Experimental Section

Materials. All reagents were used as received unless stated otherwise. Glycidyl methacrylate (GM, Acros 97%) was distilled before use. Dichloromethane (DCM) and N,N-dimethylformamide (DMF) were dried using CaH_2 and distilled. 2,2.-Azoisobutyronitrile (AIBN) and N-isopropylacrylamide (NIPAAm) were purified by recrystallization from methanol and hexane, respectively. S-1-Dodecyl-S'-(α,α'-dimethyl-α"-aceticacid)trithiocarbonate(TC)[1],2-cyanoprop-2-yl -4-cyanodithiobenzoate (CPD)[2], 4-(3-butenyl)styrene (BS)[3], phenyl 4-vinylbenzene sulfonate (PVBS)[4], 4-N-(4-vinylbenzyl)oxyethyl-N-methylaminopyridine (VEMAP)[5] and sodium prop-2-yne-1-sulfonate[6] were synthesized according to literature procedures.

Measurements. All ^{1}HNMR spectra were recorded on a Bruker AVANCEIII^{TM} 500 spectrometer (500 MHz) by using $CDCl_3$ or DMSO-d_6 as a solvent. GPC data was obtained from Waters GPC system equipped with a Waters 2414 refractive index (RI) detector, a 1515 isocratic HPLC pump, and two Waters HPLC columns. DMF (HPLC grade) with 0.1M LiBr was used as the solvent for polymers and eluent for GPC with a flow rate of 1 mL/min at 65 °C or THF (HPLC grade) with the same rate at 30 °C. The GPC instrument was calibrated with narrowly dispersed linear polystyrene standards. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F TEM instrument. Samples were prepared by dip-coating a 400 mesh carbon-coated copper grid from the dilute sample solution allowing the solvent to evaporate. GC/MS analyzed were obtained on an Agilent 6890 Series GC System with a Hewlett-Packard 5973 Mass Selective Detector (70 eV) using a HP-5MS fused silica capillary column (cross-linked 5% phenyl ethyl siloxane, 30 m ×0.25mm ID× 0.25μm film thickness) and argon as a carrier gas (1 mL/min). The split ratio was 1:50. The injector temperature was kept at 270 °C and detector was kept at 280 °C. The column temperature was held at 60 °C for 3 min, increased to 280 °C at a rate of 25 °C/min, and then kept at 280 °C for 5 min.

Synthesis

1. Synthesis of PGM backbone

GM (2mL), CPD (36mg), AIBN (2.4mg) and benzene (2mL) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 16 h. The mixture was diluted with DCM, precipitated into methanol 3 times and dried under vacuum at room temperature for 24 h. Yield = 1.67g (77%). GPC (PS standards, DMF as eluent): $M_n = 1.2\times 10^4$ g/mol, $M_w/M_n = 1.09$.

2. Synthesis of PGM-OH

PGM (1.0g), HF (20mL) and acetic acid (40mL) were mixed in a 250mL round-bottom flask. The reaction mixture was stirred and placed in an oil bath at 60 ^{o}C, followed by the slow addition of 61.5mL water over the course of 1.5 h. After stirring for 24 h, the solvent was removed on a rotary evaporator. The isolated polymer was precipitated from MeOH into diethyl ether 3 times and dried under vacuum at 25 ^{o}C for 24 h. Yield = 1.07 g (95%).

3. Synthesis of Poly(GM-g-TC)

TC (4.55g, 12.5mmol) and Oxalyl chloride (11.9mL, 125mmol) was mixed in 10 ml dry DCM under nitrogen and stirred at room temperature about 2 h. Excess reagents were then removed under vacuum, followed by the addition of PGM-OH (500mg in 40mL of dry DMF). The solvent was separated after reacted 24 h. Then, the isolated polymer was precipitated from DCM into MeOH 3 times and dried under vacuum at 25 ^{o}C overnight. Yield = 750mg (42%). ^{1}HNMR: RAFT modified ratio = 63%. GPC (PS standards, THF as eluent): $M_n = 3.6\times 10^4$ g/mol, $M_w/M_n = 1.12$.

4. Synthesis of Poly(GM-g-PVBS\BS)

Poly(GM-g-TC) (40mg), PVBS (4.1g), VPB (1.34mL), AIBN (1.29mg) and 1,4-dioxane (5.4mL) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 55 ^{o}C for 18 h. The polymer was precipitated from DCM into methanol 3 times and dried under vacuum. Yield = 715mg (12.6%). GPC (PS standards, DMF as eluent): $M_n = 6.9 \times 10^5$ g/mol, $M_w/M_n = 1.33$.

