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

Journal:	*ChemComm*
Manuscript ID	CC-COM-03-2022-001502.R1
Article Type:	Communication

ChemComm

COMMUNICATION

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A novel class of recyclable thermoset has been developed from *cis*-3,4-diphenylcyclobutane-1,2-dicarboxylic acid (CBDA-4) due to its thermocleavability at high temperature. This key CBDA-4 building block was synthesized from β-*trans*-cinnamic acid using a [2 +2] photocycloaddition reaction. CBDA-4 was subsequently linked with glycerol *via* esterification to give a thermoset with T_g of 68 °C. The thermoset was heated to 300 °C to analyze its degradation. A key intermediate was successfully obtained after purification of the degraded polymer. NMR, FT-IR, HRMS, and single crystal X-ray diffraction confirmed the intermediate was glycerol cinnamate, which was the result of splitting cyclobutane in the polymer backbone at high temperature. Glycerol cinnamate was readily hydrolyzed reforming the starting materials glycerol and *trans*-cinnamic acid to complete the recycling loop.

The tremendous growth of plastic consumption has caused serious environmental problems.[1] This is not only because plastics are mostly generated from fossil-based resources,[2] but also due to their poor or non-existent recyclability. As a result, many of these plastics can persist in nature for hundreds of years.[3] A recent study showed that only about 9% of plastics were recycled, 12% were incinerated, and the rest were accumulated in our environment (e.g., landfills and oceans).[3a] Thermosets, also known as thermosetting plastics, are cross-linked polymers.[4] They have wide applications in many fields, including printed circuit boards, computer casings, coatings, polymer composites, adhesives, electrical insulation, medical equipment, aircraft and automotive industry because of their versatility and many excellent properties such as chemical resistance, low shrink properties, corrosive resistance.[5] For example, most of the polyurethanes in insulating foams, epoxy resin in adhesives, polyimides in circuit boards are thermosets. Although thermosetting polymers have a variety of applications and occupy a significant amount of the global polymers market, they cannot be re-melted or re-moulded once they are cured through cross-linking. Therefore, most of the thermosets are still considered as a notoriously non-recyclable class of plastics.[6 7]

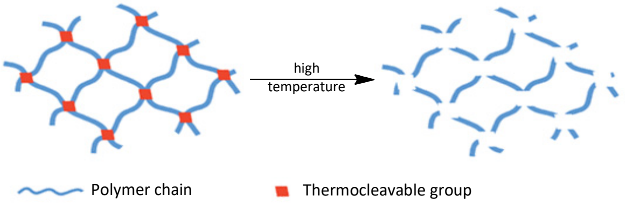

Fig. 1 Thermoset with built-in cleavable group breaking down at high temperature for chemically recycling.

Because study of recyclable thermosetting polymers has great significance for environment protection and sustainable development, numerous efforts have been made to develop recyclable thermosets.[8] The participants include companies such as IBM, Connora Technologies, etc.[9] Our research team has been exploring one aspect of the challenge by installing a thermocleavable group in the backbone of the thermoset, allowing the polymer to readily decompose at a desired high temperature for recovering the starting materials (Figure 1).[10] This advanced chemical recycling approach represents a promising way to recycle plastics that cannot be recycled via traditional mechanical recycling. It breaks thermosets down into starting materials readily, so they can be purified and used repeatedly.

In the effort of developing sustainable materials, our research group has synthesized and studied a series of biomass-derived cyclobutane diacid (CBDA) building blocks[11] and cyclobutane polymers (CBPs).[12] As an emerging building block in a variety of materials, cyclobutane-containing monomers have been able to introduce useful and novel properties into their corresponding materials.[13] For instance, some cyclobutane monomers are regarded as mechanophores, which can be readily cleaved in polymer chains upon external mechanical stimuli (e.g., sonication).[13a, 13b]

