

----- Supporting Information -----

A recyclable thermoset with built-in thermocleavable group developed from a *cis*-cyclobutane-1,2-dicarboxylic acid

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1. Material and methods

trans-Cinnamic acid was used after preprocessing. All solvents and reagents purchased from Alfa Aesar, Aldrich, Acros Organics, and Matrix Scientific were used without further purification. The irradiation source was EIKO 15526 F15T8/BL Fluorescent Blacklight Bulb 365 nm. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data were recorded on a Bruker AVANCE 500 MHz spectrometer. ^1H NMR data were reported as follows: chemical shift (ppm), s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, coupling constant (Hz), and integration. FT-IR spectra were acquired on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. Calorimetric curves were recorded on a Perkin Elmer Jade DSC at a ramping rate 10 °C/min. Thermogravimetric analysis (TGA) was performed on TA instrument SDT Q600 at a ramping rate 20 °C/min in argon or nitrogen atmosphere. The Wolff-Wilborn hardness tests were done using a Cgoldenwall pencil hardness tester. The Shore D hardness tests were carried out using a Qwork Shore D hardness digital durometer. The SEM images were taken using Hitachi SU8010 Scanning Electron Microscope. Single crystal X-ray data were recorded on Bruker Apex or Bruker Kappa Apex II Duo X-Ray Diffractometer with Mo K α ($\lambda = 0.71073 \text{ \AA}$) or Cu K α ($\lambda = 1.54178 \text{ \AA}$). SHELX2014 was used for structure solution and refinement on F². X-ray Powder Diffraction (XRD) was performed on a X'PERT-PRO X-ray diffractometer (PANalytical, Netherlands) equipped with a 3 KW copper tube X-ray generator of $\lambda = 0.1541 \text{ nm}$ under 40 mA and 45 KV. Spectra were collected at room temperature in a 2θ range of 3~35° at a scanning rate of 5°/min.

1.1. Preparation of β -*trans*-cinnamic acid and CBDA-4

The elaborate operation procedure was described in our previous work (See reference #14 in the manuscript). ^1H NMR (500 MHz, DMSO-*d*₆): δ 12.46 (s, 2H), 6.99 ~ 7.09 (m, 10H), 4.22 (d, $J = 4.5 \text{ Hz}$, 2H), 3.81 (d, $J = 4.5 \text{ Hz}$, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-*d*₆): δ 174.3, 139.6, 128.2, 128.0, 126.2, 44.8, 42.9.

1.2. Synthesis of thermoset CBDAT

Method A: CBDA-4 (0.49 g, 1.7 mmol), EDC (0.69 g, 3.7 mmol), and DMAP (0.04 g, 0.3 mmol) were added to anhydrous acetonitrile (8 mL) and stirred for 10 mins. To this mixture, a solution of glycerol (0.08 mL, 1.1 mmol) in acetonitrile (2 mL) was added dropwise. The mixture was stirred at room temperature for 48 h and then poured into 100 mL of water. The precipitates were filtered and dried in vacuum for 24 h. The obtained CBDAT was a white powder (0.3 g).

Method B: CBDA-4 (1.0 g, 3.4 mmol), glycerol (0.2 g, 2.2 mmol), *p*-toluenesulfonic acid (58 mg, 0.3 mmol; or ZnCl₂, 46 mg, 0.3 mmol), and DMF (1 mL) were added into a 10 mL round-bottom flask. The mixture was purged with argon three times and heated to 110 °C. Once the samples were dissolved, the mixture was heated at 160 °C under vacuum for a few hours with stirring to offer CBDAT as a viscous liquid or solid sample depending on the reaction time.

Method C: CBDA-4 (1.6 g, 5.4 mmol), glycerol (0.4 g, 4.3 mmol) were added to a 10 mL round-bottom flask. The flask was then purged with argon. The mixture was heated with a heat gun using the high setting. Once the mixture was fully melted, it was kept heating for about 3 minutes or

until an increase in viscosity was observed. It is important to keep the heat source in a sweeping motion to prevent the liquid from boiling over and setting too early. Once the liquid was ready to be set, the heat source was removed. The viscous liquid was allowed to release any bubbles prior to molding. The liquid was then gently poured into an aluminium foil mold and allowed to cool to room temperature. The length of heating determines the degree of crosslinking in the polymer product.

