Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Hybrid Copolymerization via Mechanisms Interconverting between Radical Vinyl-Addition and Anion Ring-Opening Polymerization

*Ze Zhang,[a] Lei Xia,[a] Tian-You Zeng,[a] De-Cheng Wu,[b] Wen-Jian Zhang,[a]**

Chun-Yan Hong,[a] and Ye-Zi You [a]**

[a]Key Laboratory of Soft Matter Chemistry, Chinese Academy of Sciences, Department of Polymer Science and Engineering University of Science and Technology of China Hefei, 230026, Anhui, China

[b]Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Polymer Physics & Chemistry, Institute of Chemistry, Chinese Academy of Science, 100190, Beijing, China

* Corresponding authors: yzyou@ustc.edu.cn (Y.Z.Y.), hongcy@ustc.edu.cn (C.Y.H.), zwj85@ustc.edu.cn (W.J.Z.)

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1. General Reagent Information

N-Isopropylmethacrylamide (NIPMAM, 97%), *N,N*-dimethylformamide (DMF, 99.9%) and dimethylacetamide (DMAc, 99.8%) were purchased from Aladdin. 2-(Phenoxymethyl) oxirane (98%), 2-(isopropoxymethyl) oxirane (96%) and tetraphenylphosphonium chloride (97%), tricaprylylmethylammonium chloride (97%), tetrabutylammonium hydrogen sulfate (99%) were purchased from Energy Chemical. Chloroform-*d* (99.8 atom % D), deuterium oxide (99.9 atom % D) and dimethyl sulphoxide-d_6 (DMSO-d_6, 99.8 atom % D) were purchased from Sigma-Aldrich. Benzyl chloride (99%) and carbon disulfide (99%) were purchased from Adamas-Beta. 2-Methyloxirane (98%), 1-dodecanethiol (98%), sodium sulfate anhydrous (99%), potassium carbonate anhydrous (99.5%), potassium thiocyanate (99%), *n*-hexane (97%), ethyl acetate (99.5%), methanol (99.7%), chloroform (99%), acetone (99.5%) and diethyl ether (99.7%) were purchased from Sinopharm Chemical Reagent Co. Ltd. *N,N*-Dimethyl acrylamide(DMA, Alfa Aesar, 99%) was purified by small aluminum oxide (basic) chromatography to remove inhibitor. *N*-Isopropyl acrylamide (NIPAM, TCI Chemical, 99%) was purified by recrystallization before use.

2. General Analytical Information

All NMR spectra were recorded on a Bruker NMR spectrometer (resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C) using the Fourier transform mode. The samples were dissolved in deuterium oxide, chloroform-*d* or DMSO-d_6 with tetramethylsilane (TMS) as an internal reference. Molecular weights and molecular weight distributions (PDI) were measured by using a Waters 150C gel permeation chromatograph (GPC) equipped with microstyragel columns and an RI 2414 detector at 30 °C. LiBr/DMF (0.1%, w/w) solution with a flow rate of 1.0 mL/min was used as eluent. The molecular weights were calibrated against monodispersed polystyrene standards. Differential scanning calorimetry (DSC) thermograms were measured on a TA Q2000 differential scanning calorimeter instrument in aluminum pans with a heating or cooling rate of 10 °C/min under a flowing nitrogen atmosphere from -70 °C to 200 °C. All T_g values were obtained from the second scan, after removing the thermal history.

3. Synthesis procedures

Synthesis of 2-methylthiirane (MT). To the solution of 2-methyloxirane (29 g, 500 mmol) in water (150 mL), potassium thiocyanate (194 g, 2 mol) was added, and the mixture was stirred at room temperature for 24 h. Subsequently, the organics were separated and dried by anhydrous sodium sulfate. 2-Methylthiirane as colorless liquid was obtained by removing the volatiles. Yield was 83%. ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 1.531 (d, 3H), δ 2.139 (d, 1H), δ 2.526 (d, 1H), δ 2.919 (m, 1H).

Synthesis of 2-(phenoxymethyl)thiirane(POMT). Potassium thiocyanate (23.2 g, 240 mmol) was added to a suspension of 2-(phenoxymethyl)oxirane (9.0 g, 60 mmol) in water (30 mL).After continuously stirring for 24 h at 40 °C, the organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined organic parts were dried by anhydrous sodium sulfate. 2-(Phenoxymethyl) thiirane was obtained as colorless viscous oil with the yield of 75%. ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 2.349 (d, 3H), δ 2.632 (d, 1H), δ 3.307 (m, 1H), δ 3.961 (m, 1H), δ 4.224 (m, 1H), δ 6.959 (m, 3H), δ 7.325 (m, 2H).

Synthesis of 2-(isopropoxymethyl)thiirane(IOMT). Potassium thiocyanate (29.1 g, 300 mmol) was added into a solution of 2-(isopropoxymethyl)oxirane (11.6 g, 100 mmol) in water (100 mL). After stirring for 24 h at 40 °C, the organic layer was separated and dried with anhydrous sodium sulfate. 2-(Isopropoxymethyl)thiirane as colorless viscous oil was obtained by removing the volatiles. The yield was 72%. ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 1.81 (dd, 6H), δ 2.209 (d, 1H), δ 2.544 (d, 1H), δ 3.07 (m, 1H), δ 3.392 (m, 1H), δ 3.645 (m, 1H), δ 3.676 (m, 1H).

Synthesis of S-1-dodecyl S'-(*α,α*-dimethylacetic acid) trithiocarbonate (DDMAT). 1-Dodecanethiol (20.2 g, 0.1 mol), acetone (58 g, 1 mol) and tricaprylylmethylammonium chloride (1.63 g, 0.004 mol) were mixed in a 500 mL bottom flask. The mixture was cooled in an ice bath. Then, sodium hydroxide (50 %, 8.4 g) was added dropwise and stirred for an additional 15 minutes. The reaction mixture turned very viscous as a white precipitate formed. Carbon disulfide (7.6 g, 0.1 mol) in acetone (10.4 g, 0.18 mol) was added dropwise to the reaction vessel. The reaction mixture turned light yellow. The mixture was subsequently stirred for an additional 10 minutes after the addition was completed. Chloroform (18 g, 0.15 mol) was added in one portion, followed by dropwise addition of sodium hydroxide (50 %, 40 g) in 30 min. The reaction was left to stir overnight and was observed to turn red. Water (150 mL) was added to the reaction vessel, followed by slow addition of concentrated HCl (25 mL) while stirring. The solid formed was collected via filtration and stirred in isopropanol (250 mL). The remaining precipitate was filtered off and the filtrate was collected. The solvent was evaporated off. The product was purified by recrystallization in *n*-hexane thrice to yield yellow crystals. Yield was 45%. ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 0.88 (t, 3H), δ 1.25 - 1.72 (m, 26H), δ 3.28 (t, 2H), δ 10.95 (s, 1H).

Synthesis of S,S'-bis(*α,α'*-dimethyl-*α''*-acetic acid) trithiocarbonate (BDMAT).Carbon disulfide (13.8 g, 0.18 mol), chloroform (58.8 g, 0.45 mol), acetone (26.3 g, 0.45 mol), tetrabutylammonium hydrogen sulfate (1.2 g, 3.6 mmol) and *n*-

hexane (60 mL) were mixed in a 250 mL bottom flask. The mixture was cooled in an ice bath. Then, solution of sodium hydroxide (50 %, 101 g) was added dropwise within 60 min. After the reaction was left to stir overnight, water (500 mL) was added to the reaction mixture, followed by slow addition of concentrated HCl (60 mL) while stirring to acidify the aqueous layer under an argon atmosphere. The precipitate was filtered, rinsed thoroughly with water, and dried under vacuum to yield brown-colored solid. The solid was purified by recrystallization in acetone/hexane (4/1, v/v) thrice to obtain a yellow crystals. Yield was 37%. ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 1.69 (s, 12H).

Synthesis of dibenzyl trithiocarbonate (DBTTC). Carbon disulfide (400 mg, 5.25 mmol) was added to a solution of benzyl chloride (633 mg, 5.0 mmol) in *N,N*-dimethylformamide (5 mL), and subsequently, potassium carbonate (691 mg, 5.0 mmol)was added. After stirred at 40 °C for 24 h, the mixture was extracted with ethyl acetate, dried over anhydrous sodium sulfate, filtered, and evaporated to give crude product as yellow oil. Going through a silica gel column chromatography with *n*-hexane gave DBTTC as a yellow crystal with the yield was 62%. ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 4.62 (s, 4H), δ 7.24 - 7.34 (m, 10H).

The synthesis of multiblock copolymer
DMA (2376 mg, 24 mmol), 2-methylthiirane (888 mg, 12 mmol), DDMAT (145 mg, 0.4 mmol), AIBN (32 mg, 0.2 mmol) and TPPCl (149 mg, 0.4 mmol) were dissolved in 24 mL DMAc and transferred into several polymerization tubes. After three freeze-pump-thaw cycles, the tubes were sealed and immersed in an oil bath at 65 °C. ^{1}H NMR spectra were recorded with NMR tubes adapted with coaxial inserts after appropriate time intervals. D_2O containing 0.03% TMS was in the inner of the concentric capillary tube, while the mixed solution in the outer capillary tube. The reaction mixture was precipitated into diethyl ether several times and the product as white or light yellow powder was obtained after dried in vacuum.

The synthesis of triblock copolymer
N,N-Dimethylacrylamide (1188 mg, 12 mmol), 2-methylthiirane (1776 mg, 24 mmol), DDMAT (145 mg, 0.4 mmol), AIBN (32 mg, 0.2 mmol) and tetraphenylphosphonium chloride (448 mg, 1.2 mmol) were dissolved in 5 mL DMAc and transferred into several polymerization tubes. After three freeze-pump-thaw cycles, the tubes were sealed and immersed in an oil bath at 70 °C. ^{1}H NMR spectra were recorded after suitable time interval with NMR tubes adapted with coaxial inserts after appropriate time intervals. D_2O was in the inner of the concentric capillary tube, while the mixed solution in the outer capillary tube. The reaction mixtures were precipitated into diethyl ether several times and the products as light yellow powder were obtained after dried in vacuum.

