Supporting Information

Durable, Acid-Resistant Copolymers from Industrial By-Product Sulfur and Microbially-Produced Tyrosine

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Synthesis of tetraallyltyrosine.

To a 500 mL round bottom flask equipped with a Teflon-coated magnetic stir bar was added 9.988 g (0.055 mol) of L-tyrosine and 150 mL of dimethylformamide, the solution was stirred until complete dissolution of tyrosine followed by the addition of 18.216 g (0.325 mol) of KOH. 54.6 g (0.451 mol) of allyl bromide was added drop-wise using an addition funnel, following complete addition of allyl bromide the flask was then equipped with a water-cooled reflux condenser and placed in a 60 °C oil bath and stirred for 24 h. The flask was cooled to room temperature and 100 mL of 0.5 *M* HCl(*aq*) was added to the reaction mixture and extracted with dichloromethane (4 × 150 mL). The organic layer was collected and washed with deionized water (4 × 200 mL) and the solvent was evaporated under reduced pressure. The remaining liquid was passed through a 5-cm high silica plug in a 150 mL fritted funnel using dichloromethane as the solvent. The product was collected as a yellow liquid (6.924 g, 37%).

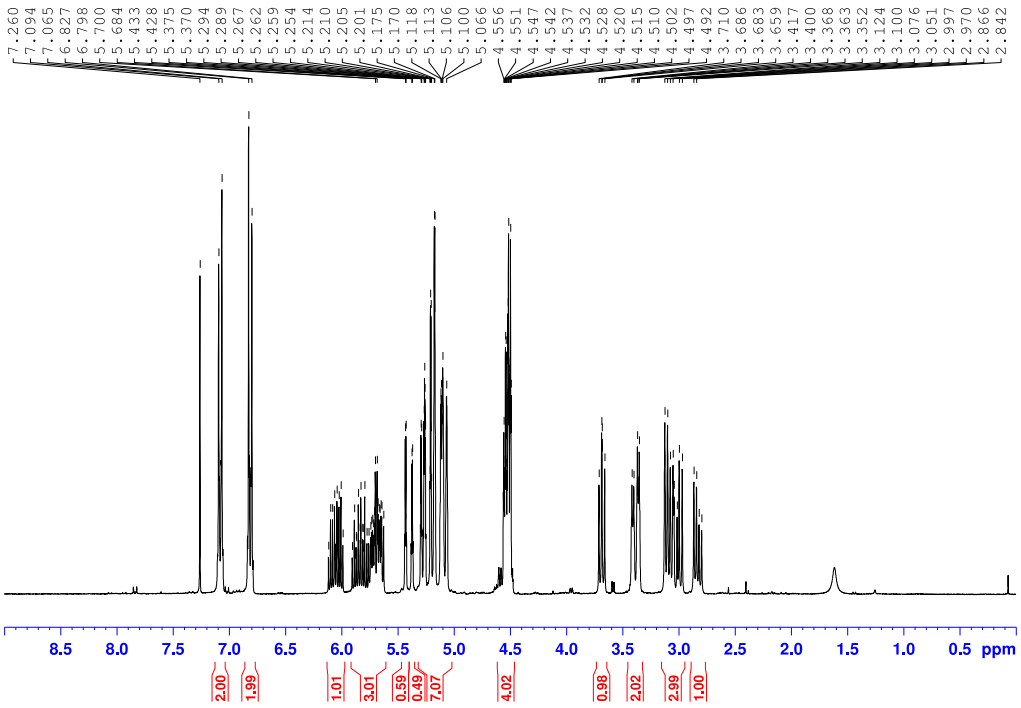

Figure S1. Proton NMR spectrum of tetrallyltyrosine in $CDCl_3$.

