Electronic Supplementary Information

Tailoring properties of guaiacol-derived high sulfur-content materials through post-polymerization modification with dithiols

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Materials and Methods

Chemicals and Materials

Guaiacol (98%, TCI America), 4,4'-biphenyldithiol (>98%, TCI America), benzene-1,4-dithiol (99%, Sigma Aldrich) and sulfur powder (Dugas Diesel, USA) were used without further purification. **GS_{80}** was prepared following the literature procedure.[1]

Instrumentation

Thermogravimetric analysis (TGA) data were recorded (Mettler Toledo TGA 2 STARe System) over 25–800 °C, with a heating rate of 10 °C min^{-1} under a flow of N_2 (100 mL min^{-1}).

Differential scanning calorimetry (DSC) data were acquired using a Mettler Toledo DSC 3 STARe System from −60 to 140 °C, with a heating rate of 10 °C min^{-1} under a flow of N_2 (200 mL min^{-1}). Each DSC measurement was carried out over three heat-cool cycles; data are reported for the third cycle.

Fourier transform infrared spectra were obtained using a Shimadzu IR Affinity-1S instrument with an ATR attachment operating over 400–4000 cm^{-1} at ambient temperature.

UV-vis data were collected over the range of 200–800 nm using an Agilent Technologies Cary 60 UV-visible spectrometer with Simple Reads software, and the dark sulfur content was reported at 275 nm.

SEM and EDS were acquired on a Schottky Field Emission Scanning Electron Microscope SU5000 operating in variable pressure mode with an accelerating voltage of 15 keV.

Shore hardness was measured using a Shore A durometer with a range of 0–100 HA, resolution of 0.5 HA, total measure force of 8.1 N, and outside pressure of 1 kg. The measurements were conducted in accordance with ISO 7619, except the sample thickness was less than the specified 6 mm, and the values in three points were recorded. The average of the three values was taken as the sample's hardness.

General Procedure for Modification of GS_{80}

GS_{80} and dithiol crosslinker were added directly into a 15 mL glass pressure tube under an atmosphere of dry nitrogen gas in a VTI glovebox. Five tubes were prepared, one for each **GS_{80}**: dithiol crosslinker mass ratios (2:1, 3:1, 4:1, 5:1 or 10:1). Each pressure tube was equipped with a magnetic stir bar and sealed under N_2 with a Teflon screwcap having a Viton O-ring. Tubes were placed into an oil bath heated to 180±2 °C, and heating was continued for 1 h with continuous stirring by a magnetic stir bar. After 1 h of heating, the pressure tubes were cooled to room temperature before opening. No mass loss was observed from any of the tubes.

*Preparation of **GS_{80}**-BPDT (2:1)*

Prepared according to the general procedure using 0.250 g of **GS_{80}** and 0.125 g (0.572 mmol) of 4,4'-biphenyldithiol. A dark brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,30.62; S, 64.21; H, 2.32%. Found: C, 27.63; S, 70.33; H, 1.55%. (Atlantic Microlab, Inc.).

*Preparation of **GS_{80}**-BPDT (3:1)*

Prepared according to the general procedure using 0.750 g of **GS_{80}** and 0.250 g (1.14 mmol) of 4,4'-biphenyldithiol. A dark brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,26.18; S, 68.56; H, 2.03%. Found: C, 22.09; S,76.09; H, 1.29%. (Atlantic Microlab, Inc.).

*Preparation of **GS_{80}**-BPDT (4:1)*

Prepared according to the general procedure using 0.800 g of **GS_{80}** and 0.200 g (0.916 mmol) of 4,4'-biphenyldithiol. A dark brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,23.52; S, 71.17; H, 1.86%. Found: C, 19.09; S, 79.07; H, 1.09%. (Atlantic Microlab, Inc.).

*Preparation of **GS_{80}**-BPDT (5:1)*

Prepared according to the general procedure using 0.250 g of **GS_{80}** and 0.050 g (0.229 mmol) of 4,4'-biphenyldithiol. A dark brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,21.75; S, 72.92; H, 1.74%. Found: C, 14.81; S, 83.68; H, 0.74%. (Atlantic Microlab, Inc.).

*Preparation of **GS_{80}**-BPDT (10:1)*

Prepared according to the general procedure using 0.910 g of **GS_{80}** and 0.090 g (0.412 mmol) of 4,4'-biphenyldithiol. A light brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,17.68; S, 76.92; H, 1.48%. Found: C, 13.86; S, 82.93; H, 0.99%. (Atlantic Microlab, Inc.).

*Preparation of **GS_{80}**-BDT (2:1)*

Prepared according to the general procedure using 0.333 g of **GS_{80}** and 0.167 g (1.17 mmol) of benzene-1,4-dithiol. A dark brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C, 25.50; S, 69.40; H, 2.20%. Found: C, 22.59; S, 75.33; H, 1.20%. (Atlantic Microlab, Inc.).

*Preparation of **GS_{80}**-BDT (3:1)*

Prepared according to the general procedure using 0.375 g of **GS_{80}** and 0.125 g (0.879 mmol) of benzene-1,4-dithiol. A dark brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,22.33; S, 72.49.; H, 1.94%. Found: C, 16.78; S, 80.78; H, 0.91%. (Atlantic Microlab, Inc.).

*Preparation of **GS_{80}**-BDT (4:1)*

Prepared according to the general procedure using 0.400 g of **GS_{80}** and 0.100 g (0.703 mmol) of benzene-1,4-dithiol. A dark brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,20.45; S, 74.32; H, 1.79%. Found: C, 15.86; S, 81.36; H, 0.96%. (Atlantic Microlab, Inc.).

*Preparation of **GS_{80}**-BDT (5:1)*

Prepared according to the general procedure using 0.416 g of **GS_{80}** and 0.084 g (0.590 mmol) of benzene-1,4-dithiol. A dark brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,19.24; S, 75.48; H, 1.69%. Found: C, 13.84; S, 81.85; H, 0.79%. (Atlantic Microlab, Inc.).

Preparation of ***GS_{80}****-BDT (10:1)*

Prepared according to the general procedure using 0.456 g of **GS_{80}** and 0.044 g (0.309 mmol) of benzene-1,4-dithiol. A light brown color composite was formed. Yield: quantitative. Elemental analysis calculated: C,16.21; S, 78.41; H, 1.44%. Found: C, 8.48; S, 89.85; H, 0.45%. (Atlantic Microlab, Inc.).

Determination of Dark Sulfur Content

A modified literature method for quantification of the dark sulfur content was employed by UV-vis spectroscopy in ethyl acetate to determine the dark sulfur content.[2] Each modified product weighed with a microbalance between 6 and 7 mg, was added to a 250 mL volumetric flask with approximately 230 mL of ethyl acetate. The mixture was allowed to stir for 30 min, after which the solution was made up to the mark of 250 mL with ethyl acetate. A 3 mL aliquot of solution was transferred to a cuvette, and 3 mL pure ethyl acetate was transferred to a separate cuvette to serve as a blank. Data were collected at 275 nm, and dark sulfur content was calculated from a calibration curve having the equation $y = 36.124x + 0.012$ ($R^2 = 0.9967$), where y is absorbance, and x is the concentration of sulfur in mg/mL.

