Supporting Information

Reversible Breakage of C-S Bond: Function of DL-Methionine in PET-RDRP Catalyzed by Zinc Protoporphyrin

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1. Experimental section.

Materials

DL-Methionine (99%, J&K), protoporphyrin (PTP, 92%, Laboratory made), *N*,*N*-dimethylformamide (DMF, 99.9%, Sigma-Aldrich), zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 99%, Sigma-Aldrich), methanol (99.5%, Sigma-Aldrich), *N*-isopropyl acrylamide (NIPAm, 99%, J&K), acrylamide (AM, 99%, J&K), *N*,*N*-Dimethylacrylamide (DMA, 99%, Leyan), tert-Butyl acrylate (tBA, 99%, J&K), butyl acrylate (BA, 99%, Kermel), methyl methacrylate (MMA, 99%, Kermel), acrylic acid (AA, industrial-grade), sodium hydroxide (NaOH, 96%, Yong Da Chemical), dimethyl sulfoxide (DMSO, 99%, Sigma-Aldrich), ascorbic acid (AH_2, 99%, Kermel), sodium trifluoroacetate (NaTFA, 99%, aladdin), tetrahydrofuran (THF, 99%, aladdin), acetone (99%, aladdin) and dichloromethane (DCM, 99%, aladdin).

Characterization

Fourier transform-infrared (FT-IR) spectra were recorded on an FT-IR Nicole spectrometer over the range of 3480-485 cm^{-1}. UV-Vis absorption spectra were acquired on Shimadzu UV-2450 spectrometer. Fluorescence spectra were recorded on F-4500 Fluorescence spectrophotometer. ^1H NMR spectroscopy was conducted on a Bruker AV 400 spectrometer with $Si(CH_3)_4$ as an internal standard. Gel permeation chromatography (GPC) measurements were carried out by an Agilent 1100 series equipped with an RI-

G1362A RI detector and a PL gel Mixed-C column using DMF as the mobile phase at a flow rate of 1 mL min^{-1} at 25 °C and carried out by an Agilent 1260 series equipped with an RI-G7162A RI detector and a PL aquagel-OH Mixed-M column using 0.05M Na_2SO_4 aqueous solution as the mobile phase at a flow rate of 1 mL min^{-1} at 30 °C. The EMX-9.5/12 X-band spectrometer was used to carry out the Electron Paramagnetic Resonance (EPR) experiments, under magnetic field modulation, at 100 kHz, and the tested power intensity was 20 mW. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry analysis was studied with a Bruker Reflex II time-of-flight mass spectrometer (Bruker-Franzen Analytik, Bremen, Germany).

2. The preparation of ZnPTP.

PTP (28.00 mg) was dissolved in DMF (10.00 mL) and stirred at 140 °C under nitrogen atmosphere in 25.00 mL three-necked flask, and then the saturated methanol solution with $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.20 g, 0.92 mmol, 10.00 mL) was dropped into the reaction solution. Next, the reaction liquid was stirred for 2 h without light. After, the product was concentrated under reduced pressure and washed by deionized water (100 mL × 3). The black and red product (ZnPTP) was centrifuged and collected by vacuum drying. Yield: 83%.

3. PET-RDRP process of DMSO as solvent.

For photo-catalyst-mediated RDRP process, a certain proportion of monomer, control agent, photocatalyst and DMSO were added into a 4 mL glass vial. The glass vial was sealed with a rubber septum without deoxygenation. The reaction mixture was then

irradiated under green LED light (λmax = 577 nm, 6 W, intensity = 0.126 mW cm^{-2}) at 25 °C. After irradiation, aliquots of the reaction mixtures were withdrawn to measure monomer conversion rate and number-average molecular weights ($M_{n,^1H\ NMR}$) by ^{1}H NMR and polymer molecular weight distributions were measured by GPC. The reaction conditions for control studies where DL-Methionine is omitted entirely were the same as those for the process of PET-RDRP with added DL-Methionine.

