

SUPPORTING INFORMATION

Fully-biobased Monomers Containing Monopyrrolidone Ring Towards the Synthesis of Renewable Polyesters with High T_g and Hydrolyzable Closed-loop Recycling

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1. General methods

Nuclear magnetic resonance (NMR): The ^1H NMR and ^{13}C NMR spectra were recorded by Bruker Avance II 500 MHz NMR spectrometer. Samples were dissolved in CDCl_3 , CD_3OD , or DMSO-d_6 . Chemical shifts were determined using solvent resonance as an internal standard (CDCl_3 : ^1H , 7.26 ppm, ^{13}C , 77.16 ppm, CD_3OD : ^1H , 3.30 ppm, DMSO-d_6 : ^1H , 2.50 ppm, ^{13}C , 39.5 ppm).

Liquid chromatography-high resolution mass spectrometry (LC-HRMS): The monomers were analyzed using an AB SCIEX Triple TOF 4600 liquid chromatography-high-resolution mass spectrometry system. Prior to testing, all monomer samples were prepared as 0.05 mg mL^{-1} solutions, filtered through a membrane filter, and then subjected to analysis. External calibration confirmed a mass accuracy below 5 ppm.

Gel Permeation Chromatography (GPC): Molecular weights and dispersions of the polymers were obtained using HP1090 high performance liquid chromatography (HPLC). Chloroform was used as the mobile phase at a flow rate of 1 mL/min . The analytical values were calibrated against a standard solution of polystyrene.

Differential Scanning Calorimetry (DSC): The thermal transition behavior of the polymer was obtained in a TA Instruments Q2000 thermal analyzer. Place the sample (5-10 mg) in the instrument, set the cycle program "heating-isothermal-cooling-isothermal-heating" and start the test in the range of $70\text{ }^\circ\text{C}$ - $180\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}$ per minute of temperature increase and decrease. All tests were performed at a nitrogen flow rate of 20 mL/min .

Thermogravimetric Analysis (TGA): The thermal properties of the polyester were determined using a CDR-34P thermogravimeter. Samples (5-10 mg) were heated from $30\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ and a nitrogen flow rate of 20 mL min^{-1} . The 5% weight loss temperatures ($T_{d,5\%}$) were recorded to assess the thermal stability of the polyesters.

X-ray Diffraction (XRD): The crystal structure of these samples was determined by a Smart Lab 9kW X-ray diffractometer with a scanning range of 5° to 45° and a scanning speed of $2^\circ/\text{s}$. The tube current was 10 mA and the tube voltage 20 kV. Prior to testing, the samples were melted and then isothermally annealed for 24 hours in a 45°C vacuum oven.

Ultraviolet-visible transmission spectroscopy (UV-vis): The UV shielding properties of polyester were determined by a METASH UV-8000 UV-vis spectrophotometer. For the test, the polyester was processed into a strip film of $1\text{ cm} \times 4.3\text{ cm} \times 0.1\text{ mm}$ (width \times length \times thickness), and the detection

band was set at 200-800 nm.

Water Contact Angle (WCA): Melt and press the polyester into a thin block of 2cm x 2cm x 1mm, drop 5 μL of deionized water on the surface of the sample with a contact angle tester Dongguan Shengding SDC-100 and measure the angle immediately.

Tensile test: Mechanical properties test using IBTC-300SL miniature in-situ mechanical experimental system for testing, the maximum tensile stress of 100N, the maximum displacement of 70mm, the control displacement rate of 20mm/min, the length, width and thickness of the sample strip were 6cm, 1.2cm, 0.2cm to test polyester-related mechanical properties.

Film Preparation: Polyester samples were melted with a JFTOOIS JF-956A thermostatic heater and then coated in a cuvette, and the films were cooled at room temperature to the measured thickness.

Intrinsic Viscosity ($[\eta]$): Approximately 0.01 g of the polyester sample was fully dissolved in a phenol/tetrachloroethane mixed solvent (mass ratio 3:2). The intrinsic viscosities ($[\eta]$) of all polyester samples were measured at 30 $^{\circ}\text{C}$ with a 0.88 mm inner diameter Ubbelohde viscometer. Before each measurement, the viscometer was thermostated in water for 15 min; measurements were performed in triplicate for an average value, and the efflux times of the blank solvent and sample solutions were recorded. The calculation formula is as follows:

$$[\eta] = [2((t/t_0 - 1) - \ln t/t_0)]^{0.5}/c \quad \text{Equation S1}$$

Where t_0 is the elution time of the blank solvent, t is the elution time of the solution, and c is the concentration of the test solution (0.1 g dL^{-1} in this case).

