Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Chemically Recyclable and Mechanically Robust Non-isocyanate Polyurethane from Resveratrol

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Materials

3-Methyl-3-oxetanemethanol (96%), 48% hydrobromic acid, 2,2-dimethoxypropane (99%), resveratrol (RE, 98%), *p*-toluenesulfonic acid monohydrate (98%), concentrated hydrochloric acid, tetrabutylammonium bromide (TBAB, 99%), *N,N*'-dimethylformamide (DMF, extra dry over molecular sieves, 99.8%), *p*-toluenesulfonyl chloride (TsCl, 99%), *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 99%), 1,3-diaminopropane, 1,6-diaminohexane, 1,12-diaminododecane, 4,7,10-trioxa-1,13-tridecanediamine (DEGDA) were obtained from Energy Chemical and used without further purification. All other chemicals were obtained from Sinopharm and used without further purification unless stated.

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were performed on the Vaian DLG400 MHz nuclear magnetic resonance spectrometer at room temperature using methyl sulfoxide-d6 (DMSO-d_6) or chloroform ($CDCl_3$) as solvent and tetramethylsilane as the internal standard.

Fourier transform infrared (FT-IR) spectra were performed on a Thermo Nicolet Nexus 470 FT-IR spectrometer through attenuated total reflectance (ATR) method with the wavelength range of 650-4000 cm^{-1}.

High-resolution time-of-flight liquid chromatography/mass spectrometry (TOF-LC/MS) was performed on an Agilent 6224 mass spectrometer.

Thermogravimetric analysis (TGA) was performed on a TA-Q500 under N_2 atmosphere with a heating heating rate of 10°C/min.

Differential scanning calorimetry (DSC) was performed on a TA-Q2000 under N_2 atmosphere with a heating heating rate of 10°C/min.

Dynamic mechanical thermal analysis was performed on TA-Q800 using dog-bone-shaped samples at a heating rate of 3°C/min and frequency of 1Hz in single cantilever mode.

Mechanical properties were measured on a universal testing machine (Instron 5567AR265) using dog-bone-shaped samples at room temperature.

Stress relaxation analysis (SRA) was performed on TA-Q800 using dog-bone-shaped

samples, and the stress decay was monitored under a strain-controlled mode at the specified temperatures (190-250°C).

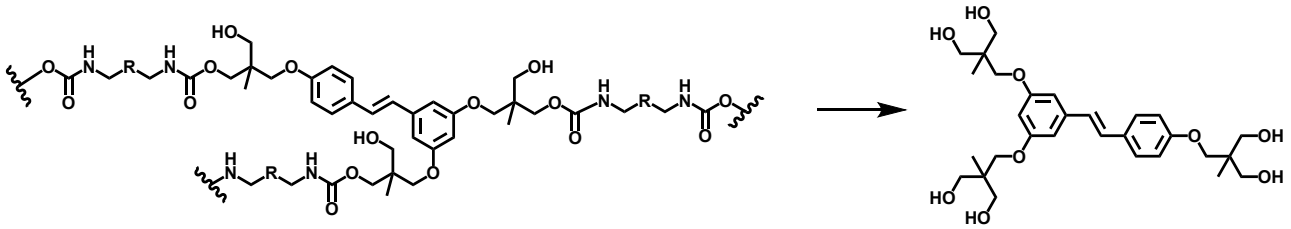
High-performance liquid chromatography (HPLC) was performed on Agilent 1100 reversed phase, the mobile phase was MeOH and H_2O.

A dissolution method was employed to measure the gel fraction of the RE-PHUs. The cross-linked samples (W1) were immersed in tetrahydrofuran (THF) for 48 h. The insoluble moieties were dried to a constant weight (W2) by vacuum drying. The gel fraction (Gf) was obtained according to the following equation:

$$G_f = \frac{W_2}{W_1} \times 100\%$$

Synthetic procedures

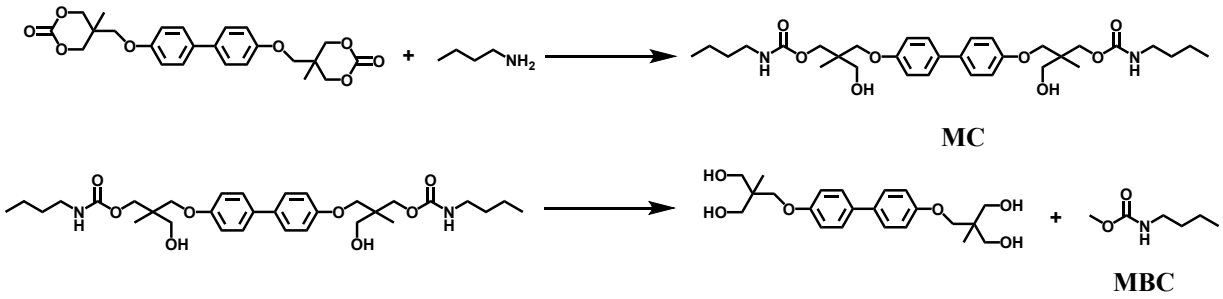
Scheme S1. Degradation of RE-PHU.