Herein, we demonstrated an engineered cyclobutane diacid thermoset (CBDAT) that poses chemical recyclability (Scheme 1). To prepare the thermoset, a *cis*-3,4-diphenylcyclobutane-1,2-dicarboxylic acid (CBDA-4) was used to serve two functions in tandem. First, as a key structural building block and second, as a cleavable (degradable) group. The latter is possible due to its thermocleavability at high temperature.[14] When the thermoset CBDAT heated at about 300 °C, it decomposed readily and no catalyst

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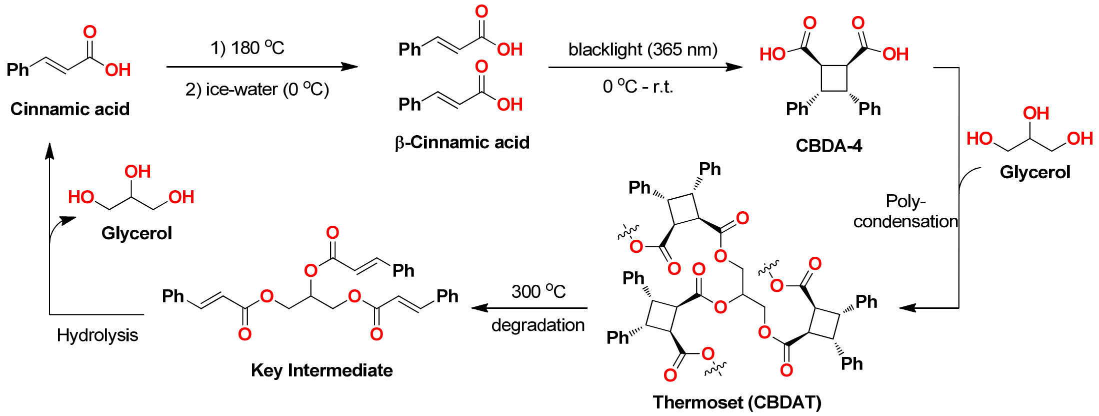
†Electronic Supplementary Information (ESI) available: Experimental details, characterization and properties of CBDA-4, CBDAT, and glycerol cinnamate, crystallographic data (CCDC: 2155526). See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of the thermoset CBDAT with built-in degradable group and its closed-loop chemical recycling process. (Only part of the repeating unit of the thermoset is shown for clarity.)

was needed. A crucial intermediate of the degraded product was captured and confirmed as glycerol cinnamate, which was readily hydrolyzed to offer the starting materials glycerol and *trans*-cinnamic acid to complete the closed loop recycling.

The building block CBDA-4 was prepared from β-*trans*-cinnamic acid via topochemical photodimerization[15] using ECO-UV (Scheme 1).[16] Specifically, *trans*-cinnamic acid was first melted and heated to 180 °C for 30 minutes and then cooled to room temperature. This preprocessed *trans*-cinnamic acid was dissolved in a small amount of DMF and added dropwise into a large amount of ice water. The precipitated crystalline powder, which was β-*trans*-cinnamic acid with head-to-head crystal packing, was kept in ice water and the slurry mixture was irradiated to give CBDA-4 as a white powder. Our previous work has elaborately described the synthetic approach of CBDA-4.[14] CBDA-4 was then connected with glycerol, a bioadvantaged chemical[11d] and waste product from the production of biodiesel from fats,[17] through an esterification reaction to form the thermoset (See Figure S5 in the ESI for images). FT-IR was used to track the synthesis of monomer CBDA-4 and the corresponding thermoset CBDAT (Fig. 2). Two peaks (1627 (C═C, stretching) and 976 (C═C–H, out of plane bending) cm^{-1}) corresponding to the double bond of *trans*-cinnamic acid vanished after photocycloaddition reaction in the FT-IR spectra. Meanwhile, the band 1671 (C═O, stretching) shifted to 1697 cm^{-1} which is attributed to the deconjugation of the carboxylic group from the rest of the molecule due to disappearance of the alkene group during the photodimerization. After esterification between CBDA-4 and glycerol, the band 1697 cm^{-1} (C═O, stretching) of CBDA-4 moved to 1729 cm^{-1} and the peak was broaden indicating the formation of the polyester.

