Supplementary Information

for

Scalable Access to Functional Nylon 6 via Ring-Opening Copolymerization of Biobased δ-Valerolactam with ε-Caprolactam

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1. Materials

L-Ornithine hydrochloride (99%), 2-piperidone, toluene, trimethylamine (Et_3N), formaldehyde (HCHO), benzoyl chloride, terephthaloyl chloride, trimesoyl chloride, Pd/C, trifluoroacetic acid, and trifluoroethanol were purchased from Energy Chemical. ε-Caprolactam was purchased from SINOPEC. Methanol (MeOH), ethyl acetate (EA), and sodium hydroxide (NaOH) were purchased from Tianjin Xinbote Chemical Co., Ltd. Diethyl ether (Et_2O) and concentrated sulfuric acid (H_2SO_4) were purchased from Xilong Scientific Co., Ltd. All chemicals were used as received without further purification.

2. Measurements

All room temperature ^{1}H NMR spectra, ^{13}C NMR spectra, and DOSY NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer, respectively. ^{1}H NMR chemical shifts were referenced as follows: δ 7.26 ppm for chloroform-d ($CDCl_3$), δ 4.79 ppm for deuteroxide (D_2O), δ 2.50 ppm for dimethyl sulfoxide-d_6 (DMSO-d_6). ^{13}C NMR chemical shifts were referenced as follows: δ 77.16 ppm for chloroform-d ($CDCl_3$), δ 39.52 ppm for dimethyl sulfoxide-d_6 (DMSO-d_6).

High Resolution Mass Spectrum (HRMS) conditions were measured by ESI Mass Spectrometry which was performed on a ThermoFisher LTQ Orbitrap Velos Pro mass spectrometer (Locality: USA) in reflectron positive mode.

Size exclusion chromatography (SEC) was carried out on a system composed of Waters 1515 Refractive Index Detector equipped with a series of connected size exclusion columns (1000 Å and 10000 Å, Shodex columns, 10 μm, 300×8.0 mm). Polymer number-average weights (M_n) and polydispersity ($Đ$) were measured at 35°C in hexafluoroisopropanol (0.02M sodium trifluoroacetate) relative to polymethyl methacrylate and a flow rate of 0.5 mL/min.

Thermal gravimetric analysis (TGA) was conducted on a Q50 thermogravimetric analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere of 60 mL/min.

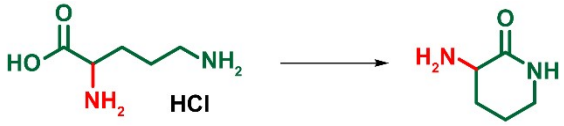
Differential scanning calorimetry (DSC) measurements, using ∼5 mg of material, were performed on a TA Q2000 DSC-7 instrument under an N_2 atmosphere of 50 mL/min at a rate of 10 ℃/min (25 to 250 °C). Data from the endothermic thermograms were recorded from the second scan and analyzed with TA Universal Analysis software.

The XRD patterns were recorded using an Empyrean diffractometer equipped with a Cu X-ray tube. A 0.5° divergence slit, a 1° anti-scatter slit, and 0.04° Soller slits were used as incident X-ray beam optics. The anti-scatter slit on the diffracted beam path was fixed at 1°. The X-Ray patterns were recorded between 5 and 75° in 2 theta with a step size of 0.01° and a time per step of 200s. The samples were placed on a zero background Si substrate. During the measurement, the samples were continuously spinning at 1rps.

Water contact angles onto the surfaces of copolymers were tested using a contact angles goniometer. The contact angles were recorded with 2 μL droplets deposited on the surfaced.

3. Synthesis of monomer and co-initiators.

3.1. Preparation of 3-aminopiperidin-2-one



The intermediate product 3-aminopiperidin-2-one was prepared according to our recent work[1]. L-ornithine hydrochloride (3 mol, 586 g) reacted with concentrated sulfuric acid (3.3mol, 330 mL) in MeOH (1.5 L) at 80 ℃ for 6 h. 28.5 L MeOH was added and then NaOH (6 mol, 240 g) was added to the solution. The mixture was stirred at RT for 6 h. After evaporation of solvent in vacuo, the crude product was recrystallized from ethyl acetate to obtain a white solid (yield, ~95%). ^{1}H NMR (400 MHz, D_2O): δ 3.25-3.35 (m, 1H), 3.15-3.25 (m, 2H), 1.50-2.15 (m, 4H). ^{13}C NMR (400 MHz, D_2O): δ 176.09, 49.92, 41.75, 28.06, 20.09.

3.2. Preparation of 3-(dimethylamino)-piperidon (M1)

114 g (1 mol) 3-aminopiperidin-2-one was dissolved in MeOH (1 L) in a round-bottomed flask (2 L). Formaldehyde (37% aqueous solution, 170 mL, 2.1 mol) and Pd/C (11.4 g) were added to the solution and attached to a hydrogen balloon. The mixture was stirred at RT for 36 h. The solution was then filtered and concentrated under a vacuum. The crude product was recrystallized from ethyl acetate to obtain a white solid (yield, ~95%). ^{1}H NMR (400 MHz, D_2O): δ 3.25-3.35 (m, 1H), 3.15-3.24 (m, 2H), 2.25-2.35 (s, 6H), 1.65-2.05 (m, 4H). ^{13}C NMR (400 MHz, D_2O): δ 173.88, 62.62, 41.33, 40.34, 21.69, 20.41. $[M+H]^+$: calcd. $C_7H_{14}N_2O$, 143.1184; found 143.1177.

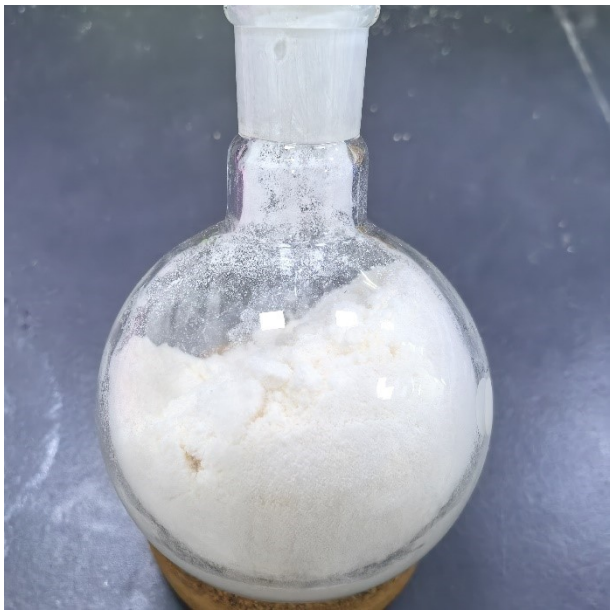


Figure S1. The crystalline of monomer **M1** (135 g) was prepared using the above procedure.

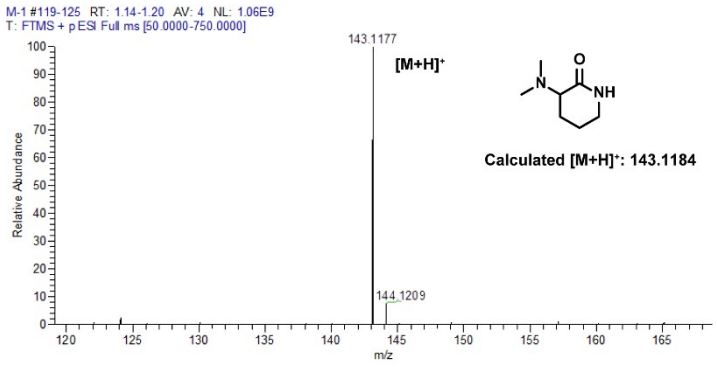
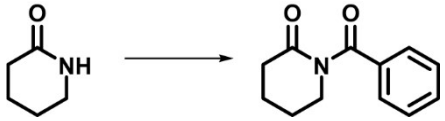


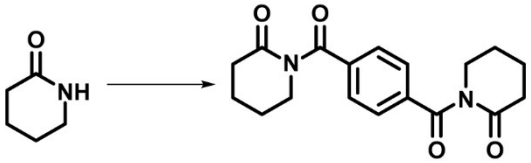
Figure S2. HRMS of monomer **M1**.

3.3. Synthesis of co-initiator 1-benzoylpiperidin-2-one (I1)



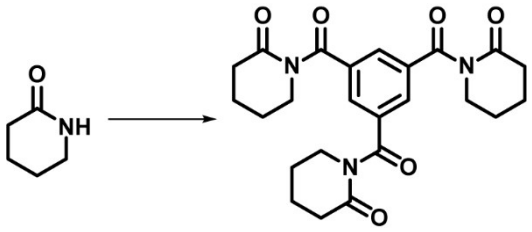
2-piperidone (0.99 g, 0.01 mol), triethylamine (1.94 mL, 0.014 mol), and benzoyl chloride (1.38 mL, 0.012 mol) were dissolved in toluene (25 mL) in a round-bottomed flask (100 mL). After stirring at 115 °C for 10 h, the resulting mixture was concentrated under vacuum, and then water (100 mL) was added. The solution was extracted with DCM (3 times) and the solvent was removed at reduced pressure. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (10/1) as eluent to afford the product as a white solid (yield, ~85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.70 (m, 5H), 3.76-3.80 (t, 2H), 2.50-2.56 (t, 2H), 1.86-2.00 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$): δ174.79, 173.60, 136.25, 131.59, 128.23, 127.98, 46.22, 34.73, 22.91, 21.55.

3.4. Synthesis of co-initiator 1,1'-terephthaloylbis(piperidin-2-one) (I2)



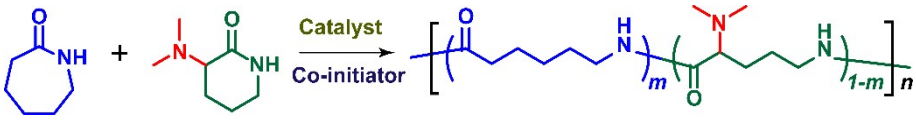
2-piperidone (0.99 g, 0.01 mol), triethylamine (1.414 mL, 0.014 mol), and terephthaloyl chloride (1.218 g, 0.006 mol) were dissolved in toluene (25 mL) in a round-bottomed flask (100 mL). After stirring at 110 °C for 10 h, the resulting mixture was concentrated under vacuum, and then water (100 mL) was added. The solution was extracted with DCM (3 times) and the solvent was removed at reduced pressure. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (10/1) as eluent to afford the product as a white solid (yield, ~85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 4H), 3.76-3.80 (t, 4H), 2.50-2.58(t, 4H), 1.86-2.00 (m, 8H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 173.85, 173.39, 138.62, 127.72, 46.19, 34.68, 22.88, 21.50.

3.5. Synthesis of co-initiator (1,1',1''-(benzene-1,3,5-tricarbonyl)tris(piperidin-2-one)) (I3)



2-piperidone (0.99 g, 0.01 mol), triethylamine (1.414 mL, 0.014 mol), and trimesoyl chloride (1.06 mL, 0.004 mol) were dissolved in toluene (25 mL) in a round-bottomed flask (100 mL). After stirring at 115 °C for 10 h, the resulting mixture was concentrated under vacuum, and then water (100 mL) was added. The solution was extracted with DCM (3 times) and the solvent was removed at reduced pressure. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (10/1) as eluent to afford the product as a white solid (yield, ~85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 3H), 3.75-3.80 (t, 6H),2.50-2.60(t, 6H), 1.86-2.00 (m, 12H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 173.22, 173.00, 136.00, 130.55, 46.33, 34.64, 22.84, 21.48.

4. General copolymerization procedure



In a typical experiment, 3-(dimethylamino)-piperidone (**M1**, 28.4 g, 200 mmol), ε-caprolactam (90.4 g, 800 mmol), and co-initiator **I1** (2.03 g, 10 mmol) were weighted and added to an autoclave (1 L). The mixture was dried in a vacuum and purged with nitrogen at 45 °C for 30 minutes, then a catalyst was added, and the polymerization was allowed to proceed at 145 °C for 48 h under a nitrogen atmosphere. After cooling to room temperature, 500 mL trifluoroethanol was added to dissolve the copolymer and then precipitated in ethyl acetate/diethyl ether (1/1) to get the copolymer **CP14** (yield ~50%). ^{1}H NMR (500 MHz, TFA/DMSO-d_6, 8:92, v:v): δ 3.57 (s, 1H), 3.01-3.22 (m, 4H), 2.60-2.71 (m, 6H), 2.13-2.31 (m, 2H), 0.80-1.80 (m, 10H). ^{13}C NMR (500 MHz, TFA/DMSO-d_6, 8:92, v:v): δ 178.58, 166.89, 68.35, 42.80, 41.42, 40.31, 33.38, 32.88, 27.07, 26.33, 24.86, 24.43.

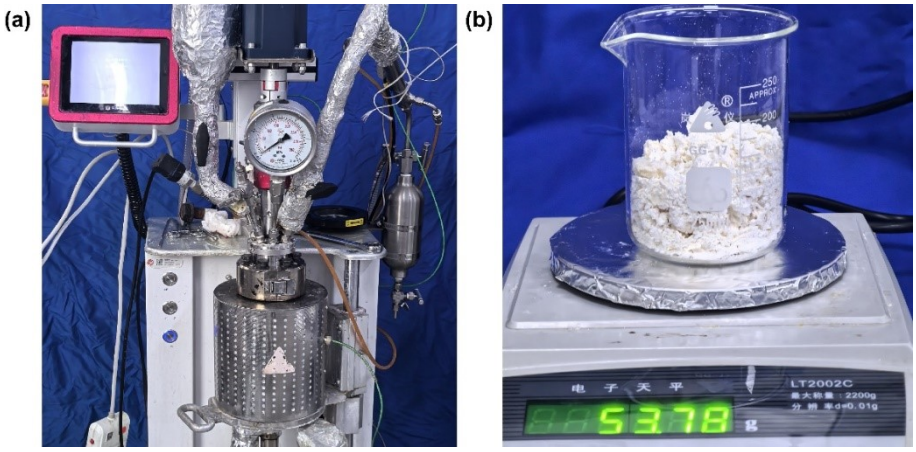
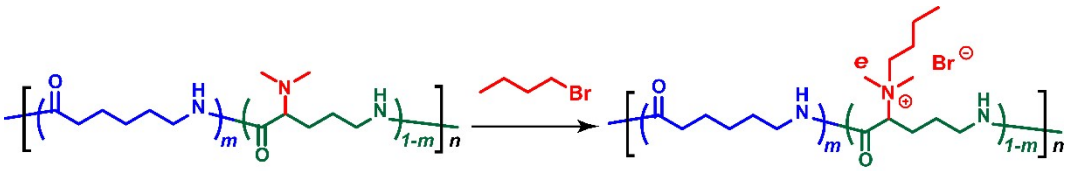


Figure S3. (a) The autoclave was used to produce the copolymers. (b) The final copolymers.