RE-PHU **Recycling RE-OH**

Degradation of RE-PHU: By mixing RE-PHU, 20 wt% aqueous NaOH, and methanol in a round bottom flask at 70°C for 3 h, a degraded solution was obtained. Adjust PH = 7 by concentrated hydrochloric acid, and remove organic solvents by rotary evaporator to collect white precipitate. Yield: 97%, purity: 98.11%. The structure of the product was determined by ^{1}H-NMR , and the spectra were presented in Figure 4b.

Scheme S2. Model reaction

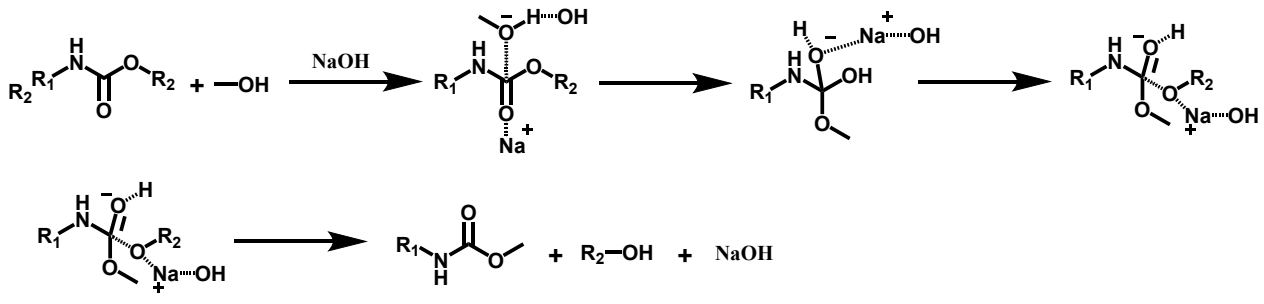


MC **MBC**

Model compound (MC): By mixing BCC-BP (1 eq), butylamine (4 eq), and anhydrous DMF (0.5 M) in a round bottom flask at 70°C overnight, a colorless and transparent solution was obtained. The solution was concentrated under reduced pressure. The crude material was dissolved in a suitable amount of CH_2Cl_2 and filtered through a plug of silica gel, eluting with 50% EtOAc in CH_2Cl_2. The filtrate was then concentrated using a rotary evaporator. Yield: 90%.

Model of degradation experiment: By mixing MC, 20 wt% aqueous NaOH, and methanol in a round bottom flask at 90°C for 3 h, a degraded solution was obtained. Adjust the pH of the solution to 7 and collect the filtrate by filtration. The excess methanol was removed by rotary evaporation. The methyl butylcarbamate (MBC) was obtained by reduced decompression distillation. Yield: >95%.

Scheme S3. Speculative mechanism for the degradation experiments.



Characterization Tables and Figures

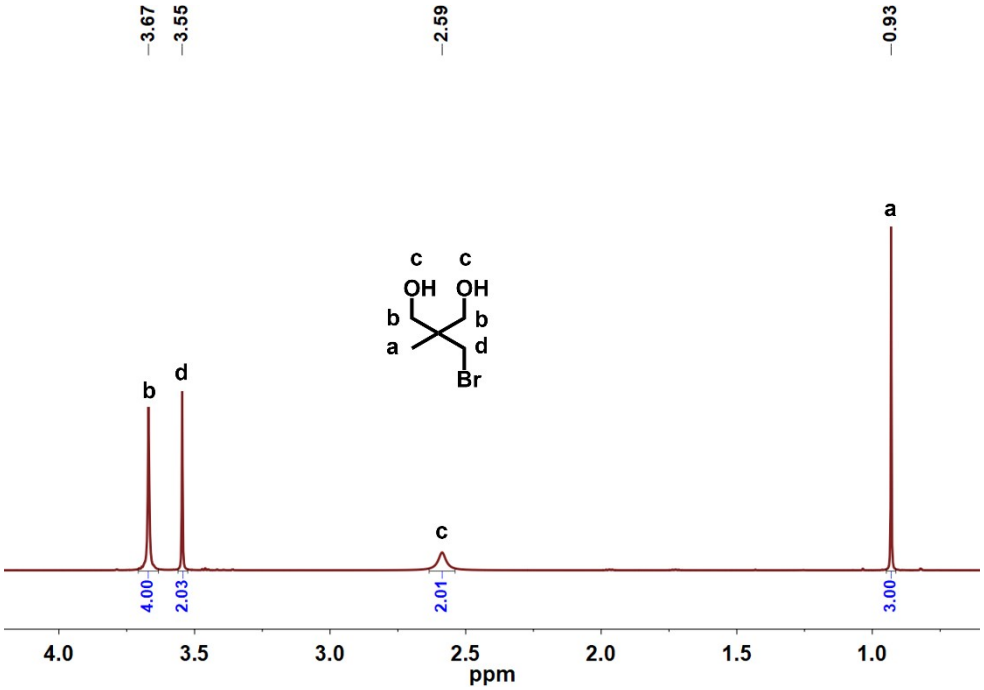


Figure S1. [1]H NMR spectra of 2-bromomethyl-2-methyl-1,3-propanediol and peak assignment.

