Electronic Supplementary Material (ESI) for Polymer Chemistry.

Hyperbranched Polypeptides Synthesized from Phototriggered ROP of a Photocaged N_{ε}-[1-(2-nitrophenyl)ethoxycarbonyl]-$_{L}$-Lysine-*N*-Carboxyanhydride: Microstructures and Effects of Irradiation Intensity and Nitrogen Flow Rate

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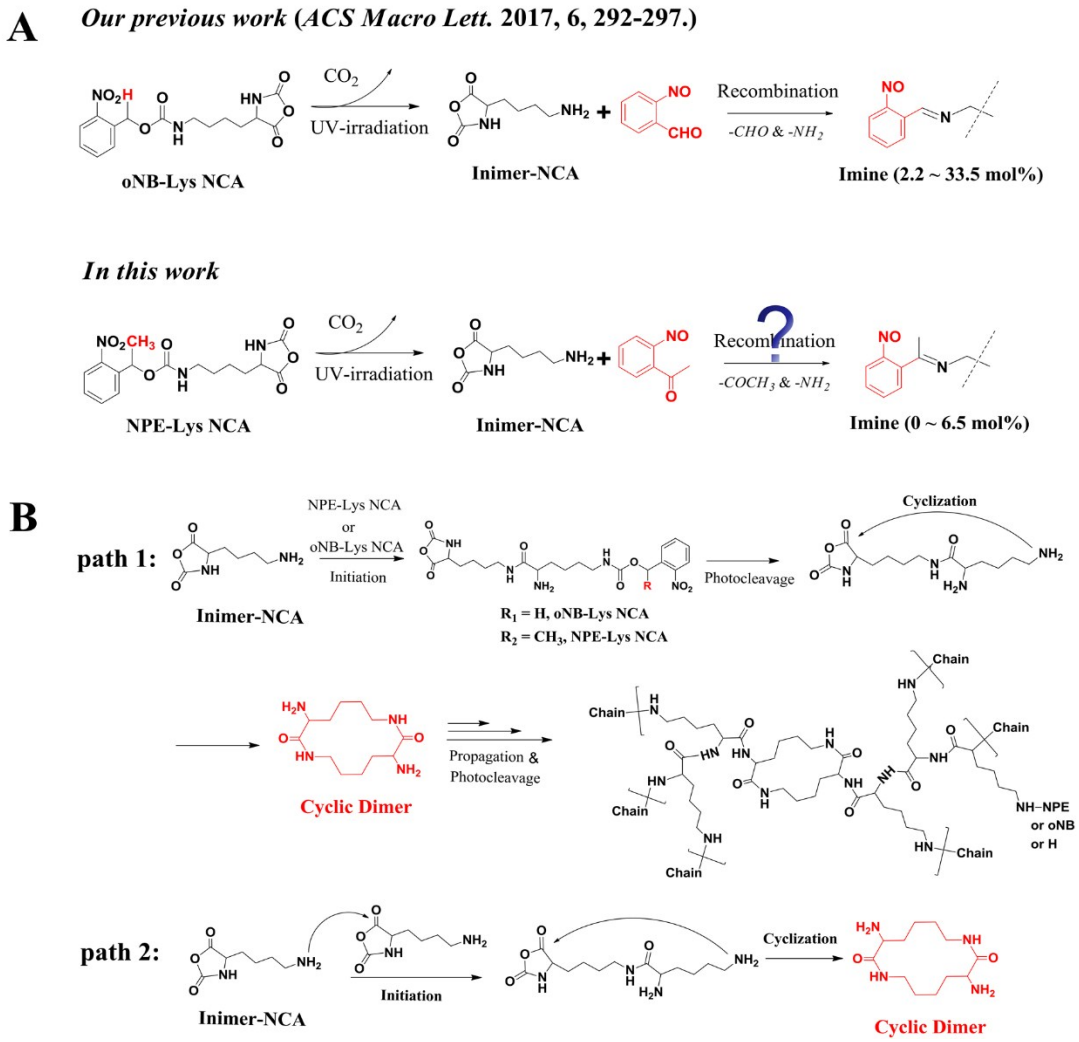
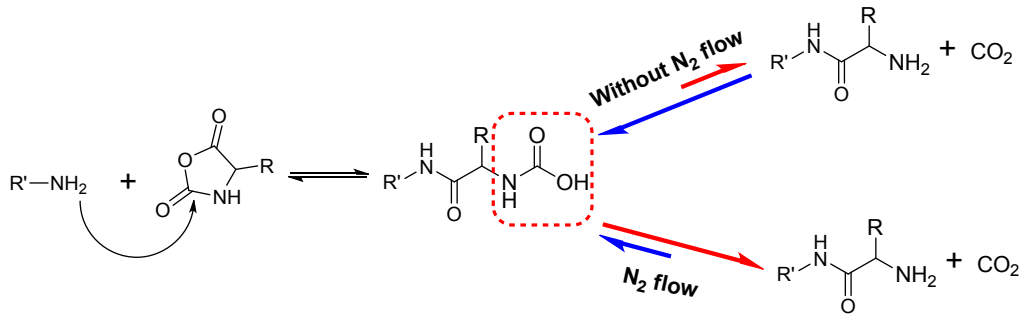


Scheme S1. The imination side reaction between photo-byproduct and amino groups during UV-triggered ROP (A) and the postulated pathways for forming the cyclic dimer initiating species during UV-triggered ROP (B).



