Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Thiolactone-Maleimide: A Functional Monomer to Synthesize Fluorescent Aliphatic Poly(amide-imide) with Excellent Solubility via In Situ PEGylation

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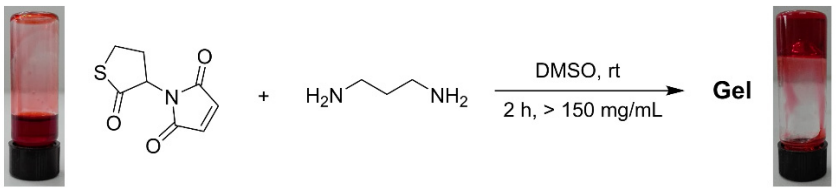
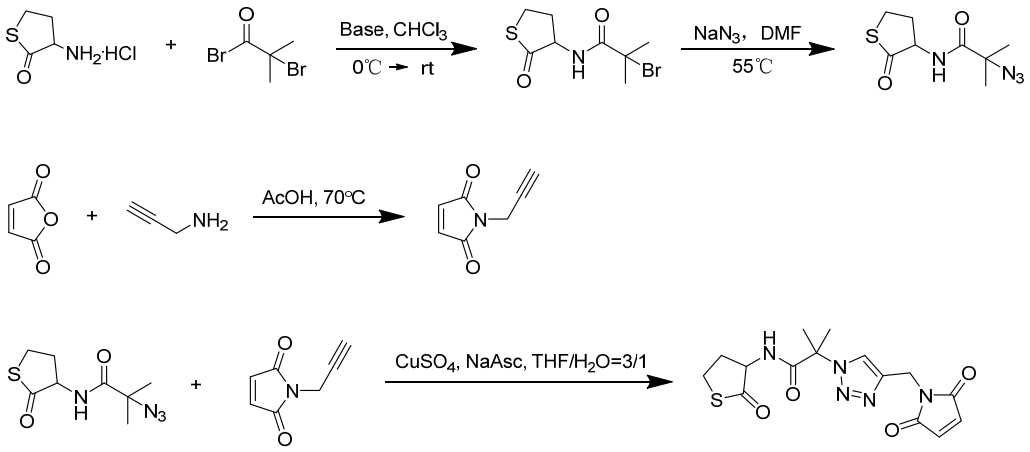
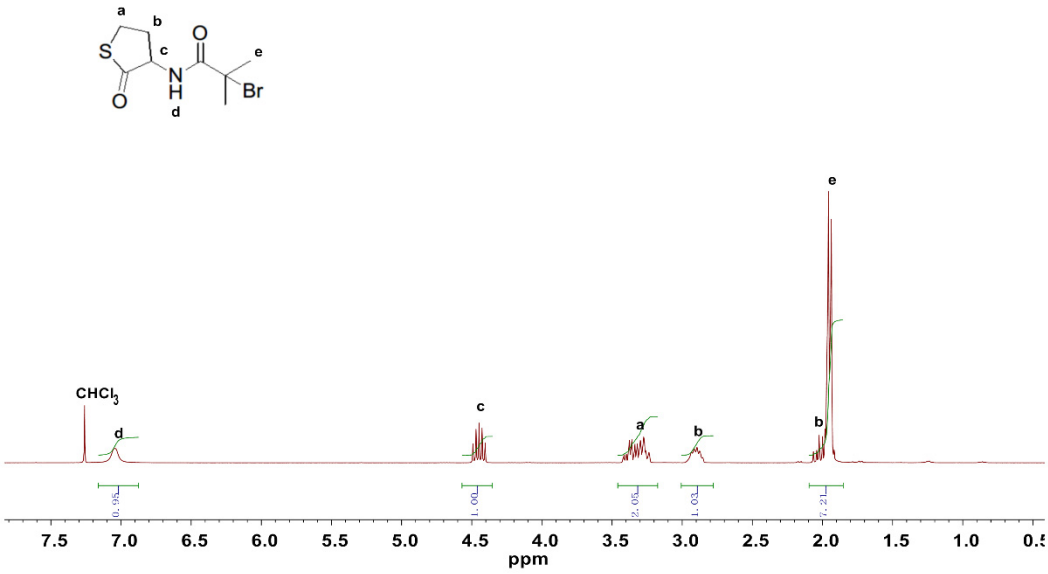


Figure S1. Gel formation during the reaction between thiolactone-maleimide (without a linker) and 1,3-diaminopropane in DMSO.



Scheme S1. Synthesis of Thiolactone-Maleimide Functional Monomer.

¹H NMR (300 MHz, Chloroform- *d*) δ 7.04 (s, 1H), 4.45 (dt, *J* = 13.0, 6.5 Hz, 1H), 3.47 – 3.20 (m, 3H), 2.89 (dt, *J* = 12.0, 6.4 Hz, 1H), 2.11 – 1.87 (m, 10H).



