

Supplementary Information

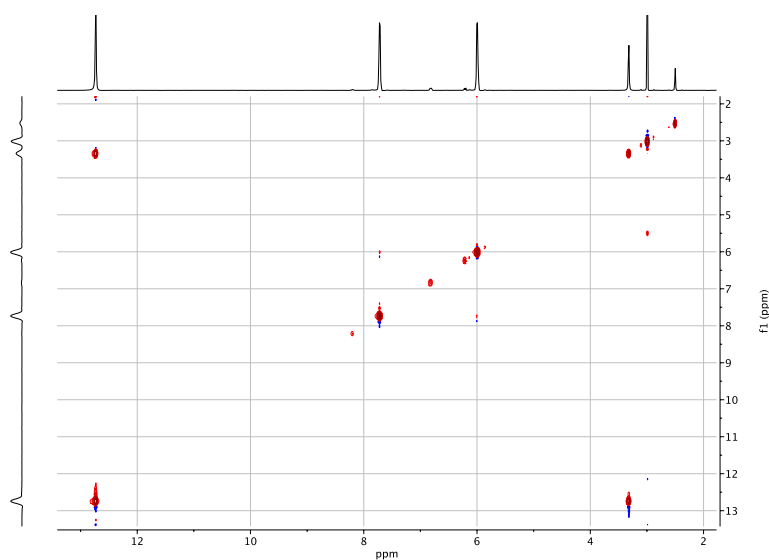
Solvent-driven isomerization of *cis,cis*-muconic acid for the production of specialty and performance-advantaged cyclic biobased monomers

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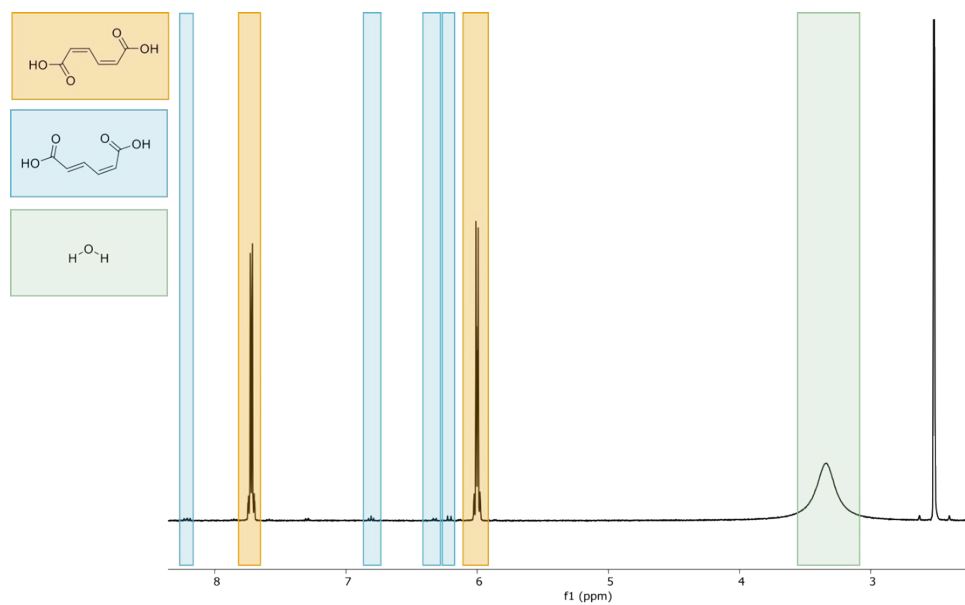
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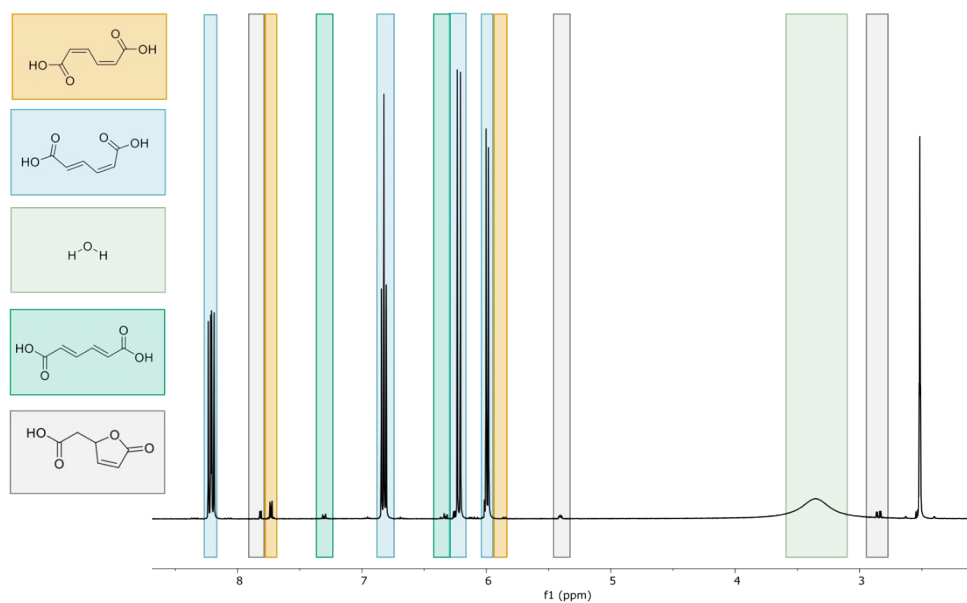
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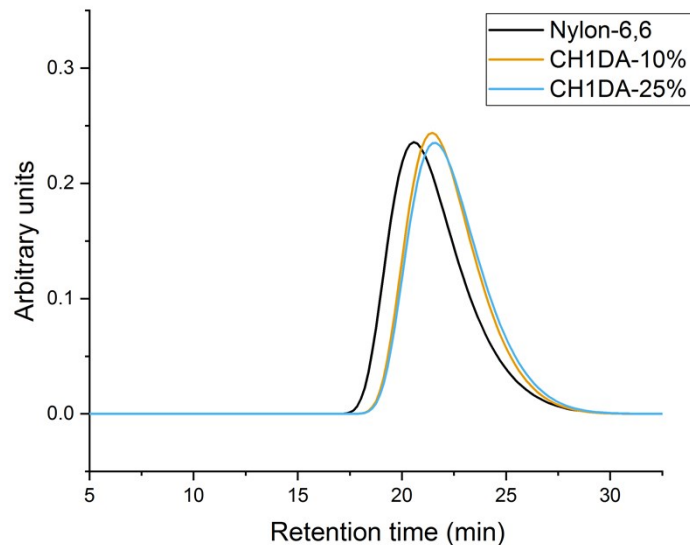
ESI 1. NOESY NMR spectrum indicating water interactions with carboxyl moieties in MA.



