# Supporting Information

## Rapid Hydrolysis of Waste and Scrap PA6 Textiles to ε-caprolactam

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# 1. Tables

## 1.1 Characterizing the melting point, crystallinity, molecular weight, and PDI of vPA6, and Was PA6 textiles

The melting behavior of vPA6 and Was PA6 textiles was examined by DSC 4000 differential scanning calorimetry (PerkinElmer, USA) under a nitrogen atmosphere to protect vPA6 and Was PA6 textiles from degradation. vPA6 and Was PA6 textiles were heated from 30 $^{o}$C to 280 $^{o}$C (first the heating scan) and then cooled to -50 $^{o}$C. The crystallized vPA6 and Was PA6 textiles were reheated to 280 $^{o}$C (second heating scan) to investigate the melting behavior of vPA6 and Was PA6 textiles. The heating and cooling rates for all runs were 10 $^{o}$C/min. The degree of crystallinity of vPA6 and Was PA6 textiles was calculated by the ratio of the measured melting enthalpy of the sample ($\triangle H_f$) to the melting enthalpy of a completely crystalline sample ($\triangle H_{f,c}$). The melting enthalpy ($\triangle H_{f,c}$) for 100% crystalline PA6 is considered to be 191 Jg$^{-1}$.[1-3]

Crystallinity is calculated by the following equation :

$$X_{DSC}(\%) = \frac{\triangle H_f}{\triangle H_{f,c}} \quad (3)$$

Where $\triangle H_f$ is the melting enthalpy of the sample and $\triangle H_{f,c}$ is the melting enthalpy of 100% crystalline sample of the same copolymer.

The molecular weight (Number-average Molecular Weight ($M_n$) and weight-average molecular weight ($M_w$)) and molecular weight distribution coefficient (PDI) of vPA6, Was PA6 textiles were determined by Agilent Technologies 1260 Infinity II gel permeation chromatography, respectively (Agilent Technologies, USA). The eluent was hexafluoroisopropanol (HFIP), the flow rate was 0.3 mL/min, and the injection volume was 10 μL.

**Table S1** Properties of vPA6 and Was PA6 textiles used in this study.

| | $T_m$ (°C) | $T_g$ (°C) | $\triangle H_f$ ($Jg^{-1}$) | $X$ (%) | $M_n$ (g/mol.) | $M_w$ (g/mol.) | PDI |
|---|---|---|---|---|---|---|---|
| vPA6 | 220 | 46 | 50 | 26 | 24000 | 56000 | 2.33 |
| Was PA6 textiles | 213/220 | 49 | 52 | 27 | 16000 | 40000 | 2.5 |

X=crystallinity.

### 1.2 Reaction conditions

**Table S2** Reaction conditions.

| entry | Temperature (°C) | Mass ratio ($H_2O$:PA6) | Time (min) | Pressure (MPa) |
|---|---|---|---|---|
| 1 | 280 | 7:1 | 60 | 6.0 |
| 2 | 290 | 7:1 | 60 | 7.0 |
| 3 | 300 | 7:1 | 60 | 8.1 |
| 4 | 310 | 7:1 | 60 | 9.4 |
| 5 | 300 | 5:1 | 60 | 8.1 |
| 6 | 300 | 9:1 | 60 | 8.1 |
| 7 | 300 | 11:1 | 60 | 8.1 |
| 8 | 300 | 7:1 | 20 | 8.1 |
| 9 | 300 | 7:1 | 40 | 8.1 |
| 10 | 300 | 7:1 | 80 | 8.1 |

The mass ratio ($H_2O$:PA6) refers to Mass ratio ($H_2O$:vPA6) or Mass ratio ($H_2O$:Was PA6 textiles).

### 1.3 Characterizing molecular weight and PDI of the solid residue that existed at entry 1 in the vPA6 hydrolysis reaction

The molecular weight ($M_n$ and $M_w$) and PDI of the solid phase that existed at entry 1 in the vPA6 hydrolysis reaction were determined by Agilent Technologies 1260 Infinity II gel permeation chromatography, respectively (Agilent Technologies, USA). The eluent was HFIP, the flow rate was 0.3 mL/min, and the injection volume was 10 μL.