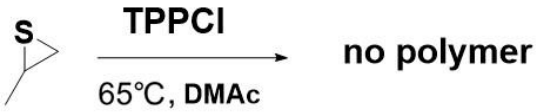
The synthesis of gradient copolymer
N,N-Dimethylacrylamide (1980 mg, 20 mmol), 2-methylthiirane (1332 mg, 18 mmol), DDMAT (72.8 mg, 0.2 mmol), AIBN (16 mg, 0.1 mmol) and tetraphenylphosphonium chloride (89.8 mg, 0.24 mmol) were dissolved in 17 mL DMAc and transferred into several polymerization tubes. After three freeze-pump-thaw cycles, the tubes were sealed and immersed in an oil bath at 65 °C. ^{1}H NMR spectra were recorded after suitable time interval with NMR tubes adapted with coaxial inserts after appropriate time intervals. D_2O was in the inner of the concentric capillary tube, while the mixed solution in the outer capillary tube. The reaction mixtures were precipitated into diethyl ether several times and the products as light yellow powder were obtained after dried in vacuum.

Incorporating more chemically distinct blocks and block types into one polymer chain
BDMAT (0.02 mmol), AIBN (0.01 mmol), TPPCl (0.02 mmol), vinyl-typed NIPAM monomer and cyclic 2-(phenoxymethyl) thiirane monomer were dissolved in DMAc to obtain clear yellow solution ([vinyl] = 1.0 M) and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 36 h. Then, the produced copolymer 1 was used in the second polymerization (DMA (150 mg, 1.5 mmol), MT (111 mg, 1.5 mmol), copolymer1 (M_w = 24100 g/mol, PDI = 1.45), AIBN (0.8 mg, 0.005 mmol) and TPPCl (11.2 mg, 0.03 mmol)) were dissolved in 4 mL DMAc and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 36 h. The reaction mixture was precipitated into diethyl ether several times and the product Copolymer 2 with M_w of 45400 was obtained and the yield was 59%.

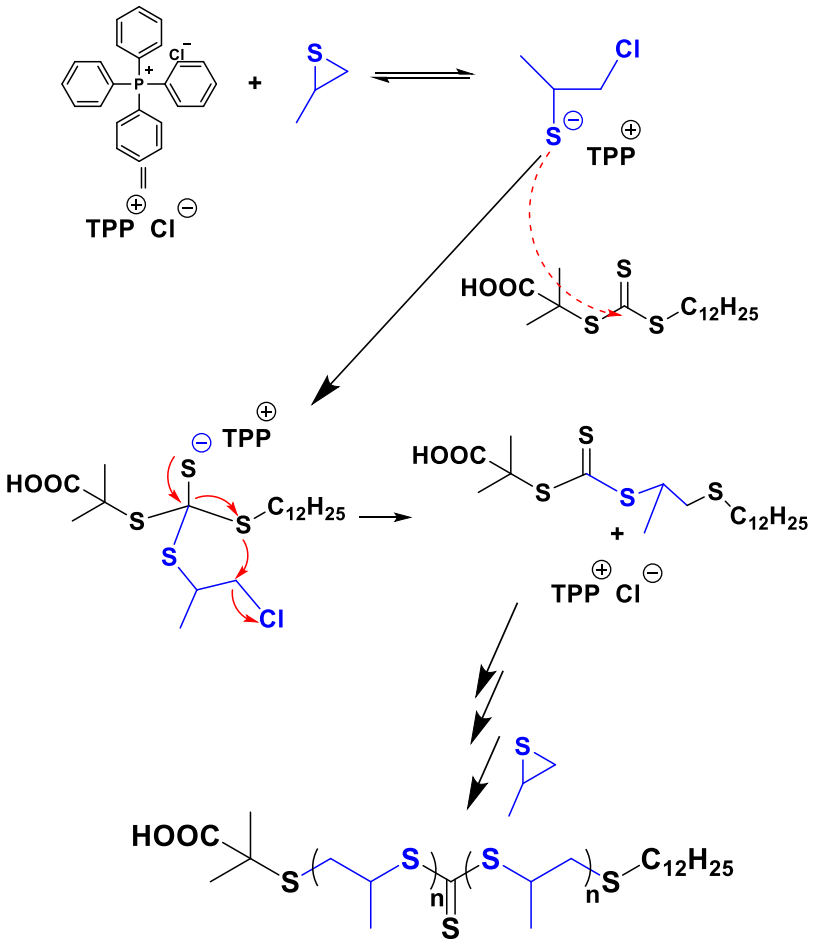
4. Supporting experiments

4.1 Trithiocarbonate-containing molecules can mediate both free radical polymerization and ring-opening polymerization

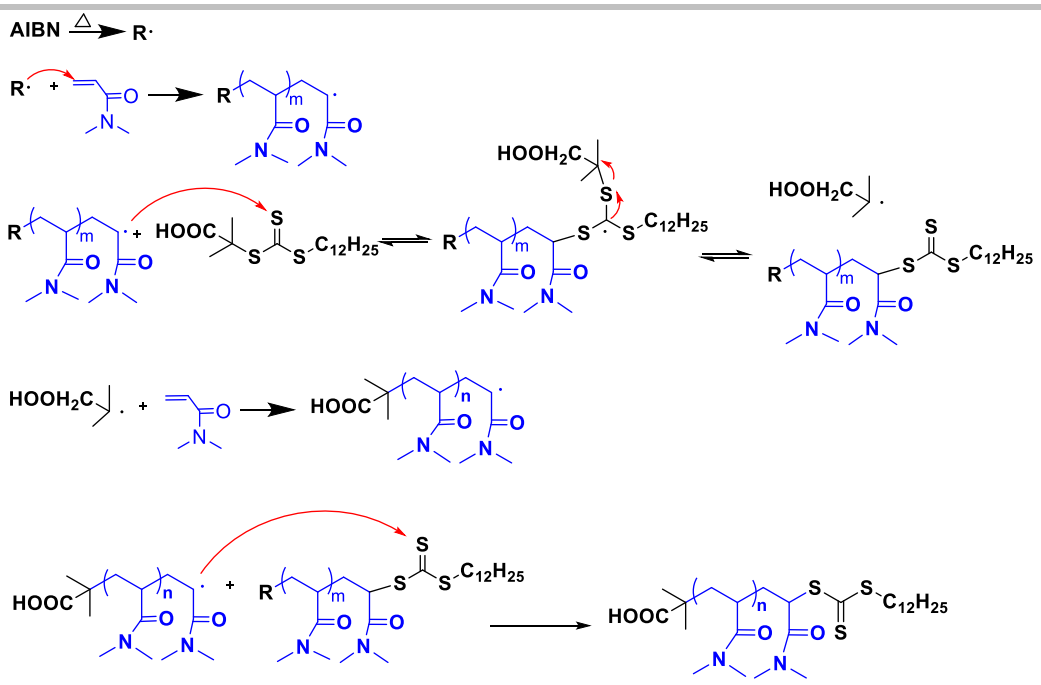
4.1.1 The polymerization of 2-methylthiirane (MT) using tetraphenylphosphonium chloride (TPPCl) as catalyst: 2-Methylthiirane (259 mg, 3.5 mmol) and TPPCl (18.7 mg, 0.05 mmol) were dissolved in 3.5 mL DMAc and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 48 h. No product could be obtained after precipitated into methanol.



4.1.2 DDMAT initiates the ring-opening polymerization of cyclic MT monomer in the presence of TPPCl as catalyst: DDMAT (18.2 mg, 0.05 mmol), 2-methylthiirane (259 mg, 3.5 mmol) and TPPCl (18.7 mg, 0.05 mmol) were dissolved in 3.5 mL DMAc and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 24 h. The reaction mixture was precipitated into methanol several times and the product (PMT) as yellow viscous oil was obtained after dried in vacuum. Yield was 82%.

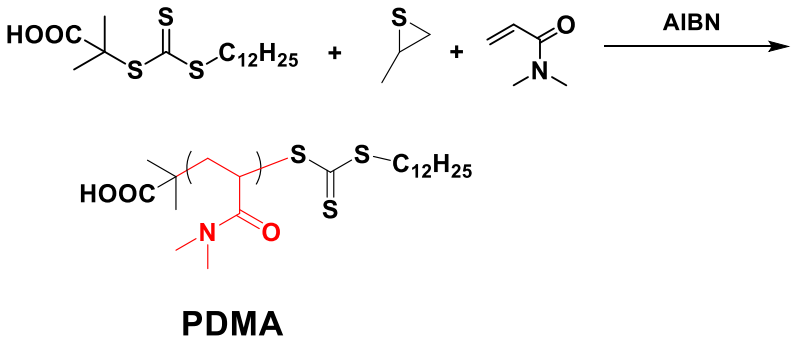


4.1.3 DDMAT mediates the free radical polymerization of vinyl-typed monomer of DMA using AIBN as initiator: DMA (347 mg, 3.5 mmol), DDMAT (18.2 mg, 0.05 mmol) and AIBN (4 mg, 0.025 mmol) were dissolved in 3.5 mL DMAc and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 24 h. The reaction mixture was precipitated into diethyl ether several times and the product (PDMA) as light yellow powder was obtained after dried in vacuum. Yield was 84%.