Biobased carbon content: The bio-based carbon contents of the monomers were evaluated in accordance with the method specified in ISO 16620. The calculation formula is as follows:

$$\text{Biobased carbon content (\%)} = N_{\text{bio-C}}/N_{\text{total-C}} \quad \text{Equation S2}$$

Where $N_{\text{bio-C}}$ is the number of carbon atoms derived from bio-based feedstocks in the molecule, and $N_{\text{total-C}}$ is the total number of carbon atoms in the molecule.

Atom economy (AE): The percentage of the molar mass of the target product relative to the total molar mass of the reactants. This indicator is applied for evaluating the atomic utilization ratio of reactants during chemical reactions. The calculation formula is as follows:

$$AE (\%) = M_{\text{target}} / \sum M_{\text{reactants}} \quad \text{Equation S3}$$

Where M_{target} is the molar mass of the target product, and $\sum M_{\text{reactants}}$ is the total molar mass of the

reactants.

C-efficiency: The ratio of total carbon atoms in the target product to total carbon atoms in all reactants.

It serves as a key quantitative metric for evaluating carbon atom utilization in green synthesis. The calculation formula is as follows:

$$C\text{-efficiency (\%)} = n_{C, \text{product}} / n_{C, \text{reactants}} \quad \text{Equation S4}$$

Where $n_{C, \text{product}}$ is the total molar amount of carbon atoms in the target product, and $n_{C, \text{reactants}}$ is the total molar amount of carbon atoms in all reactants.

2. Screening of synthesis conditions for monomers

Table S1 Optimization of pyrrolidone ring monomers

Monomer	Temperature (°C)	Time (h)	Cat. (distilled water, % mol)	Yield (Y%)
GPCA	130	18	0.2	81
L-APCA	140	18	0.2	78
L-VPCA	150	18	0.2	82
L-LPCA	150	18	0.2	84
D-PPCA	150	18	0.2	80
L-TPCA	160	18	0.2	81

3. Conversions and Selectivities of Amino Acids, and Isolated Yields and Purities of Monomers

Table S2 Conversions and selectivities of amino acids, and isolated yields and purities of monomers

Monomer	Conversion ^a (X%)	Selectivity (S%)	Theoretical output (g)	Actual output (g)	Yield (Y%)	Purity (P%)
GPCA	89	92	18.72	15.21	81	94
L-APCA	81	96	20.12	15.67	78	96
L-VPCA	87	94	22.92	18.87	82	94
L-LPCA	87	97	24.33	20.36	84	96
D-PPCA	80	98	27.23	21.67	80	98
L-TPCA	84	96	31.63	25.65	81	96

^aThe conversion was estimated by ¹H NMR spectroscopy analysis of the crude reaction mixtures.

4. Screening of polyester polymerization conditions

Table S3 Screening of polyester polymerization conditions

Polyester	Temperature (°C)	Time (h)	Catalyst loading (mol %)	$[\eta]$ (dL g ⁻¹)
PEG	150	3	0.20	0.87
	150	3	0.30	0.88
	160	3	0.20	0.91
	160	3	0.30	0.89
	160	5	0.20	1.05
	160	6	0.20	0.98

5. Green quantitative indicators of monomers

Table S4 Green metrics for the synthesis of monomers by aza-Michael addition reaction

Monomer	Biobased carbon content (%)	Atomic Economy (AE, %)	C-efficiency (%)
GPCA	100	91	100
L-APCA	100	95	100
L-VPCA	100	93	100
L-LPCA	100	93	100
D-PPCA	100	94	100
L-TPCA	100	95	100

