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Electronic Supplementary Information

Facile Route to an Organosulfur Composite from Biomass-Derived Guaiacol and Waste Sulfur

Menisha S. Karunarathna, Moira K. Lauer and Rhett C. Smith*

Department of Chemistry, Clemson University, Clemson, SC, USA 29634. E-mail: rhett@clemson.edu.

Experimental Section

Chemicals and Materials

Guaiacol (98%) was purchased from TCI America. Sulfur powder (99.5%) was purchased from Alfa Aesar. Lithium aluminum hydride and anhydrous toluene were purchased from Bean Town Chemicals and Alfa Aesar, respectively. These chemicals were used without further purification unless otherwise noted.

General Considerations

All ^{1}H NMR spectra were recorded on a Bruker Avance spectrometer operating at 300 MHz. Thermogravimetric analysis (TGA) data were recorded on a Mettler Toledo 2STARe instrument over the range 20 to 800 °C, with a heating rate of 5 °C min^{-1} under a flow of N_2 (100 mL min^{-1}). A Mettler Toledo DSC 3 STAR^e System was used to collect the differential scanning calorimetry (DSC) data over the range of –60 to 150 °C, with a heating rate of 5 °C min^{-1} under a flow of N_2 (200 mL min^{-1}). All the reported data were taken from the third heat/cool cycles.

Tensile measurements were taken with a Mark-10 ES30 mechanical test stand equipped with a Mark 1000 N Force Gauge (Model M3-2 or Model M3-200). The specimens were moulded into dog bone shapes. A cross-section of the linear portion of the dog bones was used as the area to calculate the stress on the specimen. The actual thicknesses, widths and lengths were individually measured at several areas of each sample using callipers. The average sample dimensions were 2.5 × 2.7 × 12.8 mm. Each sample was clamped down with a Mark 10 wedge grip (Model G1061-1). The data reported are an average of three runs. Fourier transform infrared spectra were obtained using a Shimadzu IR Affinity-1S instrument with an ATR attachment, operating over the range of 400-4000 cm–1 at ambient temperature.

The GC-MS analysis was carried out on a Shimadzu QP2010SE system with an auto injector (AOC-20i), equipped with mass selective detector, having interface temperature of 250°C, a solvent cut time of 3.00 min, threshold of 70eV and mass range of 45 to 900 m/z. Compounds were separated using a SH-Rxi-5 MS capillary column (Restek Company, Bellefonte, USA: crossbond 5% diphenyl/ 95% dimethyl polysiloxane) having dimensions 30 m (length) × 0.25 mm (diameter) × 0.25 µm (film thickness). The temperature of the injector was initialized to 250°C. The temperature was programmed from 40°C to 320°C at a ramp rate of 10°C/min.

Synthesis of GS_{80}

CAUTION: Heating elemental sulfur with organics can result in the formation of H_2S gas. H_2S is toxic, foul-smelling, and corrosive

Elemental sulfur (8.00 g) and guaiacol (2.00 g) were weighed directly into a glass pressure flask under an atmosphere of N_2 in an MBraun glovebox. The flask was sealed with a Teflon screwcap equipped with a Viton O-ring. The flask was then placed in an oil bath and heated to a temperature of 230°C and heating was continued for 24 h with continuous stirring by a magnetic stir bar. After 24 h the flask was cooled to room temperature. A small amount of oil had condensed on the walls of the pressure flask. This oil was removed with a Kimwipe and the remaining brown solid was collected. This solid is termed **GS_{80}** in the manuscript. Elemental combustion microanalysis: Elemental analysis found: C 10.10, H 0.70, S 85.50.

Depolymerization with $LiAlH_4$

Under an atmosphere of dry N_2 in a glove box, a powdered **GS_{80}** sample (0.100 g) and 0.175 g of $LiAlH_4$ were added into a glass vial. The solid mixture was suspended in 7 mL of anhydrous toluene. The vial was sealed with a polypropylene cap and the suspension was stirred via magnetic stir bar for 24 h at ambient temperature under N_2. At the end of the reaction time, the reaction vial was equipped with a rubber septum that was wired in place. The vial was put under a constant flow of N_2 on a Schlenk line and cooled in an ice bath. The excess $LiAlH_4$ was carefully quenched by slow addition of 5% (v/v) HCl : ethanol until no evolution of H_2 gas was noted. Insoluble inorganics were filtered, and the organic solution washed three consecutive times with washing with distilled water (acidified to pH = 5 with HCl) and then, the organic layer was separated out. Volatiles were then removed by rotary evaporation at 50 °C, followed by drying in vacuo at 40 °C. This produced a crude oil that was used for ^1H NMR analysis (Figure 1 in the main article) and in the acetylation step described below.