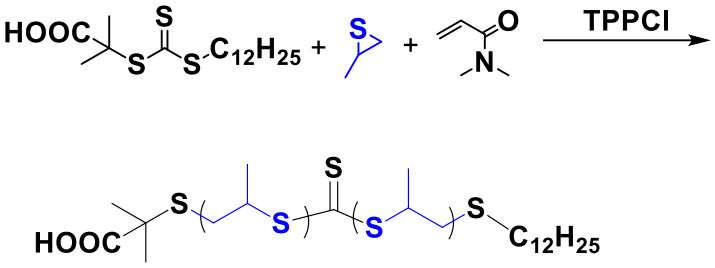
4.2 RAFT and ROP are highly selective to monomers

4.2.1 Cyclic monomer of MT does not participate in RAFT polymerization of vinyl-typed monomer of DMA without TPPCl: DMA (347 mg, 3.5 mmol), DDMAT (18.2 mg, 0.05 mmol), MT (259 mg, 3.5 mmol) and AIBN (4 mg, 0.025 mmol) were dissolved in 3.5 mL DMAc and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 24 h. The reaction mixture was precipitated into diethyl ether several times and the product was obtained after dried in vacuum.



PDMA

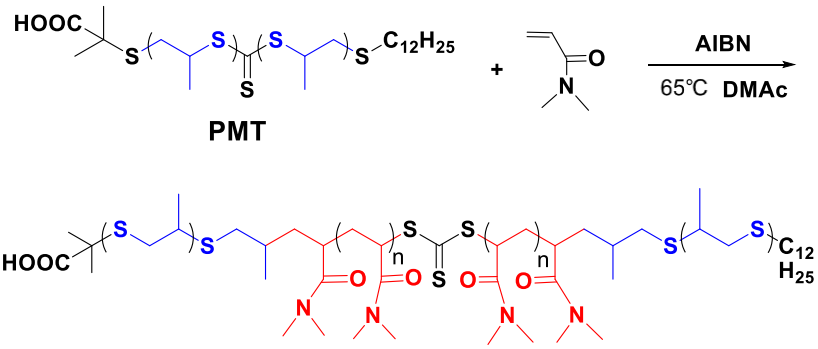
4.2.2 Vinyl-typed DMA monomer does not participate in the trithiocarbonate-mediated ROP of cyclic MT monomer without AIBN: DMA (347 mg, 3.5 mmol), DDMAT (18.2 mg, 0.05 mmol), 2-methylthiirane (259 mg, 3.5 mmol) and TPPCl (18.7 mg, 0.05 mmol) were dissolved in 3.5 mL DMAc and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 24 h. The reaction mixture was precipitated into methanol several times and the product as yellow viscous oil was obtained after dried in vacuum.



PMT

4.3 Trithiocarbonate mediated-polymerizations can be easily interconverted between ring-opening polymerization and living free radical polymerization

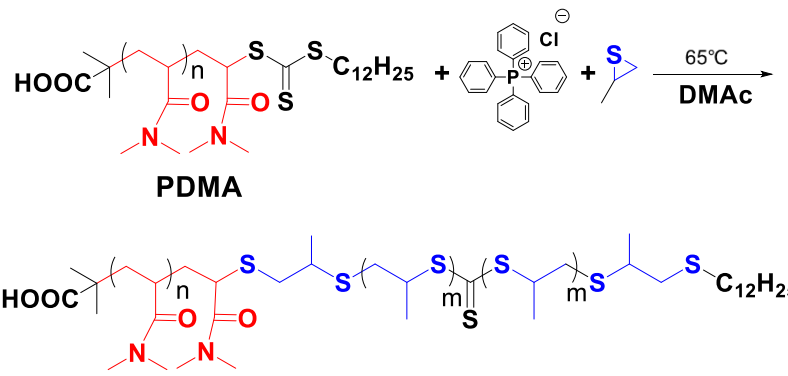
4.3.1 Poly(2-methylthiirane) bearing trithiocarbonate unit can mediate the living free radical polymerization of DMA: DMA (347 mg, 3.5 mmol), poly(2-methylthiirane) (285 mg, Mw = 8100 g/mol, PDI = 1.41) and AIBN (4 mg, 0.025 mmol) were dissolved in 3.5 mL DMAc and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 24 h. The reaction mixture was precipitated into diethyl ether several times and the product as light yellow powder was obtained after dried in vacuum. Yield was 87%, copolymer of PMT-b-PDMA-b-PMT has Mw of 15700 and PDI of 1.21.



PMT

PMT-b-PDMA-b-PMT

4.3.2 Poly(N,N-dimethylacrylamide) bearing trithiocarbonate can initiate the ring-opening polymerization of 2-methylthiirane: Poly(*N,N*-dimethylacrylamide) (355 mg, Mw = 7100 g/mol, PDI = 1.17), 2-methylthiirane (259 mg, 3.5 mmol) and TPPCl (18.7 mg, 0.05 mmol) were dissolved in 3.5 mL DMAc and transferred into a polymerization tube. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C for 24 h. The reaction mixture was precipitated into diethyl ether several times and the product as light yellow powder was obtained after dried in vacuum. Yield was 91%. Copolymer of PDMA-b-PMT has Mw of 19100 and PDI of 1.23.

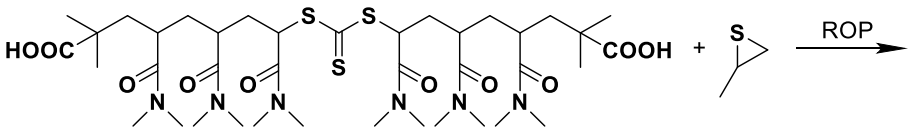


PDMA

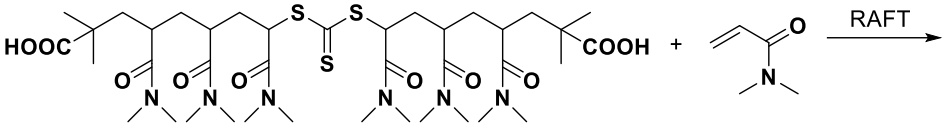
PDMA-b-PMT

4.4 The rate of monomer insertions in RAFT polymerization and ROP

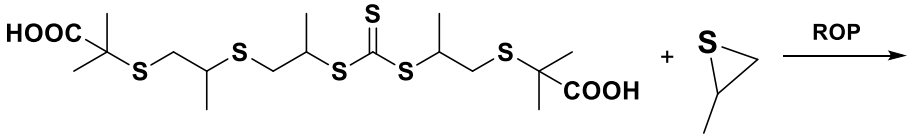
Oligomer DMA-containing trithiocarbonate (132 mg, 0.15 mmol), 2-methylthiirane (11.1 mg, 0.15 mmol) and tetraphenylphosphonium chloride (28 mg, 0.075 mmol) were dissolved in 0.6 mL DMSO-d6 and transferred into a transparent glass tube with rubber plug. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65 °C. ^{1}H NMR spectra were recorded after suitable time interval.



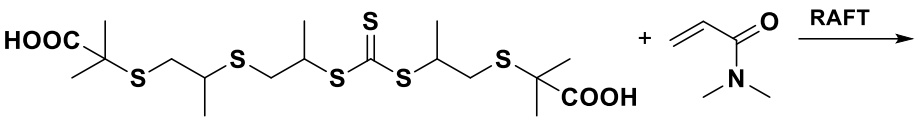
Oligomer DMA-containing trithiocarbonate (132 mg, 0.15 mmol), DMA (14.85 mg, 0.15 mmol) and AIBN (12 mg, 0.075 mmol) were dissolved in 0.6 mL DMSO-d6 and transferred into a transparent glass tube with rubber plug. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65°C. ^{1}H NMR spectra were recorded after suitable time interval.



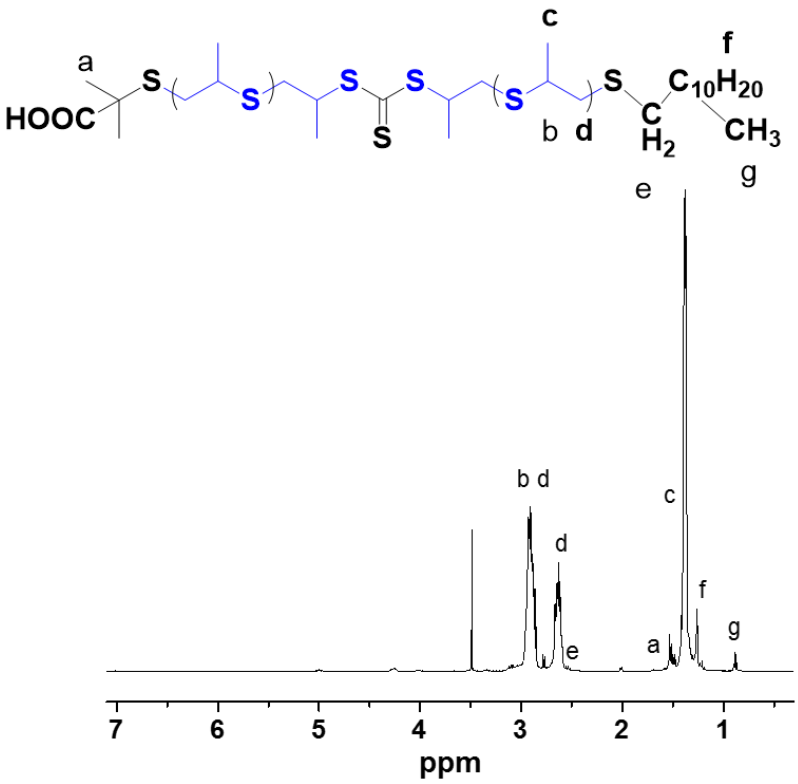
Oligomer MT-containing trithiocarbonate (75 mg, 0.15 mmol), 2-methylthiirane (11.1 mg, 0.15 mmol) and tetraphenylphosphonium chloride (28 mg, 0.075 mmol) were dissolved in 0.6 mL DMSO-d6 and transferred into a transparent glass tube with rubber plug. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65°C. ^{1}H NMR spectra were recorded after suitable time interval.