6. GPCA monomer LC-HRMS

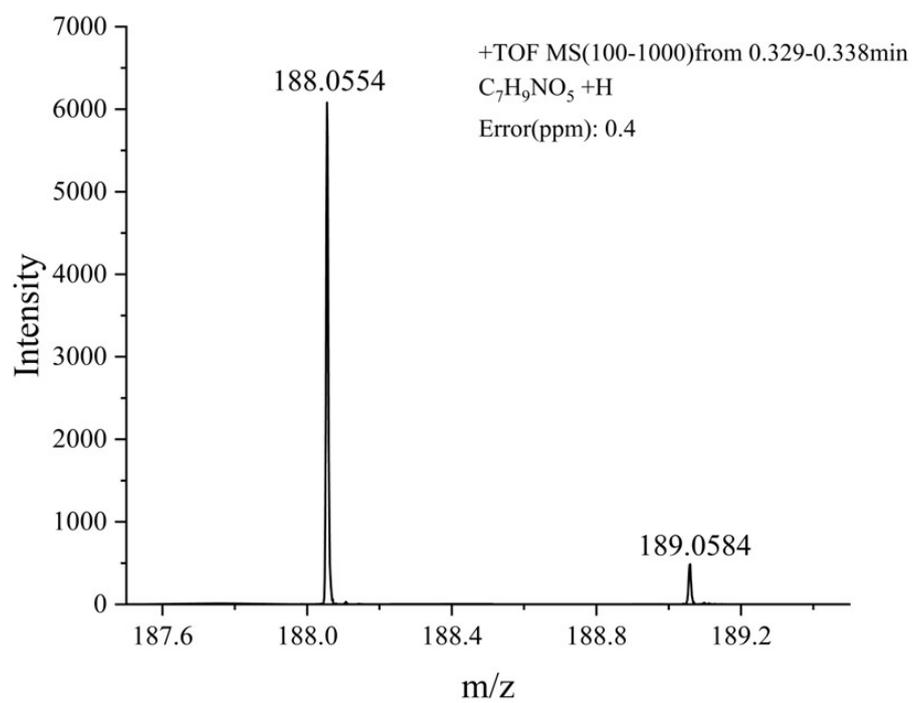


Figure S1 GPCA monomer LC-HRMS

7. L-APCA monomer LC-HRMS

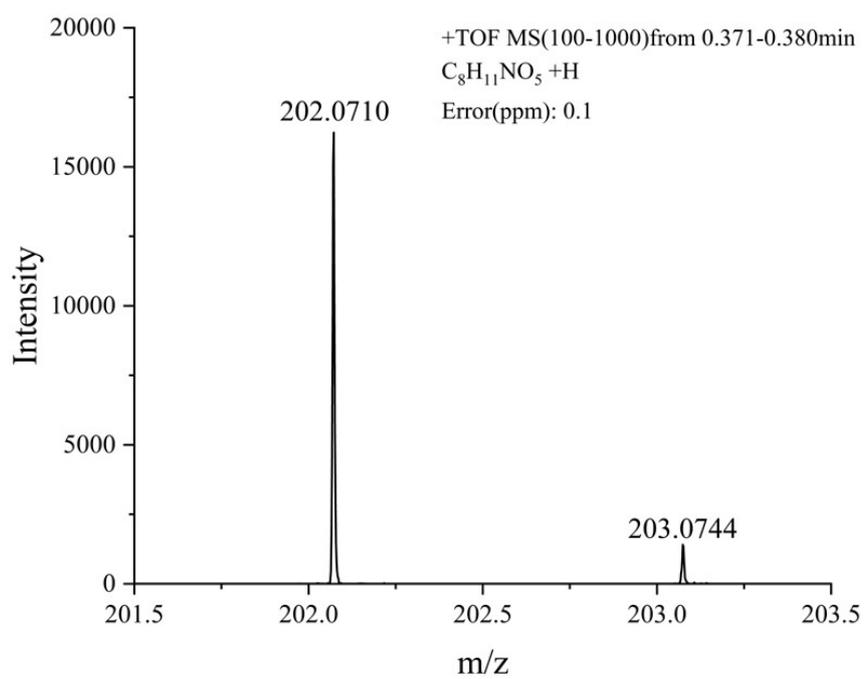


Figure S2 L-APCA monomer LC-HRMS

8. L-VPCA monomer LC-HRMS

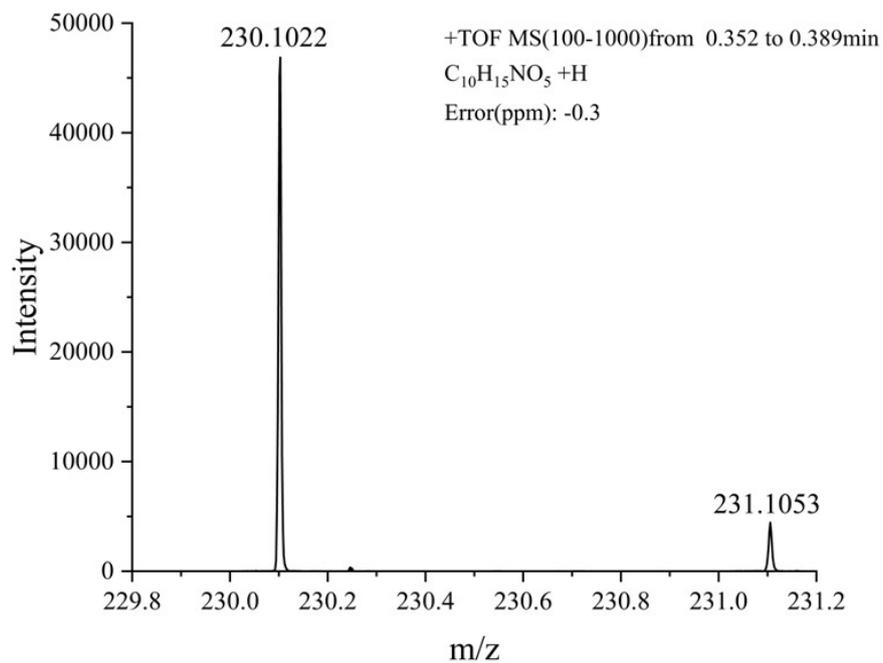


Figure S3 L-VPCA monomer LC-HRMS