Scheme S2. The promoted normal amine mechanism of NCA ROP under N_2 flow.

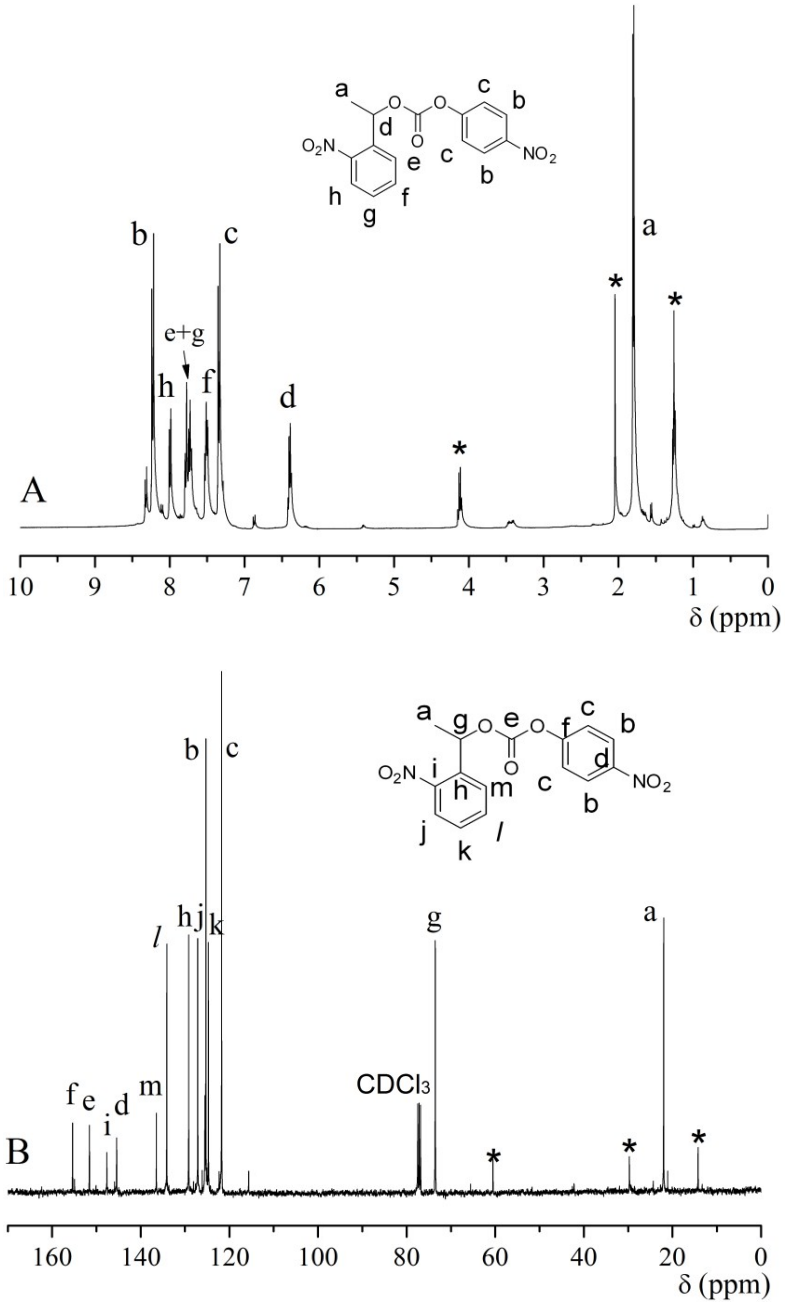


Figure S1. ^{1}H NMR (A) and ^{13}C NMR spectra of NPE-NPC ("*" denotes the EtOAc solvent peaks).