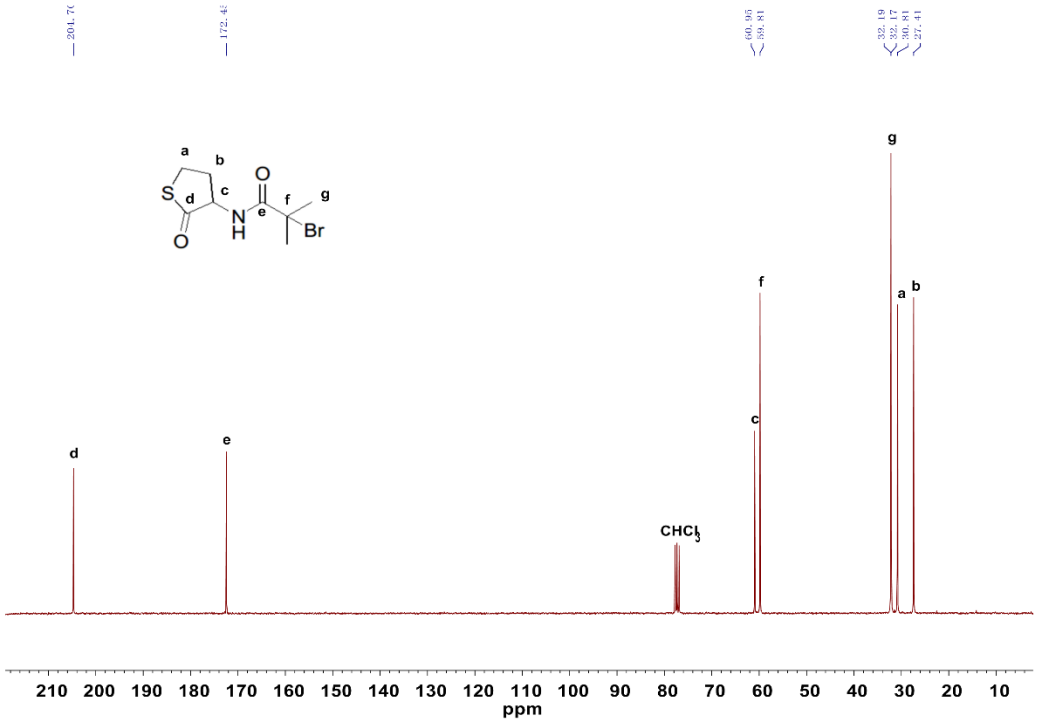
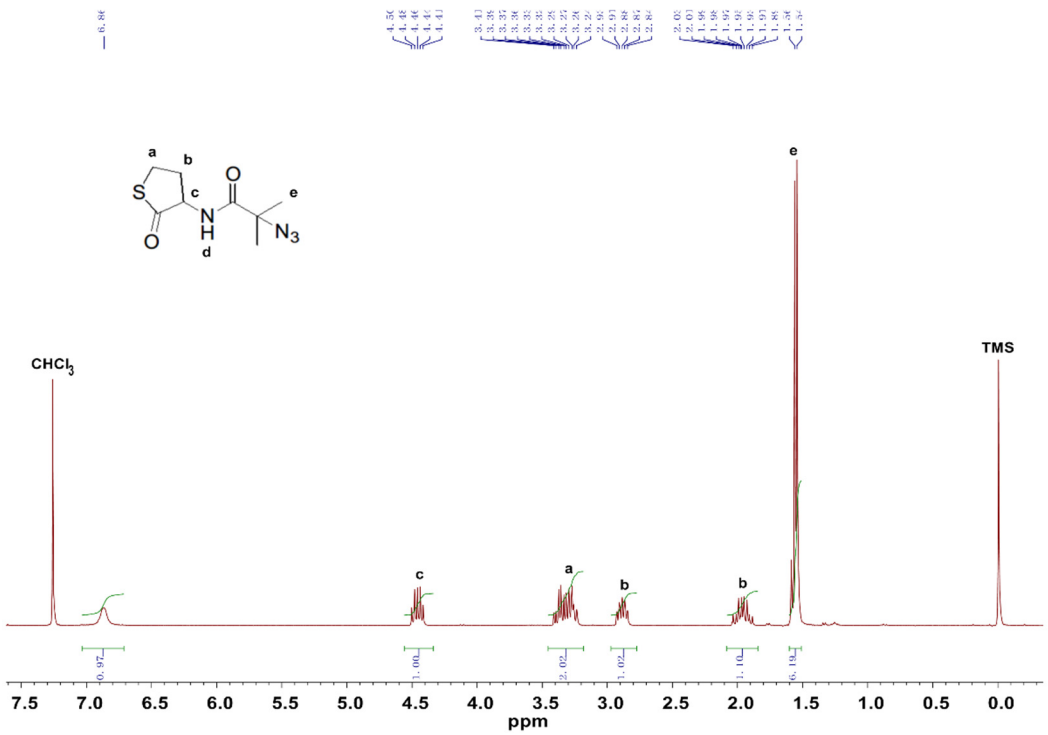


Figure S2. ^{1}H and ^{13}C NMR spectra of bromo-functionalized thiolactones in $CDCl_3$.