9. L-LPCA monomer LC-HRMS

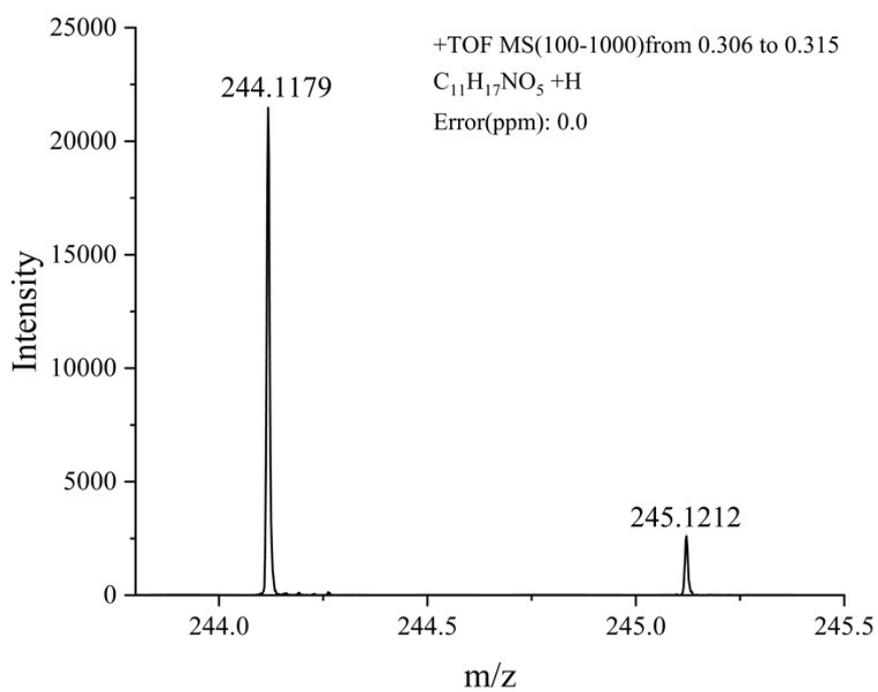


Figure S4 L-LPCA monomer LC-HRMS

10. D-PPCA monomer LC-HRMS

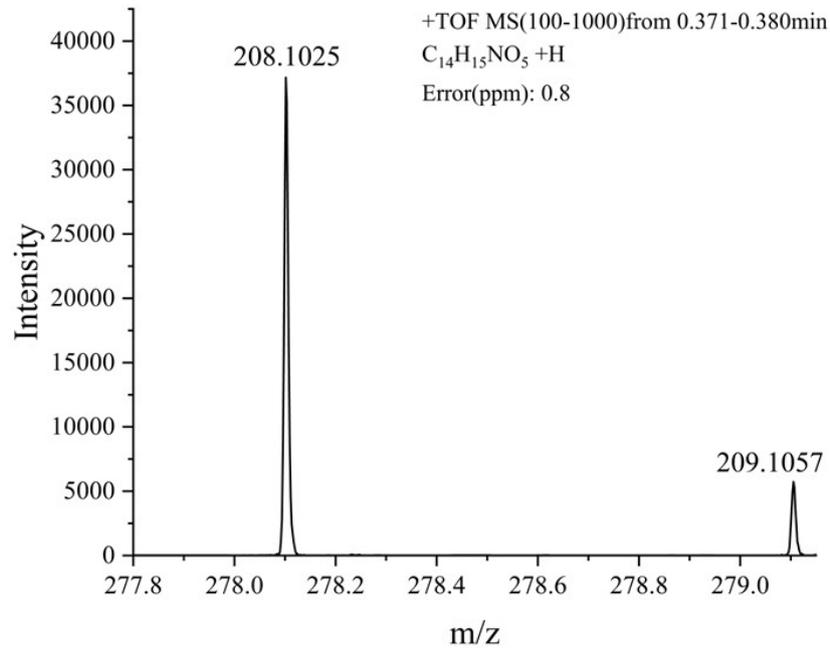


Figure S5 D-PPCA monomer LC-HRMS

11. L-TPCA monomer LC-HRMS

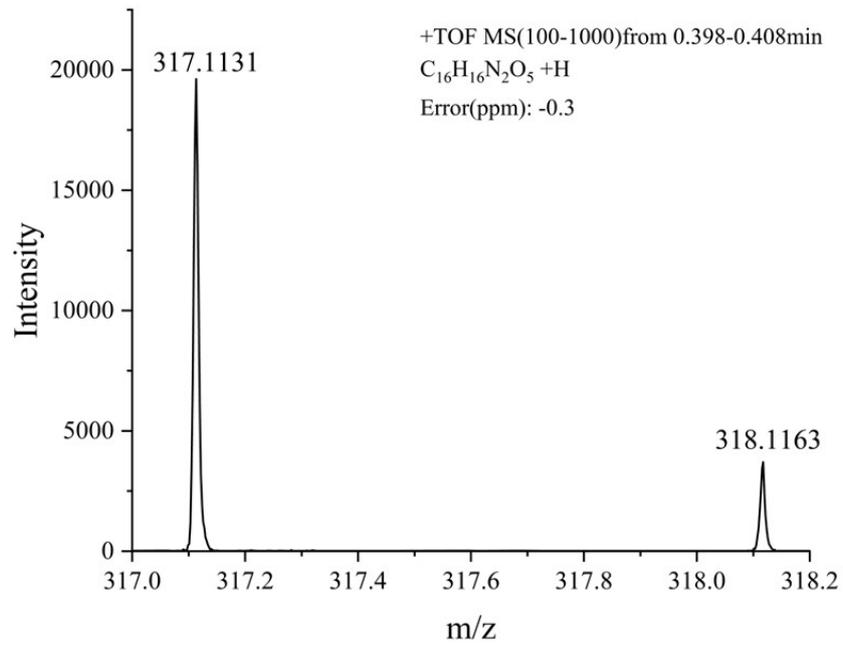


Figure S6 L-TPCA monomer LC-HRMS