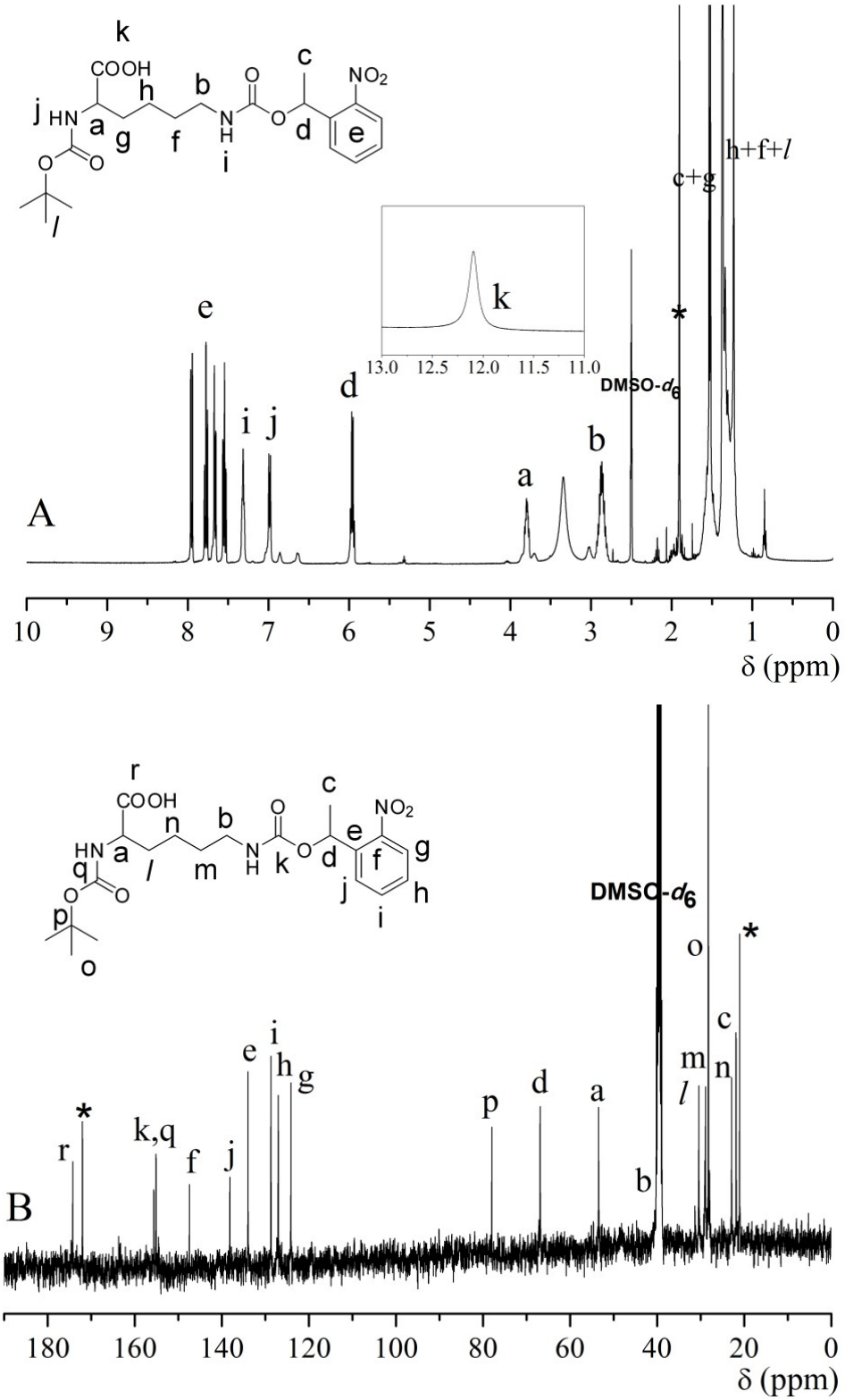


Figure S2. ^{1}H NMR (A) and ^{13}C NMR spectra of Boc-Lys(NPE)-OH ("*" denotes the AcOH solvent peaks).

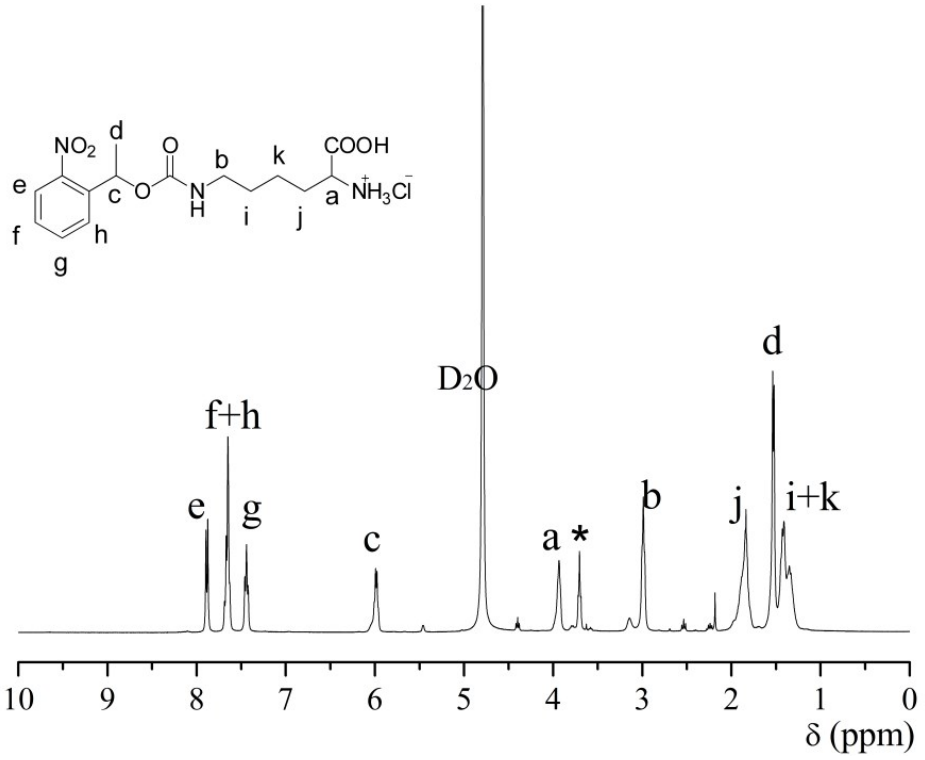


Figure S3. [1]H NMR spectrum of H-Lys(NPE)-OH·HCl ("*" denotes the THF solvent peaks).