1.3. Degradation of CBDAT

Sand bath was preheated to 300 °C. CBDAT was sealed in a Schlenk tube and purged with argon three times. This tube was placed in the sand bath for 5 mins to 300 °C, and then cooled down to room temperature. 10 mL of ethyl acetate was added to the tube and sonicated for 30 min and transferred into a 50 mL round bottom flask. Silica gel (2.0 g) was added to the flask and the solvents were evaporated. The dry samples were transferred to a silica gel column and eluted with ethyl acetate and hexane (1:20, 1:10, 1:5) to give glycerol cinnamate as a white product. ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.68 ~ 7.74 (m, 9H), 7.39 ~ 7.45 (m, 9H), 6.67 (d, *J* = 16 Hz, 2H), 6.69 (d, *J* = 16 Hz, 1H), 5.49 ~ 5.52 (m, 1H), 4.53 ~ 4.56 (m, 2H), 4.43 ~ 4.47 (m, 2H) ppm. HRMS: Calculated for [C₃₀H₂₆O₆Na]⁺ 505.1627; Found: 505.1701)

The glycerol cinnamate (100 mg), potassium hydroxide (140 mg), and a mixture of ethanol/water (3:1, 24 mL) were added into a 50 mL round-bottom flask. The mixture was refluxed for 24 hours and then cooled to room temperature. After acidified to pH 2.5 with 6M HCl, silica gel (1.0 g) was added to the flask and then the solvents were evaporated. The dry samples were transferred to a silica gel column and eluted with DCM and MeOH to give glycerol as a colorless oil (16 mg, 83% yield) and cinnamic acid as a white solid (71 mg, 86 % yield).

1.4. Stability tests of CBDAT

Test with acid: Concentrated hydrogen chloride (0.2 mL, 12 M) and distilled water (25 mL) were added into a 50 mL round-bottom flask. CBDAT (100 mg) was added into the diluted HCl solution and the mixture were stirred for 8 hours at room temperature. The polymer were filtered, dried, and weighted. CBDAT (99 mg) was recovered and FT-IR spectrum of the sample showed no obvious change compared to the one before the acid treatment.

Test with base: Sodium hydroxide (5 mg) and distilled water (25 mL) were added into a 50 mL round-bottom flask. CBDAT (100 mg) was added into the diluted NaOH solution and the mixture were stirred for 8 hours at room temperature. The polymer were filtered, dried, and weighted. CBDAT (96 mg) was recovered and FT-IR spectrum of the sample showed no obvious change compared to the one before the base treatment.

Test with sunlight: 50 mg CBDAT was placed in a beaker, and the sample was exposed to sunlight for a month when there was no rain during the day. FT-IR spectrum of the sample showed no obvious change compared to the one before the sunlight exposure.