Acetylation protocol

The oil resulting from depolymerization described above was subjected to acetylation by a modified literature procedure.[1] The crude oil (50 mg), acetic anhydride (1 mL), and powdered $NaOAc{\cdot}3H_2O$ (0.10 g) were combined in a vial and stirred at room temperature for 1 h. The acetylated product was extracted into dichloromethane and washed with water. The dichloromethane-soluble organics were then analyzed by GC-MS.

Table S1. Elemental Analysis of GS_{80}

Materials	C wt%	H wt%	S wt%
GS_{80}	10.1	0.7	85.5
GS_{80}-Insoluble Fraction	20.5	1.0	69.5

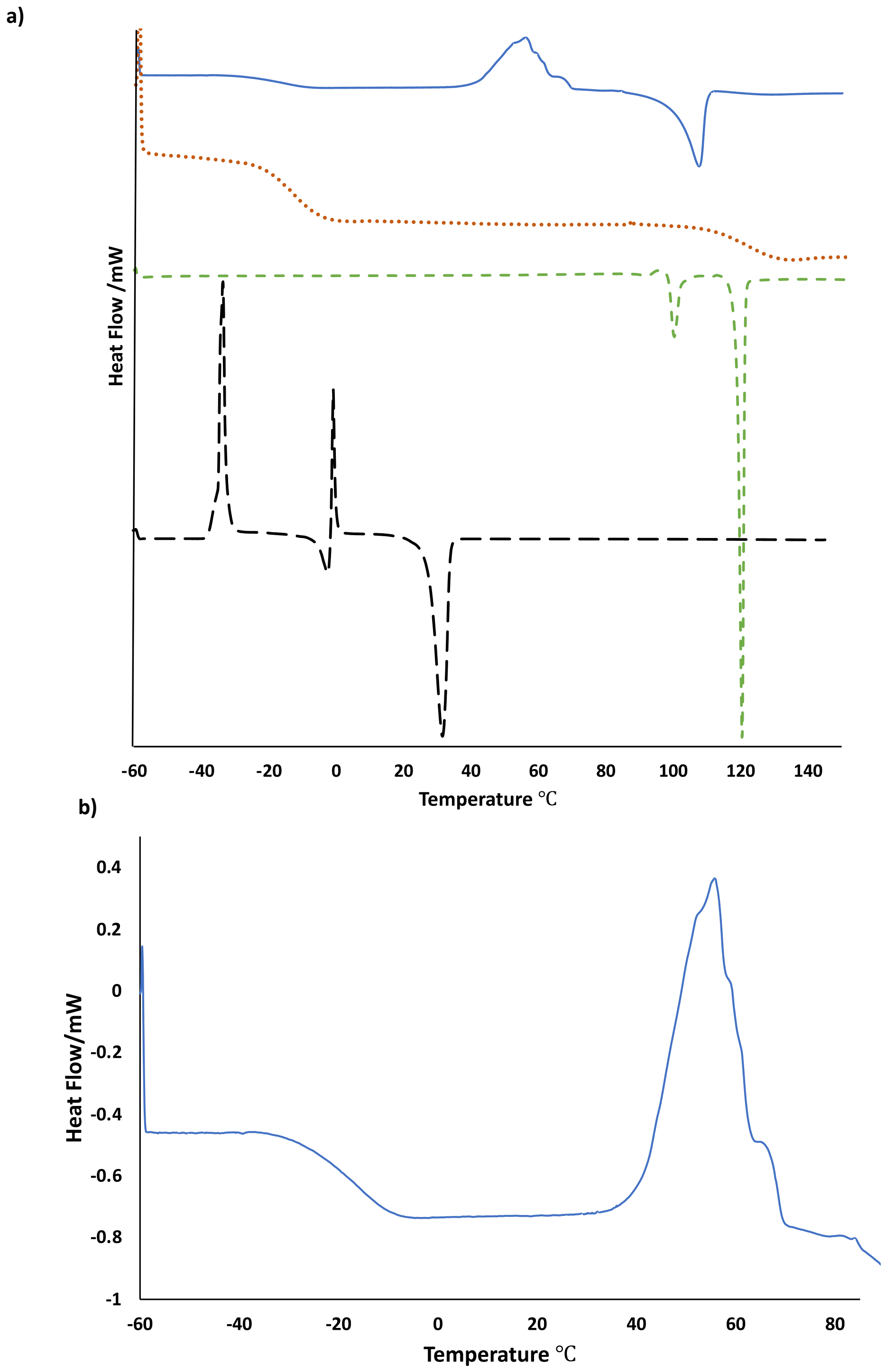


Figure S1. DSC 3rd heating curves **a) GS$_{80}$** (blue solid line), CS$_2$-Insoluble fraction of **GS$_{80}$** (orange round dot line), sulfur (green dash line), guaiacol (black long dash line)**. b)** Enlarged view of the 3rd heating curve of the **GS$_{80}$** showing the broad T_g and cold crystallization peak**.