**Table S3** $M_n$, $M_w$ and molecular weight distribution coefficient of the solid phase that existed at entry 1.

| | $M_n$ (g/mol.) | $M_w$ (g/mol.) | PDI |
|---|---|---|---|
| solid phase | 4500 | 5300 | 1.17 |

## 2. Characterization methods

The variety of chemical groups in the residual solid, vPA6, and Was PA6 textiles were examined by Fourier transform infrared spectroscopy (FTIR, Spectrum two, PerkinElmer, U.K.) with the wavenumber range of 400~4000 $cm^{-1}$ and the optical resolution 4 $cm^{-1}$.

The thermal stability of undepolymerized PA6 was determined by TGA using TGA2 SF/1100 (Mettler Toledo, Switzerland) device to obtain the corresponding thermogravimetric (TGA). The measurements were performed from 30 to 700 $^{o}C$ in a nitrogen atmosphere (50 mL/min) at 10 $^{o}C$/min.

The molecular weight ($M_n$ and $M_w$) and PDI of vPA6, Was PA6 textiles and the solid phase that existed at entry 1 in the vPA6 hydrolysis reaction were determined by Agilent Technologies 1260 Infinity II gel permeation chromatography, respectively (Agilent Technologies, USA). The eluent was HFIP, the flow rate was 0.3 mL/min, and the injection volume was 10 μL.

CPL concentration and purity were measured by high performance liquid chromatography (HPLC, Agilent Technologies 1260 Infinity II) fitted with an EC-C18 column (4 μm, 4.6 × 250 mm) and a UV detector, set at 215 nm. The column temperature was 35 $^{o}C$. The mobile phase was $H_2O$: MeOH from 90:10 to 70:30; the flow rate was 1.0 mL/min; the sample size was 5 uL.

Liquid products were analyzed by liquid chromatography-mass spectrometry (LC-MS, Agilent Technologies 1260-6120) fitted with a C18 column (1.8 μm, 2.1 × 50 mm) and a DAD detector, which was utilized to qualitatively analyze the degradation

products of vPA6 and Was PA6 textiles and study the relative content changes of intermediate products during the hydrolysis process. Chromatographic measuring conditions: gradient elution, the mobile phase was $H_2O$:MeOH from 90:10 to 70:30; the sample size was 5 μL, the flow rate was 0.3 mL/min, and the elution time was 25 min; the column temperature was 35 $^oC$. Mass spectrometry measuring conditions: ESI ionization, positive and negative ion detection of two ionization mode analysis, primary mass spectrometer for full scan mode, m/z scan range 100~1500; the $N_2$ flow rate was 12 L/min and the vaporization temperature was 350 $^oC$.