4. PET-RDRP process of H_2O as solvent.

To improve the solubility of ZnPTP in aqueous solution, a certain proportion of sodium hydroxide was added to deionized water. Photocatalyst and sodium hydroxide aqueous solution were added into a 4 mL glass vial. After ultrasonic dissolution, the mixture was mixed with hydrochloric acid solution until the pH was near neutral. Then a certain proportion of monomer and control agent were added into a 4 mL glass vial. Due to the poor stability of ascorbic acid over time under aqueous conditions, we only added ascorbic acid (AH_2) as singlet oxygen quencher to the reaction mixture prior to the start of polymerization. The glass vial was sealed with a rubber septum without deoxygenation. The reaction mixture was then irradiated under green LED light (λmax = 577 nm, 6 W, intensity = 0.126 mW cm^{-2}) at 25 ^{o}C. After irradiation, aliquots of the reaction mixtures were withdrawn to measure monomer conversion rate and number-average molecular weights ($M_{n,^1H\ NMR}$) by ^{1}H NMR and dispersity were measured by GPC. The reaction conditions for control studies where DL-Methionine is omitted entirely were the same as those for the process of PET-RDRP with added DL-Methionine.

5. EPR analysis of PET-RDRP polymerization.

200 equiv of NIPAm, 1 equiv of DL-Methionine and 0.16 equiv of ZnPTP and a certain amount of DMSO were added into a 4 mL glass vial. The glass vial was sealed with a rubber septum without deoxygenation. The reaction mixture was then added into a EPR sample tube, also without deoxygenation. Under green light irradiation (λmax = 577 nm, 6 W) for certain time of the sample.

Calculation equation for g-value.

$$g = \frac{hv}{\beta H}$$

Where h is the Planck constant (6.62607015×10^{-34} J·s), v is the microwave frequency (9.823917 GHz), β is the Bohr magneton moment value (9.274×10^{-21} erg/Gs, 1erg = 10^{-7}J), H is the magnetic field intensity (3.5 KGs in Fig.3a).

6. MALDI-TOF MS analysis of PET-RDRP process.

The PNIPAm samples (4 mg mL^{-1} in DCM), DCTB matrices (30 mg mL^{-1} in acetone) and sodium trifluoroacetate solution (19 mg mL^{-1} in THF) were all prepared for MALDI-TOF MS analysis. The above solutions were mixed in a ratio of 10:10:1 (PNIPAm:matrix:cationizing salt), and 0.5 μL of the final solution was deposited onto the MALDI sample target and was allowed to dry at room temperature and ambient atmosphere.

PAA samples (1 μg/μl in acetone and water) and sinapinic acid matrix (20 μg/μl in acetone) were prepared for MALDI-TOF MS analysis. Mix the above 1 μl sample solution and 1 μl matrix solution, deposit 1 μl of the final solution onto the MALDI

sample target, and dry at room temperature and ambient atmosphere.

7. Supplementary Figures

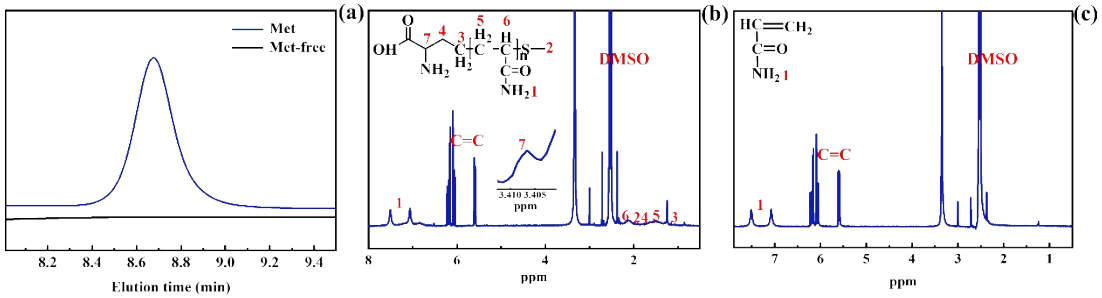

Fig. S1. PET-RDRP of AM mediated by ZnPTP in the presence (Met) or absence (Met-free) of DL-Methionine. (a) GPC curves of PAM; ^{1}H NMR spectrum of PAM (b) in the presence and (c) in the absence of DL-Methionine.