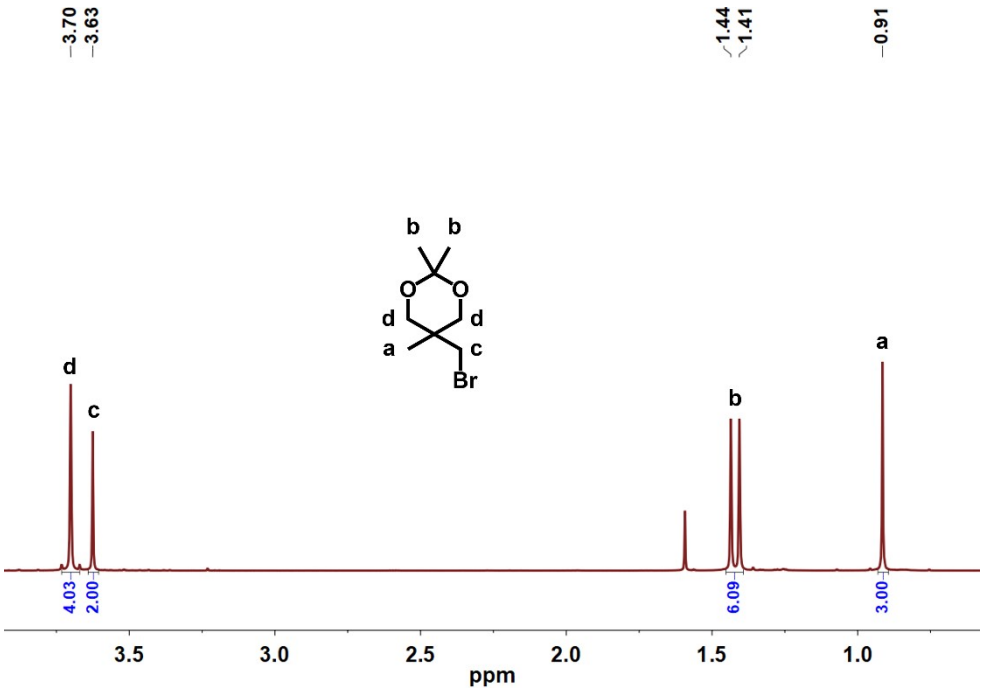


Figure S2. [1]H NMR spectra of BMTD and peak assignment.