# 3. Figures

## 3.1 Analysis of solid residue

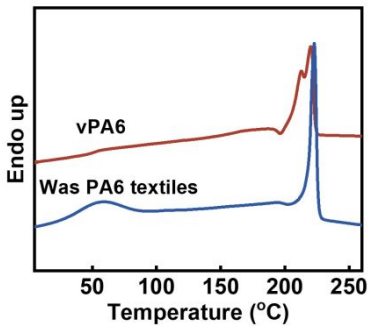


**Fig. S1** DSC heating curves of vPA6 and Was PA6 textiles

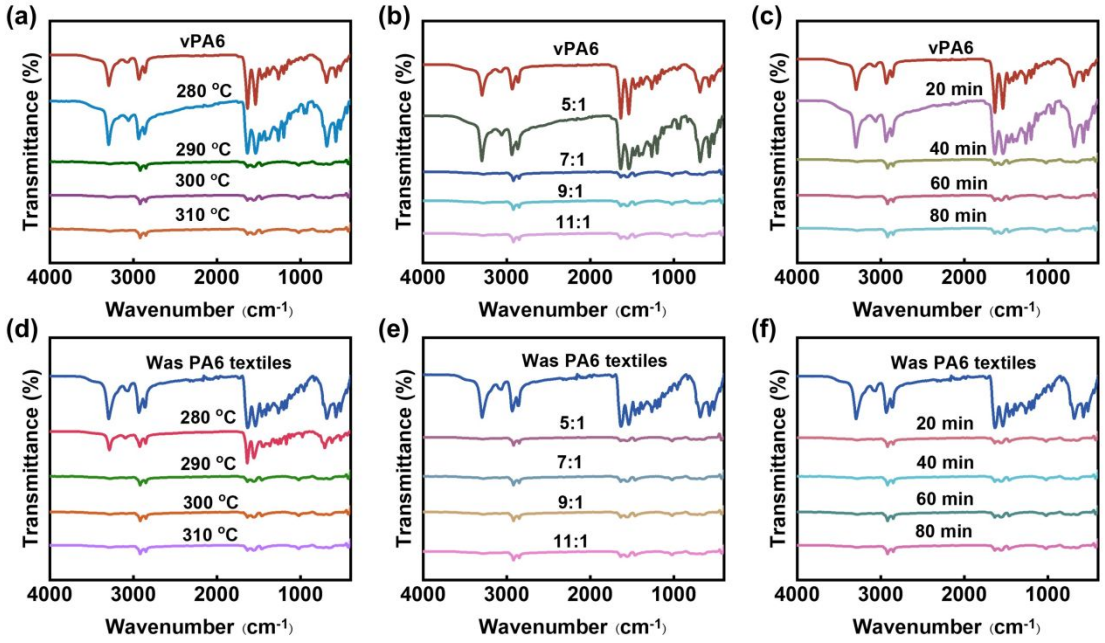


**Fig. S2** FTIR of raw PA6 samples (vPA6 and Was PA6 textiles) and solid residue, (a, d) reaction conditions: mass ratio ($H_2O$:PA6) of 7:1, 60 min, FTIR spectra of vPA6, Was PA6 textiles and solid residue at different temperatures, (b, e) reaction conditions: 300 °C, 60 min, FTIR spectra of vPA6, Was PA6 textiles and solid residue at different mass ratios, (c, f) reaction conditions: 300 °C, mass ratio ($H_2O$:PA6) of 7:1, FTIR spectra of vPA6, Was PA6 textiles and solid residue at different times.

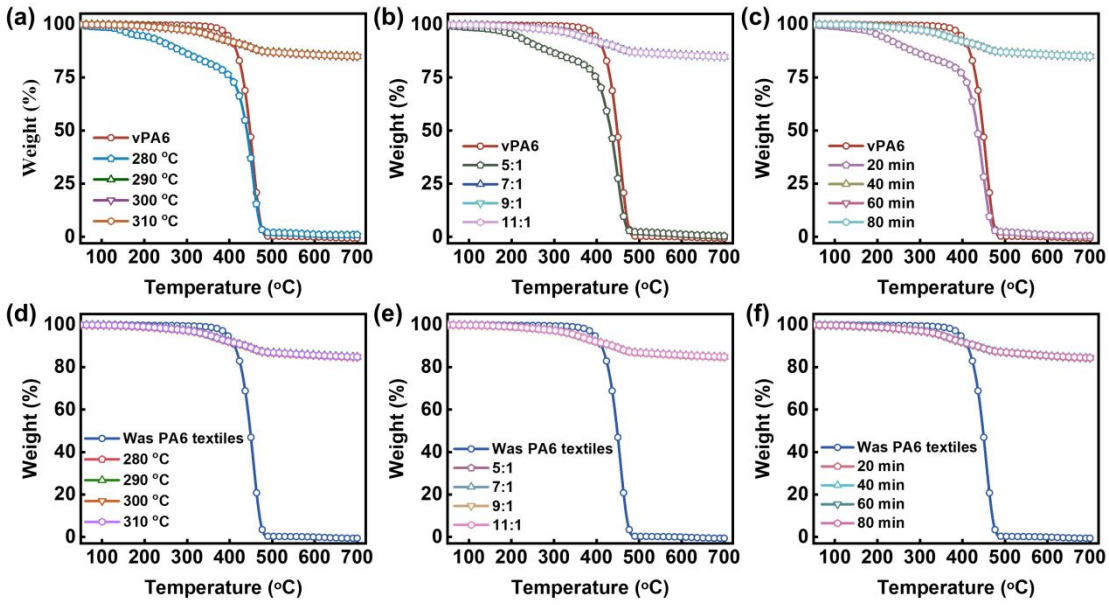


**Fig. S3** TGA curves of raw PA6 samples (vPA6 and Was PA6 textiles) and solid residue, (a, d) reaction conditions: mass ratio ($H_2O$:PA6) of 7:1, 60 min, TGA curves of vPA6, Was PA6 textiles and solid residue at different temperatures, (b, e) reaction conditions: 300 °C, 60 min, TGA curves of vPA6, Was PA6 textiles and solid residue at different mass ratios, (c, f) reaction conditions: 300 °C, mass ratio ($H_2O$:PA6) of 7:1, TGA curves of vPA6, Was PA6 textiles and solid residue at different times.