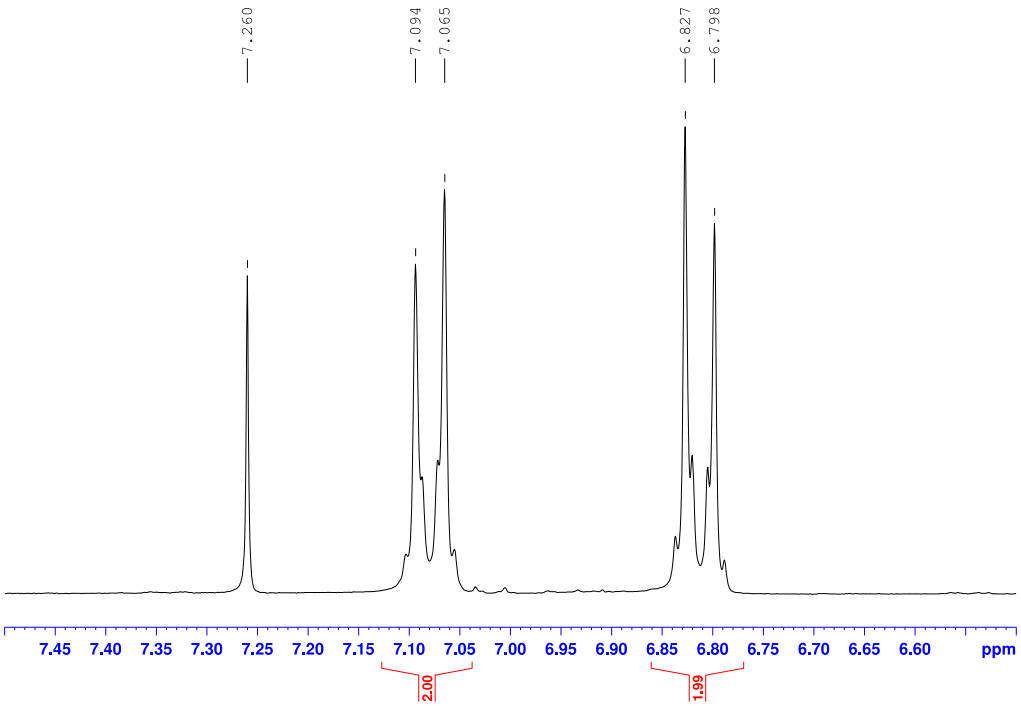

Figure S2. Inset of ^{1}H NMR spectrum between 6–7.5 ppm of tetrallyltyrosine in $CDCl_3$.

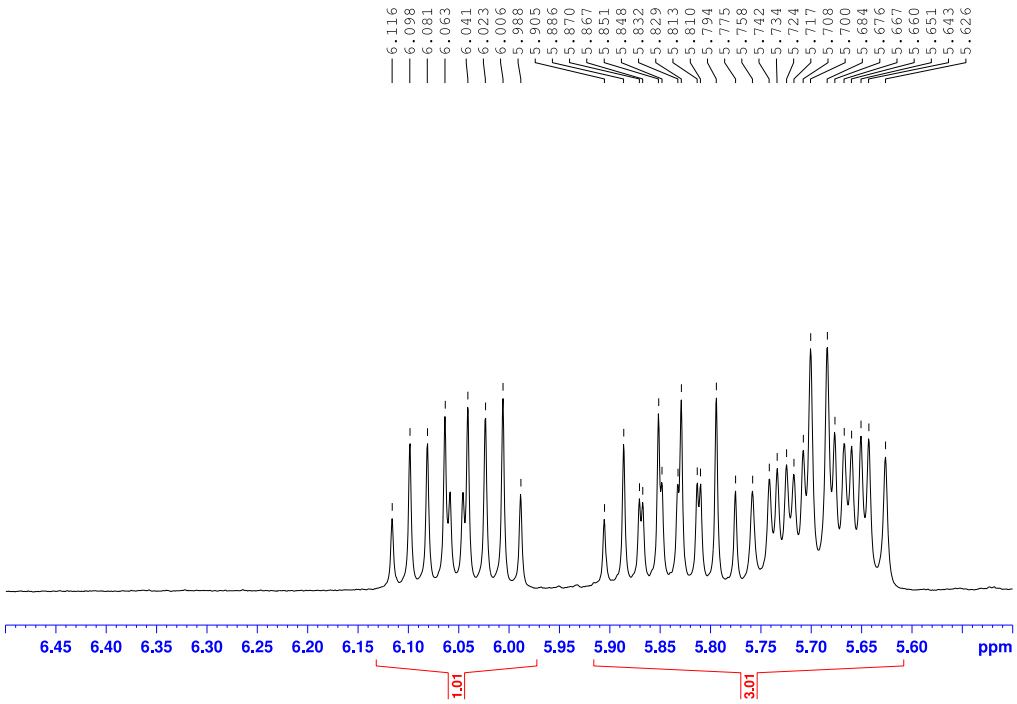

Figure S3. Inset of ^{1}H NMR spectrum between 5.5–6.5 ppm of tetrallyltyrosine in $CDCl_3$.