** Note the broader T_g with a midpoint ~12 °C observed in the DSC curve of the CS$_2$ insoluble fraction and the lack of the orthorhombic melting peak (at 120 °C in the trace for pure sulfur) due to successful extraction of the free sulfur. Pure Guaiacol also resulted in two cold crystallization peaks. The second cold crystallization peak is due to the very slow monotropic solid to solid transition from metastable to α stable crystals. The metastable crystals have already begun melting whereupon the α stable crystals crystallizes.

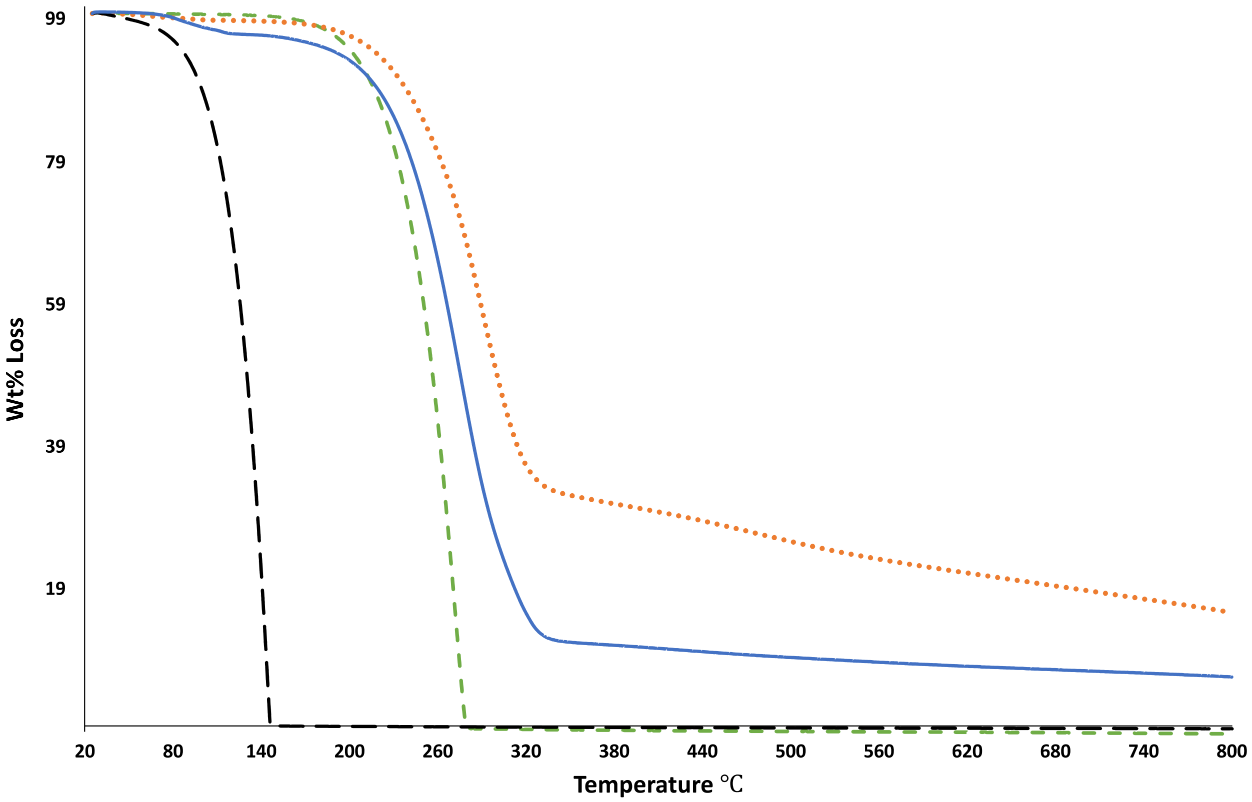


Figure S2. TGA curves **GS$_{80}$** (blue solid line), **GS$_{80}$** CS$_2$-Insoluble fraction (orange round dot line), sulfur (green dash line), guaiacol (black long dash line)**.**