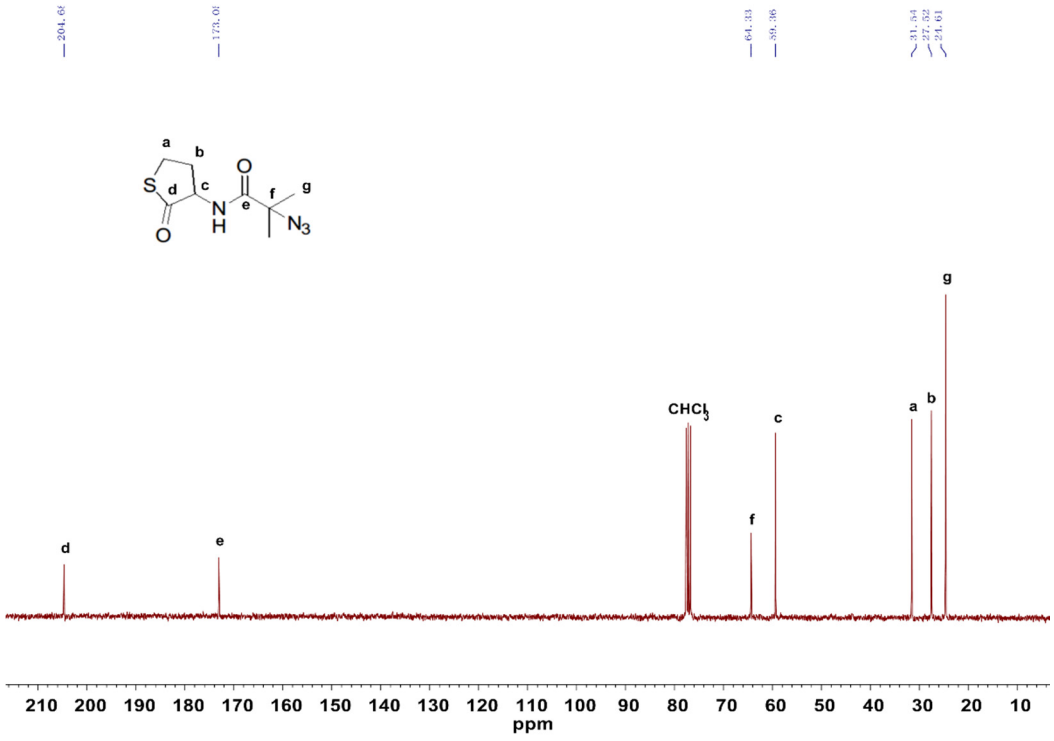
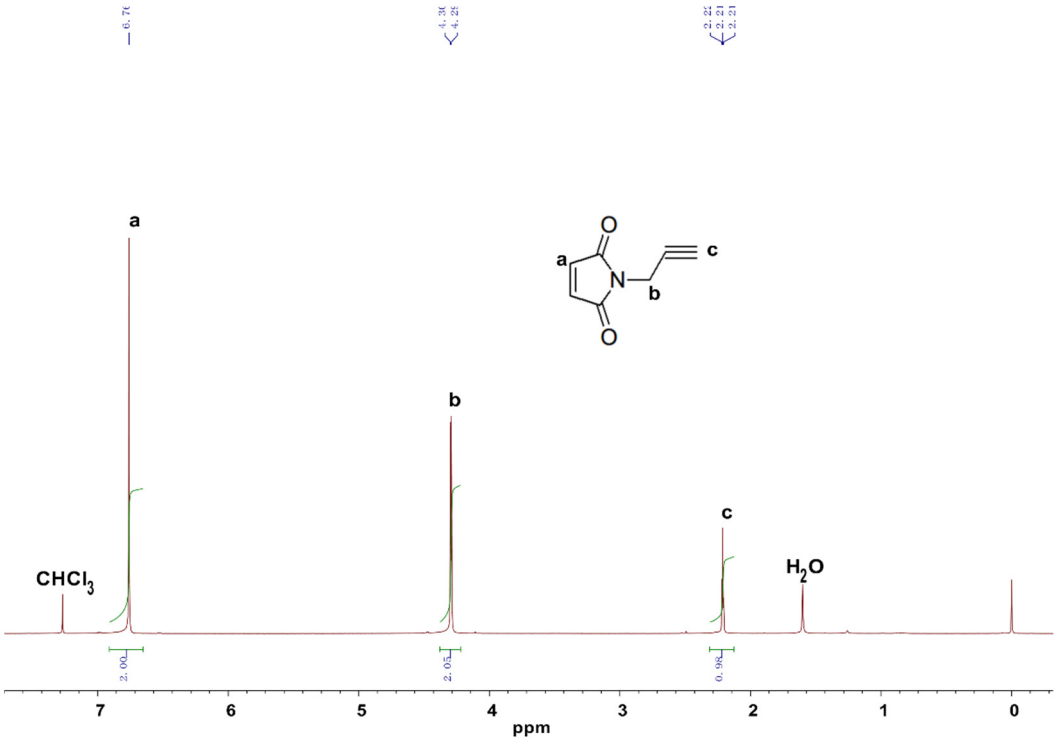


Figure S3. ^{1}H and ^{13}C NMR spectra of azide-functionalized thiolactones in $CDCl_3$.