### 3.2 Calibration curves for CPL and HPLC of CPL and CD

Firstly, 0.25 g of CPL purchased from Sigma-Aldrich was weighed and dissolved in a 250 mL volumetric flask with water purchased from Sigma-Aldrich. Then CPL solution was diluted to a series of specific concentrations to produce CPL standard solution. The calibration curves are drawn by recording the volts of the standard solutions at 215 nm.[4]

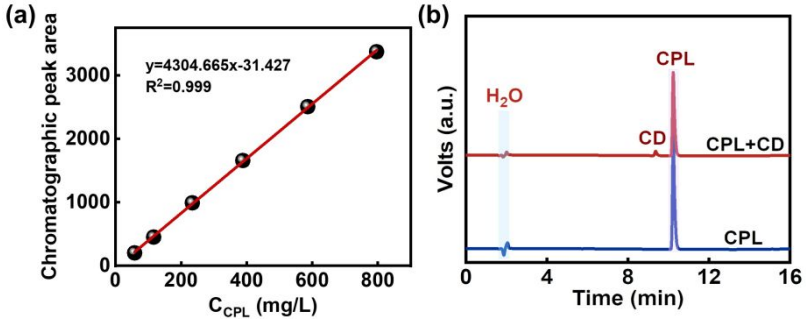


**Fig. S4** (a) Calibration curves for CPL and (b) High performance liquid chromatogram of standard solution (CPL, CD).

First of all, 0.02 g of CPL purchased from Sigma-Aldrich was weighed and dissolved in a 50 mL volumetric flask with water purchased from Sigma-Aldrich. 0.0025 g of Laboratory-made CD and 0.02 g of CPL purchased from Sigma-Aldrich were separately weighed and dissolved in a 50 mL volumetric flask with water purchased from Sigma-Aldrich. High performance liquid chromatogram of CPL and CD is drawn by recording the volts of the standard solutions at 215 nm (Figure S4b).