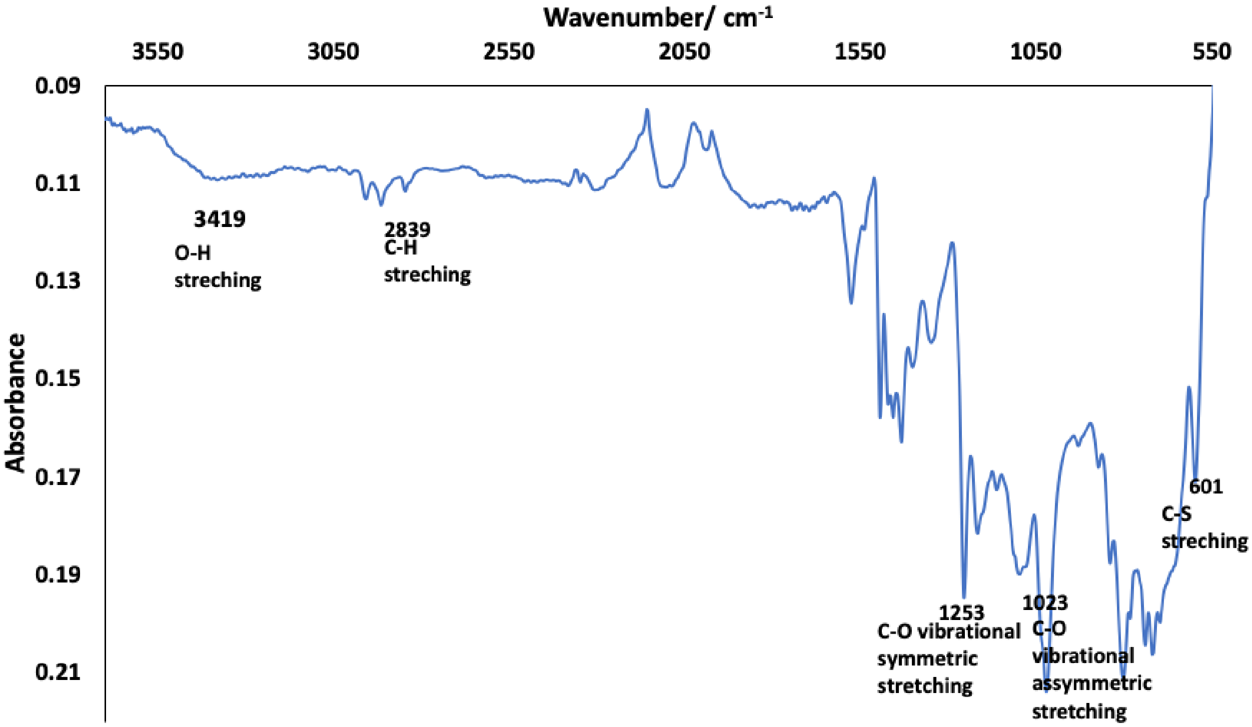


Figure S3. FTIR Spectrum of GS_{80}

Note- Most of the prominent peaks from guaiacol are present in the GS_{80} except the emergence of C-S stretching.
And reduction in the intensity of O-H stretching which imply the consumption of phenolic groups for crosslinking with sulfur.