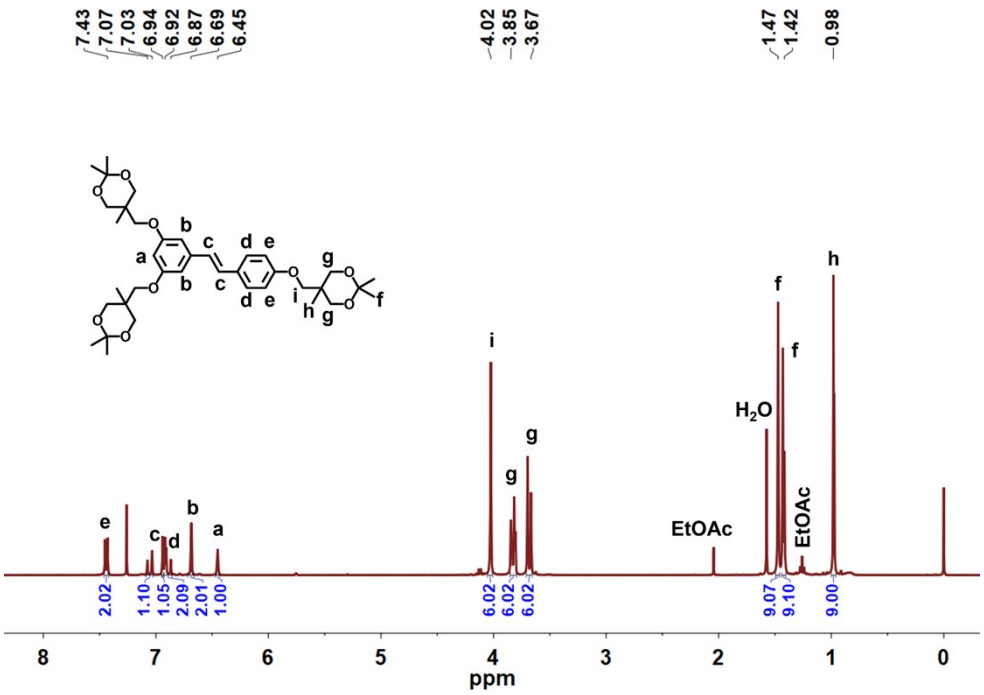


Figure S3. [1]H NMR spectra of RE-BMTD

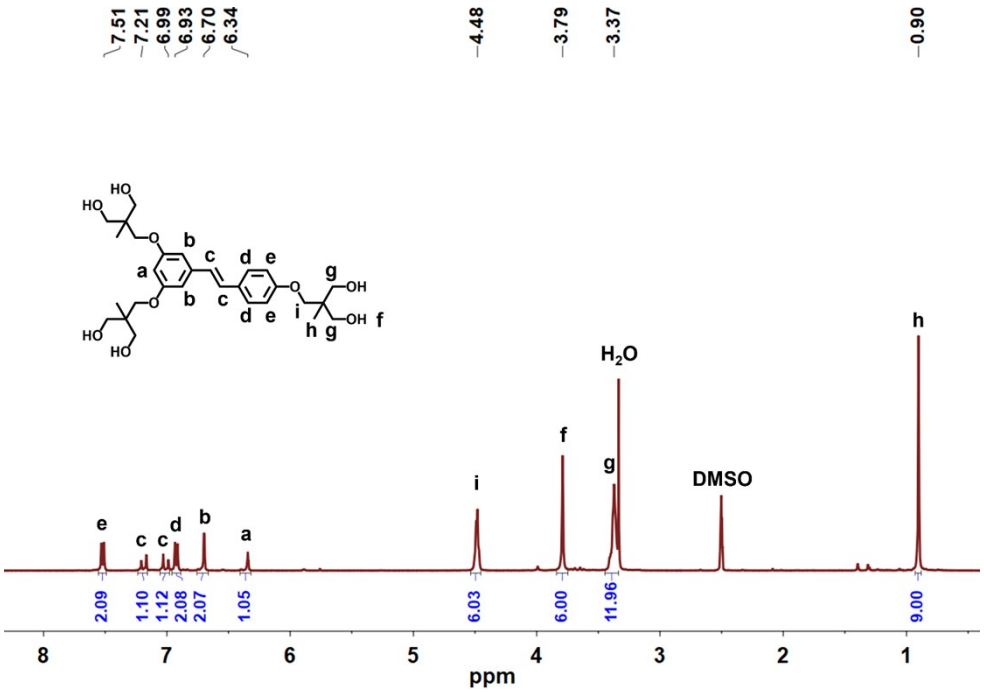


Figure S4. [1]H NMR spectra of RE-OH and peak assignment.

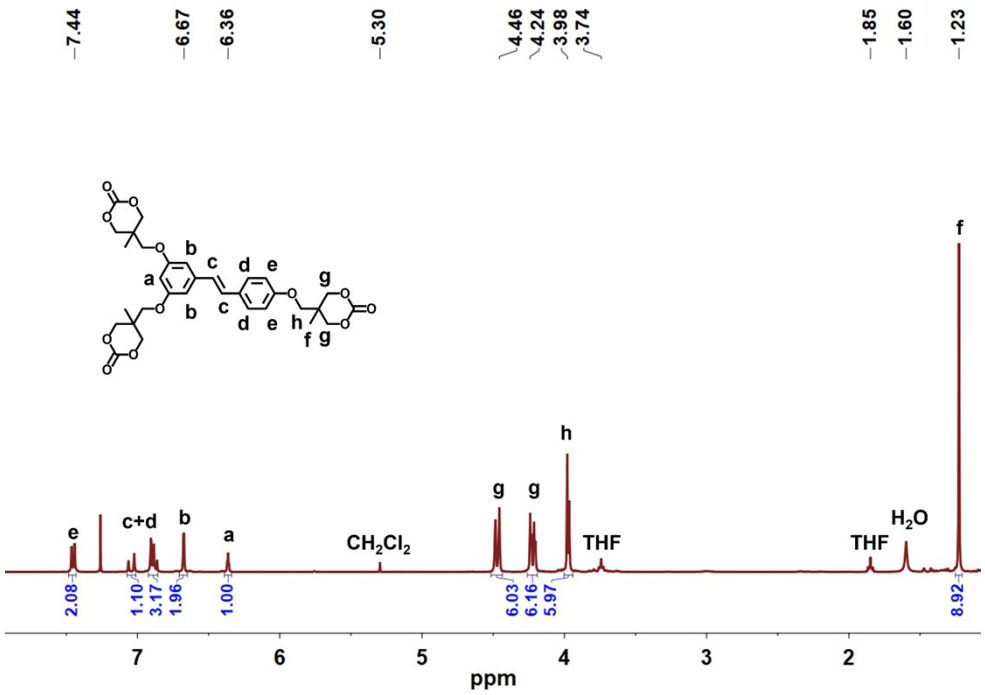


Figure S5. [1]H NMR spectra of RE-TCC and peak assignment.