### 3.3 Qualitative Analysis of Liquid Products

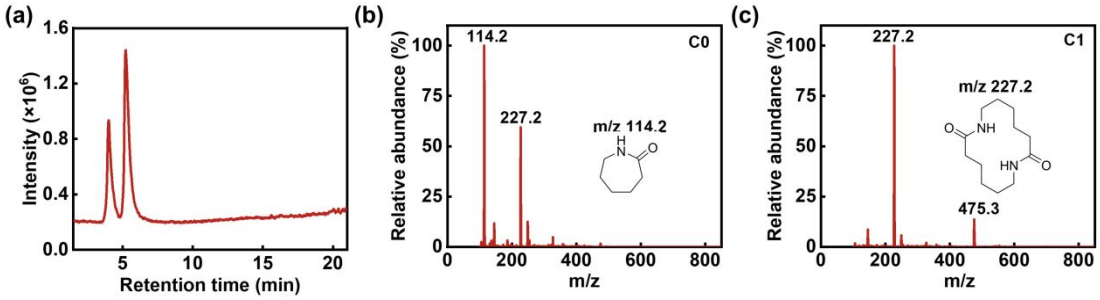


**Fig. S5** (a, b, c) Total ion chromatogram and mass spectrum of CPL and CD.

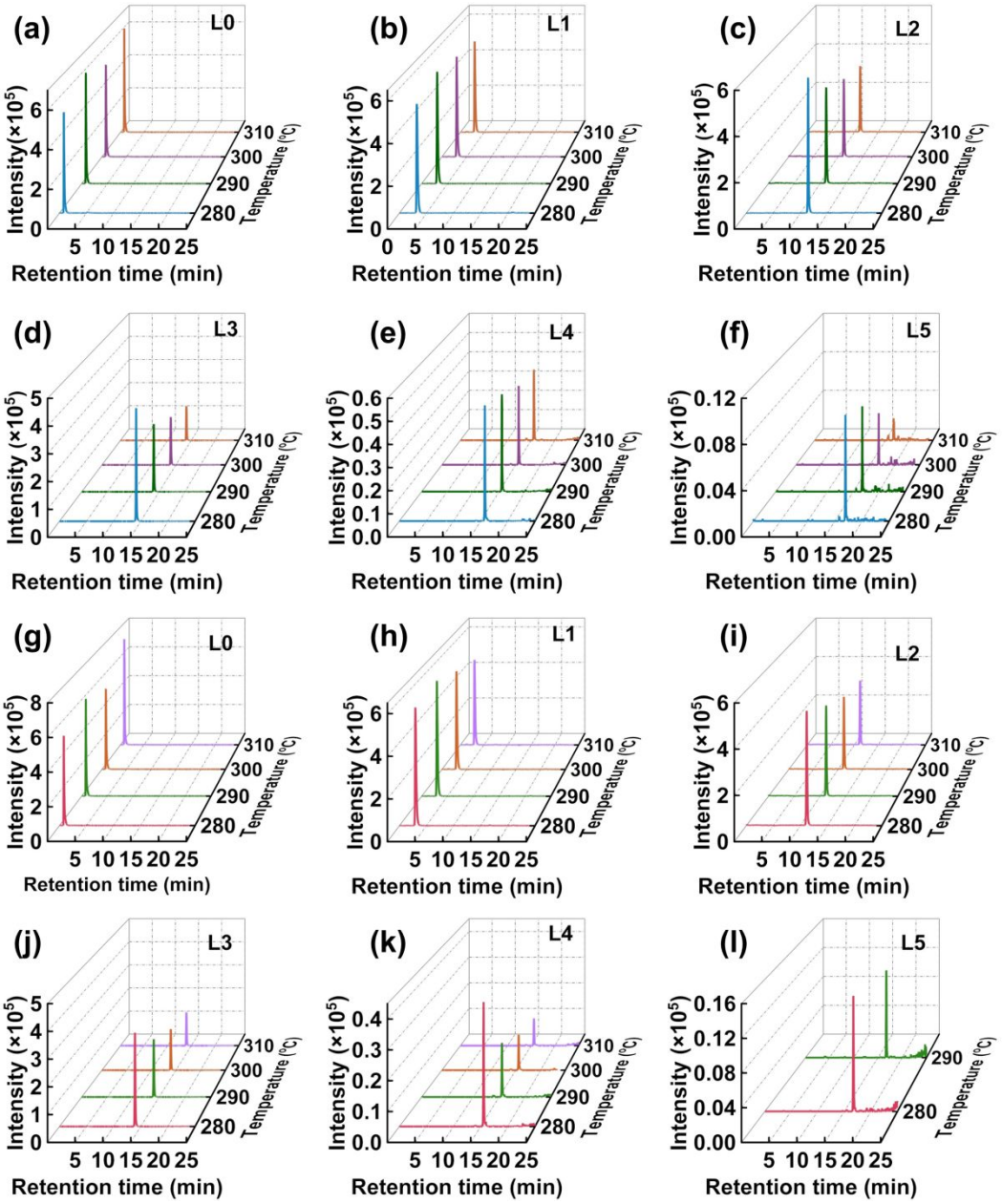


**Fig. S6** Effect of reaction temperature on hydrolysis of vPA6 and Was PA6 textiles. Reaction conditions: mass ratio ($H_2O$:PA6) of 7:1, 60 min. (a-f) extracted ion chromatography of Ln in vPA6 hydrolysis liquid products at different temperatures. (a) L0, (b) L1, (c) L2, (d) L3, (e) L4, (f) L5; (g-l) extracted ion chromatography of Ln in Was PA6 textiles hydrolysis liquid products at different temperatures. (g) L0, (h) L1, (i) L2, (j) L3, (k) L4, (l) L5.