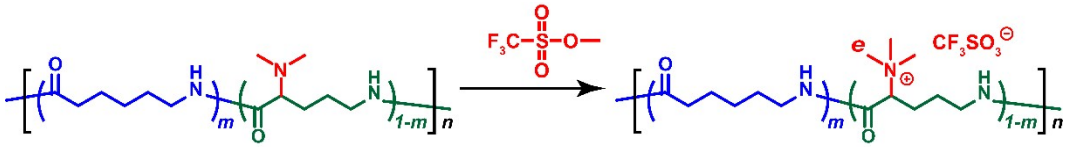
5. The post-polymerization modifications of Copolymers.

5.1. Preparation of CP14a



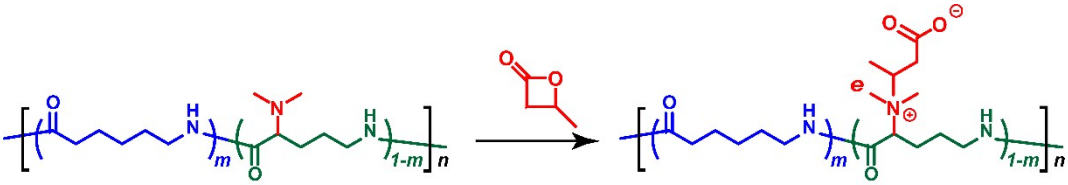
Copolymer (CP14, 114 mg, 1 mmol), and 1-bromobutane (6 mg, 0.05 mmol) were dissolved in 10 mL trifluoroethanol. The reaction was allowed to proceed at 85 °C for 12 h. After cooling to room temperature, the product CP14a was precipitated in ethyl acetate/diethyl ether (v:v=1/1). The white product was obtained by vacuum-drying. ^{1}H NMR (500 MHz, TFA/DMSO-d_6, 8:92, v:v): δ 3.60 (s, 1H), 3.01-3.32 (m, 4H), 2.76-2.84 (m, 6H), 2.12-2.32 (m, 2H), 0.90-1.58 (m, 17H).

5.2. Preparation of CP14b



Copolymer (CP14, 114 mg, 1 mmol), and methyl triflate (8 mg, 0.05 mmol) were dissolved in 10 mL trifluoroethanol. The reaction was allowed to proceed at 85 °C for 12 h under a nitrogen atmosphere. After cooling to room temperature, the product CP14b was precipitated in ethyl acetate/diethyl ether (v:v=1/1). The yellow product was obtained by vacuum-drying. ^{1}H NMR (500 MHz, TFA/DMSO-d_6, 8:92, v:v): δ 3.60 (s, 1H), 3.03-3.36 (m, 4H), 2.87 (s, 9H), 2.17-2.46 (m, 2H), 0.92-1.46 (m, 10H).

5.3. Preparation of CP14c



Copolymer (CP14, 114 mg, 1 mmol), and *β*-butyrolactone (4 mg, 0.05 mmol) were dissolved in 10 mL trifluoroethanol. The reaction was allowed to proceed at RT for 12 h under a nitrogen atmosphere. The product CP14c was precipitated in ethyl acetate/diethyl ether (v:v=1/1). The white product was obtained by vacuum-drying. ^{1}H NMR (500 MHz, TFA/DMSO-d_6, 8:92, v:v): δ 3.43 (s, 1H), 3.01-3.30 (m, 7H), 2.82-2.92 (m, 6H), 2.13-2.31 (m, 2H), 0.81-1.67 (m, 13H).

6. ^{1}H NMR and ^{13}C NMR spectra of monomer, co-initiators, and copolymer

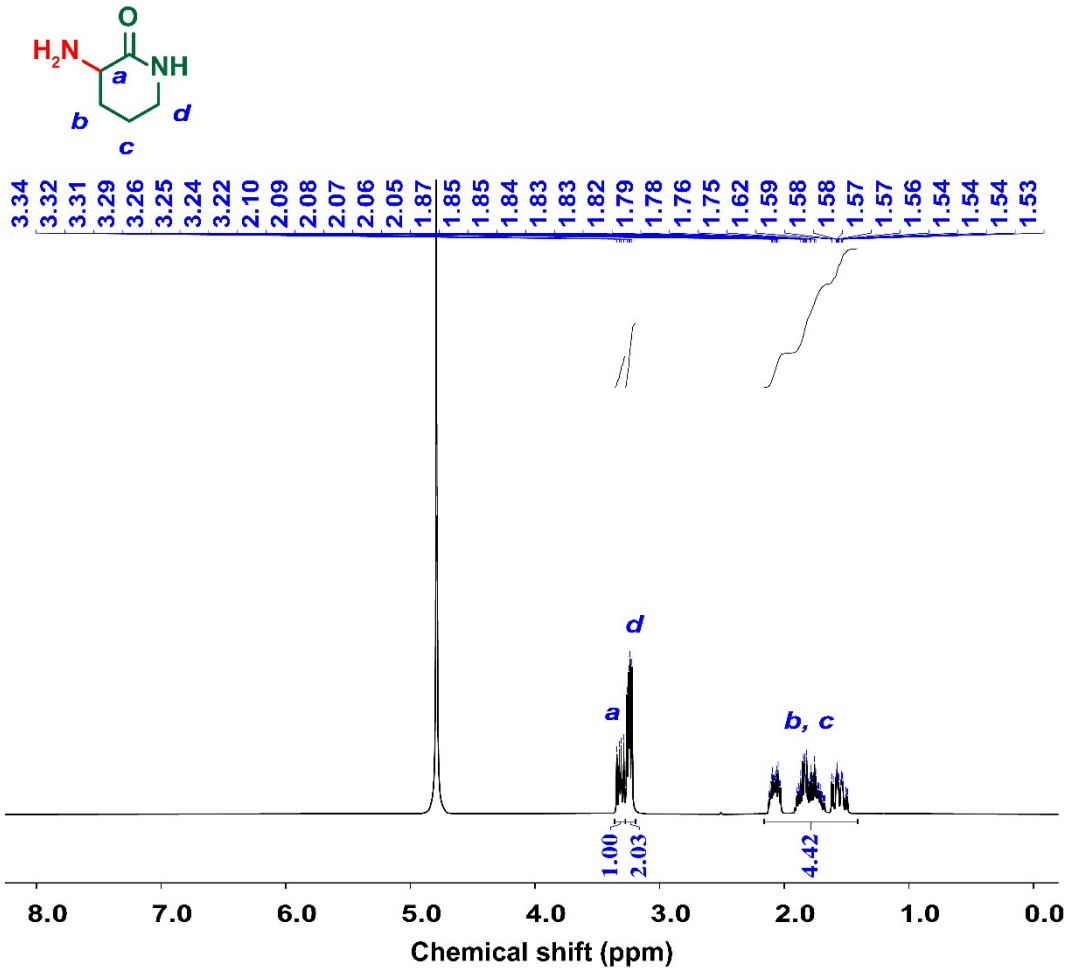


Figure S4. ^{1}H NMR spectra of 3-aminopiperidin-2-one in D_2O.

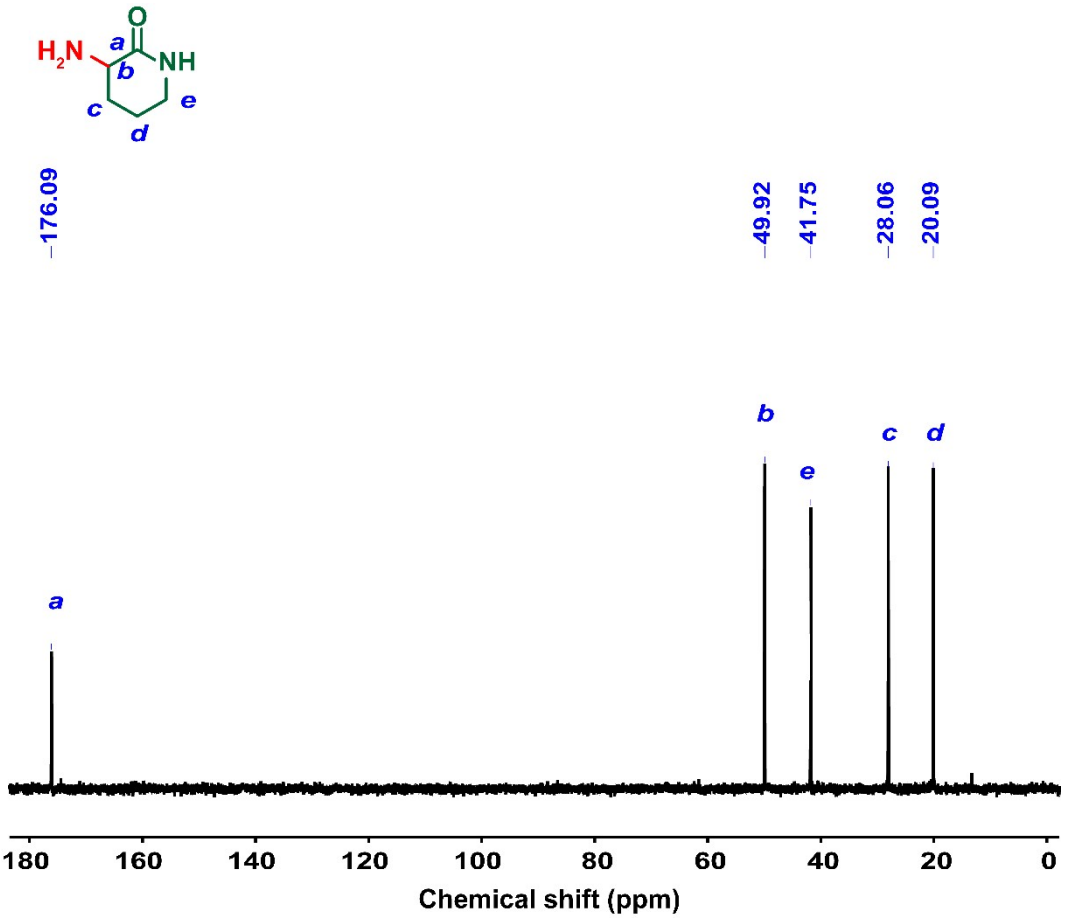


Figure S5. ^{13}C NMR spectra of 3-aminopiperidin-2-one in D_2O.

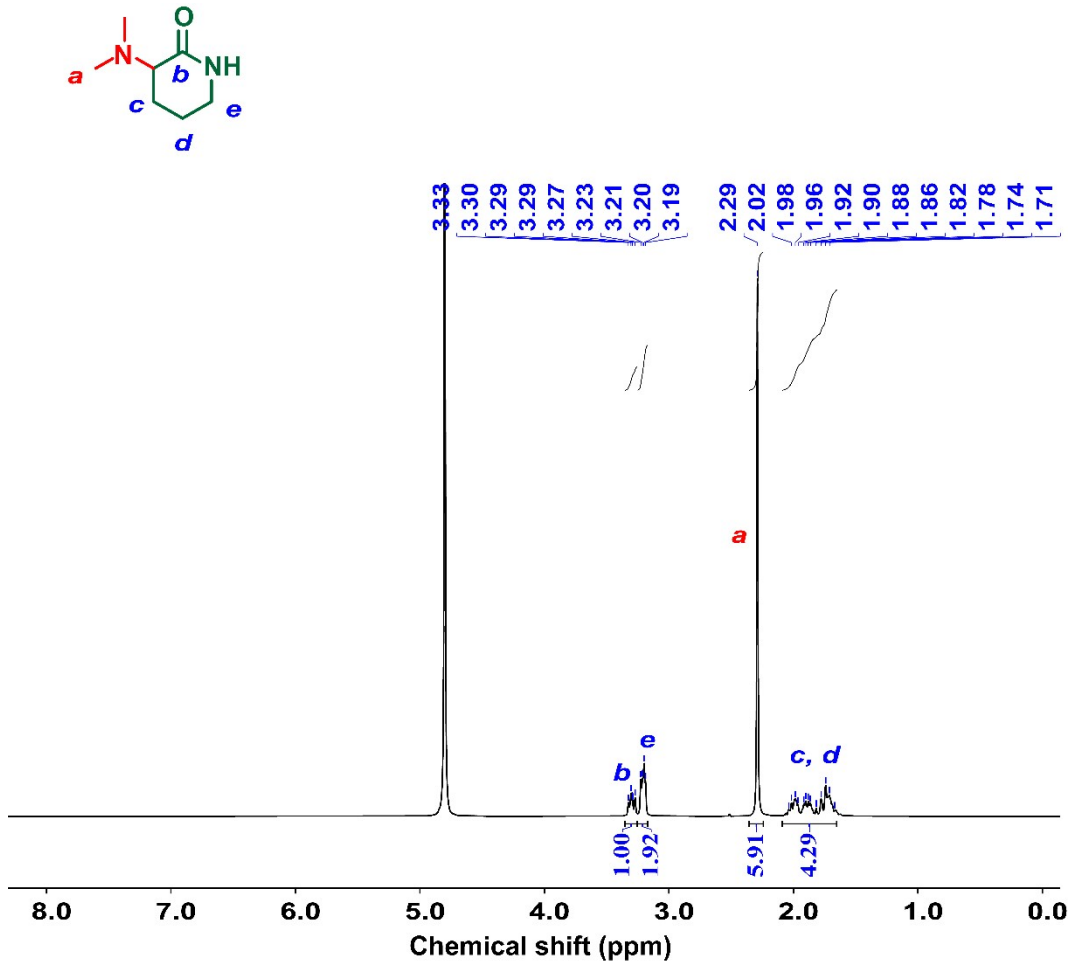


Figure S6. ^{1}H NMR spectra of 3-(dimethylamino)-piperidone (**M1**) in D_2O.

