Electronic Supporting Information

Constructing recyclable biomass-derived thermosetting polymers by a solvent-free and catalyst-free Knoevenagel condensation reaction

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Materials and Characterization

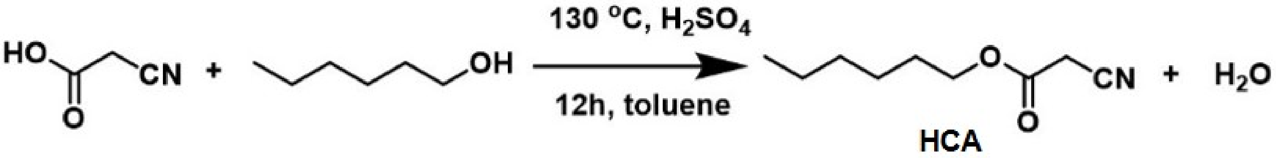
All reagents were purchased from commercial sources. *N*-hexanol (Aladdin, Shanghai, China.), cyanoacetic acid (Macklin, Shanghai, China.), *n*-hexylic acid (Macklin, Shanghai, China.), methyl cyanoacetate (Macklin, Shanghai, China), polycaprolactone diol (average Mn ~2,000, Macklin, Shanghai, China), Mg_2SO_4 (Xihua, Guangdong, China), toluene (Xihua, Guangdong, China), dichloromethane (Xihua, Guangdong, China), tetrahydrofuran (THF, Xihua, Guangdong, China), dimethylsulfoxide (Xihua, Guangdong, China), 5-hydroxymethylfurfural and 1, 10-decanedioicacid (Aladdin, Shanghai, China.), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC·HCl), and aluminium oxide (Macklin, Shanghai, China), polycaprolactone triol (M_w ~ 550, Macklin, Shanghai, China), 4-dimethylaminopyridine (DMAP, TCI chemicals, Shanghai, China) were used directly without purification.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-300 NMR spectrometer (Bruker, Bremen, Germany). Gel permeation chromatography (GPC, Waters, USA) was performed in THF (1 mL·min^{-1}) at 25 °C using a Waters chromatograph instrument equipped with three Styragel columns (HT3, HT4, and HT5; 300 mm × 7.8 mm), 1515 pump and 2414 differential refractive index detector. PS standards were employed for the GPC calibration curve. Thermogravimetric analysis (TGA) was performed on a TGA55 thermogravimetric analyzer (TA instruments, USA). Samples were heated under a nitrogen atmosphere at a rate of 10 °C/min from 50 to 800 ºC. Differential scanning calorimetry (DSC) was performed on a differential scanning calorimeter (DSC25, TA Instruments, USA). Samples were heated from 0 to 150 ^{o}C at a rate of 10 ^{o}C/min under a nitrogen atmosphere. Two cooling-heating runs were performed for each sample, and the data was obtained from the second heating curves. Uniaxial tensile measurements were performed with a 10 mm/min strain rate at 20 °C, using a dumbbell-shaped film with an effective gauge dimension: 16 mm (*L*) × 4 mm (*W*), the thickness of 0.9 ~ 1.1 mm. Each result was the average value from testing of at least three samples. Fourier transform infrared (FT-IR) spectra were measured by INVENIO-R instrument (Bruker, Germany).

Chemical synthesis

Synthesis of hexyl cyanoacetate (HCA)

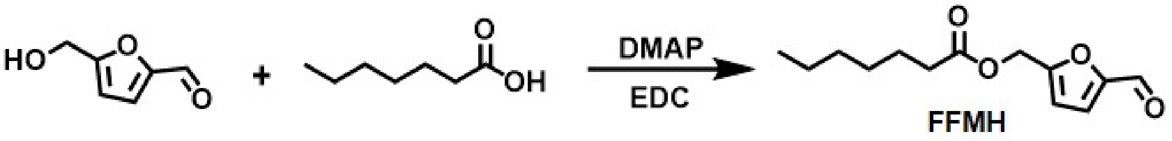
50 mL of toluene, cyanoacetic acid (1.3 g, 14.76 mmol), and n-hexanol (1 g, 9.78 mmol) were added to the single-necked flask, and then 2 drops of sulfuric acid were dropped into the flask. The solution boiled at 130 °C and the water produced was removed. The reaction was stopped after 12 h. The solution was distilled under reduced pressure after cooling, and a pale yellow oily liquid was extracted. The pale yellow oily liquid was quickly passed through a basic alumina column, and then, a colorless liquid was obtained after distillation under reduced pressure (1.3 g, 78 %).



Scheme S1. Synthesis route of HCA.

Synthesis of (5-formylfuran-2-yl)methyl hexanoate (FFMH)

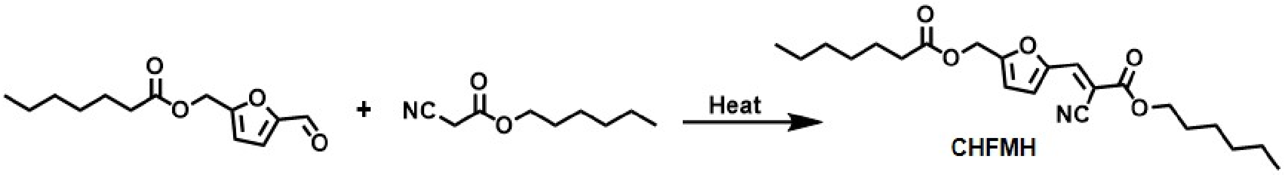
n-Hexylic acid (3 g, 25.7 mmol) and 5-hydroxymethylfurfural (3 g, 23.4 mmol) was dissolved in dichloromethane (150 mL), and DMAP (305 mg, 2.5 mmol) and EDC· HCl (4 g, 25.7 mmol) were then added under stirring. The reaction was carried out at 25 °C for 48 h. After washing with water three times, the reaction solution was dried by anhydrous $MgSO_4$ for 2 h. Following the drying process, the reaction mixture was rapidly passed through an alkaline alumina chromatographic column and subsequently subjected to distillation under reduced pressure, resulting in the isolation of a reddish brown oily liquid (3.7 g, 71 %).



Scheme S2. Synthesis route of FFMH.

Synthesis of (E)-(5-(2-cyano-3-(hexyloxy)-3-oxoprop-1-en-1-yl)furan-2-yl)methyl hexanoate (CHFMH)

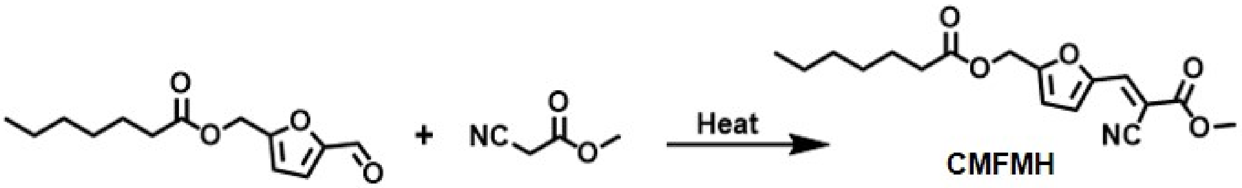
FFMH (224 mg, 1 mmol) and hexyl cyanoacetate (203 mg, 1.2 mmol) were added to a single-mouth flask, after reaction at 110 °C for 4 h, the mixture was vacuum-dried at 110 °C. The crude product was dissolved in CH_2Cl_2 and the obtained solution was subjected to column chromatography (SiO_2, CH_2Cl_2). After distillation under reduced pressure, a brownish red oily liquid was obtained (317 mg, 81 %).



Scheme S3. Synthesis route of CHFMH.

