Supporting Information

Precise Synthesis of Poly(*N*-Acryloyl Amino Acid) Through Photoinduced Living Polymerization

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1. PET-RAFT polymerization of *N*-Acryloyl-*DL*-Val-OMe (V-OMe)

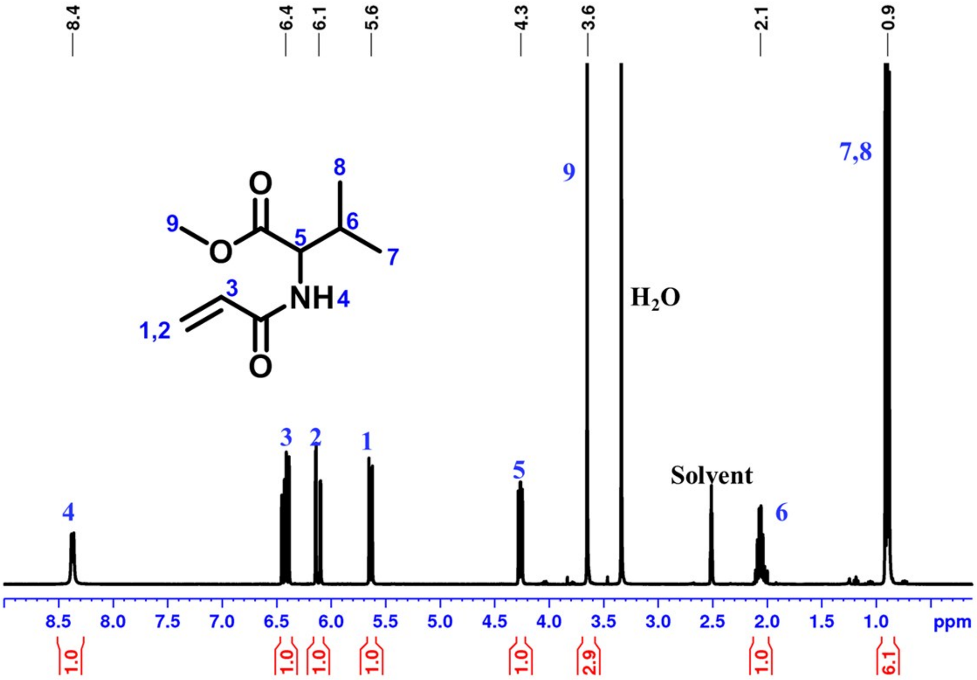

Figure S1. ^{1}H NMR spectrum of V-OMe monomer (400 MHz, DMSO-d_6 as solvent).

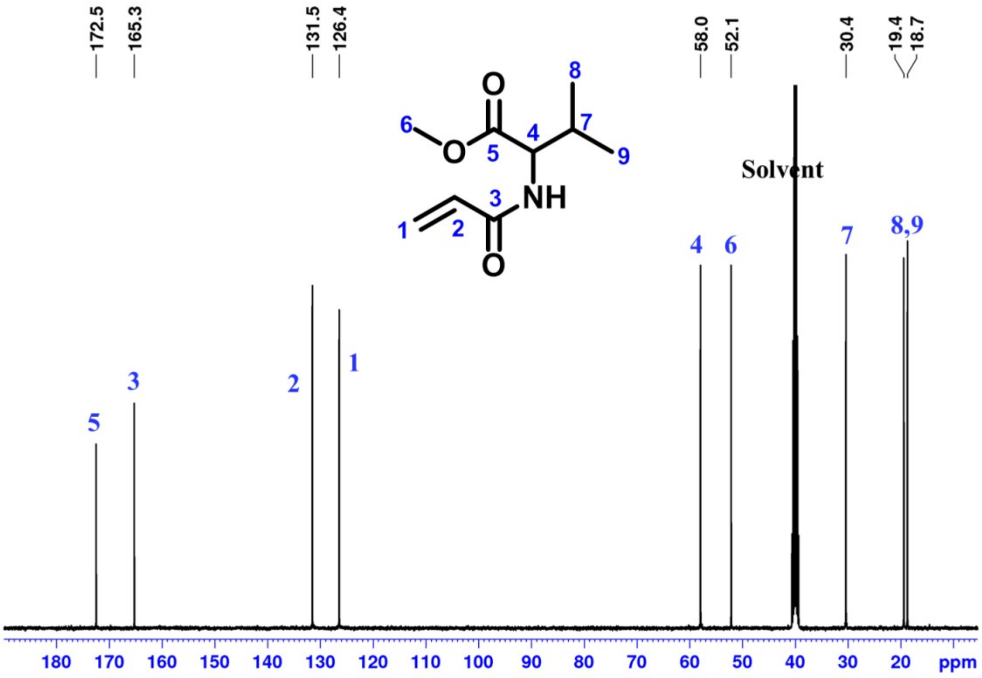

Figure S2. ^{13}C NMR spectrum of V-OMe monomer (100 MHz, DMSO-d_6 as solvent).

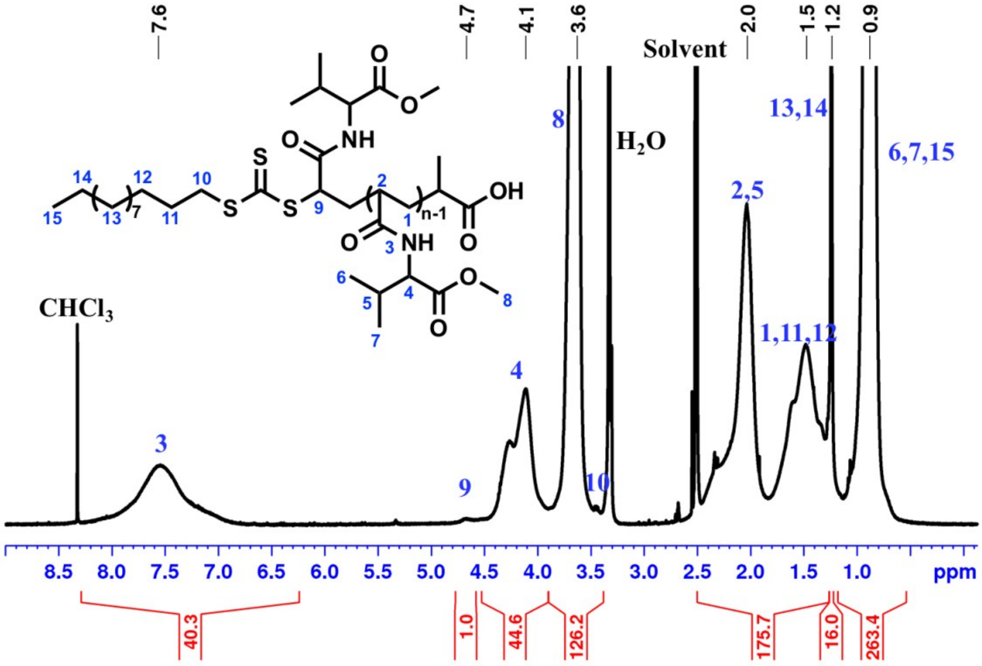

Figure S3. ^{1}H NMR spectrum of poly(V-OMe) (PV-OMe) (400 MHz, DMSO-d_6 as solvent).

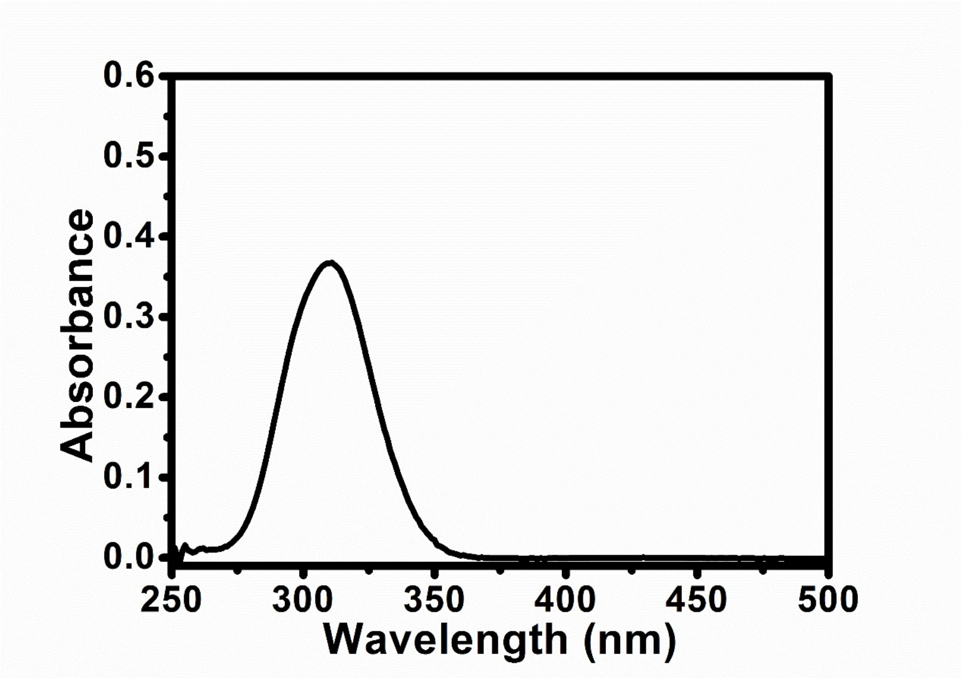

Figure S4. UV-vis spectrum of PV-OMe in DMSO, showing the typical UV absorption of the thiocarbonylthio group at the maximum of 305 nm.