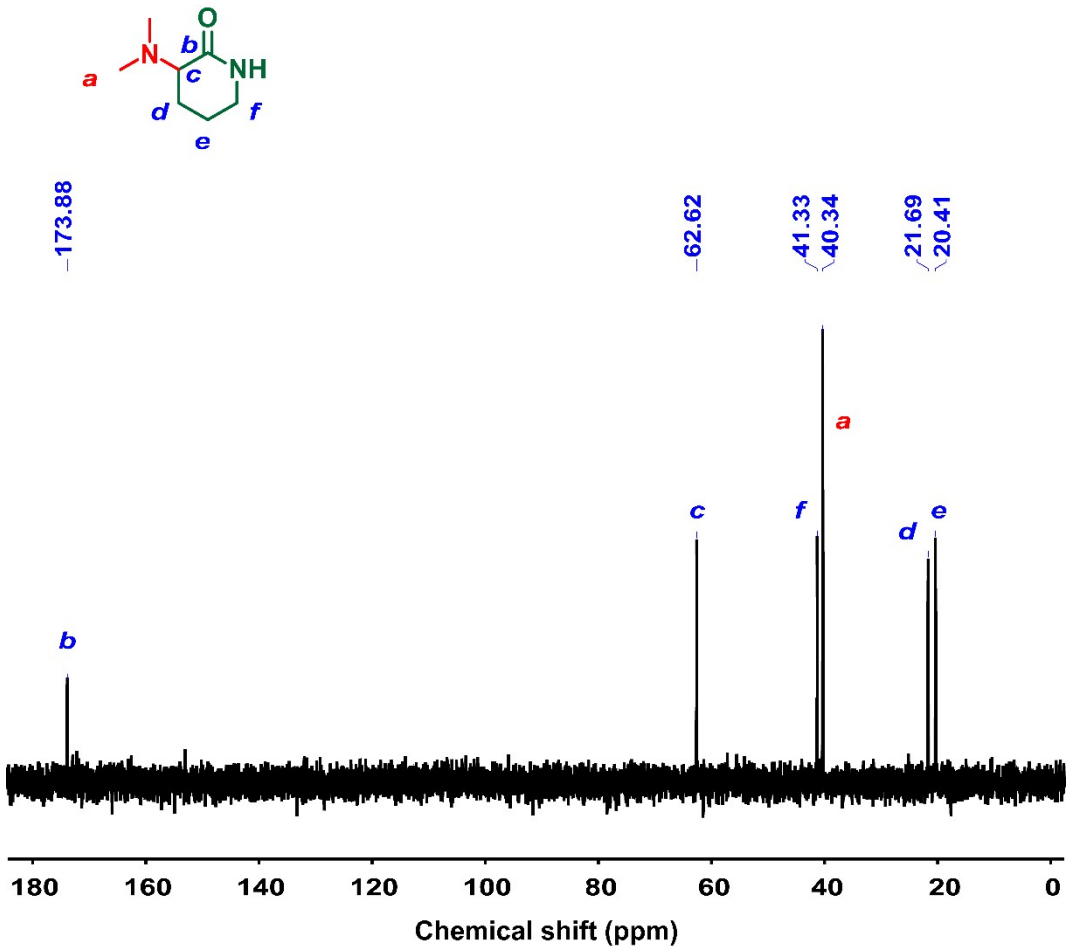


Figure S7. ^{13}C NMR spectra of 3-(dimethylamino)-piperidone (**M1**) in D_2O.

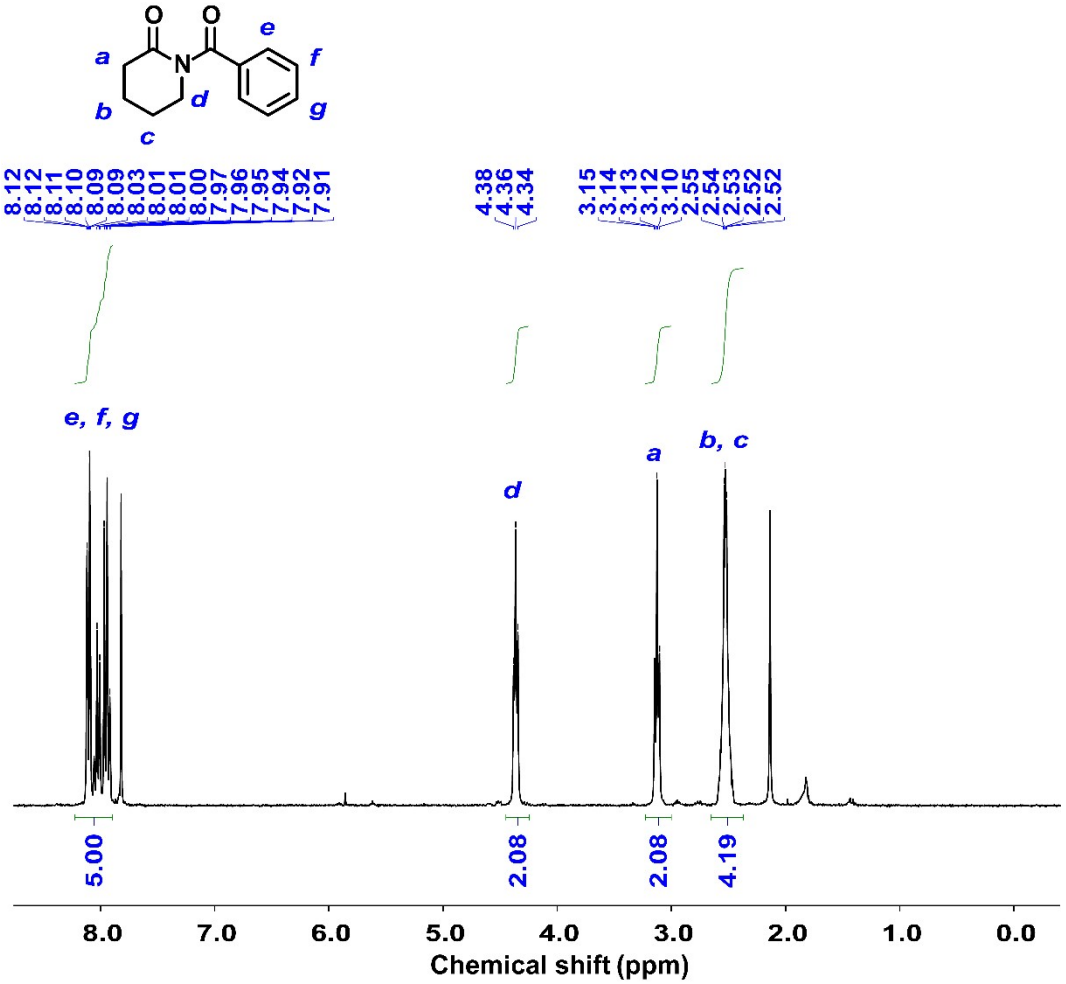


Figure S8. ^{1}H NMR spectra of 1-benzoylpiperidin-2-one (**I1**) in $CDCl_3$.

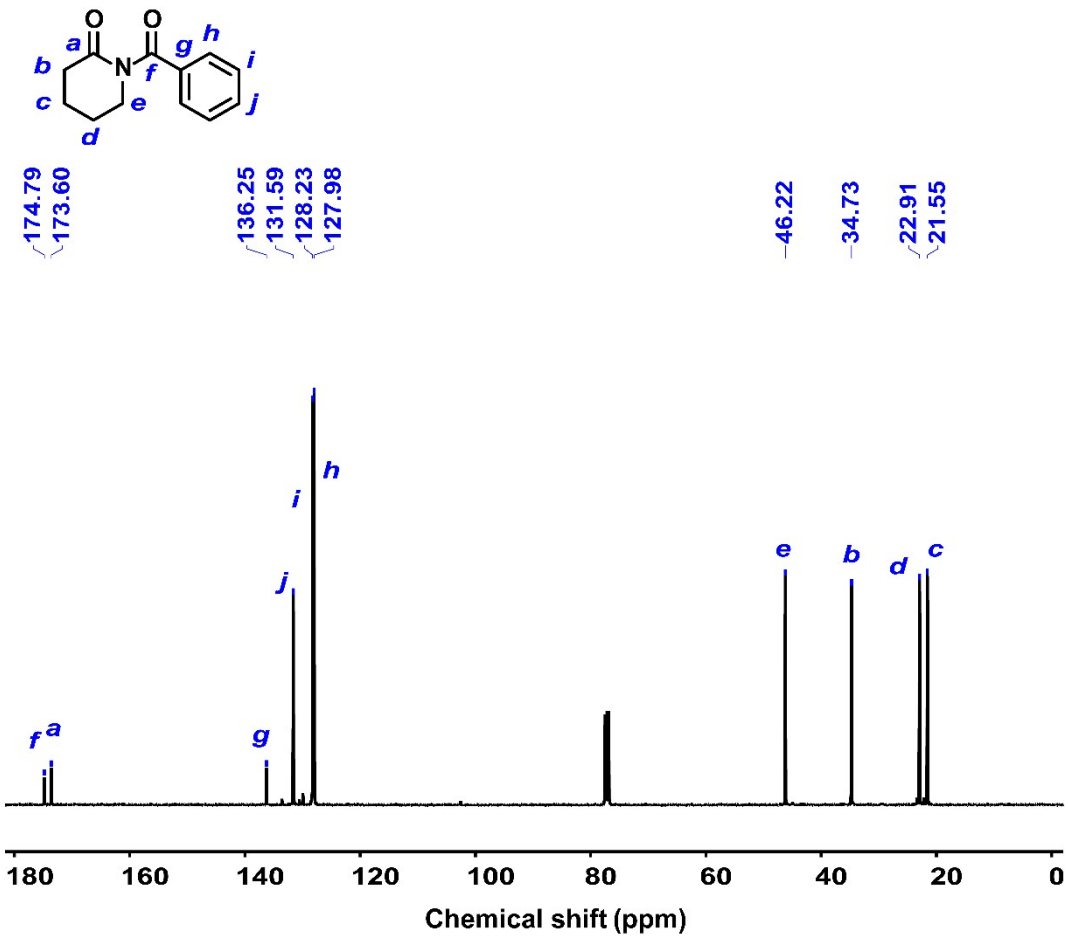


Figure S9. ^{13}C NMR spectra of 1-benzoylpiperidin-2-one (**I1**) in $CDCl_3$.

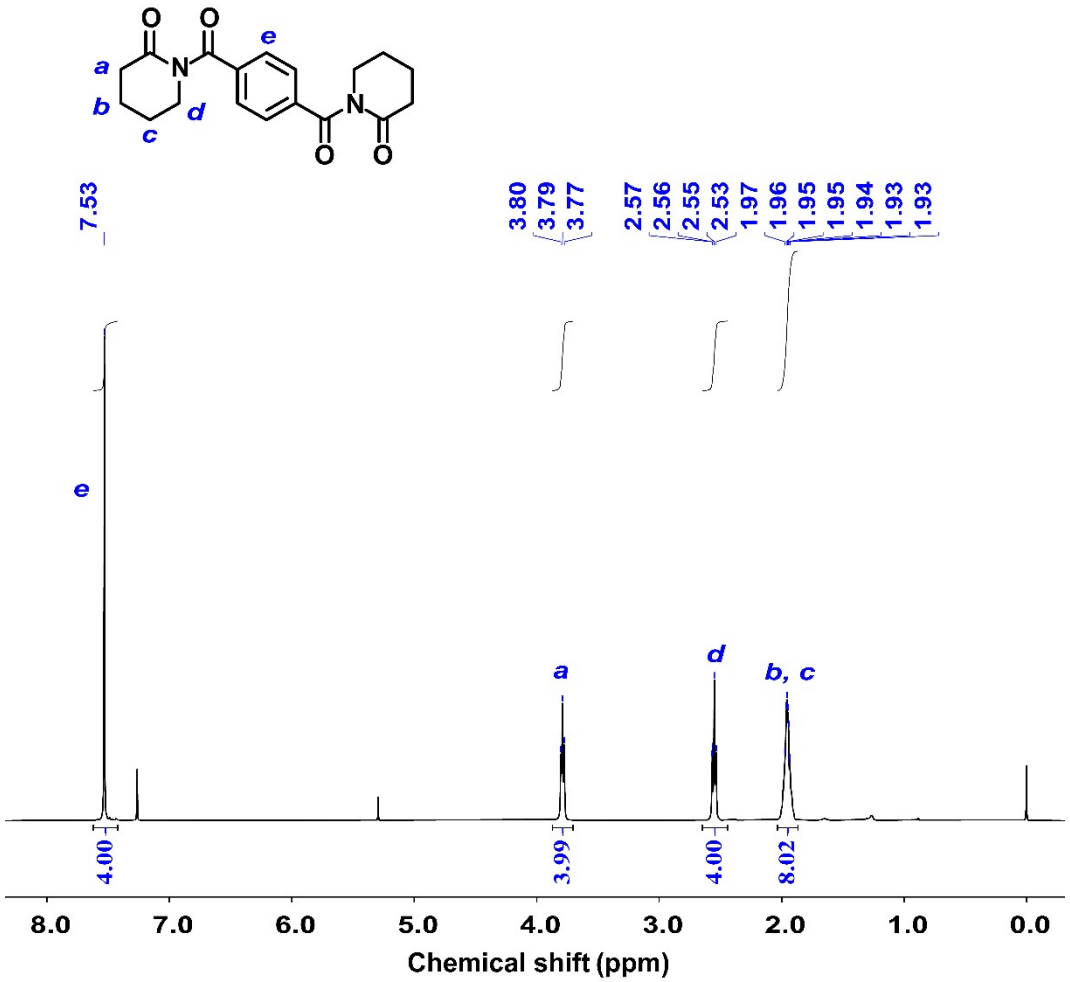


Figure S10. ^{1}H NMR spectra of 1,1'-terephthaloylbis(piperidin-2-one) (**I2**) in $CDCl_3$.