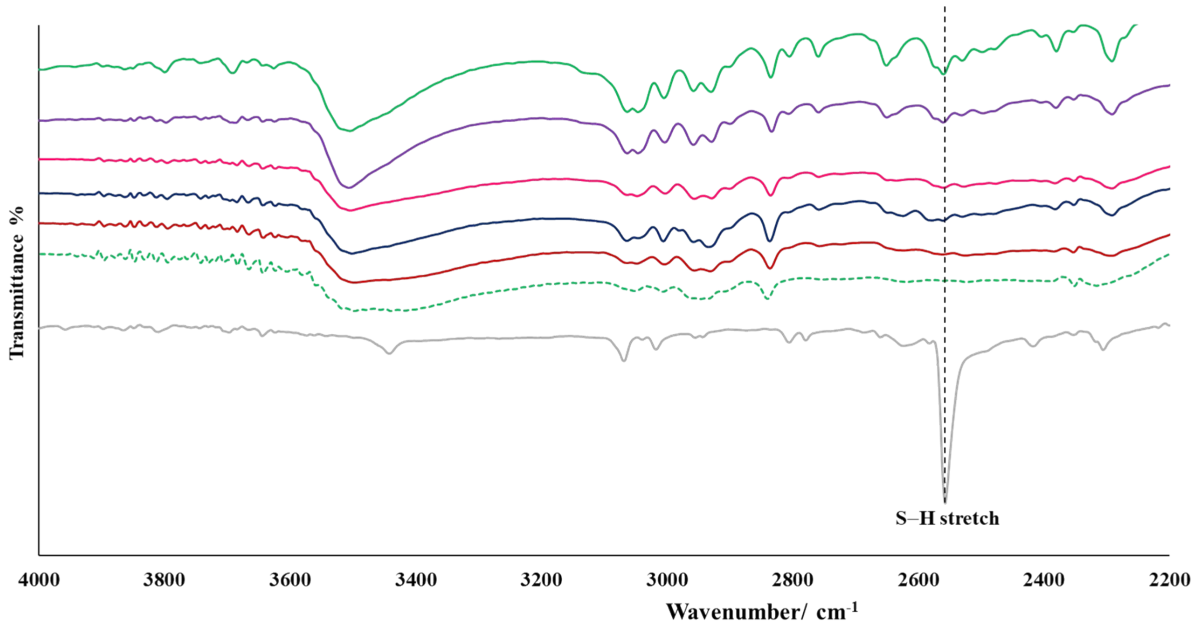

Figure S1. Fourier-transform infrared spectroscopy (FT-IR) spectra showing the wavenumber range of 4000–2200 cm^{-1} for **GS$_{80}$** (green dash line), benzene-1,4-dithiol (grey solid line), **GS$_{80}$**-BDT (2:1) (green solid line), **GS$_{80}$**-BDT (3:1) (purple solid line), **GS$_{80}$**-BDT (4:1) (pink solid line), **GS$_{80}$**-BDT (5:1) (blue solid line), and **GS$_{80}$**-BDT (10:1) (red solid line).

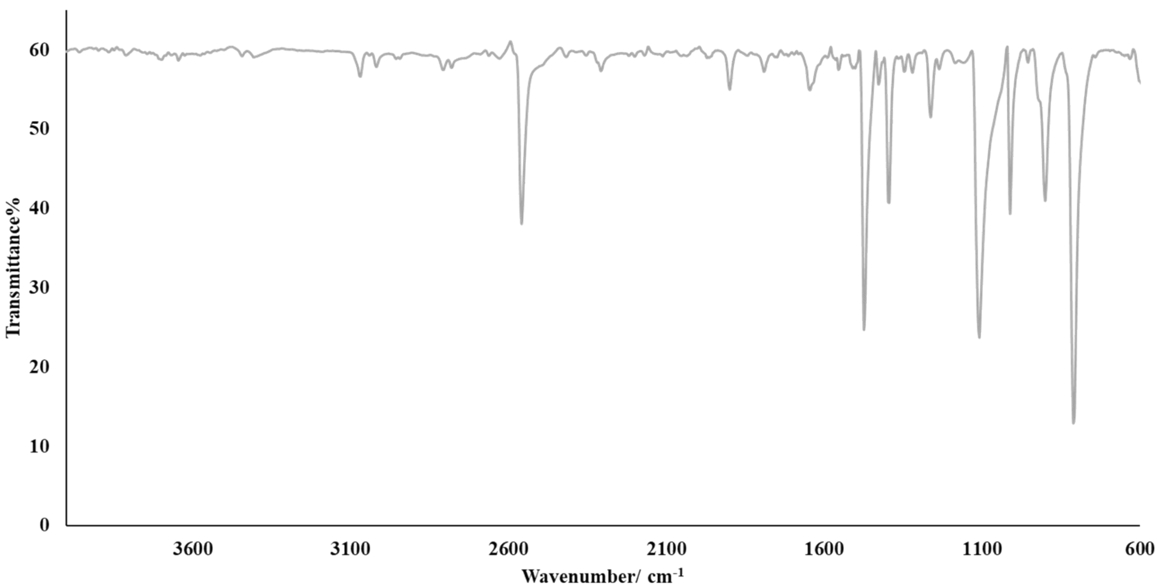

Figure S2. Infrared spectrum of benzene-1,4-dithiol.

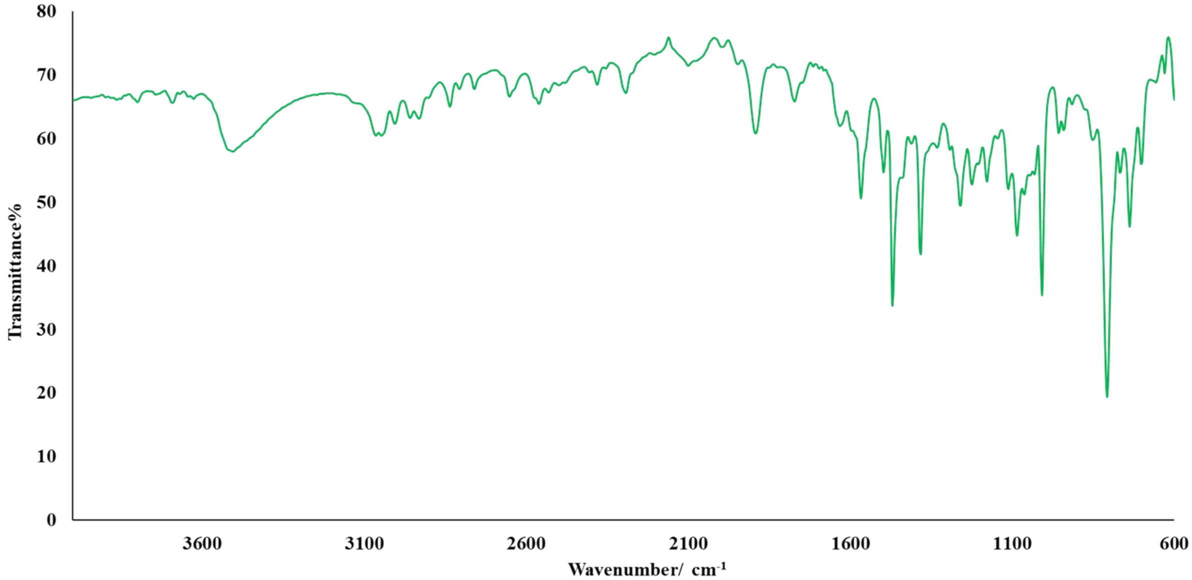

Figure S3. Infrared spectrum of $\mathbf{GS_{80}}$-BDT (2:1).