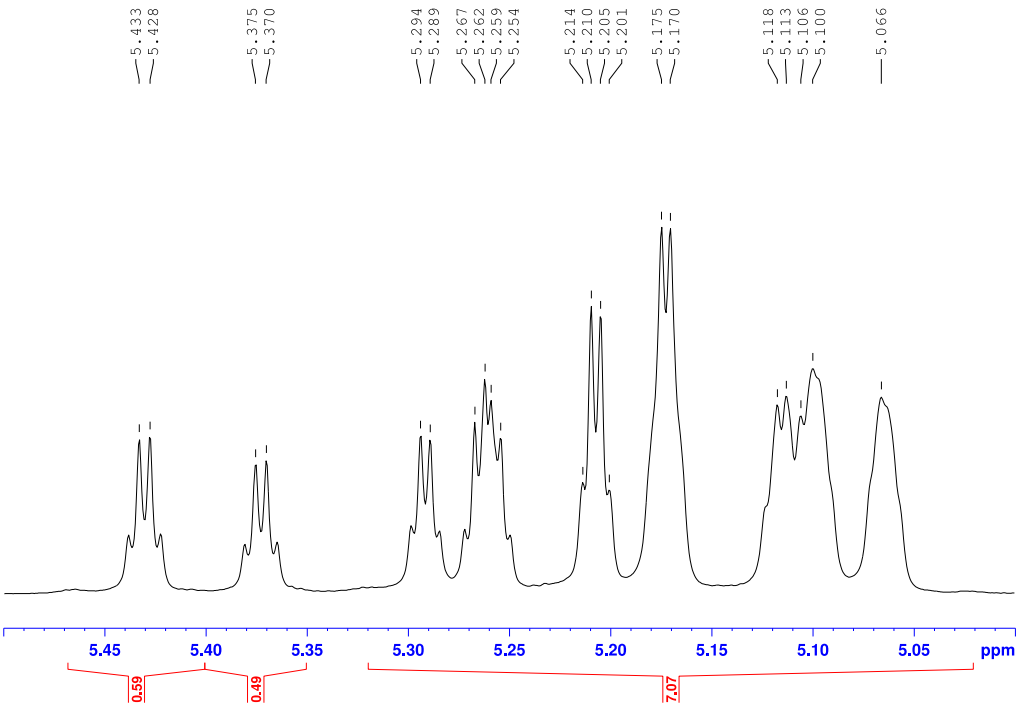

Figure S4. Inset of ^{1}H NMR spectrum between 5–5.5 ppm of tetrallyltyrosine in $CDCl_3$.