2. Spectra of NMR and FT-IR
2.1. NMR spectrum of glycerol cinnamate

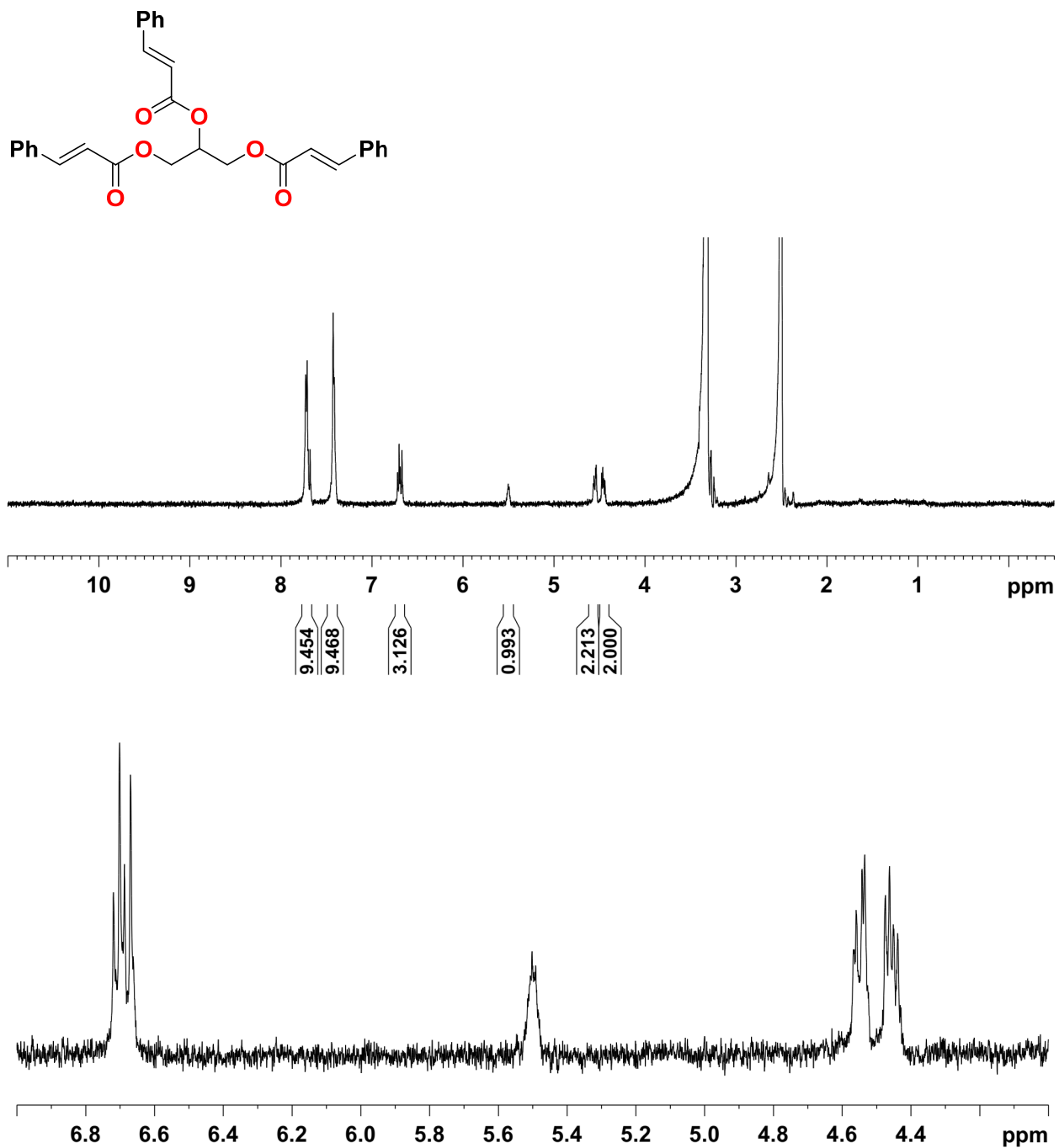


Figure S1 NMR Spectrum of the degraded intermediate - glycerol cinnamate in DMSO-*d*₆.