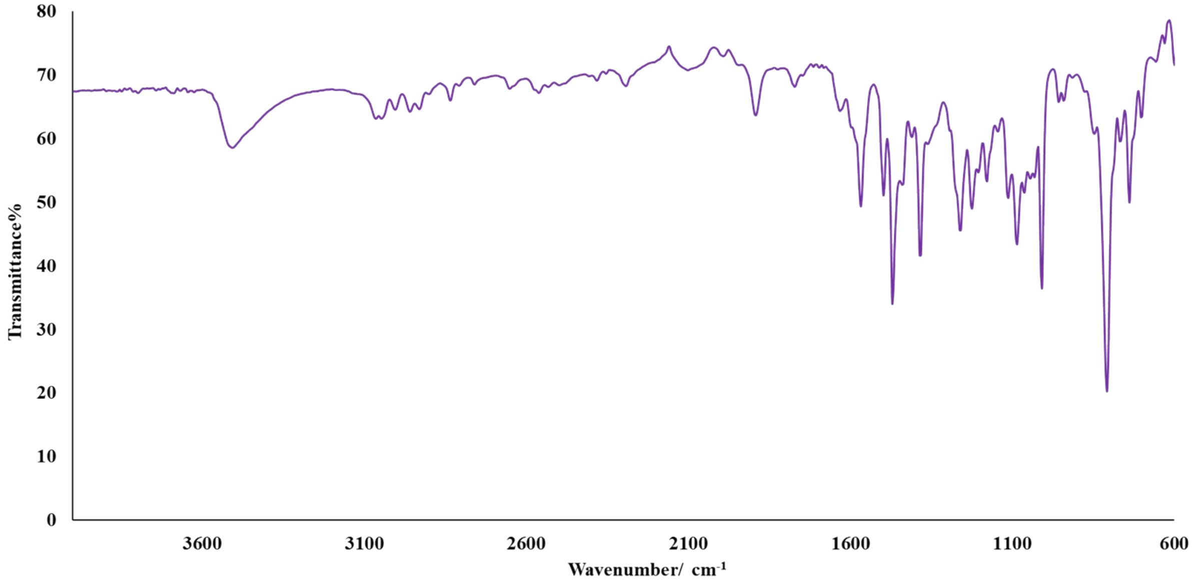

Figure S4. Infrared spectrum of $\mathbf{GS_{80}}$-BDT (3:1).

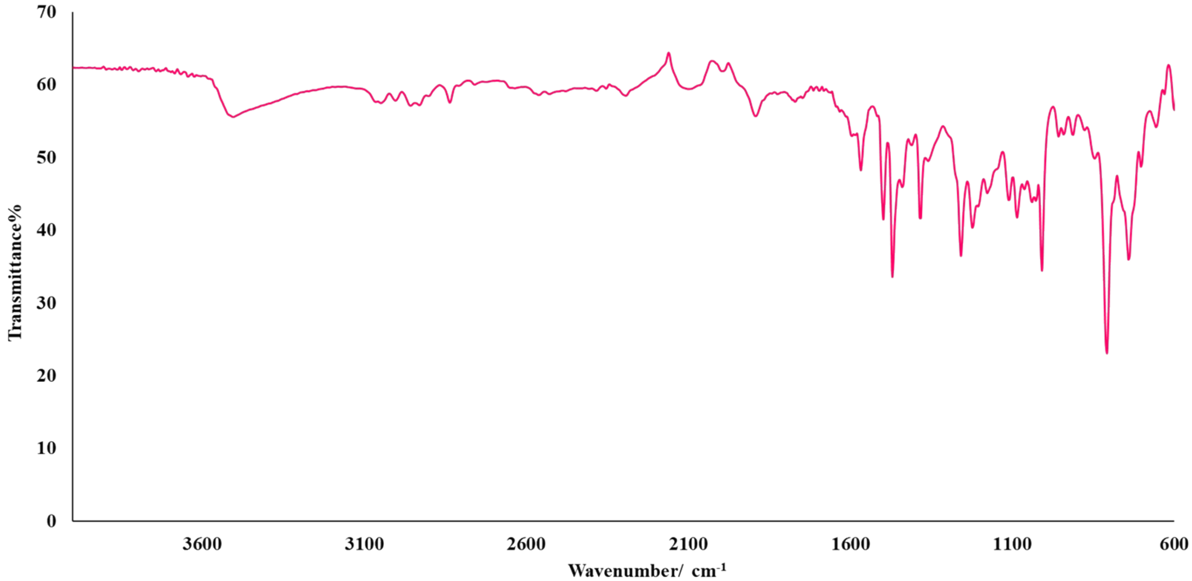

Figure S5. Infrared spectrum of **GS$_{80}$**-BDT (4:1).