5. Synthesis of Poly(GM-g-PVBS\BS-g-NIPAAm)

PolyGM-g-PVBS\BS) (200mg), NIPAAm (1.49g), AIBN (0.18mg) and 1,4-dioxane (8.9mL) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 ^{o}C for 4.5 h. The polymer was precipitated from THF into ethyl ether 3 times and dried under vacuum. Yield = 446mg (16.5%). GPC (PS standards, DMF as eluent): $M_n = 1.2 \times 10^6$ g/mol, $M_w/M_n = 1.17$.

6. Synthesis of Poly(GM-g-VEMAP\BS\St)

Poly(GM-g-TC) (40mg), VEMAP (1.27g), BS (0.54 mL), Styrene (0.54 mL), AIBN (1.29mg), 1,4-dioxane (2.4mL) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 ^{o}C for 13.5 h. The polymer was precipitated from DCM into ethyl ether 3 times and dried under vacuum. Yield = 390mg (15.4%). GPC (PS standards, DMF as eluent): $M_n = 1.6 \times 10^5$ g/mol, $M_w/M_n = 1.24$.

7. Synthesis of Poly(GM-g-VEMAP\BS\St-g-NIPAAm) (M4)

Poly(GM-g-VEMAP\BS\St) (50mg), NIPAAm (1.1g), AIBN (0.13g), 1,4-dioxane

(6.6mL) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 3 h. The polymerization was precipitated from THF into ethyl ether 3 times and dried under vacuum. Yield = 100mg (5%). GPC (PS standards, DMF as eluent): $M_n = 1.2 \times 10^6$g/mol, $M_w/M_n= 1.10$.

8. Intramolecular crosslinking of Poly(GM-g-PVBS\BS-NIPAAm) and Poly(GM-g-VEMAP\BS\St-g-NIPAAm) (M2)

Poly(GM-g-PVBS\BS-g-NIPAAm) or Poly(GM-g-VEMAP\BS\St-g-NIPAAm) (50mg) was dissolved in 50 ml DCM under nitrogen. Grubbs' first generation catalyst (4mg) was added into the reaction solution and then was stirred at room temperature under nitrogen for 12 h. Ethyl vinyl ether (0.1mL) was added to the reaction mixture to quench the catalyst. The solvent was then evaporated and cross-linked polymers were precipitated from DCM into ethyl ether 3 times.

9. Deprotection and acidify of cross-linked Poly(GM-g-PVBS\BS-NIPAAm) (M1)

Cross-linked Poly(GM-g-PVBS\BS-NIPAAm) (370mg) were dissolved in 44 mL THF:MeOH=10:1(v\v), 0.5mL of 5M KOH was added. The mixture was stirred at 50 °C for 16 h. The solvent was then evaporated and copolymers were precipitated from THF into ethyl ether. Then the copolymers were acidified in 15mL H_2O with 0.5 mL 9 M H_2SO_4 at room temperature for 12 h. The mixture was purified by dialysis using a semipermeable membrane (molecular weight cutoff, 3500).

10. Synthesis of Poly(GM-g-VBC\St)

Poly(GM-g-TC) (10mg), 1-(chloromethyl)-4-vinylbenzene(VBC) (0.56 mL), Styrene (0.23 mL), AIBN (0.32 mg), 1,4-dioxane (0.78 mL) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 9 h. The polymer was precipitated from DCM into MeOH 3 times and dried under vacuum. Yield = 59mg (6.25%). GPC (PS standards, THF as eluent): $M_n =2.1 \times 10^5$g/mol, $M_w/M_n= 1.39$.

11. Synthesis of Poly(GM-g-VBC\St-g-NIPAAm)

Poly(GM-g-VBC\St) (10mg), NIPAAm (487mg), AIBN (0.06mg), 1,4-dioxane (2.9mL) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 5 h. The polymer was precipitated from THF into ethyl ether 3 times and dried under vacuum. Yield = 70mg (12%). GPC (PS standards, THF as eluent): $M_n = 3.0 \times 10^5$g/mol, $M_w/M_n= 1.13$.

12. Synthesis ofPoly(GM-g-VBC\St-g-NIPAAm)–N_3

Poly(GM-g-VBC\St-g-NIPAAm) (50mg) and NaN_3 (19.5mg, 0.3mmol) dry DMF

(5mL) were mixed in a reaction vessel. The mixture was stirred at 50 ^{o}C for 48 h. Then, the mixture was purified by dialysis using a semipermeable membrane (molecular cutoff, 3500).