A preliminary study showed that the results of Wolff-Wilborn and Shore D hardness tests of CBDAT were 2H and 57D, respectively. Meanwhile, CBDAT has excellent chemical resistance to most solvents (e.g., acetone, ethyl acetate, toluene, THF, DCM, DMF, and DMSO.) It is also important to point out that CBDAT exhibited no obvious degradation when it was treated with diluted acid (e.g., HCl) or base (e.g., NaOH). Although ester functional groups in small organic molecules can be readily hydrolyzed under acid or base conditions, the ester groups in CBDAT are buried in the gigantic cross-linked macromolecules with only limited surface area. Thus, it is difficult degrade thermosets such as Glyptal and CBDAT via hydrolysis. CBDAT also showed no obvious degradation after being exposed to sunlight for one month.

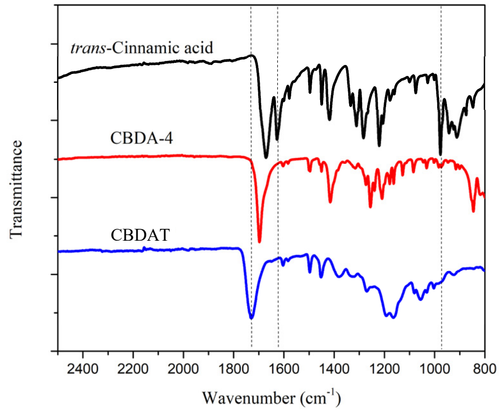


Fig. 2 FT-IR spectra of trans-cinnamic acid, monomer CBDA-4, and thermoset CBDAT.

Based on the previous study of CBDA-4,[14] we hypothesized that the thermoset CBDAT might be thermocleavable just like CBDA-4. To verify this hypothesis, the CBDAT was analyzed *via* thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA showed a 5% weight loss at 300 °C and the residue weight was 4% at 600 °C. Three heating-cooling cycles were applied to a CBDAT sample during the DSC test (Fig. 3). First two cycles were operated in the temperature range of 10 to 130 °C, which provided the glass transition temperature (T_g). T_g of the synthesized thermoset was 68 °C during the first heating process. A second T_g was observed at 74 °C which might be attributed to an annealing process that happened during the first heating and cooling cycle. A third heating-cooling cycle was used to test the thermal behavior at high temperature which was performed in temperature range of 10 to 300 °C. In the third heating process, the third T_g showed the same temperature as the second one. An endo thermal peak was observed at 265 °C. According to the thermostability of CBDA-4,[14] this peak might be corresponding to the thermocleavage of the thermoset CBDAT.

To further confirm the thermocleavability of thermoset CBDAT, a powder CBDAT sample of was placed in a Schlenk tube and purged with argon. The tube with sample were heated in a sand bath at 300 °C for five mins, and a brown solid was obtained. A key intermediate was isolated as a white powder after column chromatography. Subsequently, the structure was analyzed by using FT-IR, NMR, HRMS and single crystal X-ray diffraction. FT-IR spectrum of the intermediate showed two new bands (1635 and 971 cm^{-1}) after degradation (Fig. 4). The two new bands are similar to the C═C,

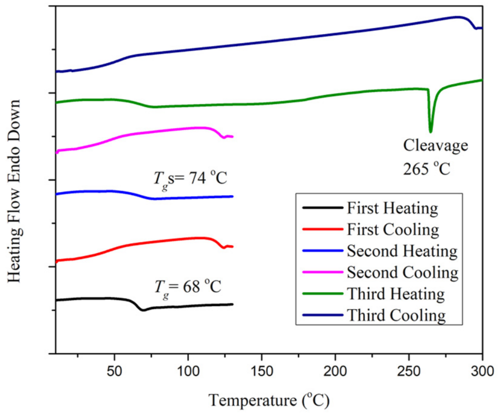


Fig. 3 DSC curves were recorded from 10 to 130 °C at the first and second heating. At the third heating-cooling cycle was recorded from 10 to 300 °C with a heating rate of 20 °C·min^{-1} under N_2 atmosphere.