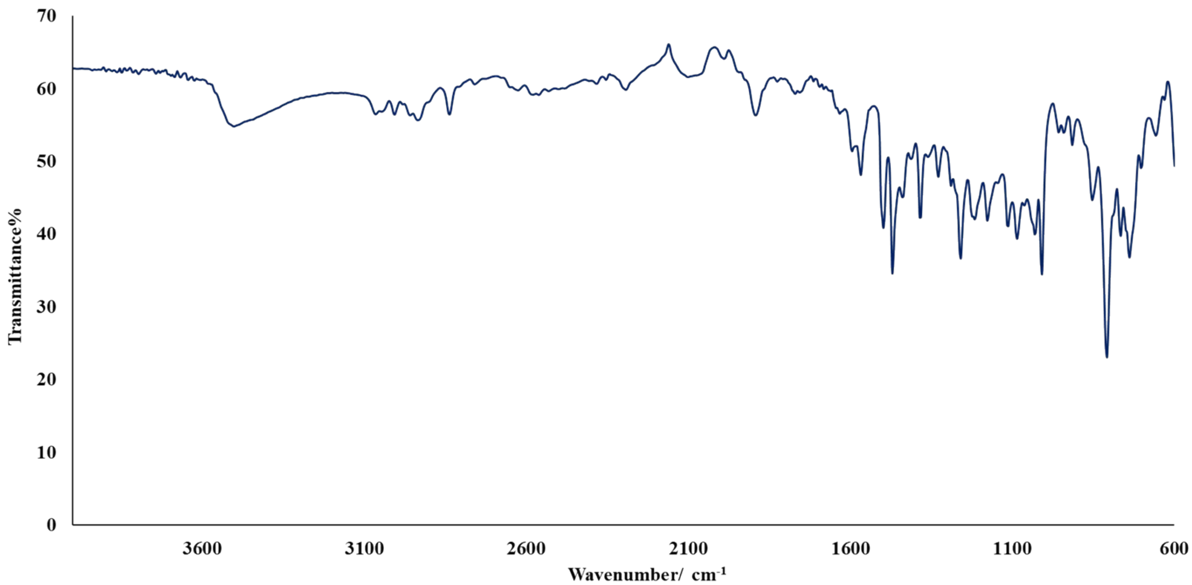

Figure S6. Infrared spectrum of $\mathbf{GS_{80}}$-BDT (5:1).

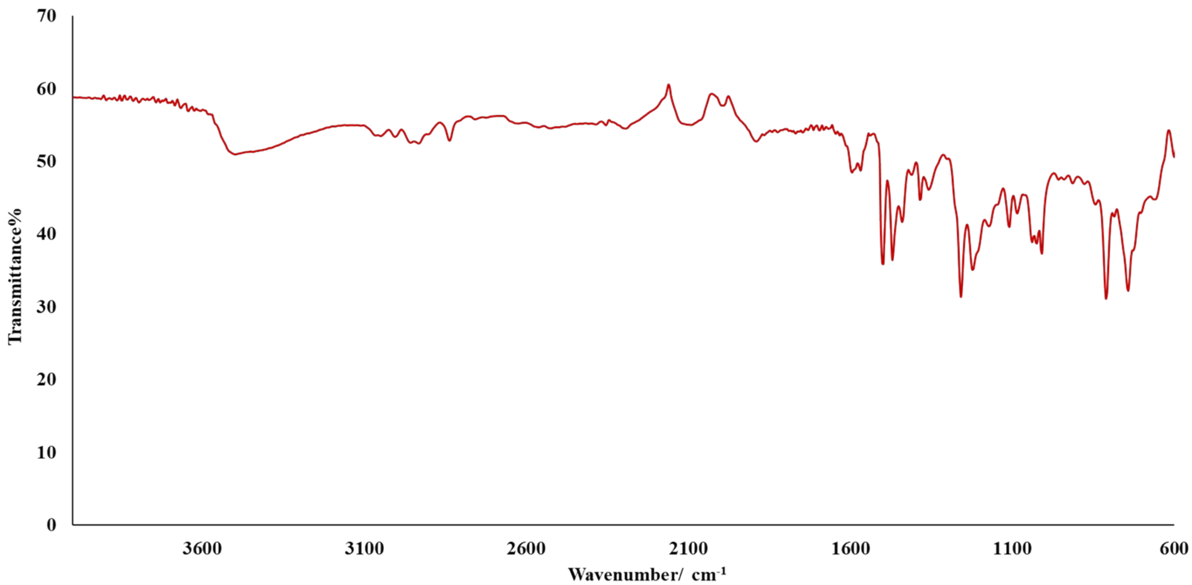

Figure S7. Infrared spectrum of **GS$_{80}$**-BDT (10:1).

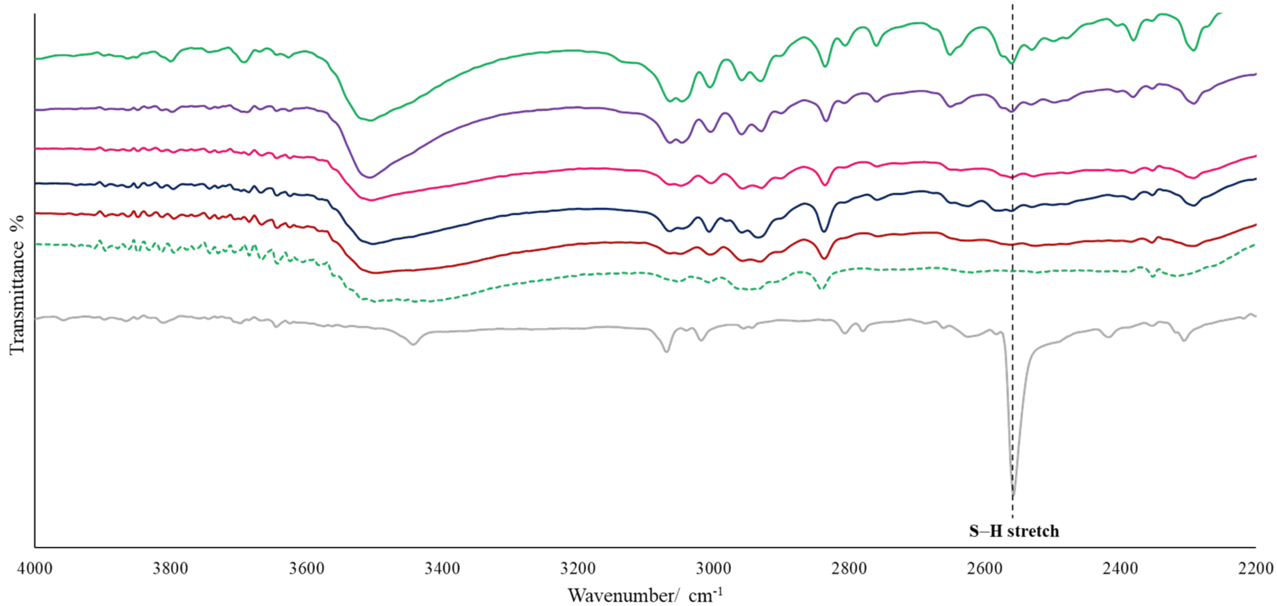

Figure S8. Fourier-transform infrared spectroscopy (FT-IR) spectra showing the wavenumber range of 4000–2200 cm^{-1} for $\mathbf{GS_{80}}$ (green dash line), 4,4'-biphenyldithiol (grey solid line), $\mathbf{GS_{80}}$-BPDT (2:1) (green solid line), $\mathbf{GS_{80}}$-BPDT (3:1) (purple solid line), $\mathbf{GS_{80}}$-BPDT (4:1) (pink solid line), $\mathbf{GS_{80}}$-BPDT (5:1) (blue solid line), and $\mathbf{GS_{80}}$-BPDT (10:1) (red solid line).

