

Supporting Information

Synthesis and Properties of Helical Polystyrene Derivatives with Amino Acid Side Groups

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Measurements

^1H and ^{13}C NMR spectra were recorded using a Bruker AVANCE 400 MHz spectrometer. The number-average molar mass (M_n), heavy-average molar mass (M_w) and polydispersity (M_w/M_n) of the polymers were estimated using a gel permeation chromatography (GPC) instrument equipped with a Waters 2414 refractive index detector. THF was used as the eluent with a flow rate of 1.0 mL/min and a temperature of 35°C. All GPC curves were calibrated against a series of monodisperse polystyrene standards. Optical rotations were measured on a JASCO Model P-1030 digital polarimeter. Circular dichroism (CD) spectra in a 1.0 mm quartz cell using a JASCO810 spectrophotometer. The polymer concentration was calculated based on 0.15 mg/ml monomer units. The chemical structures were characterized by Fourier transform infrared spectroscopy (FT-IR, NICOLET iS10) in the range of 4000-400 cm^{-1} by Traditional KBr Tableting Method. The UV-vis absorption spectra were recorded on a UNIC 4802 UV/vis double beam spectrophotometer. Transmission electron microscopy (TEM) was performed on a Japan Electronics JEOL2100. Atomic force microscopy (AFM) was recorded using Bruker Dimension ICON using highly oriented pyrolytic graphite (HOPG) as a

substrate. Dynamic light scattering (DLS) was recorded using the Malvern Mastersizer 2000.

Materials

4-vinyl benzoic acid (97%, Aladdin), 4-(4,6-dimethoxytriazin-2-yl)-4-methyl morpholine hydrochloride (98%, Macklin) and L/D-amino acid methyl ester hydrochloride (98%, Aladdin) were used without further purification. All solvents were purchased from Aladdin, Macklin and Sinopharm Holdings Ltd. 2,2'-Azobis(isobutyronitrile) (AIBN, Aladdin) was recrystallized in ethanol. The prepared PEO₄₅-DDMAT was reported according to the literature, and the structure was confirmed by ¹H NMR.¹

Synthesis of L-c : 4-vinylbenzoic acid (0.589 g, 4 mmol) and 4-(4,6-dimethoxytriazine)-4-methylmorpholine hydrochloride (DMT-MM) (1.22 g, 4.4 mmol) were dissolved in methanol (20 mL), waited for 10 min of stirring and then added L-phenylalanine methyl ester hydrochloride (0.95 g, 4.4 mmol) and appropriate amount of triethylamine. The mixture was washed with alkali, salt, water and dried after 16 h of reaction at 30 °C. Finally, the mixture was purified by silica gel column chromatography with ethyl acetate/hexane (2/5, v/v) to obtain a white solid in a yield of about 60. δ_{H} (400 MHz, Chloroform-*d*) 3.18 – 3.35 (2 H, qd, *J* 5.5, 13.8), 3.75 – 3.80 (3 H, s), 5.05 – 5.14 (1 H, dt, *J* 5.5, 7.5), 5.33 – 5.40 (1 H, d, *J* 10.9), 5.79 – 5.88 (1 H, d, *J* 17.6), 6.53 – 6.59 (1 H, d, *J* 7.5), 6.68 – 6.79

(1 H, dd, J 10.9, 17.6), 7.10 – 7.16 (2 H, m), 7.21 – 7.34 (4 H, m), 7.42 – 7.48 (2 H, d, J 8.2), 7.66 – 7.72 (2 H, d, J 8.3). δ_C (126 MHz, Chloroform-*d*) 37.76 – 37.97, 52.32 – 52.53, 53.41 – 53.64, 55.22 – 55.47, 115.98 – 116.22, 126.21 – 126.47, 127.12 – 127.27, 127.27 – 127.43, 128.55 – 128.70, 129.26 – 129.42, 132.82 – 132.94, 135.78 – 136.01, 140.81 – 141.01, 166.32 – 166.55, 172.02 – 172.17. FT-IR (KBr, 25 °C): 3268, 3077, 3032, 2937, 2845, 1745, 1645, 997, 913 cm^{-1} . MS m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 310.1443; Found: 310.1441. Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.71; H, 5.24; N, 4.84. The same synthetic procedure prepared the L-a, L-b, L-d, and D-c monomers. Their characterization data are given below.

L-a: δ_H (400 MHz, Chloroform-*d*) 0.95 – 1.03 (6 H, dd, J 6.0, 7.9), 1.60 – 1.82 (3 H, m), 3.75 – 3.80 (3 H, s), 4.82 – 4.92 (1 H, td, J 5.0, 8.4), 5.33 – 5.40 (1 H, d, J 10.9), 5.80 – 5.89 (1 H, d, J 17.6), 6.47 – 6.54 (1 H, d, J 8.3), 6.69 – 6.80 (1 H, dd, J 10.9, 17.6), 7.44 – 7.50 (2 H, d, J 8.2), 7.73 – 7.80 (2 H, m). FT-IR (KBr, 25 °C) : 3265, 3064, 3037, 2953, 2874, 1755, 1634, 993, 918 cm^{-1} . MS m/z calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 276.1600; Found: 276.1599. Calcd. for $\text{C}_{16}\text{H}_{21}\text{NO}_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 68.61; H, 7.32; N, 5.15.

L-b: δ_H (400 MHz, Chloroform-*d*) 0.96 – 1.05 (6 H, dd, J 6.8, 8.8), 2.22 – 2.34 (1 H, pd, J 4.9, 6.9), 3.76 – 3.80 (3 H, s), 4.01 – 4.06 (2 H, d, J 1.0), 4.75 – 4.83 (1 H, dd, J 4.9, 8.6), 5.33 – 5.40 (1 H, dd, J 0.8, 10.9), 5.80 –

5.89 (1 H, dd, J 0.9, 17.6), 6.58 – 6.65 (1 H, d, J 8.6), 6.69 – 6.81 (1 H, dd, J 10.9, 17.6), 7.44 – 7.51 (2 H, m), 7.74 – 7.81 (2 H, m). δ_{C} (101 MHz, Chloroform-*d*) 17.90 – 18.10, 18.91 – 19.10, 31.57 – 31.77, 52.19 – 52.33, 55.29 – 55.43, 57.32 – 57.52, 115.98 – 116.18, 126.29 – 126.44, 127.29 – 127.50, 133.10 – 133.29, 135.86 – 136.02, 140.86 – 140.99, 166.78 – 166.99, 172.66 – 172.79, 173.52 – 173.67. FT-IR (KBr, 25 °C): 3324, 3092, 2958, 2865, 1750, 1634, 993, 910 cm^{-1} . MS m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 262.1443; Found: 262.1442. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 64.21; H, 6.57; N, 7.26.

L-d: δ_{H} (400 MHz, Chloroform-*d*) 1.22 – 1.32 (3 H, t, J 7.1), 3.19 – 3.34 (2 H, m), 4.17 – 4.27 (2 H, q, J 7.2), 5.02 – 5.11 (1 H, dt, J 5.6, 7.6), 5.32 – 5.39 (1 H, d, J 10.9), 5.79 – 5.88 (1 H, d, J 17.6), 6.55 – 6.61 (1 H, d, J 7.6), 6.68 – 6.79 (1 H, dd, J 10.9, 17.6), 7.11 – 7.18 (2 H, m), 7.20 – 7.34 (2 H, m), 7.42 – 7.51 (2 H, m), 7.66 – 7.73 (2 H, m). δ_{C} (101 MHz, Chloroform-*d*) 14.07 – 14.24, 37.86 – 38.05, 53.45 – 53.64, 61.60 – 61.75, 115.98 – 116.19, 126.26 – 126.47, 127.09 – 127.24, 127.26 – 127.44, 128.49 – 128.66, 129.37 – 129.52, 132.93 – 133.07, 135.81 – 136.06, 140.86 – 140.99, 166.33 – 166.49, 171.60 – 171.74. FT-IR (KBr, 25 °C): 3339, 3028, 2995, 2935, 1750, 1643, 984, 918 cm^{-1} . MS m/z calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 324.1600; Found: 324.1594. Calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 73.48; H, 6.2; N, 4.91.

D-c: δ_{H} (400 MHz, Chloroform-*d*) 1.23 – 1.30 (1 H, m), 3.18 – 3.34 (2 H,

qd, J 5.6, 13.8), 3.75 – 3.79 (3 H, s), 5.05 – 5.14 (1 H, dt, J 5.6, 7.6), 5.32 – 5.39 (1 H, d, J 10.9), 5.79 – 5.88 (1 H, d, J 17.5), 6.52 – 6.59 (1 H, d, J 7.6), 6.68 – 6.79 (1 H, dd, J 10.9, 17.6), 7.09 – 7.16 (2 H, m), 7.21 – 7.34 (4 H, m), 7.42 – 7.48 (2 H, m), 7.66 – 7.72 (2 H, m). δ_c (101 MHz, Chloroform-*d*) 37.81 – 38.02, 52.37 – 52.51, 53.42 – 53.62, 116.03 – 116.21, 126.29 – 126.46, 127.15 – 127.29, 127.29 – 127.43, 128.58 – 128.72, 129.29 – 129.44, 132.84 – 132.99, 135.80 – 135.93, 135.85 – 135.99, 140.90 – 141.03, 166.31 – 166.52, 172.02 – 172.17. FT-IR (KBr, 25 °C): 3269, 3083, 3028, 2953, 1736, 1639, 989, 914 cm^{-1} . MS m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 310.1443; Found: 310.1439. Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.56; H, 5.86; N, 4.68.

Synthesis of Poly-L-c₅₀ : To a 10 mL argon-filled dry Schlenk bottle was added the monomer L-c (0.124 g, 0.4mmol), azo diisobutyronitrile (AIBN) (0.4 mg, 0.0024mmol), PEO₄₅-DDMAT (0.019 g, 0.008mmol) and tetrahydrofuran (2.5 mL). The obtained mixture was stirred at 70°C for 24h and poured into a large amount of methyl tert-butyl ether to form a white solid, which was separated by filtration and dried under vacuum to obtain Poly-L-c₅₀. δ_H (400 MHz, Chloroform-*d*) 0.74 – 0.79 (1 H, s), 2.80 – 2.88 (3 H, d, J 12.9), 4.13 – 4.17 (1 H, s), 5.34 – 5.39 (1 H, s), 5.49 – 5.54 (1 H, s), 6.35 – 6.40 (3 H, s), 6.42 – 6.46 (1 H, s). FT-IR (KBr, 25 °C): 3431, 3306, 3032, 2930, 2851, 1741, 1643 cm^{-1} . $[\alpha]_D^{20} = -69.2$ ($c=1\text{mg/mL}$ THF). Other polymers were synthesized following the same synthesis procedure.

Characterization data are shown below.

Poly-L-a_{50 H} (400 MHz, Chloroform-*d*) -3.83 – -3.79 (1 H, s), 0.96 – 1.01 (2 H, s), 1.39 – 1.44 (1 H, s), 3.69 – 3.74 (1 H, s), 6.28 – 6.32 (1 H, s), 7.39 – 7.44 (1 H, s). FT-IR (KBr, 25 °C): 3316, 3028, 2958, 2865, 1745, 1643 cm⁻¹. $[\alpha]_{\text{D}}^{20} = -52.8$ (*c*=1mg/mL THF).

Poly-L-b_{50 H} (400 MHz, Chloroform-*d*) 0.98 – 1.05 (5 H, d, *J* 9.7), 1.38 – 1.43 (4 H, s), 2.32 – 2.37 (1 H, s), 3.62 – 3.67 (1 H, s), 3.71 – 3.75 (3 H, s), 4.64 – 4.68 (1 H, s), 6.32 – 6.37 (2 H, s), 7.38 – 7.42 (3 H, s). FT-IR (KBr, 25 °C): 3320, 3028, 2985, 2874, 1745, 1643 cm⁻¹. $[\alpha]_{\text{D}}^{20} = -57.6$ (*c*=1mg/mL THF).

Poly-L-d_{50 H} (400 MHz, Chloroform-*d*) 1.14 – 1.18 (4 H, s), 3.27 – 3.32 (2 H, s), 3.62 – 3.67 (1 H, s), 4.10 – 4.15 (2 H, s), 4.94 – 4.99 (1 H, s), 6.12 – 6.16 (1 H, s), 6.31 – 6.36 (1 H, s), 7.21 – 7.25 (6 H, s). FT-IR (KBr, 25 °C): 3436, 3306, 3028, 2986, 2925, 2865, 1741, 1648 cm⁻¹. $[\alpha]_{\text{D}}^{20} = -70.6$ (*c*=1mg/mL THF).