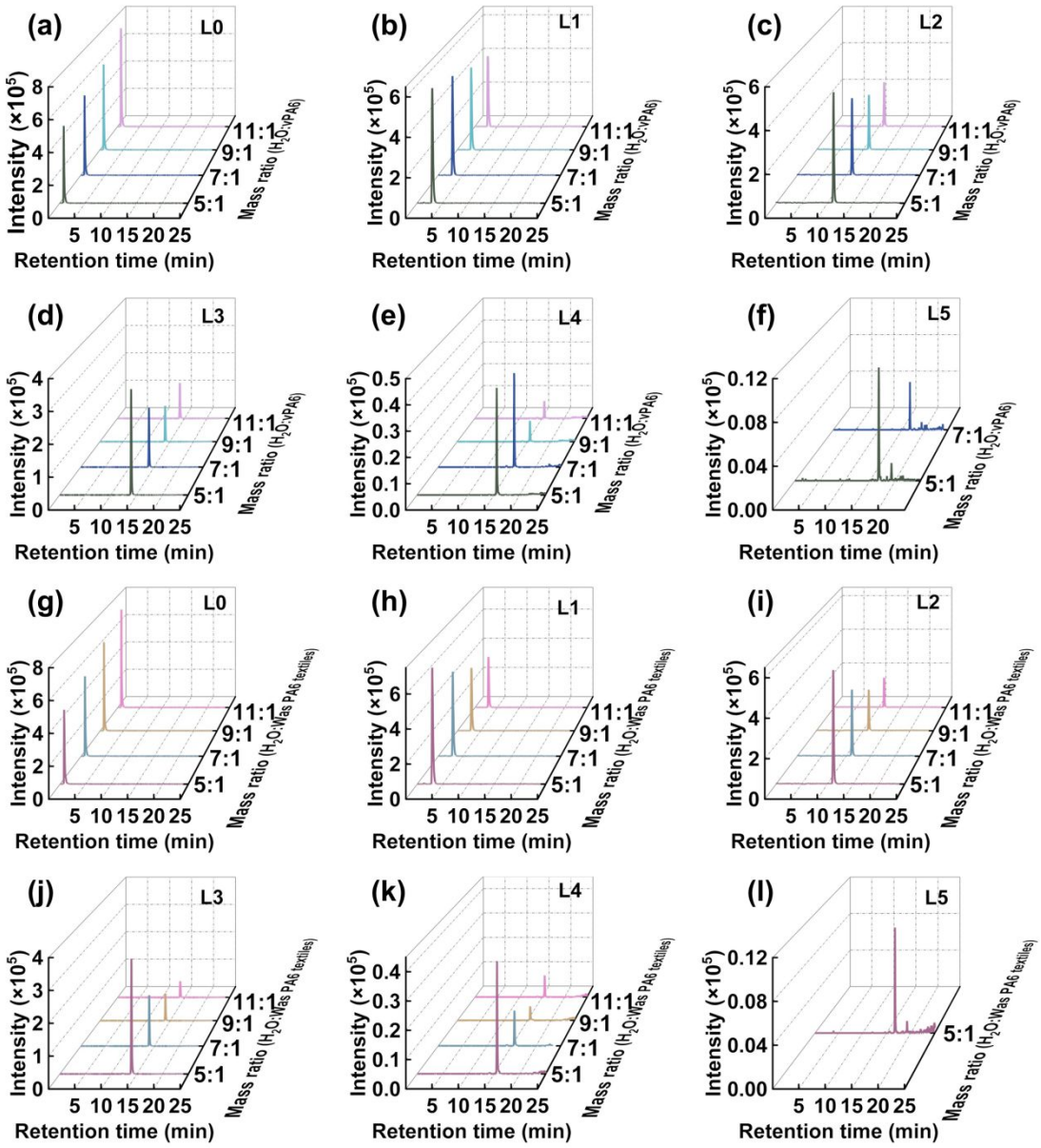


**Fig. S7** Effect of mass ratio ($H_2O$:PA6) on hydrolysis of vPA6 and Was PA6 textiles. Reaction conditions: 300 °C, 60 min. (a-f) extracted ion chromatography of Ln in vPA6 hydrolysis liquid products at different mass ratios ($H_2O$:vPA6). (a) L0, (b) L1, (c) L2, (d) L3, (e) L4, (f) L5; (g-l) extracted ion chromatography of Ln in Was PA6 textiles hydrolysis liquid products at different mass ratios ($H_2O$:Was PA6 textiles). (g) L0, (h) L1, (i) L2, (j) L3, (k) L4, (l) L5.