Oligomer MT-containing trithiocarbonate (75 mg, 0.15 mmol), DMA (14.85 mg, 0.15 mmol) and AIBN (12 mg, 0.075 mmol) were dissolved in 0.6 mL DMSO-d6 and transferred into a transparent glass tube with rubber plug. After three freeze-pump-thaw cycles, the tube was sealed and immersed in an oil bath at 65°C. ^{1}H NMR spectra were recorded after suitable time interval.



5. Supporting figures and table



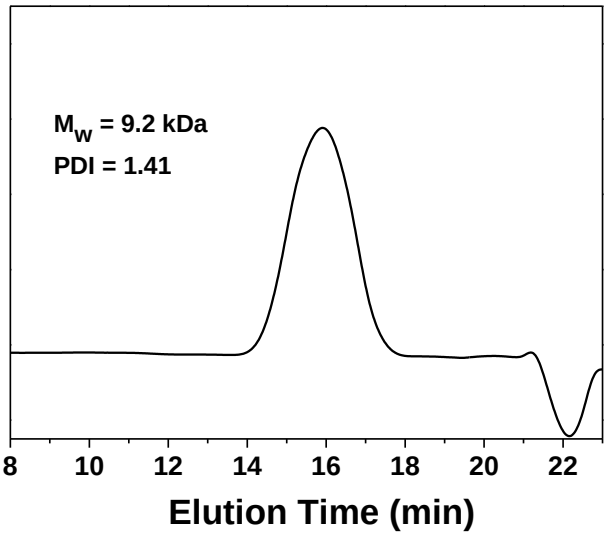


Figure S1. ^{1}H NMR spectrum and GPC curve of PMT produced by DDMAT-mediated ring-opening polymerization of cyclic MT monomer in the presence of TPPCl

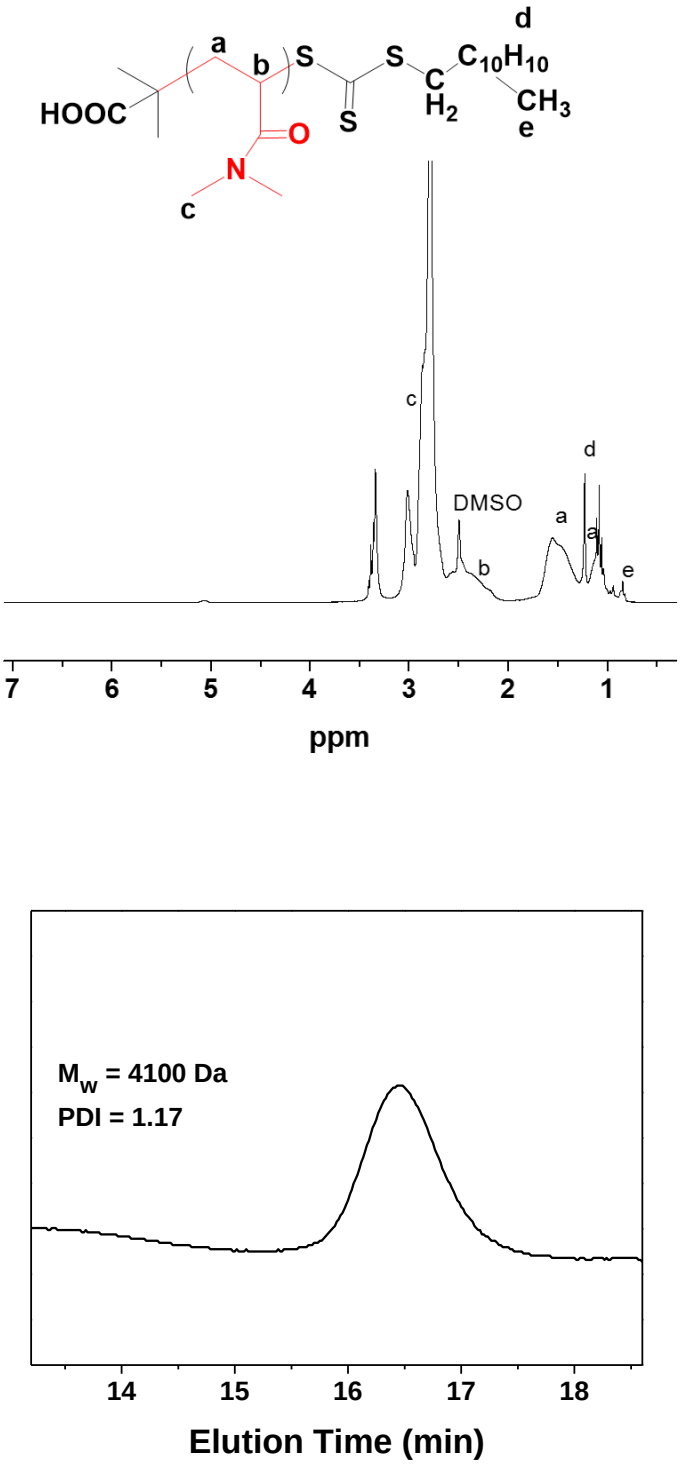


Figure S2. ^{1}H NMR spectrum and GPC curve of PDMA produced by DDMAT-mediated RAFT polymerization of vinyl-typed DMA monomer

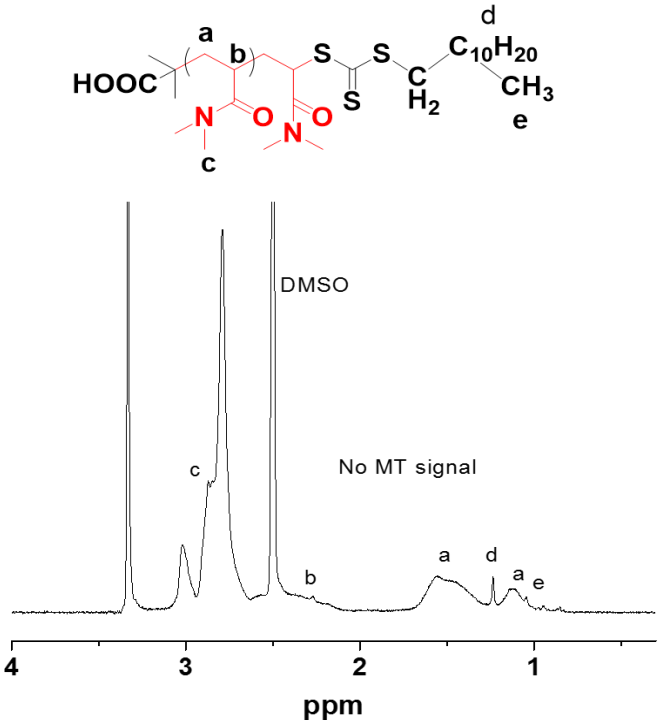
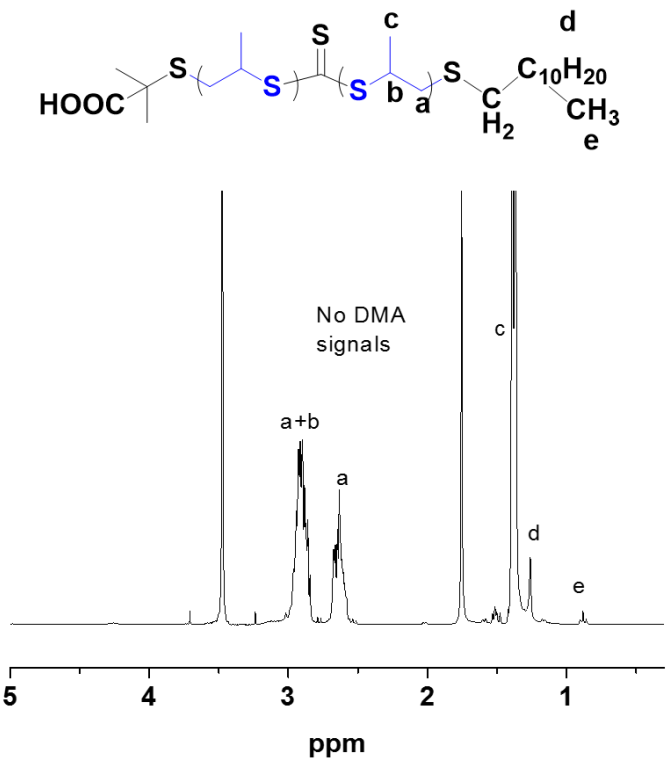


Figure S3. [1]HNMR spectrum for the resulting polymer via RAFT polymerization of vinyl DMA monomer in the presence of cyclic MT monomer



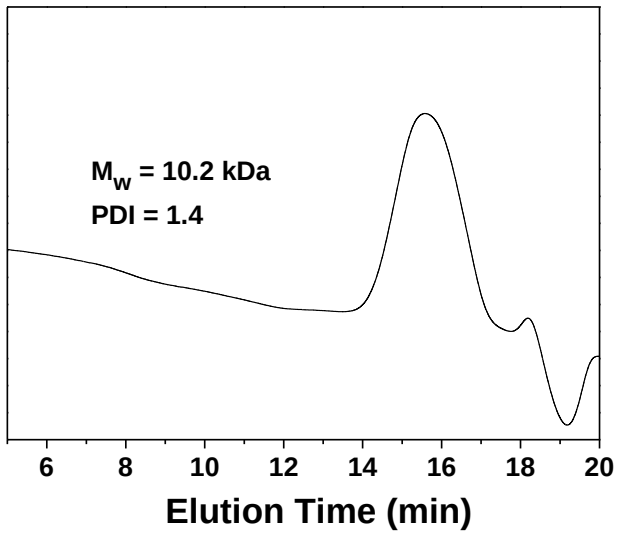


Figure S4. ^{1}HNMR spectrum and GPC curve of the resulting polymer via trithiocarbonate-mediated ROP of cyclic MT monomer in the presence of vinyl-typed DMA monomer without AIBN