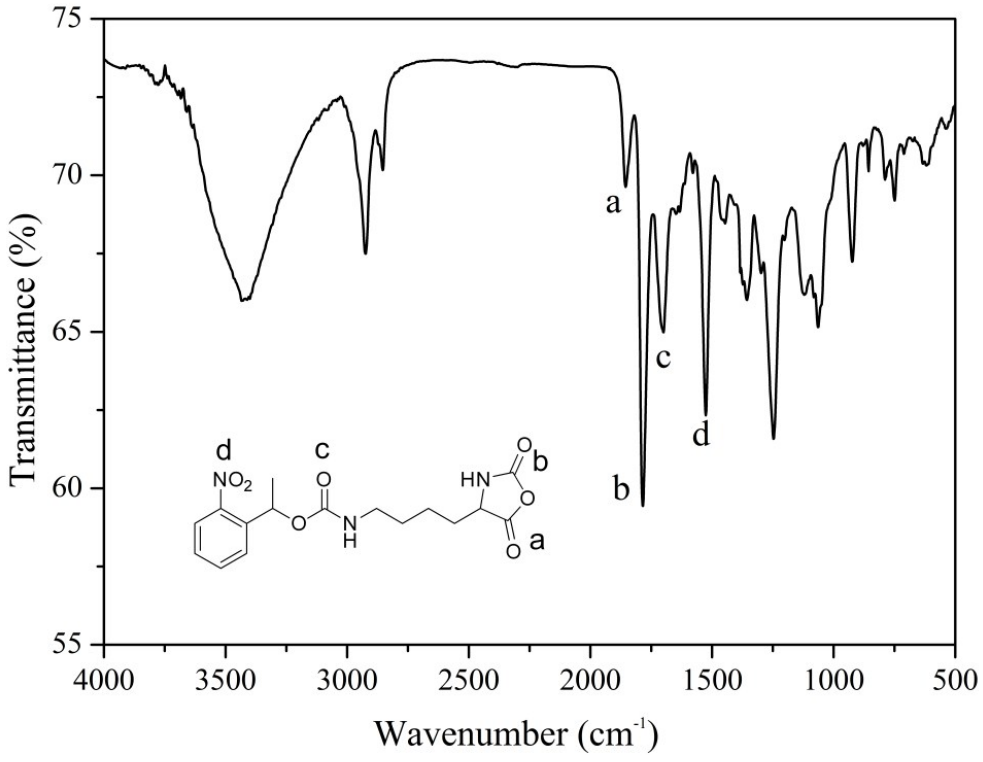


Figure S4. FT-IR spectrum of NPE-Lys NCA.

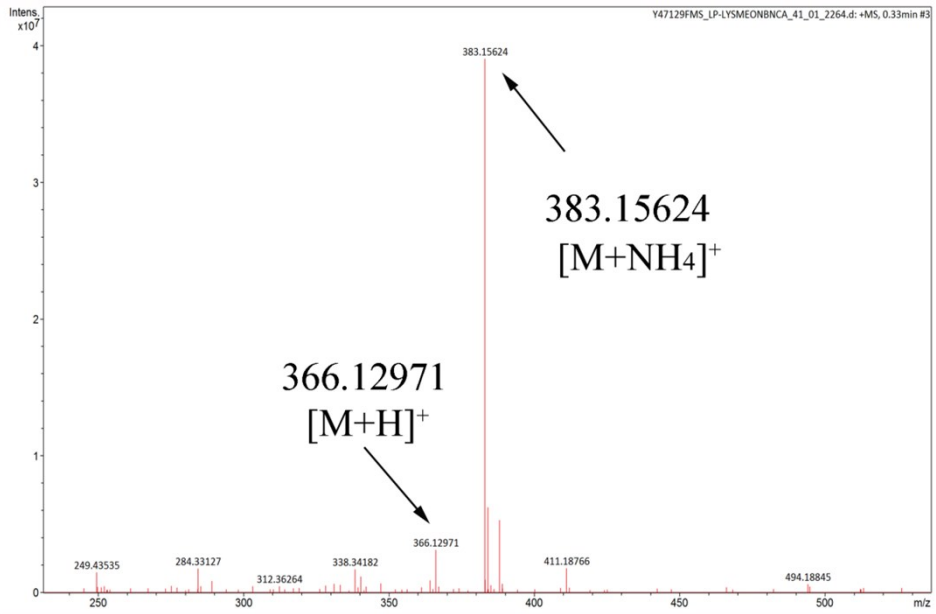


Figure S5. ESI-MS spectrum of NPE-Lys NCA.