12. ^{13}C NMR of PEG polyester

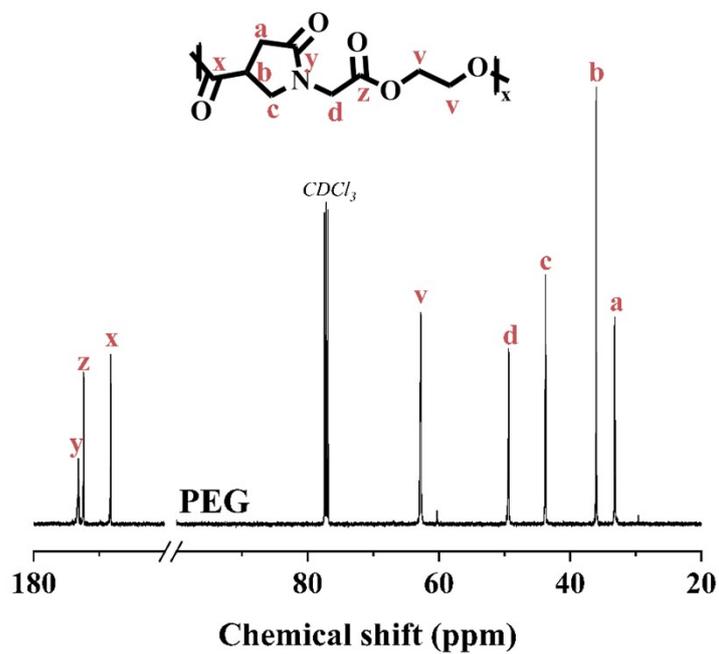


Figure S7 ^{13}C NMR of PEG polyester

13. ^{13}C NMR of PEL-A polyester

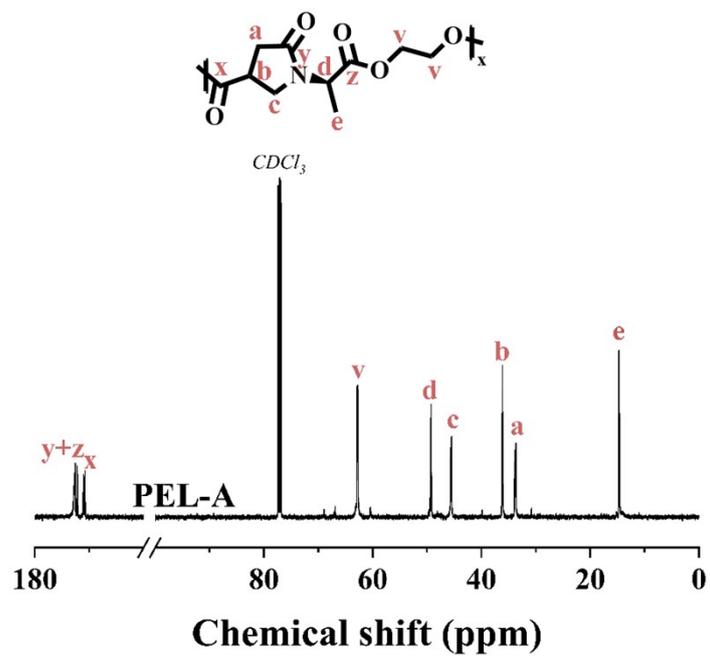


Figure S8 ^{13}C NMR of PEL-A polyester

14. ^{13}C NMR of PEL-V polyester