Poly-D-c_{50 H} (400 MHz, Chloroform-*d*) -3.75 – -3.71 (2 H, s), 0.03 – 0.17 (2 H, dd, *J* 8.5, 21.8), 0.82 – 0.87 (1 H, s), 1.23 – 1.28 (1 H, m), 3.28 – 3.32 (2 H, s), 3.62 – 3.70 (5 H, d, *J* 13.3), 4.95 – 5.00 (1 H, s), 6.16 – 6.20 (1 H, s), 6.32 – 6.37 (1 H, s), 7.16 – 7.21 (5 H, s), 7.90 – 7.94 (1 H, s). FT-IR (KBr, 25 °C): 3427, 3311, 3032, 2925, 2846, 1736, 1639 cm⁻¹. $[\alpha]_{\text{D}}^{20} = +74.4$ (*c*=1mg/mL THF).

Synthesis of PEO₄₅-DDMAT: PEG monomethyl ether (mPEG₂₀₀₀) (1 g,

0.5 mmol), 2-(dodecylthio)-2-methylpropanoic acid (0.455 g, 1.248 mmol) and 4-dimethylamino pyridine (DMAP) (25 mg, 0.205 mmol) were dissolved in dry DMC. A solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) (240 mg, 1.252 mmol) was added dropwise to the premixed solution at 0 °C. The mixture was stirred for one day and monitored by ¹H NMR. The crude product was washed three times with brine and dried with MgSO₄. The product was purified by silica gel column chromatography with ethyl acetate/hexane (5/2, v/v) to give a yellow powder. δ_{H} (400 MHz, Chloroform-*d*) 1.25 – 1.28 (10 H, s), 1.28 – 1.35 (5 H, d, *J* 13.5), 3.63 – 3.67 (147 H, s), 3.64 – 3.69 (20 H, d, *J* 1.9). FT-IR (KBr, 25 °C): 3423, 2893, 1736, 1462 cm⁻¹.

Synthesis of Poly(L-c₅₀-co-e₁₀): To a 10 mL argon-filled Schlenk bottle was added ethylene glycol dimethacrylate (0.0076 mL, 0.04 mmol), AIBN (0.66 mg, 0.004 mmol), PEO₄₅-b-Poly-L-c₅₀ (0.07 g, 0.004 mmol) and THF (2.5 mL). The obtained mixture was stirred at 70 °C for three hours, poured into a large amount of methyl tert-butyl ether to obtain a white solid, separated by filtration and dried under vacuum to obtain Poly(L-c₅₀-co-e₁₀). δ_{H} (400 MHz, Chloroform-*d*) 0.77 – 1.46 (1 H, t, *J* 9.5), 3.06 – 3.94 (5 H, m), 4.86 – 5.14 (1 H, s), 6.01 – 6.58 (2 H, d, *J* 72.6). FT-IR (KBr, 25 °C): 3427, 3316, 3027, 2950, 2927, 2855, 1735, 1650, 1529, 1496 cm⁻¹. $[\alpha]_{\text{D}}^{20} = -69.2$ (*c* = 1 mg/mL THF). $M_{\text{n}} = 19.4$ kg/mol, $\text{Đ} = 1.46$.

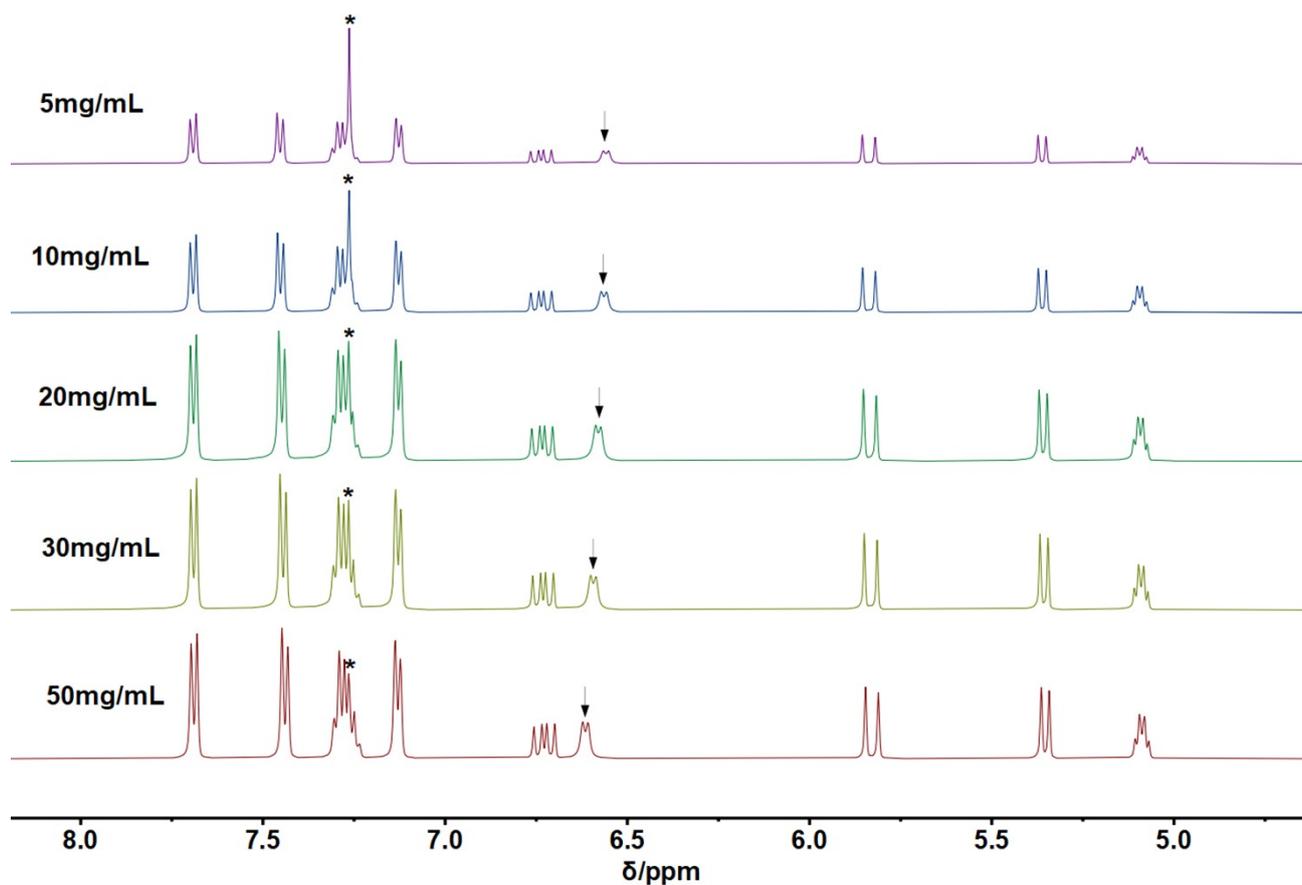


Fig. S1 ^1H NMR (400 MHz) spectra of different concentrations of L-c were measured in CDCl_3 at 25°C .

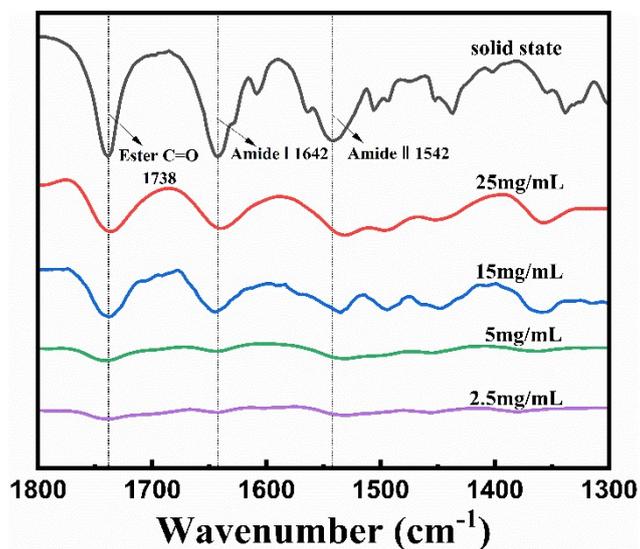


Fig. S2 FT-IR spectra of different concentrations of L-c were measured in CDCl_3 at 25°C .

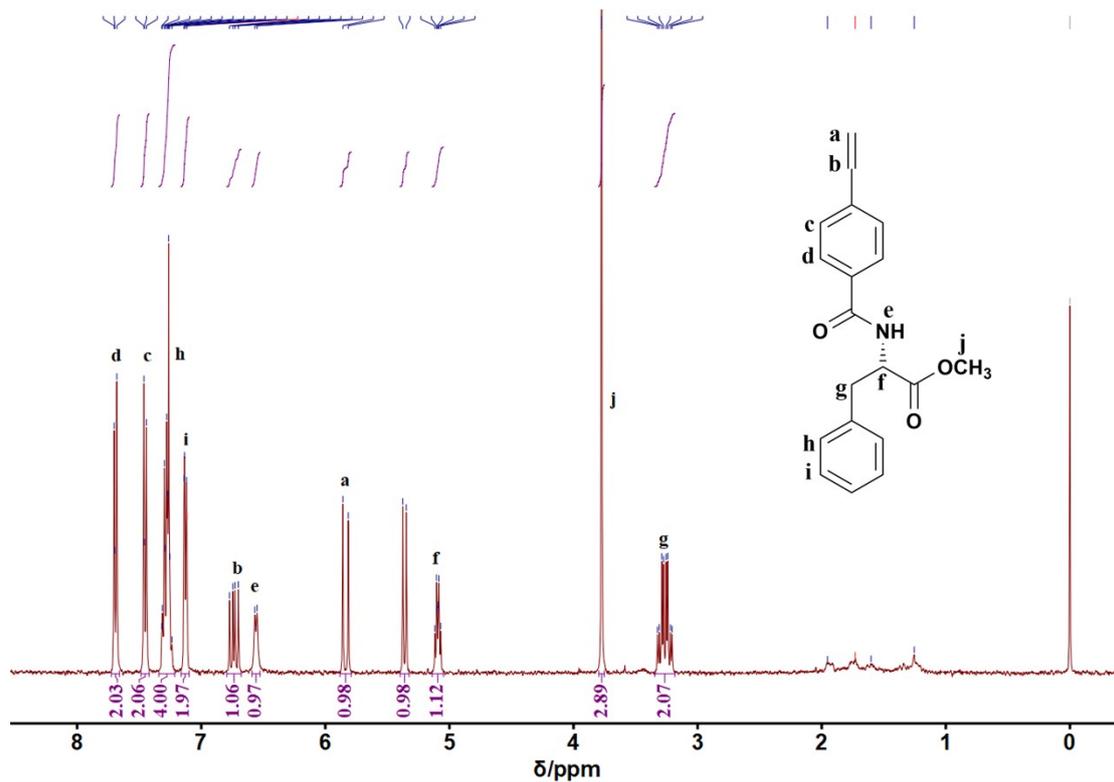


Fig. S3 ¹H NMR (400 MHz) spectra of L-c were measured in CDCl₃ at 25 °C.