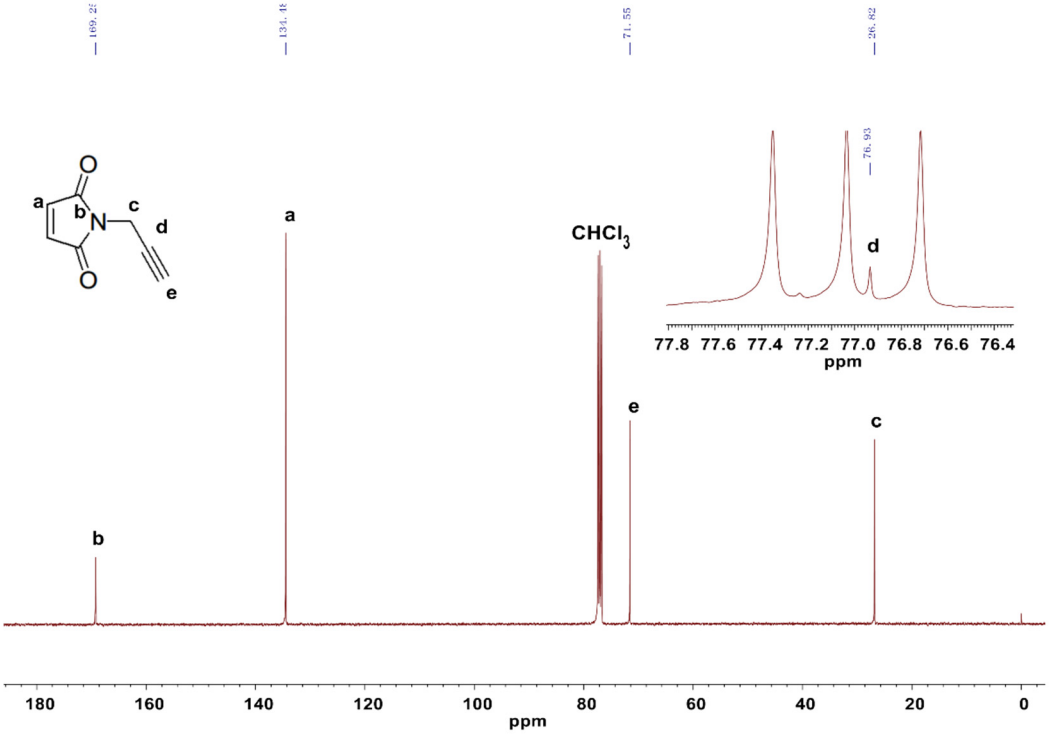
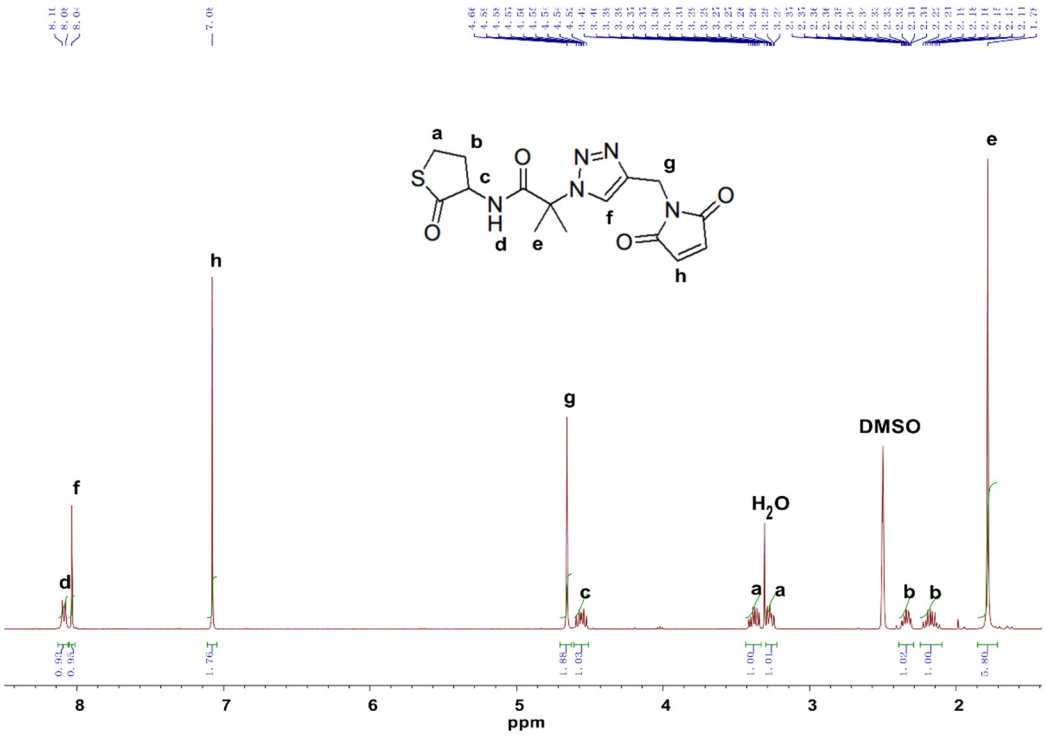


Figure S4. ^{1}H and ^{13}C NMR spectra of *N*-propargylmaleimide in $CDCl_3$.



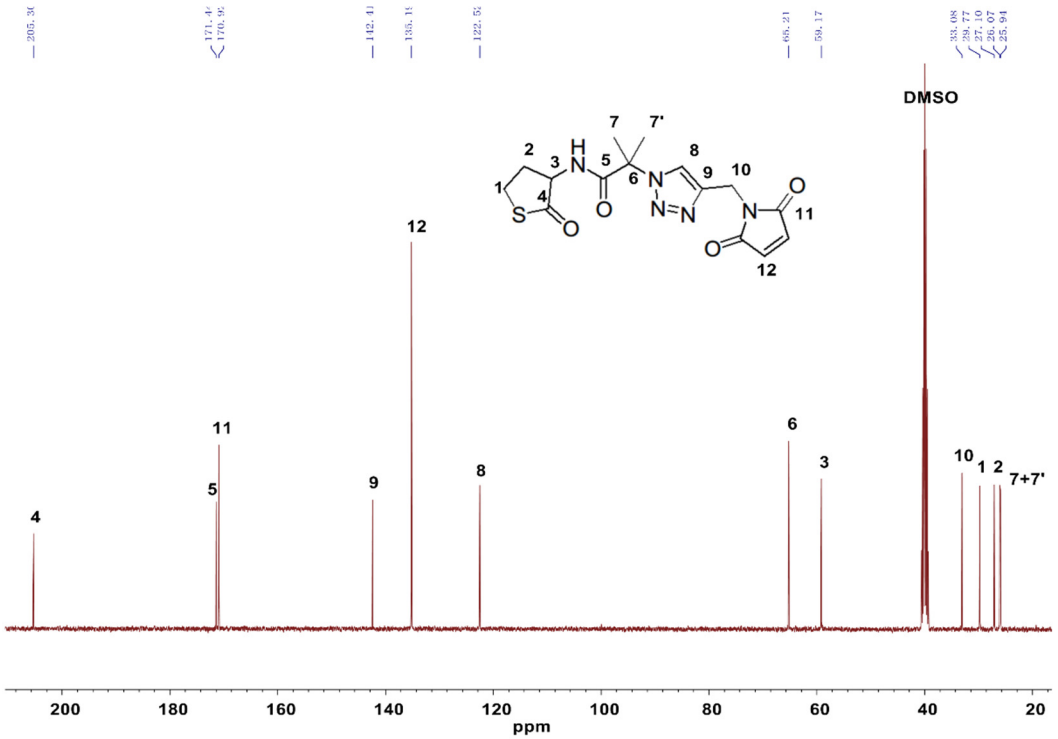


Figure S5. ^{1}H and ^{13}C NMR spectra of thiolactone-momaleimide monomer in DMSO-d_6.