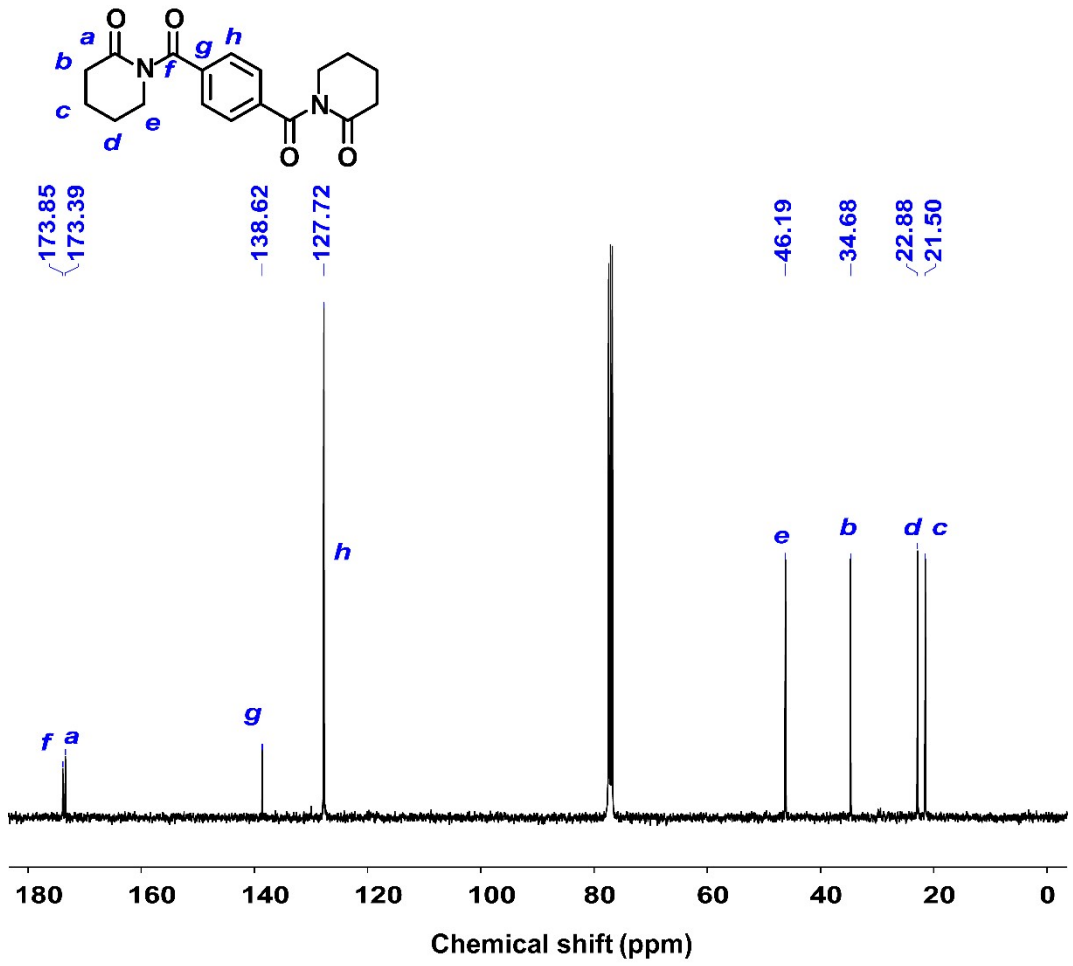


Figure S11. ^{13}C NMR spectra of 1,1'-terephthaloylbis(piperidin-2-one) (**I2**) in $CDCl_3$.

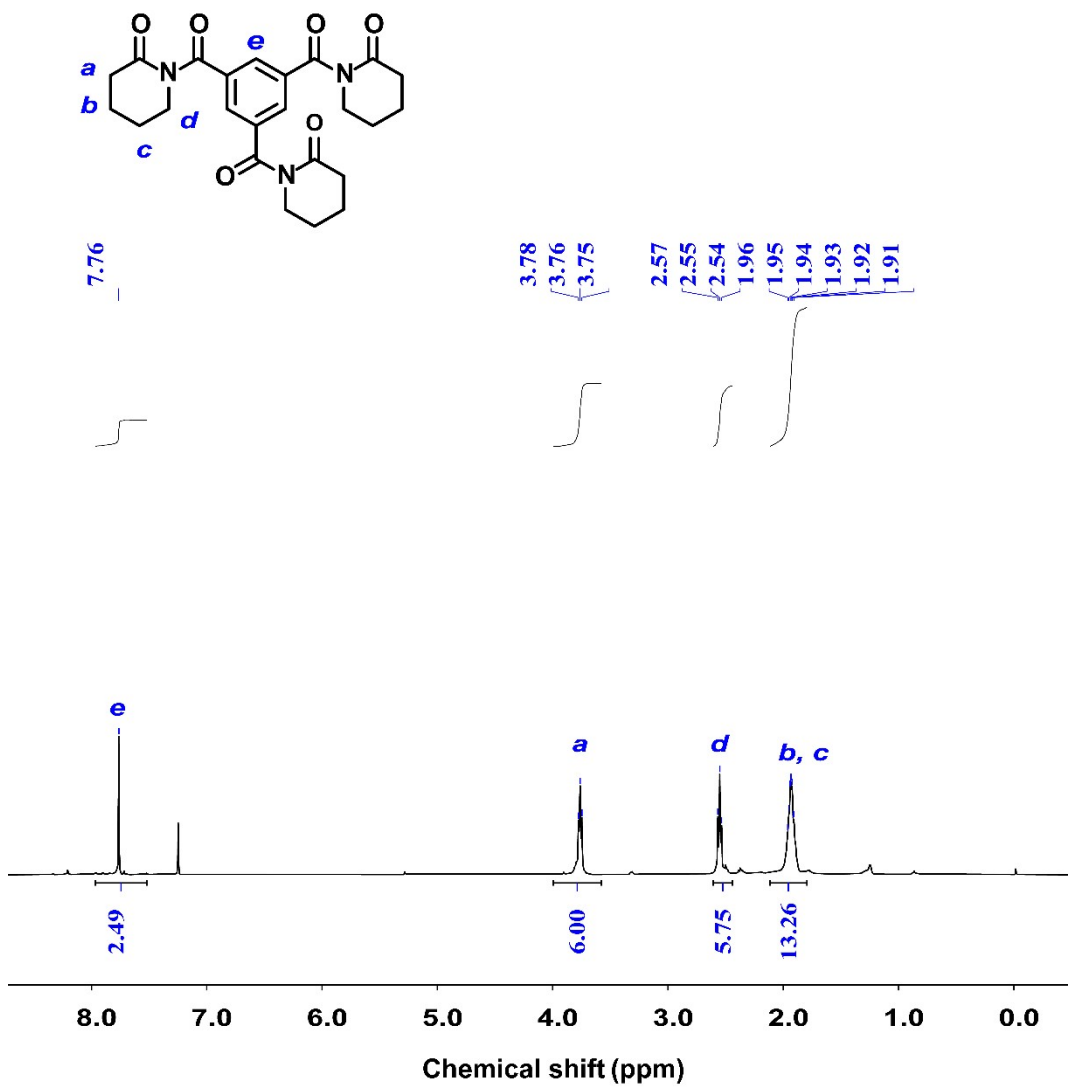


Figure S12. ^{1}H NMR spectra of (1,1',1"-(benzene-1,3,5-tricarbonyl)tris(piperidin-2-one)) (**I3**) in $CDCl_3$.

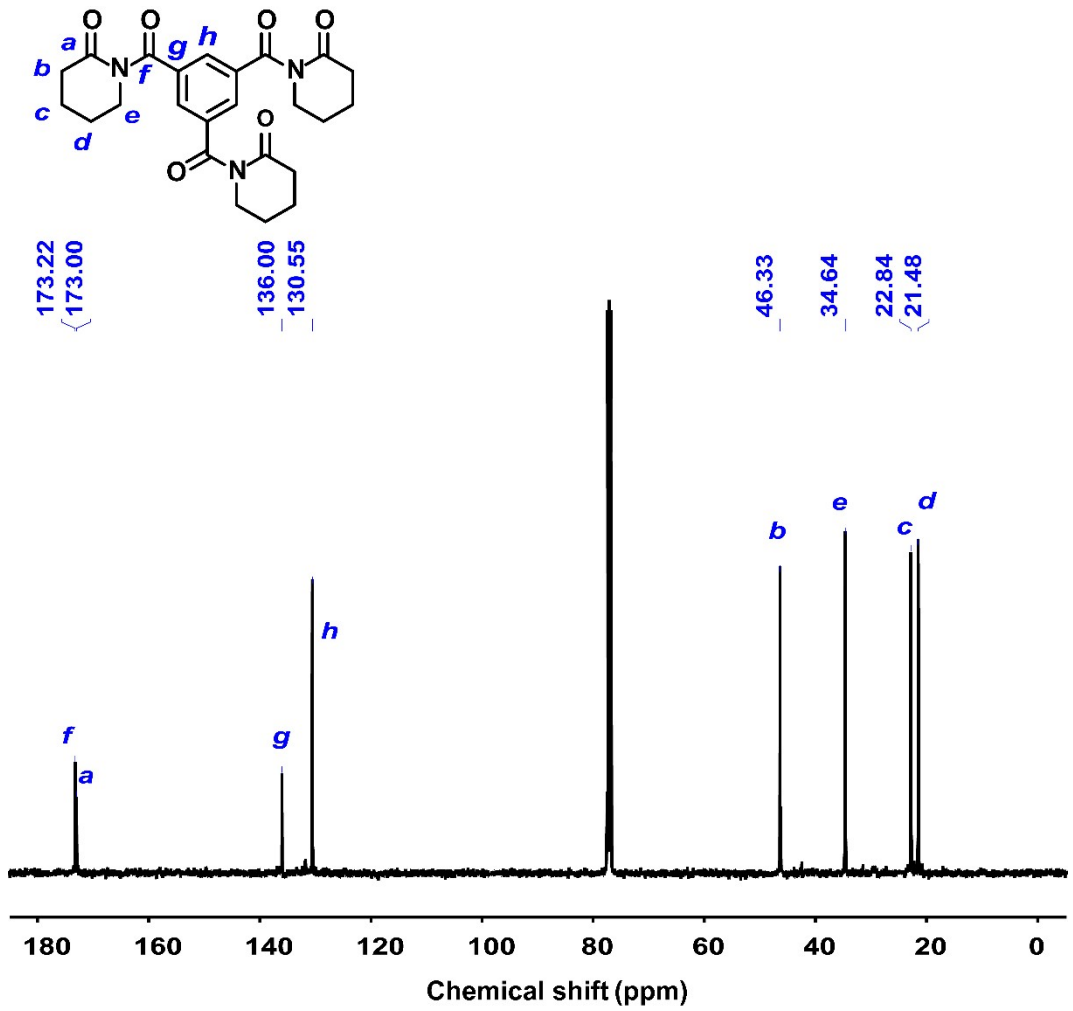


Figure S13. ^{13}C NMR spectra of (1,1',1"-(benzene-1,3,5-tricarbonyl)tris(piperidin-2-one)) (**I3**) in $CDCl_3$.

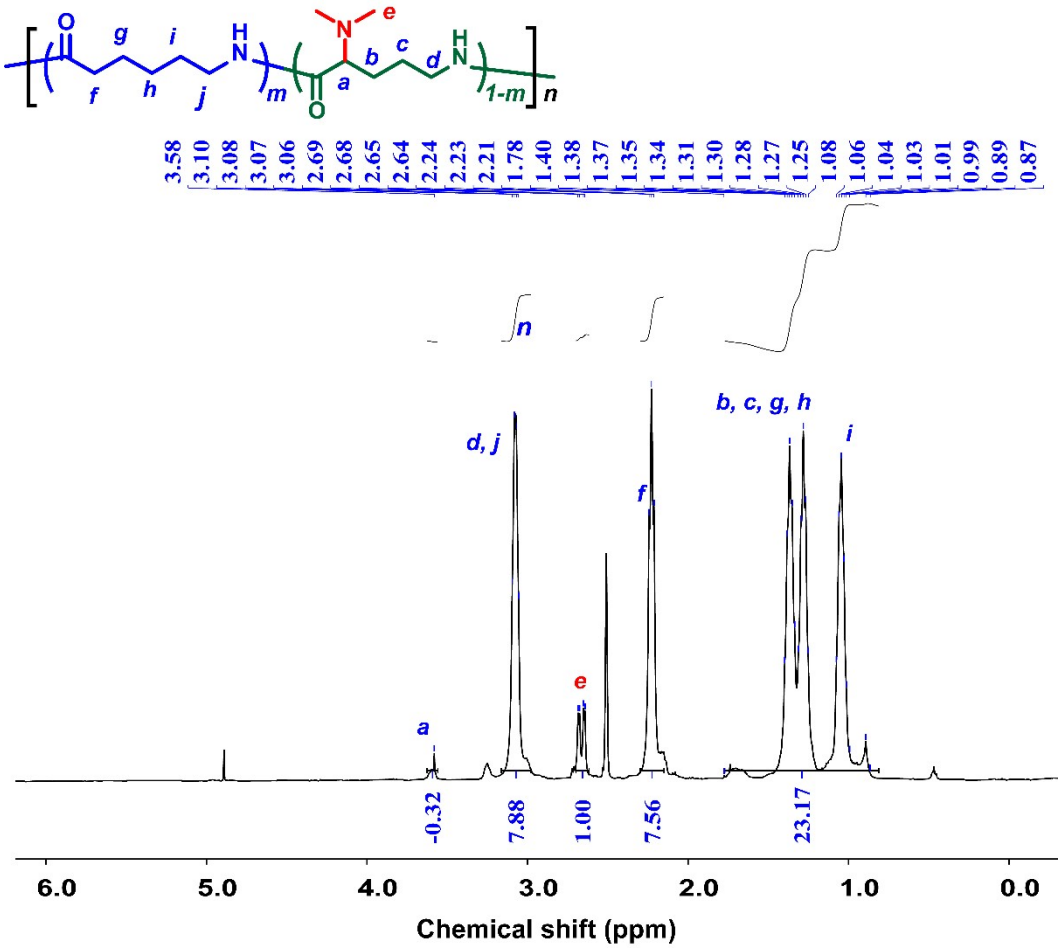


Figure S14. ^{1}H NMR spectra of copolymer **CP14** in DMSO-d_6.