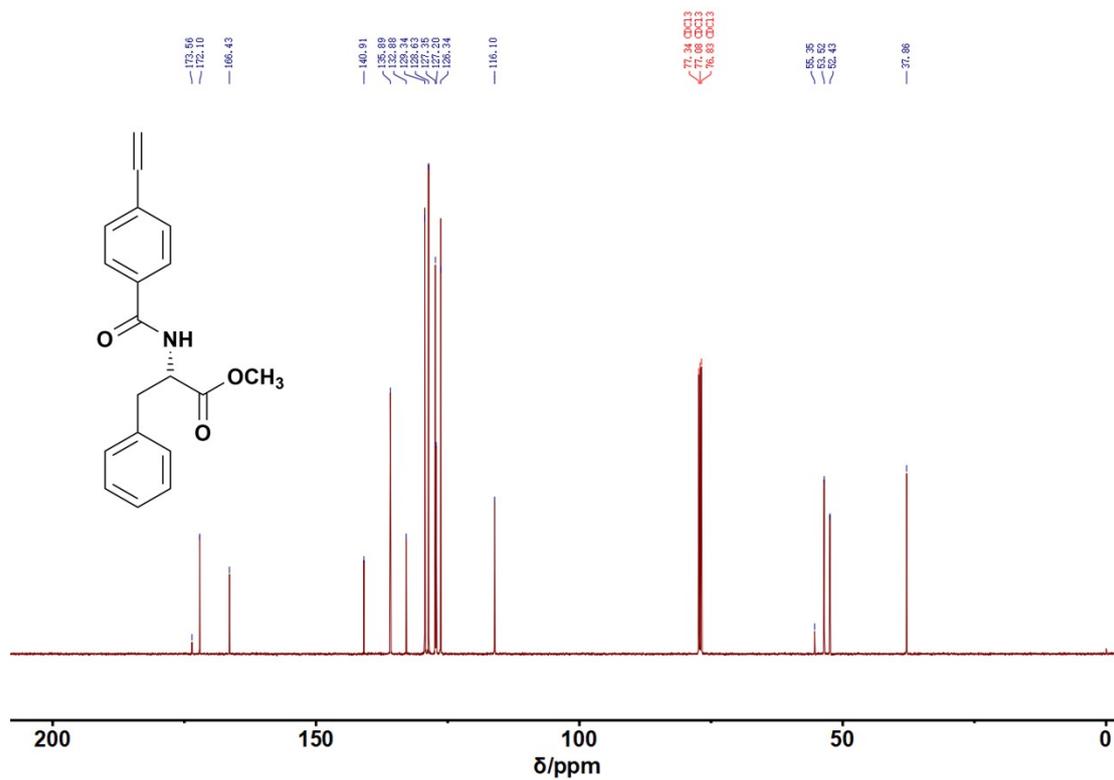


Fig. S4 ¹³C NMR (101 MHz) spectra of L-c were measured in CDCl₃ at 25 °C.

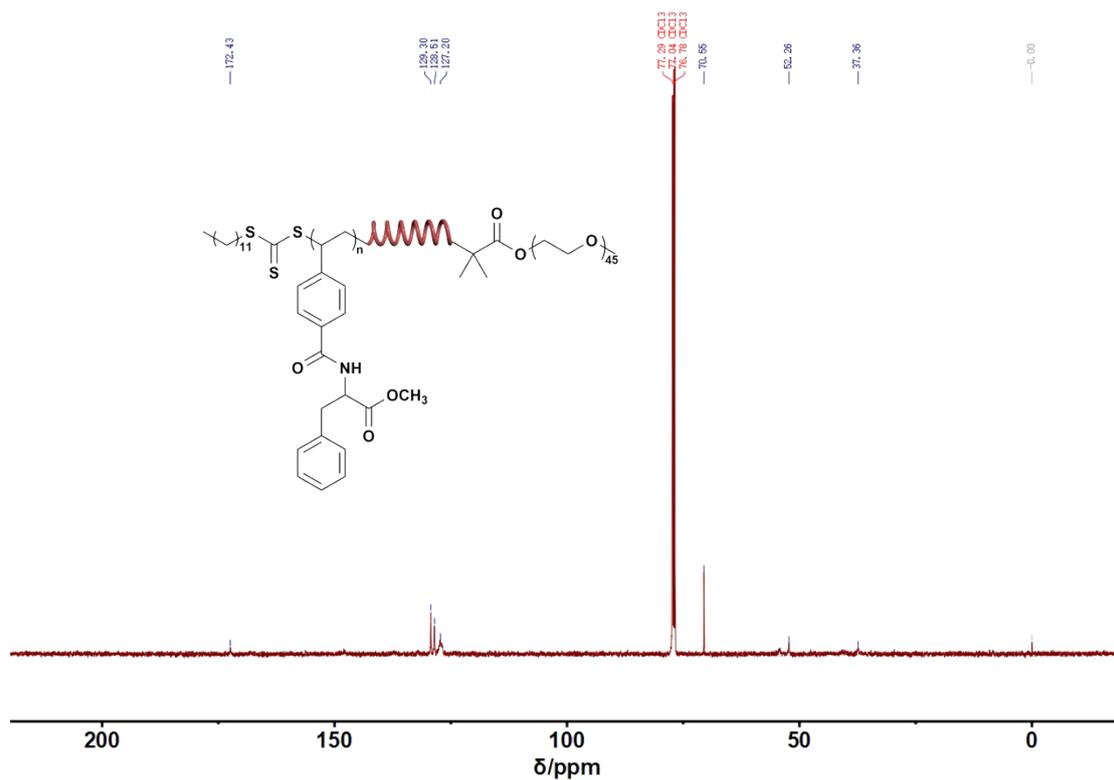


Fig. S5 ¹³C NMR (101 MHz) spectra of Poly-L-c₅₀ were measured in CDCl₃ at 25 °C.

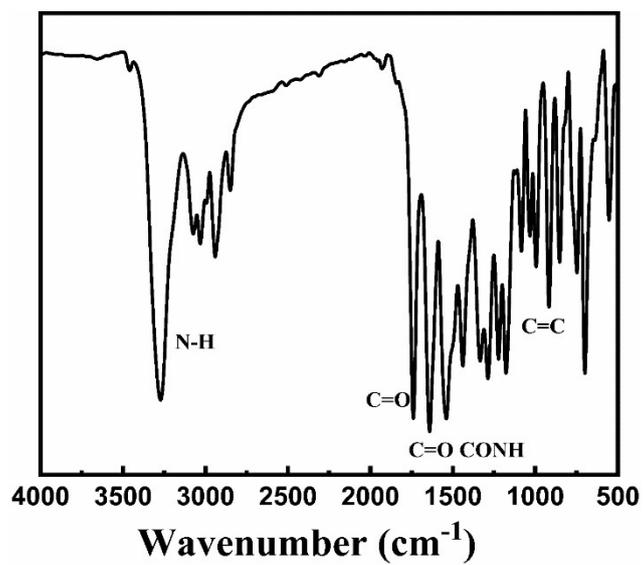


Fig. S6 FT-IR spectra of L-c were measured using KBr at 25 °C.

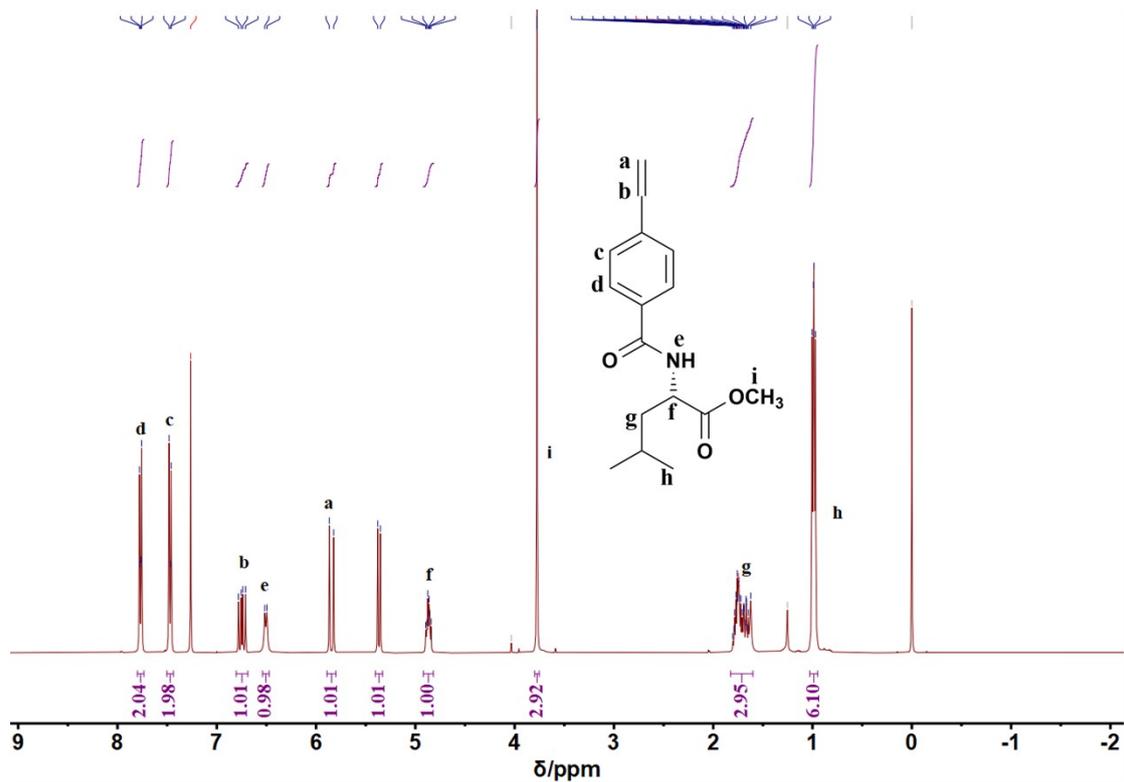


Fig. S7 ¹H NMR (400 MHz) spectra of L-a were measured in CDCl₃ at 25 °C.

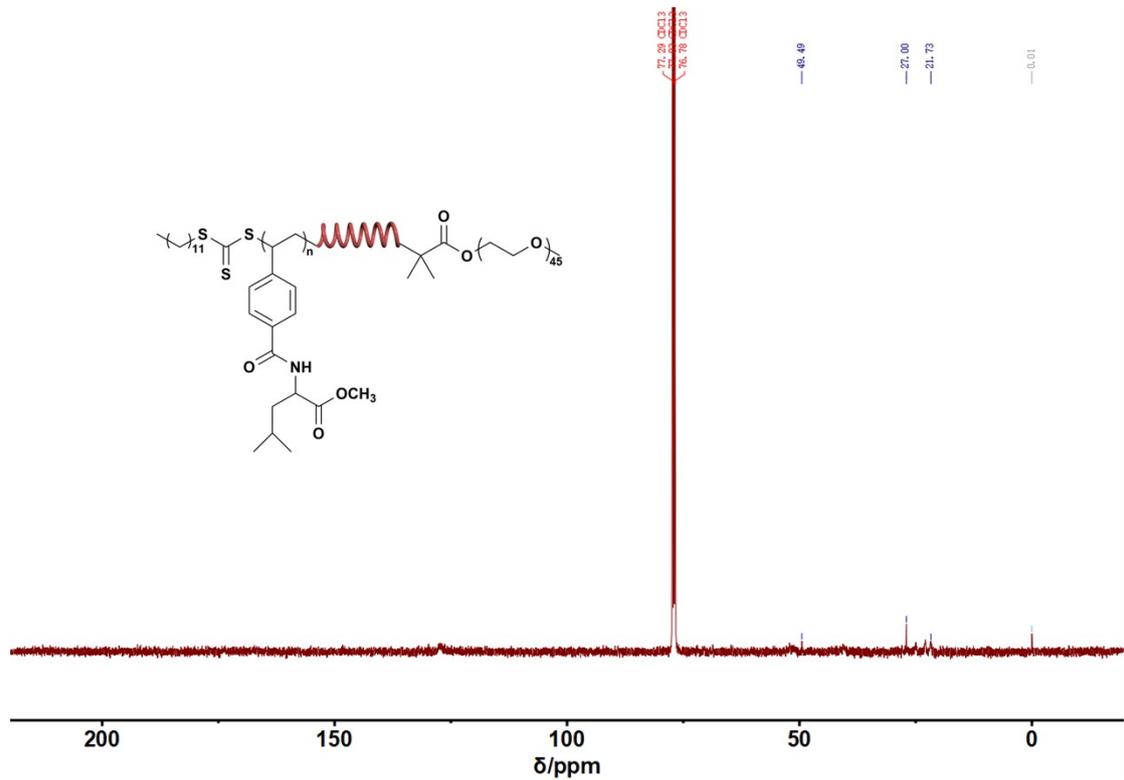


Fig. S8 ¹³C NMR (101 MHz) spectra of Poly-L-a₅₀ were measured in CDCl₃ at 25 °C.