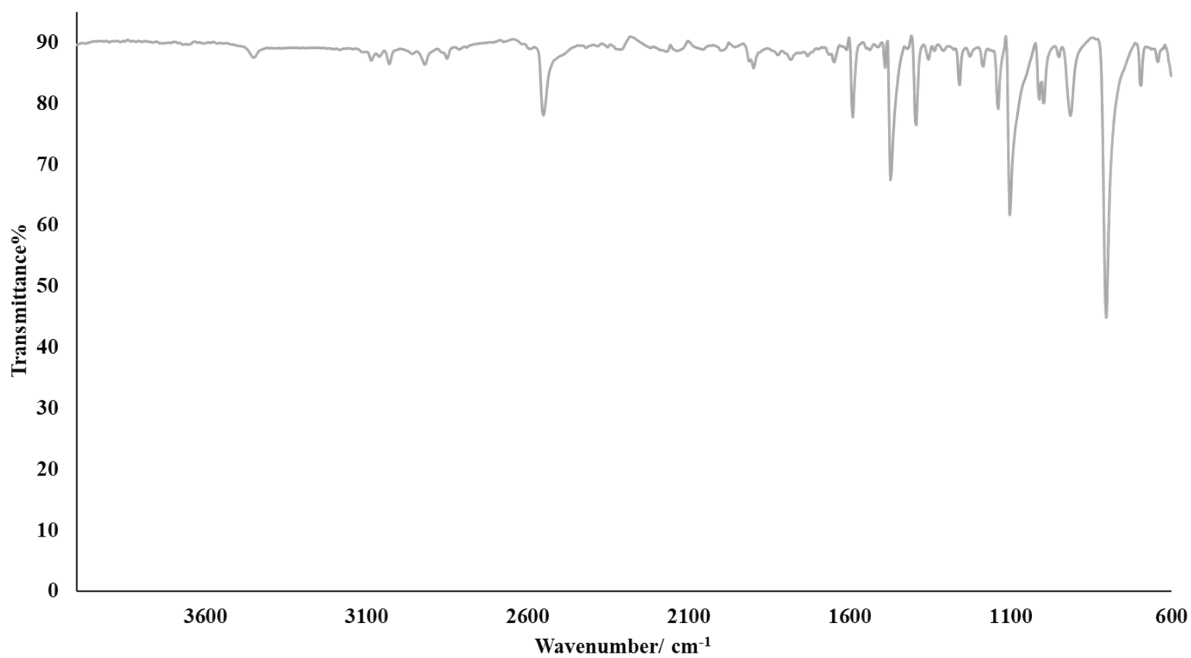

Figure S9. Infrared spectrum of 4,4'-biphenyldithiol.

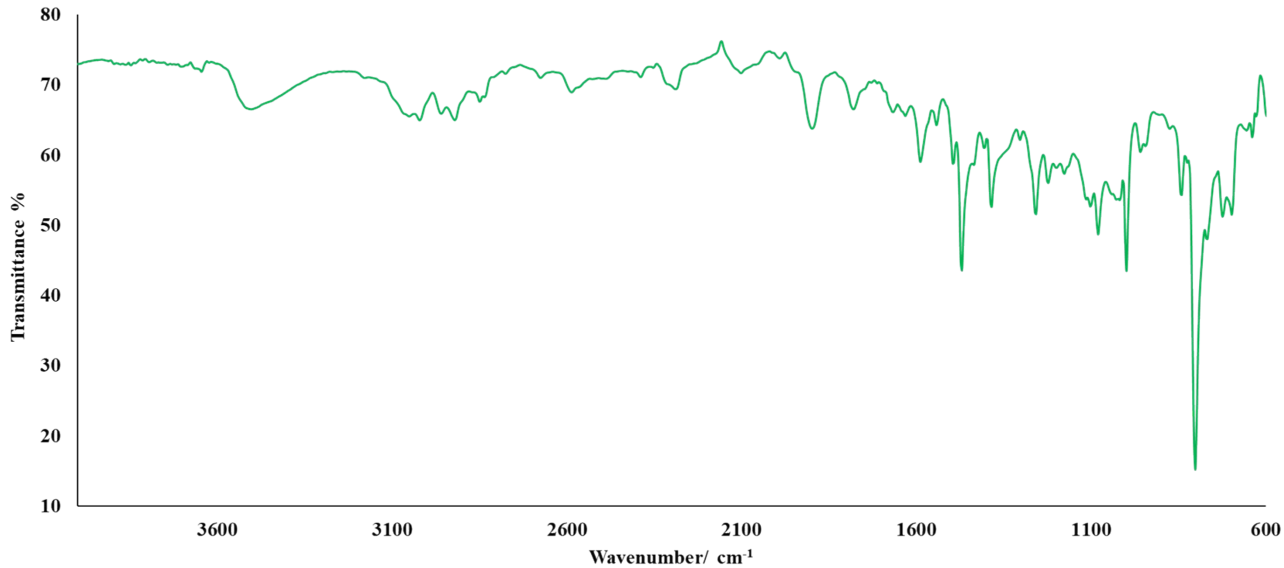

Figure S10. Infrared spectrum of **GS$_{80}$**-BPDT (2:1).

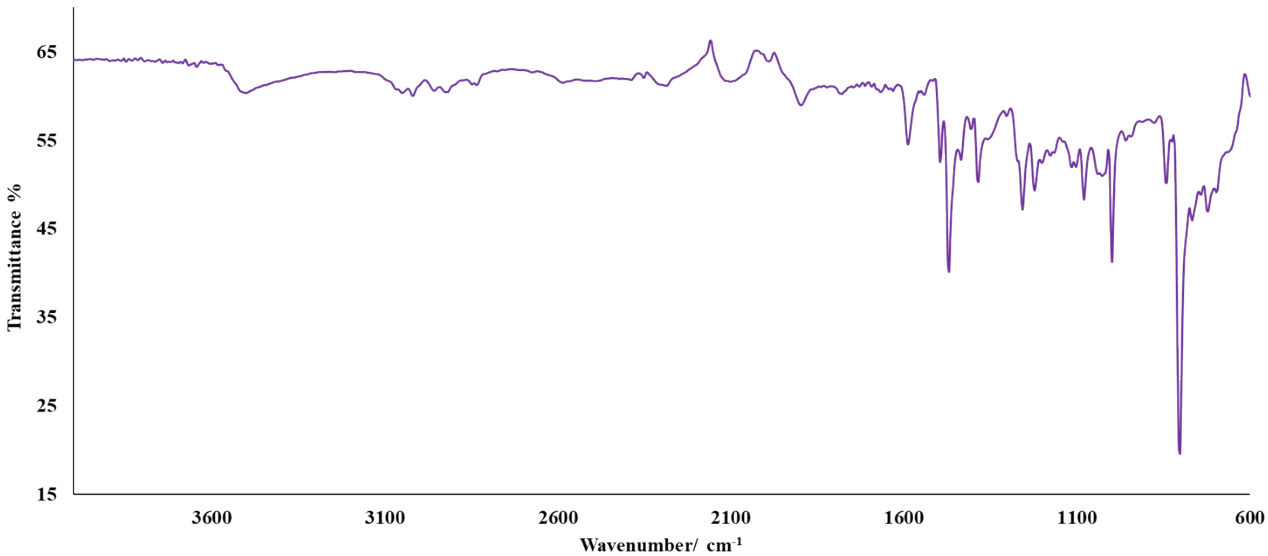

Figure S11. Infrared spectrum of $\mathbf{GS_{80}}$-BPDT (3:1).