2. PET-RAFT polymerization of *N*-Acryloyl-*L*-Val (*L*V)

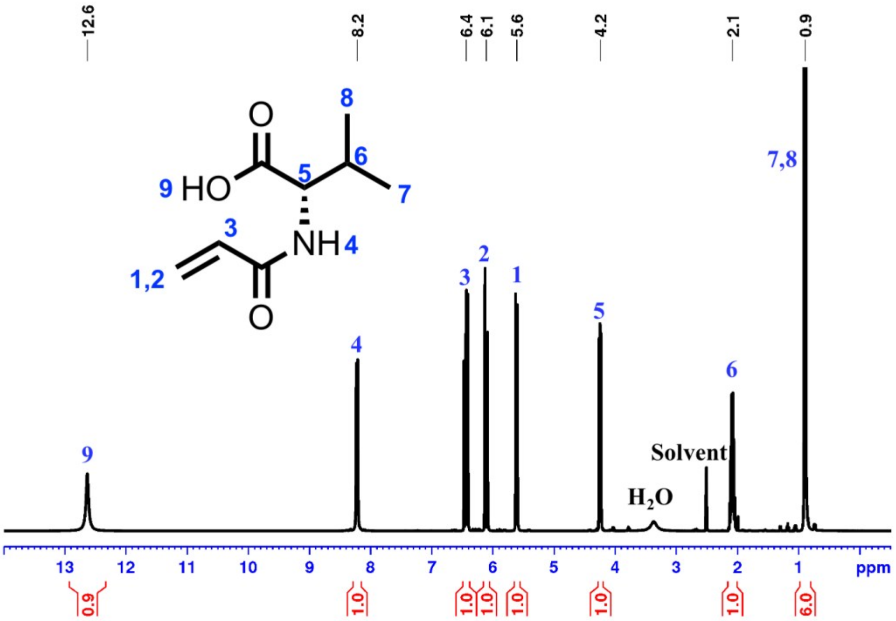

Figure S5. ^{1}H NMR spectrum of *L*V monomer (400 MHz, DMSO-d_6 as solvent).

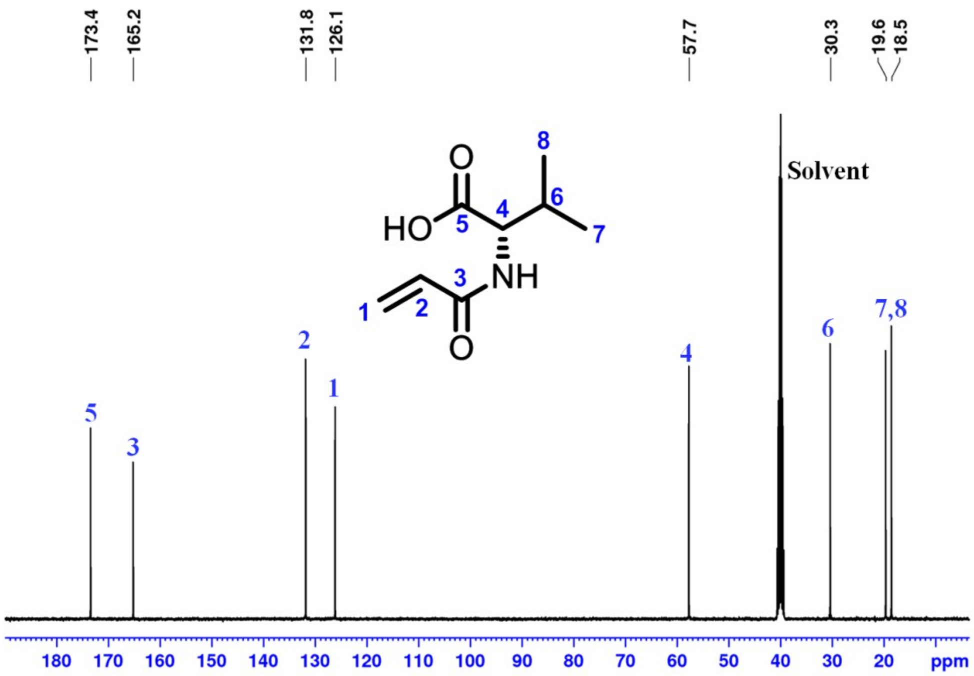

Figure S6. ^{13}C NMR spectrum of *L*V monomer (100 MHz, DMSO-d_6 as solvent).

Table S1. PET-RAFT polymerization of *L*V using different solvents.[a]

#	Solvent	CTA	[M]/[CTA]/[PC]	[I]/[M] (ppm)	Time (h)	a[b] (%)	$M_{n,GPC}$[c] (g/mol)	M_w/M_n
1	DMF	DDMAT	150:1:7.5×10^{-4}	5	4	76	13 690	1.40
2	THF	DDMAT	150:1:7.5×10^{-4}	5	4	60	10 560	1.46
3	Diox	DDMAT	150:1:7.5×10^{-4}	5	4	93	19 220	1.35

[a] The reactions were performed using Ir(ppy)$_3$ as catalyst under blue LED light irradiation (λ_{max} = 460 nm, 0.7 mW/cm^2) at room temperature. [b] Monomer conversion determined by ^1H NMR spectroscopy. [c] Molecular weight and dispersity determined by GPC analysis (DMAc used as eluent) using polymethyl methacrylate (PMMA) standards for calibration. The resulting polymer was methylated using TMSCHN$_2$.

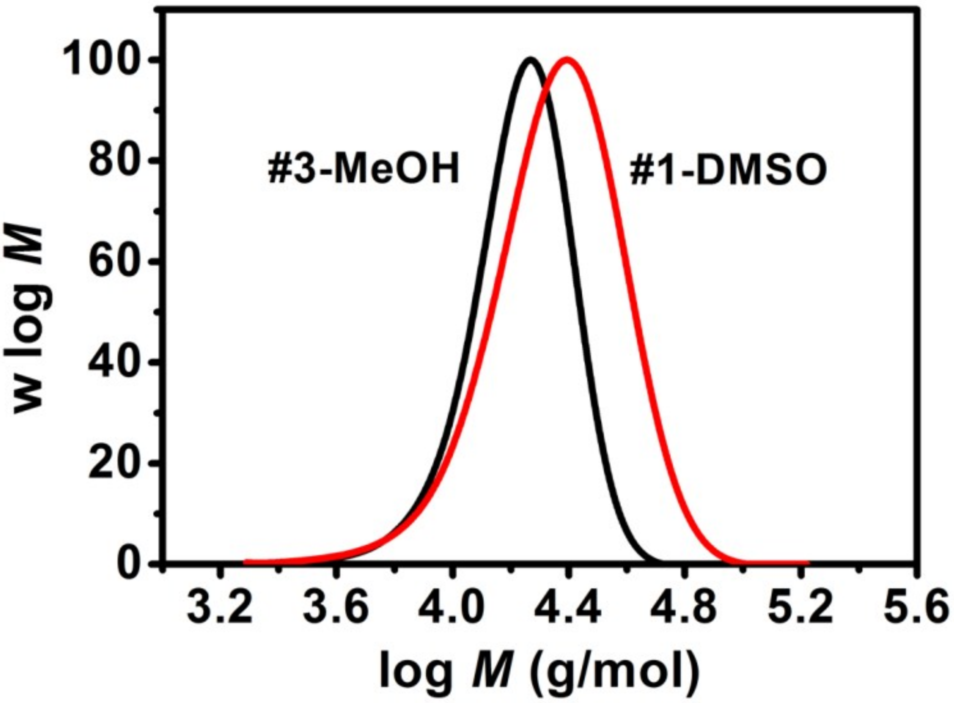

Figure S7. GPC curves for poly(*L*V) (P*L*V)s prepared in DMSO and MeOH (#1 and #3 in Table 2).