Synthesis of (E)-(5-(2-cyano-3-methoxy-3-oxoprop-1-en-1-yl)furan-2-yl)methyl hexanoate (CMFMH)

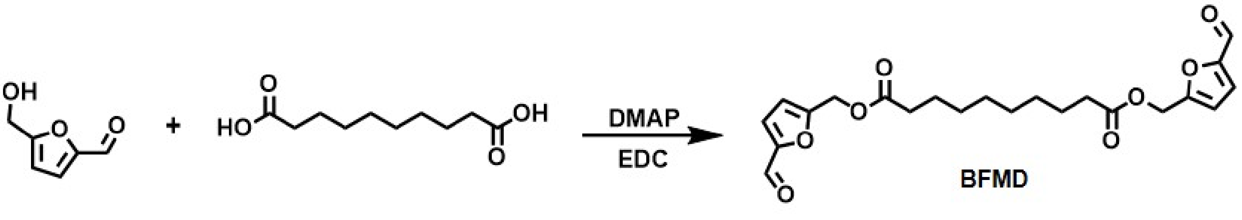
FFMH (224 mg, 1 mmol) and methyl cyanoacetate (198 mg, 2 mmol) were added to the single-mouth flask, and reacted at 110 °C for 4 h. The crude product was dissolved in CH_2Cl_2 and the obtained solution was subjected to column chromatography (SiO_2, CH_2Cl_2). After vacuum distillation, a brown red oily liquid was obtained (357 mg, 91%).



Scheme S4. Synthesis route of CMFMH

Synthesis of bis((5-formylfuran-2-yl)methyl) decanedioate (BFMD)

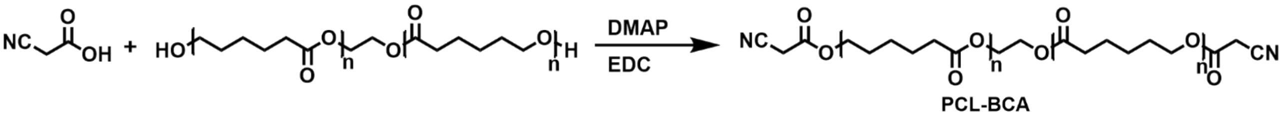
Decanedioic acid (1 g, 4.94 mmol) and 5-hydroxymethylfurfural (2.55g, 12.36 mmol) were dissolved in dichloromethane (200 mL). Then, DMAP (61mg, 0.5 mmol) and 1.55 g of EDC·HCl (1 mmol) were added. The reaction was carried out at 25 °C for 48 h. After that, the solvent was evaporated and a brown substance was obtained. The crude product was dissolved in dichloromethane and washed three times with water. The organic phase was collected and dried over anhydrous $MgSO_4$. The organic phase was subjected to column chromatography (basic alumina, chloroform). After the eluent was collected and concentrated, a brown solid was obtained (1.46 g, 71 %).



Scheme S5 Synthesis route of BFMD.

Synthesis of polycaprolactone bis(2-cyanoacetate) (PCL-BCA)

The synthesis route of PCLBCA is shown in Scheme S6. Polycaprolactone diol with two hydroxyl end groups (10.0 g, 5 mmol, $M_w = 2000$) and cyanoacetic acid (1.27 g, 15 mmol) were dissolved in dichloromethane (200 mL). Then, 61 mg of DMAP (0.5 mmol) and 1.55 g of EDC·HCl (1 mmol) were added. The reaction was carried out at 25 °C for 48 h. After that, the solvent was evaporated and a white sticky substance was obtained. The crude product was dissolved in dichloromethane and washed three times with water. The organic phase was collected and dried over anhydrous $MgSO_4$. The organic phase was subjected to column chromatography (basic alumina, chloroform). After the eluent was collected and concentrated, a white waxy solid was obtained (8.6 g, 75 %).

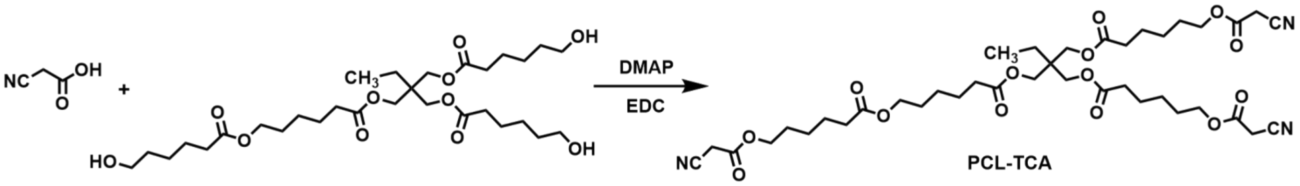


Scheme S6. Synthesis route of PCL-BCA.

Synthesis of cyanoacetic acid modified polycaprolactone triol (PCL-TCA)

Firstly, the PCLT was characterized by ^{1}H NMR and ESI-MS (Figures S13a and S13b). The number-average molecular weight was determined to be ~540 g/mol, and the mass spectrometry data revealed a distribution primarily consisting of species containing 3 to 5 caprolactone repeating units, which is consistent with the nominal molecular weight and confirms its well-defined triol functionality. Cyanoacetic acid (5.74 g, 67.5 mmol), DMAP (0.82 g, 6.75 mmol), and EDC·HCl (25.88 g, 135 mmol) were dissolved in 150 mL of CH_2Cl_2 and reacted at room temperature for 3 h. Then, polycaprolactone triol (5 g, 9 mmol) was added to the reaction system. After reacting at room temperature for 48 h, the mixture was washed three times with 50 mL of saturated sodium chloride solution. Subsequently, the organic phase was collected, and excess anhydrous magnesium sulfate was added to dry for 2 h. Remove anhydrous magnesium sulfate by filtration. The filtrate was distilled under reduced pressure to remove the solvent, and dried under vacuum at 35 °C overnight to obtain an orange-red oily liquid

(3.5 g, 52%).



Scheme S7. Synthesis route of PCL-TCA.

Synthesis of thermosetting polymer

PCL-TCA and bis((5-formylfuran-2-yl)methyl) decanedioate were added to a single-mouth flask and reacted at 110 °C. A vacuum pump was used to remove the by-product water during the reaction. The reaction stoped until there were no more bubbles in the mixture. The obtained polymer was hot pressed in a plate vulcanizer (110 °C, 10 MPa, 20 min), and the dark red polymer BFMD-PCLT was obtained.

Monitoring the reaction progress by ^{1}H NMR spectroscopy

A model reaction between (5-formylfuran-2-yl)methyl hexanoate and hexyl cyanoacetate was investigated by time-dependent ^{1}H NMR spectroscopy at room temperature, 70, 90, and 110 °C. In detail, (5-formylfuran-2-yl)methyl hexanoate (224 mg, 1 mmol) and hexyl cyanoacetate (169 mg, 1 mmol) were added to a single-mouth flask. Then, the time-dependent ^{1}H NMR spectra were collected at 5, 10, 20, 60, and 120 min at different temperatures. The reaction was performed in an open reactor. The obtained data are shown in Figures 1 and S5-7.

Monitoring the dynamic exchange process by ^{1}H NMR spectroscopy

A model reaction between (5-formylfuran-2-yl)methyl hexanoate and hexyl cyanoacetate was investigated by time-dependent ^{1}H NMR spectroscopy at 110 °C. In detail, (E)-(5-(2-cyano-3-methoxy-3-oxoprop-1-en-1-yl)furan-2-yl)methyl hexanoate (305 mg, 1 mmol), and hexyl cyanoacetate (118 mg, 0.7 mmol) were added to a single-mouth flask at 110 °C. Then, the time-dependent ^{1}H NMR spectra were collected at 10, 60, and 120 min.

Swelling ratio and gel fraction of BFMD-PCL

BFMD-PCL were soaked in different solvents (water, ethanol, n-hexane, dichloromethane, THF and N, N-dimethylformamide) for 24 h to conduct swelling experiments. After 24 h, the swollen samples were taken out, and the surface solvent was wiped and weighed. Finally, the samples were dried at 120 °C for 24 hours to a constant weight. Swelling ratio (SR) and gel fraction (GF) were calculated according to the following formula:

$$\mathrm{SR} = (W_2 - W_1)/W_1 \times 100\%$$

$$\mathrm{GF} = W_3 / W_1 \times 100\%$$

Where W_3 is the weight of the dried sample, W_2 is the weight of the swollen sample, and W_1 is the weight of the original sample.

Reprocessing experiments

BFMD-PCL were cut into pieces and then placed into a rectangular mold (ca. 80 mm (*L*) × 80 mm (*W*)) under a hot press (The processing temperature is 110 °C, 10 MPa) for 20 min. The mold was cooled to room temperature at 10 MPa (10 min) and the reprocessed samples were de-molded.