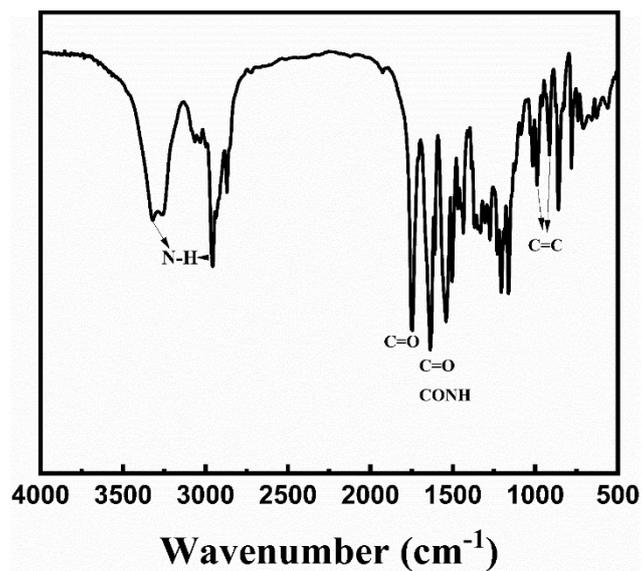


Fig. S9 FT-IR spectra of L-a were measured using KBr at 25 °C.

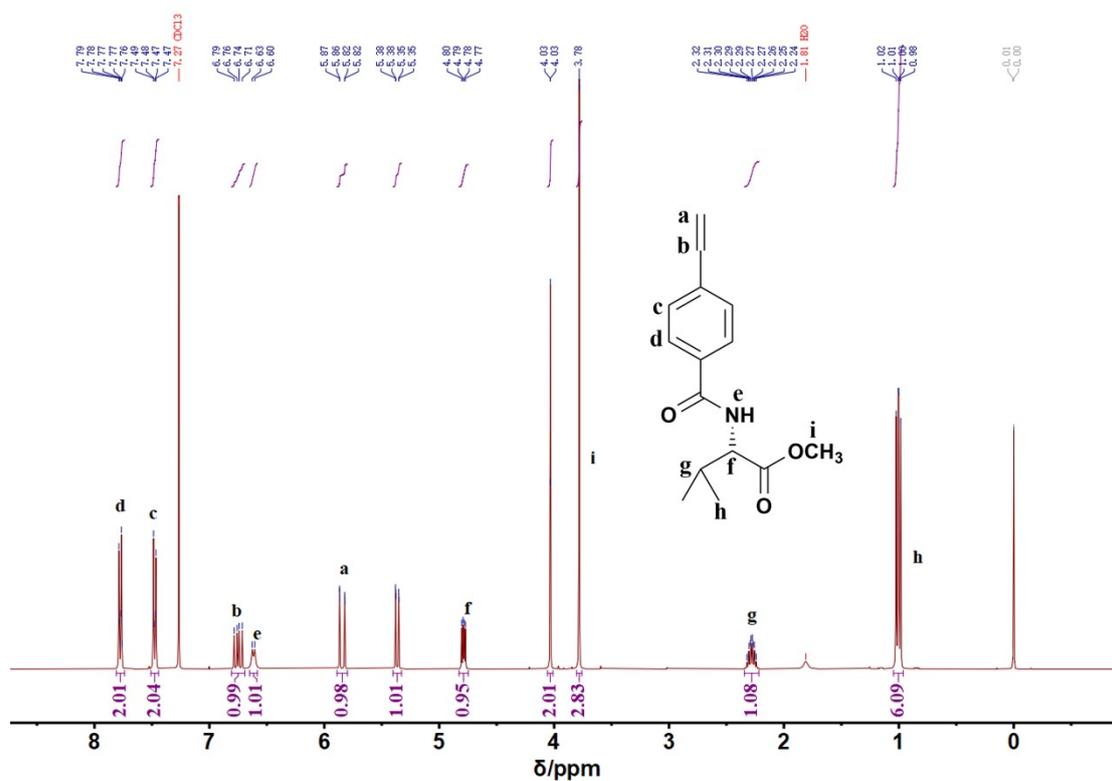


Fig. S10 ^1H NMR (400 MHz) spectra of L-b were measured in CDCl_3 at 25 °C.

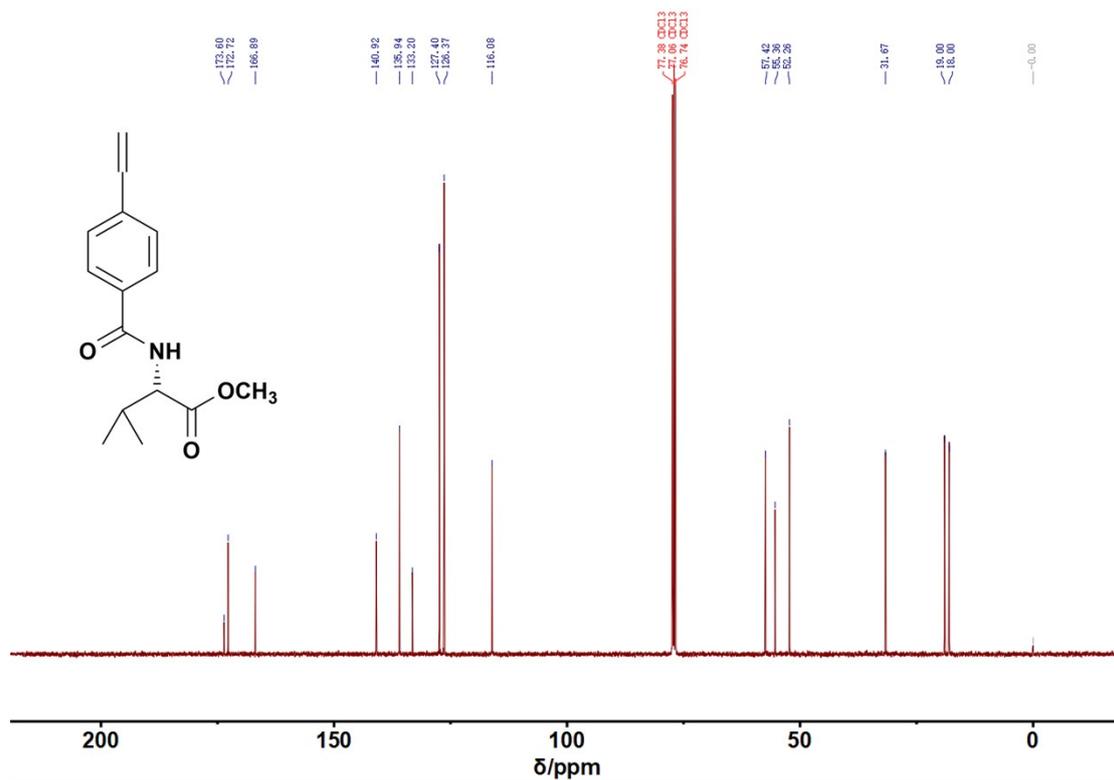


Fig. S11 ^{13}C NMR (101 MHz) spectra of L-b were measured in CDCl_3 at 25 °C.

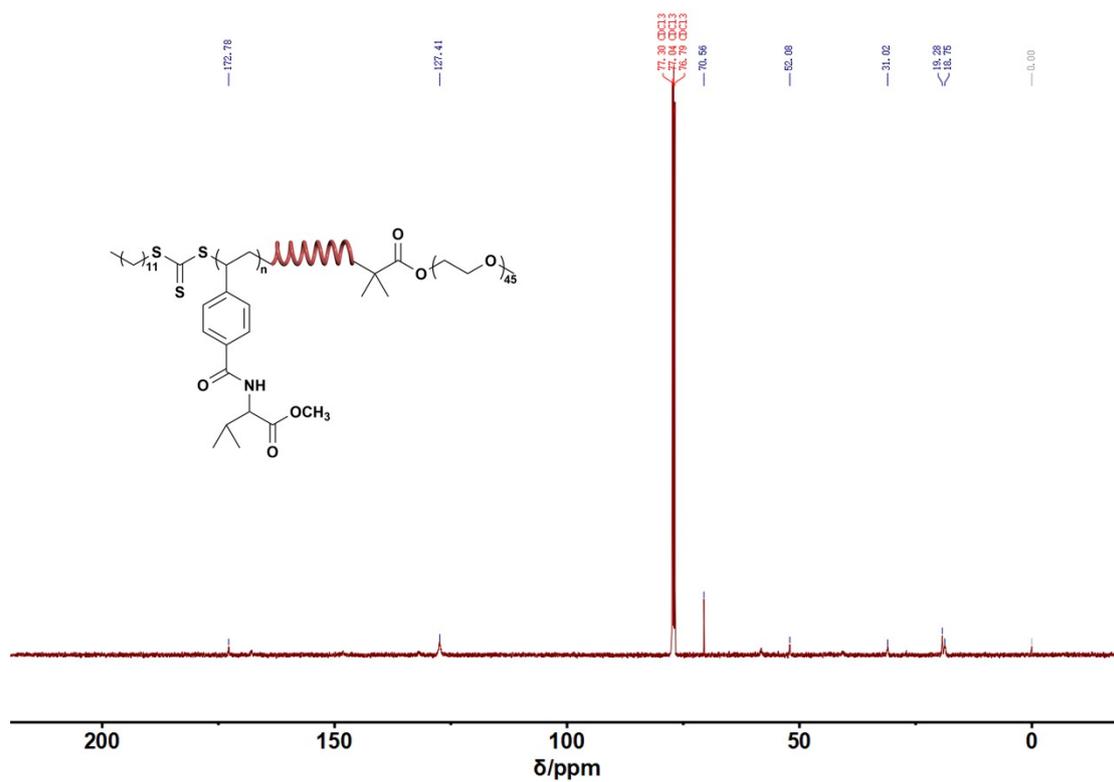


Fig. S12 ^{13}C NMR (101 MHz) spectra of Poly-L-b₅₀ were measured in CDCl_3 at 25 °C.

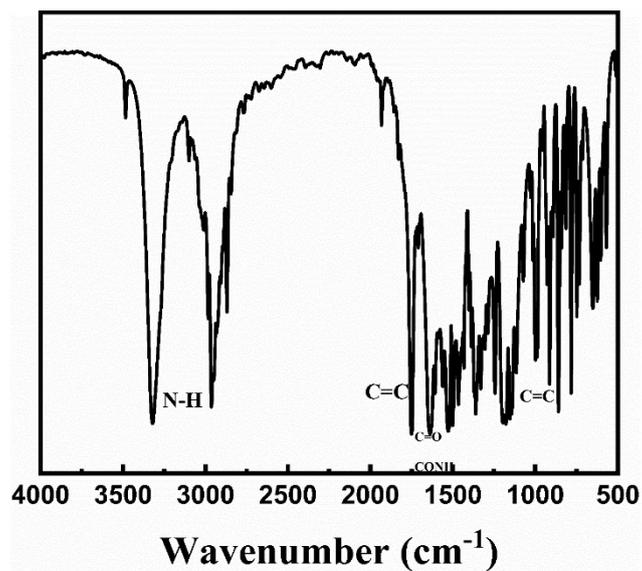


Fig. S13 FT-IR spectra of L-b were measured using KBr at 25 °C.

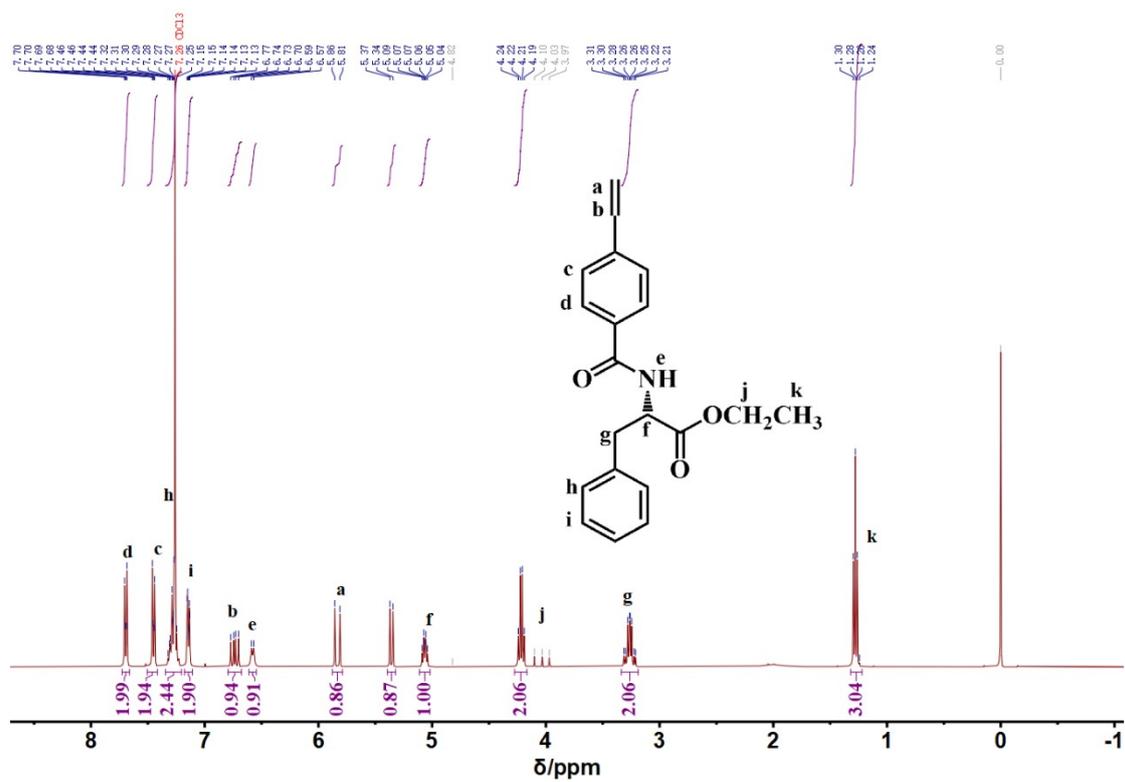


Fig. S14 ^1H NMR (400 MHz) spectra of L-d were measured in CDCl_3 at 25 °C.