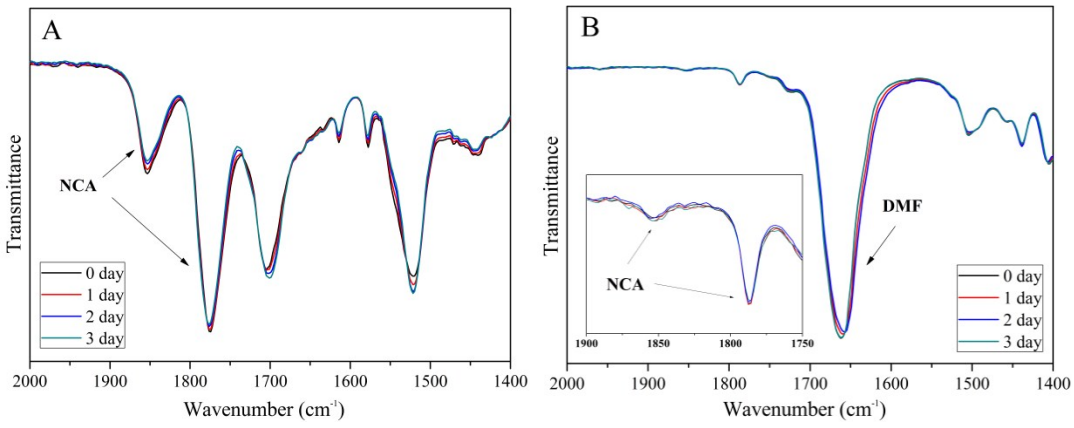


Figure S6. FT-IR monitoring the NPE-Lys NCA monomer consumption in the dark at 25 ^{o}C in both acetone (A) and DMF solution (B).

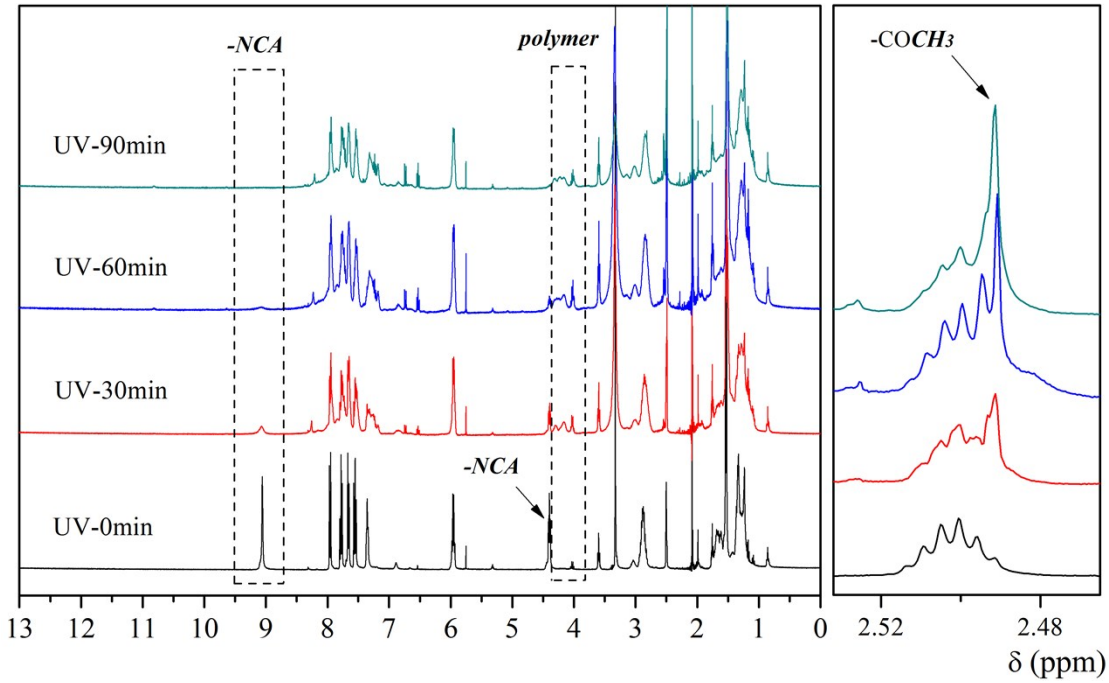


Figure S7. ^{1}H NMR spectra of NPE-Lys NCA in acetone upon 365 nm UV-irradiation at 16 mW/cm^2 for different irradiation times.

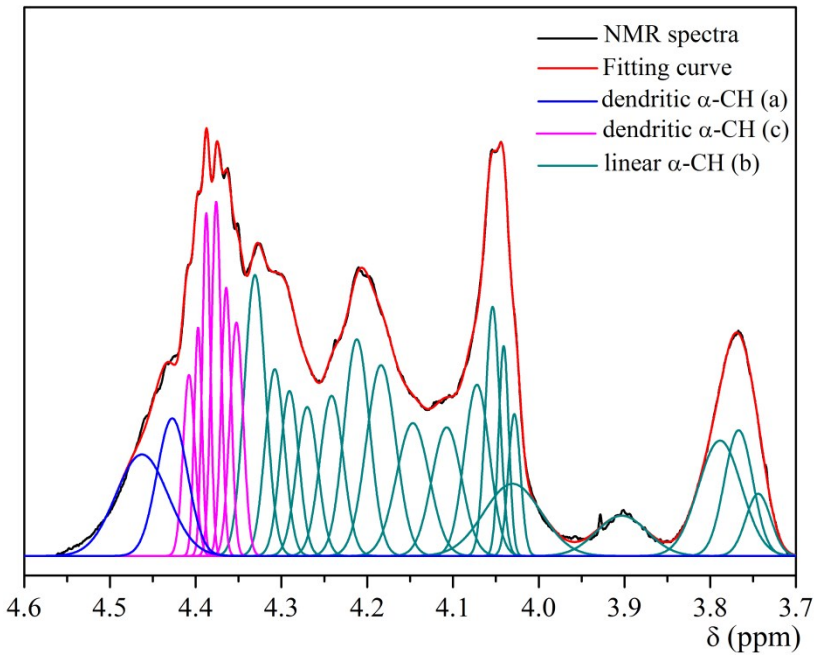


Figure S8. Peak fitting for α-CH in the ^{1}H NMR spectrum of sample P12 to calculate DB value by using software PeakFit (v 4.12).