Chemically recycling

BFMD-PCL (0.24 g) were mixed with PCLTCA (1.19 g, 1.5 mmol), and then, the mixture was heated to 110 °C and formed dark red viscous oil. Subsequently, BFMD (0.94 g, 2.25) was incorporated into the mixture, heating for 4 h. The solidified mixture was hot-pressed at 110 °C and 10 MPa. After the material cools naturally, it is cut into a dumbbell shape.

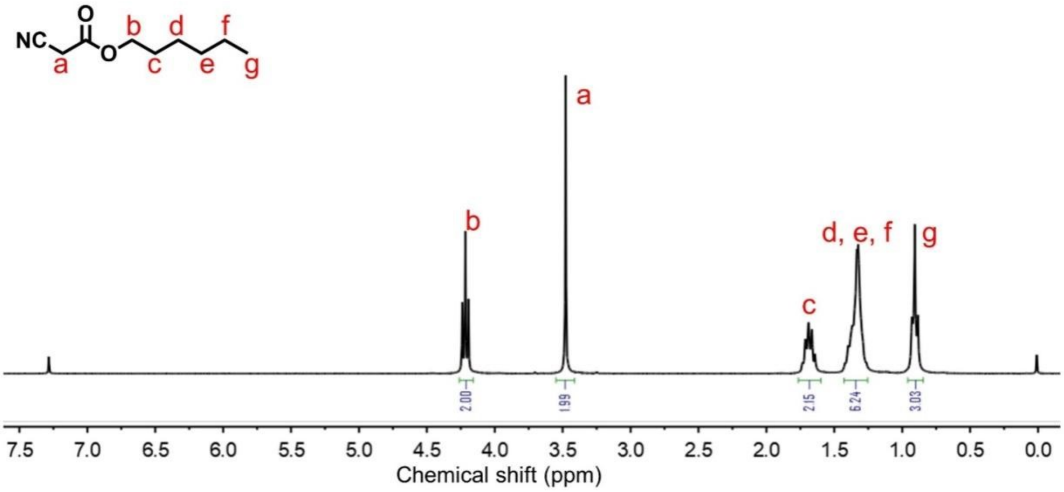


Figure S1 ^{1}H NMR spectrum of HCA in $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.22 (t, *J* = 6.7 Hz, 2H), 3.48 (s, 2H), 1.77 – 1.60 (m, 2H), 1.43 – 1.25 (m, 6H), 0.91 (t, *J* = 6.7 Hz, 3H).

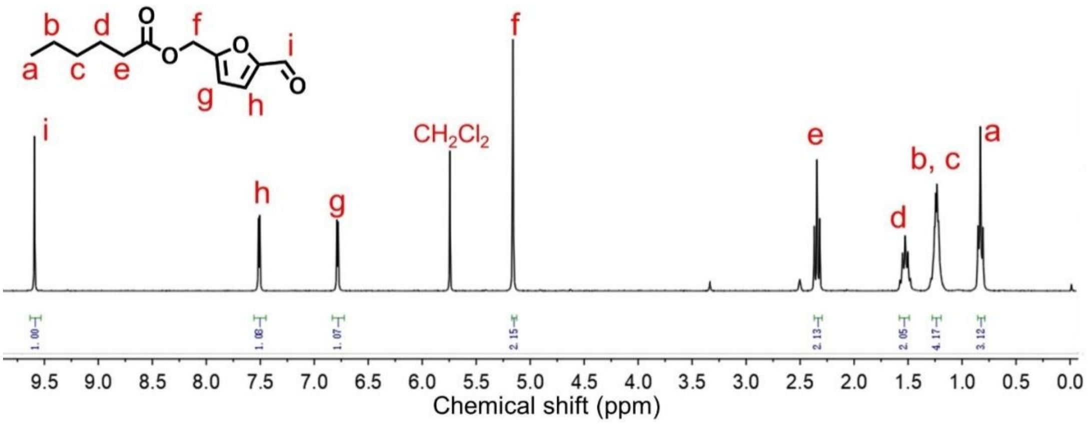


Figure S2 ^{1}H NMR spectrum of FFMH in DMSO-D6. ^{1}H NMR (300 MHz, DMSO) δ 9.59 (s, 1H), 7.51 (d, *J* = 3.5 Hz, 1H), 6.78 (d, *J* = 3.5 Hz, 1H), 5.16 (s, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.54 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.24 (dd, *J* = 7.2, 3.7 Hz, 4H), 0.83 (t, *J* = 6.8 Hz, 3H).

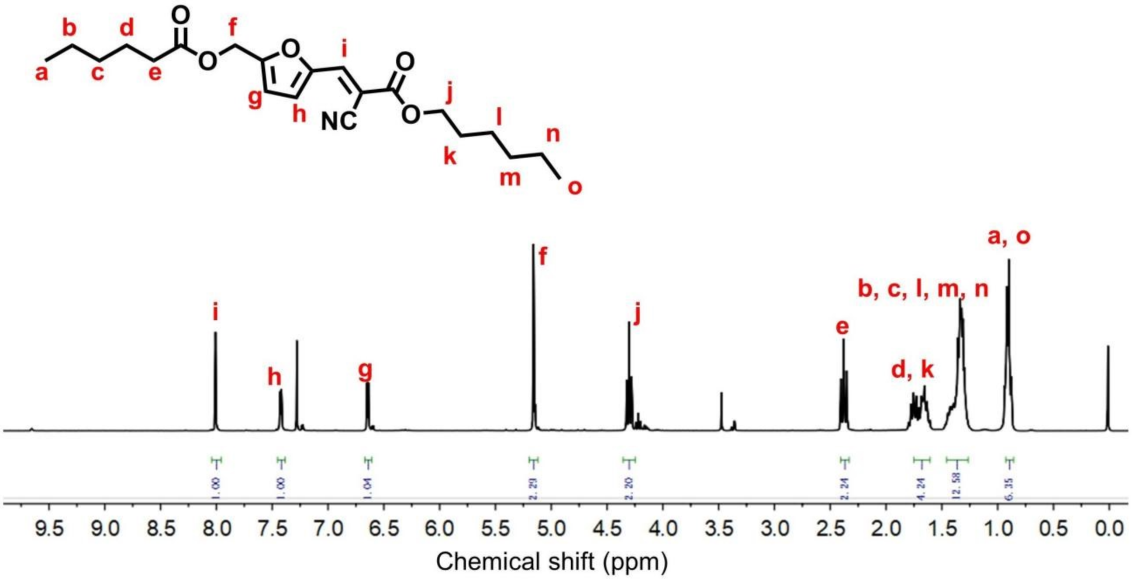


Figure S3 ^{1}H NMR spectrum of CHFMH in $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.42 (d, *J* = 3.6 Hz, 1H), 6.64 (d, *J* = 3.6 Hz, 1H), 5.15 (d, *J* = 3.8 Hz, 2H), 4.30 (t, *J* = 6.7 Hz, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 1.74 – 1.60 (m, 4H), 1.50 – 1.21 (m, 12H), 0.91 (q, *J* = 6.5 Hz, 6H).

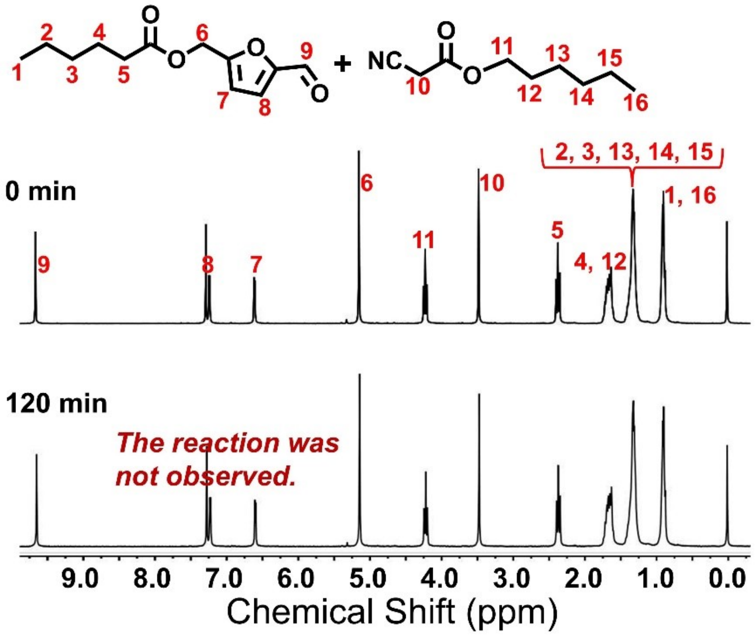


Figure S4 ^{1}H NMR spectra of solvent-free and catalyst-free KC reaction at 0 and 120 min in $CDCl_3$ (room temperature, the molar ratio of FFMH to HCA is 1: 1).

