

Electronic Supplementary Information for:

One Pot Route to Aryl Halide/Sulfur/Olefin Terpolymers via Sequential Crosslinking by Radical-Initiated Aryl Halide-Sulfur Polymerization, Inverse Vulcanization, and Sulfenyl Chloride Formation

*Nawoda L. Kapuge Dona and Rhett C. Smith**

Department of Chemistry, Clemson University, Clemson, SC, 29634, USA; rhett@clemson.edu

**Email: rhett@clemson.edu*

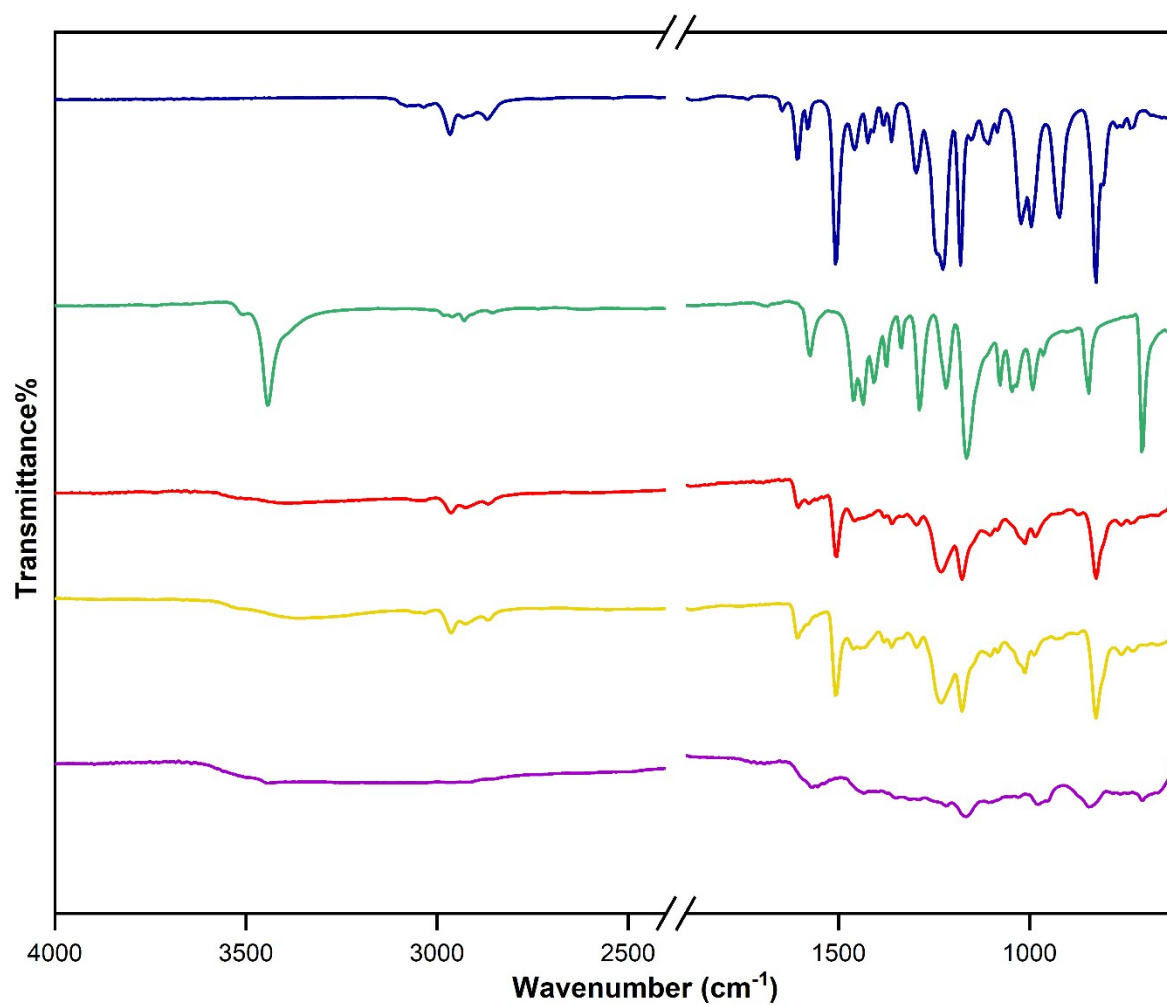


Figure S1. Infrared spectra of *O*, *O*'-diallylbisphenol A (blue line), 2,4-dichloro-3,5-dimethylphenol (green line), **DACIS**₅₁ (red line), **DAS**₅₀ (yellow line), and **DS**₈₁ (purple line).