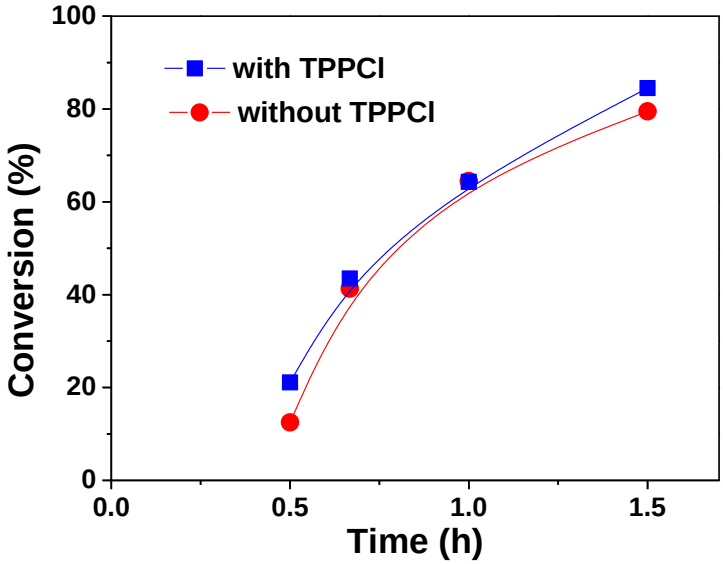


Figure S5. The effect of TPPCl on RAFT polymerization of vinyl-typed DMA monomer

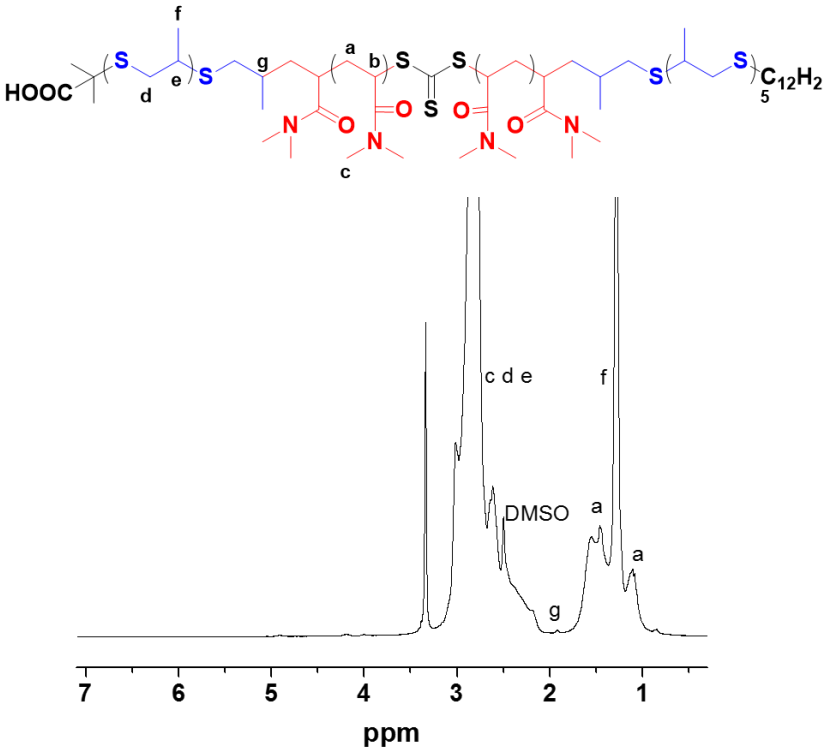


Figure S6. ^{1}HNMR spectrum of the resulting polymer via RAFT polymerization of vinyl-typed DMA monomer mediated PMT bearing trithiocarbonate

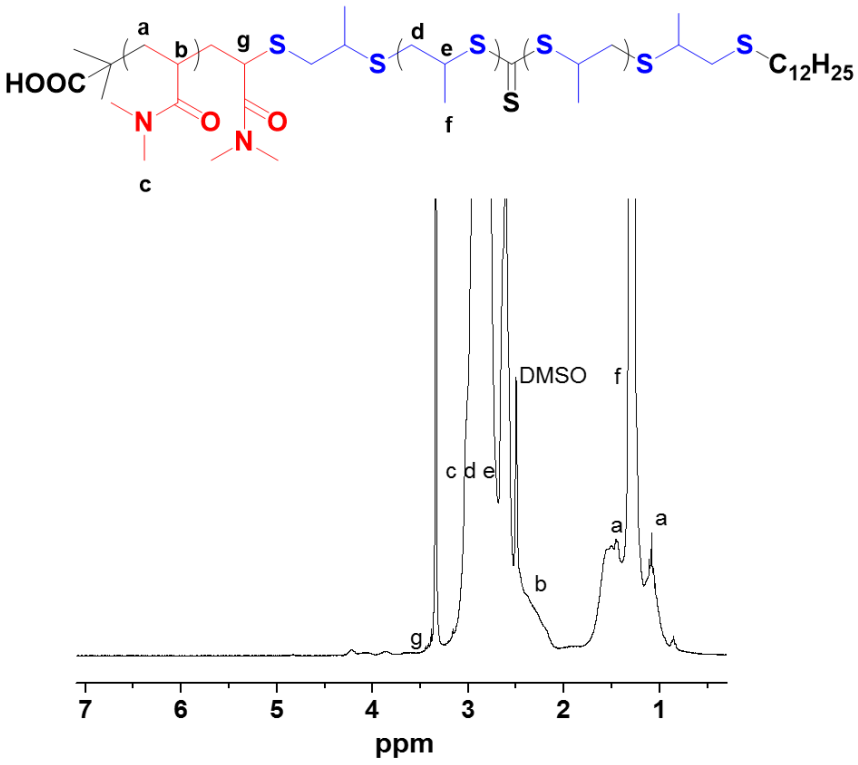


Figure S7. ^{1}H NMR spectrum of the resulting polymer via ROP of cyclic MT monomer mediated PDMA bearing trithiocarbonate

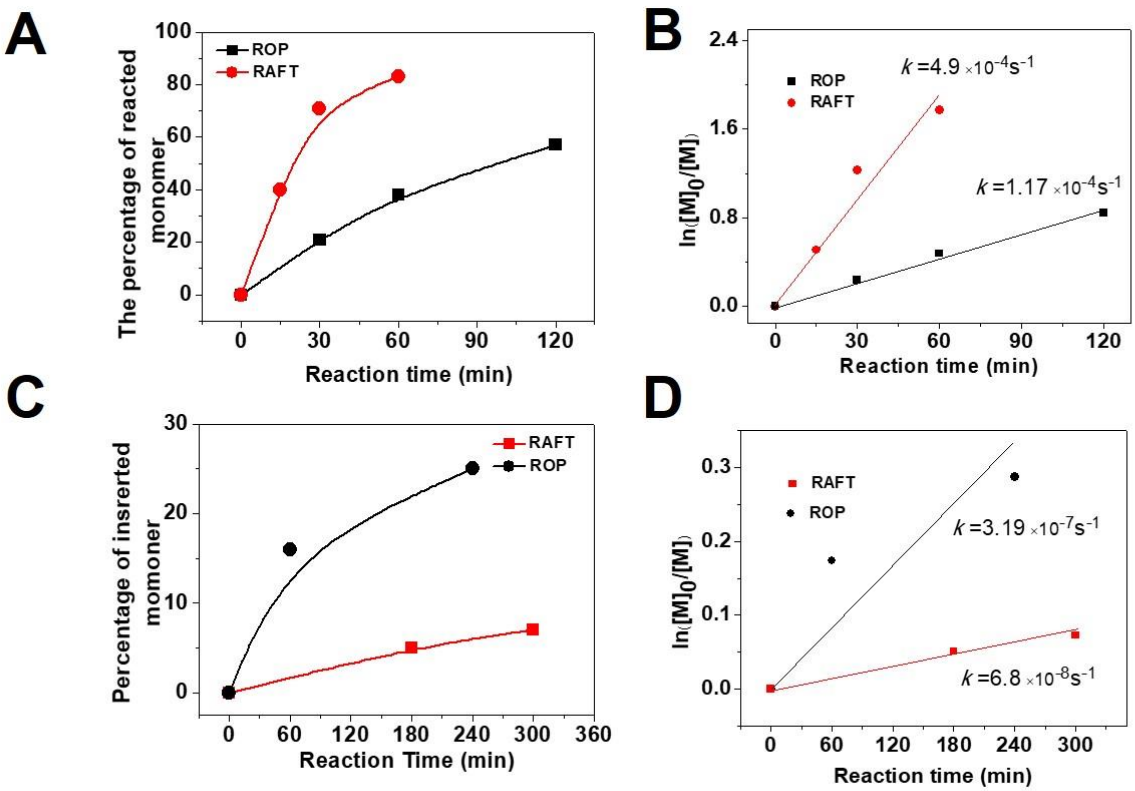


Figure S8. (A) and (B) The percentage of monomer insertion and apparent rate constant *k* mediated by oligomer DMA-containing trithiocarbonate; (C) and (D) The percentage of monomer insertion and apparent rate constant *k* mediated by oligomer MT-containing trithiocarbonate.