2.2. FT-IR spectra of CBDAT and glycerol cinnamate

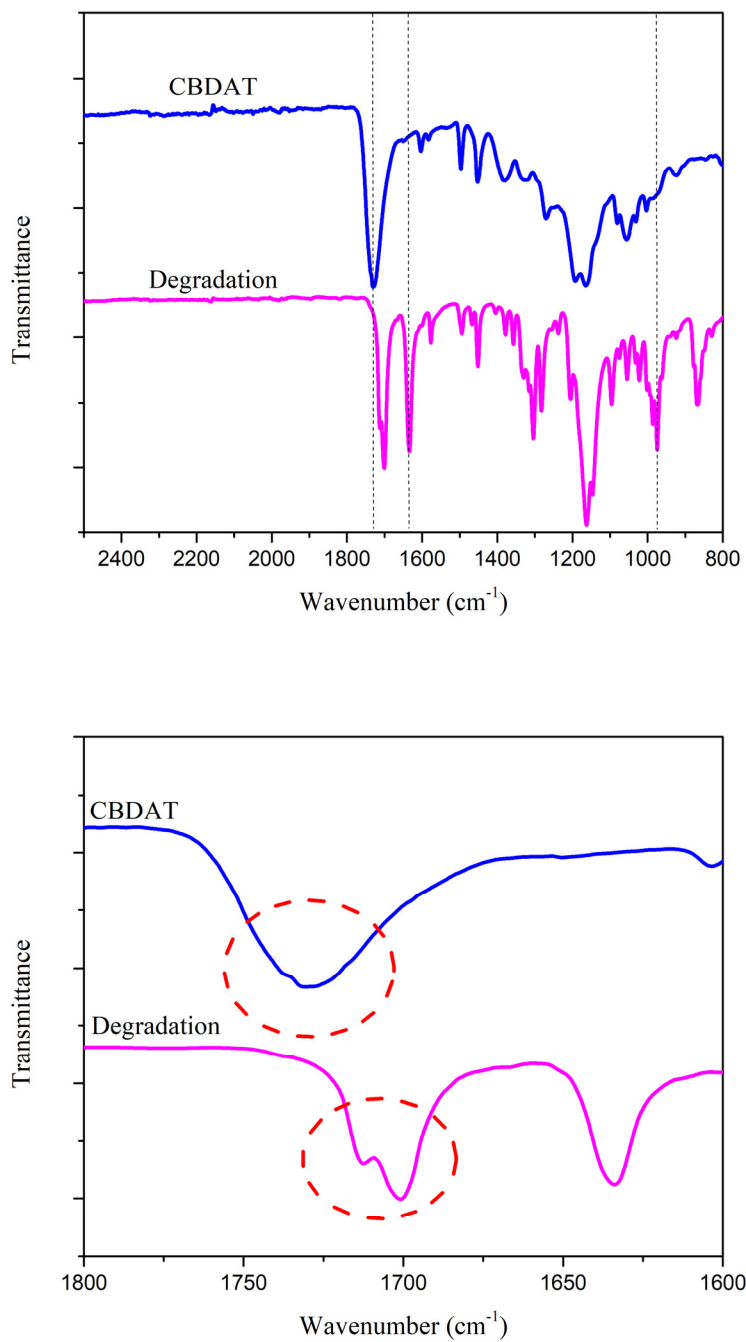


Figure S2 FT-IR spectra of thermoset CBDAT and the degraded intermediate. The bottom image is the magnification of the two carbonyl (C=O) stretching peaks in the spectra.