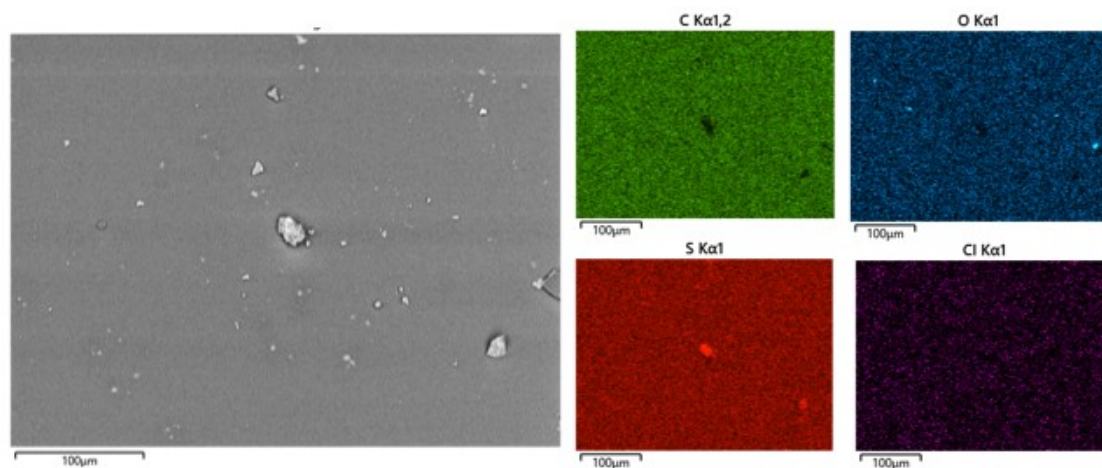


Figure S2. Scanning electron microscopy (SEM, gray image) with elemental mapping by energy dispersive X-ray analysis (EDX) of **DACIS₅₁**. Carbon is shown in green, oxygen in blue, sulfur in red, and chlorine in purple.

a) EDS Quantitative Analysis Table

Map Sum Spectrum			
Element	Signal Type	Line	Atomic Composition
C	EDS	K series	37.0%
O	EDS	K series	15.1%
S	EDS	K series	50.5%
Cl	EDS	K series	5.0%

b) EDS Spectrum

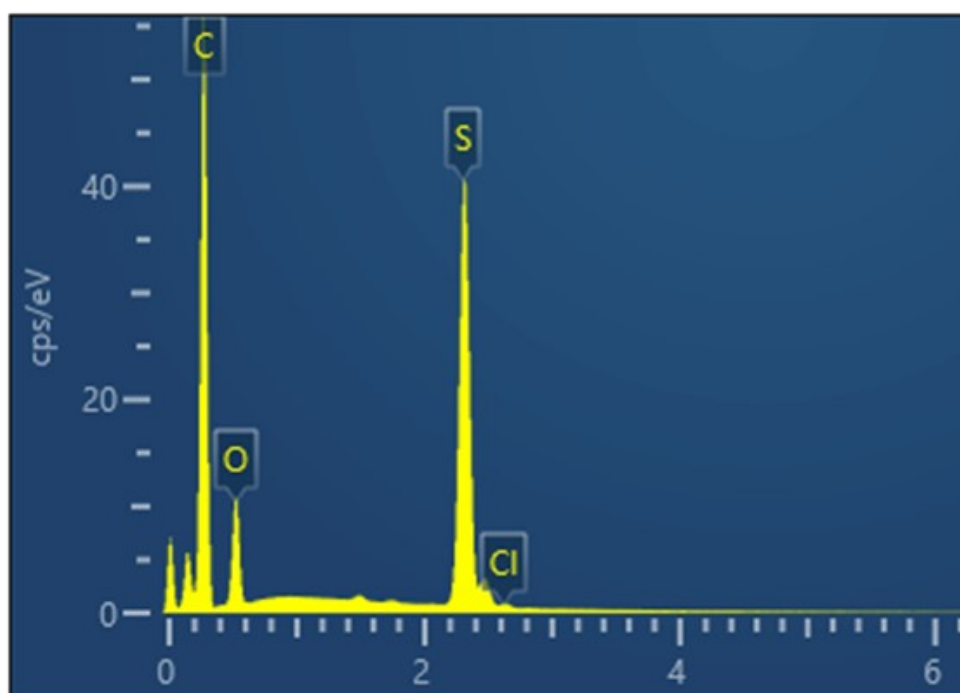


Figure S3. Results of an Energy Dispersive X-ray Spectroscopy (EDS) analysis of **DACIS₅₁**. (a) Quantitative analysis table providing the elemental composition in weight percentages. This table highlights the presence of key elements detected in the sample. (b) EDS spectrum showing characteristic X-ray emission peaks corresponding to the detected elements.