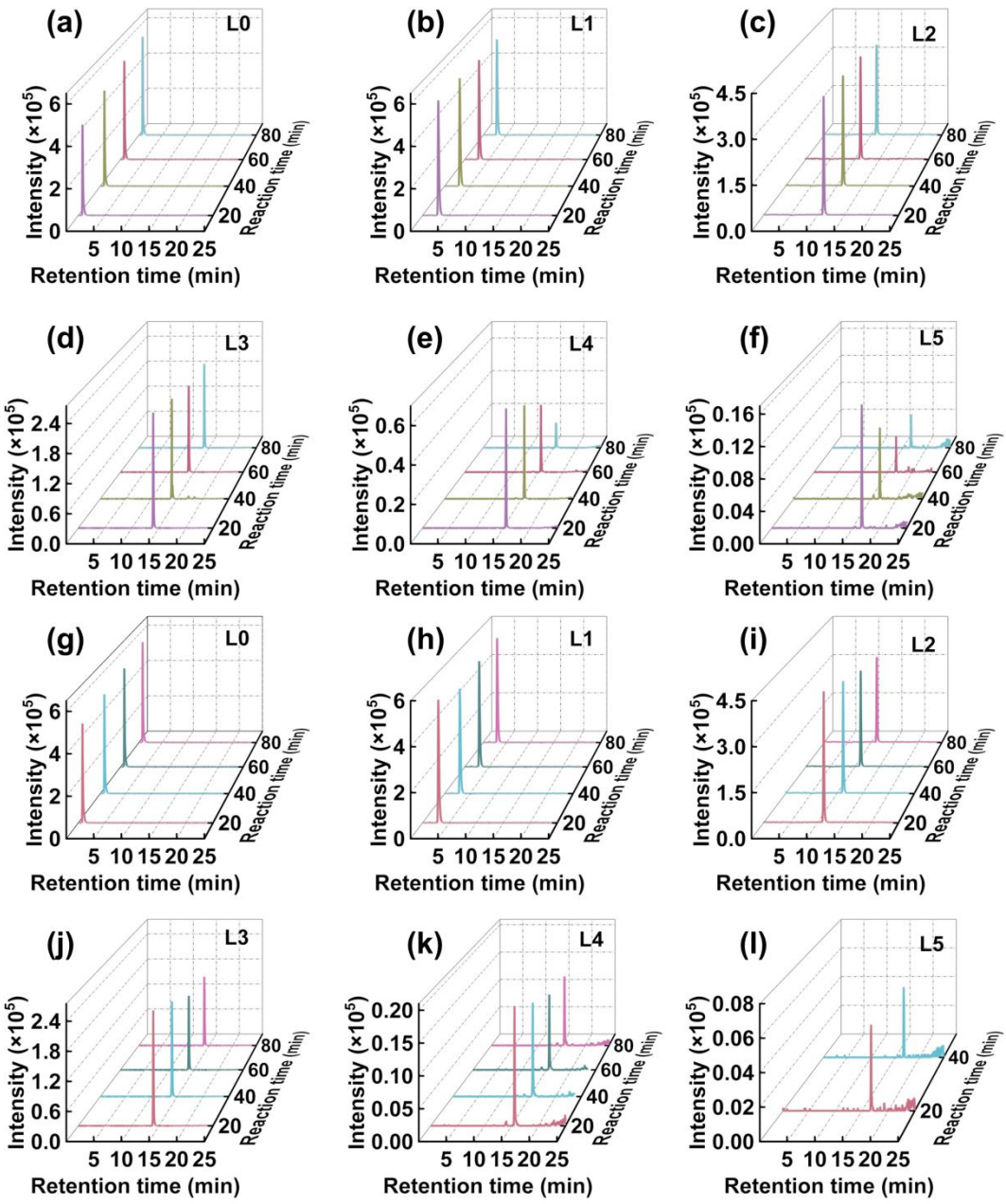


**Fig. S8** Effect of reaction time on hydrolysis of vPA6 and Was PA6 textiles. Reaction conditions: 300 °C, mass ratio ($H_2O$:PA6) of 7:1. (a-f) extracted ion chromatography of Ln in vPA6 hydrolysis liquid products at different times. (a) L0, (b) L1, (c) L2, (d) L3, (e) L4, (f) L5; (g-l) extracted ion chromatography of Ln in Was PA6 textiles hydrolysis liquid products at different times. (g) L0, (h) L1, (i) L2, (j) L3, (k) L4, (l) L5.

## 4. References

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