Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information
Fully Biomass-Derived Vitrimeric Material with Water-Mediated Recyclability and Monomer Recovery

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Small molecule NMR model studies of acetal exchange

All small molecule studies were performed in an NMR tube with furfural-acetyl (0.2 mmol, 1 eq), sorbitol, (0.2 mmol, 1 eq), and 1,3,5-trimethoxybezene (0.06 mmol, 0.3 eq) as an internal standard in DMSO-d_6 (0.55 mL).

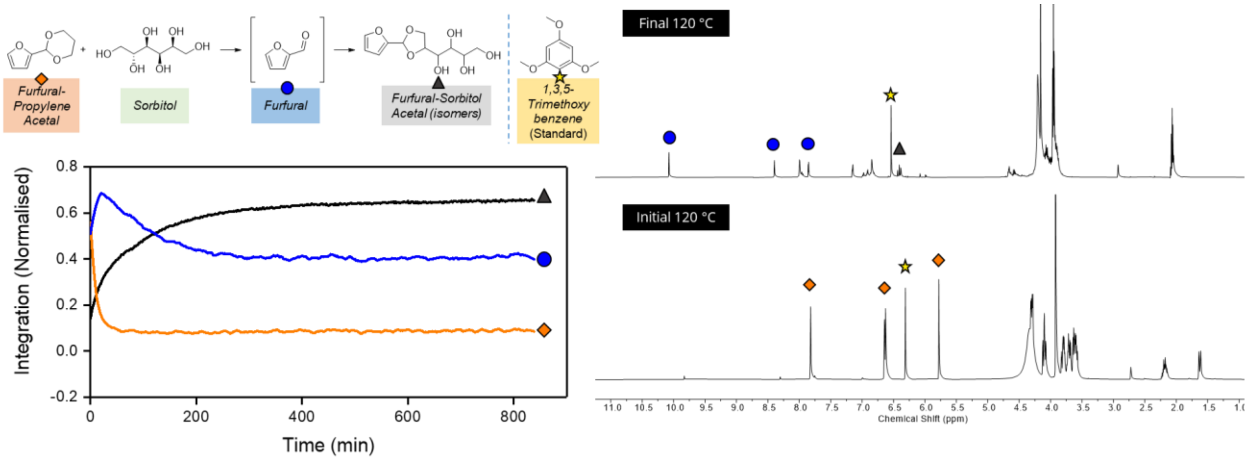


Figure S1: Reaction profile of Furfural-propylene acetal with sorbitol, with TsOH catalyst (5 mol%) at 120 °C.

Small molecule GC-MS model studies of acetal exchange

Furfural-ethylene acetal (1.2 mmol, 1 eq), sorbitol (1.2 mmol, 1 eq), and 1,3,5-trimethoxybenzene (0.36 mmol, 0.3 eq) as an internal standard was stirred in DMSO (3.3mL) at 120°C. GC-MS samples of the reaction mixture was taken every 3 hours and quenched by cooling. Trace furancarboxylic acid, together with acetal exchange products, was found after 9h.