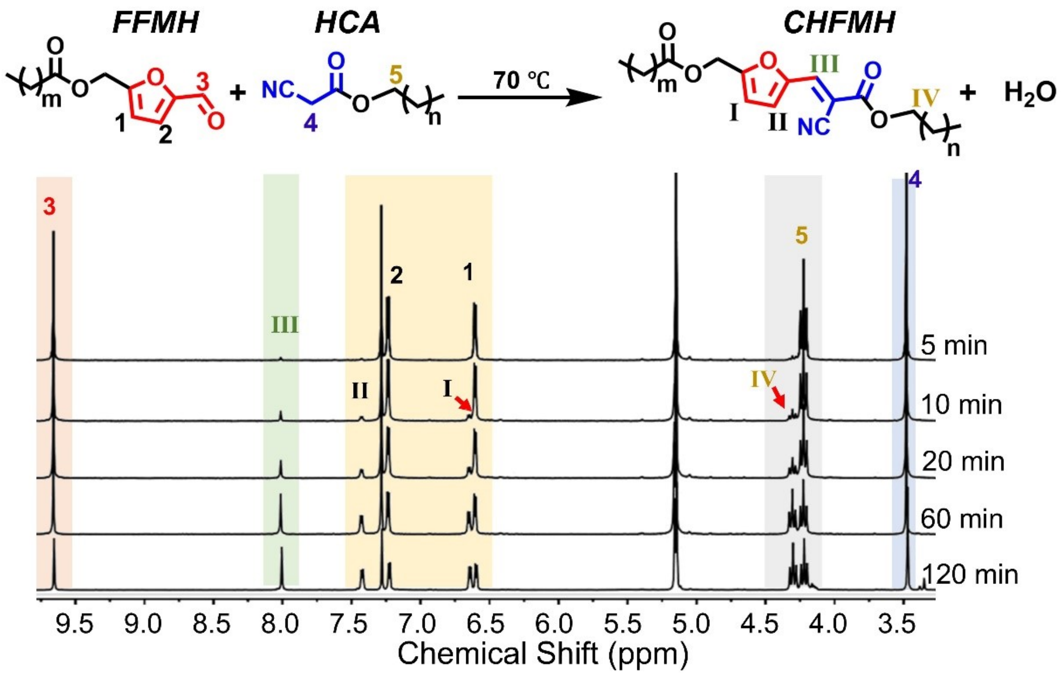


Figure S5 Time-dependent ^{1}H NMR spectra of solvent-free and catalyst-free KC reaction at 70 ℃ (the molar ratio of FFMH to HCA is 1: 1). The reaction was monitored by ^{1}H NMR spectroscopy at 5, 10, 20, 60, and 120 min in $CDCl_3$.

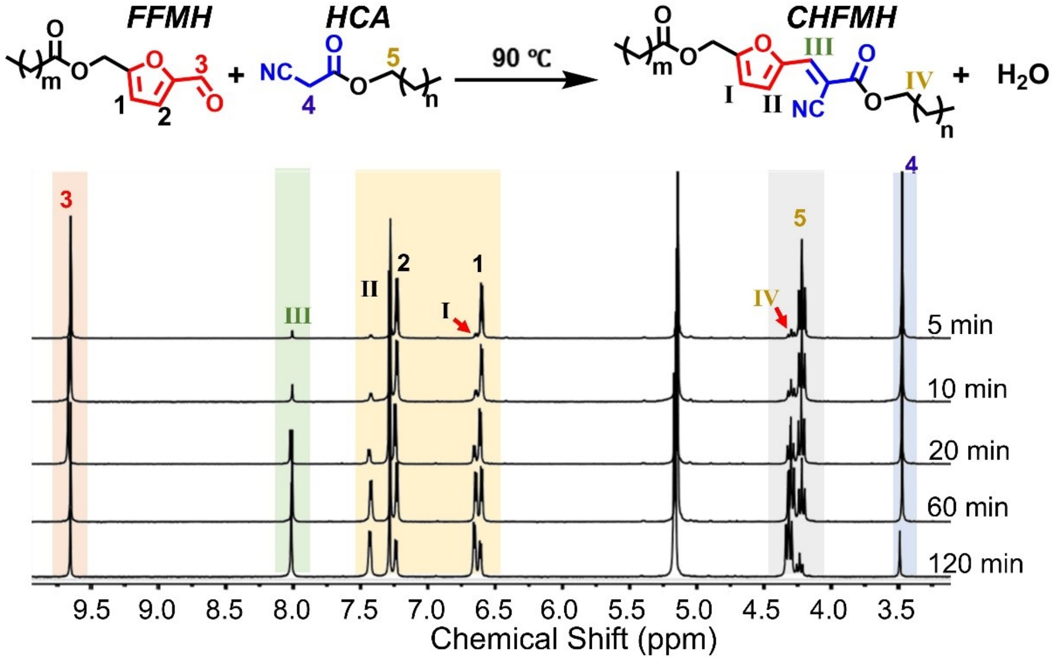


Figure S6 Time-dependent ^{1}H NMR spectra of solvent-free and catalyst-free KC reaction at 90 °C (the molar ratio of FFMH to HCA is 1: 1). The reaction was monitored by ^{1}H NMR spectroscopy at 5, 10, 20, 60, and 120 min in $CDCl_3$

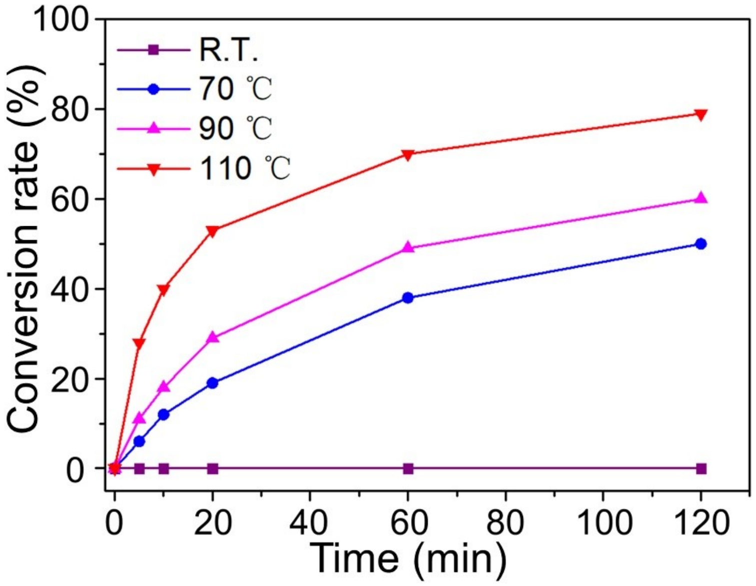


Figure S7 Conversion of solvent-free and catalyst-free KC reaction at room temperature, 70, 90, and 110 °C.