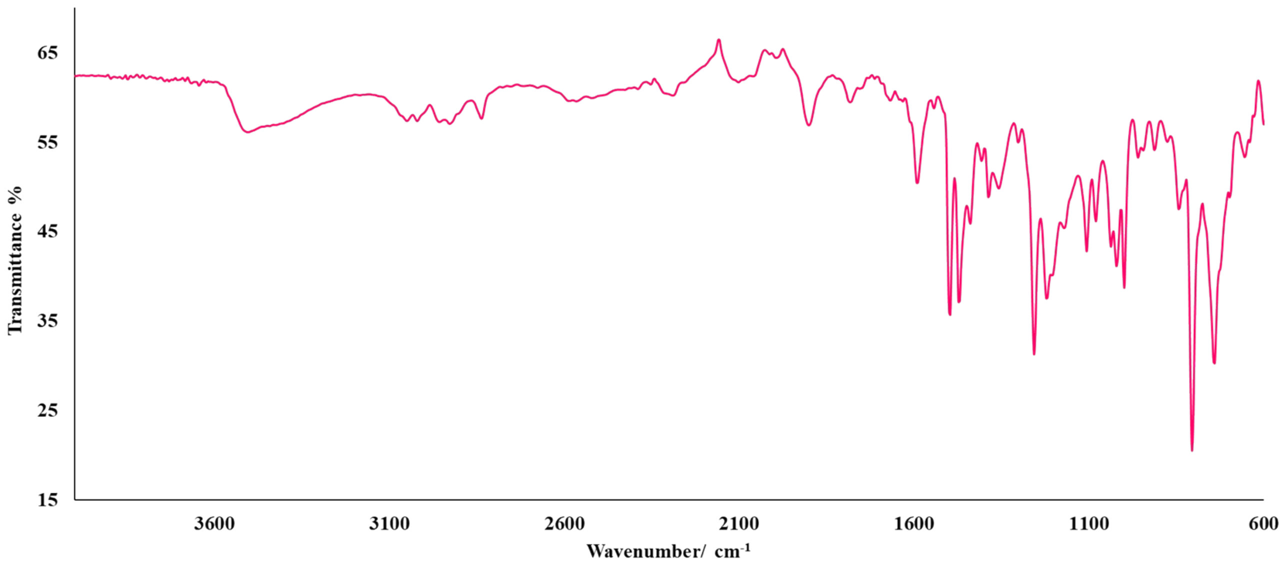

Figure S12. Infrared spectrum of **GS$_{80}$**-BPDT (4:1).

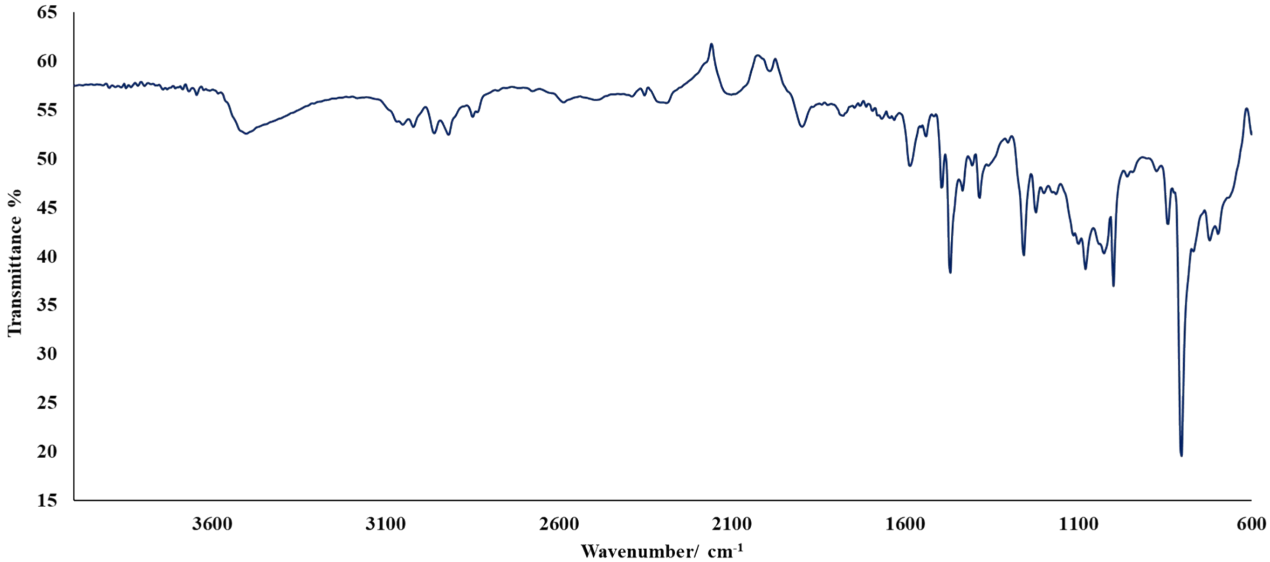

Figure S13. Infrared spectrum of **GS$_{80}$**-BPDT (5:1).

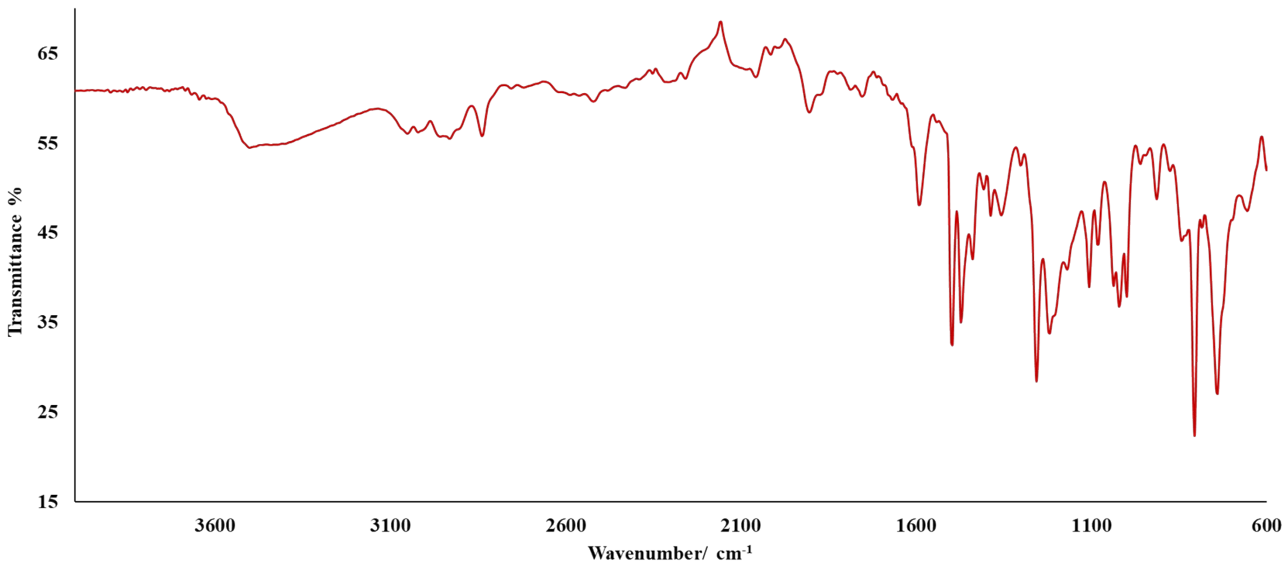

Figure S14. Infrared spectrum of $\mathbf{GS_{80}}$-BPDT (10:1).