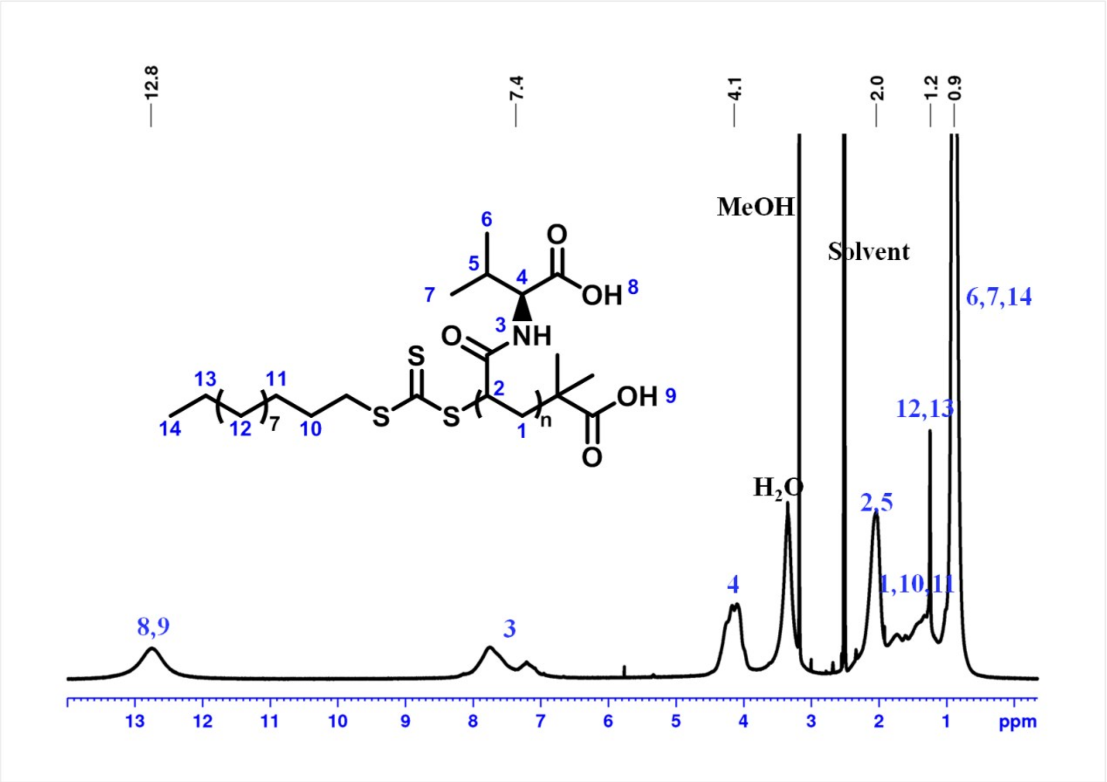

Figure S8. ^{1}H NMR spectrum of poly(*L*V) (P*L*V) (400 MHz, DMSO-d_6 as solvent).

Figure S9. UV-vis spectrum of P*L*V in DMSO, showing the typical UV absorption of the thiocarbonylthio group at the maximum of 305 nm.

3. PET-RAFT polymerization of *N*-Acryloyl-*D*-Phe (*D*F)

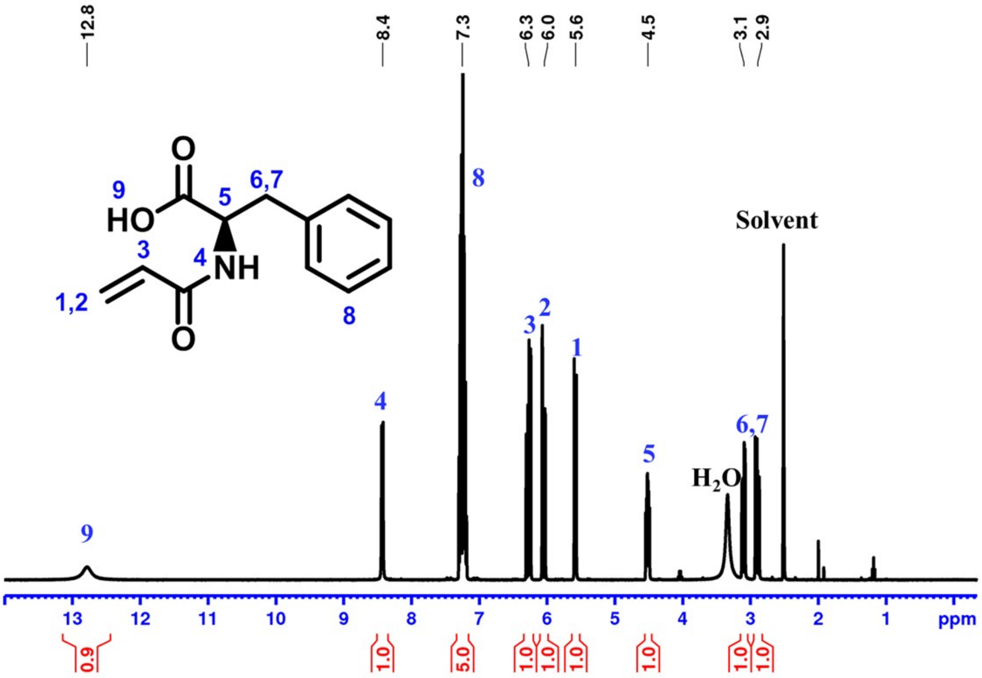

Figure S10. ^{1}H NMR spectrum of *D*F monomer (400 MHz, DMSO-d_6 as solvent).

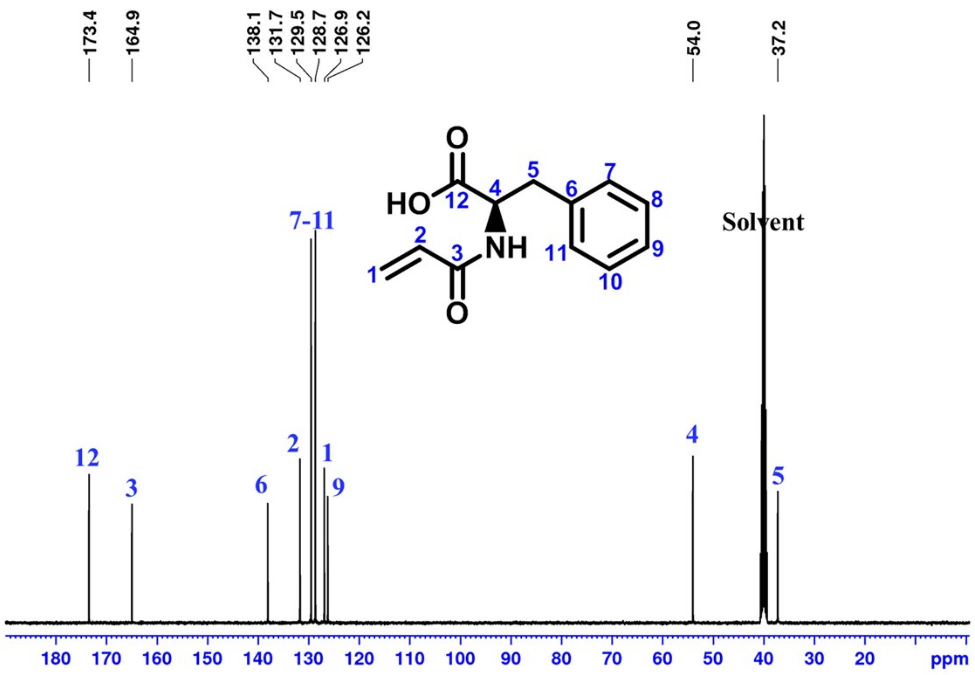

Figure S11. ^{13}C NMR spectrum of *D*F monomer (100 MHz, DMSO-d_6 as solvent).

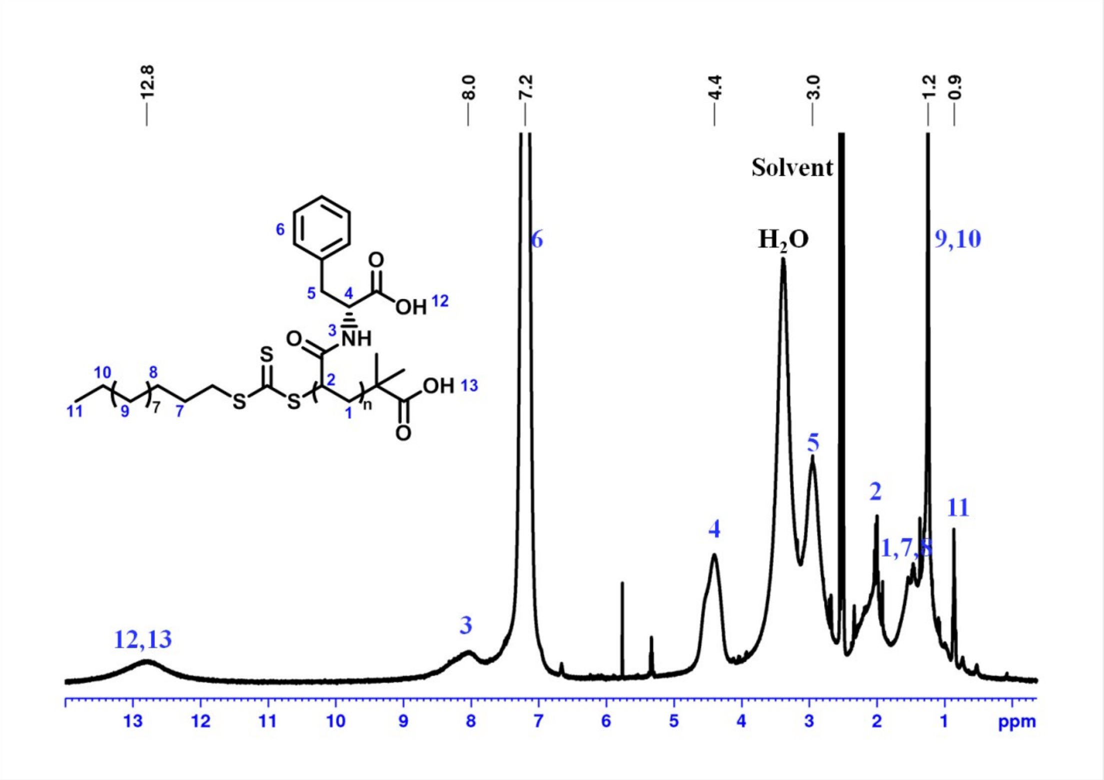

Figure S12. ^{1}H NMR spectrum of poly(*D*F) (P*D*F) (400 MHz, DMSO-d_6 as solvent)