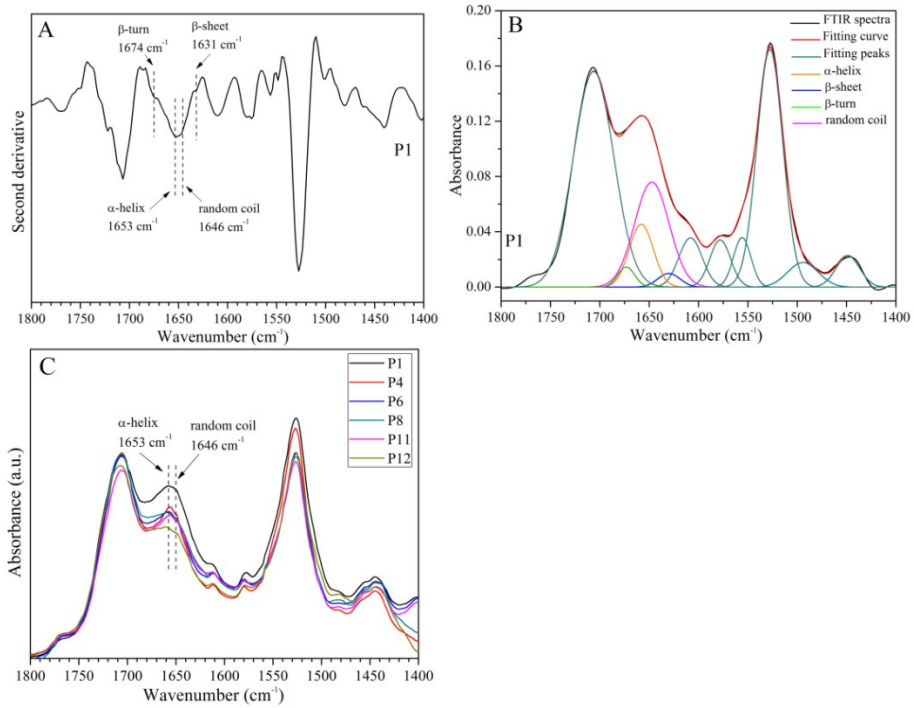


Figure S9. Second derivative (A) and FT-IR peak fitting results (B) of P1 in the solid state; and FT-IR spectra of P1, P4, P6, P8, P11 and P12 (C).

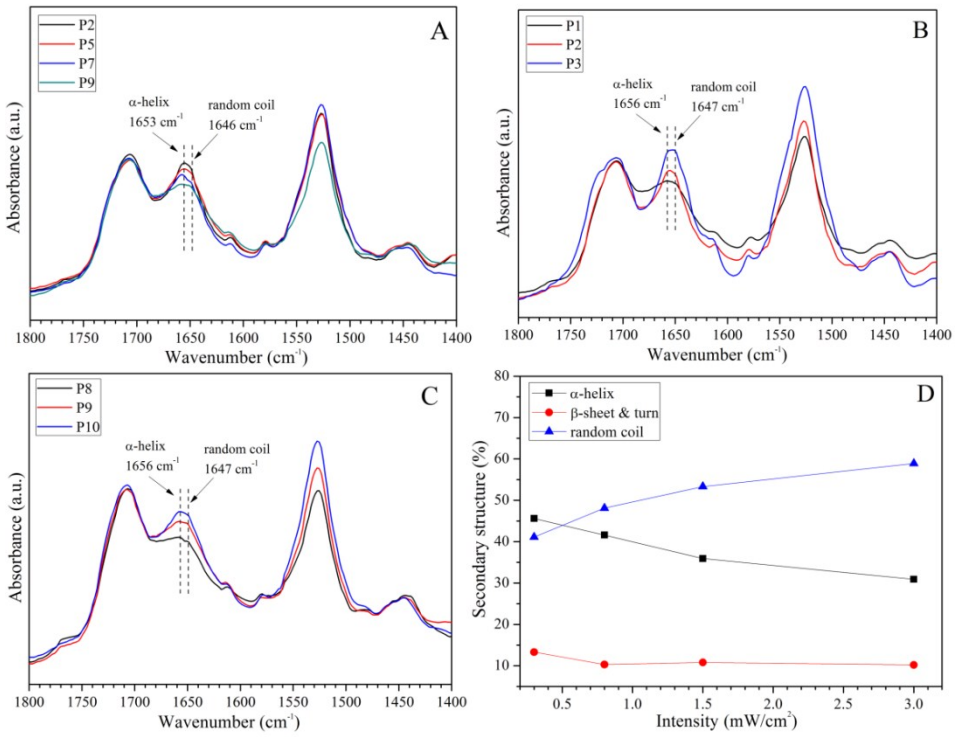


Figure S10. FT-IR spectra of P2, P5, P7 and P9 (A), P1-P3 (B) and P8-P10 (C) in the solid state, and the secondary structures of P2, P5, P7 and P9 synthesized at different irradiation intensities (D).