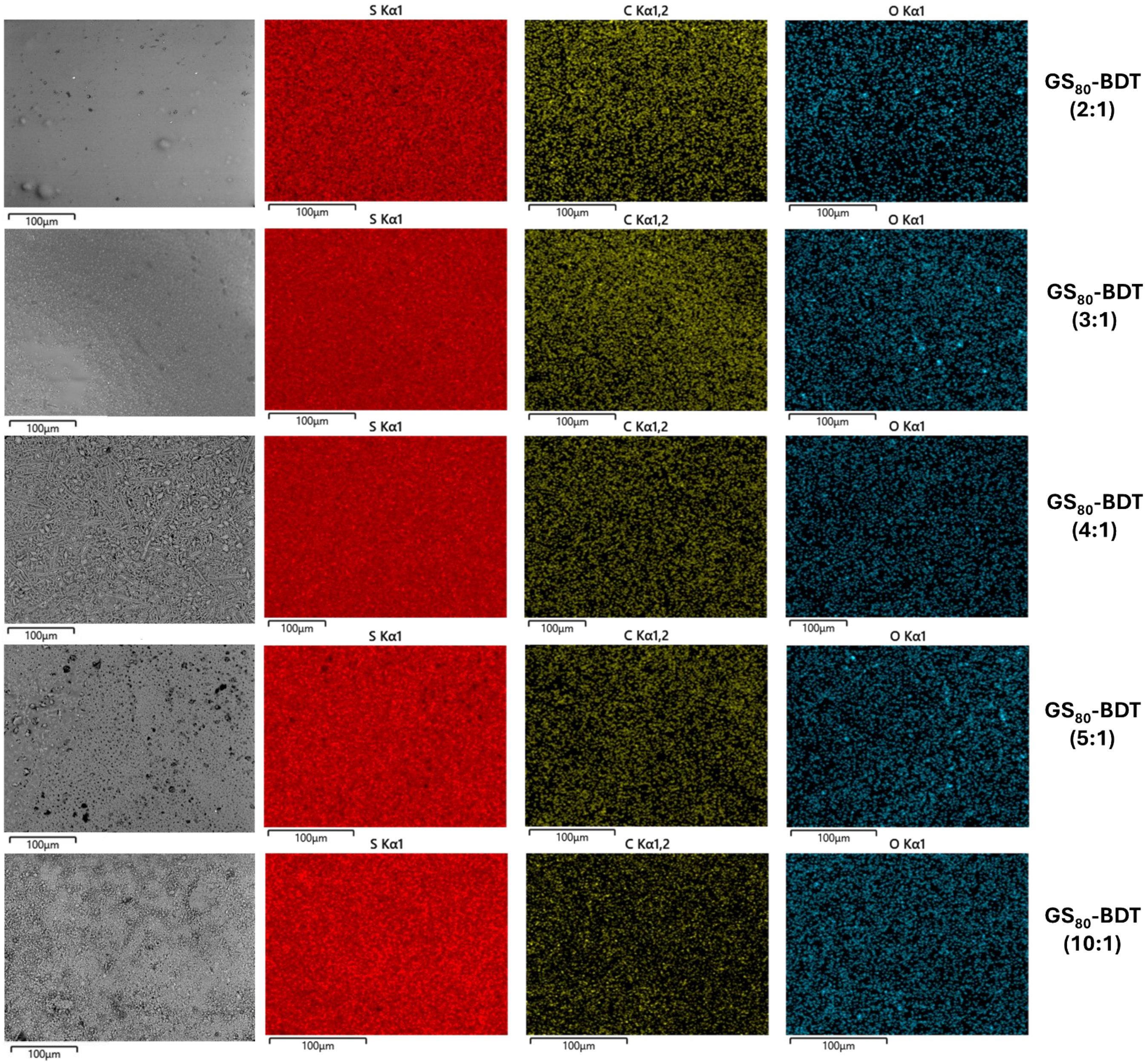

Figure S15. Scanning electron microscopy (SEM, gray image) with elemental mapping by energy dispersive X-ray spectroscopy (EDS) of **GS_{80}**-BDT modified materials. Sulfur is shown in red, carbon in yellow, and oxygen in blue.