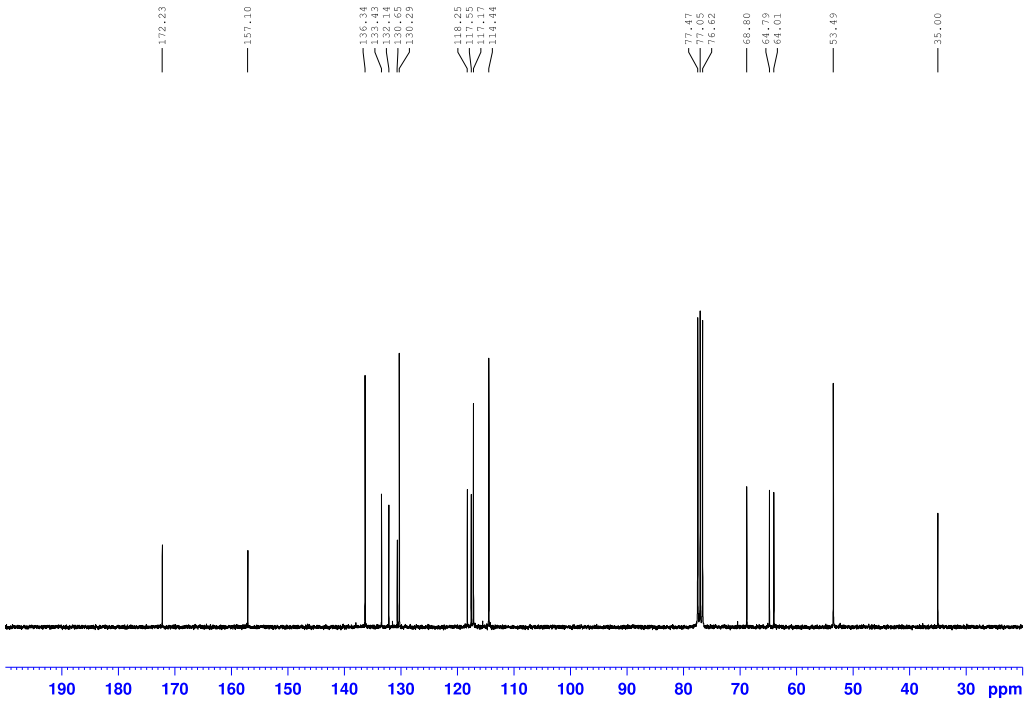

Figure S5. Carbon-13 NMR spectrum of tetrallyltyrosine in $CDCl_3$.

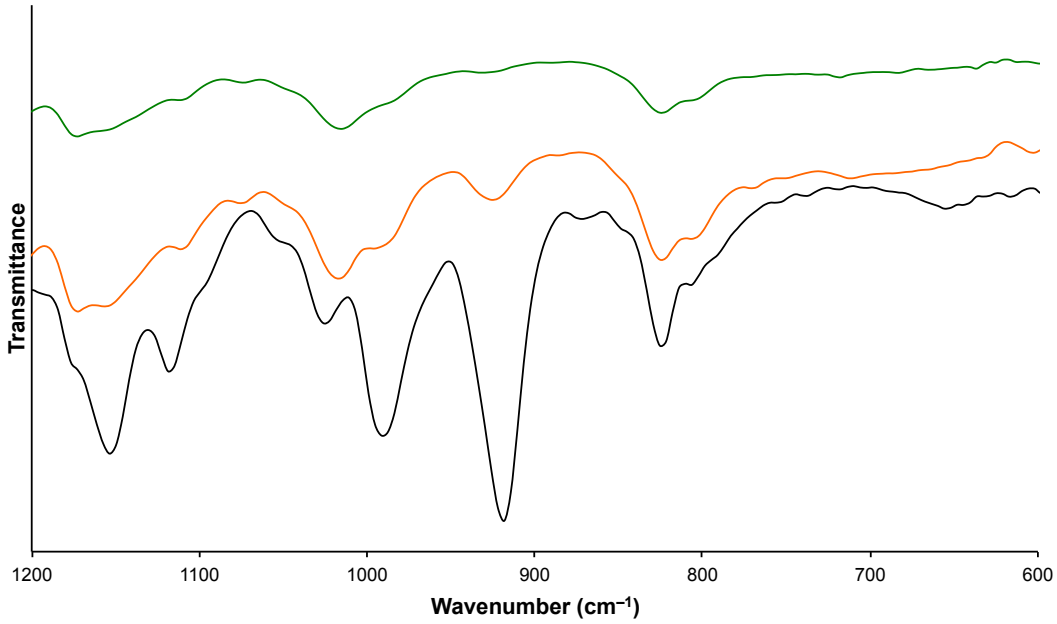

Figure S6: Infrared spectra of **TTS_{30}** (green), **TTS_{50}** (orange), and **tetraallyltyrosine** (black) between 600-1200 cm^{-1}.