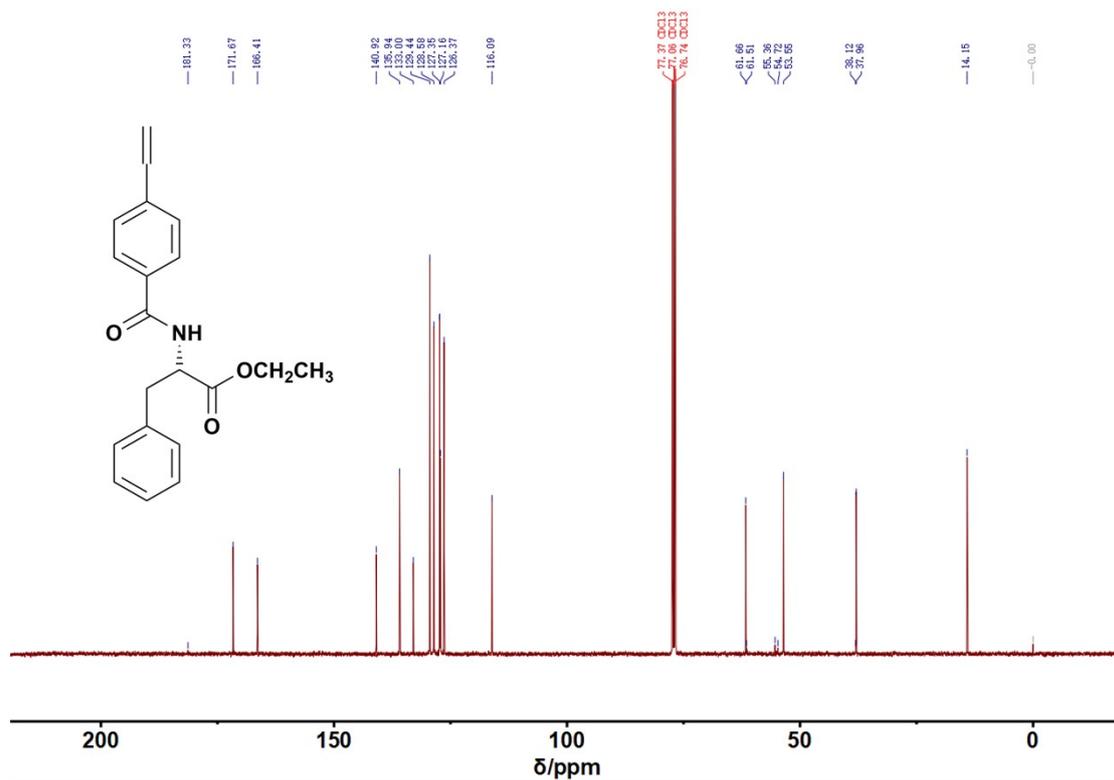


Fig. S15 ^{13}C NMR (101 MHz) spectra of L-d were measured in CDCl_3 at 25 °C.

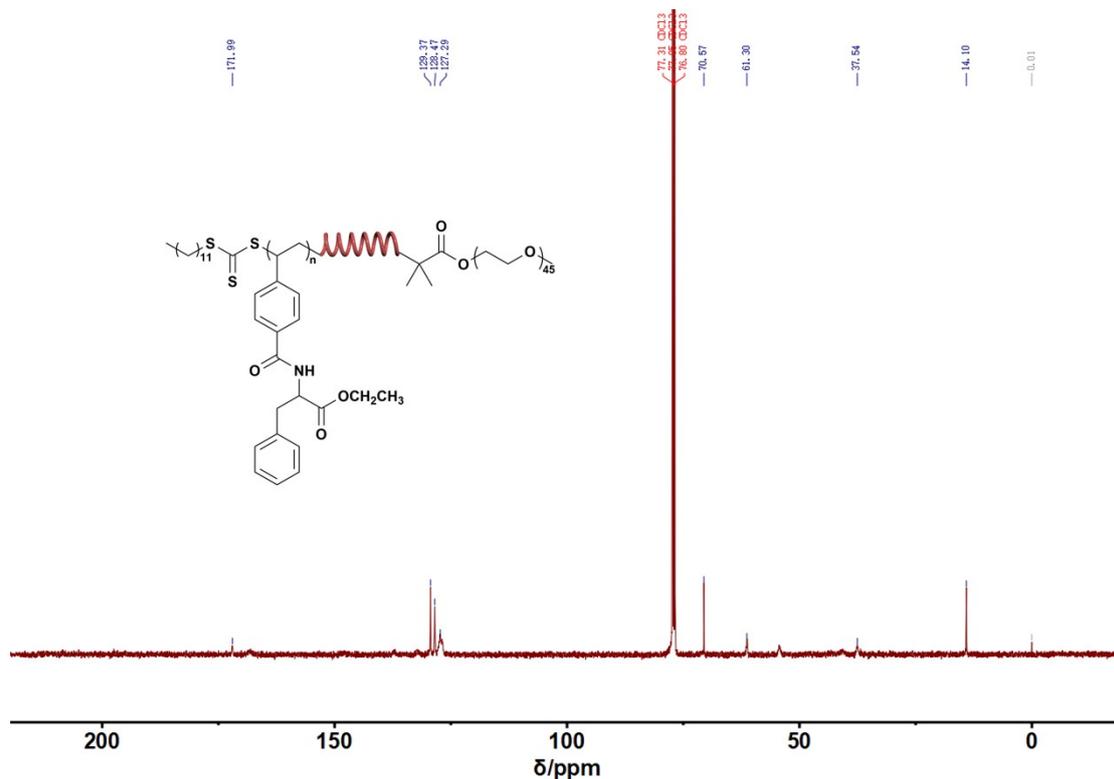


Fig. S16 ^{13}C NMR (101 MHz) spectra of Poly-L-d₅₀ were measured in CDCl_3 at 25 °C.

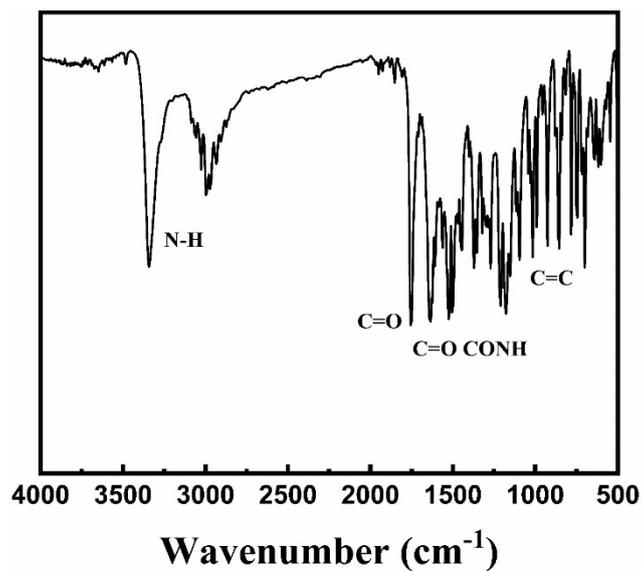


Fig. S17 FT-IR spectra of L-d were measured using KBr at 25 °C.

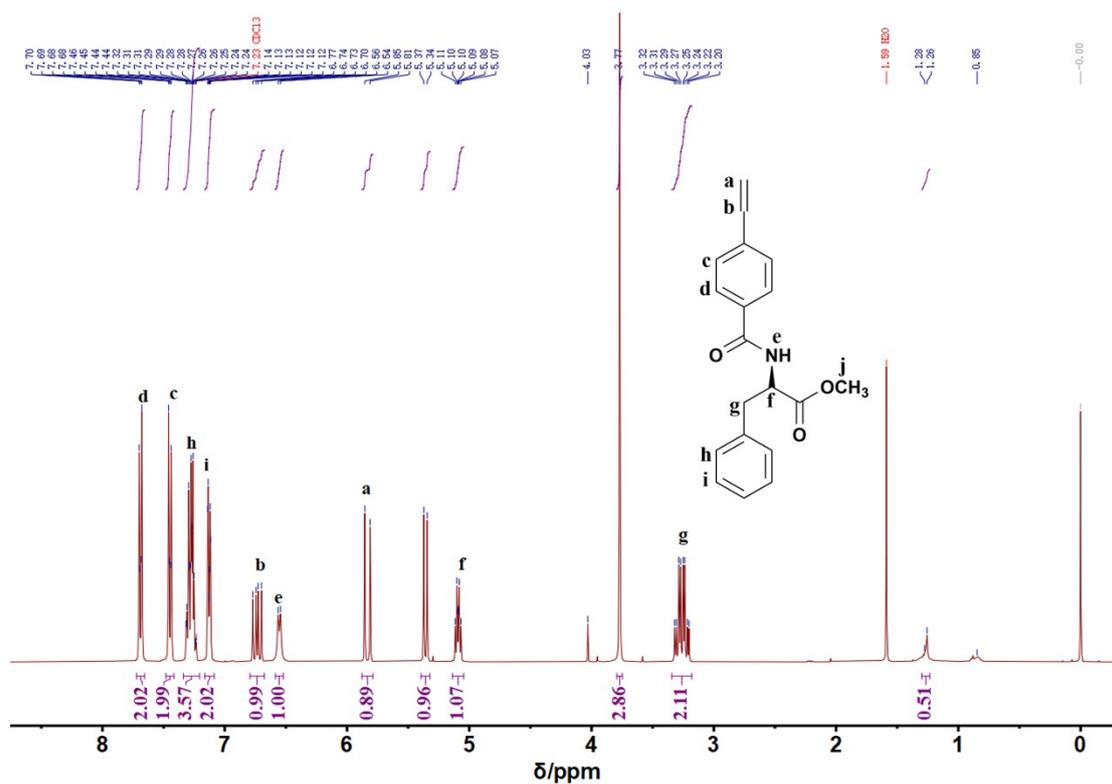


Fig. S18 ^1H NMR (400 MHz) spectra of D-c were measured in CDCl_3 at 25 °C.