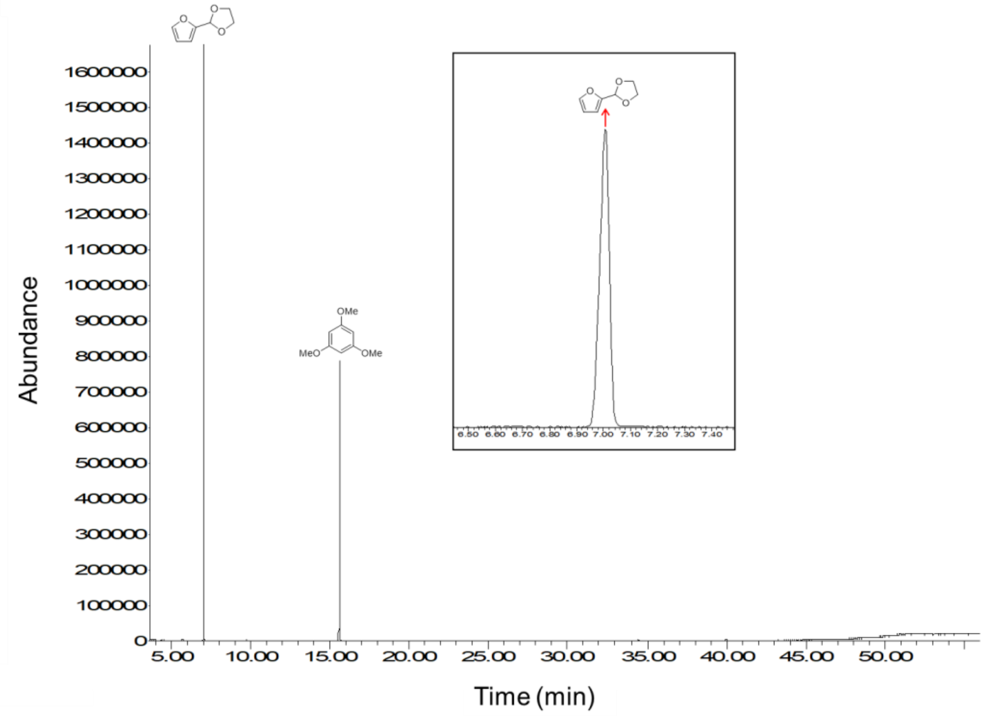


Figure S2a: GCMS spectrum of uncatalyzed acetal exchange at 0 h.

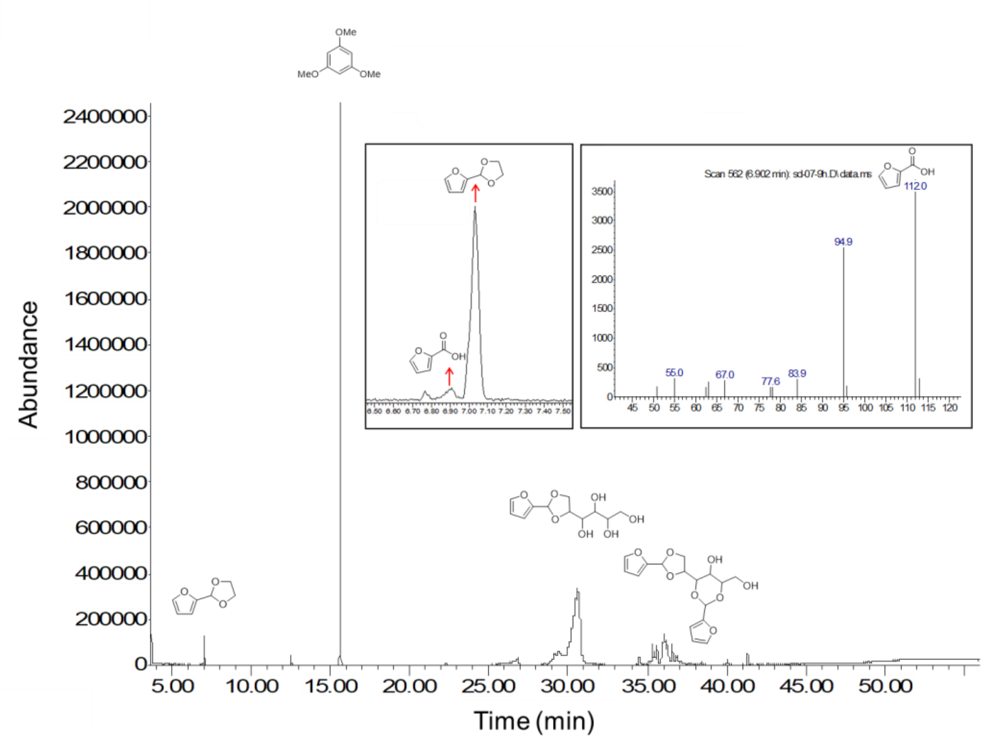
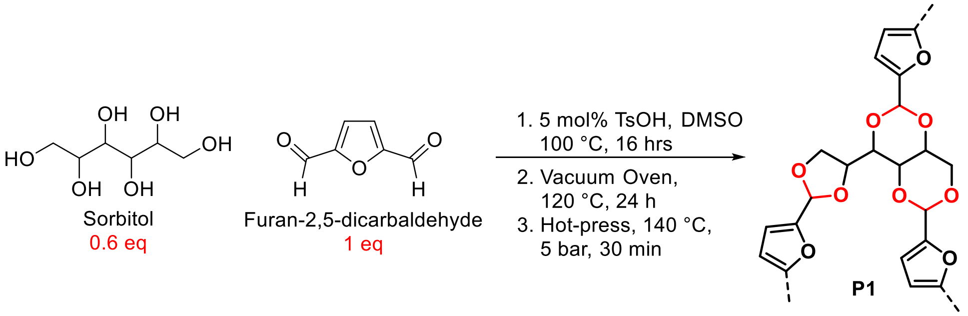


Figure S2b: GCMS spectrum of uncatalyzed acetal exchange at 9 h.

