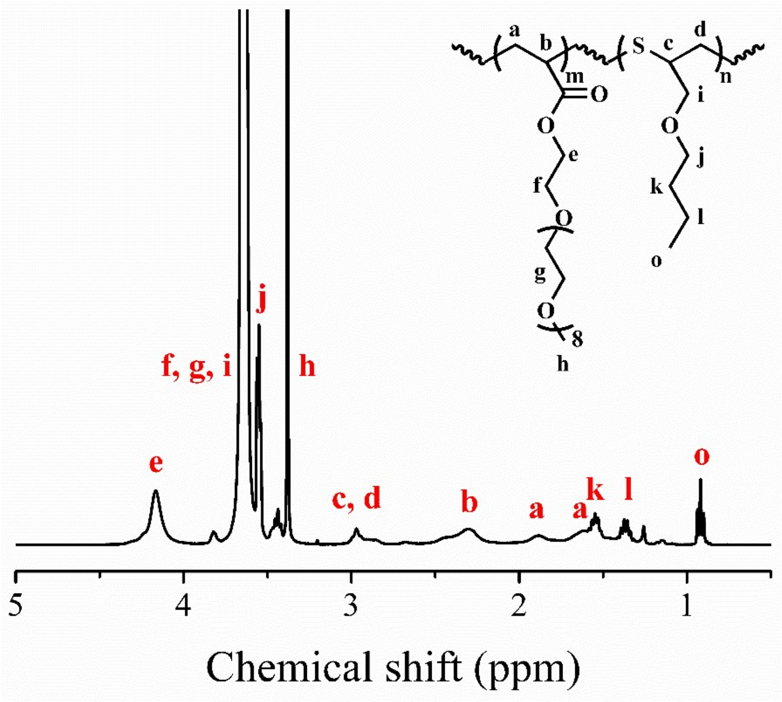

Figure S13. ^{1}H NMR spectrum of hybrid copolymer P(OEGA-*co*-BOMT).

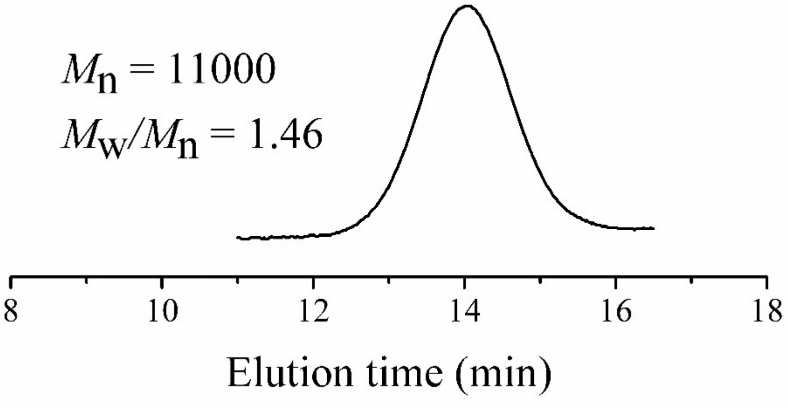

Figure S14. GPC curve of hybrid copolymer P(OEGA-*co*-BOMT).

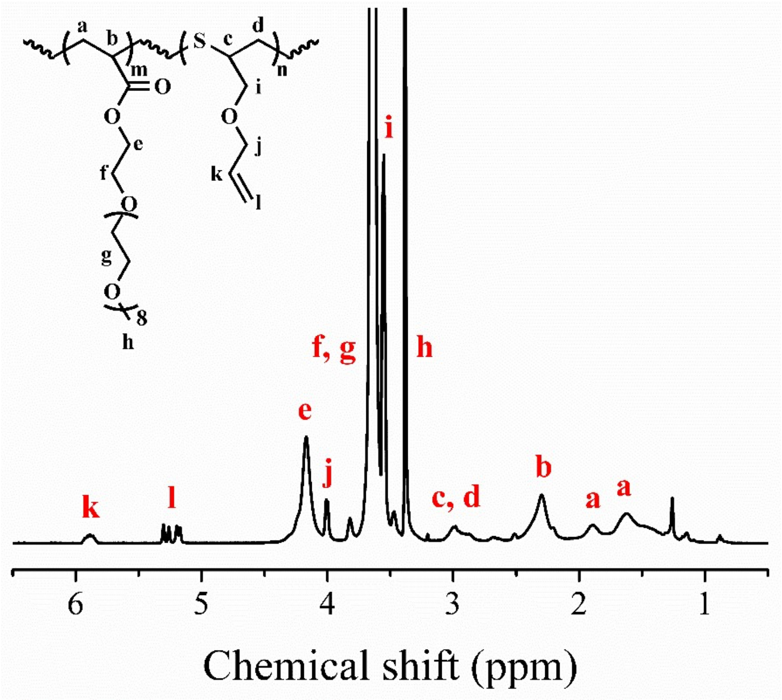

Figure S15. ^{1}H NMR spectrum of hybrid copolymer P(OEGA-*co*-AOMT).