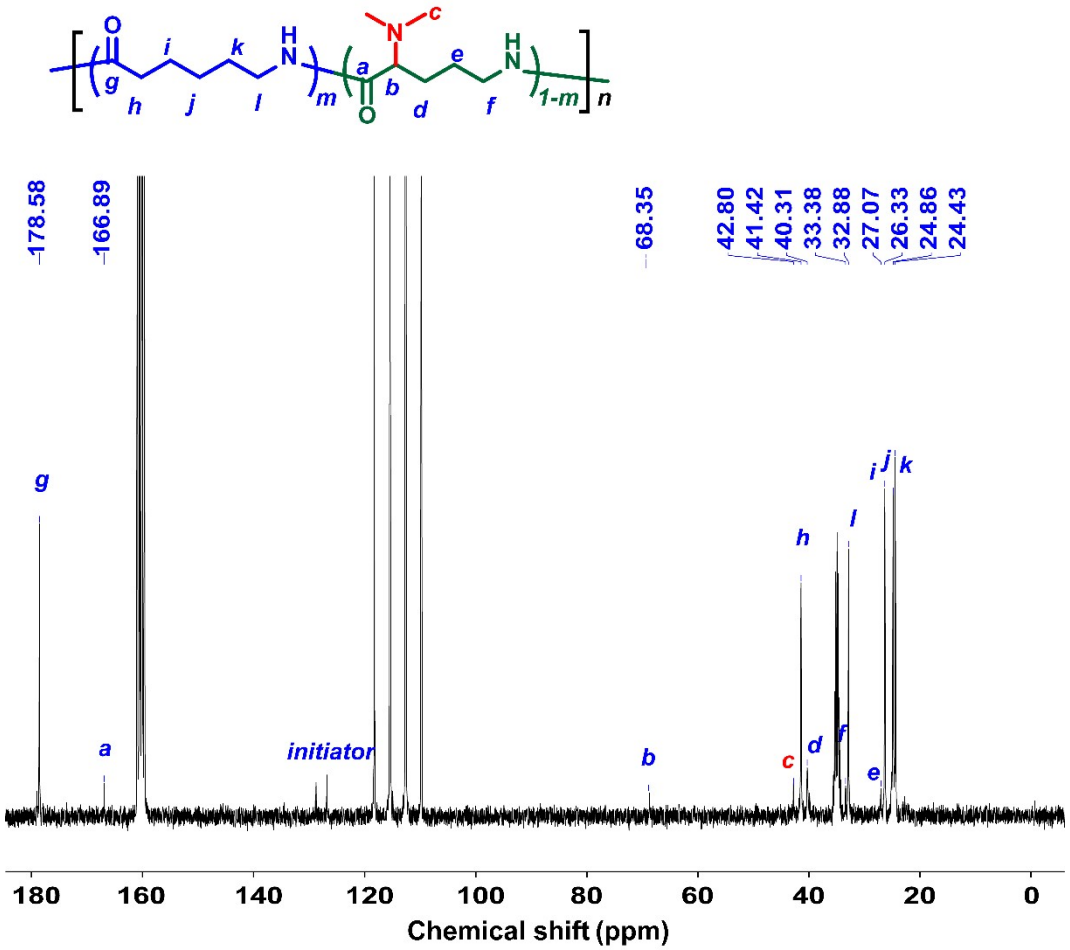


Figure S15. ^{13}C NMR spectra of copolymer **CP14** in DMSO-d_6.

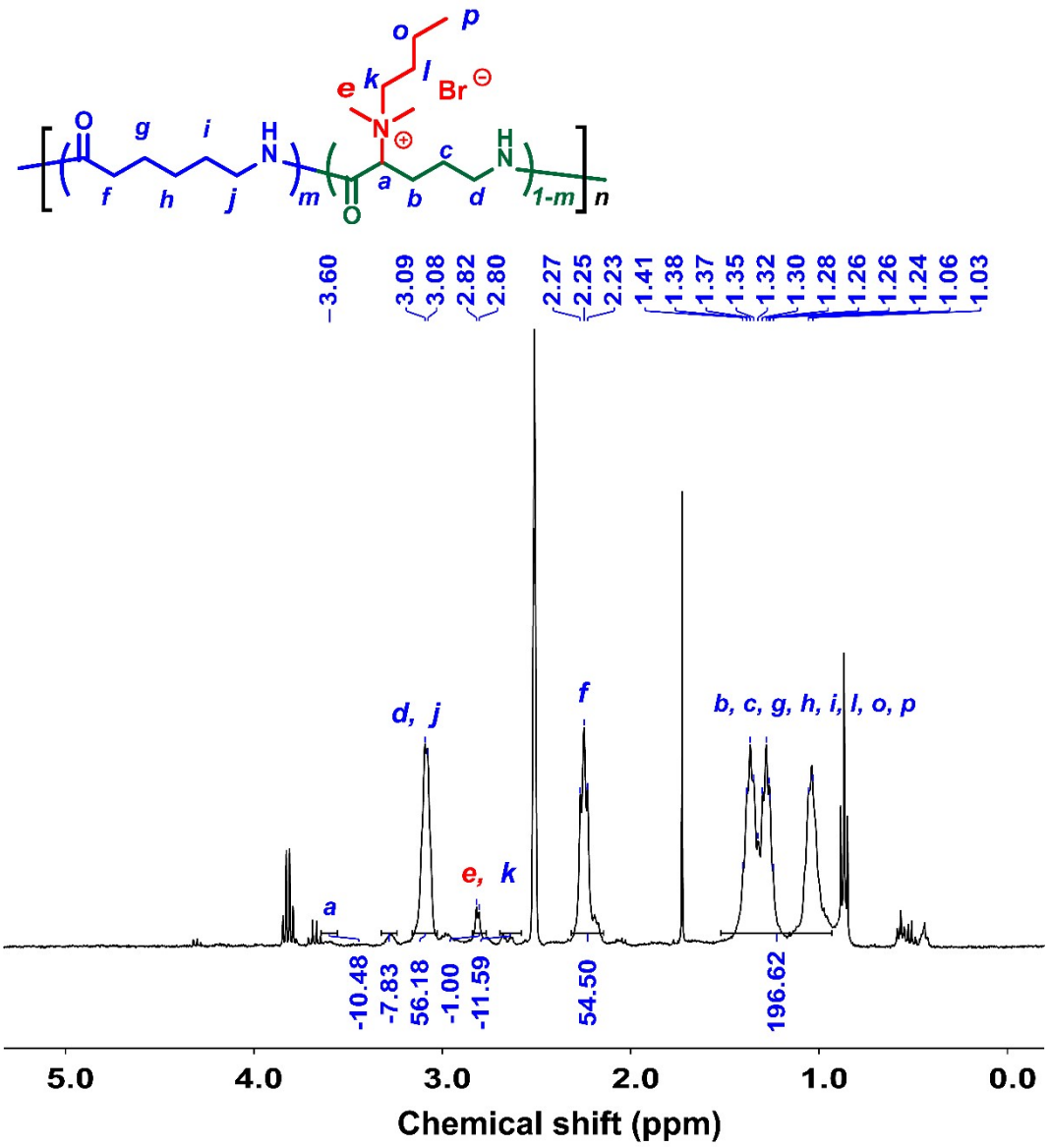
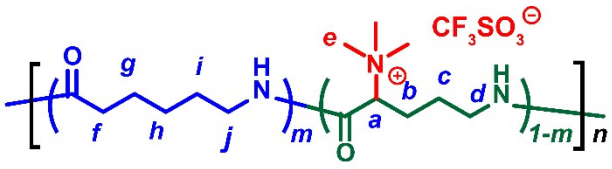


Figure S16. ^{1}H NMR spectra of copolymer **CP14a** in DMSO-d_6.



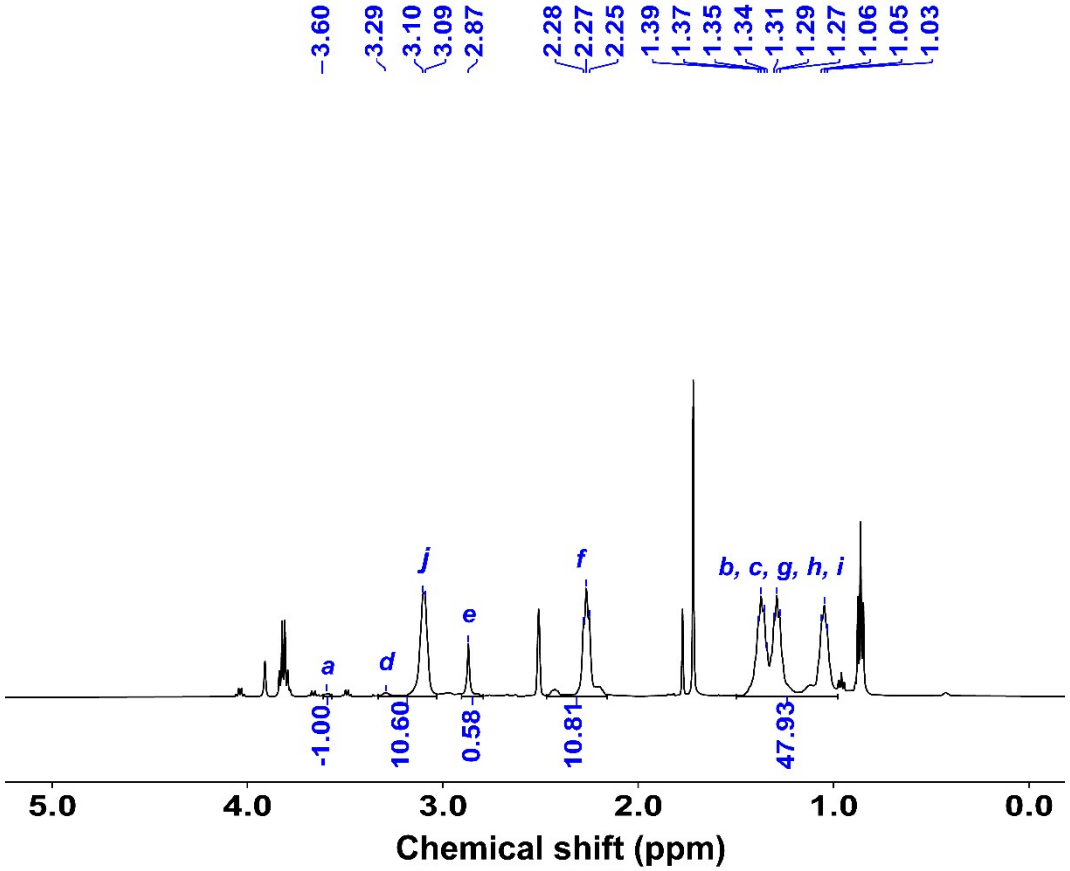


Figure S17. ^{1}H NMR spectra of copolymer **CP14b** in DMSO-d_6.

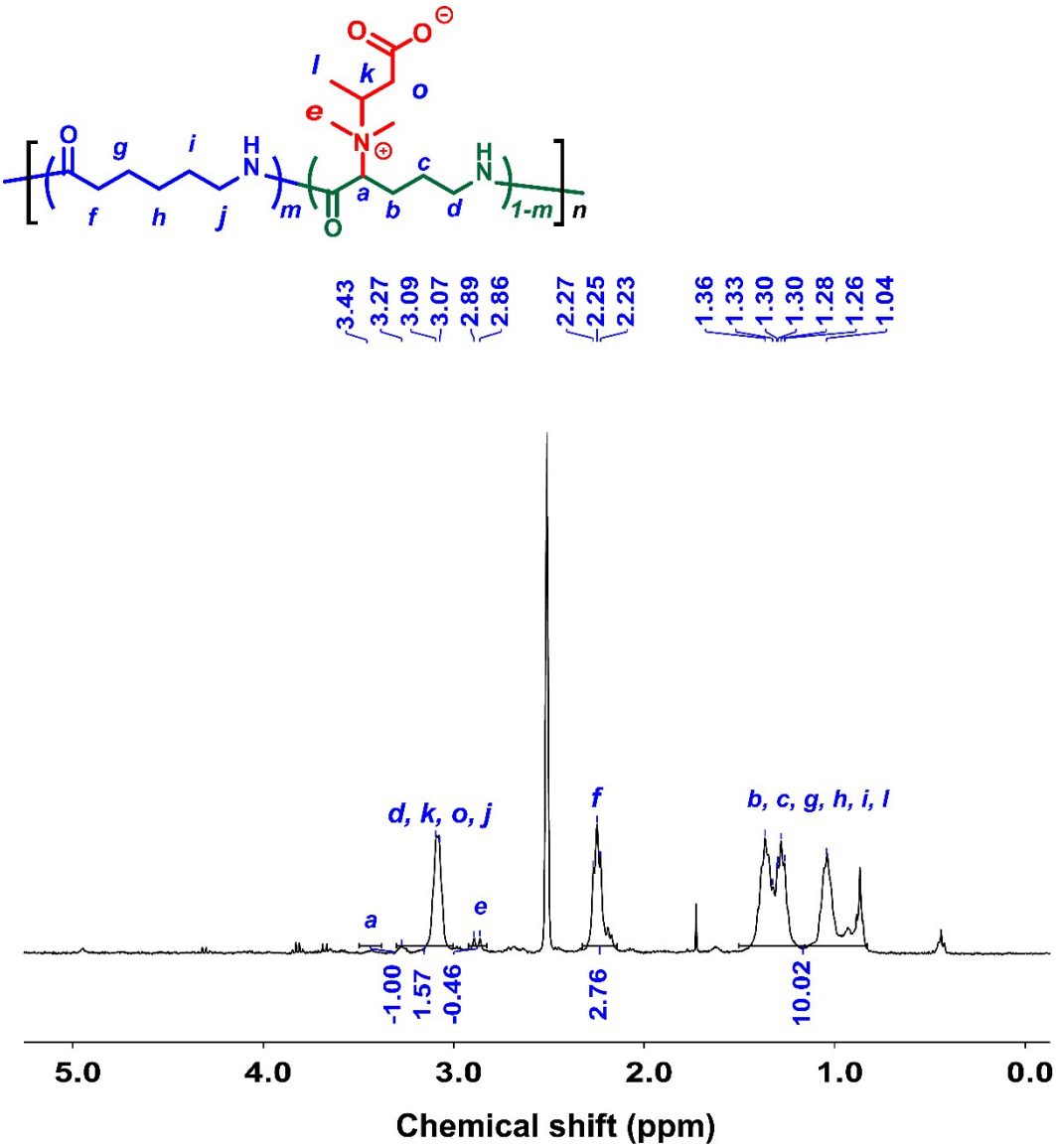


Figure S18. ^{1}H NMR spectra of copolymer **CP14c** in DMSO-d_6.