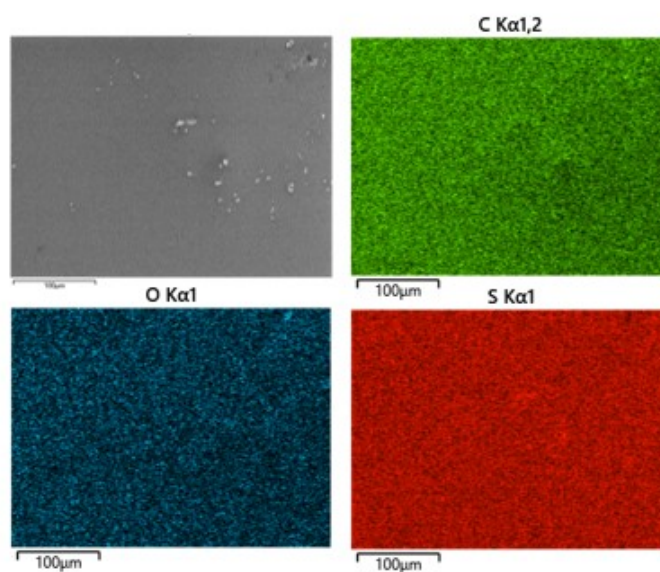


Figure S4. Scanning electron microscopy (SEM, gray image) with elemental mapping by energy dispersive X-ray analysis (EDX) of **DAS₅₀**. Carbon is shown in green, oxygen in blue, and sulfur in red.

a) EDS Quantitative Analysis Table

Map Sum Spectrum			
Element	Signal Type	Line	Atomic Composition
C	EDS	K series	35.2%
O	EDS	K series	14.6%
S	EDS	K series	52.3%
Cl	EDS	K series	0.0%

b) EDS Spectrum

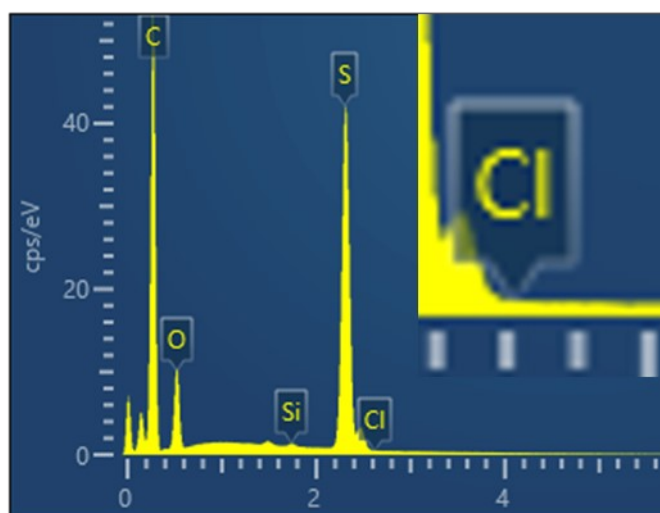


Figure S5. Results of an Energy Dispersive X-ray Spectroscopy (EDS) analysis of **DAS₅₀**. (a) Quantitative analysis table providing the elemental composition in weight percentages. The table clearly indicates the absence of chlorine (Cl), with a weight percentage of zero. (b) EDS spectrum showing characteristic X-ray emission peaks corresponding to the detected elements, with an inset showing where the Cl peak would be (note it is indicating baseline, consistent with the table of concentrations generated by the instrument software).