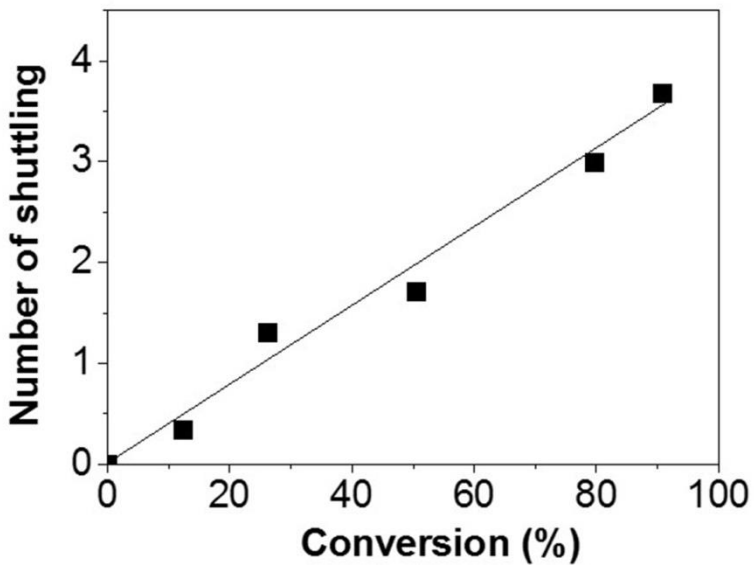


Figure S9. The variation of interconverting times with comonomer conversion during the formation of multiblock copolymer via the hybrid copolymerization

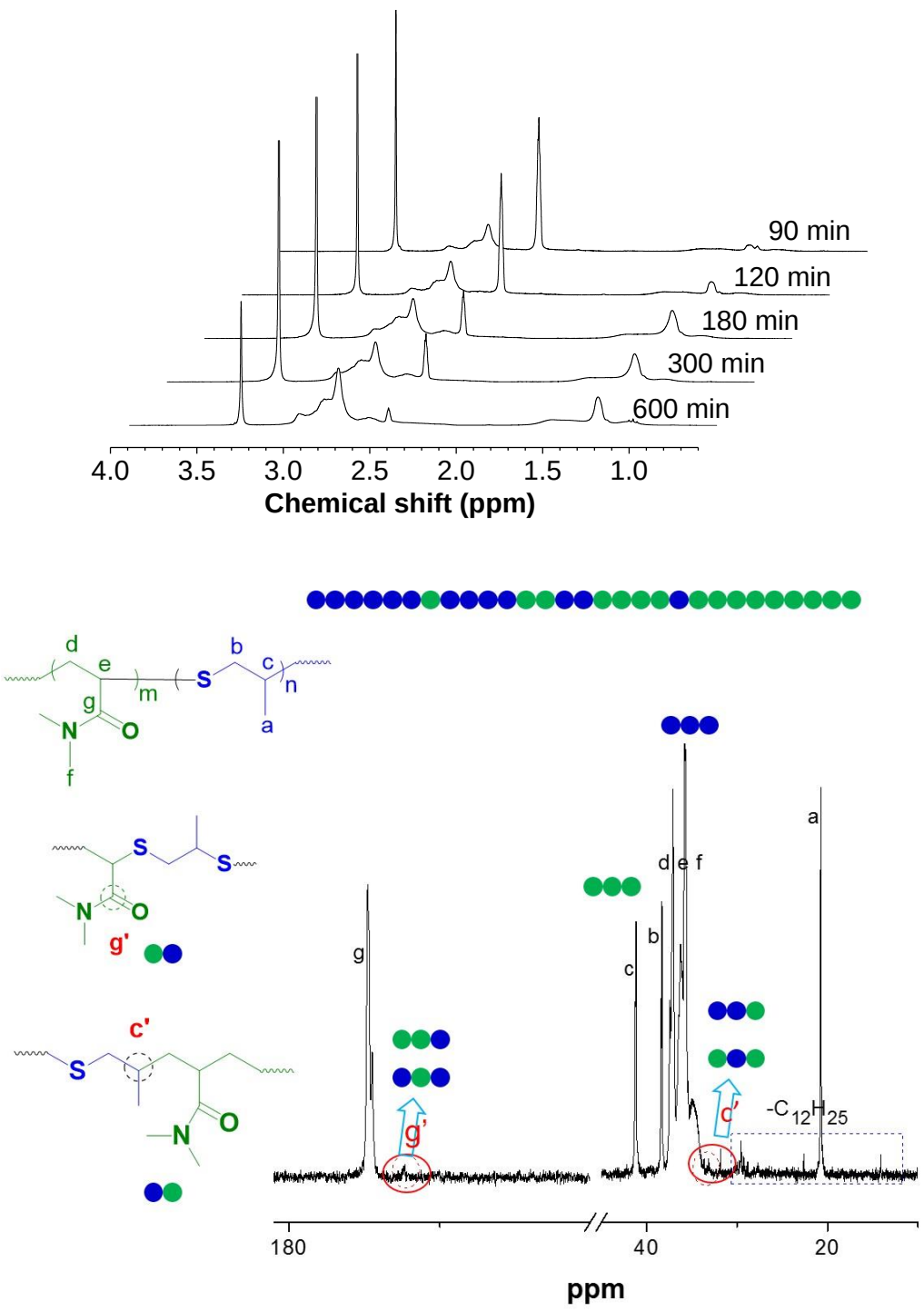


Figure S10. ^{1}H NMR spectra of the resulting gradient polymers and ^{13}C NMR spectrum of the resulting gradient polymers via the hybrid copolymerization in DMSO-d6

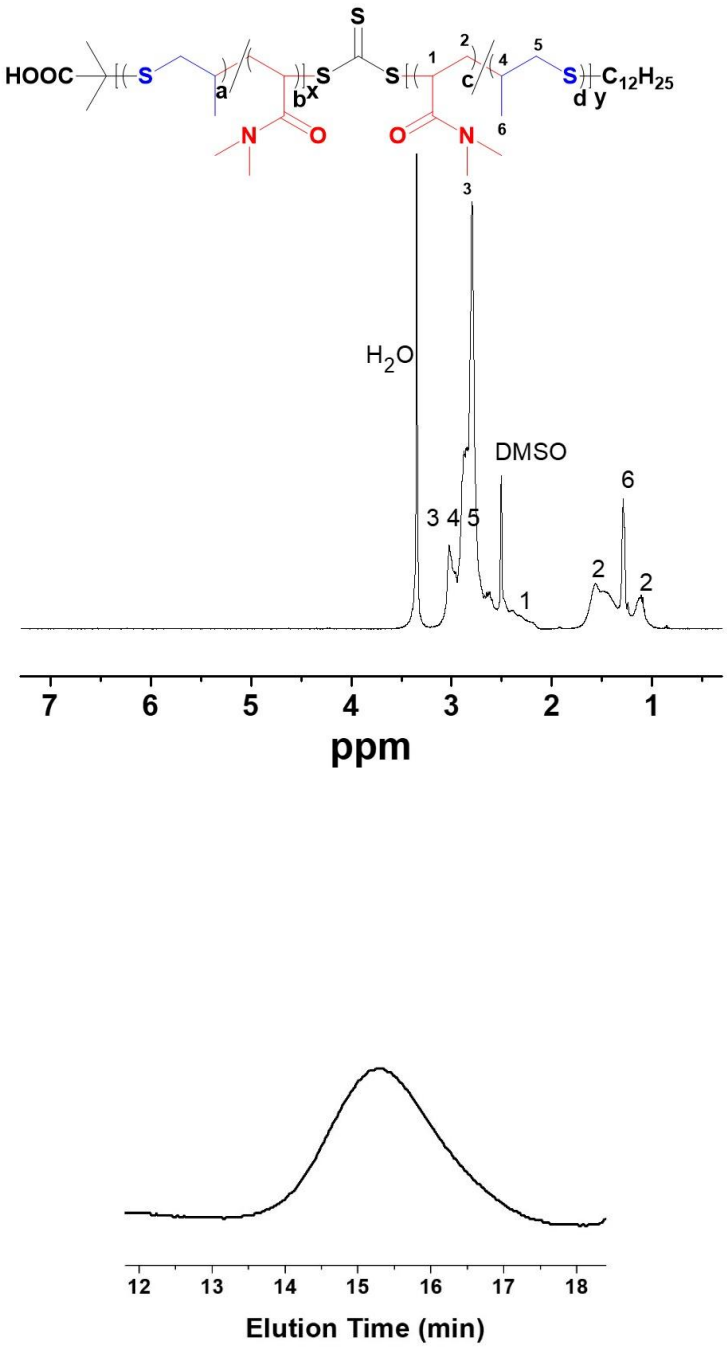


Figure S11. ^{1}H NMR spectrum and GPC curve of the copolymer (entry 1 in Table 1)

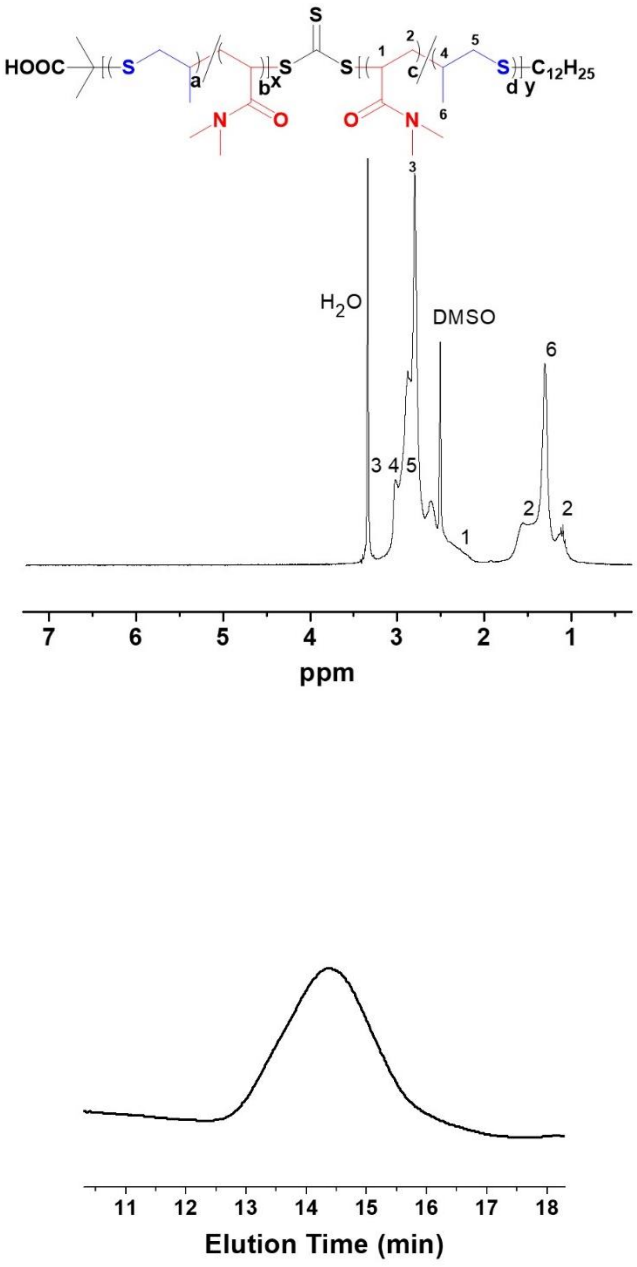


Figure S12. ^{1}H NMR spectrum and GPC curve of the copolymer (entry 2 in Table 1)