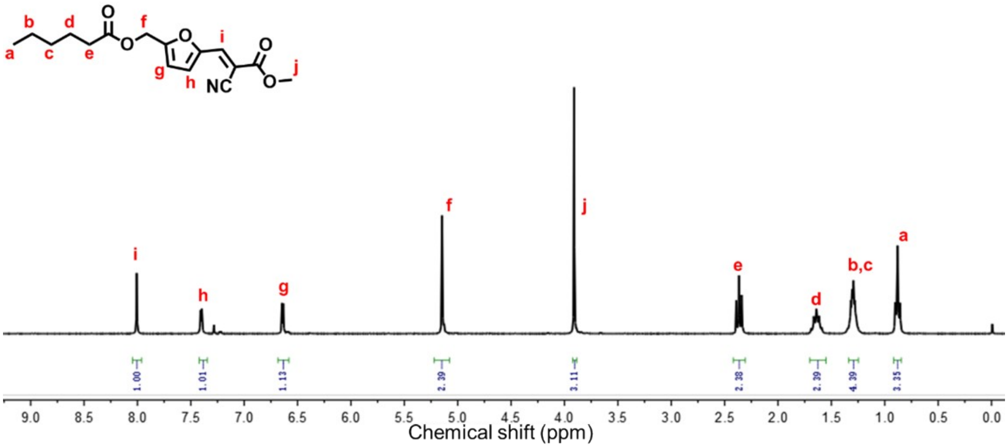


Figure S8 ^{1}H NMR spectrum of CMFMH in $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.39 (t, J = 6.3 Hz, 1H), 6.62 (dd, J = 14.6, 3.6 Hz, 1H), 5.14 (d, J = 5.1 Hz, 2H), 3.90 (d, J = 6.5 Hz, 3H), 2.42 – 2.31 (m, 2H), 1.70 – 1.55 (m, 2H), 1.29 (td, J = 7.4, 3.9 Hz, 4H), 0.88 (t, J = 6.9 Hz, 3H).

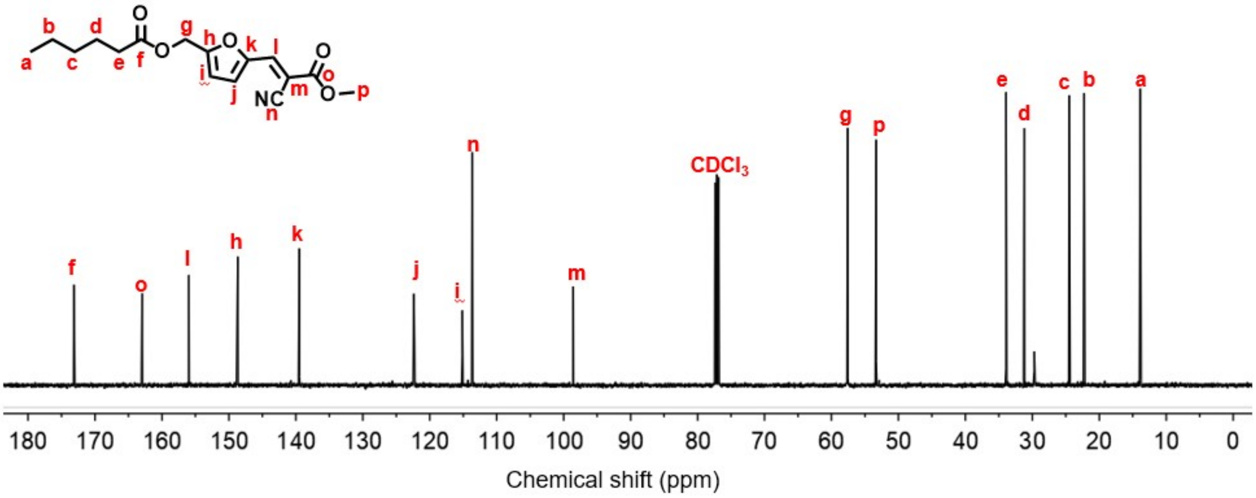


Figure S9 ^{13}C NMR spectrum of CMFMH in $CDCl_3$. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.16 (s), 162.97 (s), 155.99 (s), 148.68 (s), 139.48 (s), 122.36 (s), 115.14 (s), 113.67 (s), 98.56 (s), 57.58 (s), 53.33 (s), 33.92 (s), 31.22 (s), 24.50 (s), 22.27 (s), 13.89 (s).

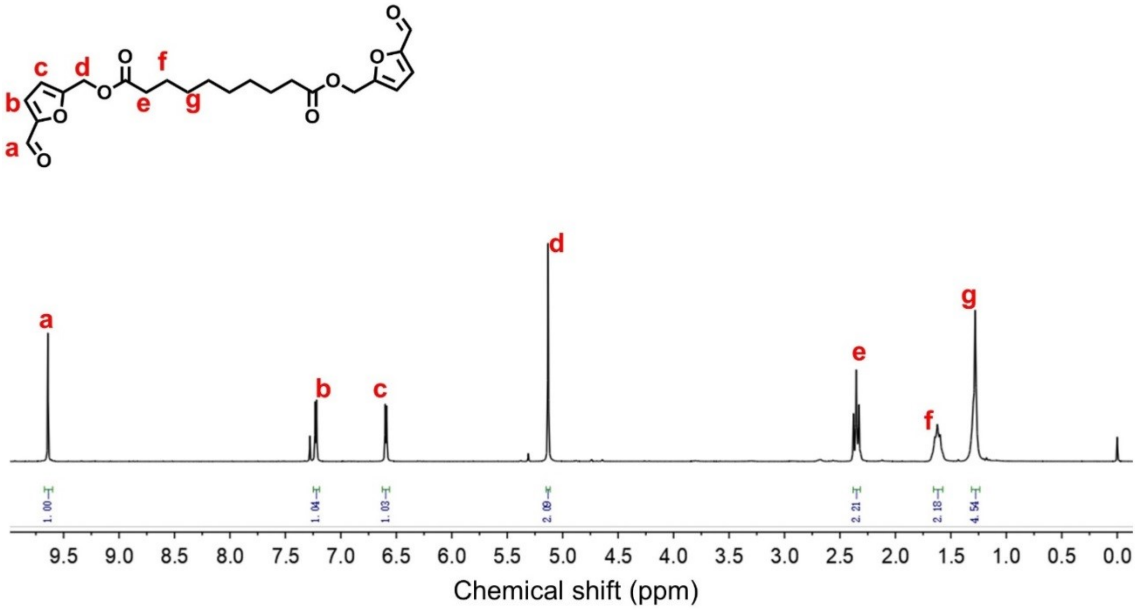


Figure S10 ^{1}H NMR spectrum of BFMD in $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.64 (s, 2H), 7.23 (d, *J* = 3.5 Hz, 2H), 6.59 (d, *J* = 3.5 Hz, 2H), 5.13 (s, 4H), 2.35 (dd, *J* = 9.8, 5.2 Hz, 4H), 1.66 – 1.57 (m, 4H), 1.29 (d, *J* = 4.1 Hz, 8H).

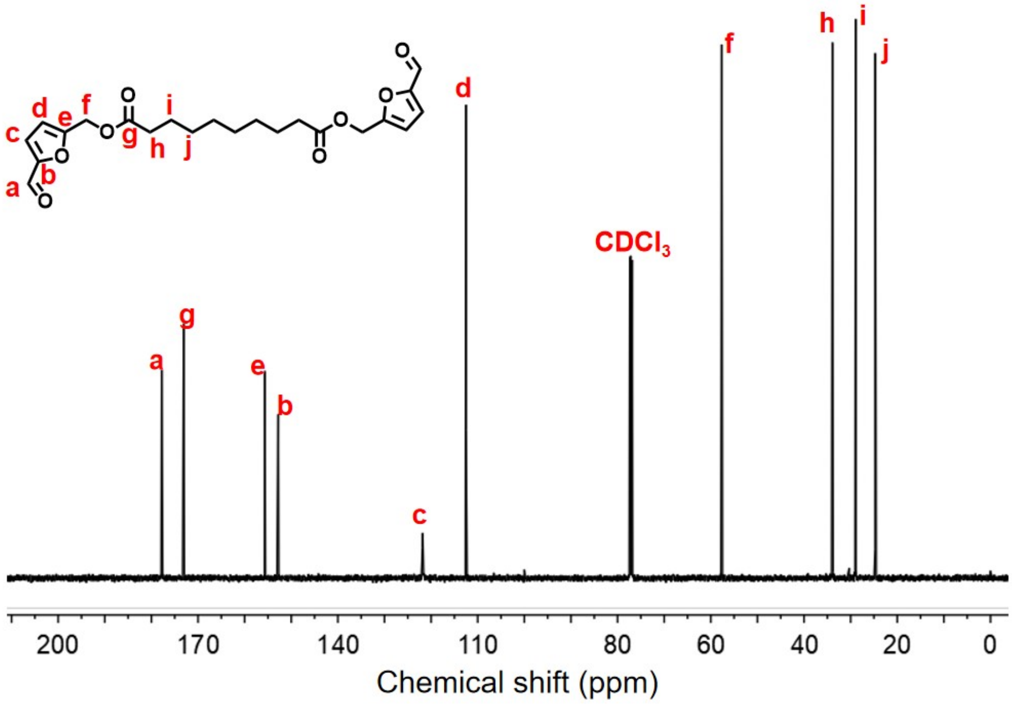


Figure S11 ^{13}C NMR spectrum of BFMD in CDCl$_3$. ^{13}C NMR (126 MHz, CDCl$_3$) δ 177.80 (s), 173.08 (s), 155.65 (s), 152.80 (s), 121.80 (s), 112.51 (s), 57.65 (s), 33.91 (s), 28.94 (d, *J* = 4.1 Hz), 24.73 (s).