7 Data

Table S1. Copolymerization of **M1** and ε-CLa [a]

entry	Time	**M1** Conv. (%) [b]	**ε-CLa** Conv. (%) [b]	**M1** Incorp. (%) [c]
1	10 min	4	26	0.6
2	0.5 h	5	35	0.8
3	1 h	7	83	0.5
4	2 h	8	85	0.6
5	3 h	10	86	0.8
6	4 h	13	88	0.9
7	6 h	17	88	1.1
8	12 h	17	89	0.8
9	24 h	18	90	1.5
10	36 h	18	92	1.4

Condition: **M1** = 3-(dimethylamino)-piperidone, ε-CLa = ε-caprolactam, Catalyst = KHMDS, Co-initiator = **I1**, (**M1**+ε-CLa)/KHMDS/**I1** = (5+45)/1/1, Temperature=145 ℃, N_2 atmosphere. [a] Abbreviation: Conv., conversion. [b] The conversion of monomer **M1** and ε-CLa were determined by ^{1}H NMR. [c] The content of monomer **M1** was determined by ^{1}H NMR.

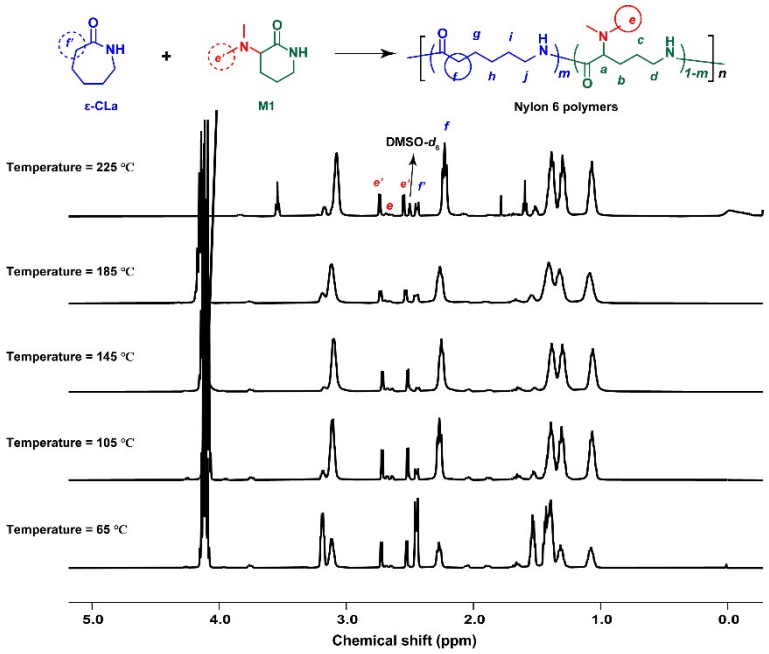


Figure S19. Overlay of ^{1}H NMR spectra in DMSO-d_6 of CP1, CP7-CP10 after ring-opening polymerization (Table 1, entry 1, 7-10).

Table S2. Experiment data of reactivity ratio [a]

entry	f_1	F_1 [b]	x	y	F	G	α	η	ξ
1	0.1	0.64%	0.1111	0.0064	1.9167	-17.1389		-2.2833	0.2553
2	0.2	1.35%	0.2500	0.0137	4.5671	-18.0185		-1.7741	0.4497
3	0.3	2.53%	0.4286	0.0260	7.0761	-16.0824	5.5896	-1.2698	0.5587
4	0.4	4.00%	0.6667	0.0417	10.6667	-15.3333		-0.9432	0.6562
5	0.5	5.78%	1.0000	0.0613	16.3010	-15.3010		-0.6990	0.7447

[a] Condition: **M1** = 3-(dimethylamino)-piperidone, ε-CLa = ε-caprolactam, Catalyst = KHMDS, Co-initiator = **I1**, (**M1**+ε-CLa)/KHMDS/**I1** = 50/1/1, Temperature=145 ℃, Time=10 min, N_2 atmosphere. $x= f_1/(1- f_1)$, $y= F_1/(1- F_1)$, $F=x^2/y$, $G=x(y-1)/y$, $\alpha=\sqrt{F_{max} * F_{min}}$. $\eta=G/(\alpha+F)$, $\xi=F/(\alpha+F)$. [b] The content of **M1** (F_1) was determined by ^{1}H NMR.

Table S3. Thermodynamic property of copolymers

entry	Copolymer	$M_{n,SEC}$ (KDa)	$T_{d,5\%}$ (℃)	T_g(℃)	T_c(℃)	T_m(℃)
1	**CP11**	35.0	373	-	179	214
2	**CP12**	35.4	364	-	180	212
3	**CP13**	32.7	368	-	183	211
4	**CP14**	33.0	370	-	186	209

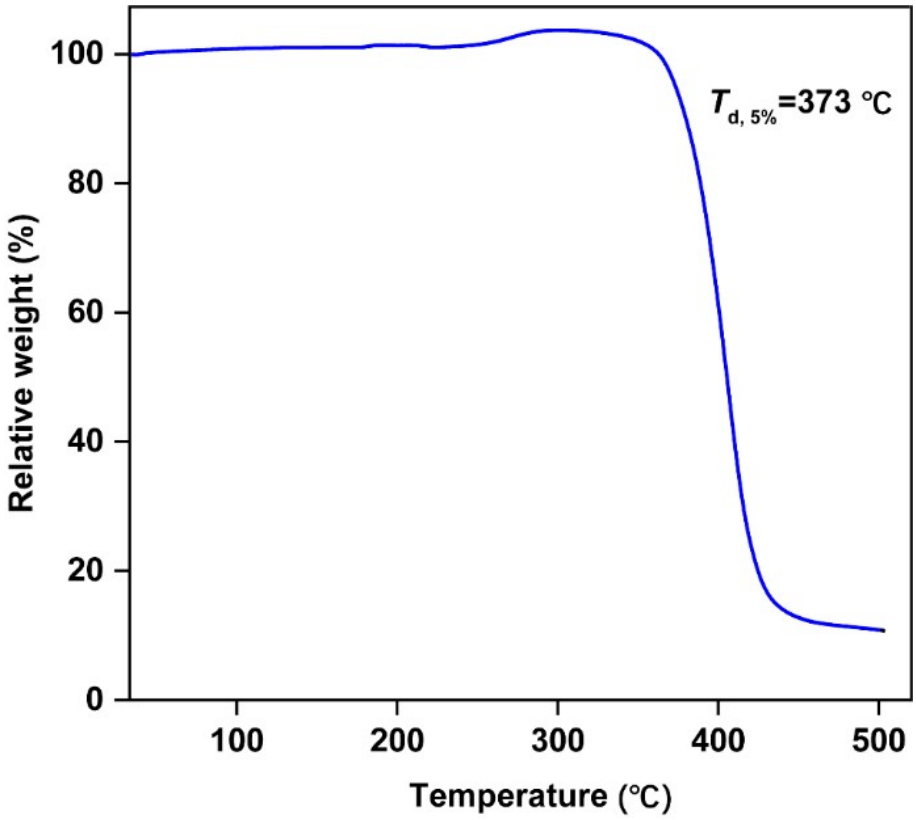


Figure S20. TGA profiles of **CP11**.

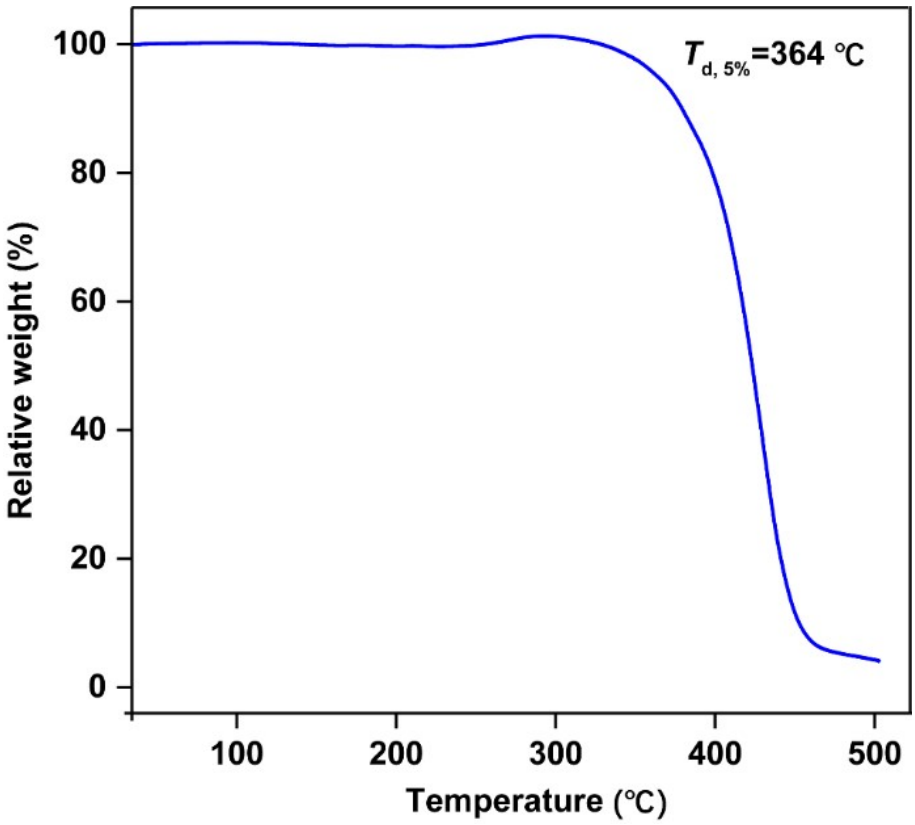


Figure S21. TGA profiles of **CP12**.

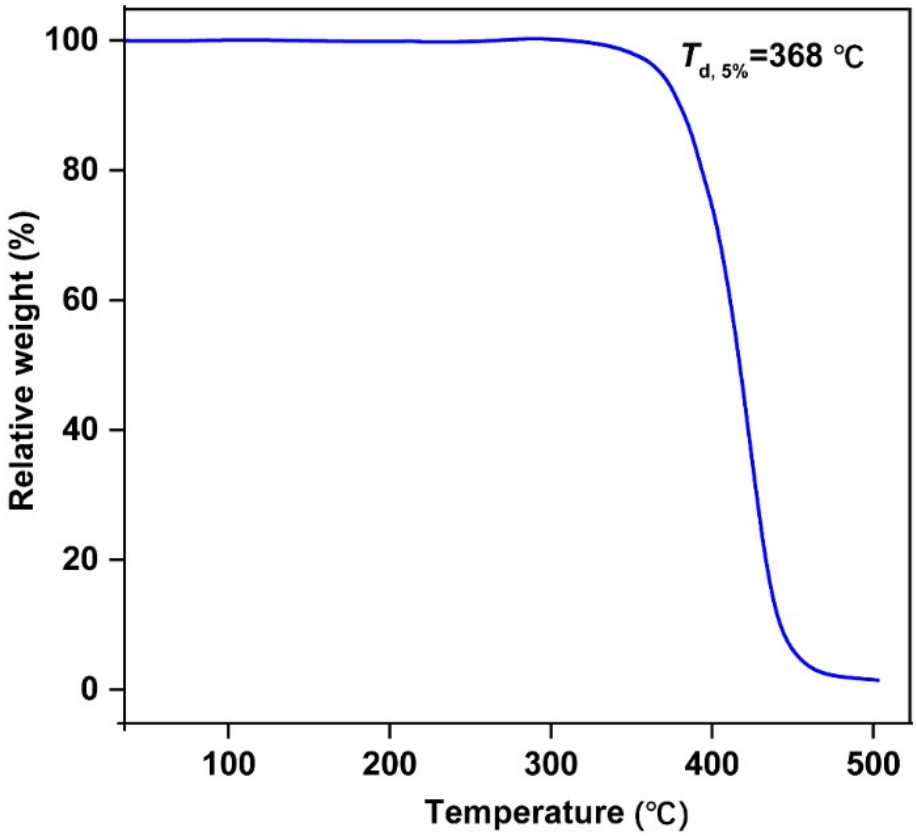


Figure S22. TGA profiles of **CP13**.

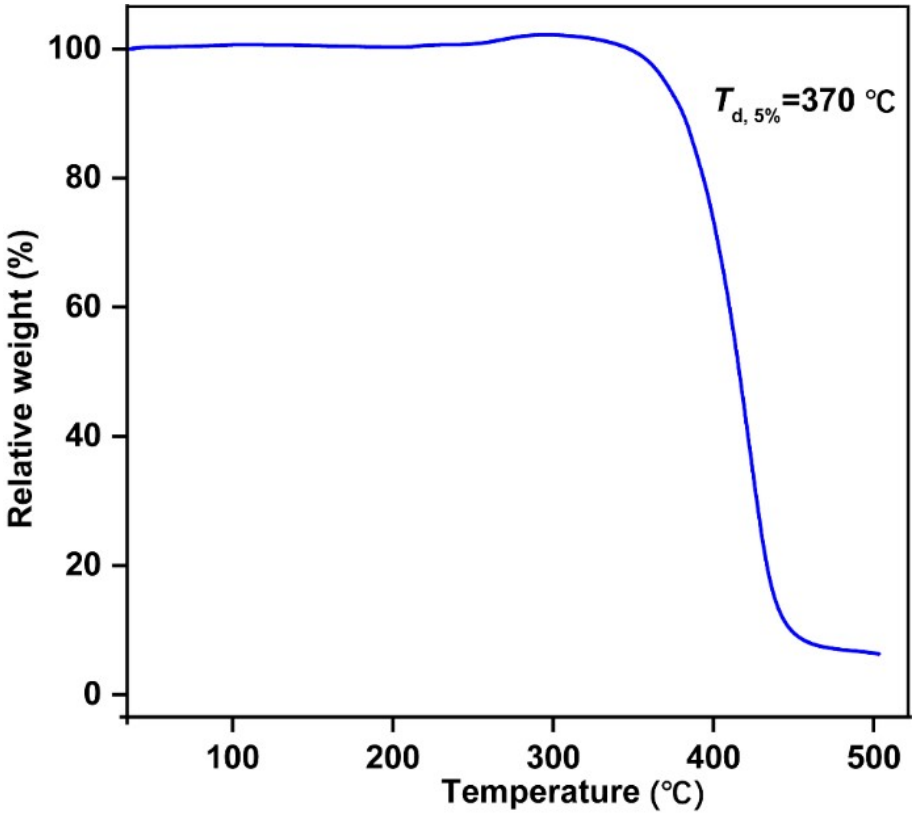


Figure S23. TGA profiles of **CP14**.