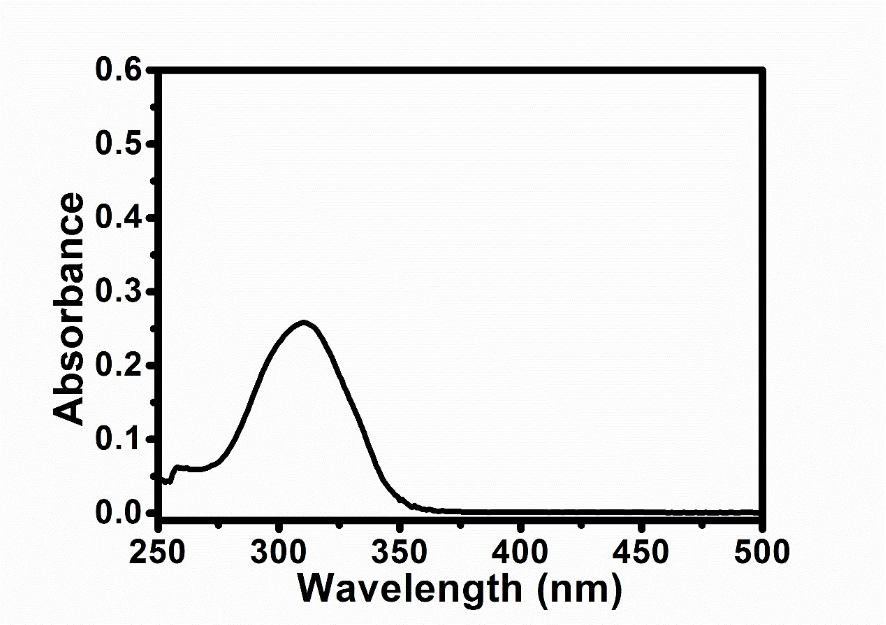

Figure S13. UV-vis spectrum of P*D*F in DMSO, showing the typical UV absorption of the thiocarbonylthio group at the maximum of 305 nm.

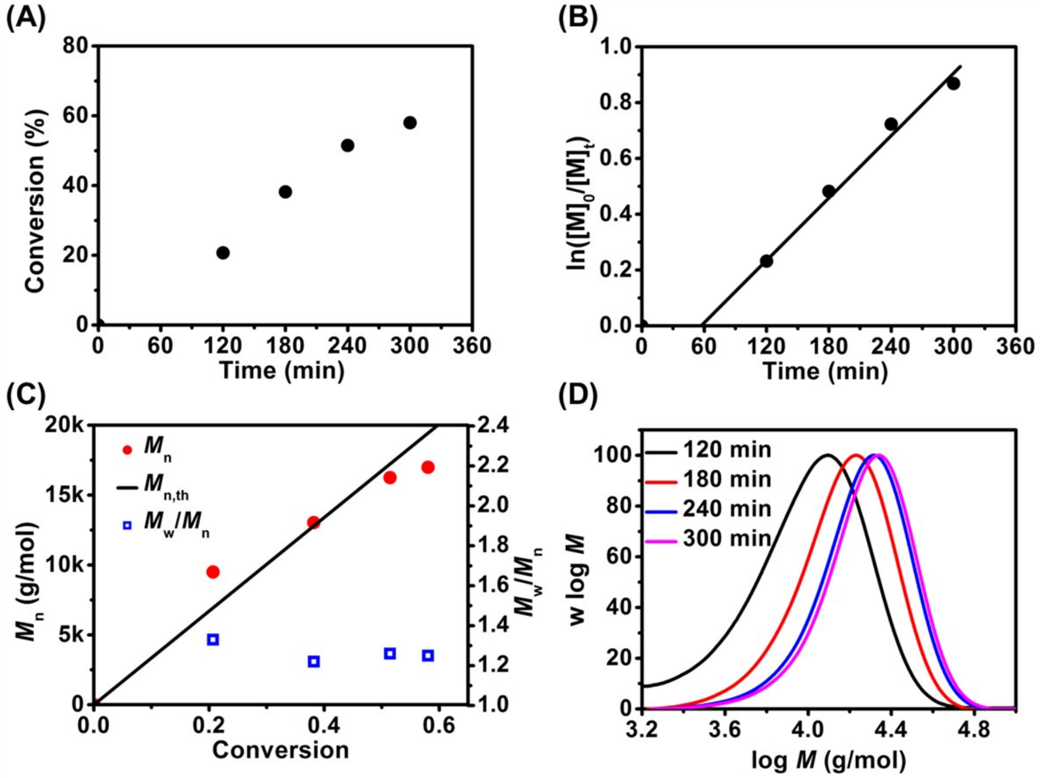

Figure S14. Kinetic study of the PET-RAFT polymerization of *D*F using DDMAT as the CTA and Ir(ppy)$_3$ as catalyst under blue light irradiation ($\lambda_{\max}$ = 460 nm, 0.7 mW/cm^2), a molar ratio of [*D*F]/[DDMAT]/[Ir(ppy)$_3$] = 150:1:7.5×10^{-4} in MeOH. (A) Monomer conversion *versus* polymerization time. (B) ln([M]$_0$/[M]$_t$) *versus* polymerization time. (C) $M_{n,\text{ GPC}}$ and M_w/M_n *versus* monomer conversion. (D)

Molecular weight distributions at different polymerization time intervals. The resulting polymer was methylated by TMSCHN$_2$.

4. PET-RAFT polymerization of *N*-Acryloyl-*L*-Ser (*L*S)

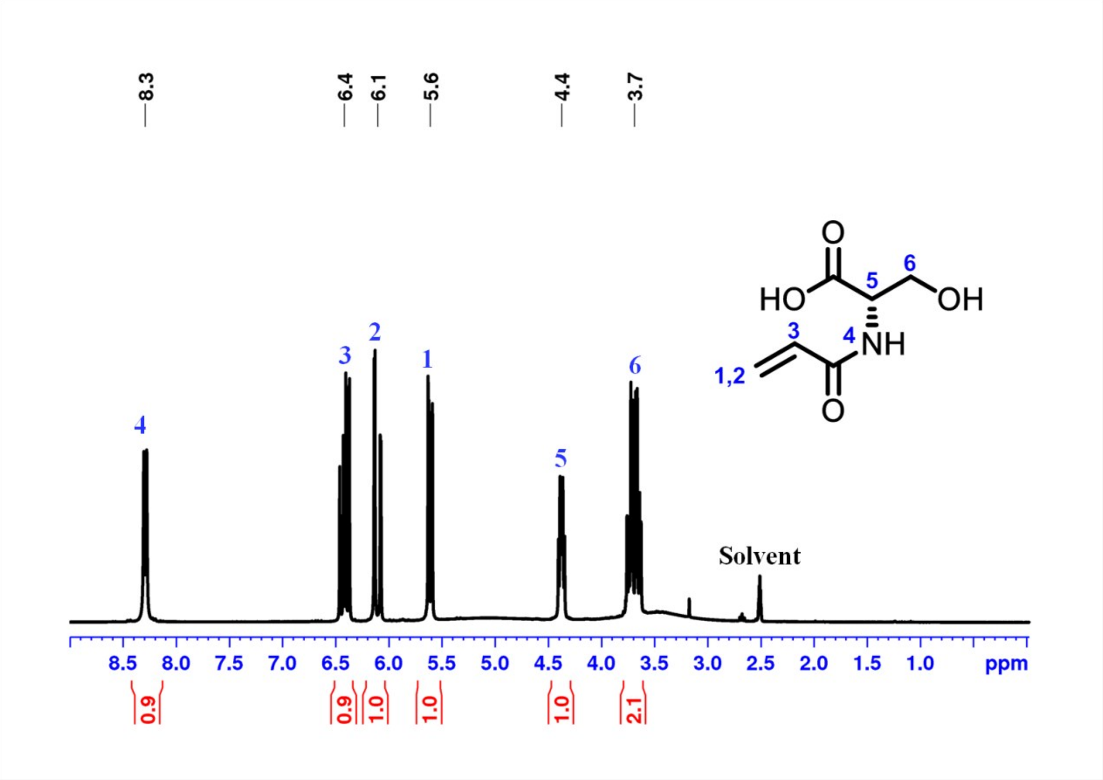

Figure S15. ^{1}H NMR spectrum of *L*S monomer (400 MHz, DMSO-d_6 as solvent).