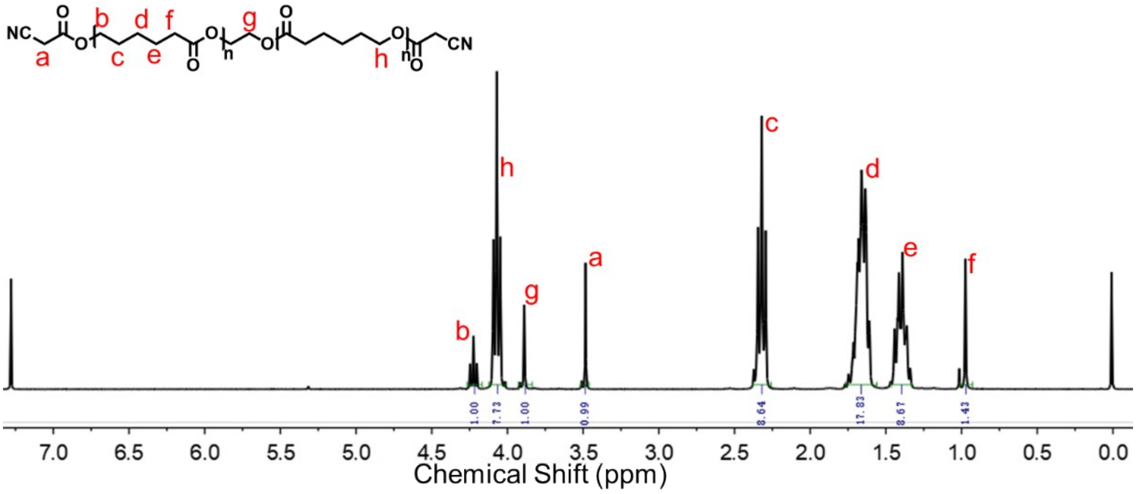


Figure S12 ^{1}H NMR spectrum of PCLBCA in $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.22 (t, *J* = 6.6 Hz, 4H), 4.07 (t, *J* = 6.7 Hz, 28H), 3.90 (d, *J* = 8.4 Hz, 4H), 3.50 (d, *J* = 7.6 Hz, 4H), 2.32 (dd, *J* = 9.9, 5.2 Hz, 34H), 1.66 (dq, *J* = 15.1, 7.6 Hz, 70H), 1.46 – 1.35 (m, 32H), 0.97 (s, 6H).

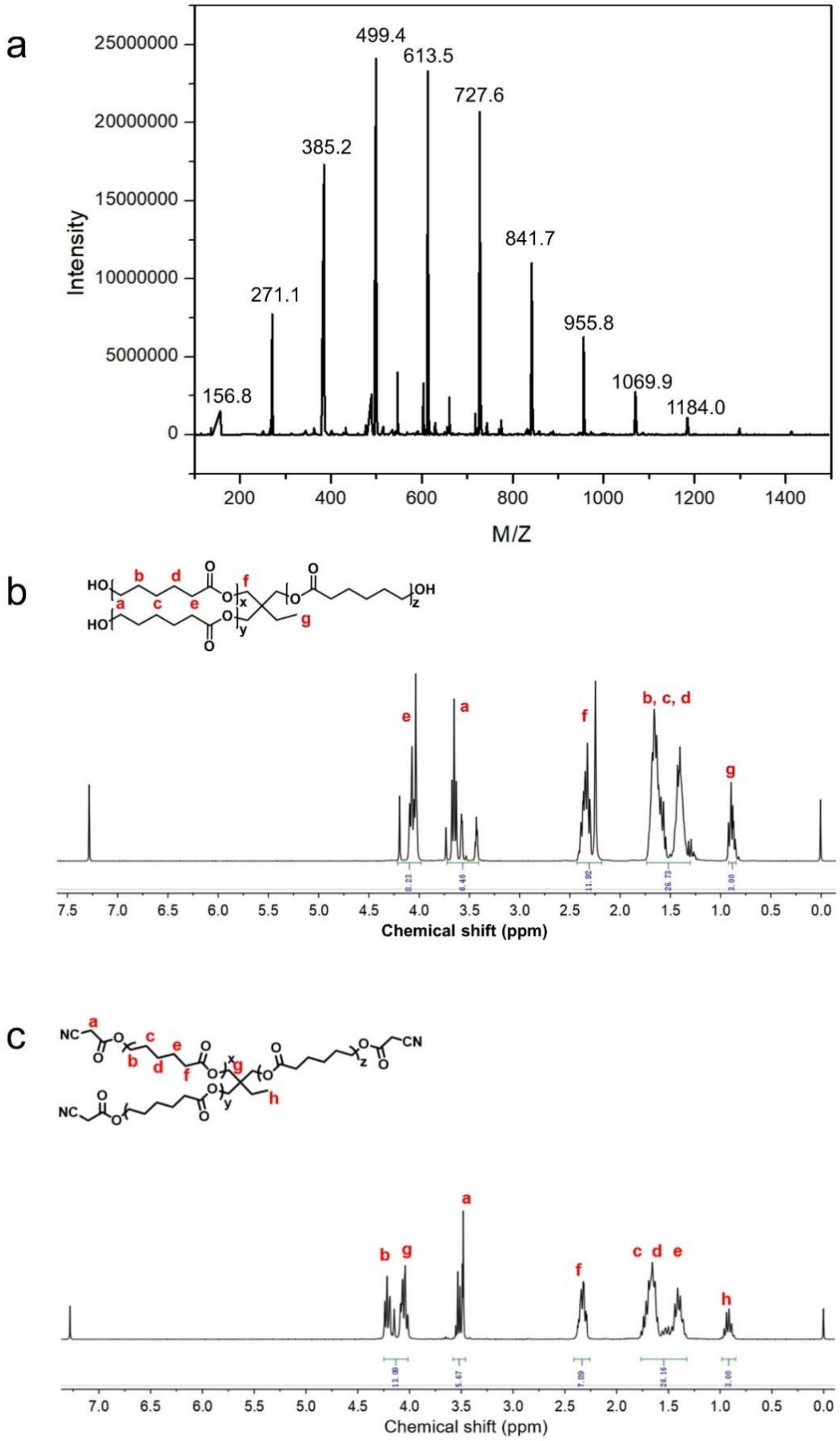


Figure S13 (a) The ESI-MS spectrum of PCLT. (b) The ^{1}H NMR spectrum of PCLT in $CDCl_3$. (c) ^{1}H NMR spectrum of PCL-TCA in $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27 – 3.99 (m, 14H), 3.60 – 3.42 (m, 6H), 2.41 – 2.27 (m, 8H), 1.76 – 1.33 (m, 26H), 0.98 – 0.85 (m, 3H).