3. X-ray single crystal data and images of glycerol cinnamate

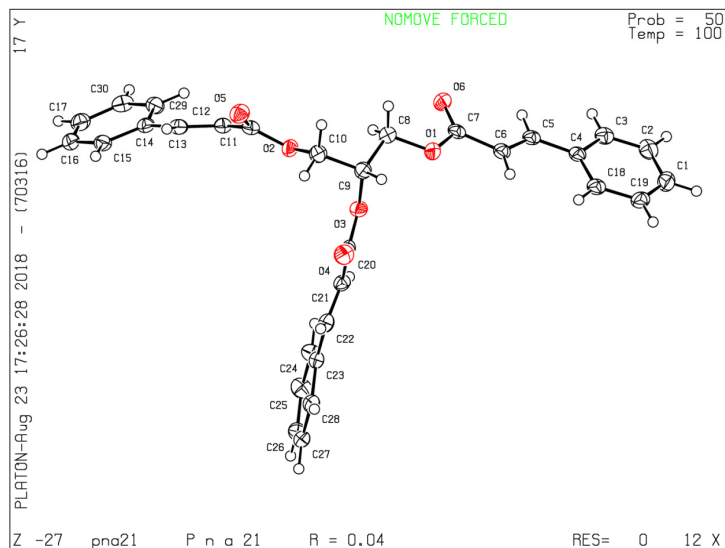


Table S1. Crystal data of Glycerol Cinnamate

| Crystal | Glycerol Cinnamate |
|---|--|
| CCDC # | 2155526 |
| Formula | C ₃₀ H ₂₆ O ₆ |
| FW | 482.51 |
| Crystal size [mm] | 0.25 × 0.04 × 0.03 |
| Crystal system | Orthorhombic |
| Space group | Pna2 ₁ |
| a (Å) | 14.6141(4) |
| b (Å) | 29.7385(10) |
| c (Å) | 5.6446(2) |
| α (°) | 90 |
| β (°) | 90 |
| γ (°) | 90 |
| V (Å ³) | 2453.15(14) |
| Temp. (K) | 100 |
| Z | 4 |
| ρ _{calc} (g·cm ⁻³) | 1.306 |
| μ (mm ⁻¹) | 0.740 |
| Radiation type | MoKα (λ = 0.71073) |
| F(000) | 1016.0 |
| Reflections collected | 9222 |
| Independent reflections | 3599 |
| R1/wR2 (I ≥ 2σ) (%) | 3.60/8.10 |
| R1/wR2 (all data) (%) | 4.26/8.52 |

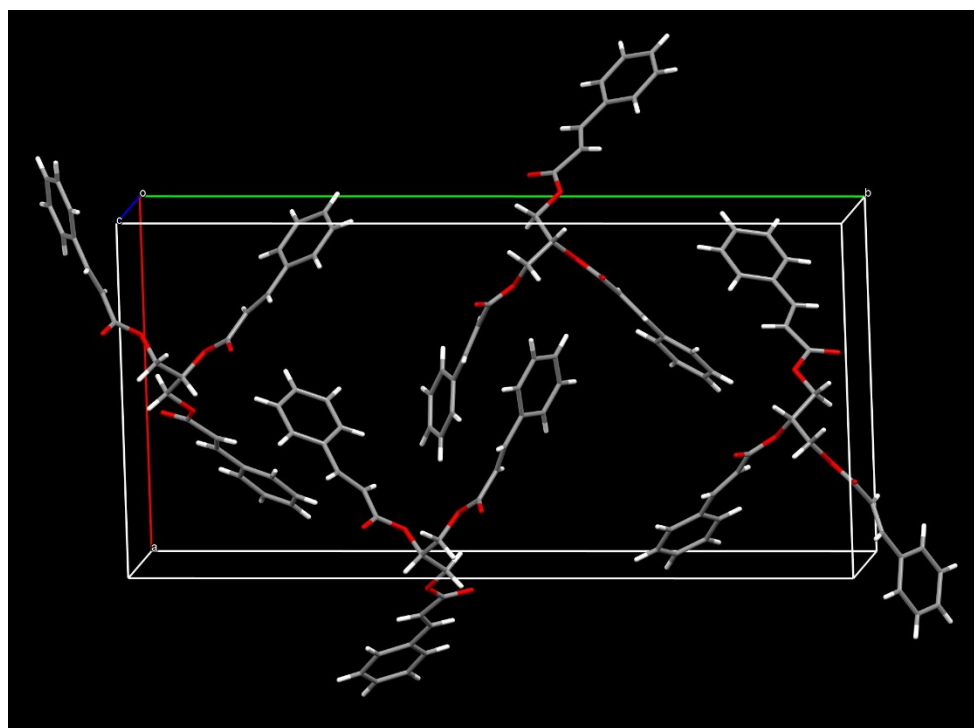
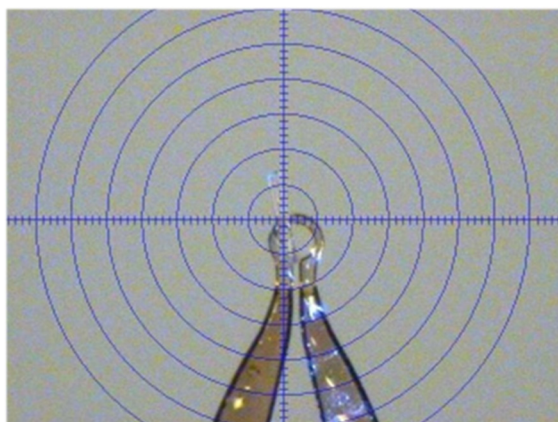


Figure S3 Image of a single crystal of glycerol cinnamate (top) and unit cell of glycerol cinnamate crystal structure (bottom).