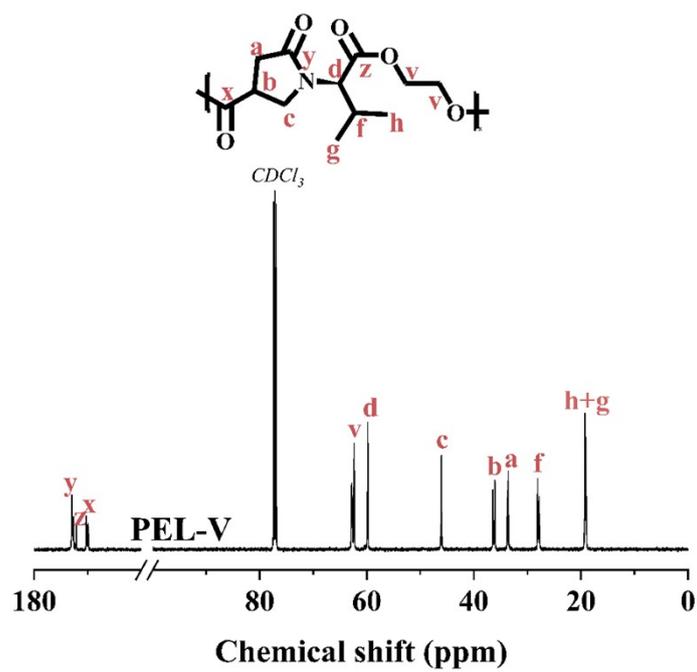


Figure S9 ^{13}C NMR of PEL-V polyester

15. ^{13}C NMR of PEL-L polyester

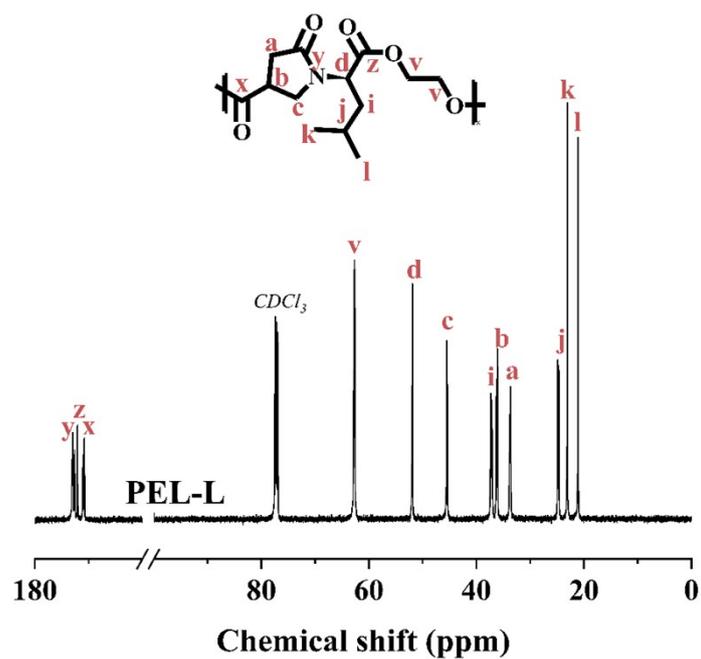


Figure S10 ^{13}C NMR of PEL-L polyester

16. ^{13}C NMR of PED-P polyester

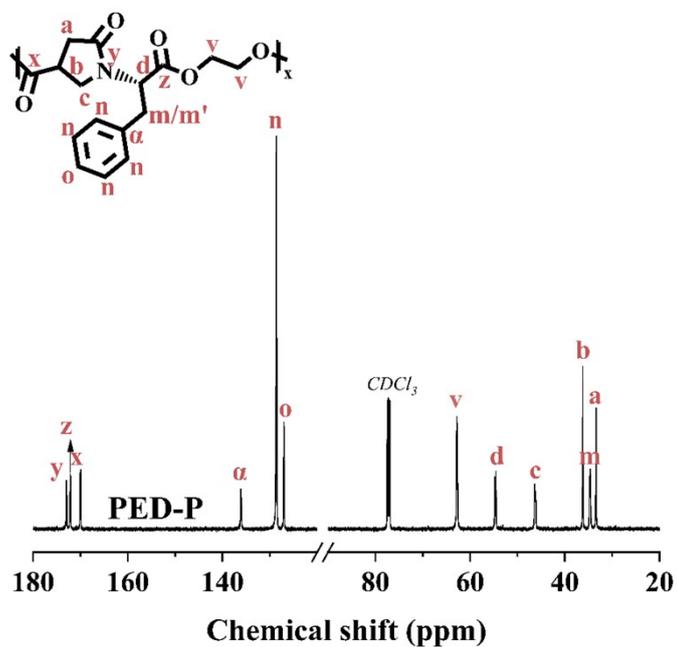


Figure S11 ^{13}C NMR of PED-P polyester.