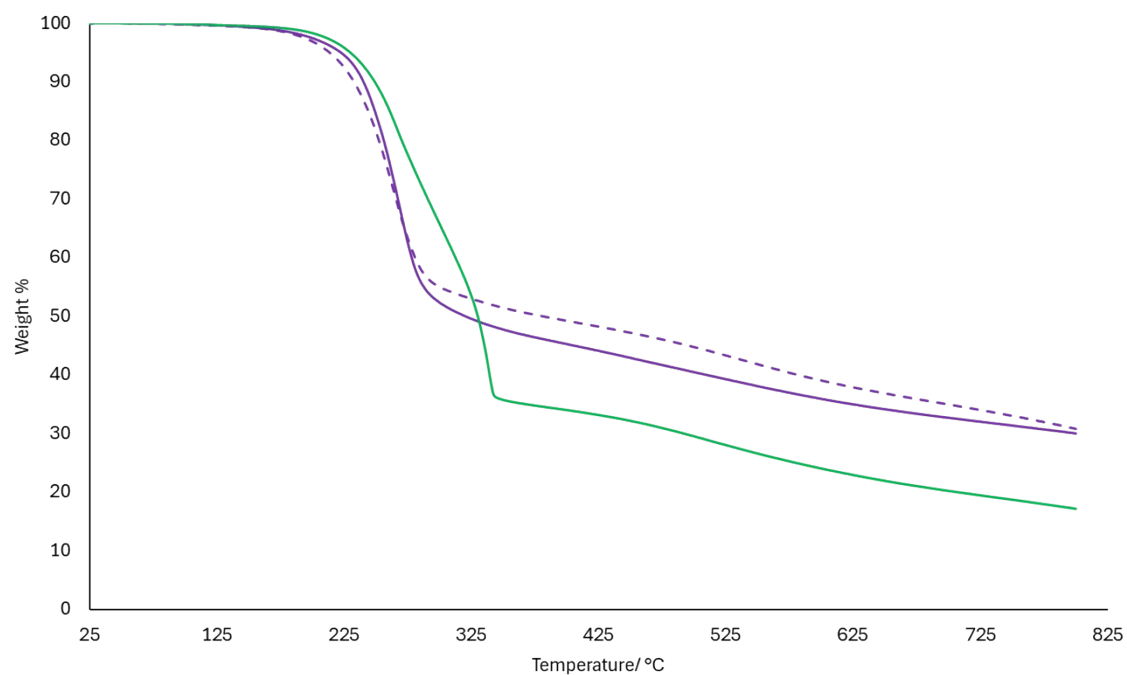


Figure S6. Thermogravimetric analysis (TGA) curves for **DACIS₅₁** (purple solid line), **DAS₅₀** (purple dash line), and **DS₈₁** (green solid line).

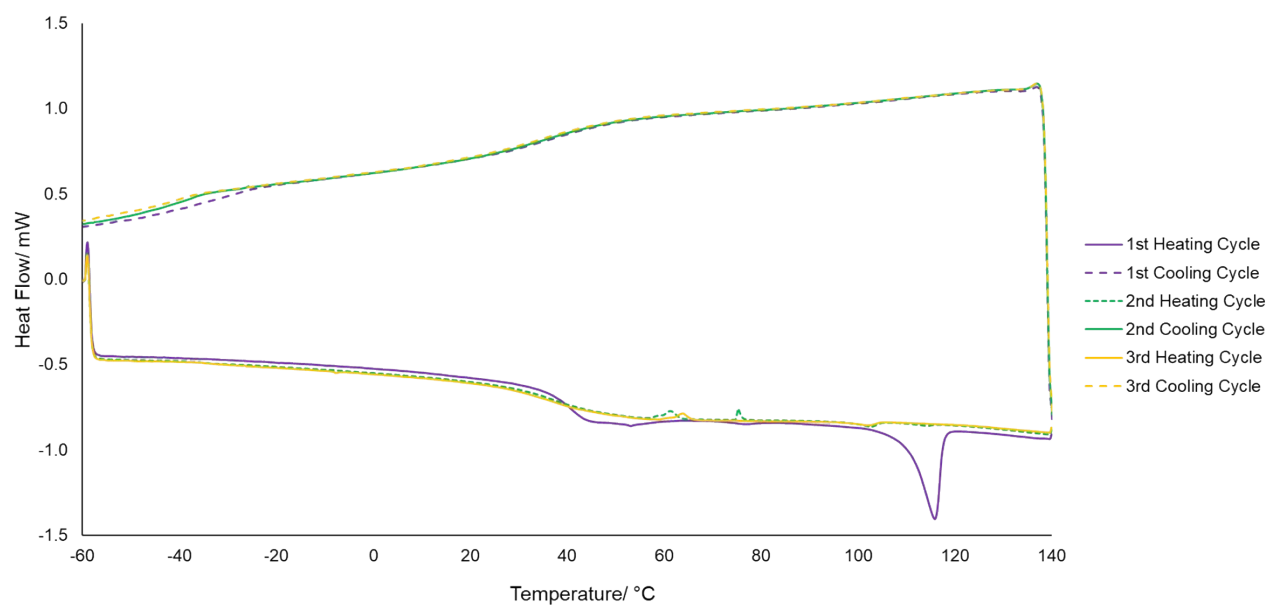


Figure S7. Differential scanning calorimetry (DSC) traces for **DACIS₅₁**. Three heating cycles and three cooling cycles were collected. Endothermic transitions are downward in this thermogram.