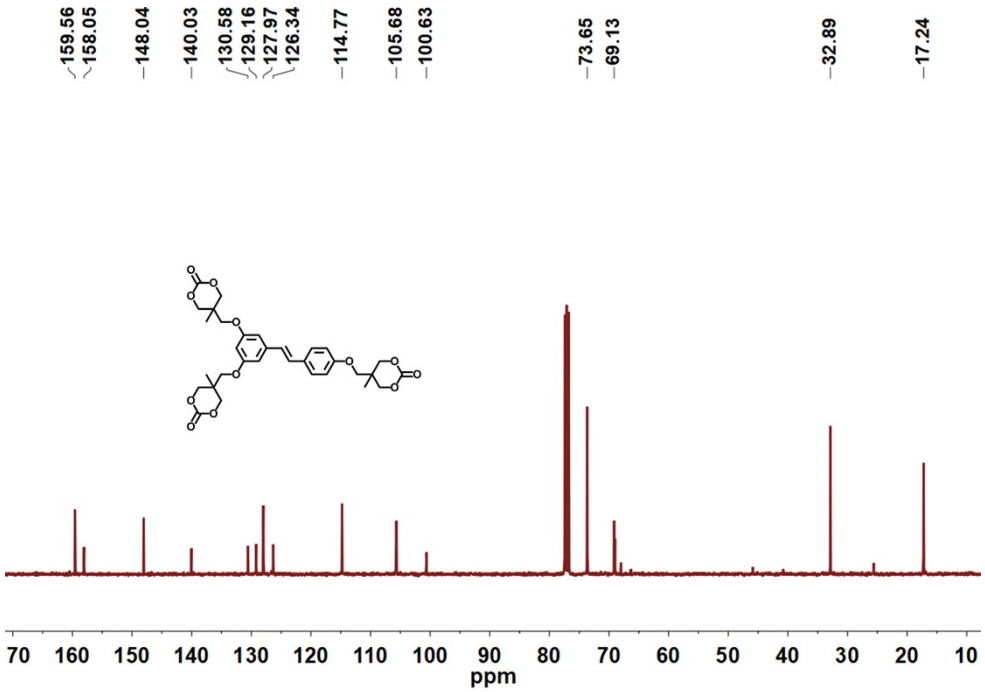


Figure S6. [13]C NMR spectra of RE-TCC.

Table S1. Formulas for the preparation of RE-PHUs

Sample	Diamine	Ratio [a]
RE-PHU-3	1,3-diaminopropane	1
RE-PHU-6	1,6-diaminohexane	1
RE-PHU-12	1,12-diaminododecane	1
RE-PHU-13	4,7,10-trioxa-1,13-tridecanediamine	1

[a]Ratio=amino molar content/cyclic carbonate molar content.

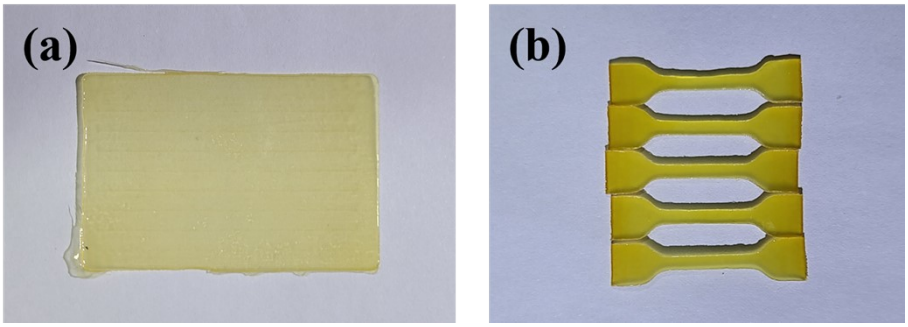


Figure S7. Photos of (a) the RE-PHU films and (b) the dog-bone RE-PHU samples.

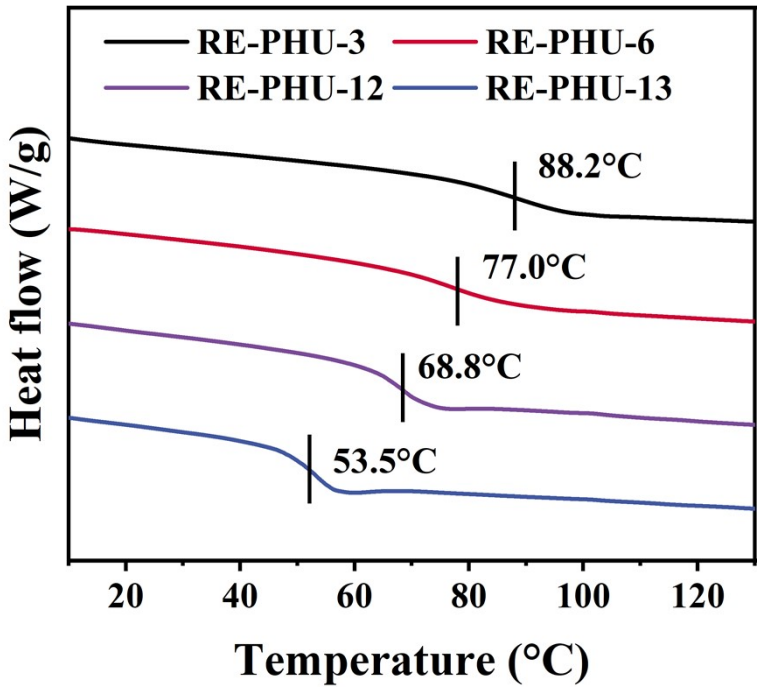


Figure S8. DSC curves of RE-PHUs with different diamines.