Polymerization of thiolactone-maleimide and monoamine. Thiolactone-maleimide functional monomer (36.3 mg, 0.1 mmol) was dissolved in 1.0 mL DMSO and the solution was purged with argon for 10 min. Then, n-butylamine (7.3 mg, 0.1 mmol) was added, and the mixture immediately turned from slight yellow to deep red. The reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy.

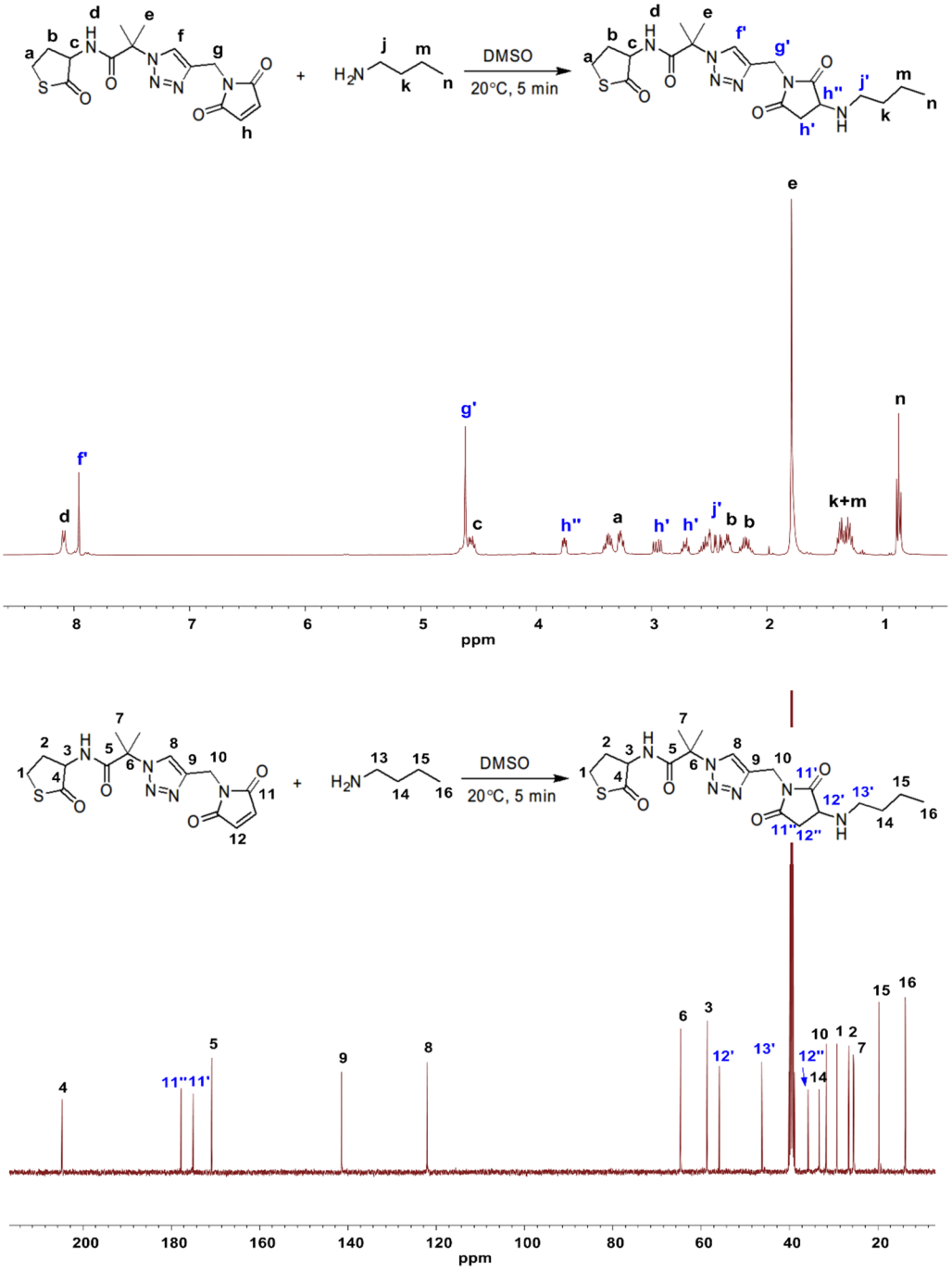


Figure S6. ^{1}H and ^{13}C NMR spectra of reaction between thiolactone-momaleimide monomer and *n*-butylamine.

As shown in Figure S6, *n*-butylamine selectively and quantitatively reacted with maleimide unit and obtained complete conversion within 5 min, while no ring-opening reaction of thiolactone unit was detected. Also, no additional new carbon signals were observed in ^{13}C NMR spectrum except the carbons of the product, precluding the possible by-product from the Michael addition between the formed secondary amine and the maleimide unit.

Polymerization of thiolactone-maleimide and diamine. Thiolactone-maleimide functional monomer (36.3 mg, 0.1 mmol) was dissolved in 1.0 mL DMSO and the solution was purged with argon for 10 min. Then, 1,3-diaminopropane (7.4 mg, 0.1 mmol) was added, and the mixture gradually turned from yellow to orange red. The mixture was stirred at room temperature and the reaction was monitored by ^{1}H NMR and ^{13}C NMR. After the polymerization, the product was purified by precipitating to acetone twice, and the product was vacuum dried at 35℃ for 3 h. Yield: 94.2%.