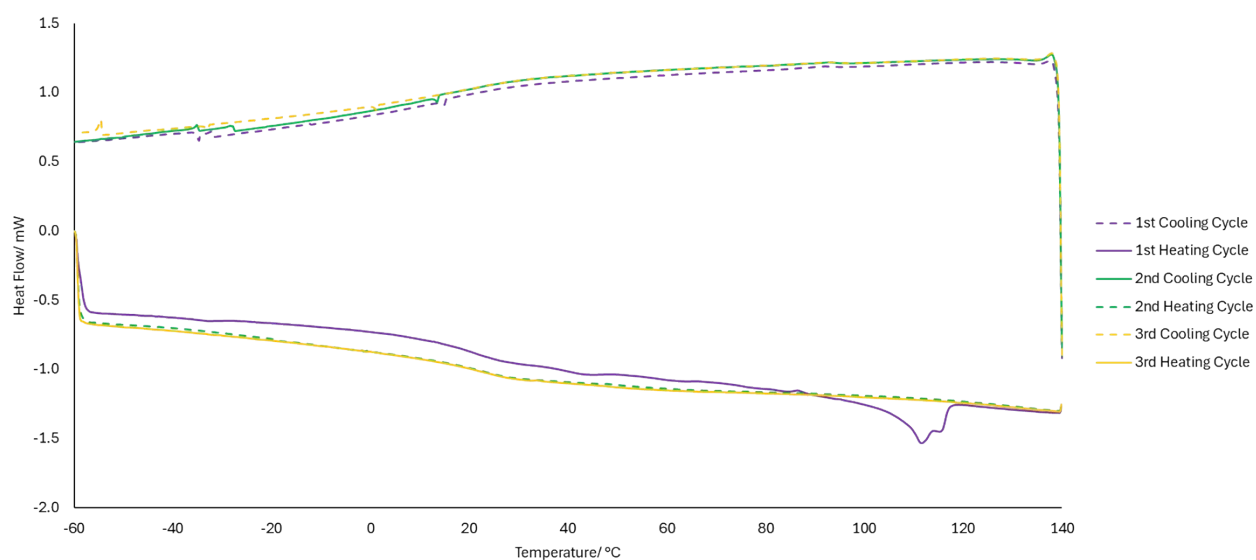


Figure S8. Differential scanning calorimetry (DSC) traces for **DAS₅₀**. Three heating cycles and three cooling cycles were collected. Endothermic transitions are downward in this thermogram.

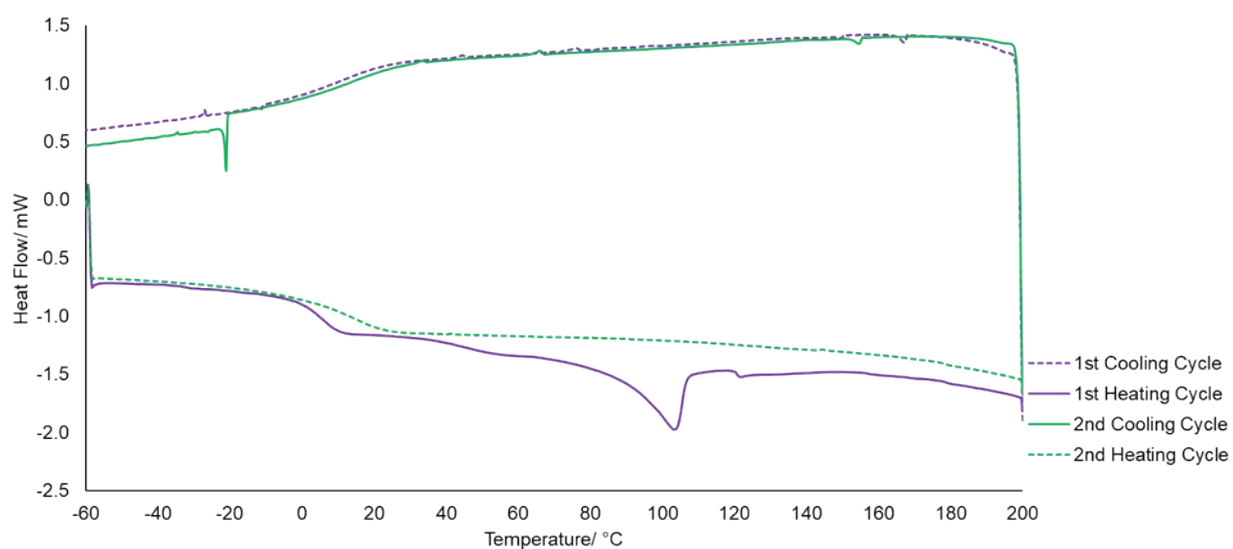


Figure S9. Differential scanning calorimetry (DSC) traces for AS₅₀. Two heating cycles and two cooling cycles were reported. Endothermic transitions are downward in this thermogram.