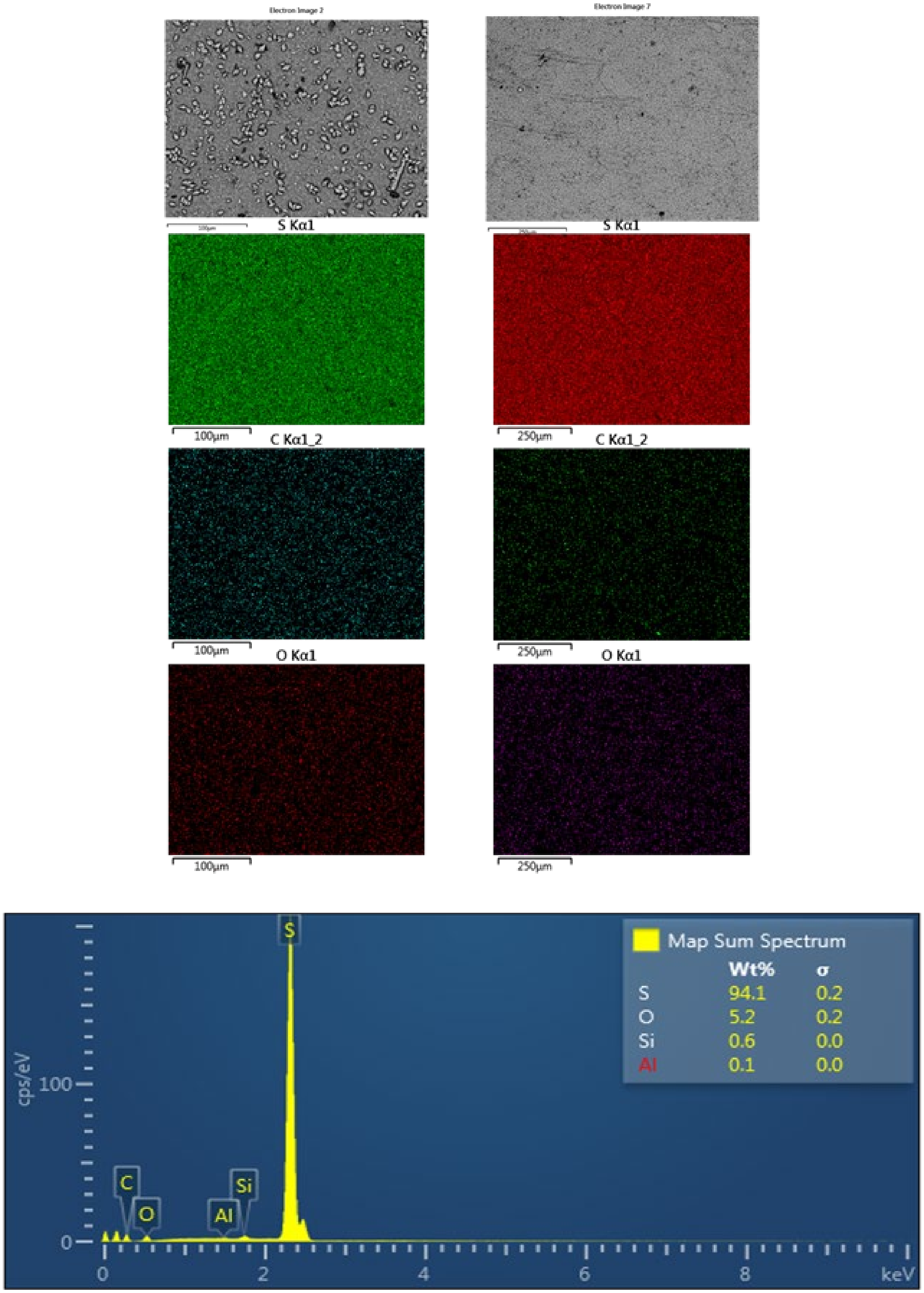
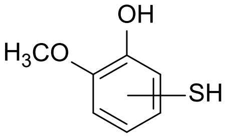


Figure S4. Images of **GS$_{80}$** generated by scanning electron microscopy (upper) with 100 μm (left) or 250 μm (right) scale bars. with element mapping by energy-dispersive X-ray analysis showing sulfur, carbon, and oxygen. The XPS spectrum is also provided (lower).



Chemical Formula: $C_7H_8O_2S$
Exact Mass: 156.0245
m/z: 156.0245 (100.0%), 157.0279 (7.6%), 158.0203 (4.5%)