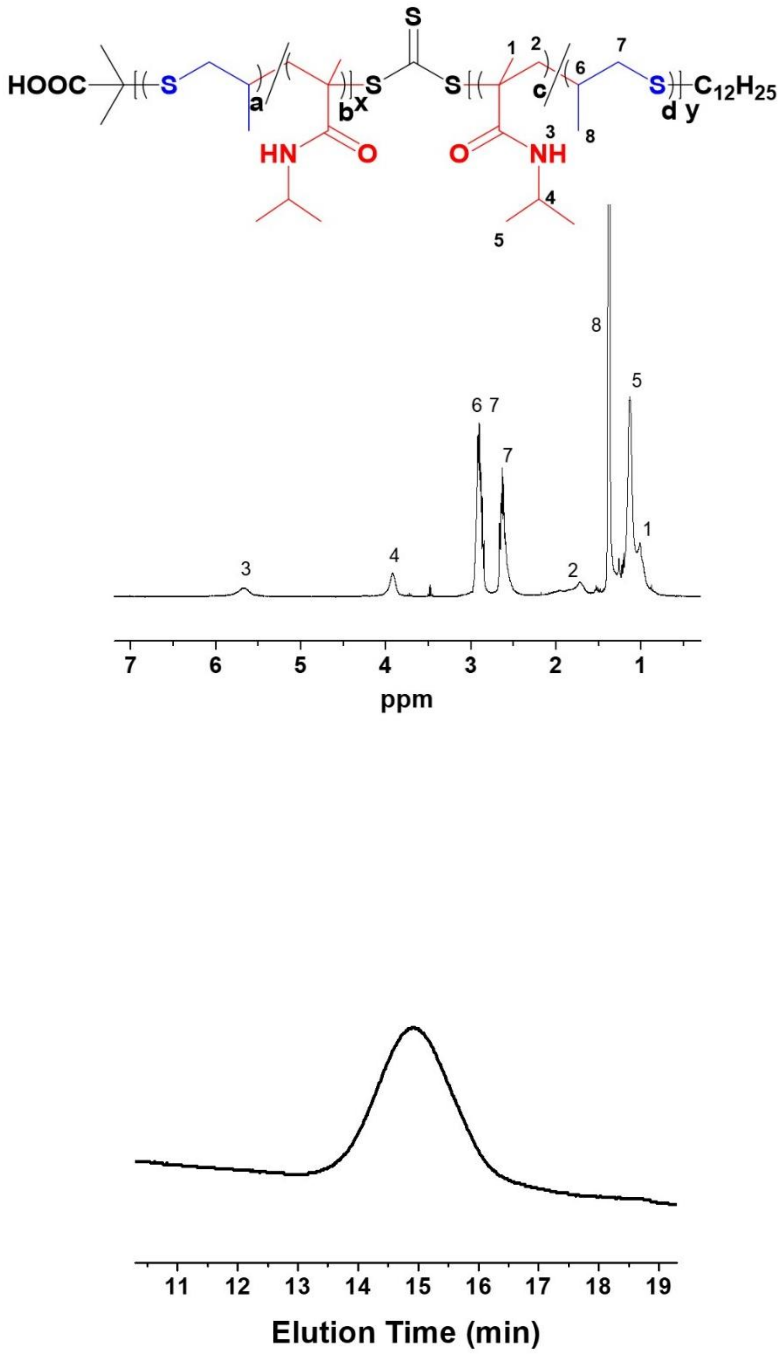
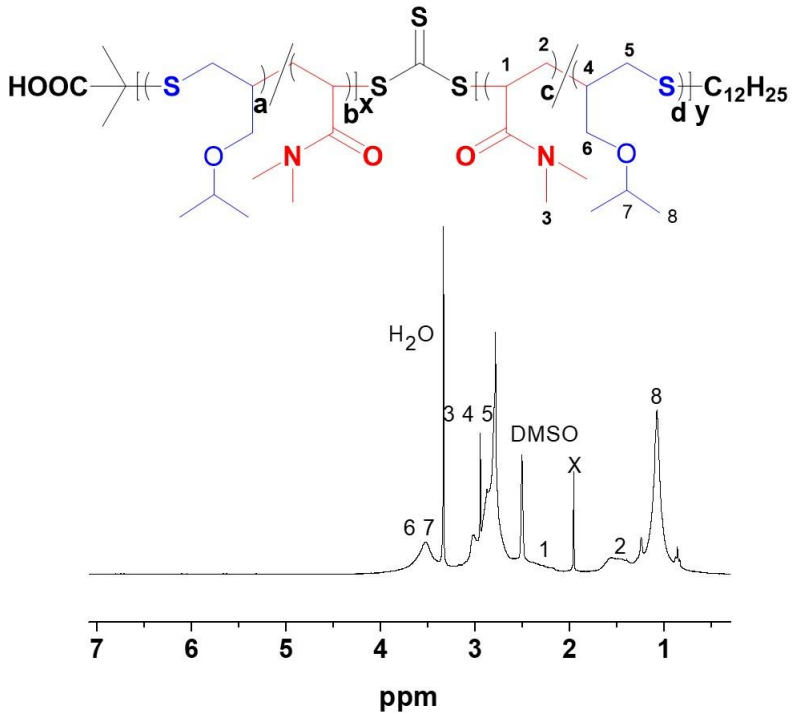


Figure S13. ^{1}H NMR spectrum and GPC curve of the copolymer (entry 3 in Table 1)



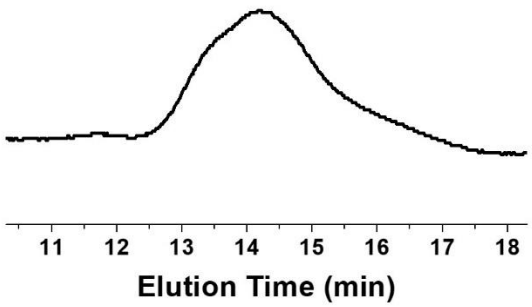
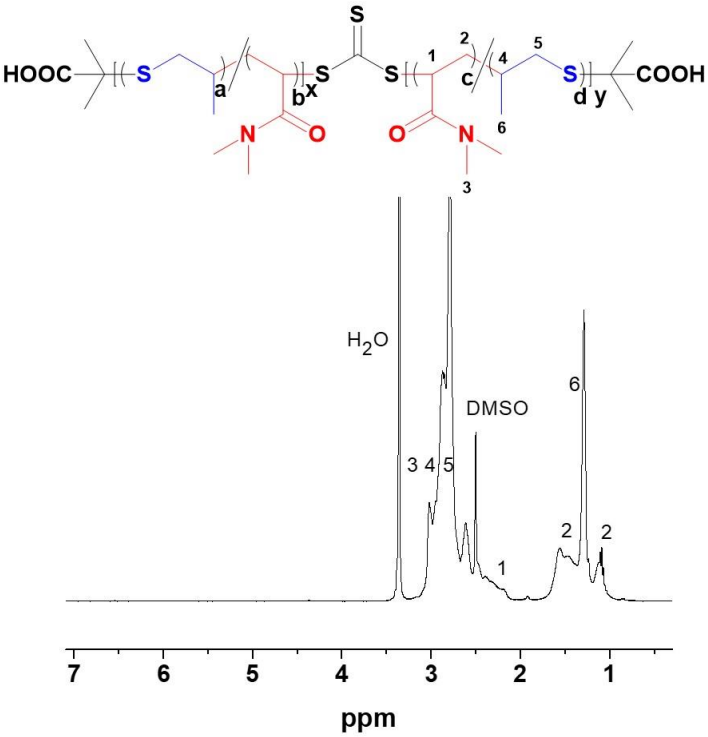


Figure S14. ^{1}H NMR spectrum and GPC curve of the copolymer (entry 4 in Table 1)



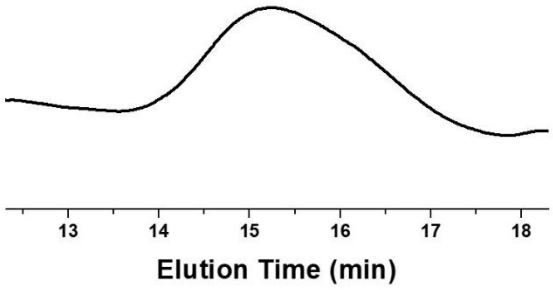


Figure S15. ^{1}H NMR spectrum and GPC curve of the copolymer (entry 5 in Table 1)