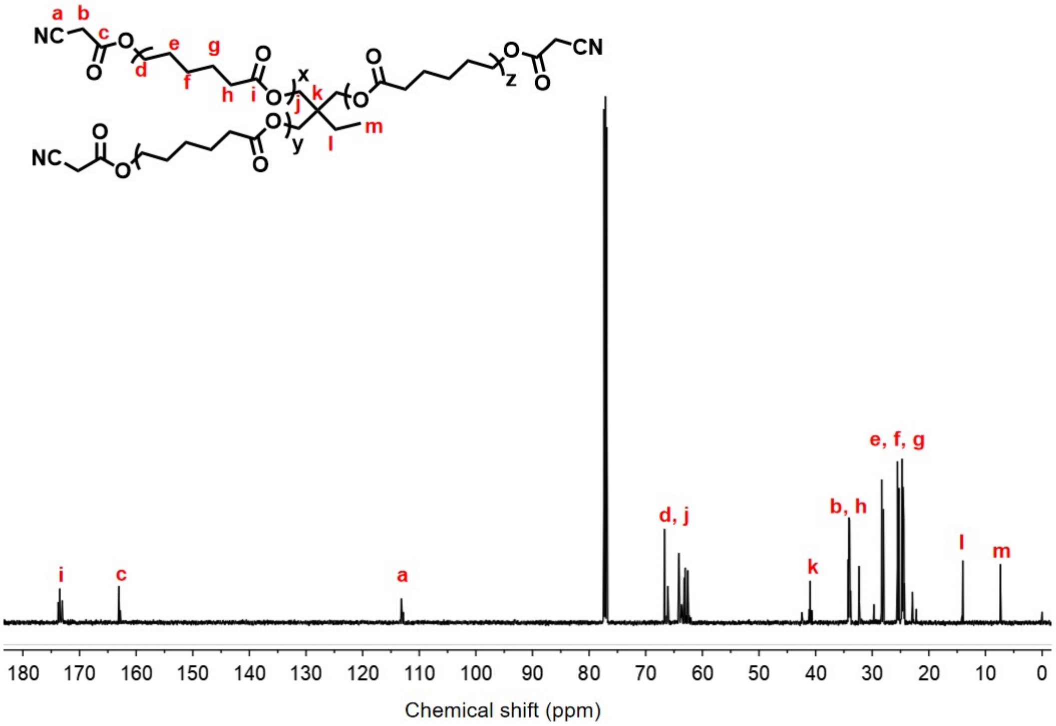


Figure S14 ^{13}C NMR spectrum of PCLTCA in $CDCl_3$. ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.38 – 171.47 (m), 163.00 (d, *J* = 7.3 Hz), 162.81 (s), 113.14 (s), 112.80 (s), 66.93 – 61.51 (m), 40.92 (t, *J* = 28.9 Hz), 34.35 – 31.26 (m), 25.43 (dddd, *J* = 28.3, 25.3, 22.7, 20.7 Hz), 14.00 (s), 7.35 (t, *J* = 5.3 Hz).

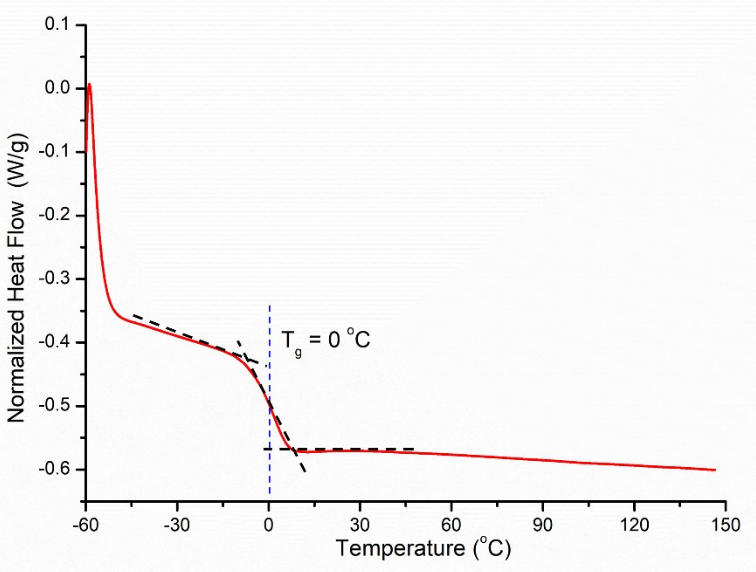


Figure S15 DSC curve of BFMD-PCLT.

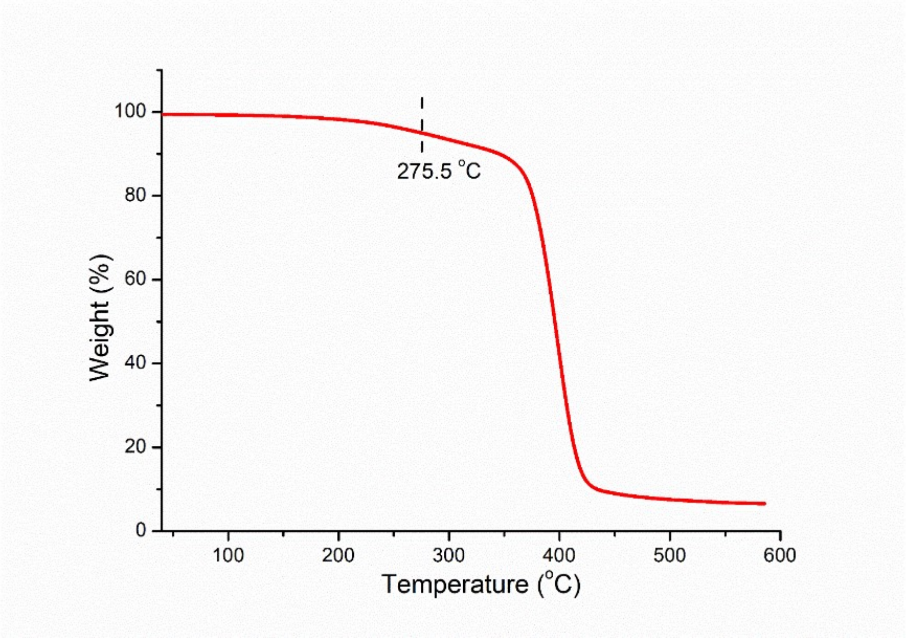


Figure S16 TGA curves of BFMD-PCLT.

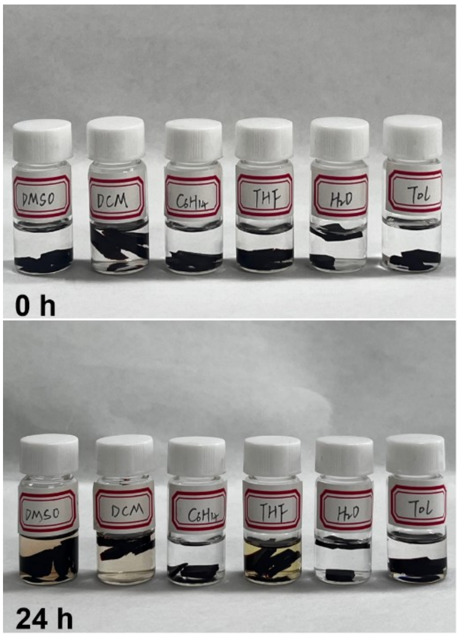


Figure S17 Photos of BFMD-PCLT in DMSO, DCM, C_6H_{14}, THF, water, and Tol at 0 and 24 h.

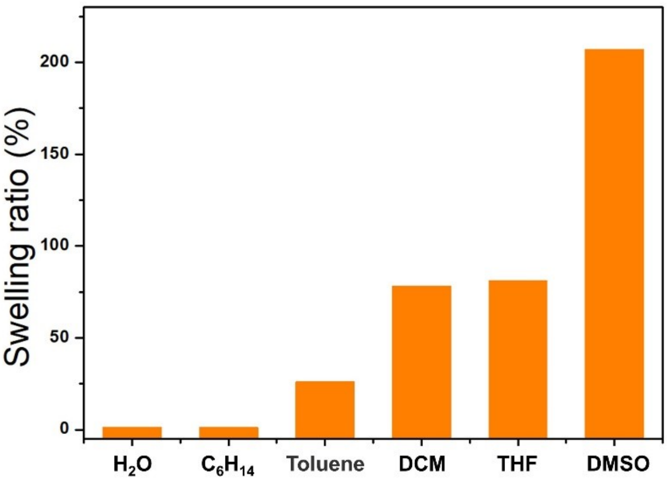


Figure S18 Swelling ratios of BFMD-PCLT in water, C_6H_{14}, toluene, DCM, THF, and DMSO.