M1
Two isomers observed

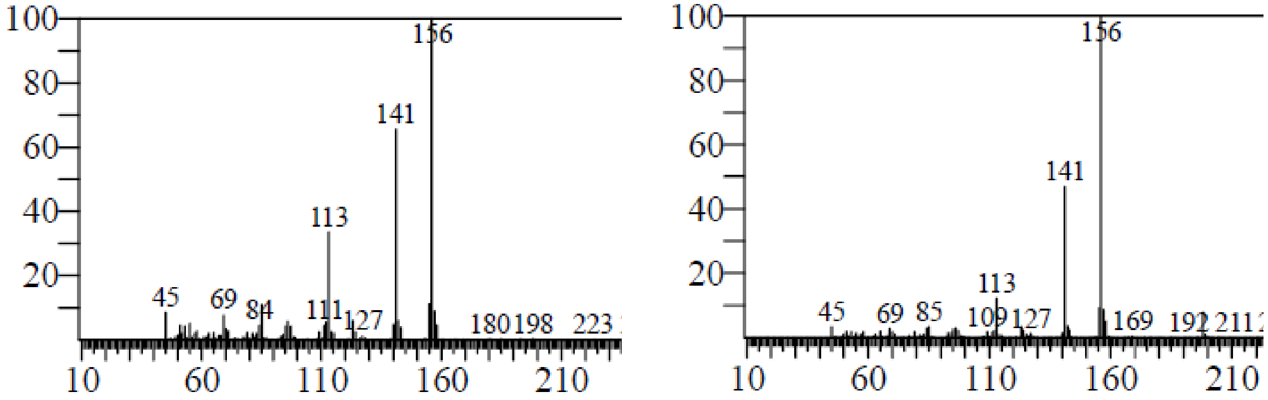
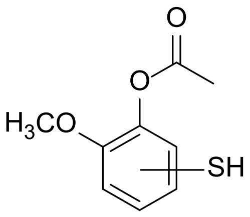


Figure S5. Mass spectra for two isomers of a depolymerization product of **GS$_{80}$** (shown in Chart 2 in the main text)



M1-Ac

Chemical Formula: $C_9H_{10}O_3S$
Exact Mass: 198.0351
m/z: 198.0351 (100.0%), 199.0384 (9.7%), 200.0309 (4.5%)

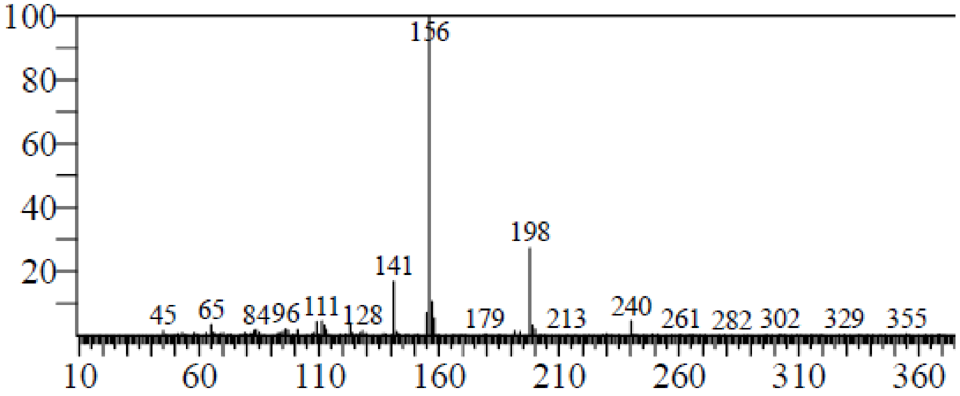
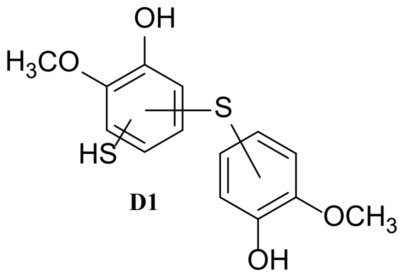


Figure S6. Mass spectrum for depolymerization product of **GS$_{80}$** (shown in Chart 2 in the main text)



D1

Chemical Formula: $C_{14}H_{14}O_4S_2$
Exact Mass: 310.0334
m/z: 310.0334 (100.0%), 311.0367 (15.1%), 312.0291 (9.0%), 311.0327 (1.6%), 312.0401 (1.1%)