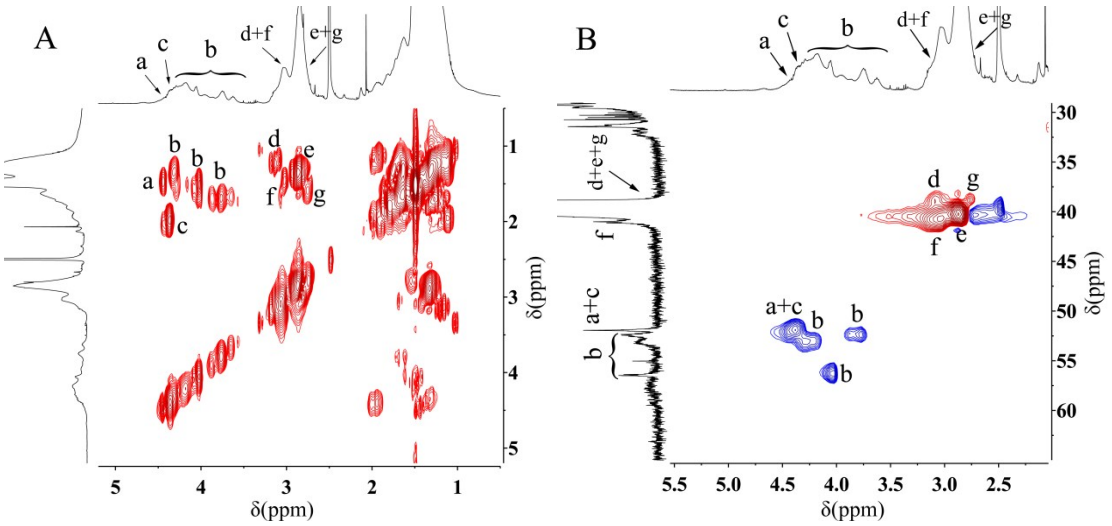


Figure S11. $^{1}H,^{1}H$-COSY spectrum (A) and $^{1}H,^{13}C$-HSQC spectrum (B) of P10.

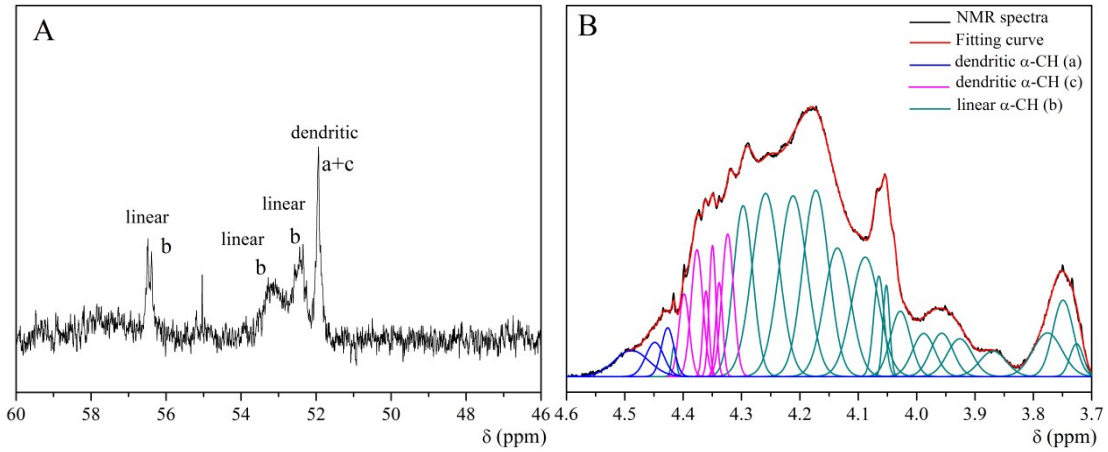


Figure S12. Quantitative ^{13}C NMR spectrum of P10 (A) and the peak fitting for α-CH in the ^{1}H NMR spectrum of P10 to calculate DB value (B).