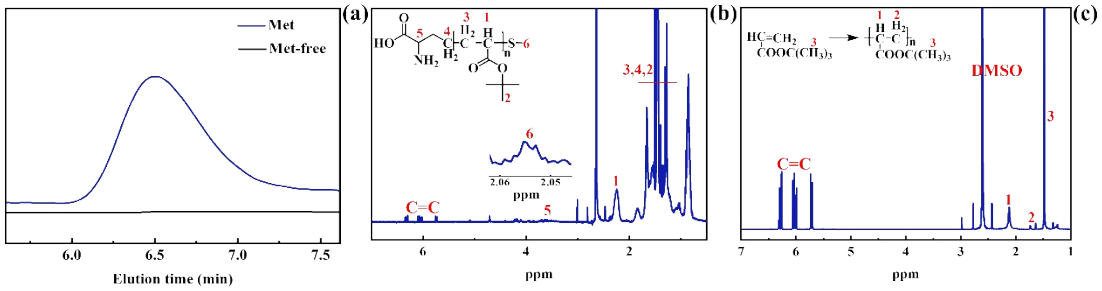

Fig. S2. PET-RDRP of tBA mediated by ZnPTP in the presence (Met) or absence (Met-free) of DL-Methionine. (a) GPC curves of PtBA; ^{1}H NMR spectrum of PtBA (b) in the presence and (c) in the absence of DL-Methionine.

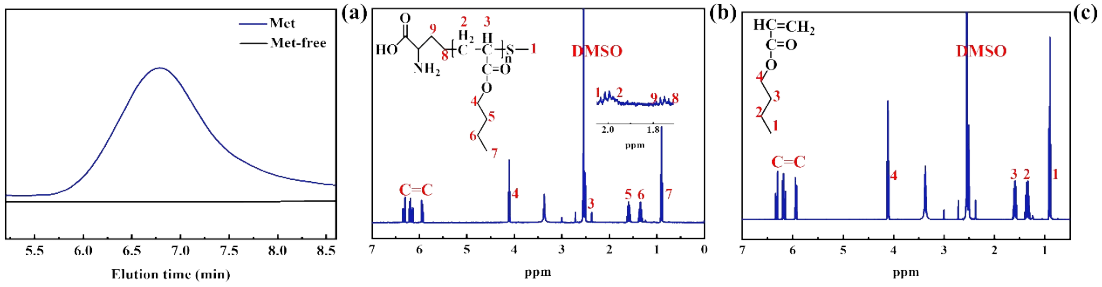

Fig. S3. PET-RDRP of BA mediated by ZnPTP in the presence (Met) or absence (Met-

free) of DL-Methionine. (a) GPC curves of PBA; ^{1}H NMR spectrum of PBA (b) in the presence and (c) in the absence of DL-Methionine.

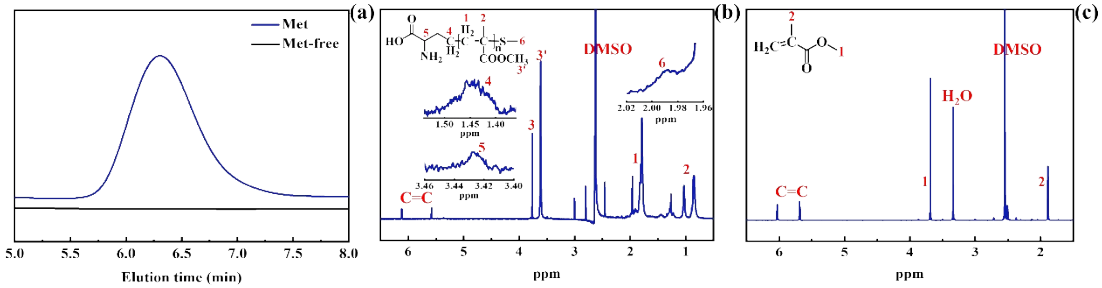

Fig. S4. PET-RDRP of MMA mediated by ZnPTP in the presence (Met) or absence (Met-free) of DL-Methionine. (a) GPC curves of PMMA; ^{1}H NMR spectrum of PMMA (b) in the presence and (c) in the absence of DL-Methionine.