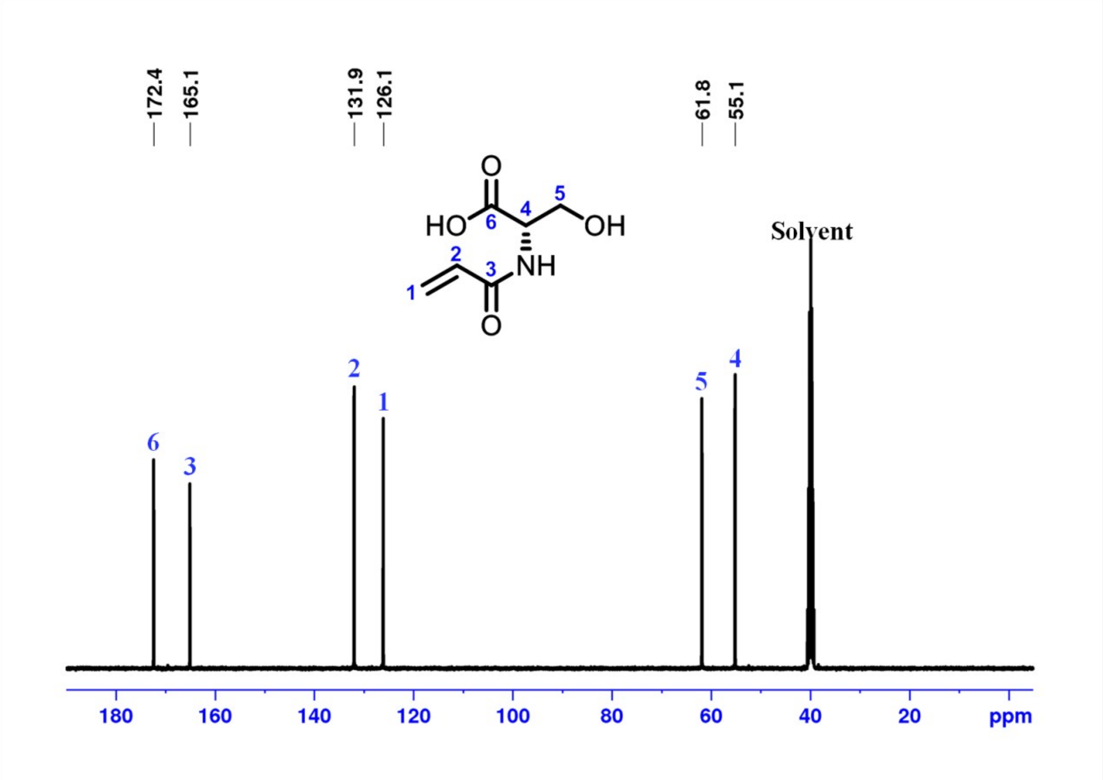

Figure S16. ^{13}C NMR spectrum of *L*S monomer (100 MHz, DMSO-d_6 as solvent).

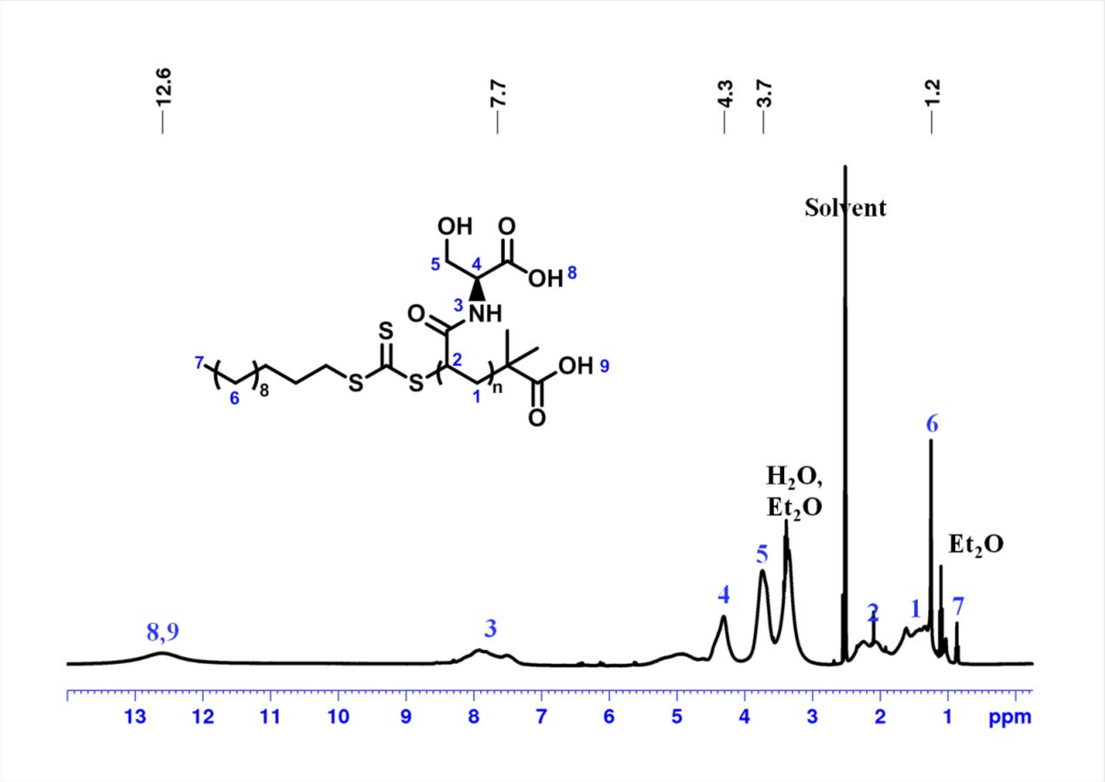

Figure S17. ^{1}H NMR spectrum of poly(*L*S) (P*L*S) (400 MHz, DMSO-d_6 as solvent)

5. PET-RAFT polymerization of *N*-Acryloyl-*D*-Asp (*D*D)

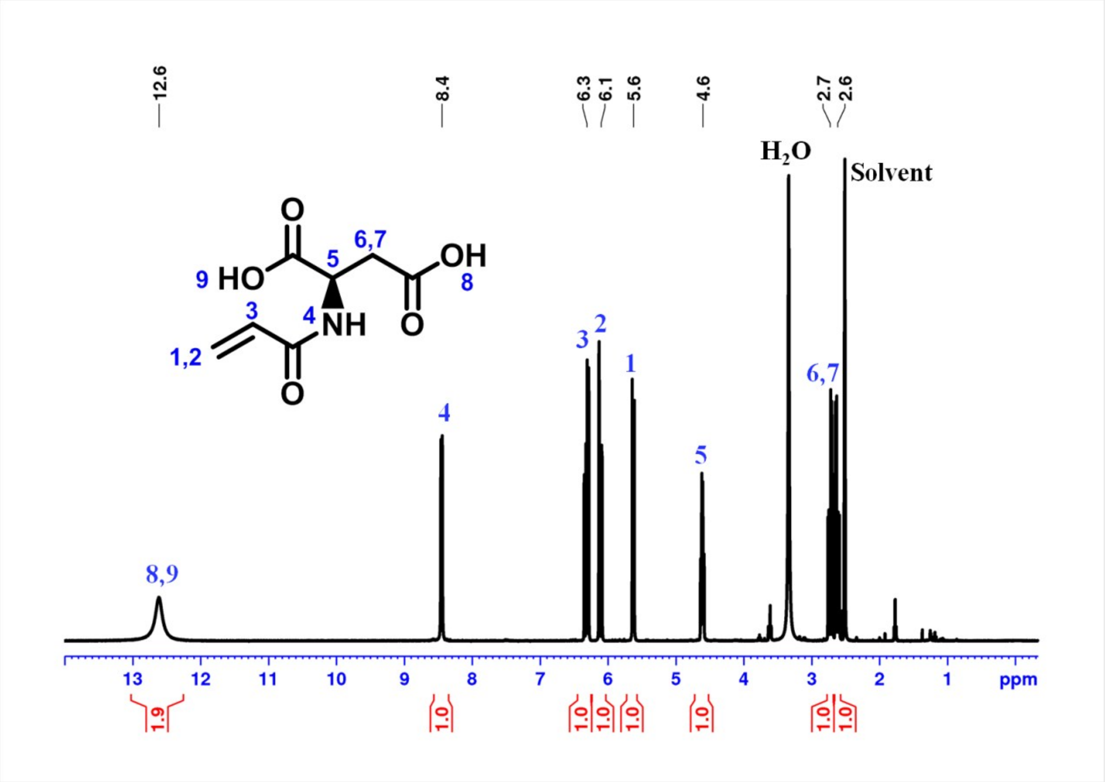

Figure S18. ^1H NMR spectrum of *D*D monomer (400 MHz, DMSO-d_6 as solvent).

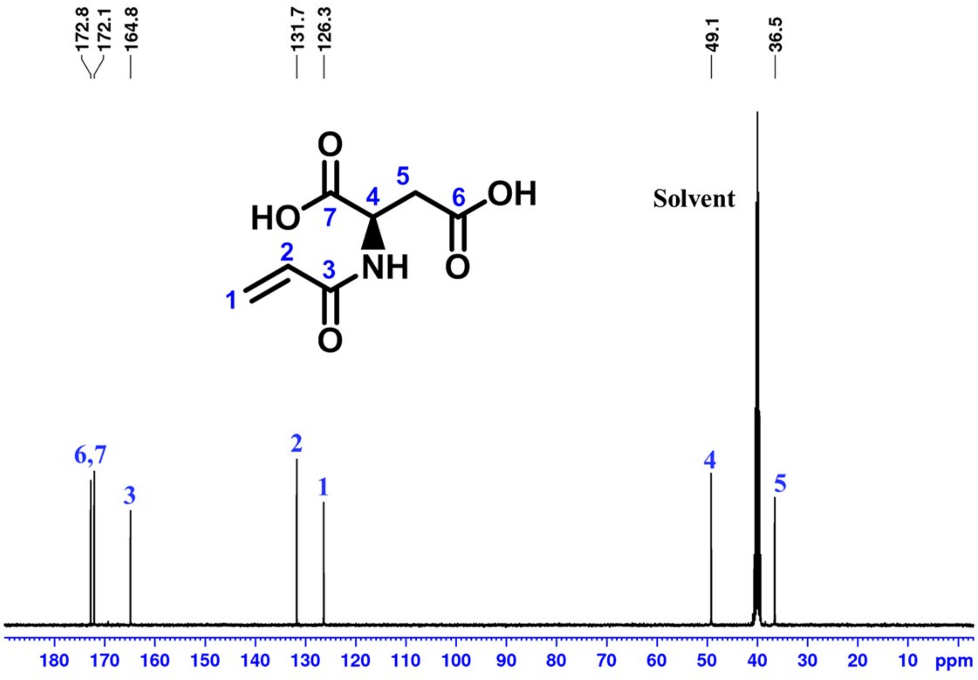

Figure S19. ^{13}C NMR spectrum of *D*D monomer (100 MHz, DMSO-d_6 as solvent).