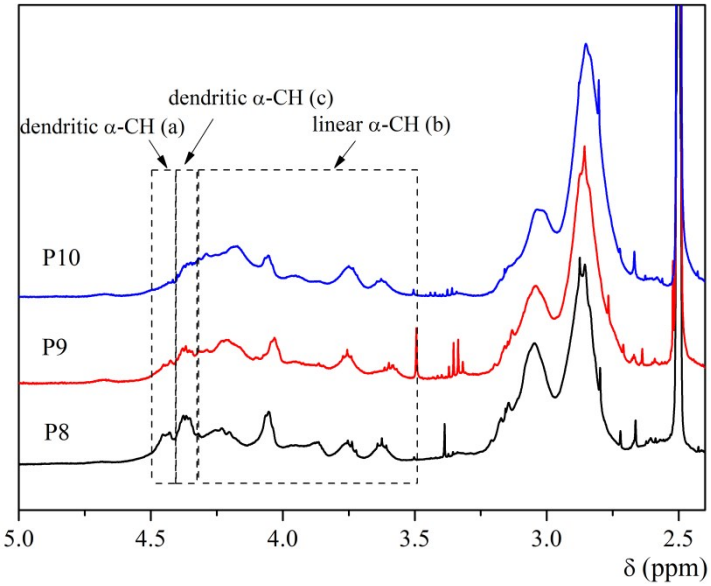


Figure S13. ^{1}H NMR spectra of P8-P10 synthesized under different N_2 flow rates.

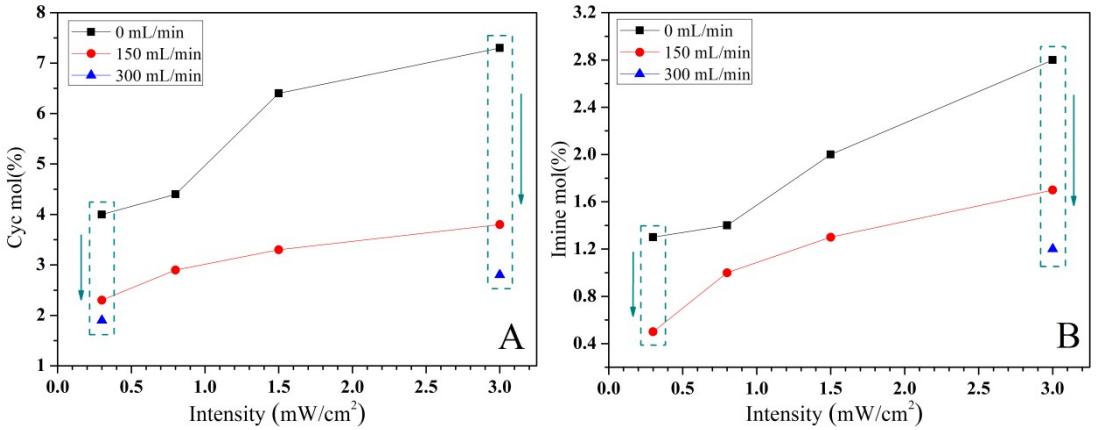


Figure S14. The effects of the irradiation intensity and/or N_2 flow rate on the contents of the cyclic dimer (A) and the imine (B).

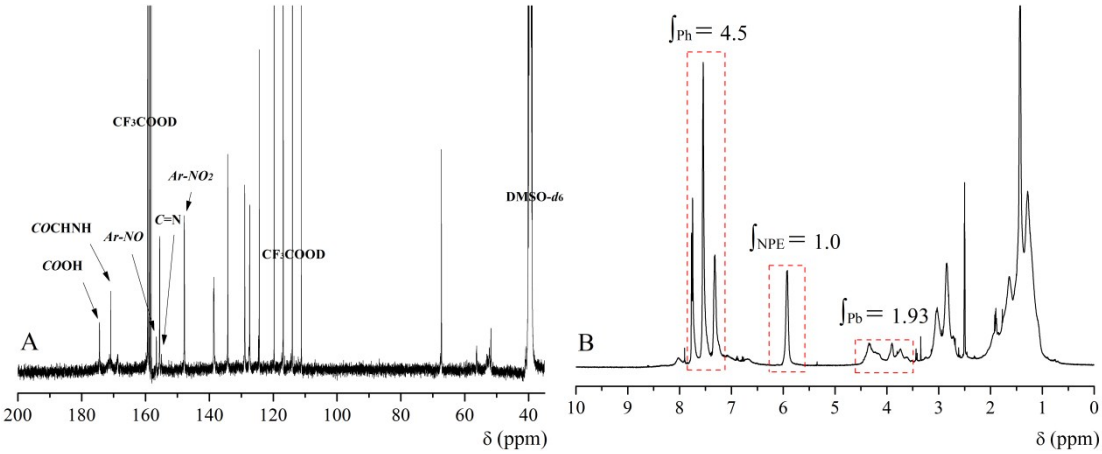


Figure S15. Both ^{13}C NMR spectrum (A) and ^{1}H NMR spectrum in mixed solvents of DMSO-d_6 and CF_3COOD (v:v = 3:2) of P12.

Note: Imine molar percentage is calculated according to the following procedure. The integration of peak at 5.93 ppm attributable to the methine proton of NPE group is set as the reference $\int_{NPE} = 1.0$; the theoretical integrated area of phenylic region 7.77~7.31 ppm should be $\int_{Ph} = 4.0$ if without imination, so the extra area compared to the theoretical integration (Δ=4.5-4.0=0.5) comes from the phenylic signals of imination. Therefore, imine mole percentage in the whole polypeptide backbone, $\int_{Pb} = 1.93$ integrated from 4.50~3.70 ppm, was calculated as $f = \frac{(\int NPE - \int Ph)/4}{\int Pb} = \frac{(4.5-4)/4}{1.93} = 6.5$ mol%.