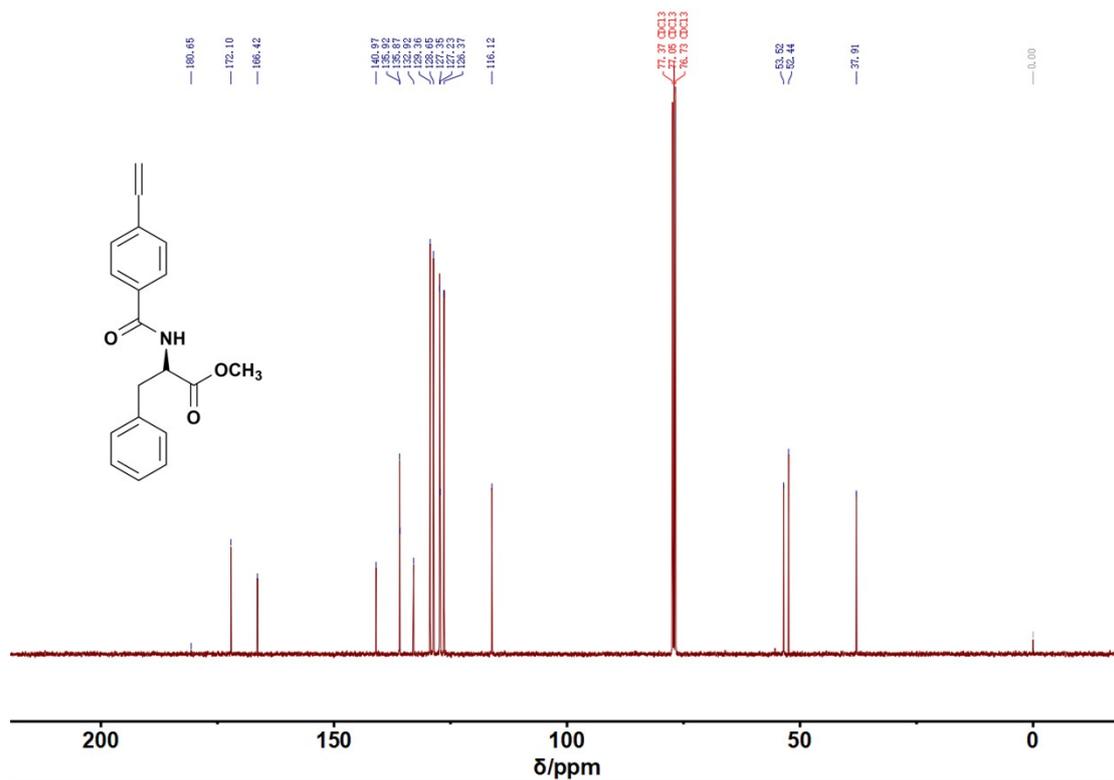


Fig. S19 ^{13}C NMR (101 MHz) spectra of D-c were measured in CDCl_3 at 25 °C.

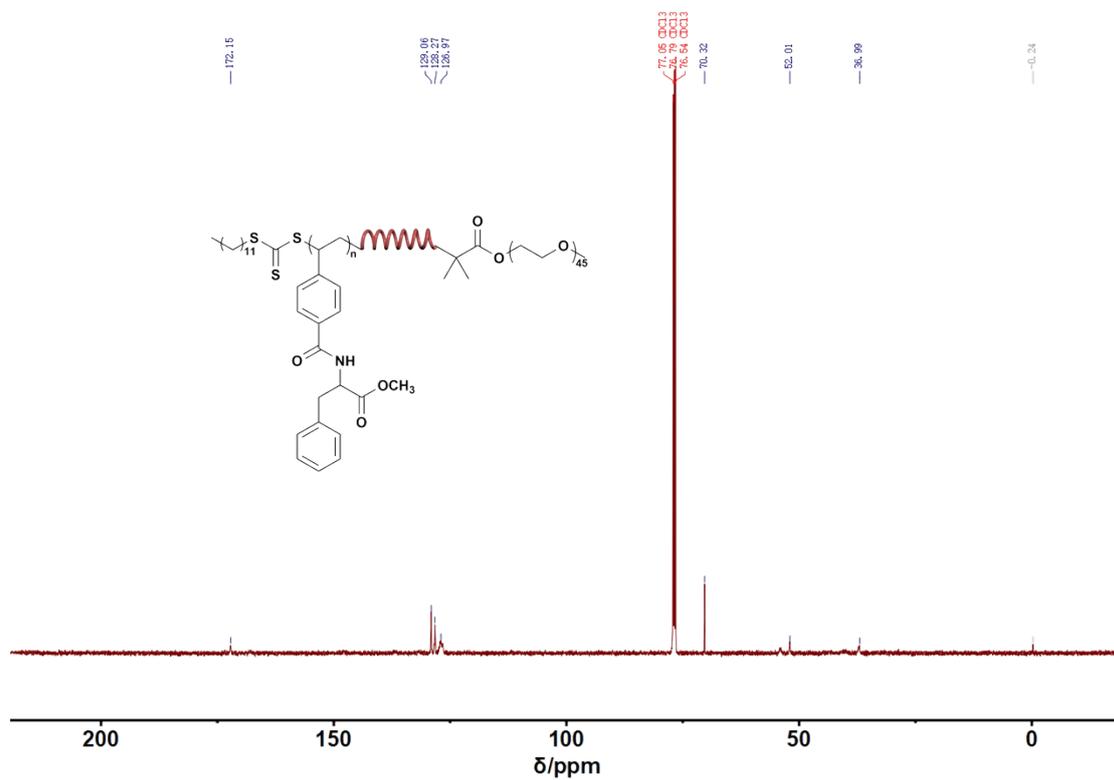


Fig. S20 ^{13}C NMR (101 MHz) spectra of Poly-D-c₅₀ were measured in CDCl_3 at 25 °C.

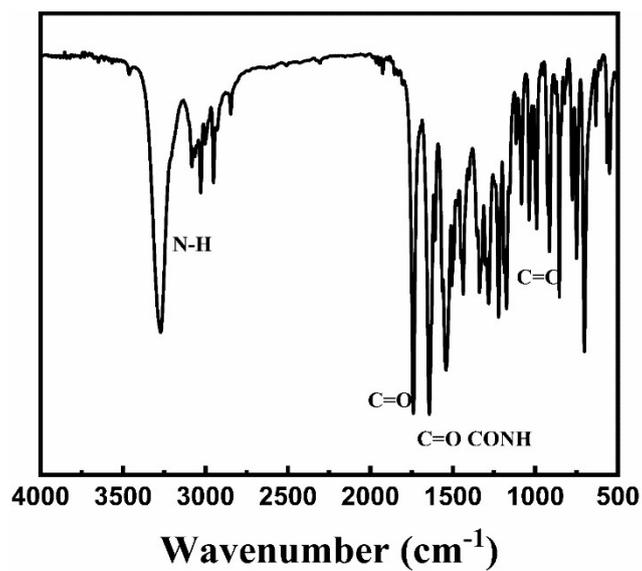


Fig. S21 FT-IR spectra of D-c were measured using KBr at 25 °C.

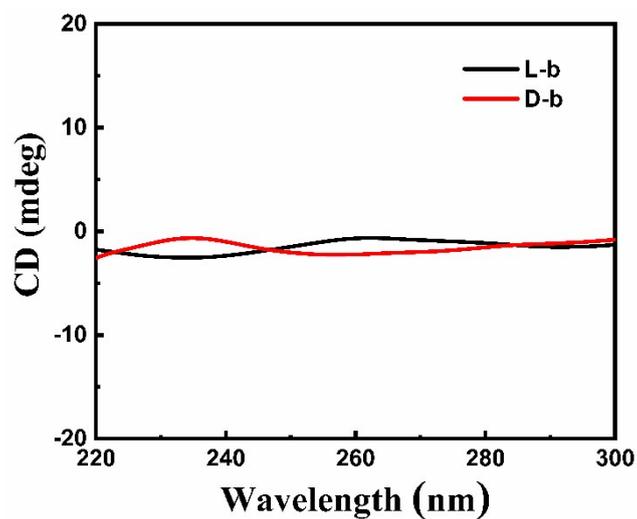


Fig. S22 CD and UV-vis spectra of L-b and D-b were measured in THF at 25°C ($c=0.15\text{mg/mL}$).

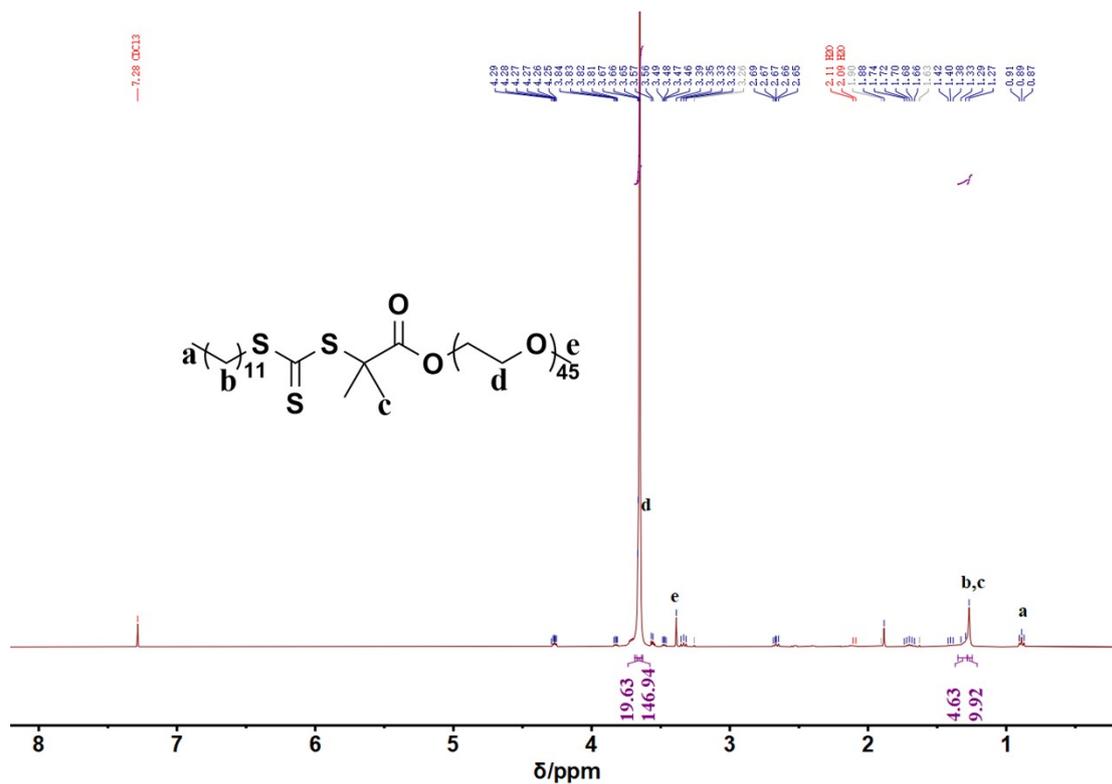


Fig. S23 ¹H NMR (400 MHz) spectra of PEO₄₅-DDMAT were measured in CDCl₃ at 25 °C.

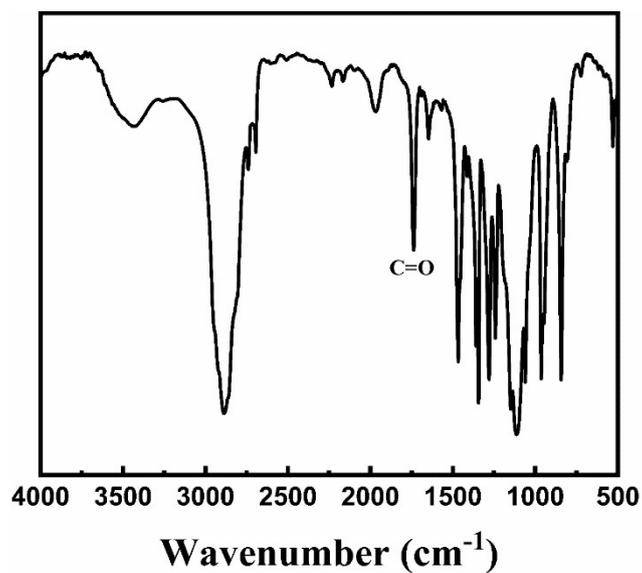


Fig. S24 FT-IR spectra of PEO₄₅-DDMAT were measured using KBr at 25 °C.