13. Synthesis of M3

Poly(GM-g-VBC\St-g-NIPAAm)–N_3 (10mg), sodium prop-2-yne-1-sulfonate (2.84mg, 0.02mmol), $CuSO_4 \cdot 5H_2O$ (5mg,0.02mmol), sodium ascorbate (19.8mg, 0.1mmol) were mixed in 3mL DMF\H_2O(1:2) under N_2protection. The reaction mixture was stirred and placed in an oil bath at 60 ^{o}C for 24 h. And then 0.1 mL of 9 M H_2SO_4 was added to the mixture for 5 h to generate M3. The mixture was purified by dialysis using a semipermeable membrane (molecular cutoff, 3500).

Reference:

1. J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.
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5. B. Zhao, X. M. Jiang, D. J. Li, X. G. Jiang and H. G. O'Lenick, *J Polym Sci Pol Chem*, 2008, **46**, 3438-3446.
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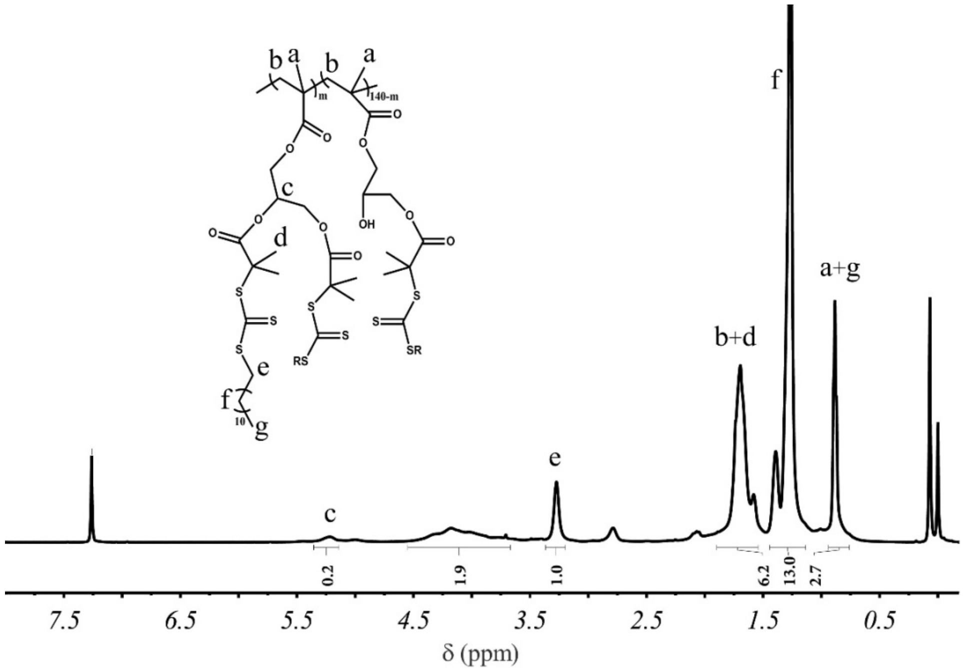

Fig.S1. ^{1}HNMR ($CDCl_3$) spectrum of RAFT modified PGM.