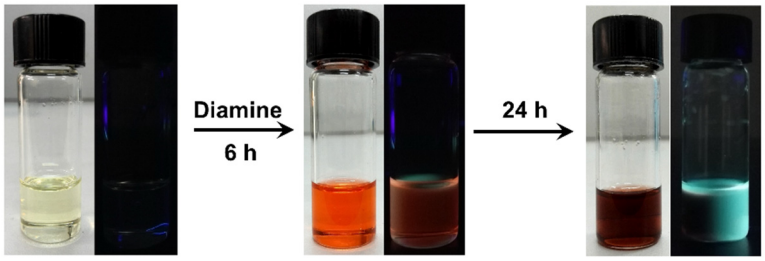


Figure S7. Optical change of PAI1 during synthesis.

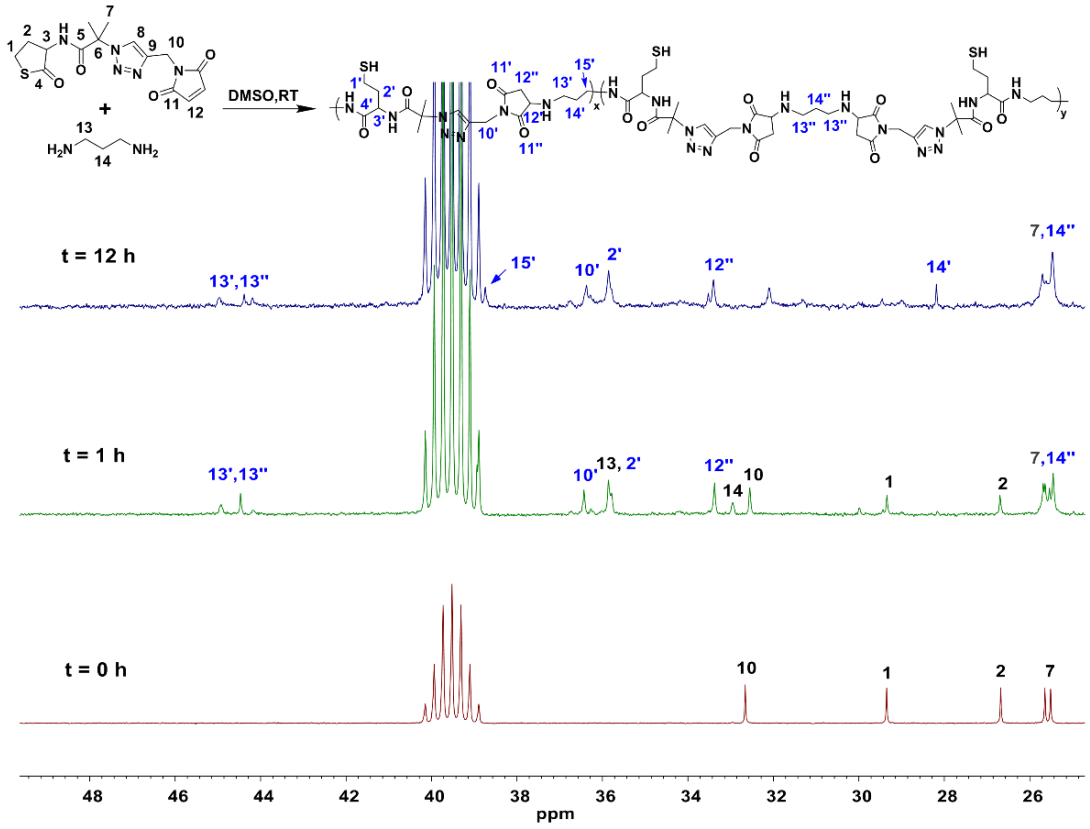


Figure S8. Enlarged ^{13}C NMR spectra between 24 and 50 ppm (complete spectra, see Figure 1B) for the polymerization of thiolactone-maleimide and 1,3-diaminopropane.