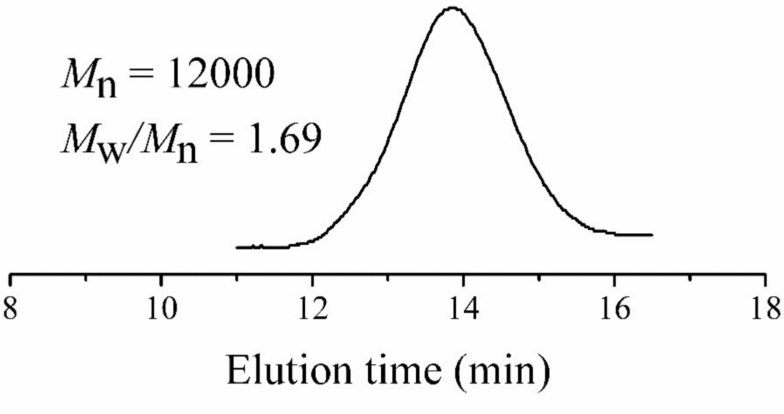

Figure S16. GPC curve of hybrid copolymer P(OEGA-*co*-AOMT).

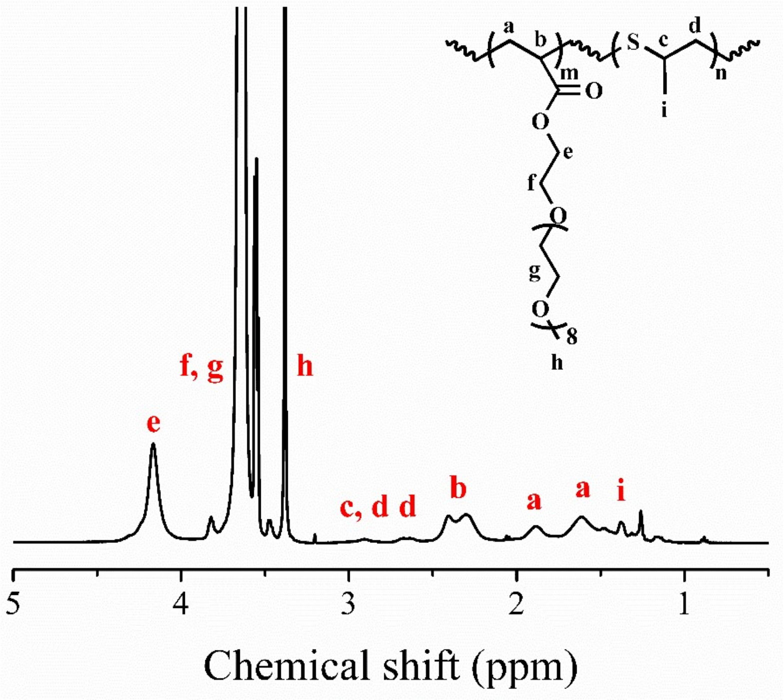

Figure S17. ^1H NMR spectrum of hybrid copolymer P(OEGA-*co*-MT).

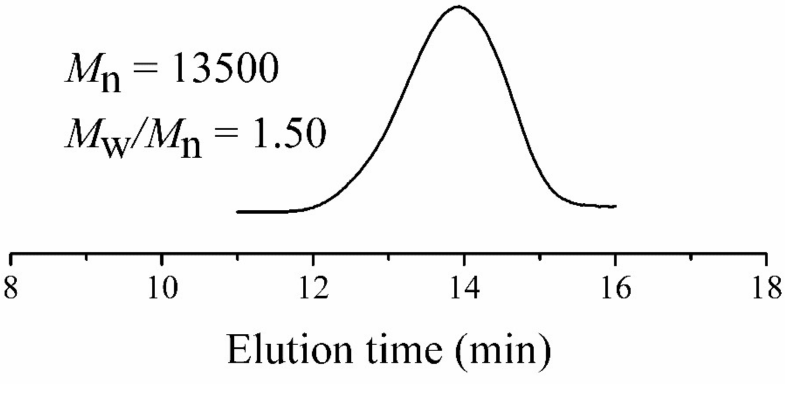

Figure S18. GPC curve of hybrid copolymer P(OEGA-*co*-MT).