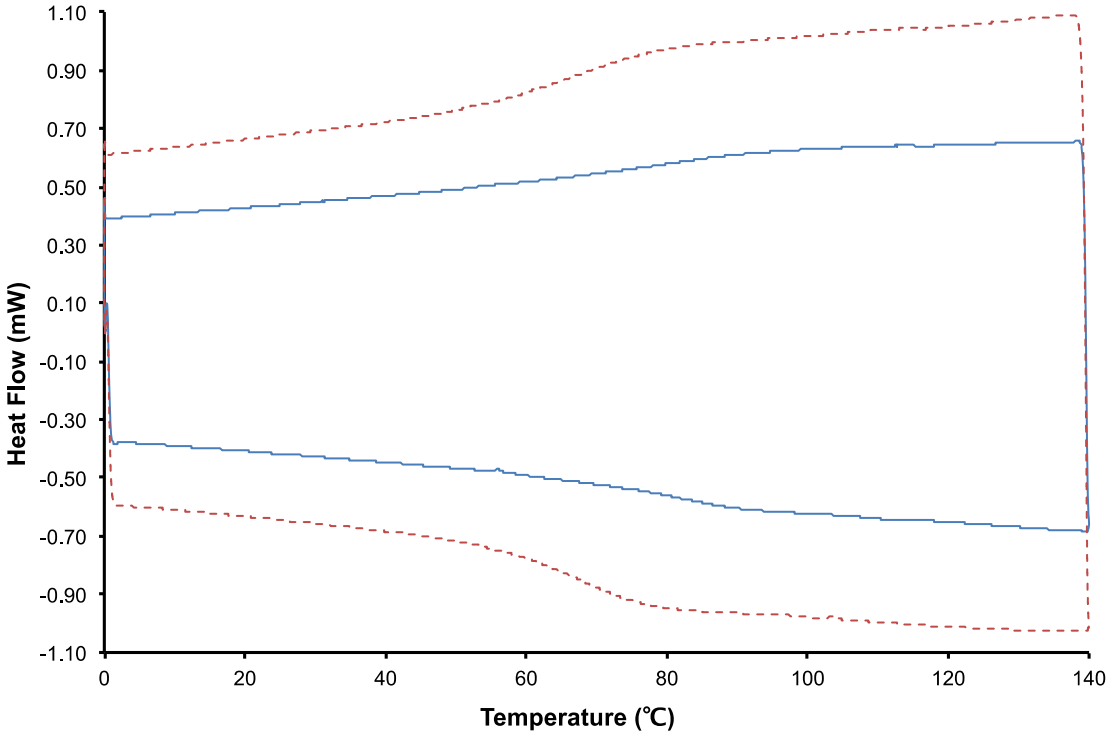

Figure S7: DSC curves for **TTS_{30}** (blue line) and **TTS_{50}** (red dashed line). Curves represent the third heat/cool cycles.

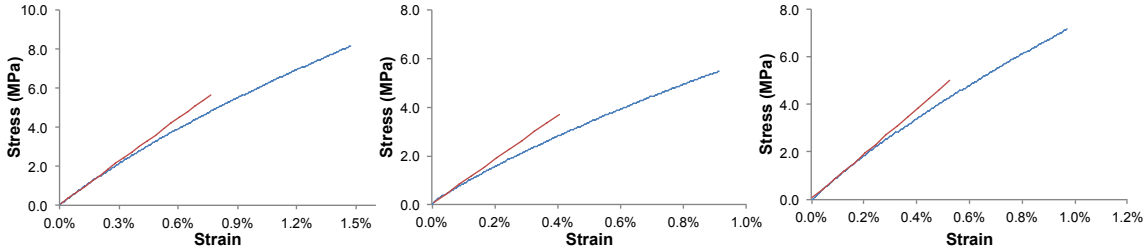

Figure S8: Trials 1, 2, and 3 of **TTS_{30}** stress strain measurements where the red line is the propagation of the linear region of the respective stress strain curve.

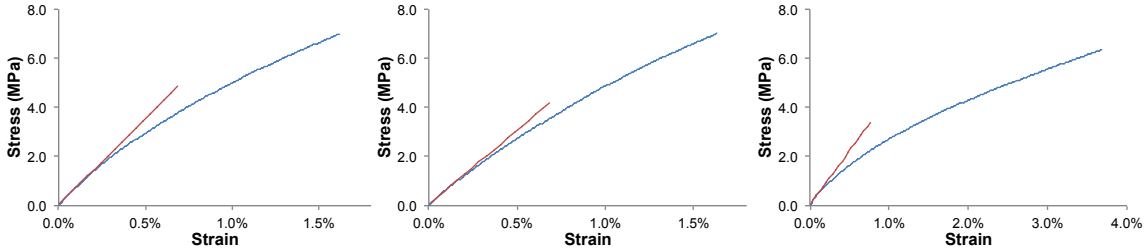

Figure S9: Trials 1, 2, and 3 of **TTS_{50}** stress strain measurements where the red line is the propagation of the linear region of the respective stress strain curve.