Supporting Information

Efficient “depolymerization-polymerization” closed-loop recycling strategy for Selective-degradation of polycaprolactone

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1. Experimental Section

1.1. Materials.

Polycaprolactone (PCL6000C) was obtained from Guanghua Weiye Co., Ltd. (Shenzhen, China). $Sn(Oct)_2$, $CsOH·H_2O$ and $MgCl_2·6H_2O$ were purchased from Aladdin Chemicals Co., Ltd. (Shanghai, China).The solid acid catalyst (HND-580) comes from the Catalyst Research Center of Nanda in Jiangsu.

1.2. Thermal catalyzed depolymerization of PCL

Melt thermal degradation was used to degrade PCL. The samples were dried in a vacuum oven at 40 °C until constant weight.80 g of dried PCL was added to a 250 ml reaction flask and heated at 120 °C until molten. Subsequently, a certain proportion of catalyst was added and the reaction was carried out at a certain temperature and depressurized to 0.01-0.02 MPa, and the resulting liquid sample was collected as the depolymerization product.

1.3. Synthesis of re-PCL

The depolymerization product was distilled under reduced pressure at 100 °C. 80 g of the purified product and 0.5 mol% $Sn(Oct)_2$ were added to a 250 ml reaction flask. Under N_2 atmosphere, the temperature was raised to 160 °C and the reaction was carried out for 48 h. The product obtained from polymerization was purified to obtain re-PCL.

1.4. Characterization.

The proton nuclear magnetic resonance (^1H NMR) spectra of the samples were recorded using an AVANCE III HD 600 spectrometer from Bruker, Germany, with $CDCl_3$ as solvent. Before testing, the samples were dissolved in $CHCl_3$, precipitated by adding into cold methanol, and dried for 12 hours using an FTFDS freeze dryer.

Liquid Chromatography-Mass Spectrometry (LC-MS): The depolymerization products were analyzed using an Agilent 1290/Bruker maXis impact ultrahigh-performance liquid chromatography-high-resolution mass spectrometry (UHPLC-HRMS) system for LC-MS analysis. The samples to be tested were mixed with methanol (CH_3OH) at a concentration of 100 ug/mL to prepare the solution to be tested, and an electrosprayed positive ion source was used and scanned at a scanning range of

20~600 m/z with a dry N_2 flow rate of 4.0 L/min, a temperature of 180 °C, the capillary voltage was 2000 V.

Gel permeation chromatography (GPC) was used for molecular weight analysis and dispersibility determination using a GPC-20A from Shimadzu, Japan, equipped with an Eclipse Plus-C18 column and a UV-visible detector (DAD). The samples were dissolved in tetrahydrofuran (THF) at a concentration of 3 mg/mL at a flow rate of 1.0 mL/min and a column temperature of 10-50°C.

Gas chromatography (GC) was performed using a Trace 1300 gas chromatograph from Thermo Fisher Scientific, USA. The samples were dissolved in methanol (CH_3OH) at a concentration of 100 ug/mL, and were scanned using an electrospray positive ionization source and a scanning range of 20~600 m/z with a dry N_2 flow rate of 4.0 L/min, a temperature of 180 °C, and a capillary voltage of 2000 V.

Thermogravimetric analysis (TG) was performed using a STA 449 F5 thermogravimetric analyzer from Netzsch, Germany. The PCL mixtures with different $Sn(Oct)_2$ additions were prepared by melt blending at 70 °C, and the mass of the test samples ranged from 5.0 to 10.0 mg.

Dynamic mechanical analysis (DMA) was performed using a DMA 1 from Mettler-Toledo, Switzerland, to analyze the viscoelastic behavior of the samples in uniaxial stretching mode, with the sample size of 20 mm×4 mm×1 mm, the test temperature range of -70~60 °C, the heating rate of 5 °C /min, the amplitude of 3 μm, and the fixed frequency of 1 Hz.

Differential scanning calorimetry (DSC) was carried out using a DSC3 Differential Scanning Calorimeter from Mettler-Toledo, Switzerland. The temperature range of the test was set at -60~100 °C, and the cooling/raising rate was 5 °C /min.

The relevant thermal performance data are summarized in Table S3. Calculation of the degree of crystallinity is based on equation.

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (1)$$

Where ΔH_m is the enthalpy of melting of the sample and ΔH_m^0 is the standard

enthalpy of melting corresponding to 100% crystallized PCL (ΔH_m^0=139 J/g).

X-ray diffraction (XRD) was analyzed using X'pert Powder from Malvern Panalytical, Netherlands. The scanning range was 2θ = 5~40° and the X-ray wavelength was 1.5405 Å. The XRD data were analyzed using Jade 6.5 software.

Polarized optical microscope (POM) was used to determine the spherical crystal size and the growth rate of spherical crystals of PCL using a STEMI 2000 high magnification video microscope from Carl Zeiss, Germany. The hot stage temperature was 80 °C and cooled down to 35 °C, while the changes in the spherical crystal size of the samples were observed and recorded under a 50x microscope.

The mechanical properties were tested using the 104B universal testing machine of Shenzhen Wanjie Equipment Co. The tensile rate was set at 50 mm/min, and the dumbbell-shaped sample strips (75×4×1 mm^3) were tensile tested according to GB/T 1040-2006, and at least three sample strips were tested for each sample.