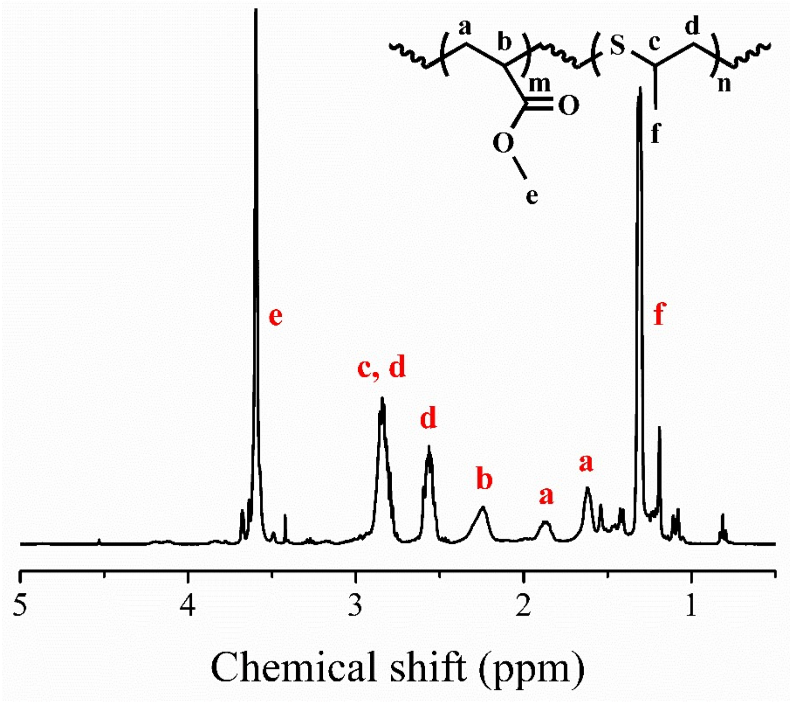

Figure S19. ^{1}H NMR spectrum of hybrid copolymer P(MA-*co*-MT).

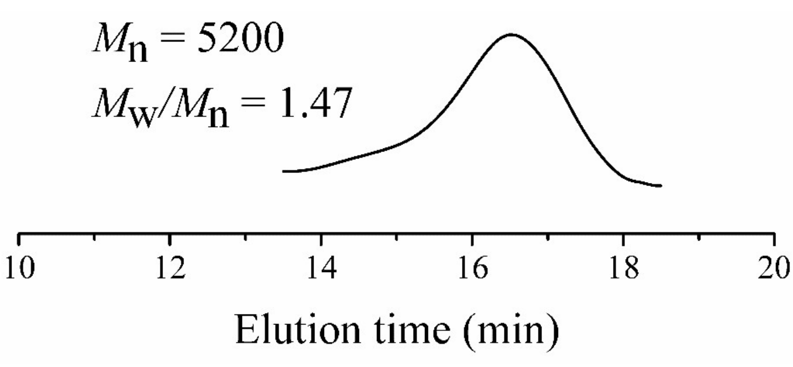

Figure S20. GPC curve of hybrid copolymer P(MA-*co*-MT).

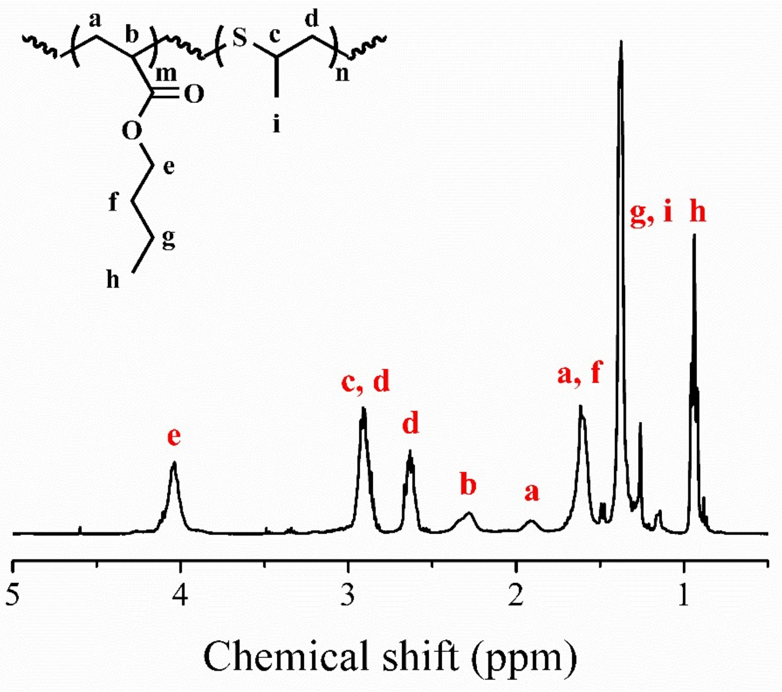

Figure S21. ^{1}H NMR spectrum of hybrid copolymer P(BA-*co*-MT).