17. ^{13}C NMR of PEL-T polyester

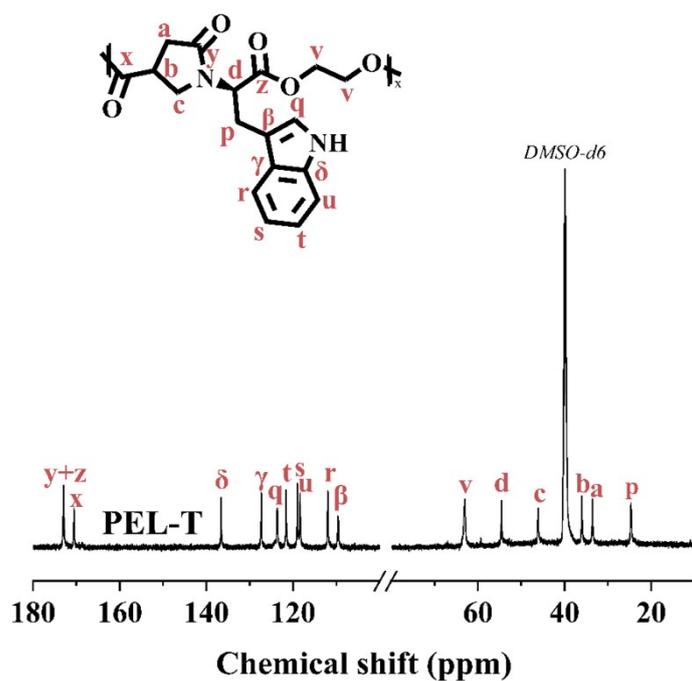


Figure S12 ¹³C NMR of PEL-T polyester

18. Polyesters' DTG traces

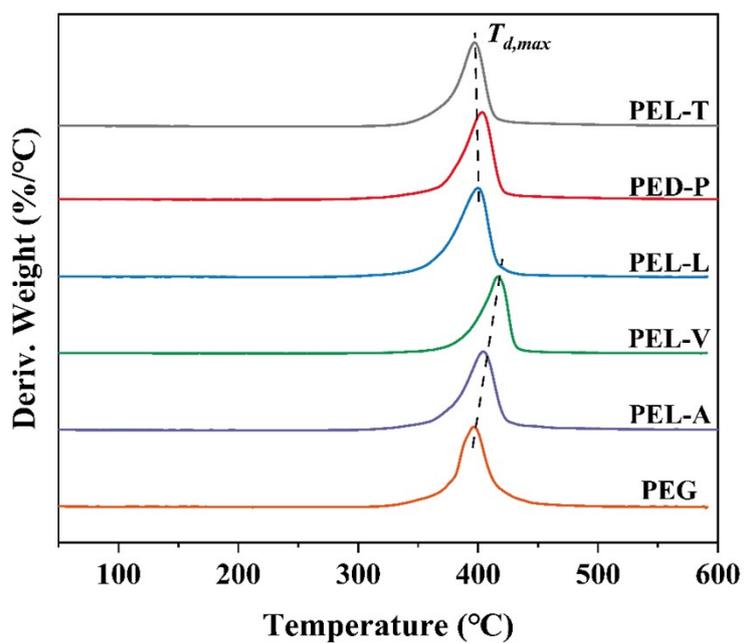


Figure S13 Polyesters' DTG traces

19. Polyesters' DSC Curve of Second Heating Melting

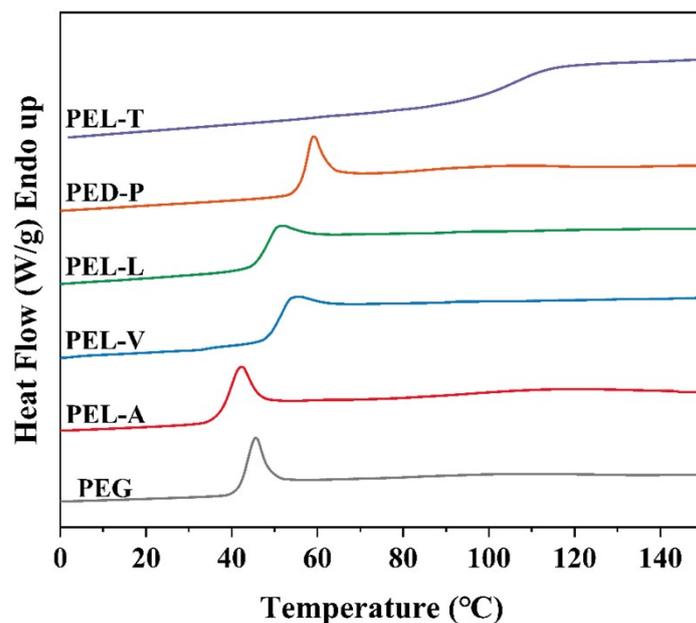


Figure S14 Polyesters' DSC Curve of Second Heating Melting

20. Mechanical Properties of Polyesters

Table S5 Mechanical Properties of Polyesters