2. Supplementary Figures and Tables

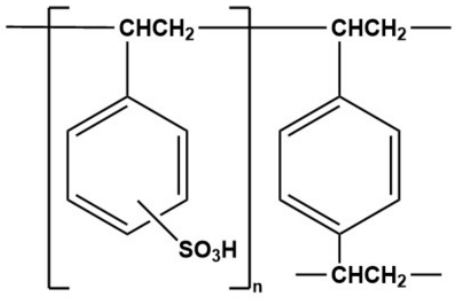

Figure S1 Chemical structure of HND-580.

Table S1 Data on the degradation of PCL by different catalysts

Entry	Catalyzer [b]	Temperature（℃）	Catalyst dosage（mol%）	Reaction time（h）	Total yield [c]（wt%）
1	1	270	0.5	2	80.0
2	2	270	0.5	7	12.7
3	3	270	0.5	4	92.4
4	4	270	0.5	6	20.0
5	3-4 [d]	270	0.25-0.25	13	84.8

a. Reaction conditions: the PCL feeding amount was 80 g and the reaction vacuum was 80 Pa;

b. Catalysts 1, 2, 3, and 4 corresponded to $CsOH·H_2O$, $MgCl_2·6H_2O$, $Sn(Oct)_2$, and HND-580, respectively;

c. The total yield is the mass ratio of liquid product to PCL feedstock;

d. 0.5 mol% $Sn(Oct)_2$ was added to PCL, followed by 0.5 mol% solid acid.

Table S2 Degradation activation energy of PCL0.05

X（wt%）	slope	correlation coefficient	ΔE_{td}（kJ/mol）
10	4.53	0.99	37.67
20	6.33	0.98	52.64
30	7.46	0.98	62.05
40	8.11	0.98	67.43
50	8.53	0.97	70.95
60	8.69	0.97	72.28
70	8.78	0.96	73.02
80	8.76	0.96	72.82
90	8.53	0.94	70.90

The activation energy for thermal degradation of PCL, ΔEtd, was calculated using the following equation recommended by MacCallum et al:

$$ln\,(t) = ln\left[F\left(1 - \frac{X}{100}\right)\right] - ln\,(A) + \Delta E_{td}/RT \qquad 2$$

where X (wt%) is the mass loss rate; t (min) is the degradation time corresponding to a mass loss rate of X (wt%); F(1-X/100) is a function of X; R is a gas constant; A is a constant; T is the temperature (K); and ΔE_{td} (kJ/mol) is the isothermal degradation activation energy corresponding

to a mass loss rate of X (wt%). The corresponding thermal degradation times at different mass loss rates were read from the isothermal heat loss curves, plotted as ln(t)-1/T, and a straight line was fitted, and $\Delta E_{td}=R-K_x$ could be calculated from the slope of the straight line, K_x. After regression analysis the ln(t)-1/T curve for PCL is shown in Fig. 1i and the associated degradation activation energy data are in Table S2.

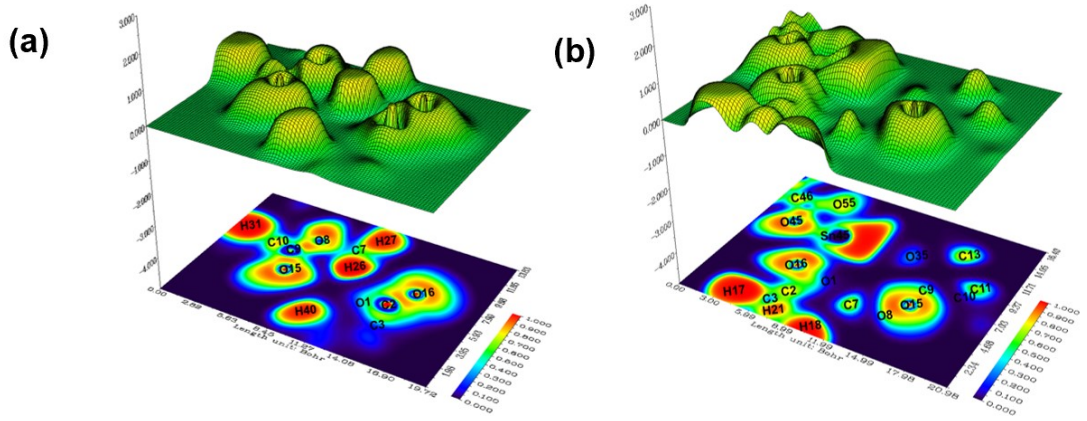

Figure S2: (a) Shaded surface map with projection effect of ELF; (b) Shaded surface map with projection effect of ELF.

Table S3 Thermal properties and crystallization properties of re-PCL and pure PCL

Sample	Tensile strength (MPa)	Fracture strength (MPa)	Elongation at break (%)
re-PCL	13.1±2.1	28.4±1.8	913±13
Pure PCL	10.6±3.6	27.2±2.7	1000±16

Table S4 Thermal properties and crystallization properties of re-PCL and pure PCL

Sample	T_c（℃）	ΔH_c（J/g）	T_m（℃）	ΔH_m（J/g）	X_c（%）

re-PCL	29.1	56.3	53.3	59.6	42.9
Pure PCL	24.7	52.9	53.4	59.5	42.8