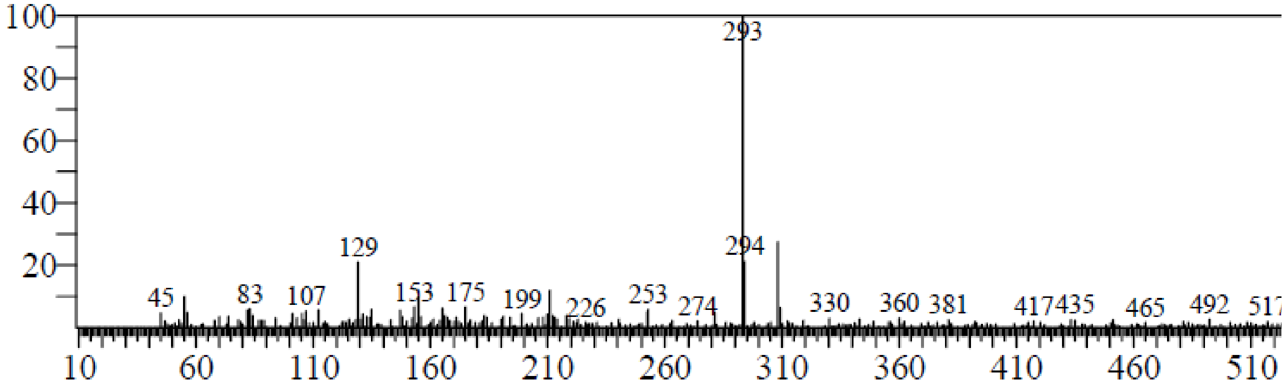
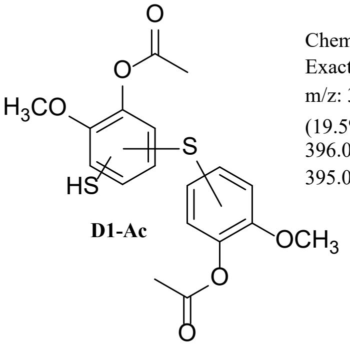


Figure S7. Mass spectrum for depolymerization product of **GS$_{80}$** (shown in Chart 2 in the main text)



D1-Ac

Chemical Formula: $C_{18}H_{18}O_6S_2$
Exact Mass: 394.0545
m/z: 394.0545 (100.0%), 395.0578
(19.5%), 396.0503 (9.0%),
396.0612 (1.8%), 397.0536 (1.8%),
395.0539 (1.6%), 396.0587 (1.2%)

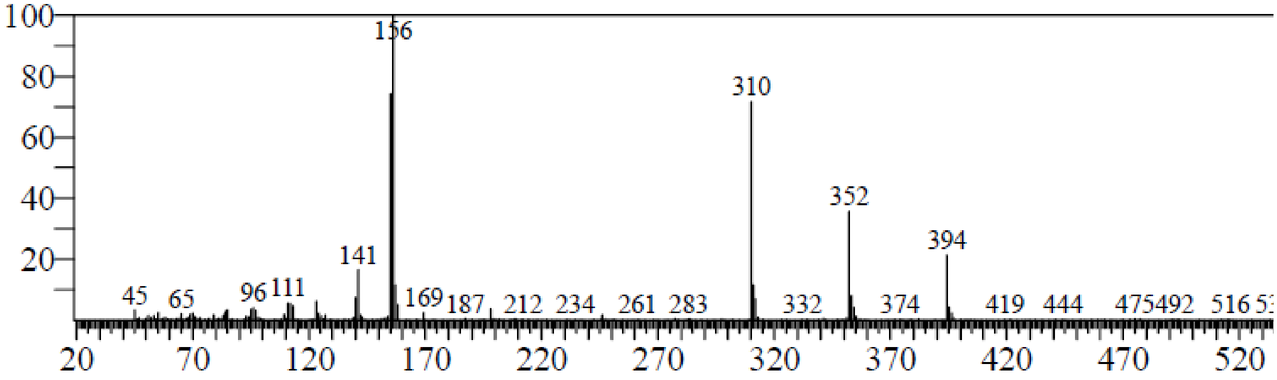


Figure S8. Mass spectrum for depolymerization product of **GS$_{80}$** (shown in Chart 2 in the main text)

Figure S9. Digital images of **GS$_{80}$** samples and the image of tensile strength tested dog bone shaped **GS$_{80}$** sample, clamped down with a Mark 10 wedge grip.