Table S2. Detailed data on thermal properties of RE-PHUs.

Sample	T_g/°C[a]	T_g/°C[b]	E'/MPa	υ/(mol/m^3)[c]
RE-PHU-3	88.2	117.2	4.60	418.3
RE-PHU-6	77.0	108.1	3.71	344.9
RE-PHU-12	68.8	91.3	3.08	298.0
RE-PHU-13	53.5	76.2	2.80	281.1

[a]Determined by DSC. [b]Determined by DMA. [c]Calculated from eq 1.

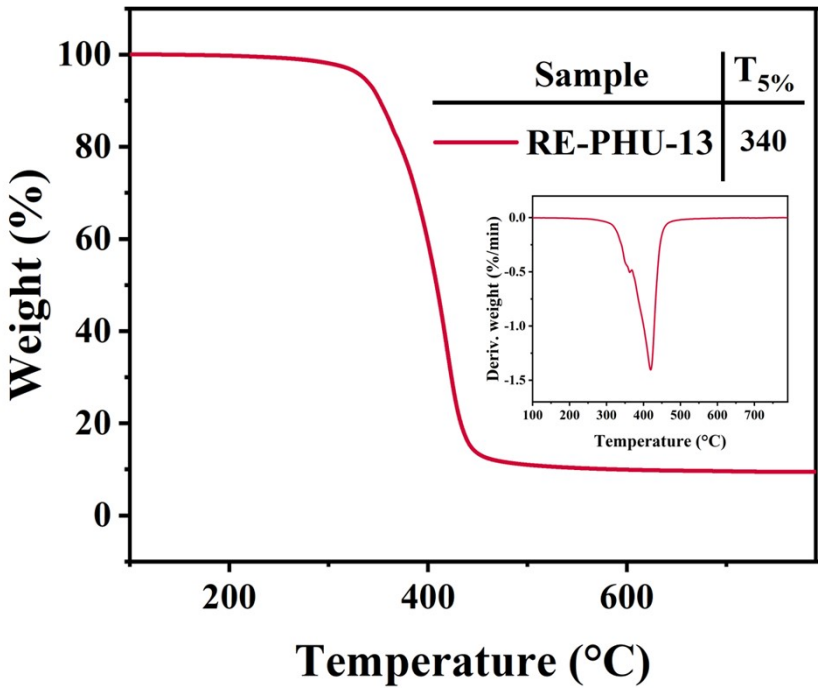


Figure S9. TGA curves of RE-PHU-13.

Table S3. Dynamic data of RE-PHU-13.

Sample	E_a/(kJ/mol)	ln(τ_0)	τ*/min			
			190	210	230	250
RE-PHU-13	107.5	-18.8	160.7	48.2	17.7	6.4
RE-PHU-12	103.9	-18.0	140.3	45.4	16.1	6.4
RE-PHU-6	98.1	-16.7	103.8	40.6	14.1	5.7
RE-PHU-3	90.6	-15.2	65.7	28.7	10.6	4.6

Calculations for stress relaxation derived activation energy.

RE-PHU-13:

Equation obtained from Arrhenius law: y = 12.93x - 18.76, R^2 = 0.99944

Corresponding equation: ln(τ*) = 12.93 × 1000/T - 18.76

Identifying this to the experimental equation: $E_a/R = 12.93$

$E_a = 12.93 \times 8.314 = 107.50$ kJ/mol

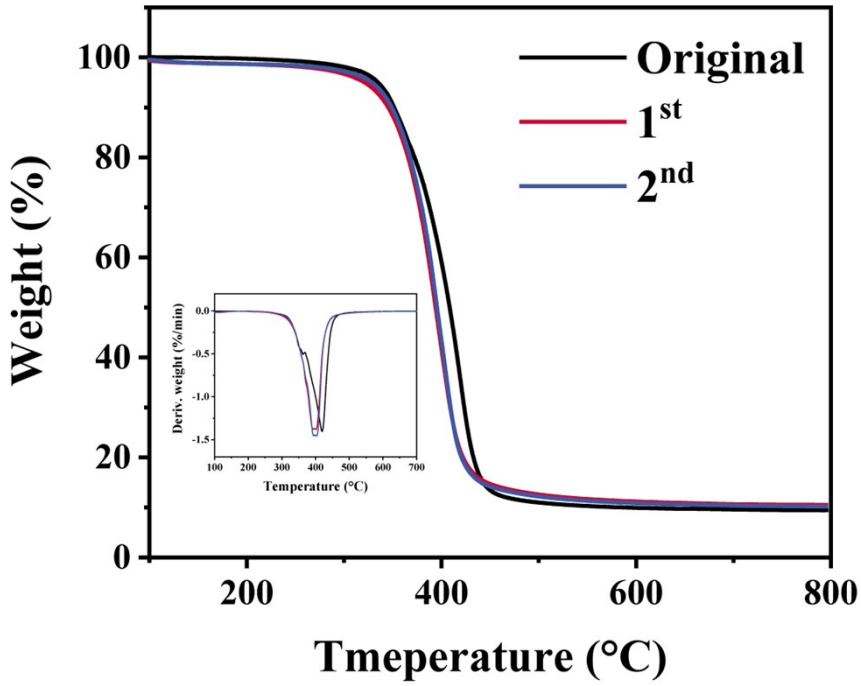


Figure S10. TGA curves of original and remolding RE-PHU-13.

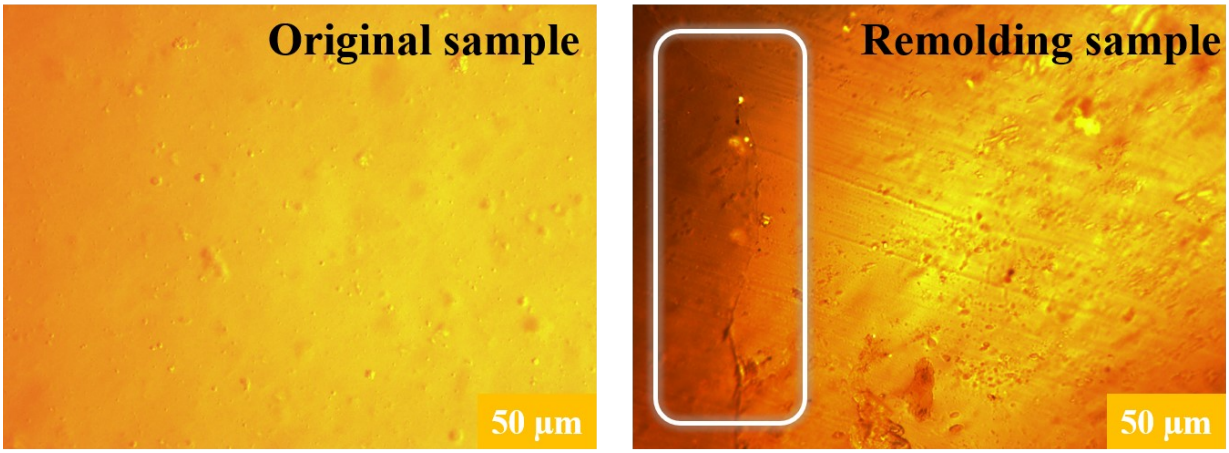


Figure S11. POM (50 μm) images of original and remolding samples (boundary of clipped pieces).

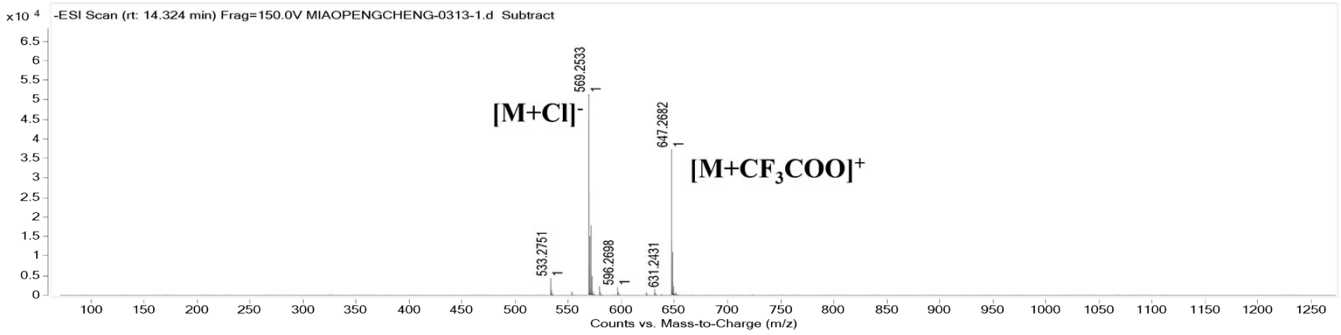


Figure S12. MS spectrum of regenerated RE-OH.