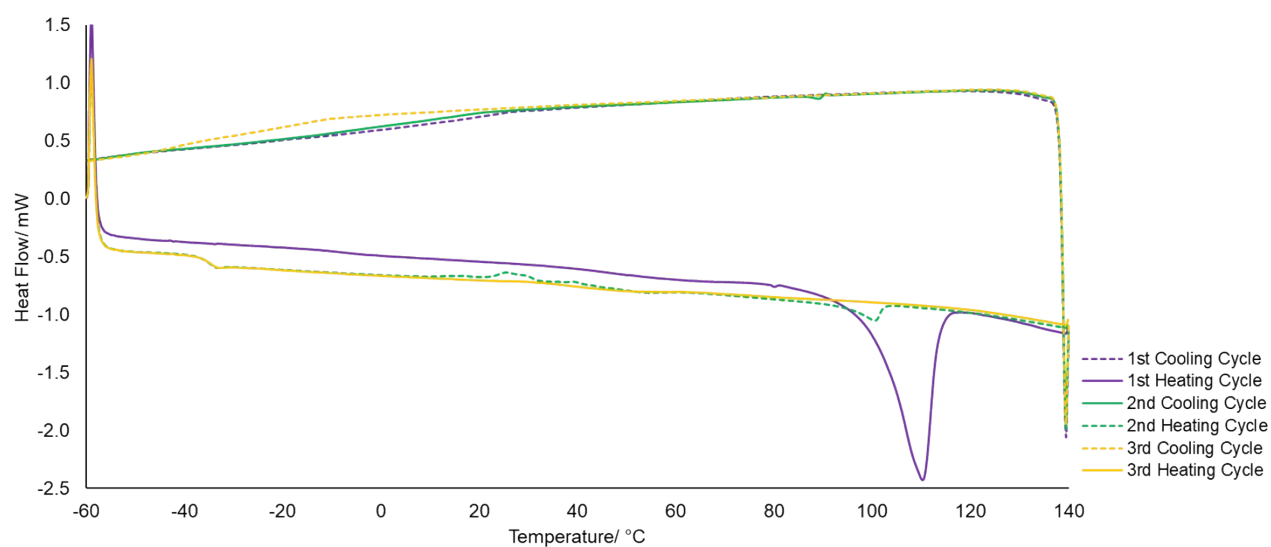


Figure S10. Differential scanning calorimetry (DSC) traces for **DS₅₁**. Three heating cycles and three cooling cycles were collected. Endothermic transitions are downward in this thermogram.

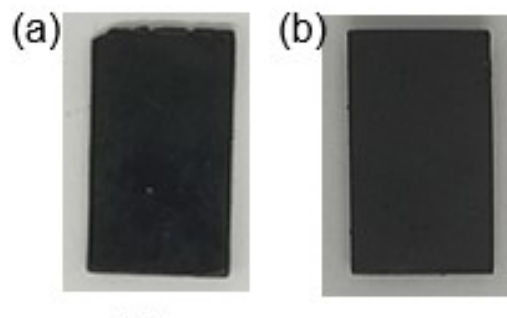


Figure S11. Photos of rectangular prisms (a) **DACIS₅₁** and (b) **DAS₅₀** that have been shaped for DMA and flexural strength analysis.

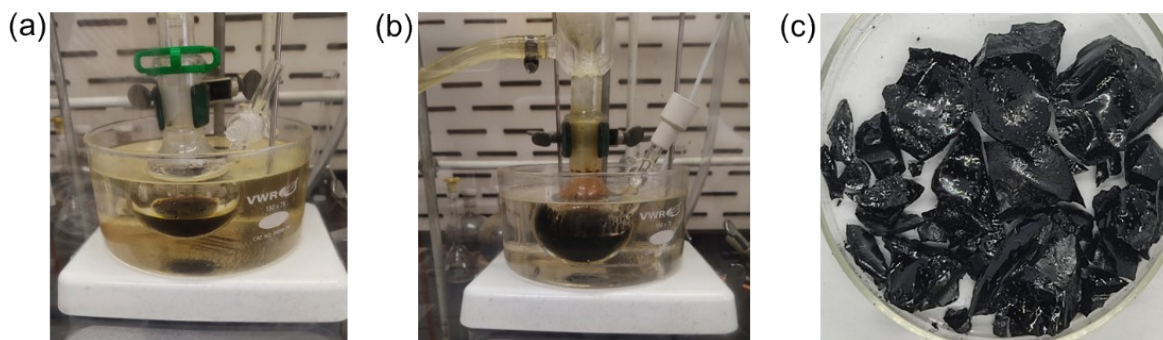


Figure S12. Different stages of reaction in **DACIS₅₁** preparation process (a) reaction setup heating at 230 °C (liquid stage, reaction is under dynamic flow of N₂ supplied via needles inserted into a septum at the top of the water-cooled reflux condenser) with 2,4-dichloro-3,5-dimethylphenol and elemental sulfur (b) reaction setup after cooling to room temperature then adding *O, O'*-diallylbisphenol A via syringe through the white septum after opening the stopcock (viscous liquid stage) and (c) final product obtained after cooling to room temperature (homogeneous solid).