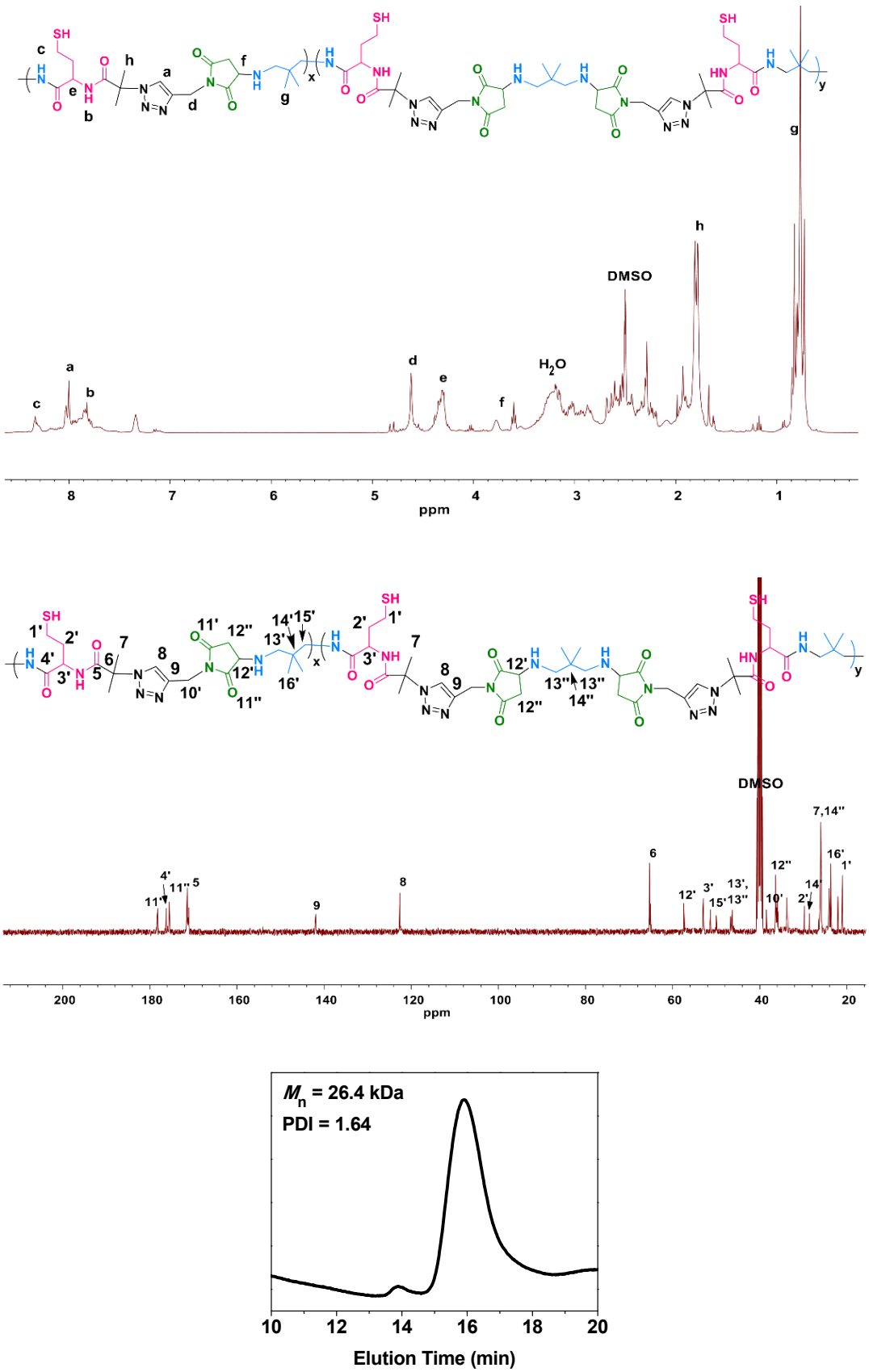


Figure S9. ^{1}H, ^{13}C NMR spectra and GPC curve of PAI2.

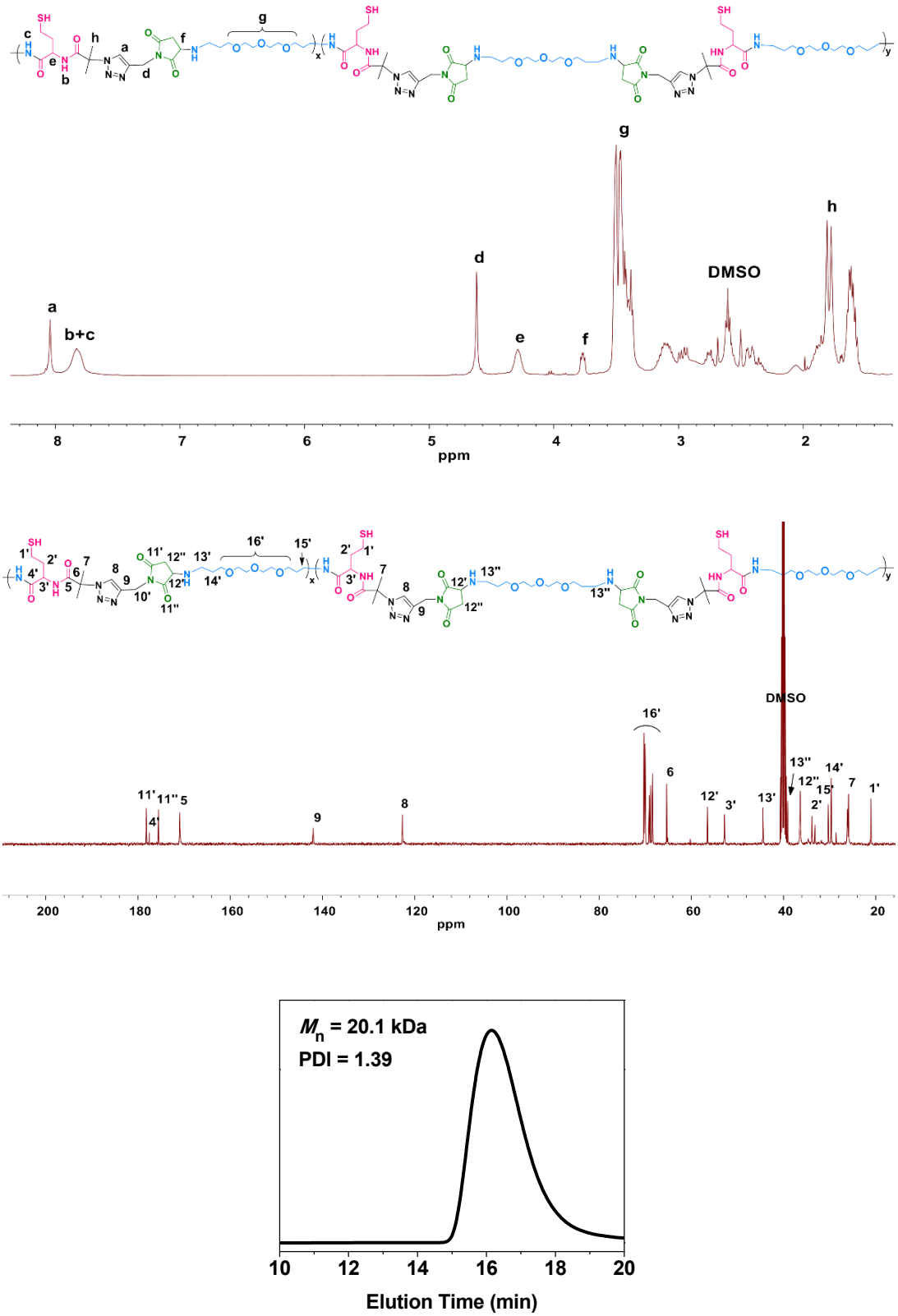


Figure S10. ^{1}H, ^{13}C NMR spectra and GPC curve of PAI3.