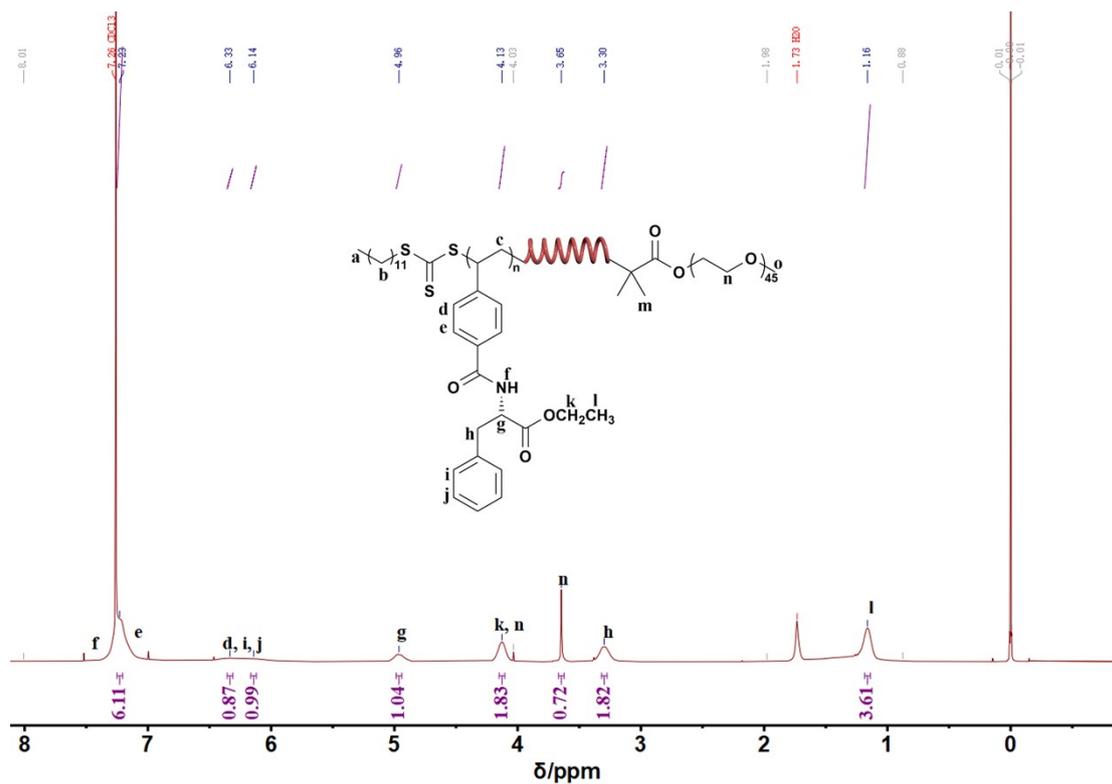


Fig. S25 ^1H NMR (400 MHz) spectra of Poly-L-c₅₀ were measured in CDCl_3 at 25 °C.

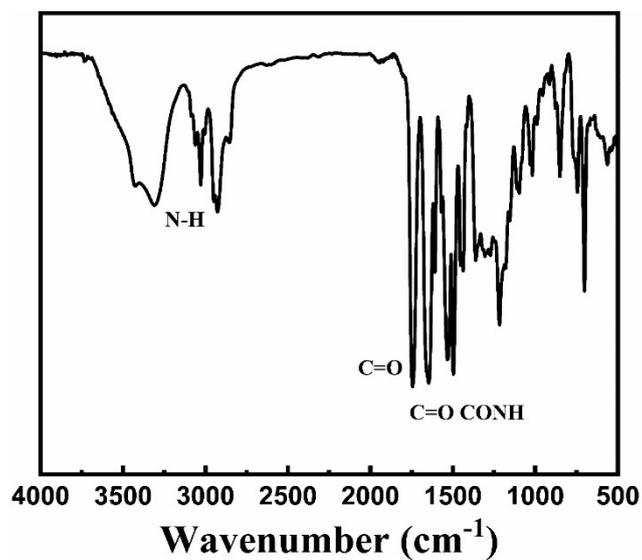


Fig. S26 FT-IR spectra of Poly-L-c₅₀ were measured using KBr at 25 °C.

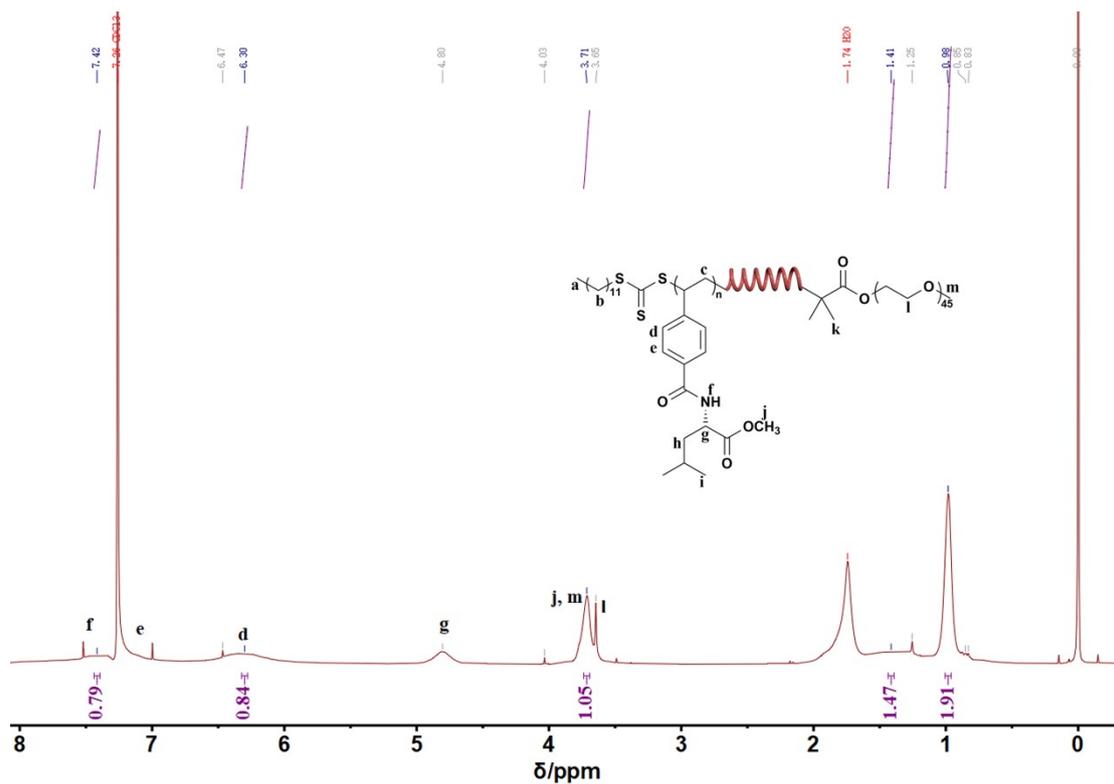


Fig. S27 ^1H NMR (400 MHz) spectra of Poly-L-a₅₀ were measured in CDCl_3 at 25 °C.

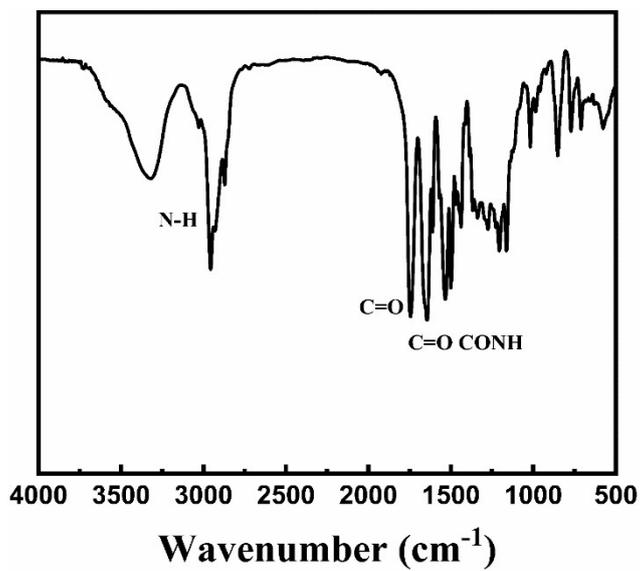


Fig. S28 FT-IR spectra of Poly-L-a₅₀ were measured using KBr at 25 °C.

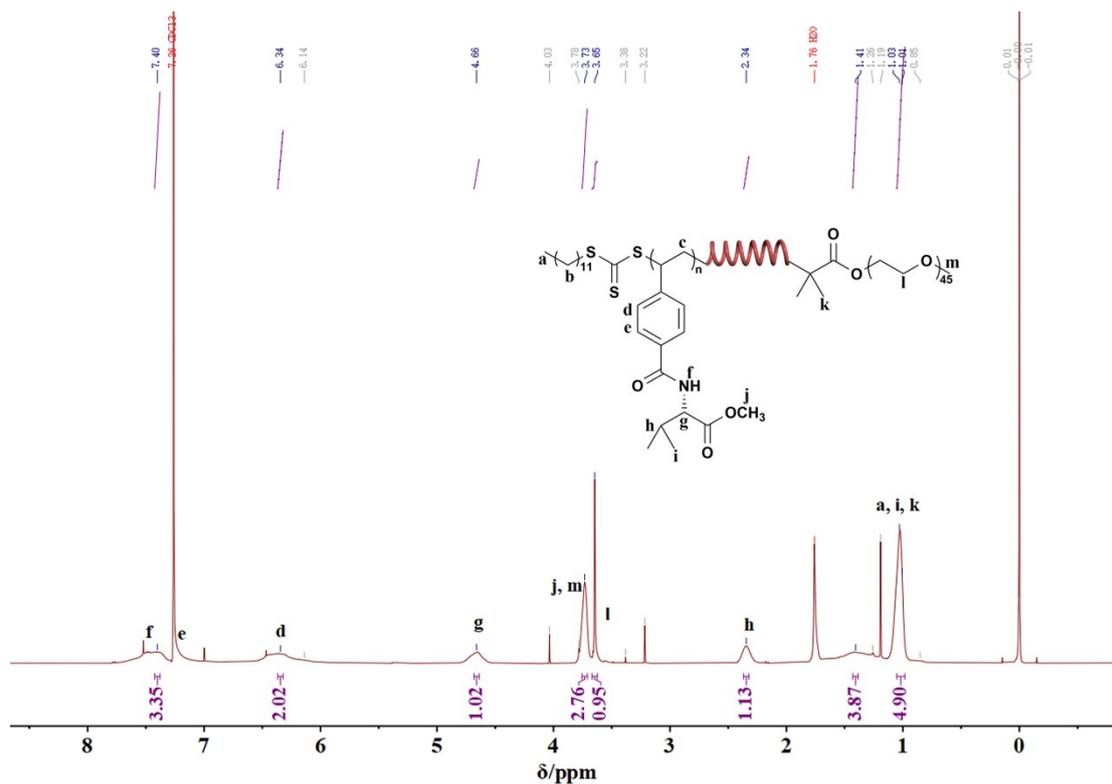


Fig. S29 ¹H NMR (400 MHz) spectra of Poly-L-b₅₀ were measured in CDCl₃ at 25 °C.

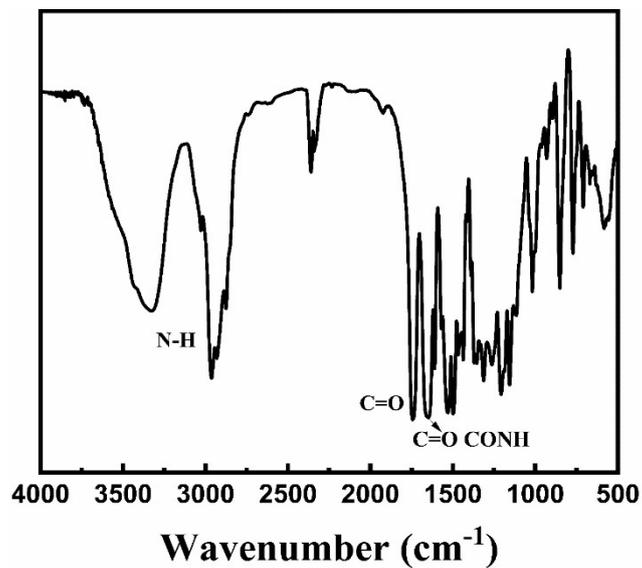


Fig. S30 FT-IR spectra of Poly-L-b₅₀ were measured using KBr at 25 °C.



Fig. S31 ^1H NMR (400 MHz) spectra of Poly-L-d₅₀ were measured in CDCl_3 at 25 °C.

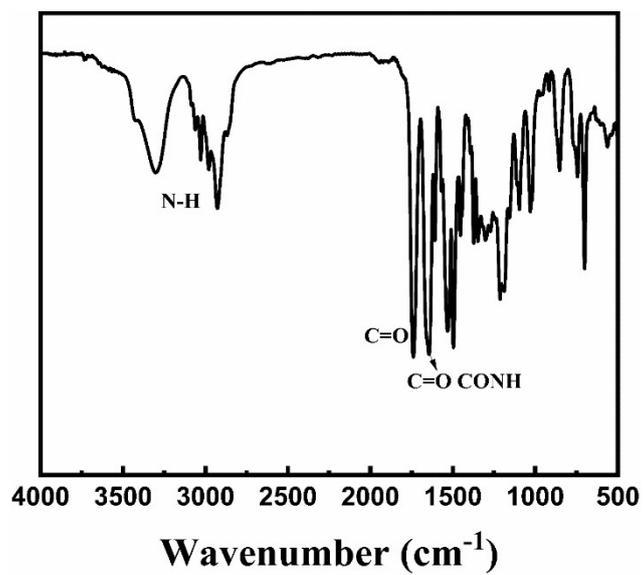


Fig. S32 FT-IR spectra of Poly-L-d₅₀ were measured using KBr at 25 °C.