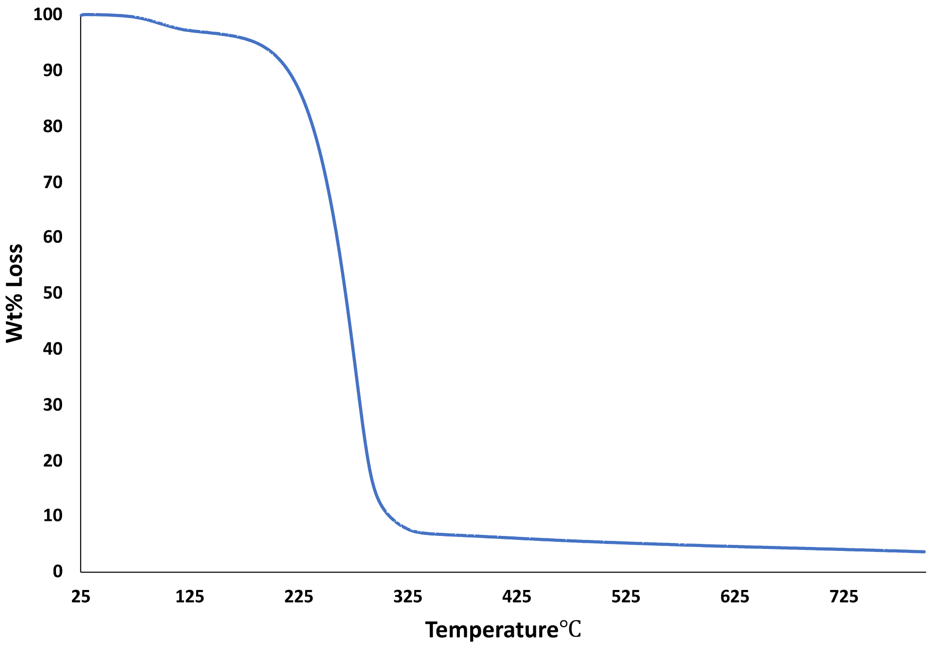


Figure S10. TGA curve of GS_{90}

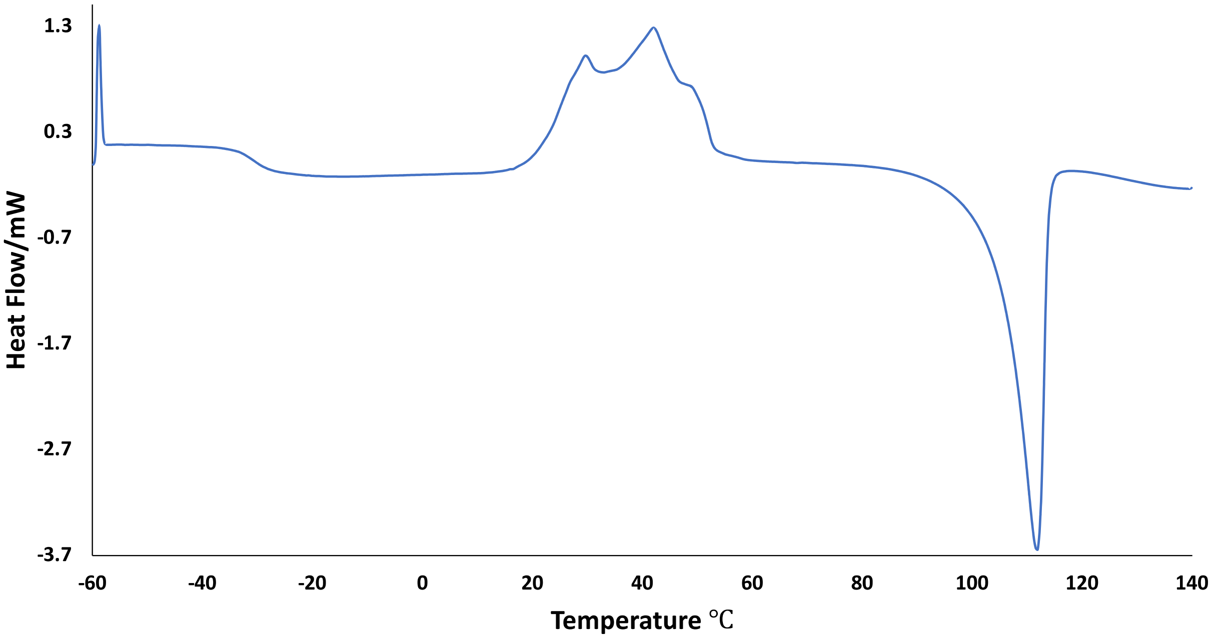


Figure S11. DSC 3rd Heating Curve of GS_{90}, consisted of broader $T_{g.}$, and cold crystallization peak followed by a melting peak

Supporting Information References

1. M. M. Mojtahedi, S. Samadian. *Journal of Chemistry* **2013**, *2013*, 642479.