4. TGA curve of CBDAT and glycerol cinnamate

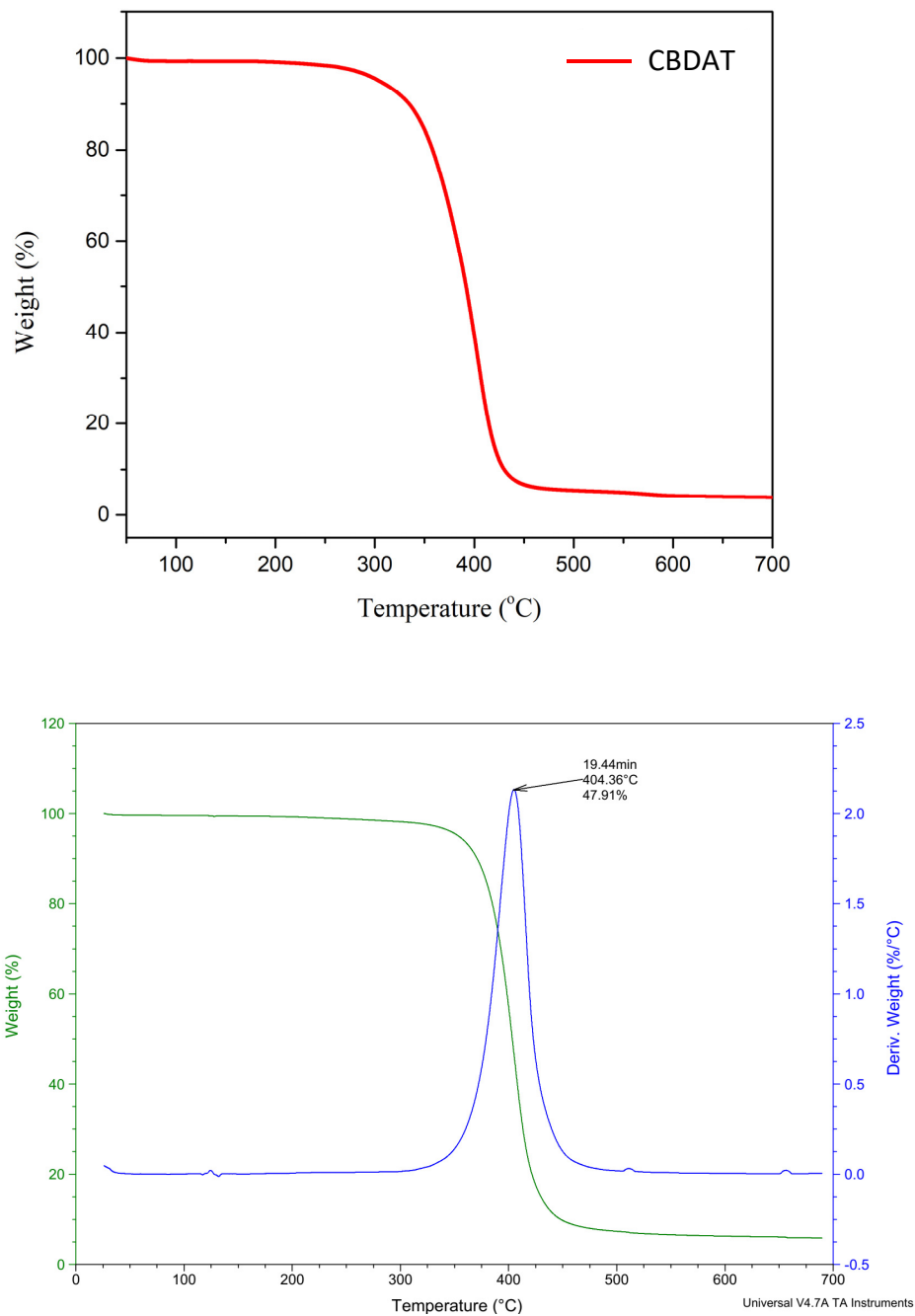


Figure S4 TGA curve of CBDAT (top). TGA and DTG curves of the degraded intermediate - glycerol cinnamate (bottom).