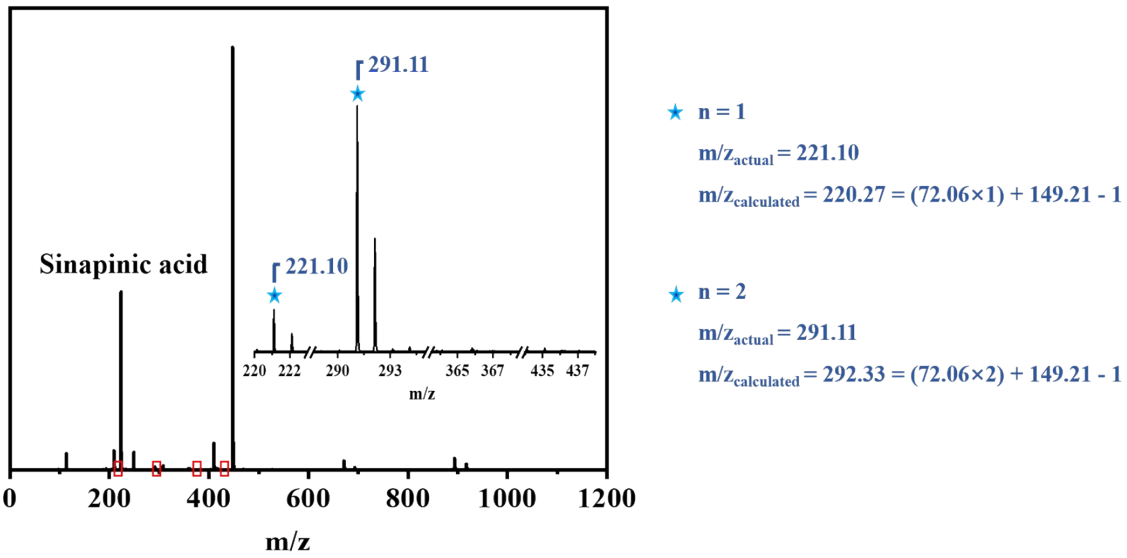

Fig. S5. MALDI-TOF MS of low-conversion PAA mediated by DL-Methionine.

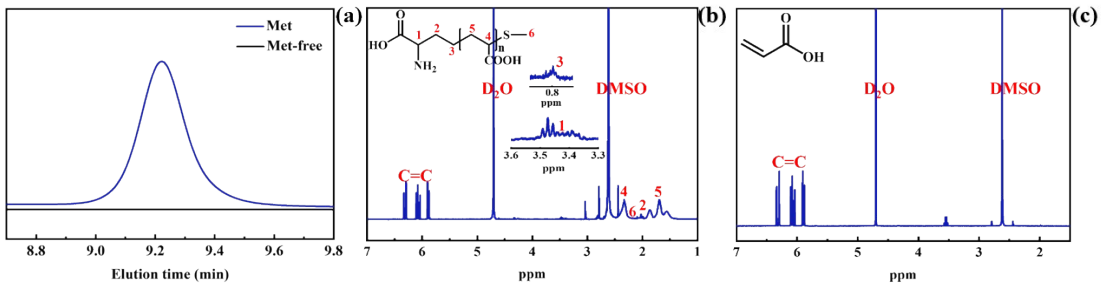

Fig. S6. ^{1}H NMR spectrum of PAA (a) in the presence and (b) in the absence of DL-Methionine.

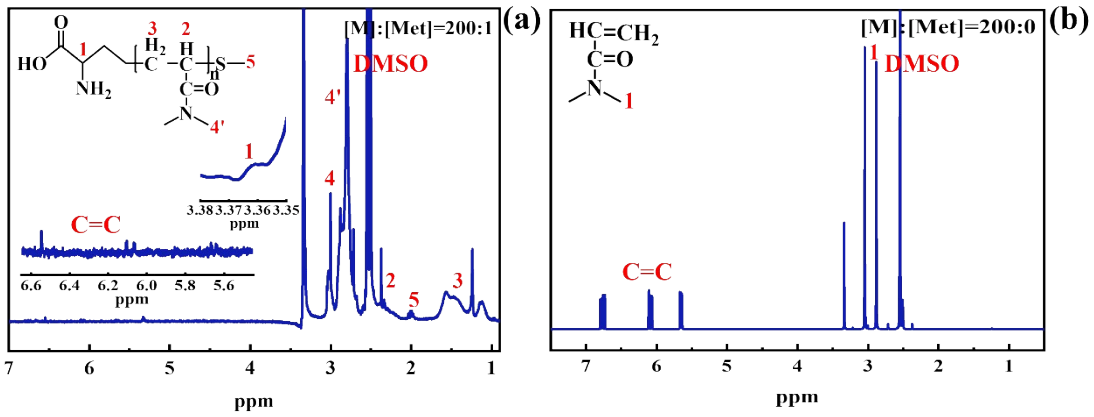

Fig. S7. ^{1}H NMR spectrum of 200 ratios of PDMA (a) in the presence and (b) in the absence of DL-Methionine.