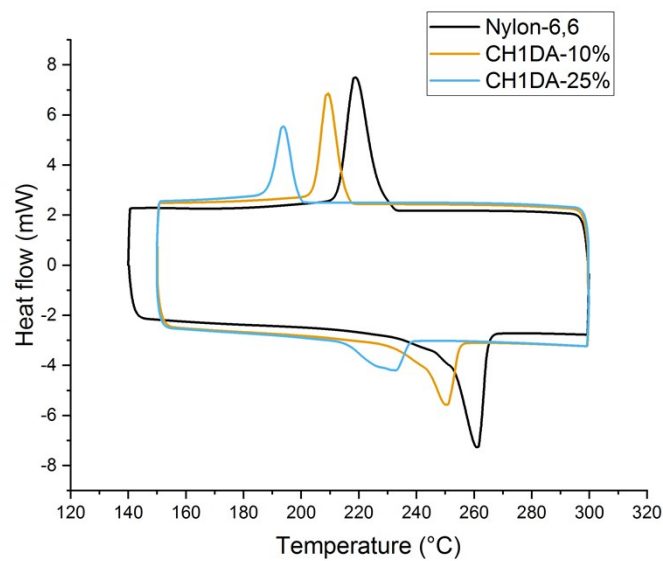
ESI 2. ^1H NMR spectrum of biobased *cc*MA in DMSO-d_6 obtained after filtration of fermentation broth over activated carbon followed by precipitation using sulfuric acid, rinsing, and drying.



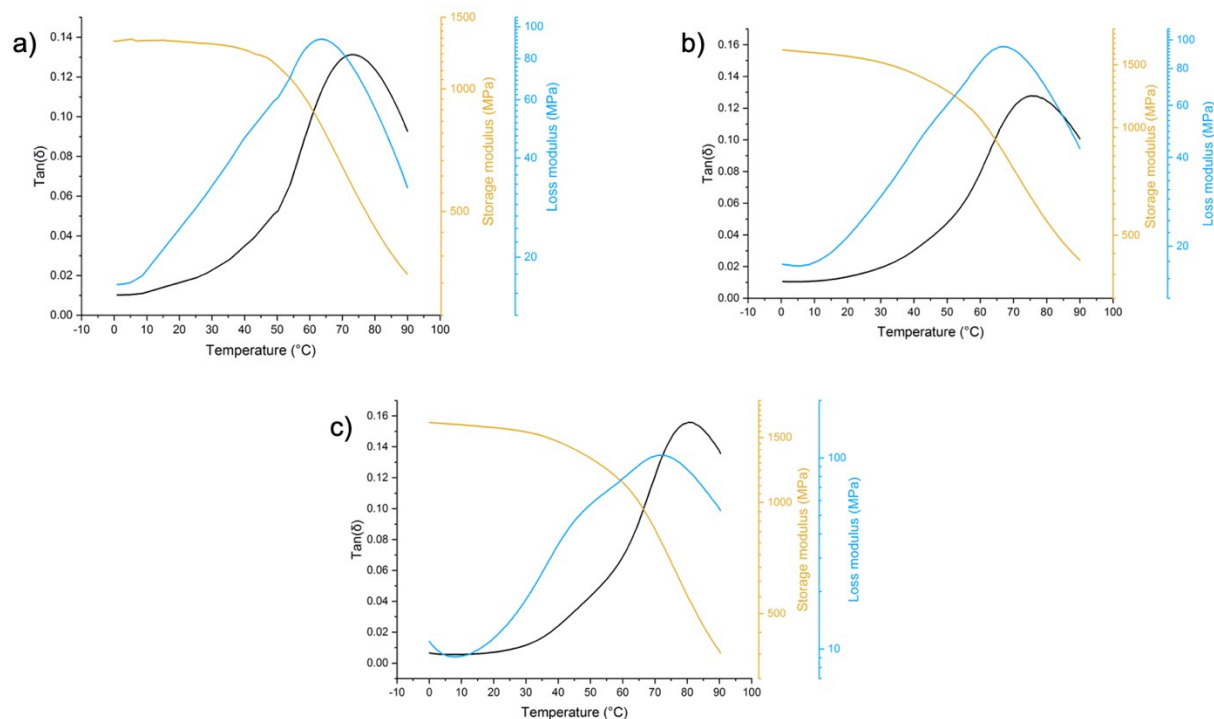
ESI 3. ^1H NMR spectrum of biobased *ct*MA in DMSO-d_6 obtained through isomerization of biologically-produced *cc*MA. Residual sulfuric acid from the initial separation-purification of *cc*MA catalyzed the lactonization of *cc*MA during the isomerization to *ct*MA.