5. A Photo and SEM images of CBDAT

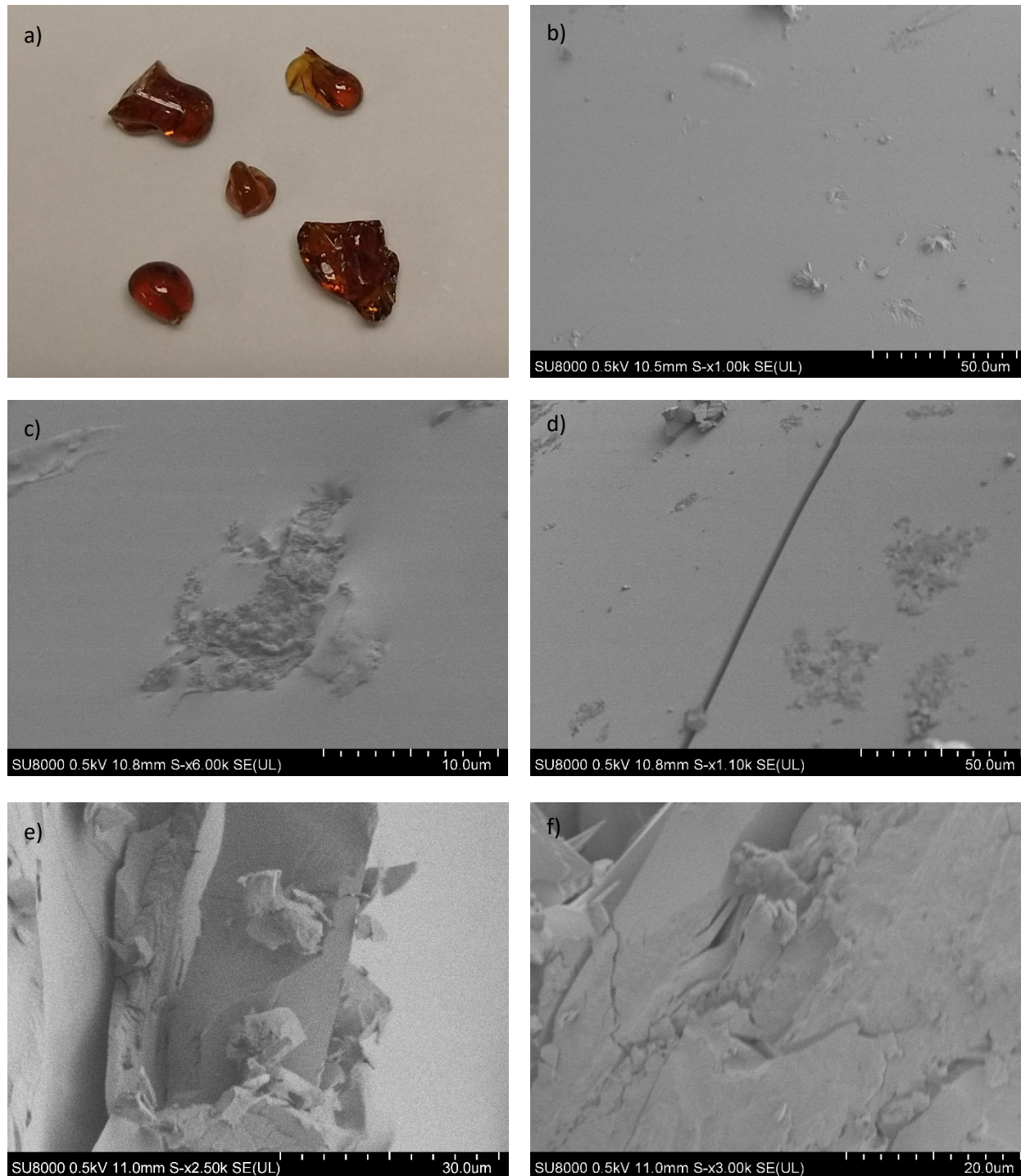


Figure S5 a) a photo of CBDAT obtained by melting polymerization without catalyst; b) SEM image showing the polymer surface; c) SEM image showing defects on the surface; d) SEM image showing a crack on the polymer; e-f) SEM images showing the cross-section of the polymer.