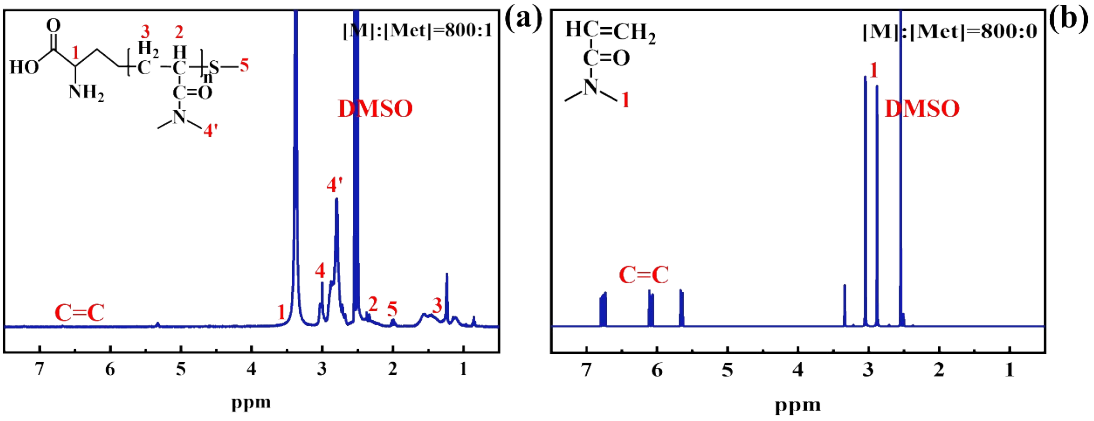

Fig. S8. ^{1}H NMR spectrum of 800 ratios of PDMA (a) in the presence and (b) in the absence of DL-Methionine.

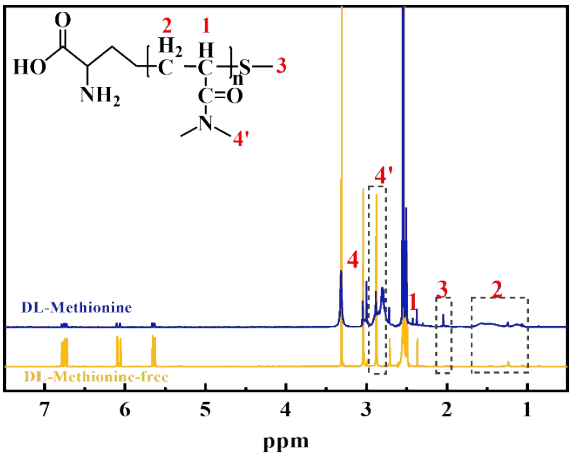

Fig. S9. ^{1}H NMR spectrum of low molecular weight PDMA in the presence and in the absence of DL-Methionine.

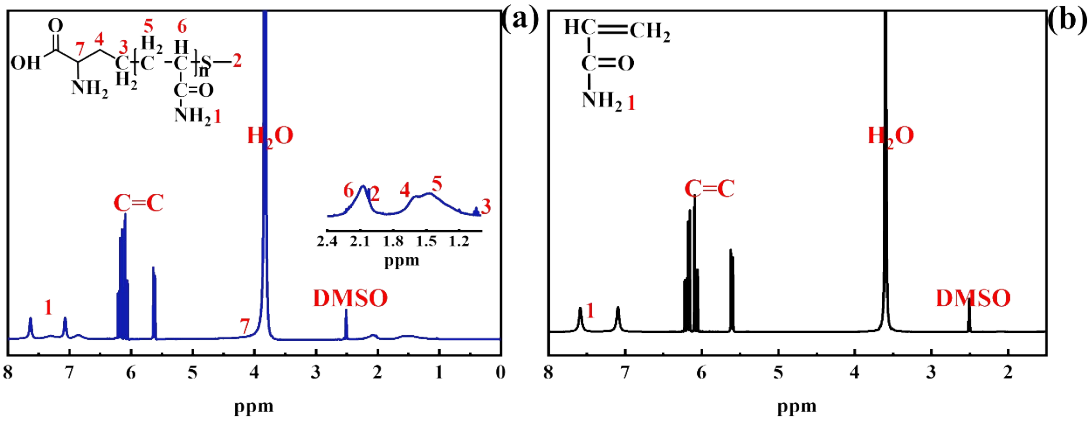

Fig. S10. ^{1}H NMR spectrum of 800 ratios of PAM (a) in the presence and (b) in the absence of DL-Methionine.