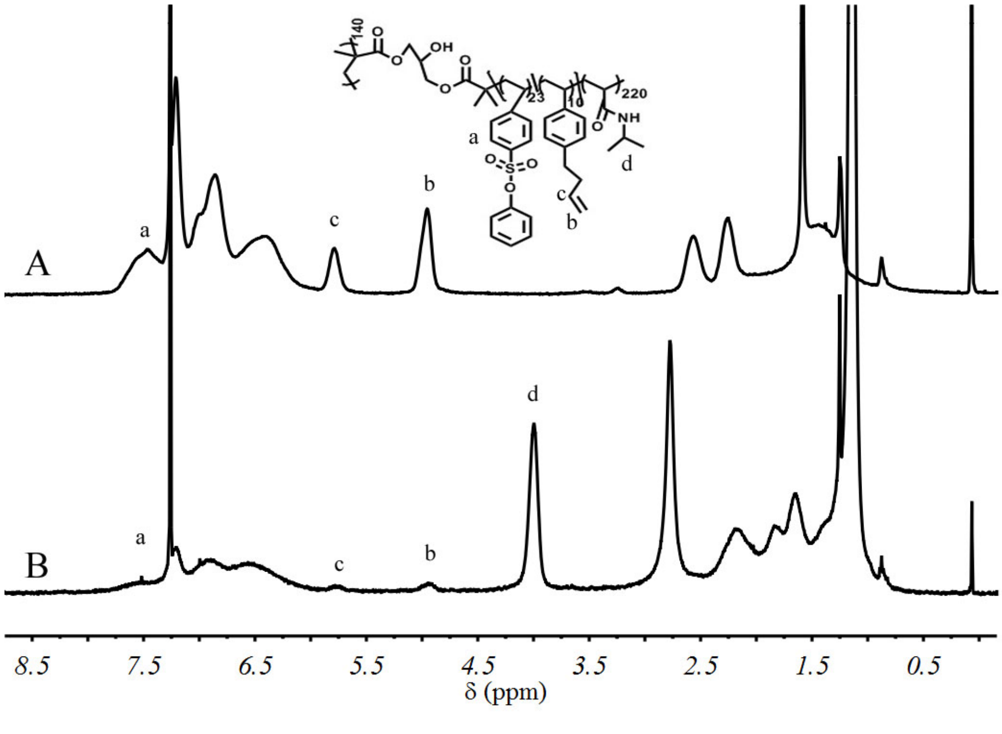

Fig.S2. ^{1}HNMR ($CDCl_3$) spectra of Poly(GM-g-PVBS\BS) (A), Poly(GM-g-PVBS\BS-g-NIPAAm) (B).

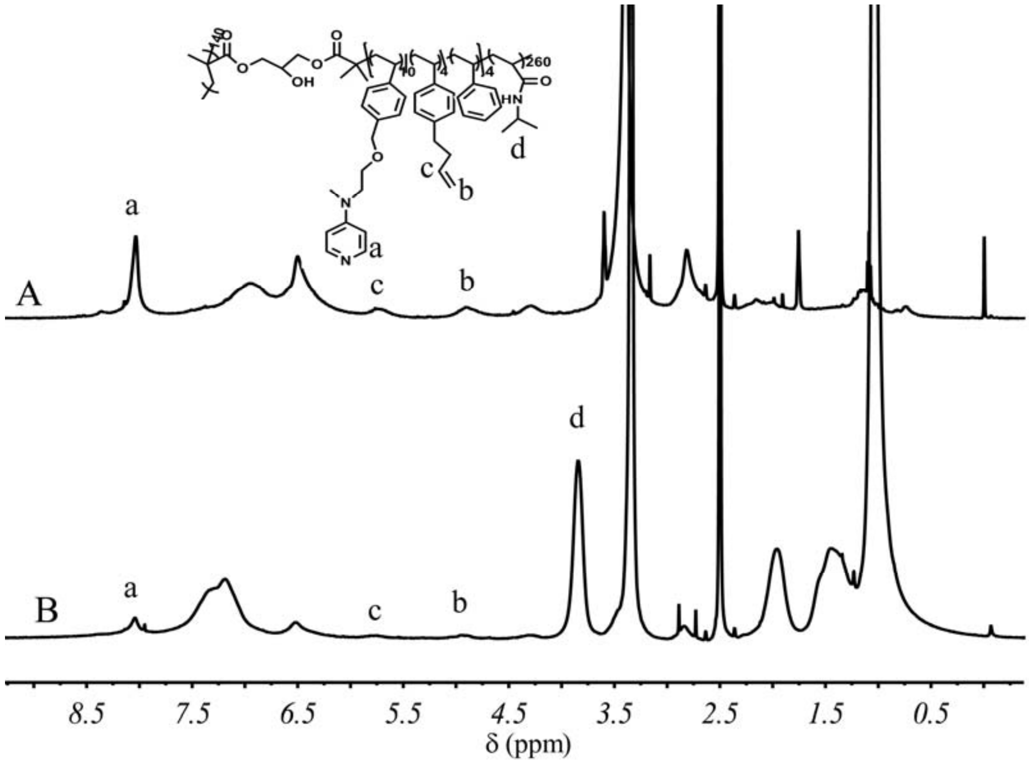

Fig.S3. ^{1}HNMR ($CDCl_3$) spectra of Poly(GM-g-VEMAP\BS\St) (A), Poly(GM-g-VEMAP\BS\St-g-NIPAAm) (B).