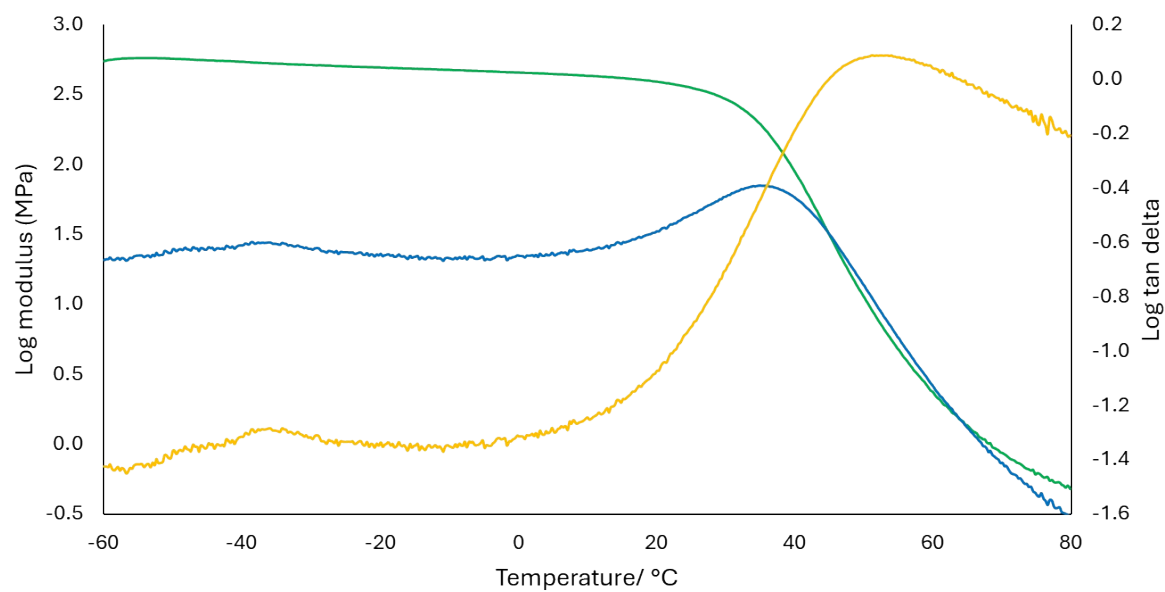


Figure S13. DMA analysis of **DACIS₅₁** showing logarithmic-scale curves for storage modulus (green line), loss modulus (blue line) and tan delta (yellow line) after 4 d at room temperature.