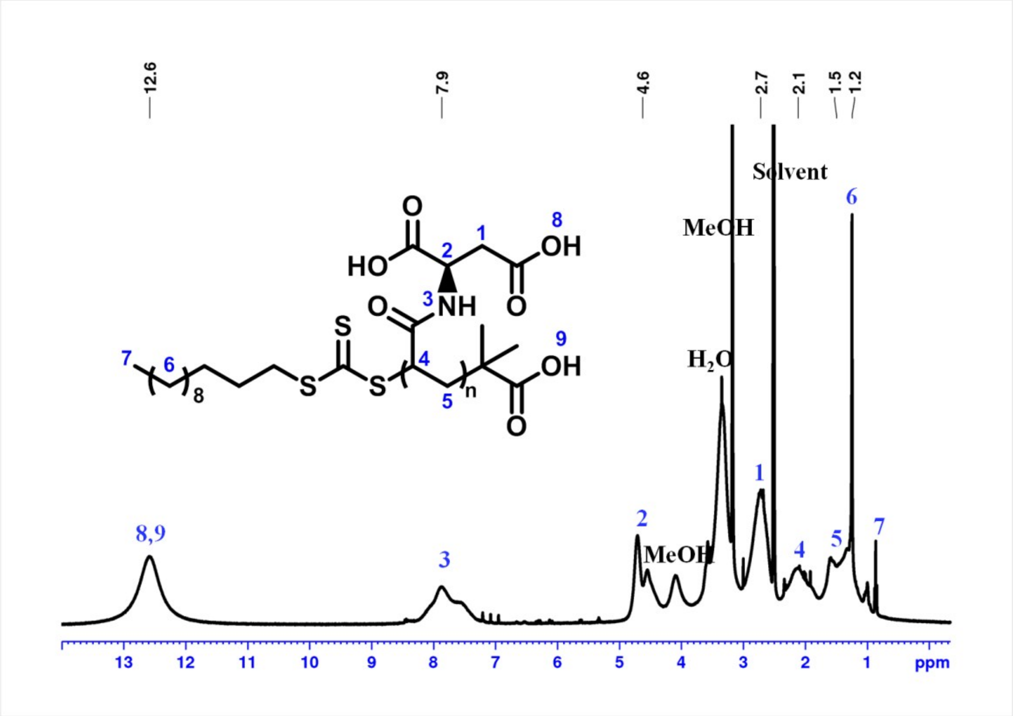

Figure S20. ^{1}H NMR spectrum of poly(*D*D) (P*D*D) (400 MHz, DMSO-d_6 as solvent).

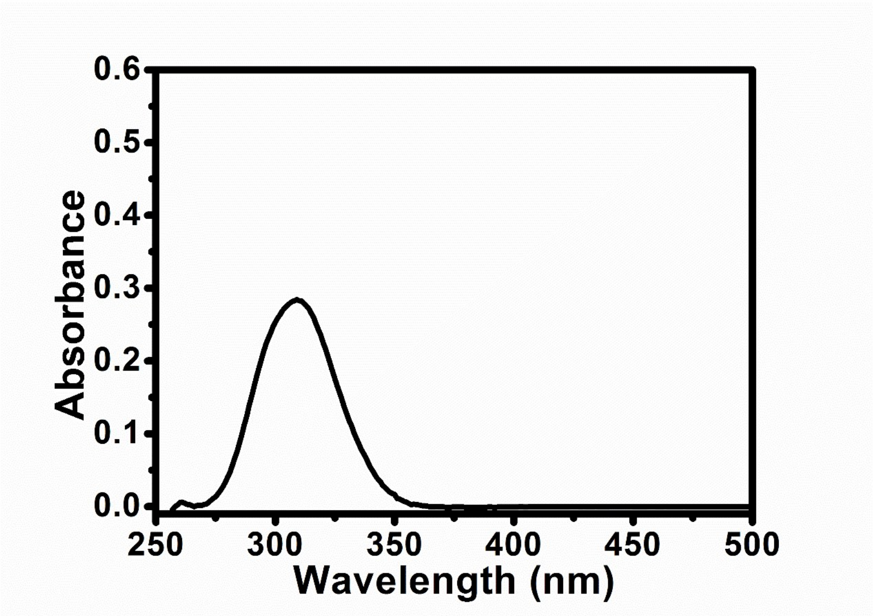

Figure S21. UV-vis spectrum of P*D*D in DMSO, showing the typical UV absorption of the thiocarbonylthio group at the maximum of 305 nm.

Table S2. Thermally initiated RAFT polymerization of *D*D using AIBN as catalyst.[a]

#	Catalyst	CTA	[M]/[CTA]/[PC]	Time (h)	a^b (%)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n
1	AIBN	DDMAT	150:1:1	8	93	19 650	1.24
2	AIBN	DDMAT	150:1:0.5	16	88	18 550	1.20

[a]The reactions were performed using AIBN as catalyst at 60 °C. [b]Monomer conversion determined by ^{1}H NMR spectroscopy. [c]Molecular weight and dispersity determined by GPC analysis (DMAc used as eluent) using polymethyl methacrylate (PMMA) standards for calibration. The resulting polymer was methylated using $TMSCHN_2$.

Experimental procedure for thermally initiated RAFT polymerization: A reaction stock solution consisting of MeOH (0.65 mL), *N*-Acryloyl-*D*-Asp (100 mg, 0.54 mmol), DDMAT (1.26 mg, 0.0036 mmol) and AIBN (0.59 mg, 0.0036 mmol) was prepared in a 4 mL glass vial. The glass vial was sealed with a rubber septum, and the reaction mixture was degassed with nitrogen for 20 minutes. The glass vial was stirred in an oil bath at 60 °C for 8 h. The other polymerization was performed in the presence of half amount of AIBN (0.3 mg, 0.0018 mmol) under otherwise identical conditions.

6. PET-RAFT polymerization of *N*-Acryloyl-*L*-Glu (*L*E)

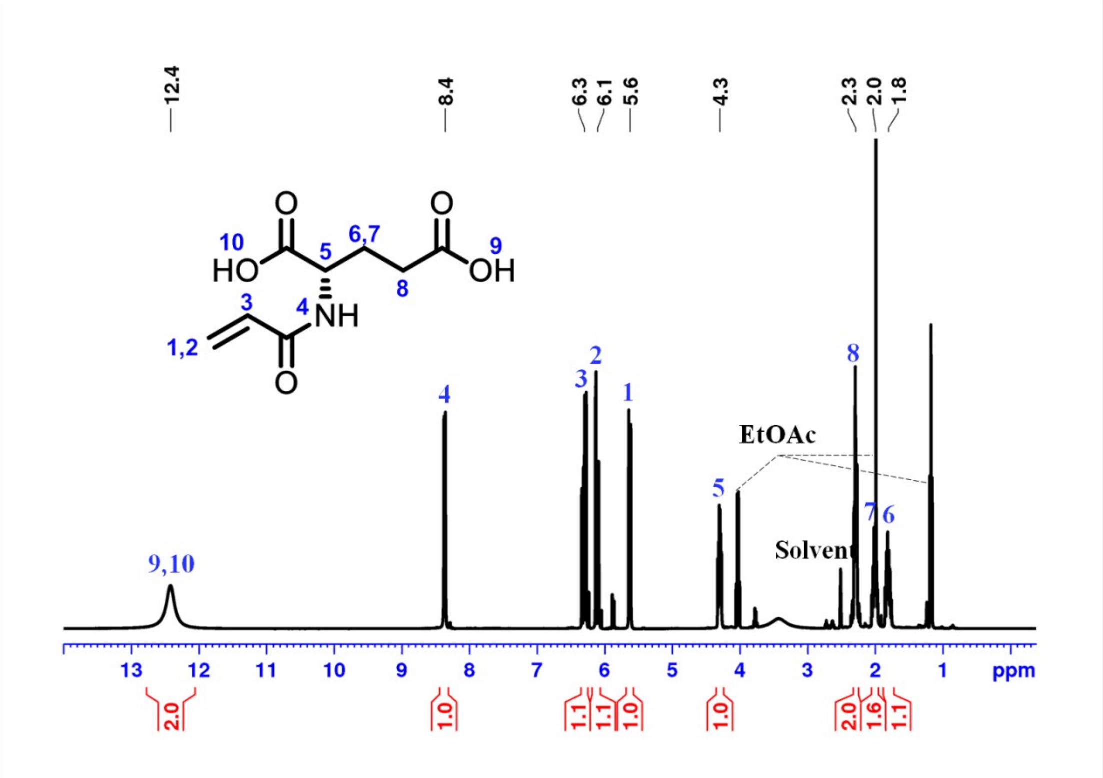

Figure S22. ^{1}H NMR spectrum of *L*E monomer (400 MHz, DMSO-d_6 as solvent).