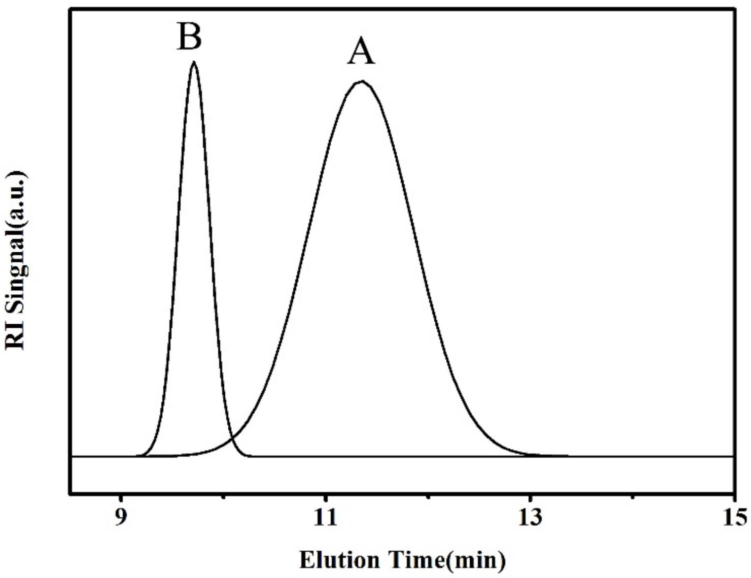

Fig.S4. GPC traces of Poly(GM-g-PVBS\BS) (A), Poly(GM-g-PVBS\BS-g-NIPAAm) (B).

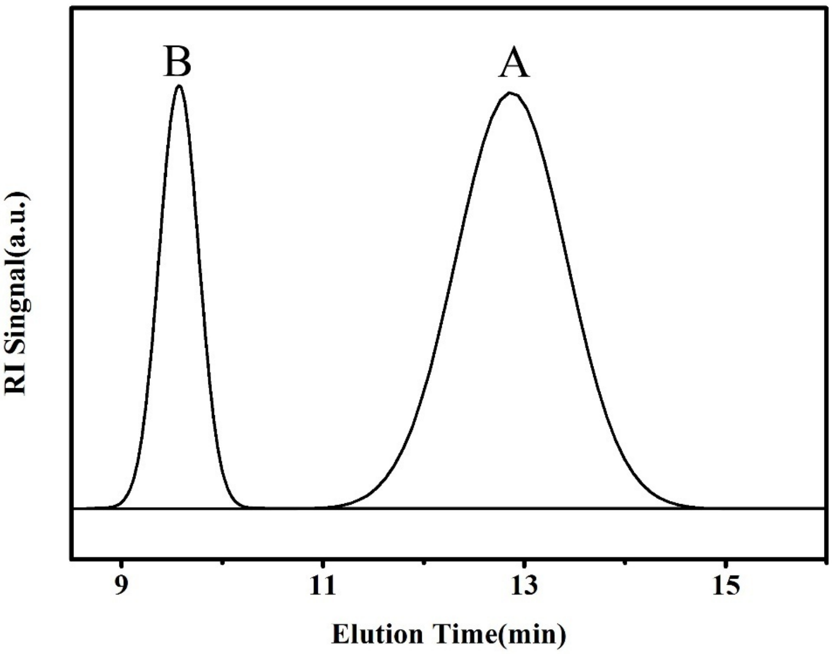

Fig.S5. GPC traces of Poly(GM-g-VEMAP\BS\St) (A), Poly(GM-g-VEMAP\BS\St-g-NIPAAm) (B).

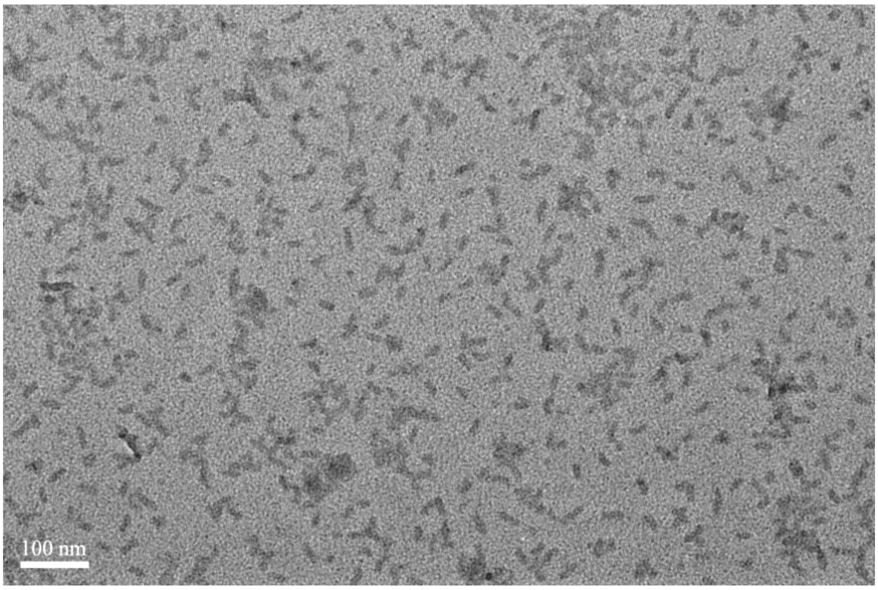

Fig.S6. TEM characterization of base-containing CCBCs.