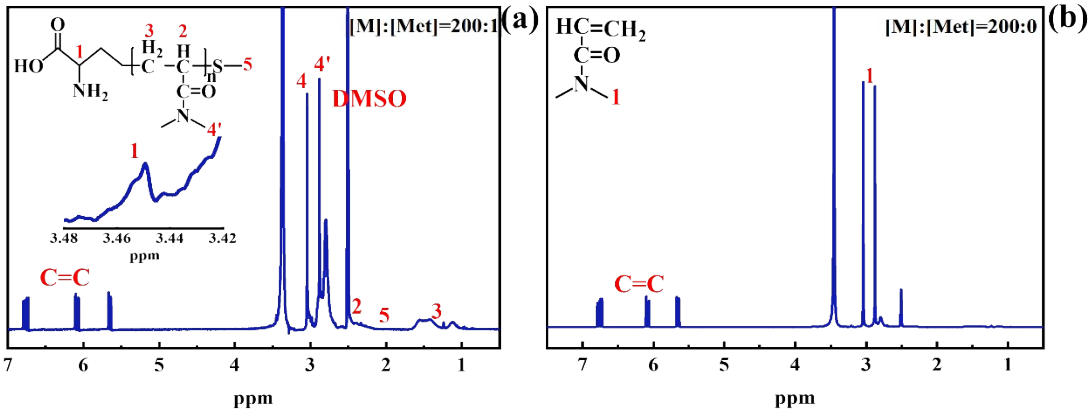

Fig. S11. ^{1}H NMR spectrum of 200 ratios of PDMA (a) in the presence and (b) in the absence of DL-Methionine.

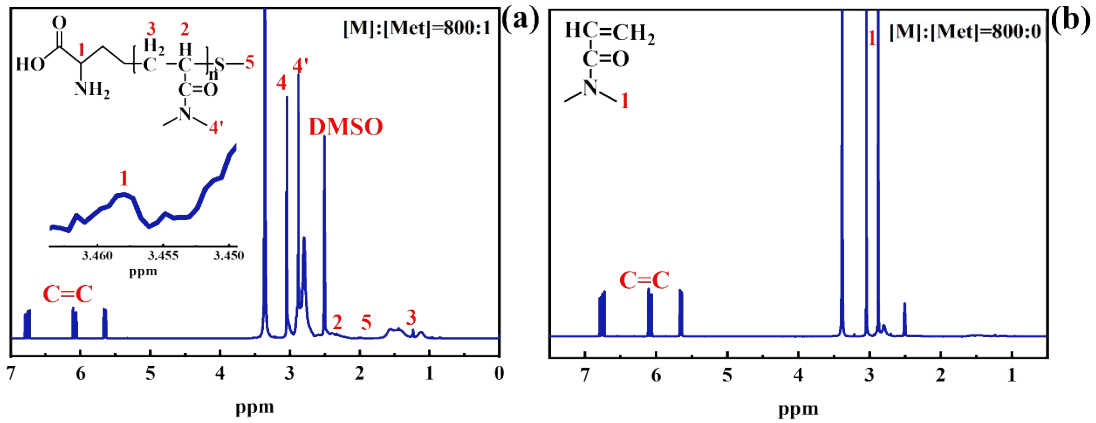

Fig. S12. ^{1}H NMR spectrum of 800 ratios of PDMA (a) in the presence and (b) in the absence of DL-Methionine.

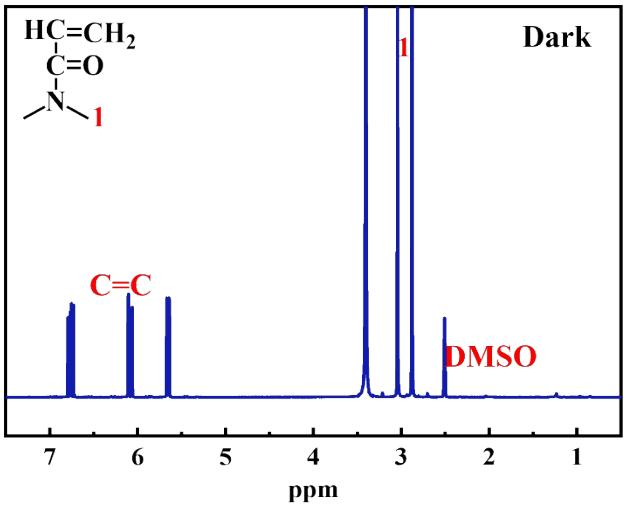

Fig. S13. ^{1}H NMR spectrum of PDMA mediated by ZnPTP with a mole ratio of DMA:DL-Methionine = 200:1 under dark condition.