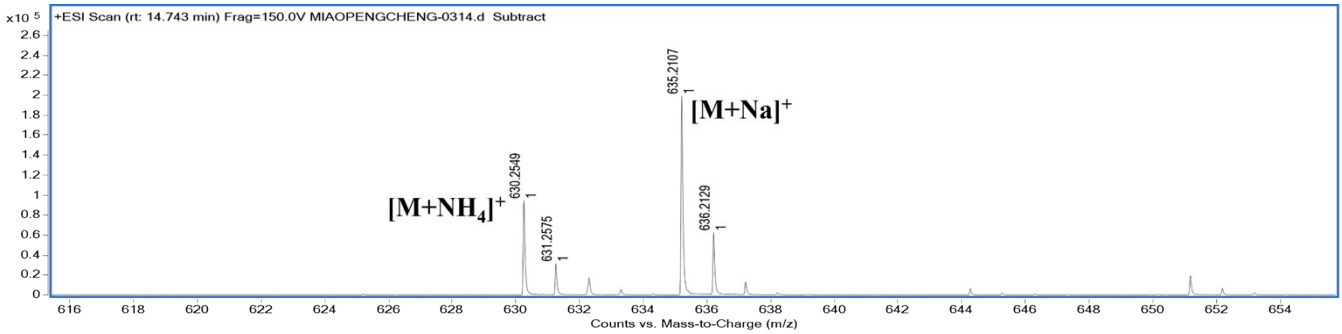


Figure S13. MS spectrum of regenerated RE-TCC.

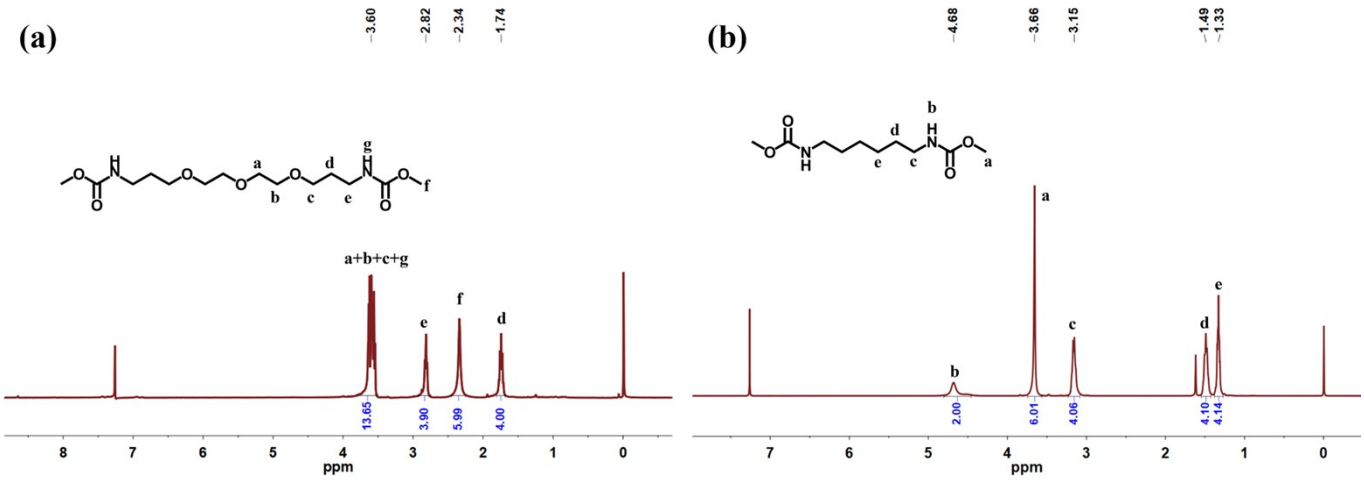


Figure S14. ^{1}H NMR spectra of the by-product of degradation.

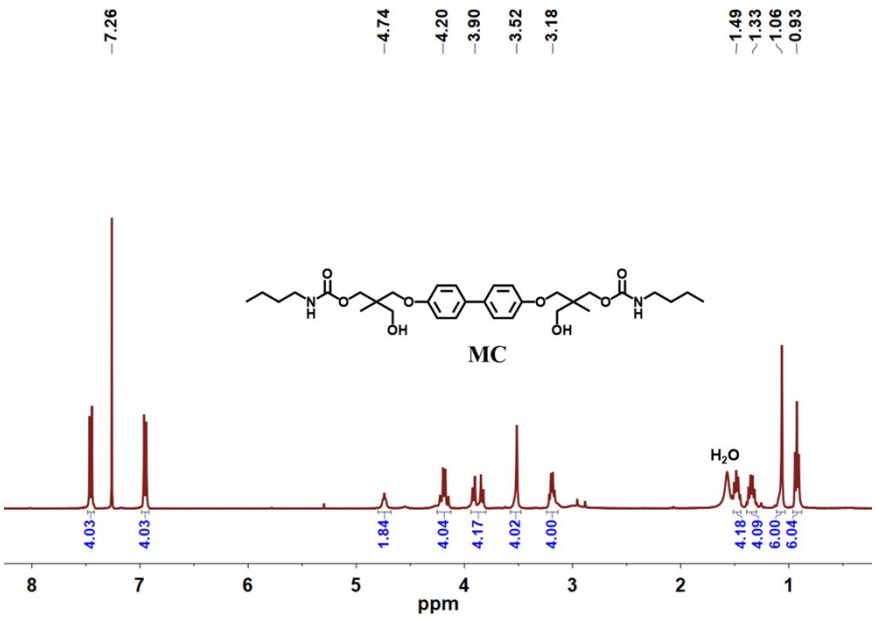


Figure S15. ^{1}H NMR spectra of MC.