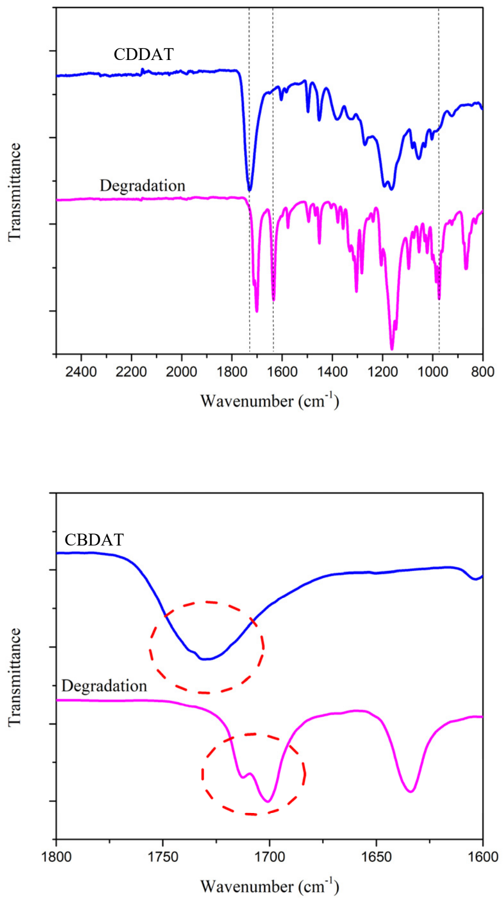


Fig. 4 FT-IR spectra of thermoset CBDAT and the degraded intermediate. The bottom image is the magnification of the two carbonyl (C=O) stretching peaks in the spectra.

stretching and C═C–H, out of plane bending in the spectrum of *trans*-cinnamic acid (1627 (C═C, stretching) and 976 (C═C–H, out of plane bending) cm^{-1}). Peaks at 1714 and 1701 cm^{-1} show two carbonyl groups with different chemical environment, which is similar to the two bands of thermoset CBDAT. ^{1}H NMR spectrum of CBDA-4 has two *sp*^{3}C peaks from the cyclobutane ring (δ: d, 4.22 ppm, J = 4.5 Hz and d, 3.82 ppm, J = 4.5 H) while *trans*-cinnamic acid contains two C=C bond peaks (Fig. 5). After degradation ofCBDAT, two pairs of new C=C bond peaks appeared in the spectrum of the intermediate, and the peaks corresponding to ones next to the carbonyl groups at 6.67 (d, J = 16 Hz) and 6.69 (d, J = 16 Hz) ppm are showed in the inset of Figure 5. The integration of the peak at 6.67 ppm was as twice as the one at 6.69 ppm, which indicated two equal double bonds and one unequal double bond. The peaks at 4.44 and 4.53 pm are corresponding to the -C$\underline{H}_2$-O- in glycerol moiety, and the one at 5.50 ppm is the -C$\underline{H}$-O- group. The three protons of the Ph-C$\underline{H}$═CH- and three phenyl groups appear between 7 and 8 ppm. Therefore, it was proposed that the intermediate is glycerol cinnamate. HRMS (found: 505.1701) was also consistent with the molecular weight of glycerol cinnamate (calculated $[C_{30}H_{26}O_6Na]^+$ 505.1627).

High quality single crystals of the degraded intermediate, glycerol cinnamate, were yielded from its DMF solution. The crystal data were collected at 100 K. The glycerol cinnamate adopts a cone shape conformation in the crystal with orthorhombic crystal system and Pna2$_1$ space group (Figure 6 and ESI). The repeating distance on *c* axis was 5.64 Å.