Synthesis and Characterization of polymer



Scheme S1. Synthesis of **P1** from furan-2,5-dicarbaldehyde and sorbitol

To a Teflon beaker with stirrer bar was added furan-2,5-dicarbaldehyde (6.2 g, 50 mmol, 1 eq), sorbitol (5.45 g, 30 mmol, 0.6 eq) and DMSO (10 mL). The mixture was then heated at 100 °C for 16 hours under steady stream of nitrogen. The gel-like mixture was then transferred to a Teflon dish and further cured in a vacuum oven at 120 °C overnight. The sample was obtained as a brown solid (**P1**, 9.44g, 85%).

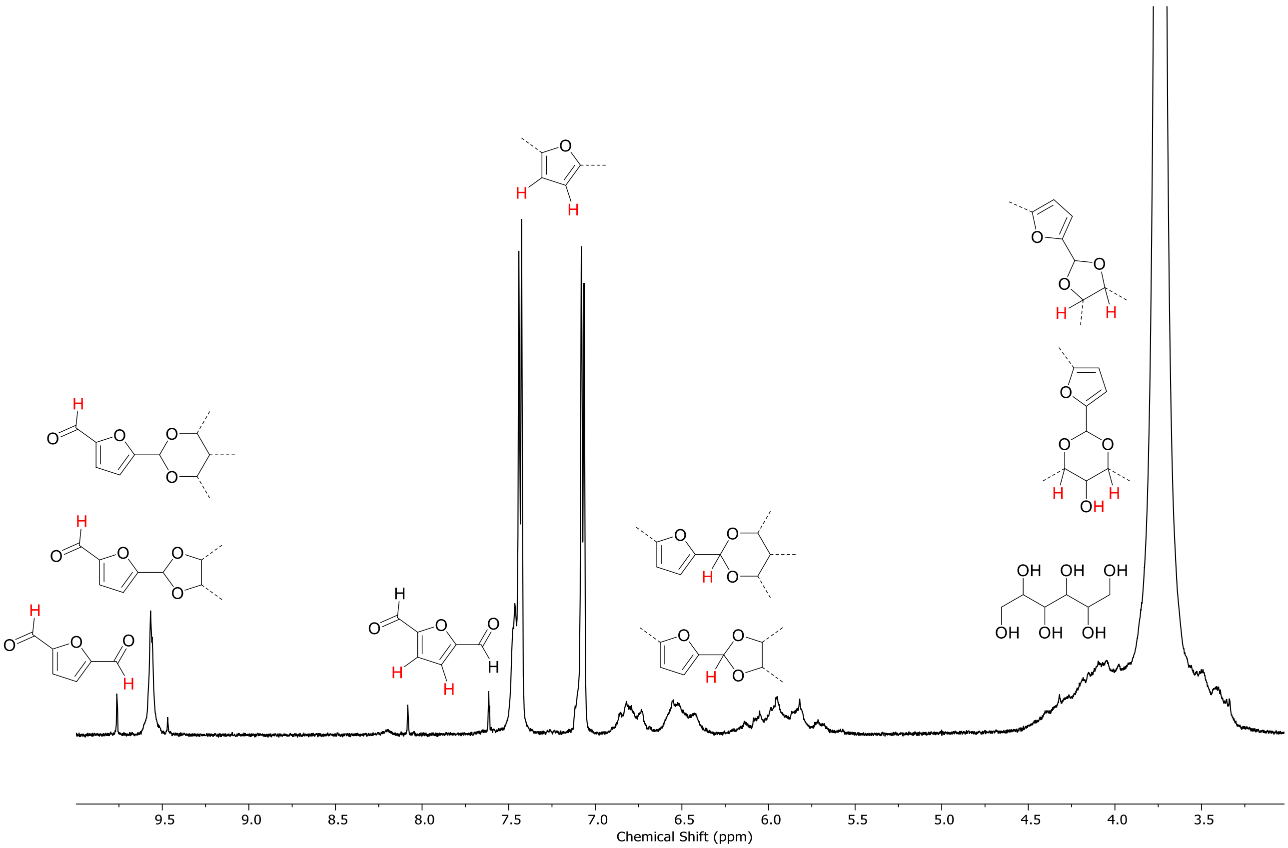


Figure S3: NMR of pre-cured oligomers of **P1**.