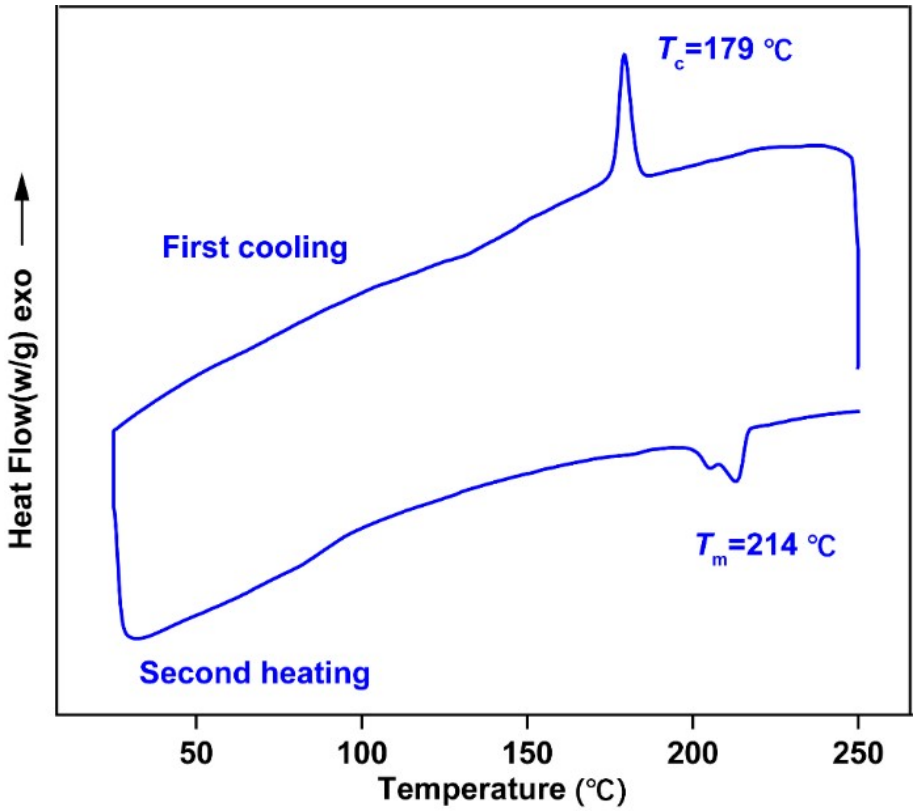


Figure S24. DSC profiles of **CP11**.

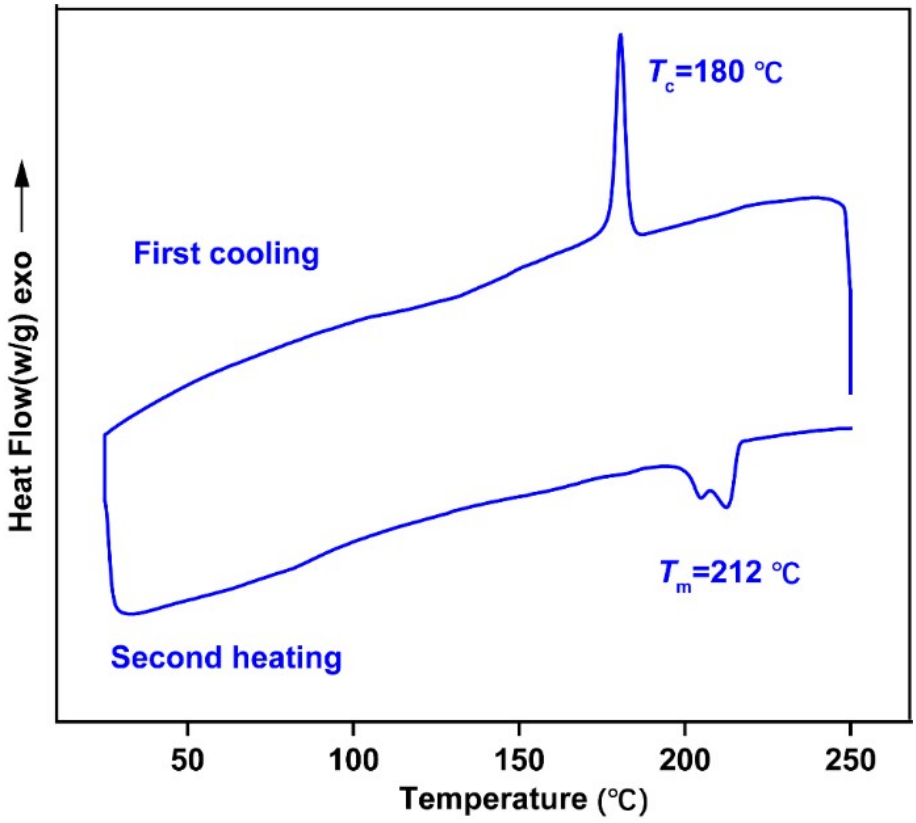


Figure S25. DSC profiles of **CP12**.

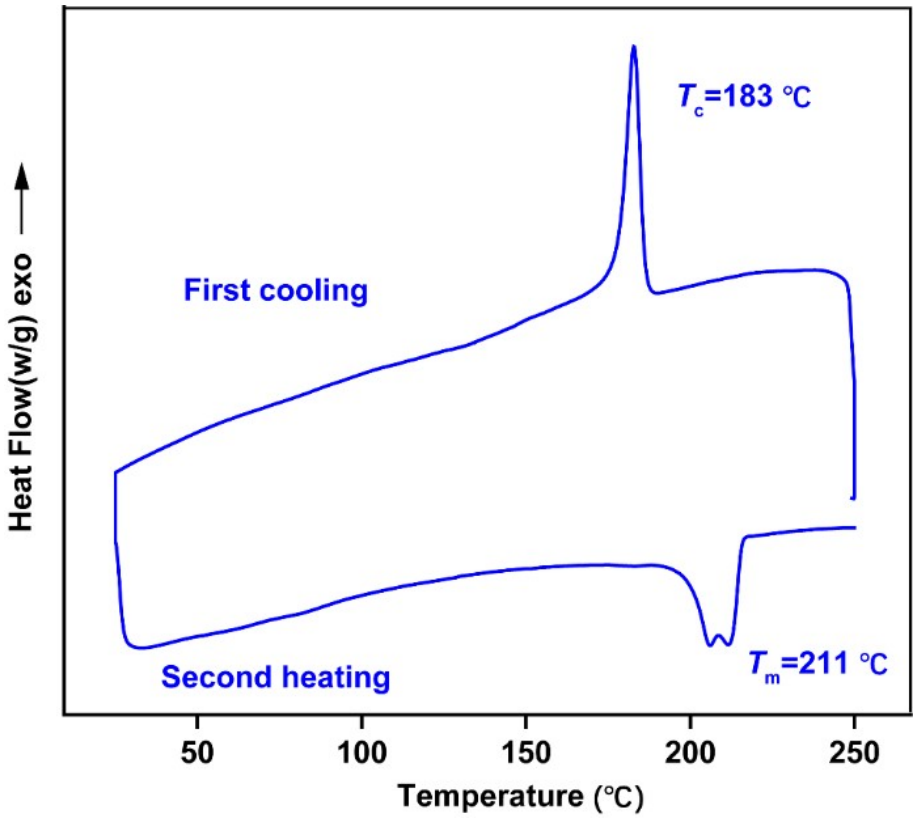


Figure S26. DSC profiles of **CP13**.

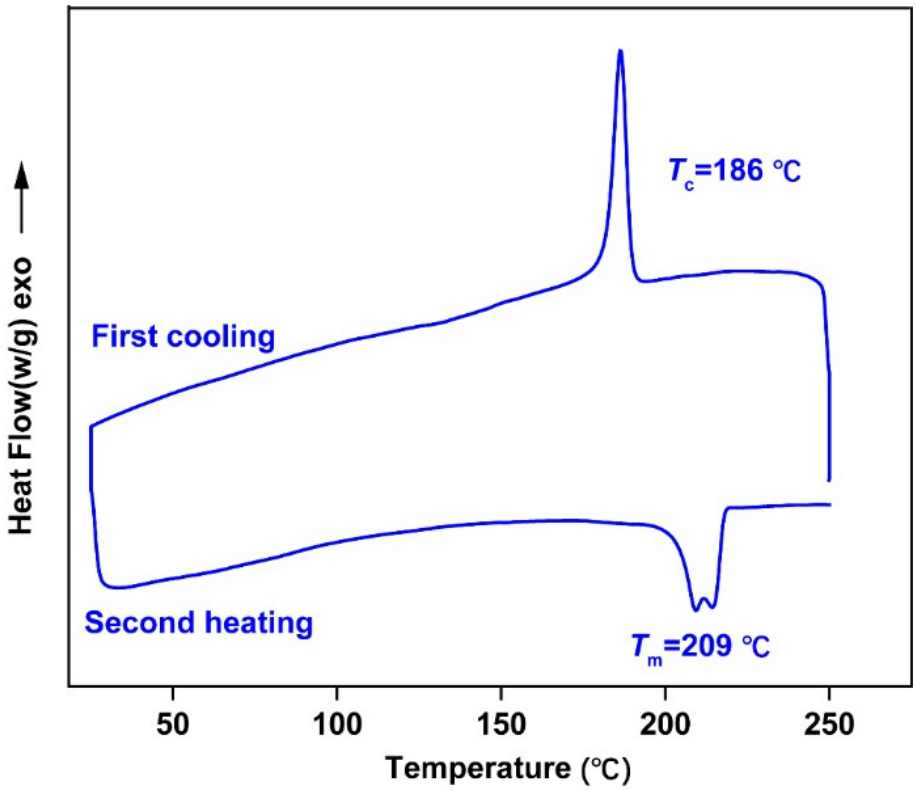


Figure S27. DSC profiles of **C14**.

Table S4. Thermodynamic property of CP14a, CP14b, and CP14c

entry	Copolymer	$T_{d,5\%}$ (°C)	T_g(°C)	T_c(°C)	T_m(°C)
1	**CP14a**	375	-	164	205
2	**CP14b**	366	-	170	208
3	**CP14c**	364	-	164	204

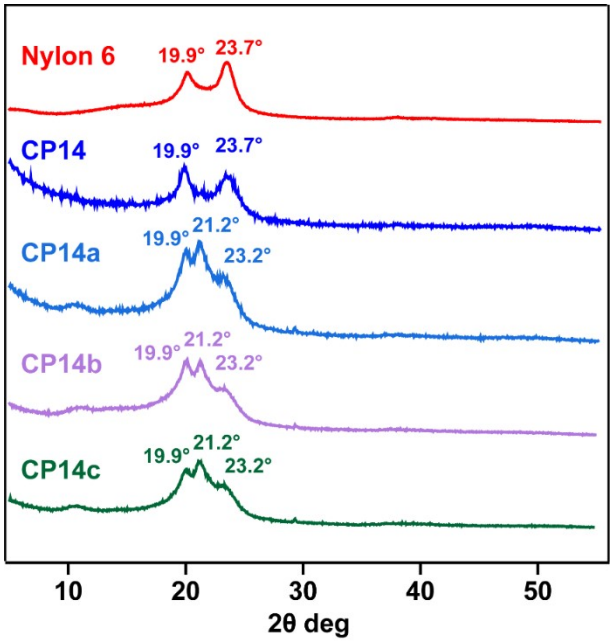


Figure S28. XRD profiles of nylon 6, **CP14, C14a, CP14b, and CP14c**.