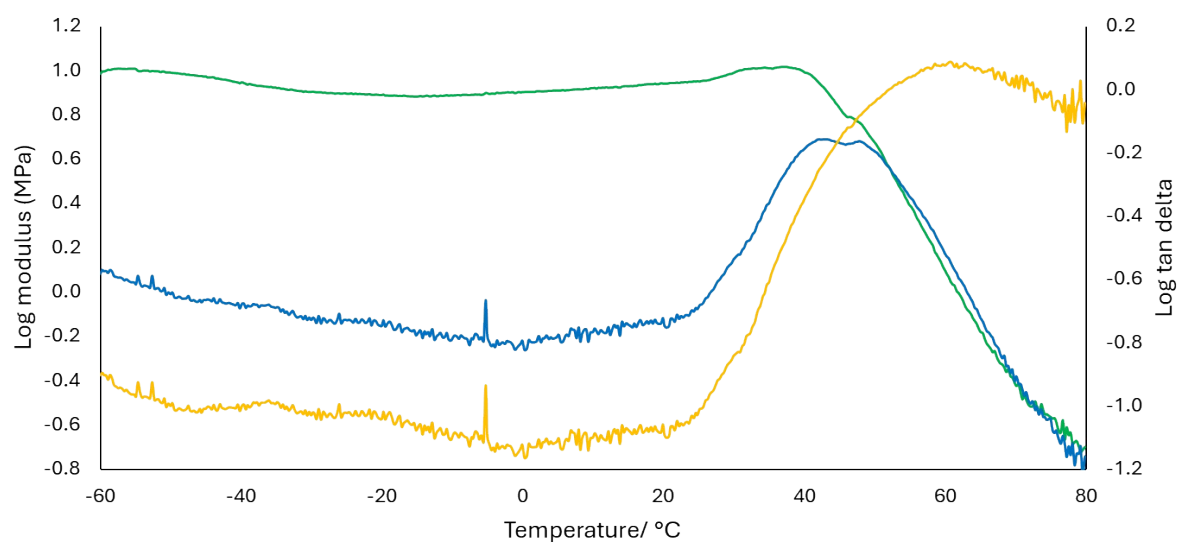


Figure S14. DMA analysis of **DAS₅₀** showing logarithmic-scale curves for storage modulus (green line), loss modulus (blue line) and tan delta (yellow line) after 4 d at room temperature.

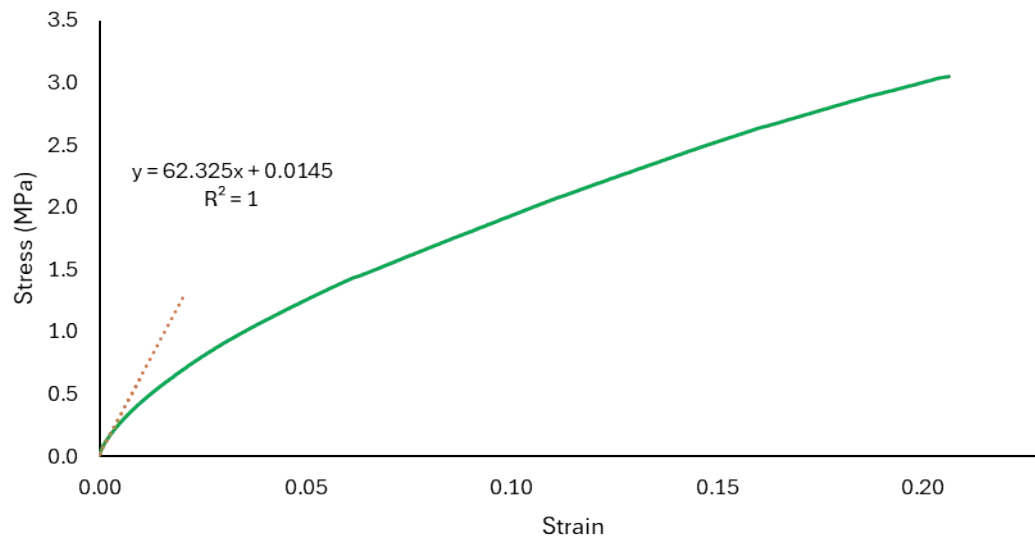


Figure S15. Stress-strain plots for flexural strength of **DACIS₅₁** after 4 d at room temperature.

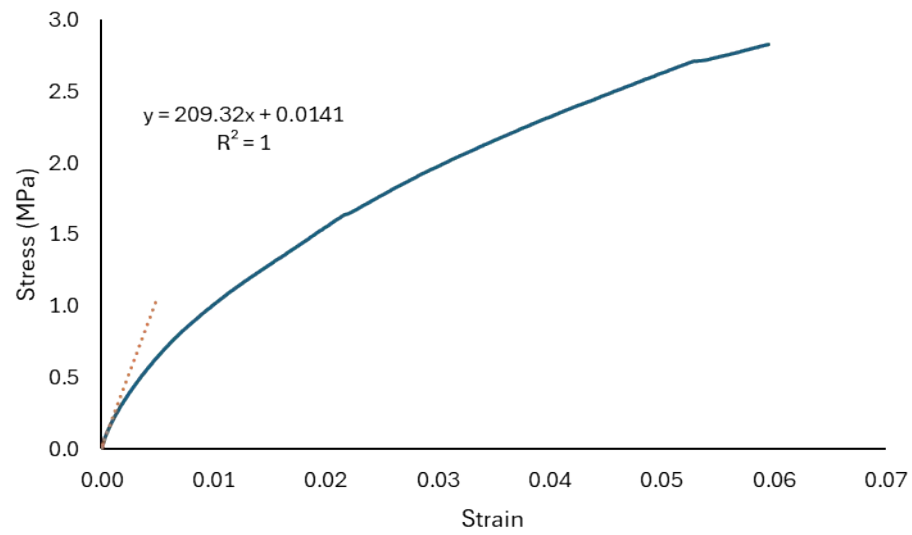


Figure S16. Stress-strain plots for flexural strength of **DAS₅₀** after 4 d at room temperature.