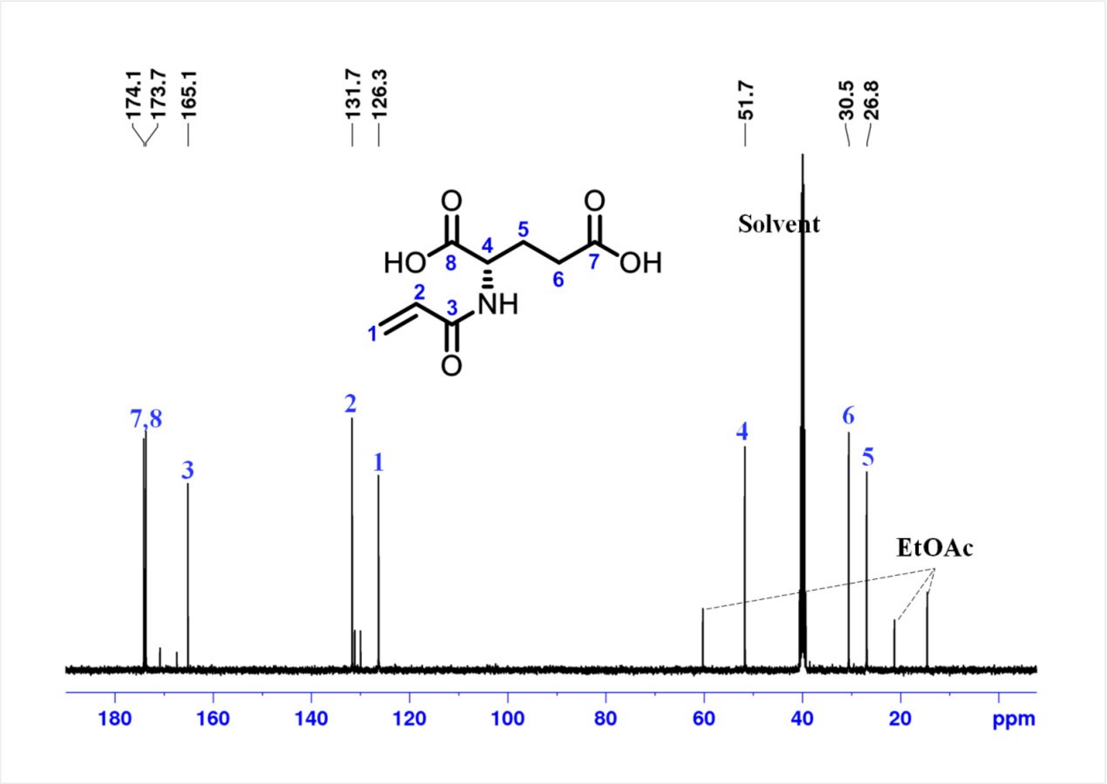

Figure S23. ^{13}C NMR spectrum of *L*E monomer (100 MHz, DMSO-d_6 as solvent).

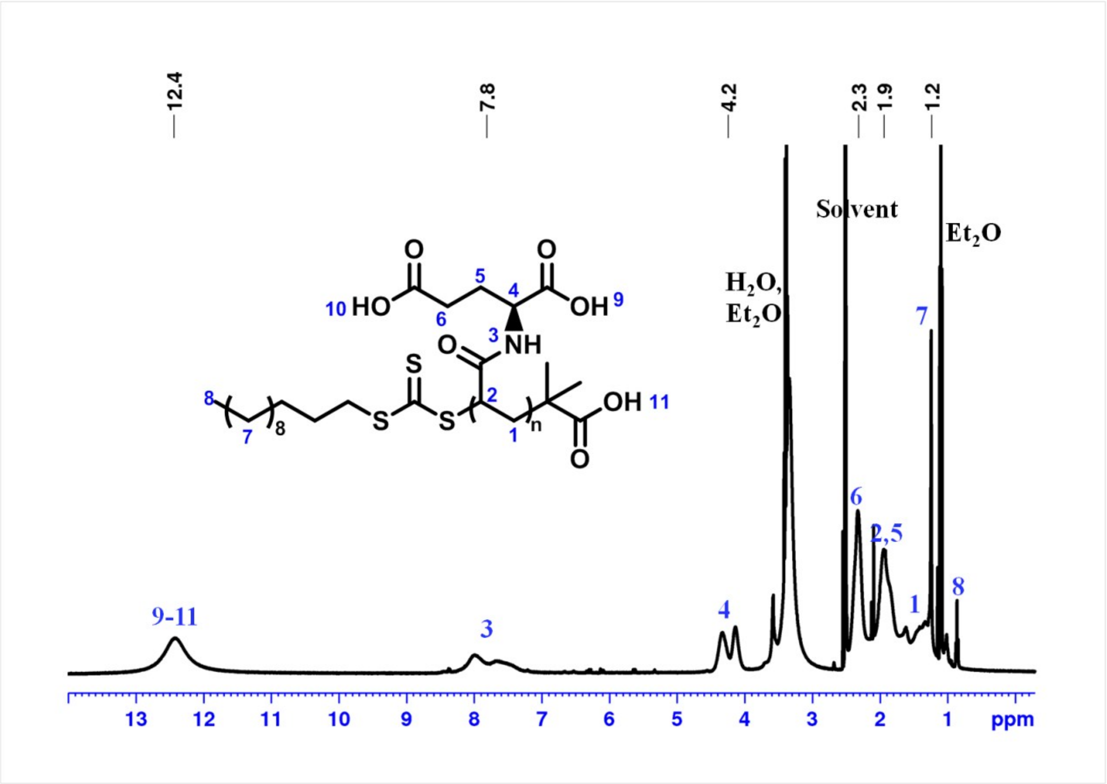

Figure S24. ^{1}H NMR spectrum of poly(*L*E) (P*L*E) (400 MHz, DMSO-d_6 as solvent).

7. PET-RAFT polymerization of *N*-Acryloyl-*L*-Glu-O*t*Bu (*L*E-O*t*Bu)

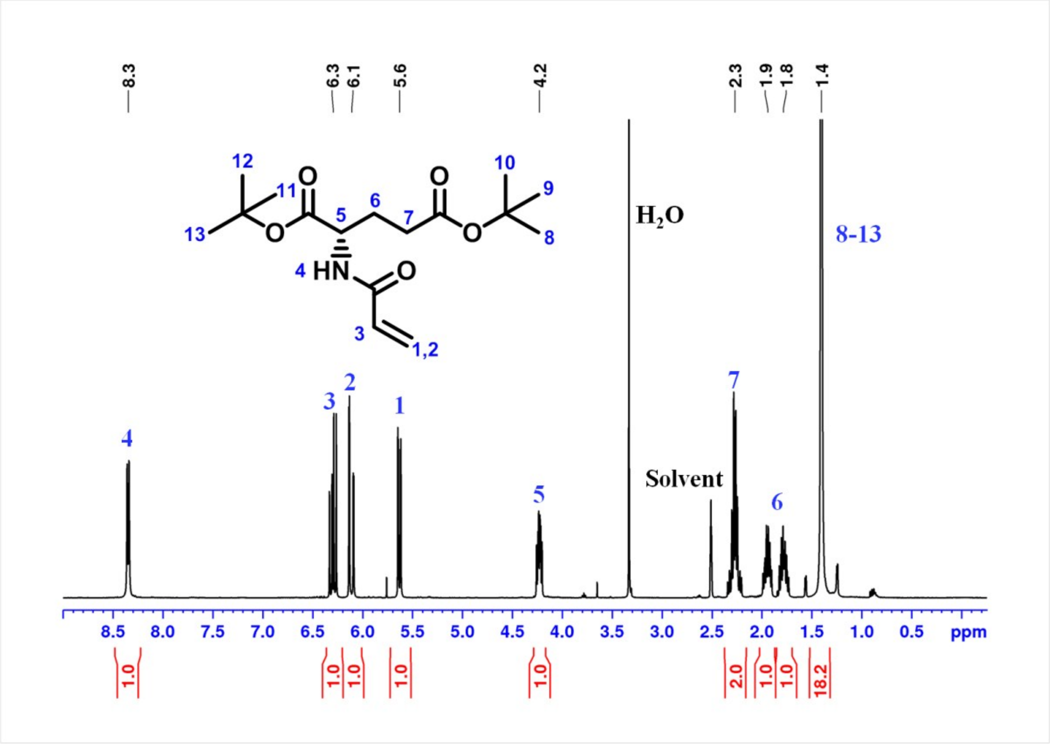

Figure S25. ^{1}H NMR spectrum of *L*E-O*t*Bu monomer (400 MHz, DMSO-d_6 as solvent).