Polyester	Mechanical parameters		
	E_t (MPa)	σ_m (MPa)	ϵ_b (%)
PEL-V	464.7	16.9	281.2
PEL-L	166.1	8.5	228.0
PED-P	99.3	5.7	68.0

21. Hydrolysis mechanism diagram

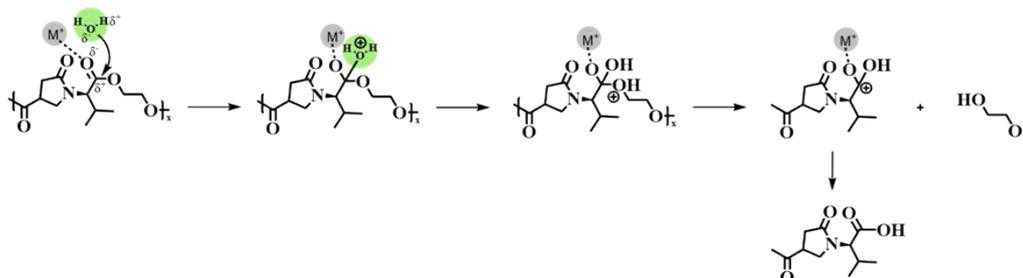


Figure S15 Schematic diagram of the hydrolysis mechanism of PEL-V polyester

22. PEL-V polyester water environment stability test

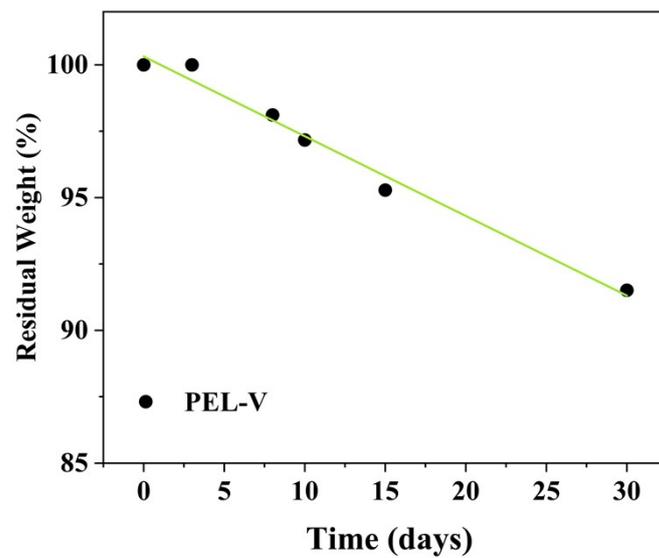


Figure S16 The weight loss curve of PEL-V polyester in deionized water at 25 °C