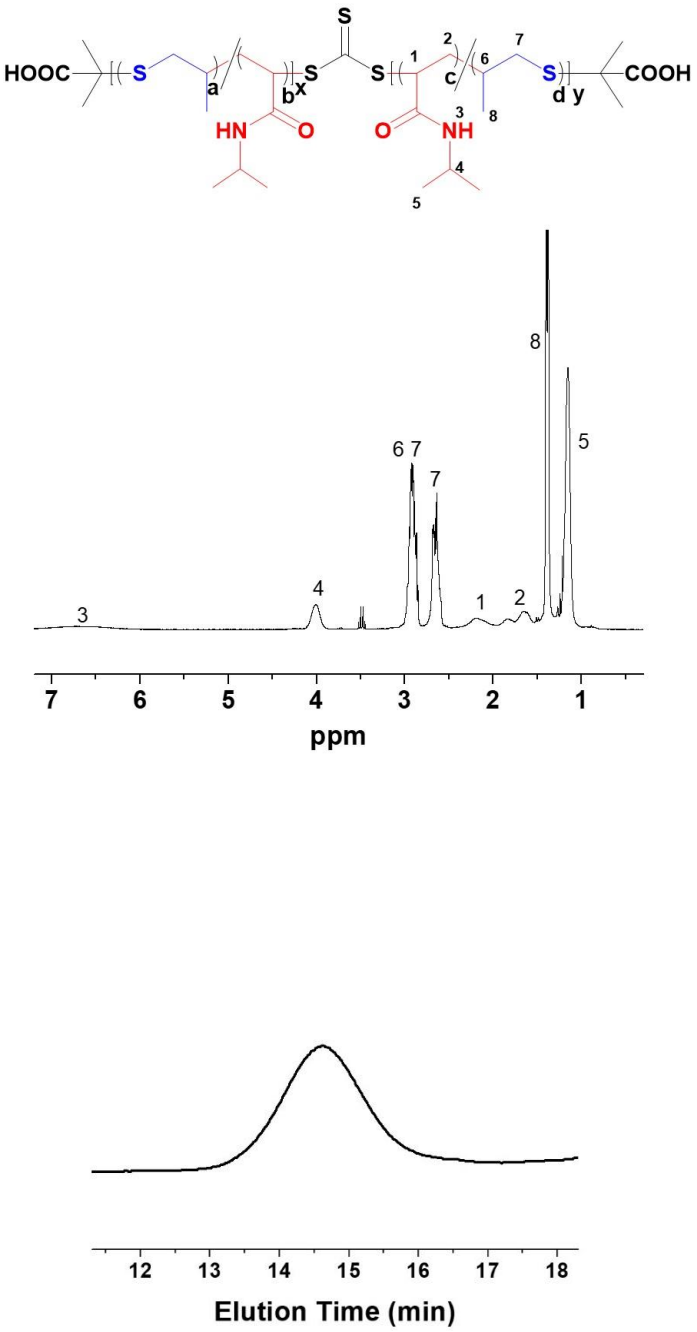


Figure S16. ^{1}H NMR spectrum and GPC curve of the copolymer (entry 6 in Table 1)

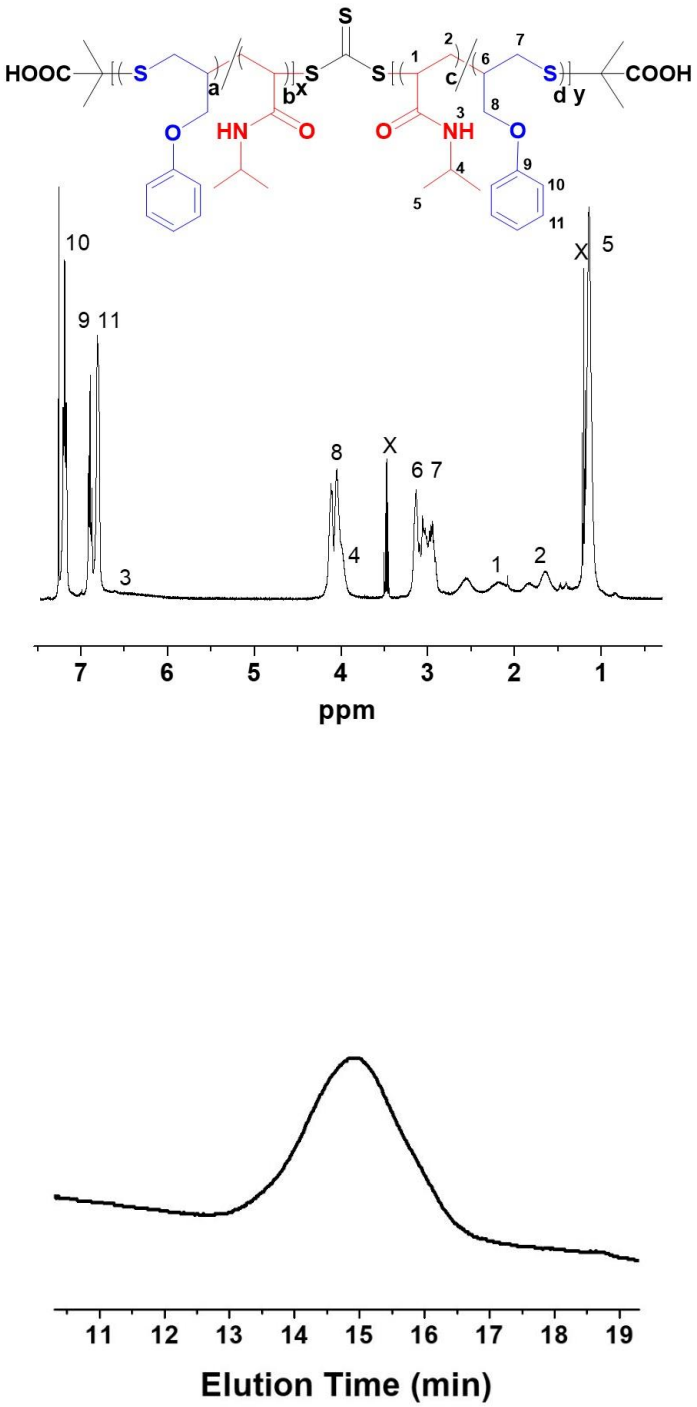


Figure S17. ^{1}H NMR spectrum and GPC curve of the copolymer (entry 7 in Table 1)

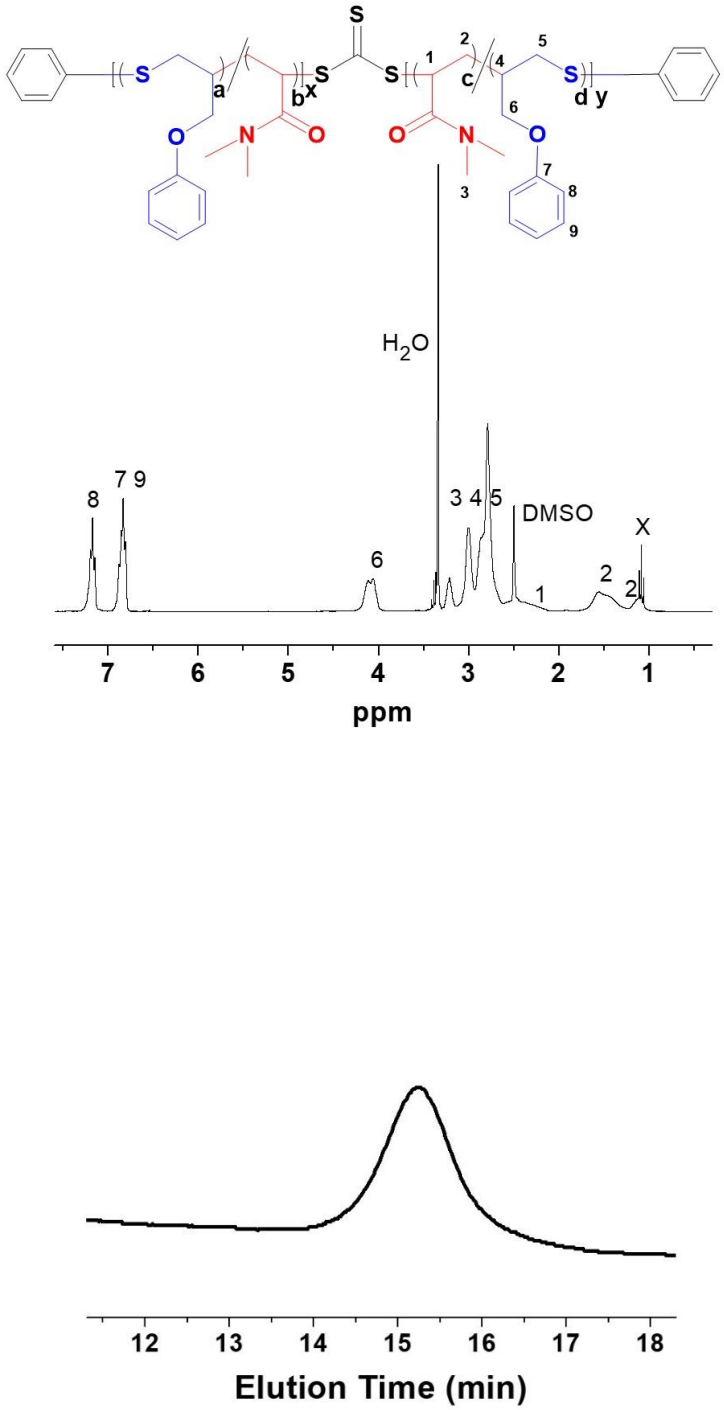


Figure S18. ^{1}H NMR spectrum and GPC curve of the copolymer (entry 8 in Table 1)

6. References

[1] A Gooch, N S Murphy, N H Thomson, A J Wilson, *Macromolecules*, **2013**, 46, 9634–9641
[2] Z Zhang, TY Zeng, L Xia, CY Hong, DC Wu, YZ You, *Nature communications,* **2018**, 9, 2577