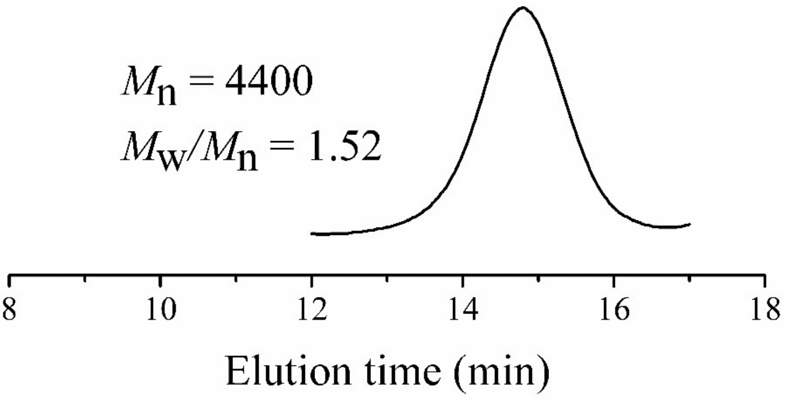

Figure S22. GPC curve of hybrid copolymer P(BA-*co*-MT).

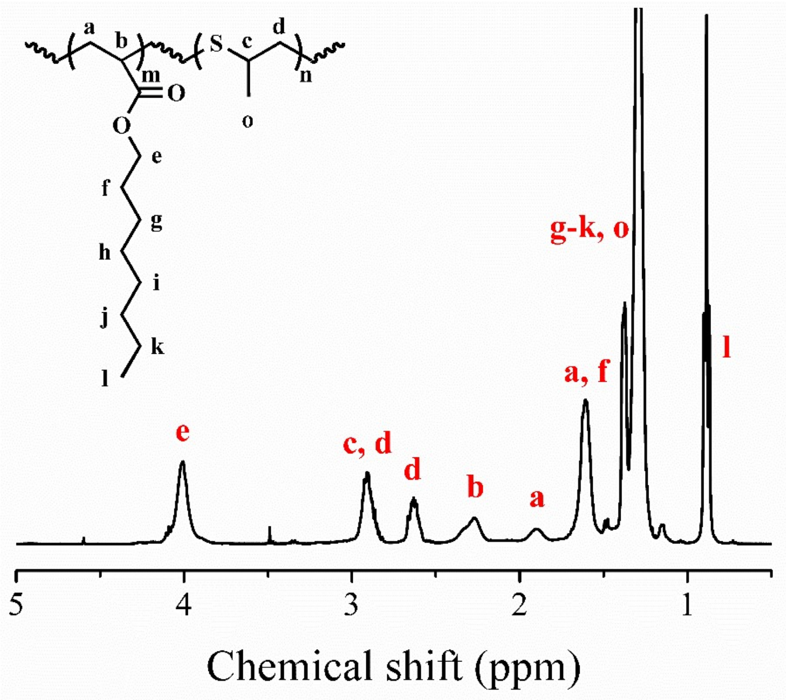

Figure S23. ^1H NMR spectrum of hybrid copolymer P(OA-*co*-MT).

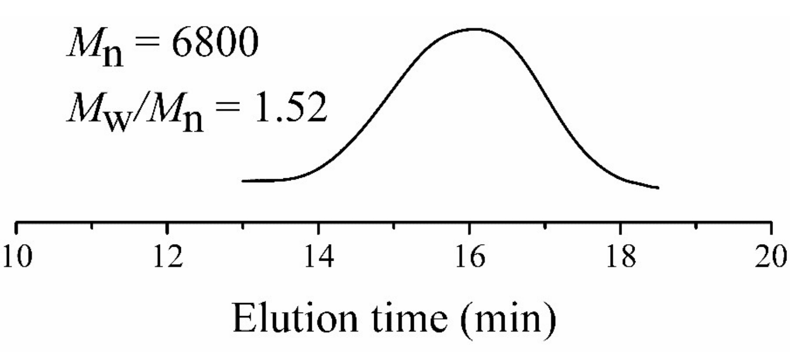

Figure S24. GPC curve of hybrid copolymer P(OA-*co*-MT).