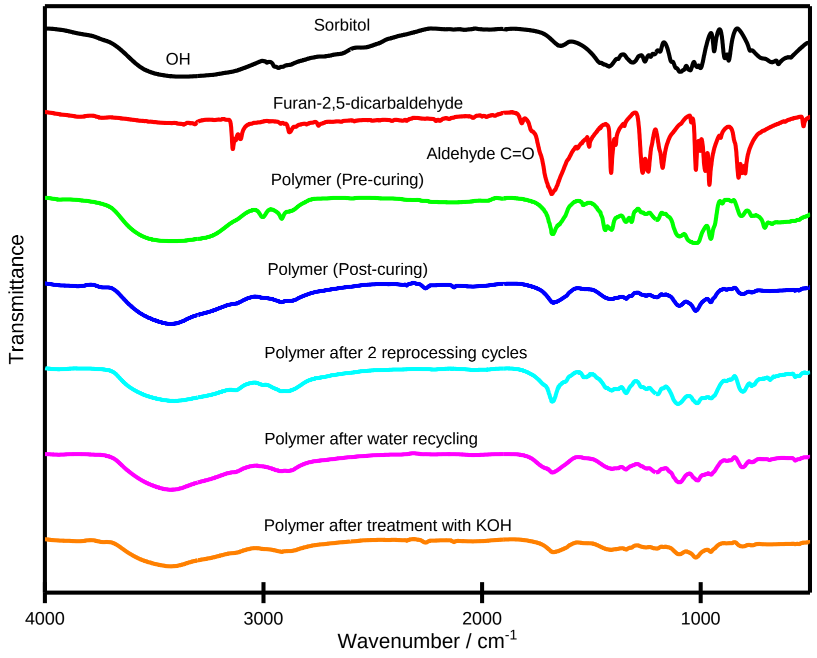


Figure S4: FTIR of the starting materials, the polymer network pre and post curing, as well as after 2 reprocessing cycles, water-mediated recycling, and treatment with KOH.

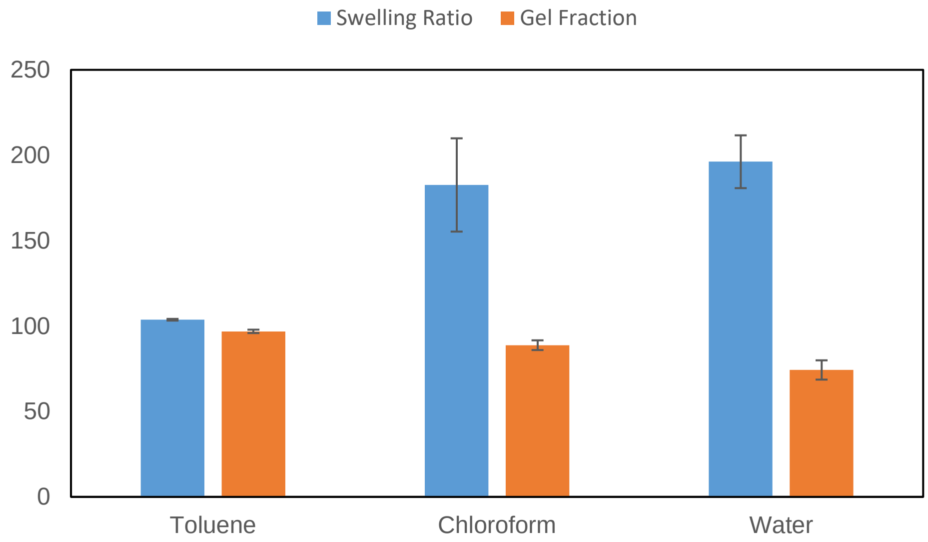


Figure S5: Swelling ratio and gel fraction of **P1** in toluene, chloroform, and water.

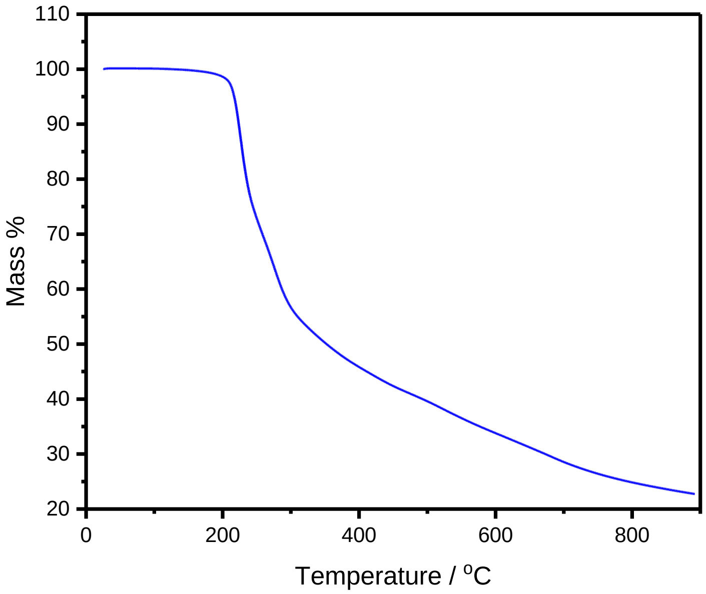


Figure S6: TGA of polymer **P1**. $T_{d5\%}$ was found to be 216 °C.