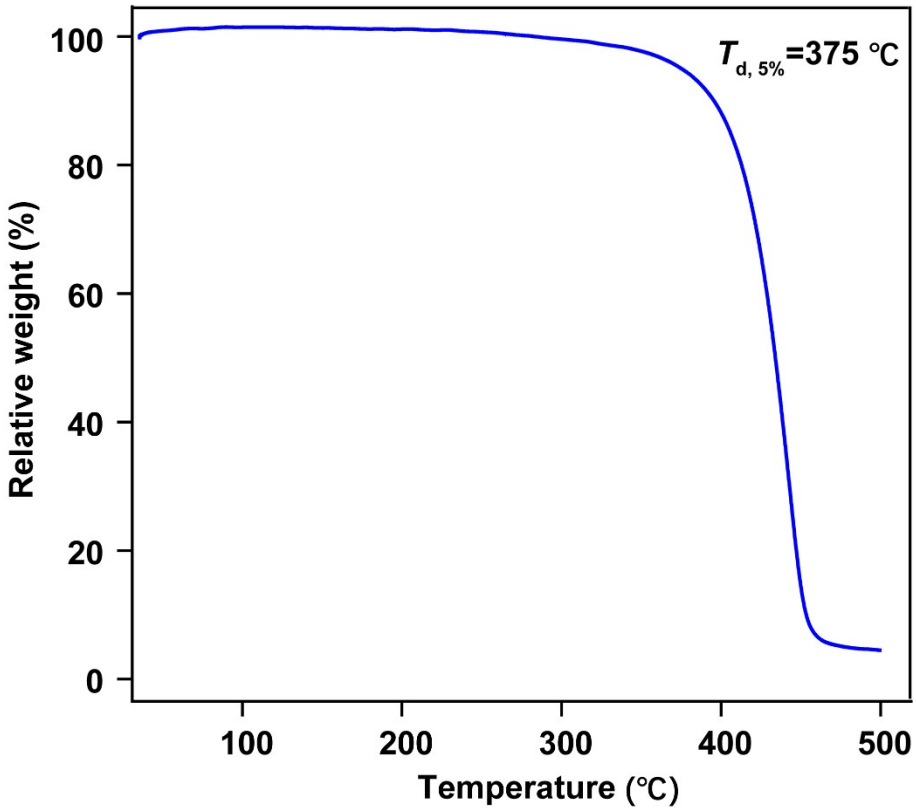


Figure S29. TGA profiles of **C14a.**

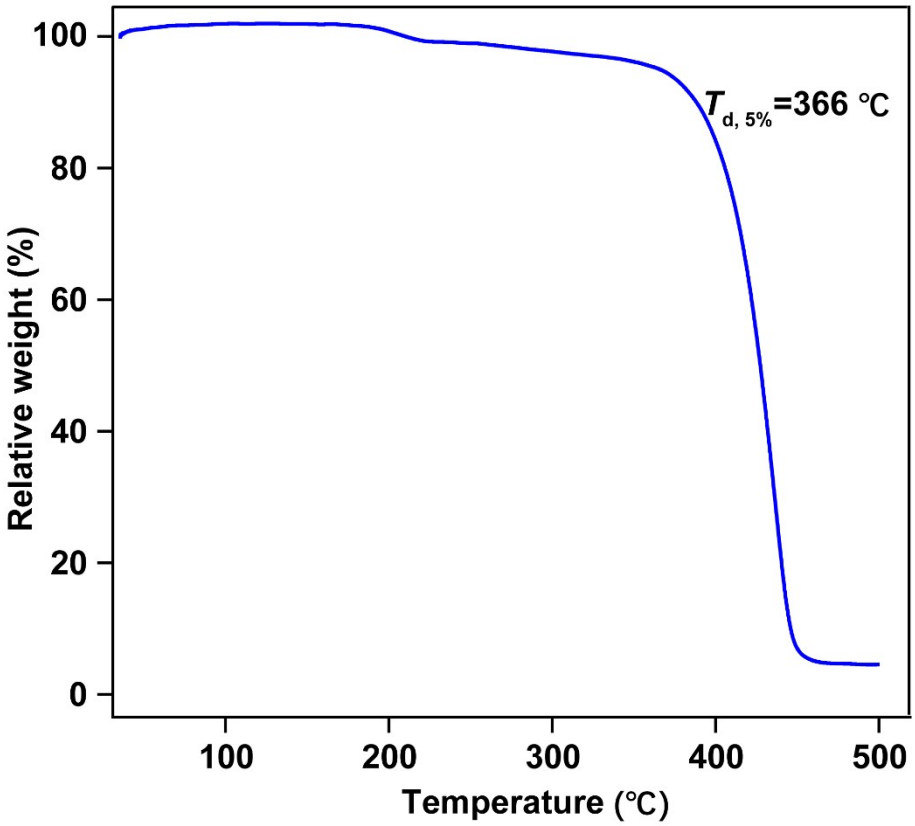


Figure S30. TGA profiles of **C14b.**

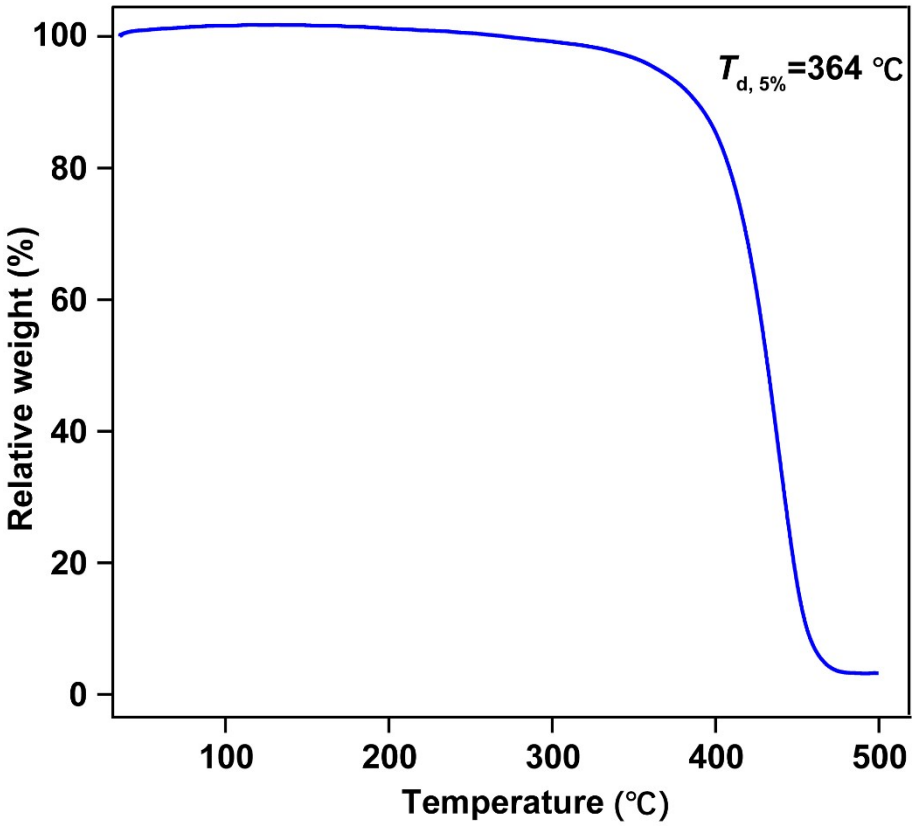


Figure S31. TGA profiles of **C14c.**

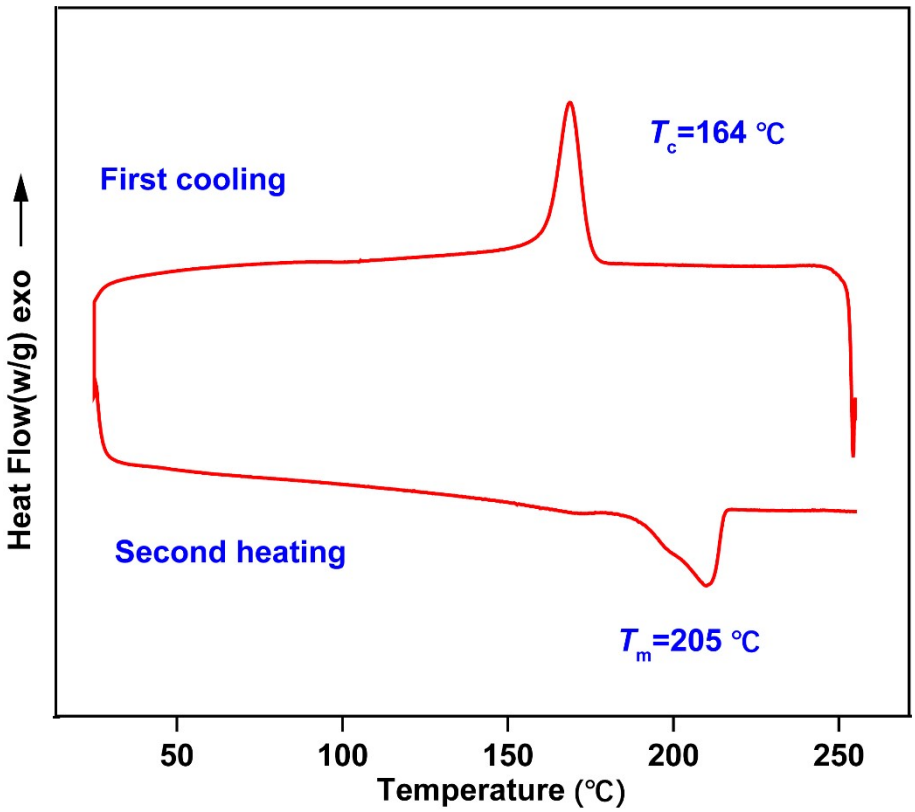


Figure S32. DSC profiles of **C14a.**

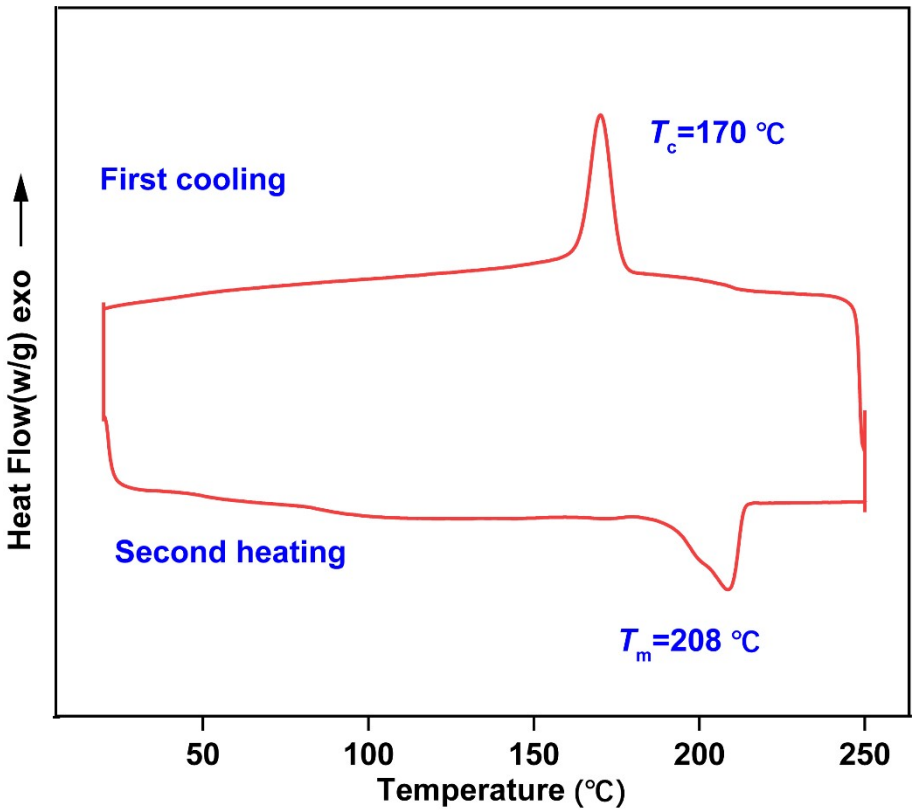


Figure S33. DSC profiles of **C14b.**

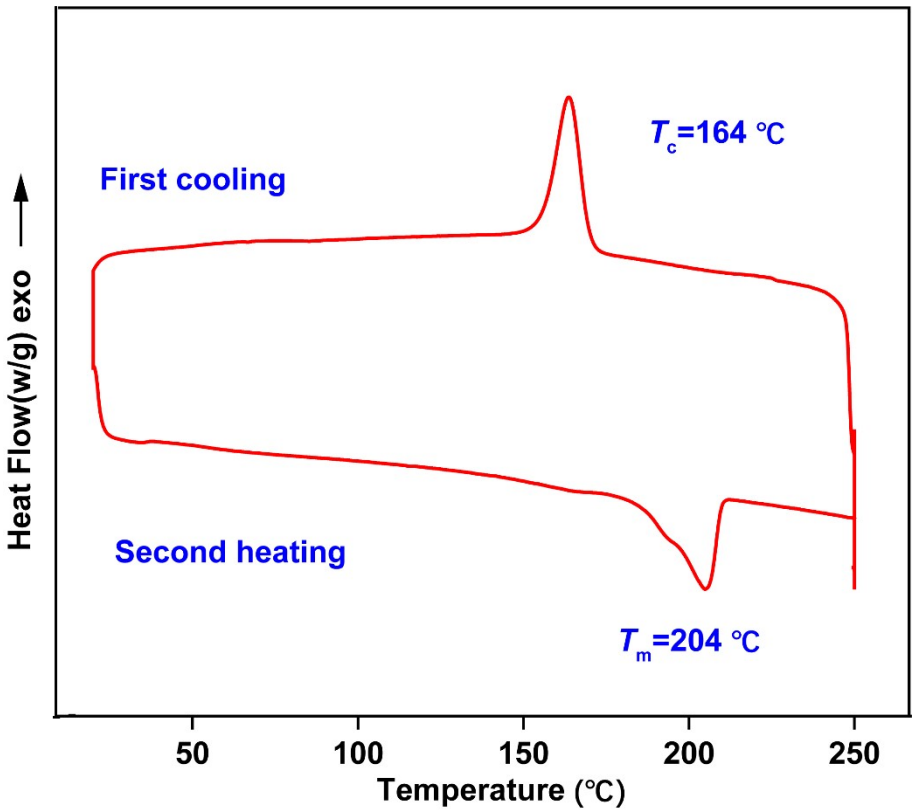


Figure S34. DSC profiles of **C14c.**

Table S5. Water contact angles of nylon 6, CP14, CP14a, CP14b, and CP14c

Sample	Water contact angles
Nylon 6	63.9 ± 0.3
CP14	58.1 ± 0.9
CP14a	51.7 ± 1.4
CP14b	49.6 ± 1.8
CP14c	53.5 ± 1.5

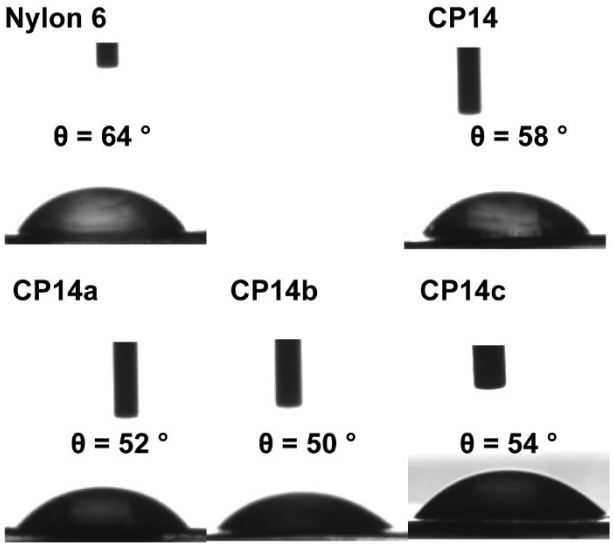


Figure S35. Water contact angles profiles of nylon 6, CP14, CP14a, CP14b, and CP14c **.**

REFERENCE

1. Y. Tao, X. Chen, F. Jia, S. Wang, C. Xiao, F. Cui, Y. Li, Z. Bian, X. Chen and X. Wang, *Chem. Sci.*, 2015, **6**, 6385-6391.