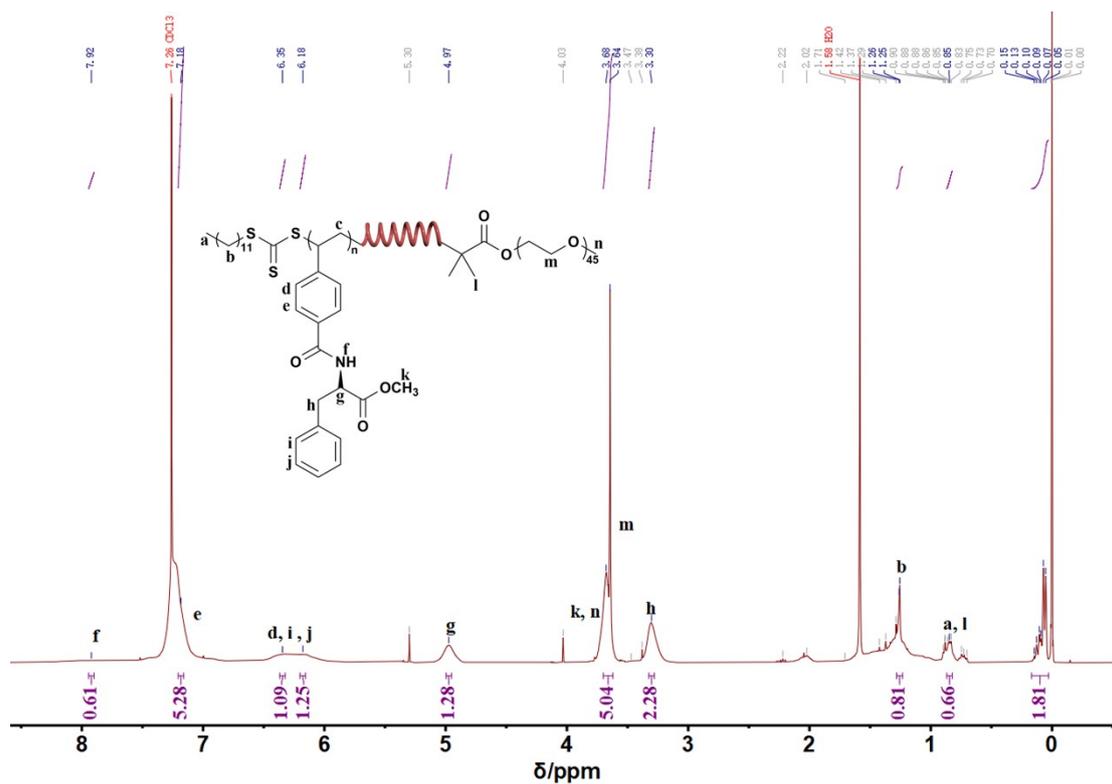


Fig. S33 ¹H NMR (400 MHz) spectra of Poly-D-c₅₀ were measured in CDCl₃ at 25 °C.

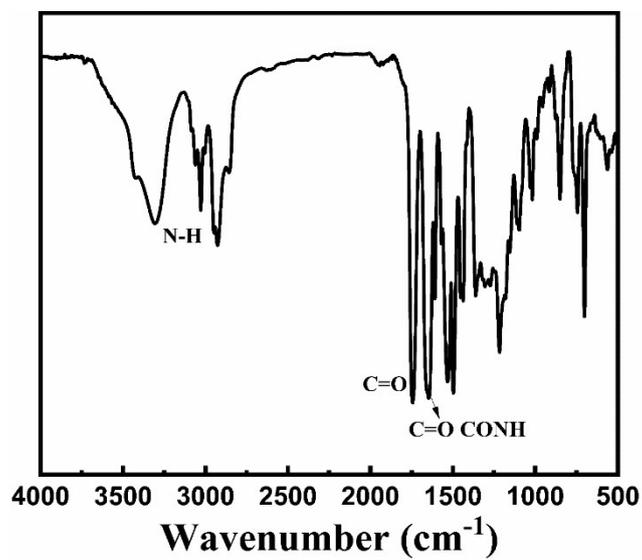


Fig. S34 FT-IR spectra of Poly-D-c₅₀ were measured using KBr at 25 °C.

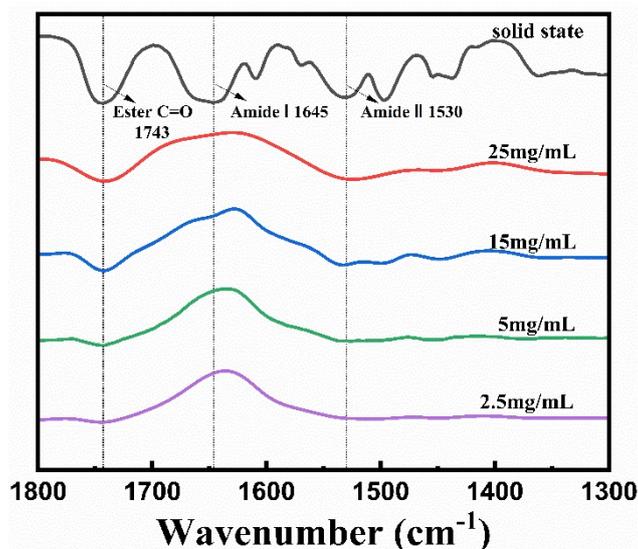


Fig. S35 FT-IR spectra of different concentrations of Poly-L-c₅₀ were measured in CDCl₃ at 25 °C.

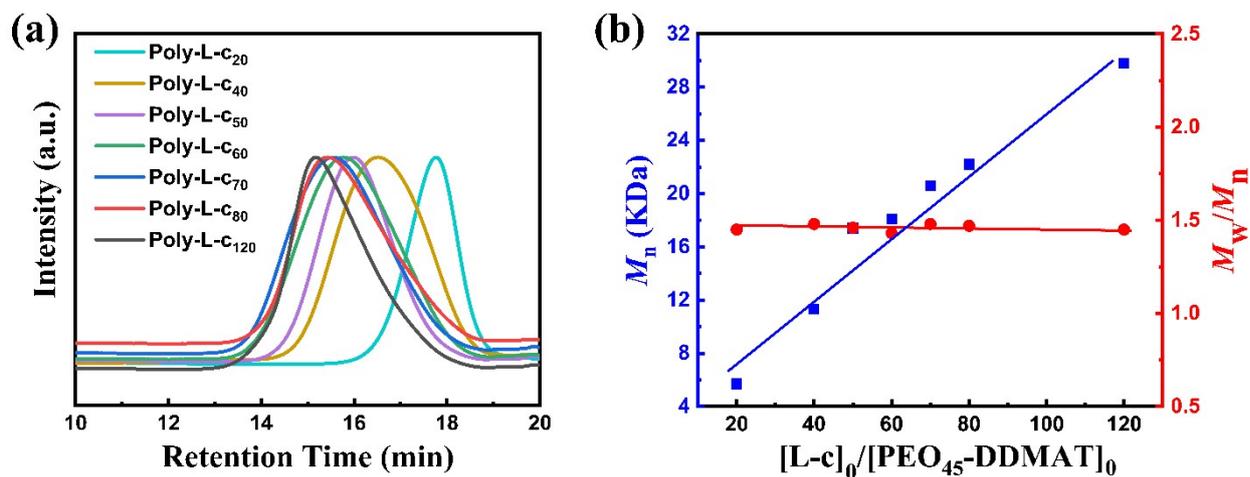


Fig. S36 (a) SEC chromatograms of Poly-L-c_n prepared from L-c with different initial feed ratio of monomer to CAT. (b) Plot of M_n and M_w/M_n values of the isolated Poly-L-c_n as a function of the initial feed ratios of L-c to the PEO₄₅-DDMAT CTA. M_n and M_w/M_n values were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).

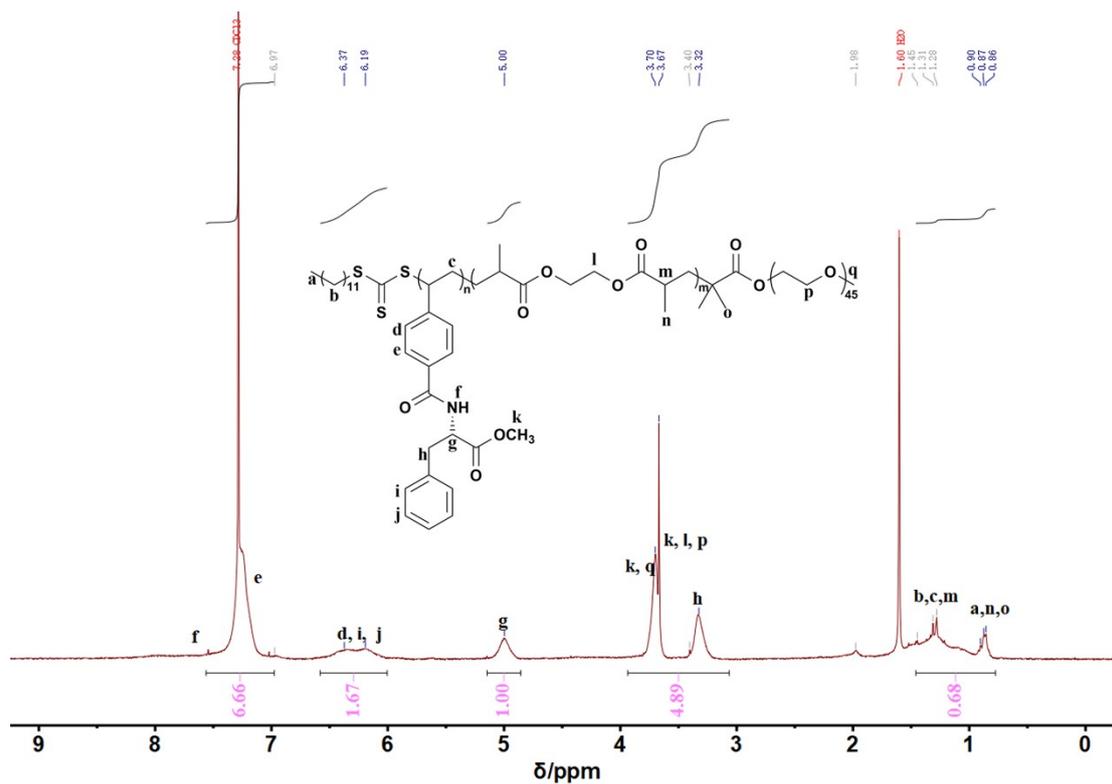


Fig. S37 ^1H NMR (400 MHz) Poly(L-c₅₀-co-e₁₀) spectra were measured in CDCl_3 at 25 °C.

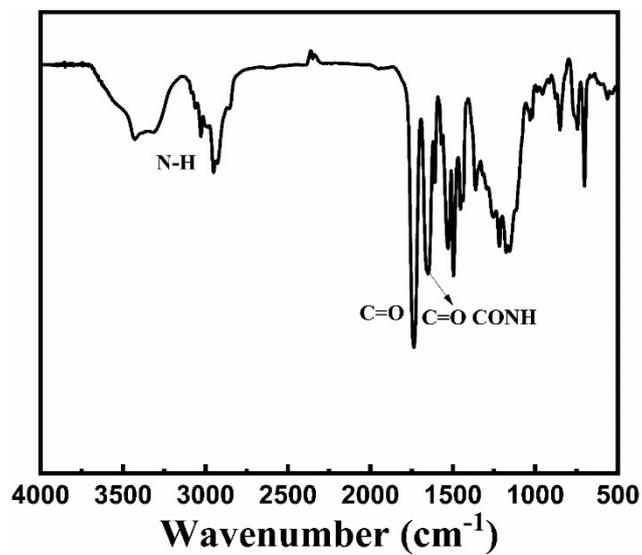


Fig. S38 FT-IR spectra of Poly(L-c₅₀-co-e₁₀) were measured using KBr at 25 °C.

References

1. J. Kim and K. T. Kim, *ACS Appl Mater Interfaces*, 2020, **12**, 23502-23513.