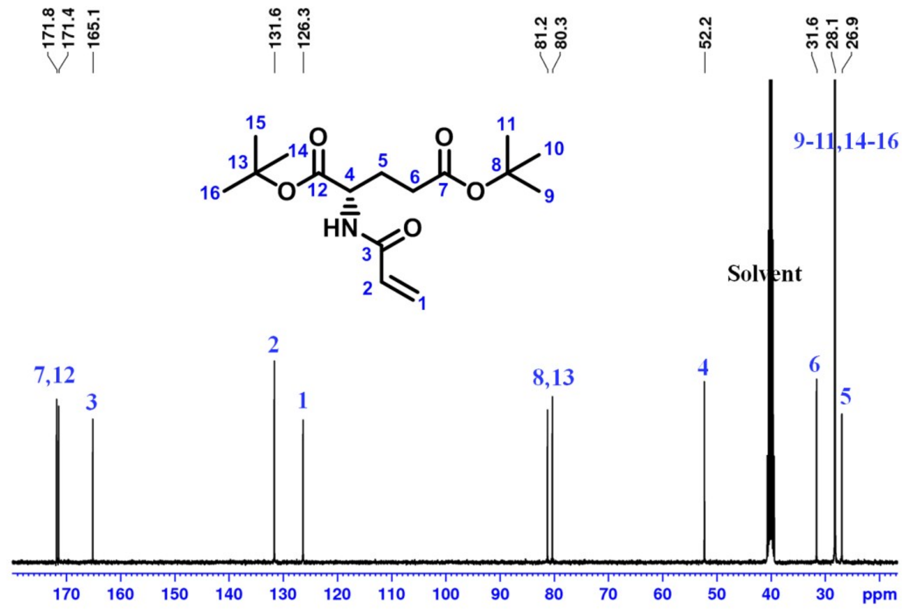

Figure S26. ^{13}C NMR spectrum of *L*E-O*t*Bu monomer (100 MHz, DMSO-d_6 as solvent).

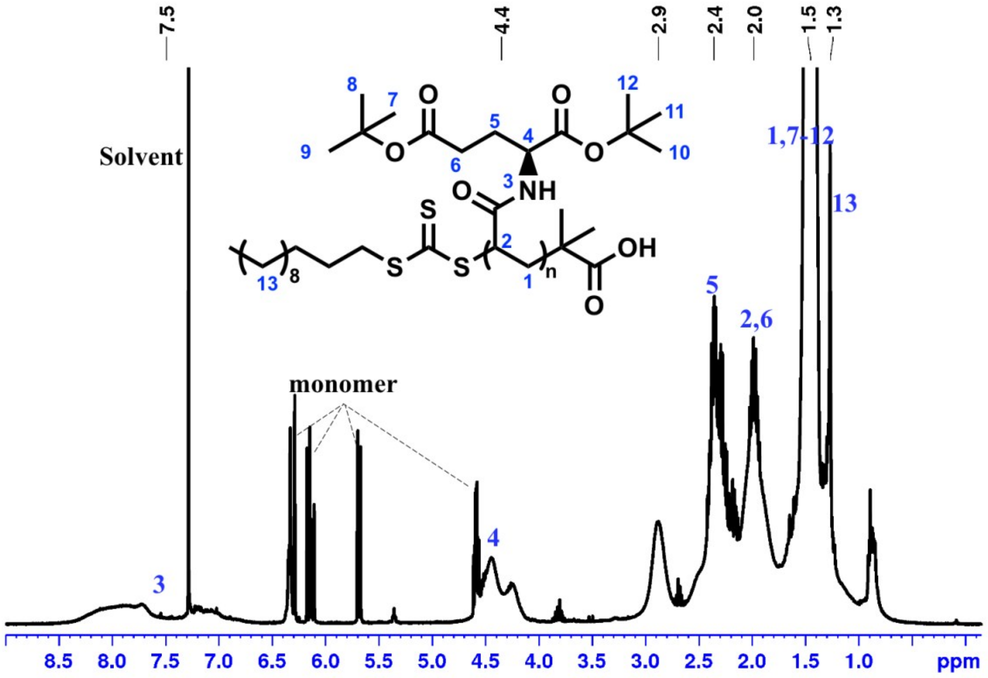

Figure S27. ^{1}H NMR spectrum of poly(*L*E-O*t*Bu) (P*L*E-O*t*Bu) (400 MHz, CDCl$_3$ as solvent).

8. Chain extension of various *N*-acryloyl amino acid monomers

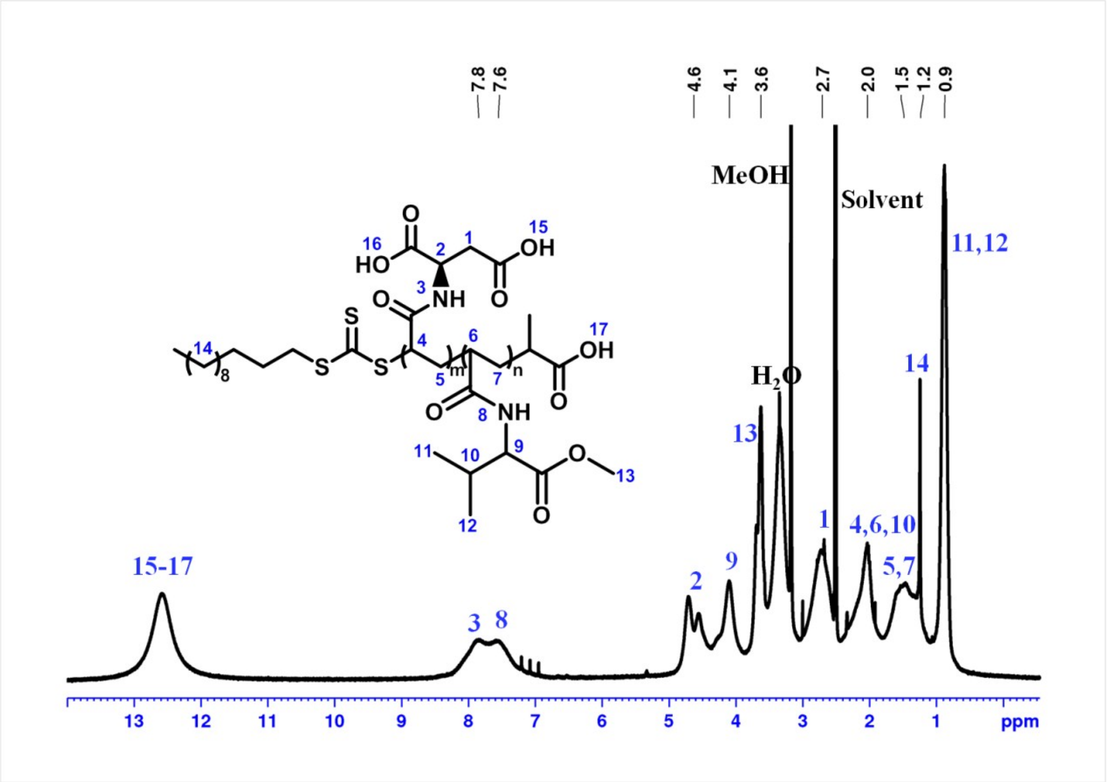

Figure S28. ^{1}H NMR spectrum of poly(V-OMe)-*b*-poly(*D*D) (PV-OMe-*b*-P*D*D) (400 MHz, DMSO-d_6 as solvent).

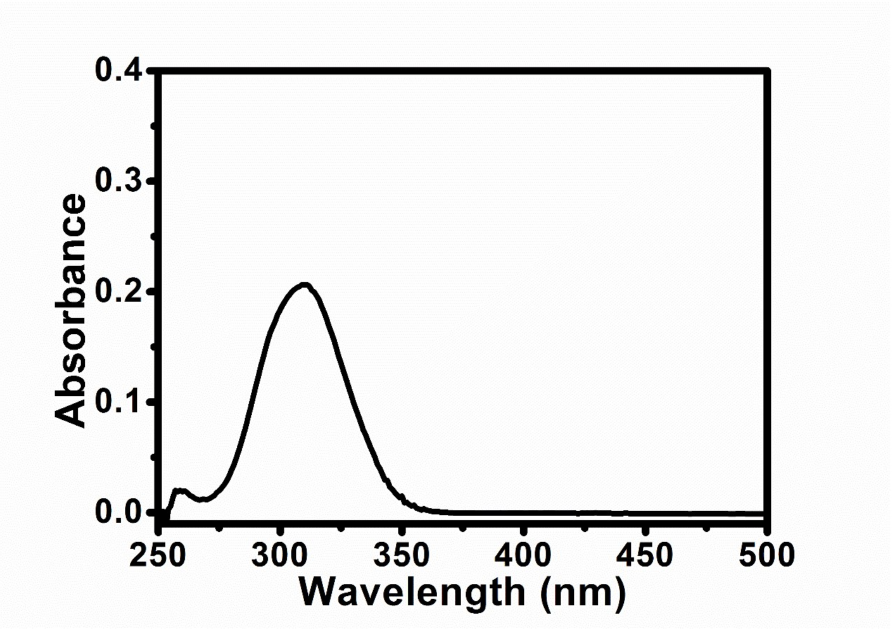

Figure S29. UV-vis spectrum of PV-OMe-*b*-P*D*D in DMSO, showing the typical UV absorption of the thiocarbonylthio group at the maximum of 305 nm.