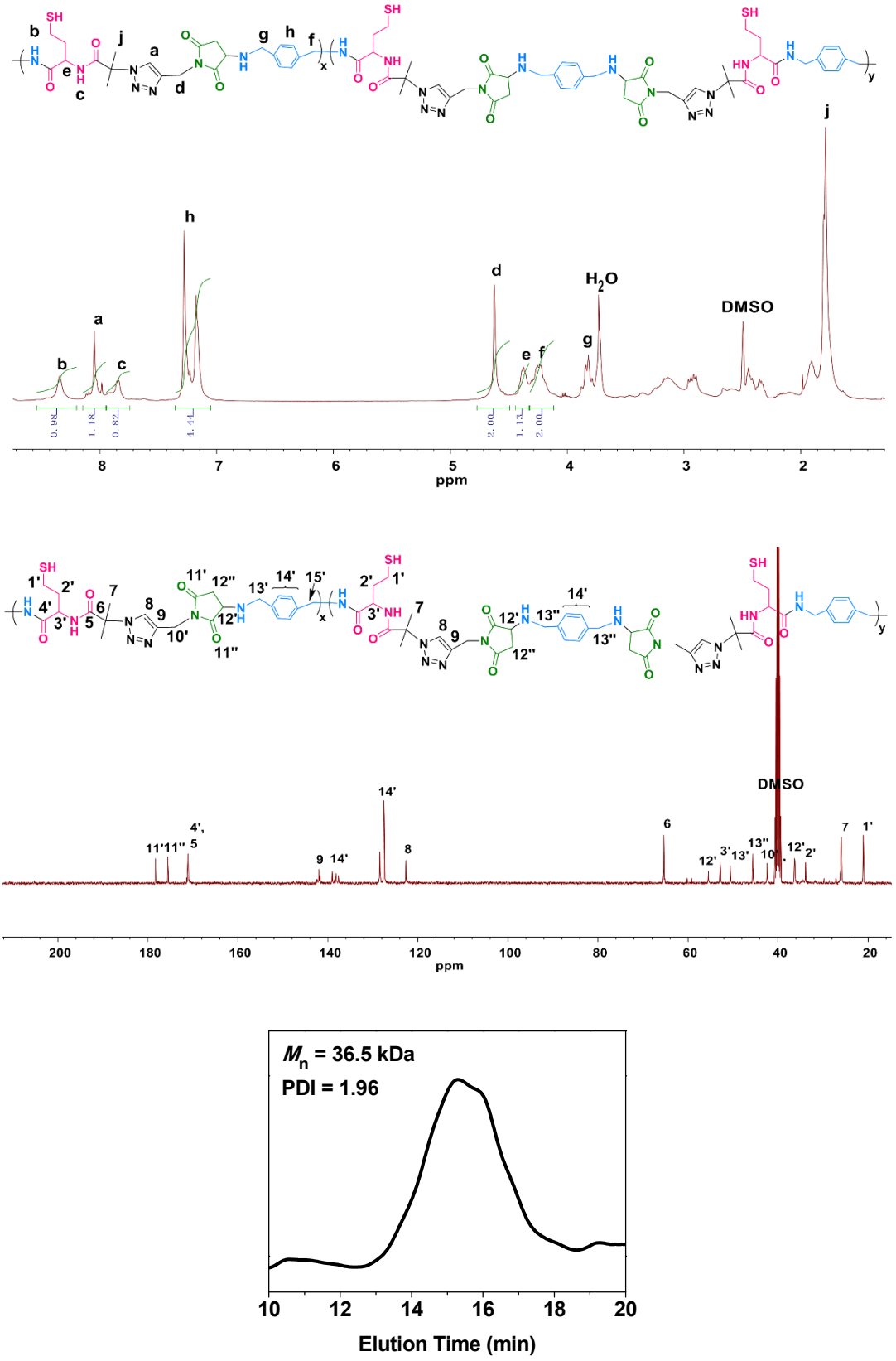


Figure S11. ^{1}H, ^{13}C NMR spectra and GPC curve of PAI4.

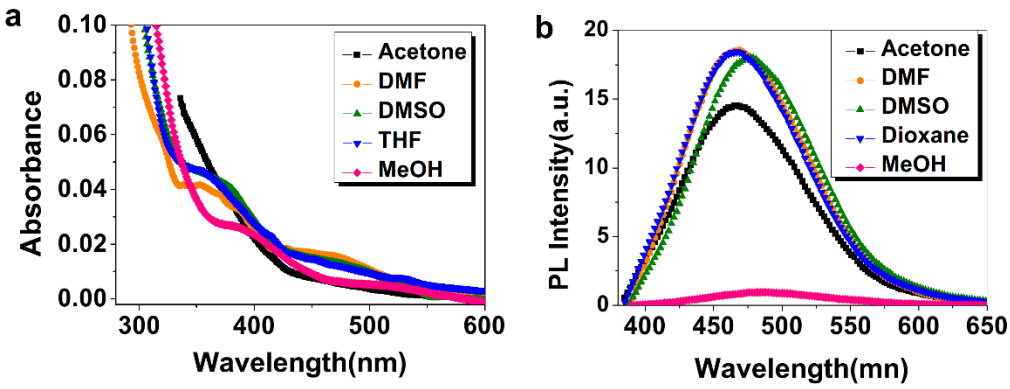


Figure S12. UV-vis (a) and fluorescence spectra (b) of PEGylated PAI1 in different solvents.