ESI 4. Gel-permeation chromatograms (GPC) of cyclo-aliphatic polyamides were carried out in hexafluoroisopropanol (HFIP) with respect to poly(methyl methacrylate) standards fitted to Nylon-6,6 standards purchased from American Polymer Standards. A Tosoh Ecosec HLC-8320GPC equipped with RI and UV detectors was used to determine the molecular weight of each sample. The GPC column included a Tosoh TSKgel SuperH6000 (150 x 6.0 mm) in series with two Agilent PL HFIPgel columns (250 x 4.6 mm). HFIP was used as the eluent in combination with sodium trifluoroacetate to prevent sample aggregation at a concentration of 0.02 mol/L HFIP (1.7 g/kg HFIP). Each sample had an injection volume of 10 μ L and was analyzed at 45 $^{\circ}$ C under a 0.3 mL/min flow rate.



ESI 5. Differential scanning calorimetry (DSC) measurements of the synthesized polyamides were carried out with sample sizes of around 5 mg using a TA Q100 instrument. Samples were held isothermally at 150 °C for 2 minutes, heated to 300°C, and cooled back down at 10 K/min and repeated thrice. Results shown here are for the 3rd cycle.



ESI 6. Dynamic Mechanical Analysis (DMA) of polyamide series with varying CH1DA incorporation: (a) Nylon-6,6 (b) CH1DA-10% (c) CH1DA-25%. DMA specimens were prepared by injection molding with a Haake MiniLab extruder into ISO 527-2-1BB model, followed by annealing for 6 h at 150 °C. DMA experiments were conducted using a TA Ares G2 in torsion mode heating at 5 °C min⁻¹ from 0 to 90 °C in the linear viscoelastic regime at $\omega = 10$ rad s⁻¹.

Isomerization of biobased ccMA

Biologically-produced *ccMA* was recovered from a high-titer fermentation broth at neutral pH. In addition to muconate, the broth contained a range of biogenic impurities, unreacted sugars, and inorganic salts. 200 ml of broth were first filtered over 20 g of activated carbon (DARCO® KB-WJ) to remove the organic impurities that give the broth its characteristic brown color. A clear solution was recovered and *ccMA* was subsequently precipitated by acidifying the filtrate using 5 M sulfuric acid until reaching pH 0. *ccMA* was filtered, rinsed with 10 ml of 5 M sulfuric acid, and dried at room temperature overnight. The sample was further isomerized to *ctMA* using the same procedure as for commercial, high-purity, *ccMA*.

Hydrogenation of CH1DA

CH1DA was esterified with methanol in the presence of H_2SO_4 to obtain cyclohex-2-ene-1,4-dimethyl ester (CH2DAME2) (>94% yield). This esterification resolved the solubility challenges that were due to CH1DA, thereby facilitating the hydrogenation step. The hydrogenation was then performed in a stainless-steel three-phase plug flow reactor using 10 mg of 5% Pt/C catalyst, diluted with 100 mg of glass beads (45–90 μm). The reaction was conducted at 250 °C and 20 ml min^{-1} of gas flow. The reaction temperature was maintained using a PID controller and the gas flow was regulated using a Brooks SLA5850 flow controller. The reactor was operated in an up-flow configuration, and the reactant dissolved in dioxane (11.4 mg ml^{-1}) was pumped at 0.4 ml min^{-1} using a Lab Alliance Series I HPLC pump. Product samples were collected every 15 minutes and were analyzed using ^1H NMR. The corresponding saturated ester (CHDAME2) was obtained with 92% yield at 97% conversion.