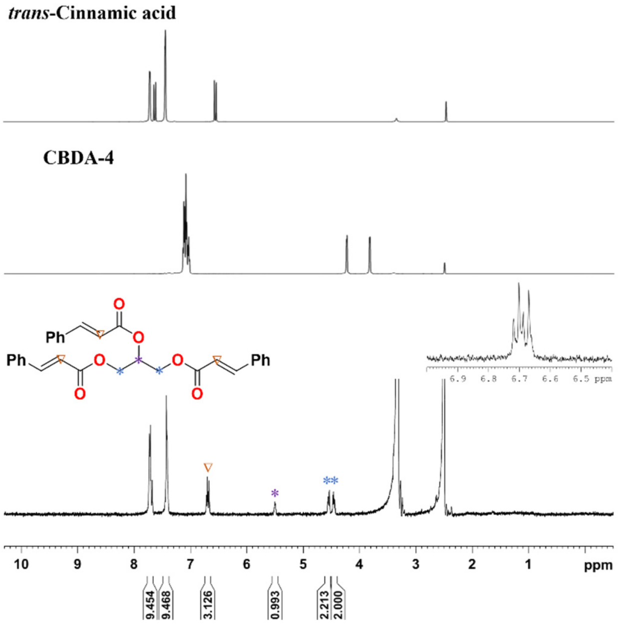


Fig. 5. ^{1}H NMR spectra of *trans*-cinnamic acid (top), CBDA-4 (middle), and glycerol cinnamate (bottom). The inset is the magnification of glycerol cinnamate spectrum (6.4 - 7.0 ppm). ^{1}H NMR was performed in DMSO-d_6.

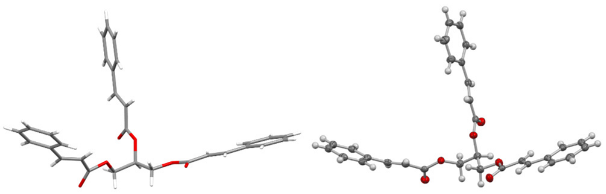
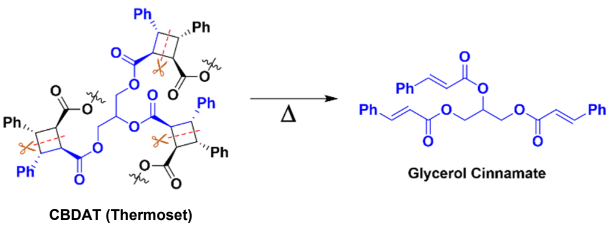


Fig. 6 the X-ray structures of glycerol cinnamate: a) Capped Stick Style of the key intermediate, b) Oak Ridge Thermal Ellipsoid Plot (ORTEP) representing at 50% electron density. (Hydrogens are shown in 25% electron density for clarity.)



Scheme 2. Proposed route for the thermoset degradation.

The isolated glycerol cinnamate was then hydrolyzed in the presence of KOH to offer the starting materials *trans*-cinnamic acid and glycerol in high yields. Thermoset CBDAT synthesized using the recycled monomers showed identical chemical and physical properties with "freshly" prepared thermoset CBDAT, showing the completion of the closed loop chemical recycling.

In summary, we synthesized a potentially recyclable thermoset CBDAT from β-*trans*-cinnamic acid and glycerol. The preliminary test of the chemical recyclability of the thermoset was carried out and the structure of a degraded key intermediate, glycerol cinnamate, was confirmed by several independent techniques including single crystal X-ray diffraction. The cyclobutane moiety served as a built-in cleavable group in the backbone of the thermoset. At about 300 ^{o}C, the cyclobutane was split into two double bonds allowing the polymer to decompose readily (Scheme 2). The glycerol cinnamate was further hydrolyzed back to the initial starting materials readily to complete the recycling loop. The approach of breaking down polymers with embedded cyclobutane thermocleavable groups at high temperature avoids the use of any expensive ligand and metal catalyst, which can be poisoned by the impurity introduced to the plastics during their use. This promising chemical recycling approach paves the way for facile and scalable chemical recycling of polymers that are traditionally difficult or impossible to recycle mechanically.

The authors are grateful for financial support of this work by the National Science Foundation Grant (NSF EPSCoR Award IIA-1355466) and United States Department of Agriculture (USDA–NIFA, Sun Grant Funding Award 3TN372).

Conflicts of interest

There are no conflicts to declare.

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