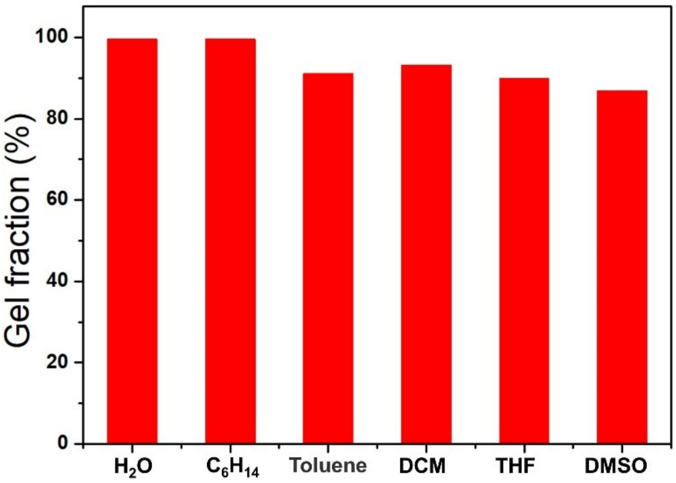


Figure S19 Gel fractions of BFMD-PCLT in water, C_6H_{14}, toluene, DCM, THF, and DMSO.

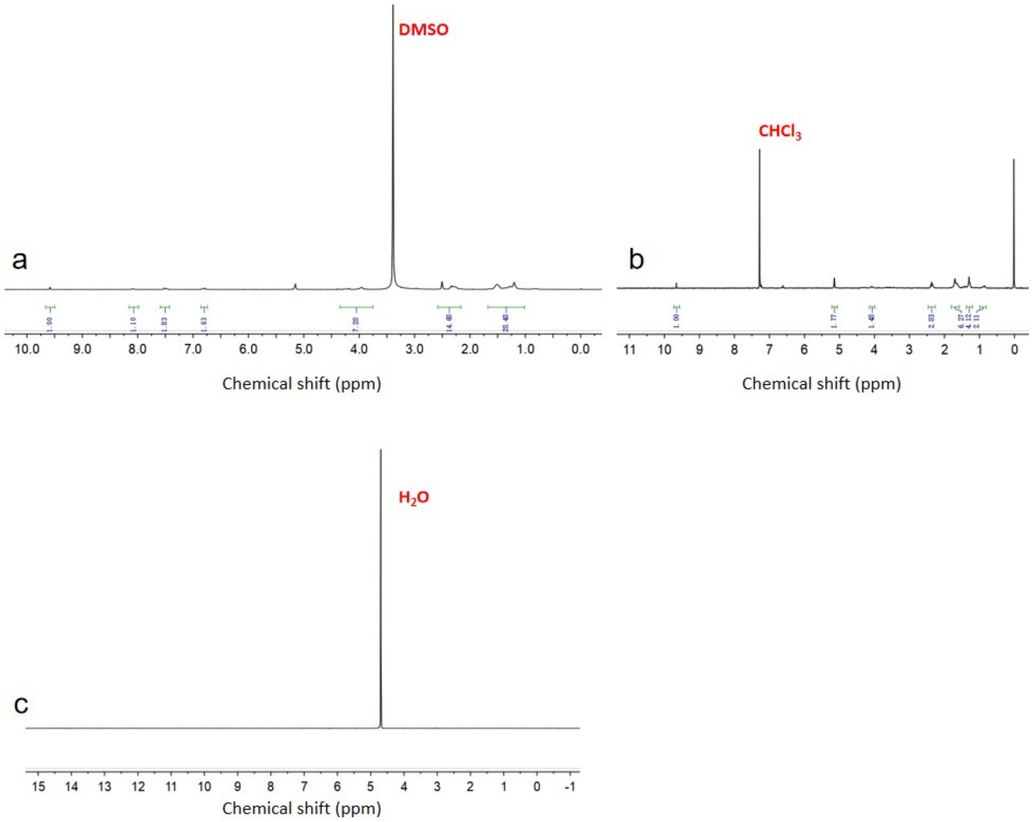


Figure S20 The ^1H NMR spectrum of BFMD-PCLT in the leaching solutions of DMSO-d_6, $CDCl_3$ and D_2O.

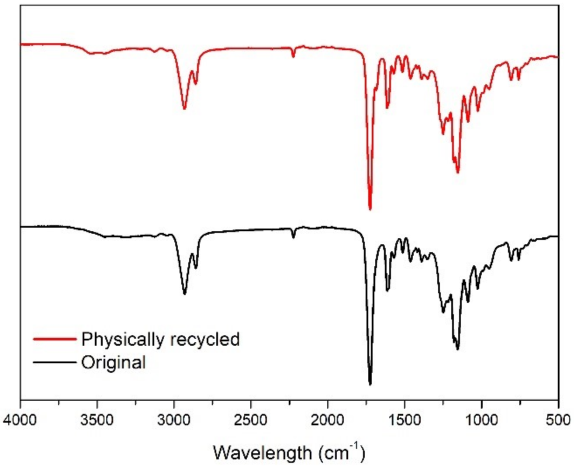


Figure S21 The FTIR spectra of the original and physically recycled BFMD-PCLT.

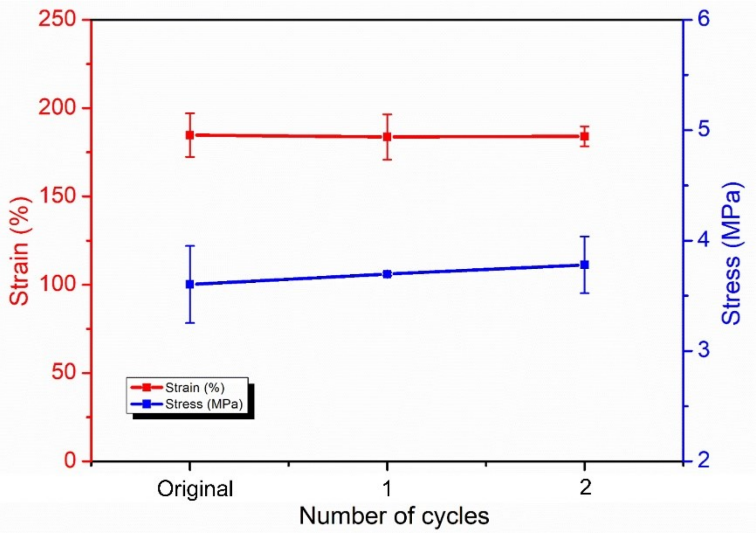


Figure S22 Change of breaking strength and elongation at break of BFMD-PCLT in three recycling cycles.

Table S1 Conversion data for the reaction at different temperatures

Temperature (°C)	5 min	10 min	20 min	60 min	120 min
R. T.	0	0	0	0	0
70	6%	12%	19%	38%	50%
90	11%	18%	29%	49%	60%
110	28%	40%	53%	70%	79%

R.T. stands for "room temperature"

Table S2 Molecular weight data from GPC-THF analysis for the samples in Figure 4

Stage	Time (min)	*M*p (kDa)	*M*n (kDa)	*M*w (kDa)	*M*z (kDa)	Dispersity
I	10	13	10	17	26	1.68
	20	23	15	27	40	1.74
	40	37	25	42	60	1.71
	90	58	43	69	102	1.48
II	20	9	7	13	21	1.88
	40	15	11	19	30	1.76
	60	16	12	22	34	1.79
III	30	31	20	35	51	1.74
	90	55	42	70	110	1.56
IV	20	4.4	4.7	5.6	6.7	1.19
	40	4.4	4.6	5.5	6.5	1.18

Table S3 Experimental data of swelling tests.

Solvent	W_1（mg）	W_2（mg）	W_3（mg）
Water	106	108	105
Toluene	99	125	90
n-Hexane	107	108	106
Tetrahydrofuran	108	137	93
Dichlormethane	95	173	79
Dimethyl sulfoxide	102	154	92

Table S4 Mechanical properties of BFMD-PCL after hot-pressing.

Name	Recycle number	Tensile modulus（MPa）	Breaking stress（MPa）	Elongation at break（%）
BFMD-PCL	1	4.41 ± 0.49	3.60 ± 0.35	184.67 ± 12.34
	2	4.44 ± 0.31	3.69 ± 0.02	183.66 ± 12.89
	3	4.39 ± 0.20	3.78 ± 0.26	184.00 ± 5.57

Table S5 Mechanical properties of BFMD-PCL after recycling.

Name	Recycle number	Tensile modulus（MPa）	Breaking stress（MPa）	Elongation at break（%）
BFMD-PCL	1	4.32 ± 0.18	3.69 ± 0.26	184.98 ± 6.86