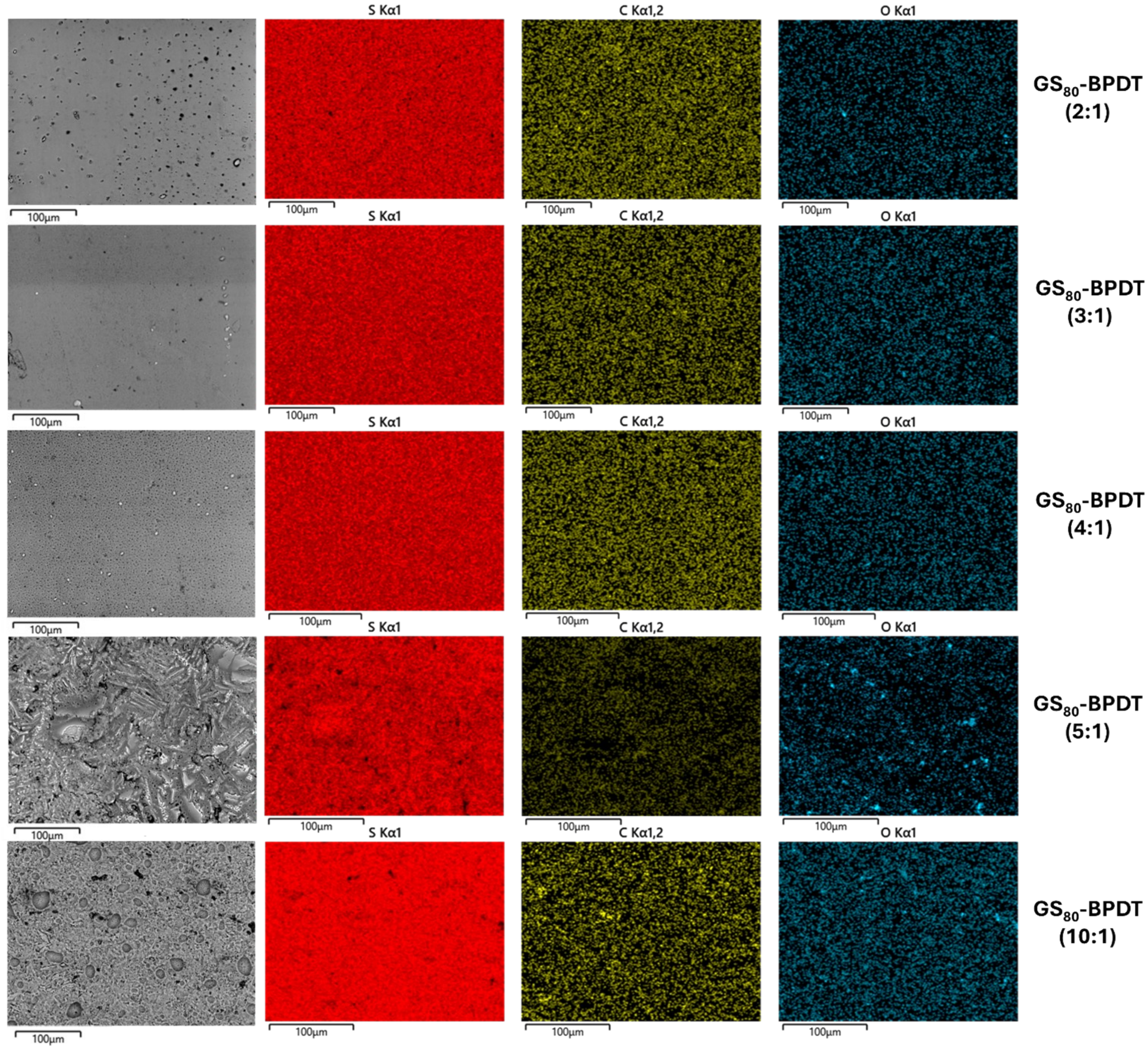

Figure S16. Scanning electron microscopy (SEM, gray image) with elemental mapping by energy dispersive X-ray spectroscopy (EDS) of **GS$_{80}$**-BPDT modified materials. Sulfur is shown in red, carbon in yellow, and oxygen in blue.

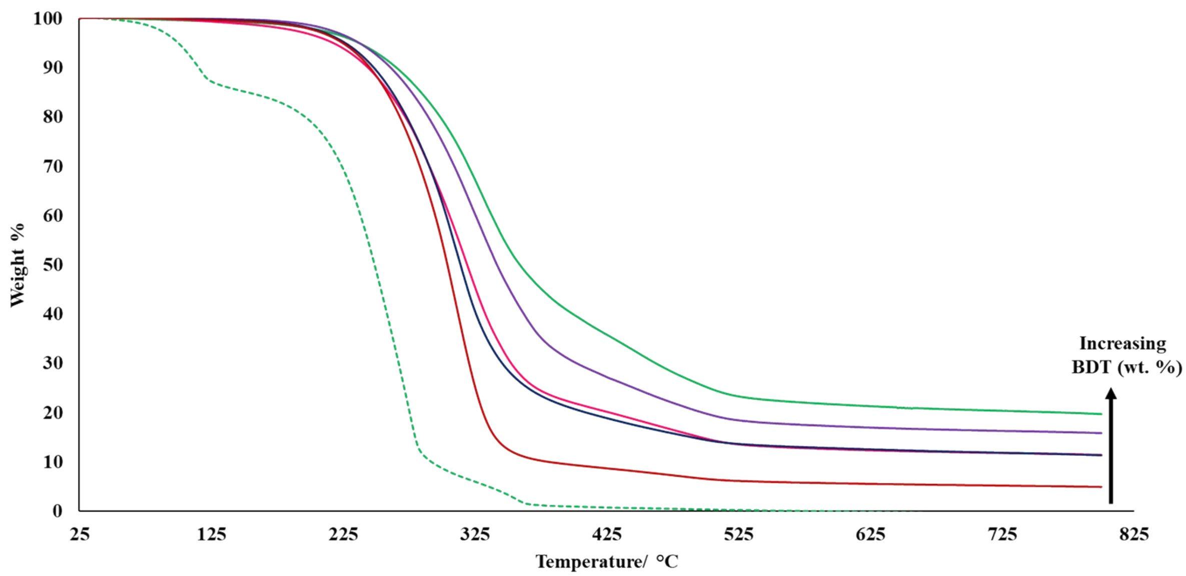

Figure S17. Thermogravimetric analysis (TGA) curves for **GS$_{80}$** (green dash line), **GS$_{80}$**-BDT (2:1) (green solid line), **GS$_{80}$**-BDT (3:1) (purple solid line), **GS$_{80}$**-BDT (4:1) (pink solid line), **GS$_{80}$**-BDT (5:1) (blue solid line), and **GS$_{80}$**-BDT (10:1) (red solid line).

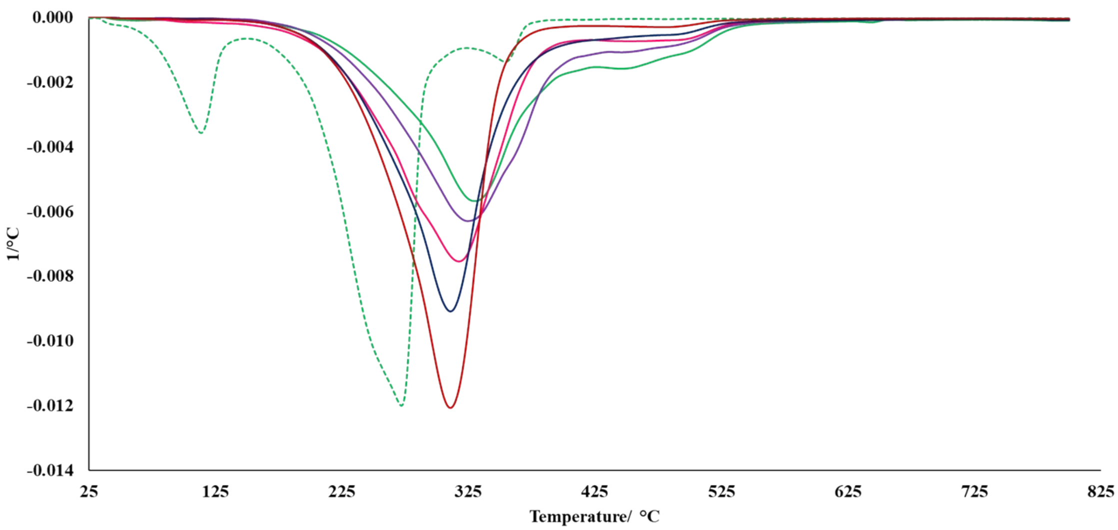

Figure S18. Thermogravimetric analysis – first derivative (DTG) curves for **GS$_{80}$** (green dash line), **GS$_{80}$**-BDT (2:1) (green solid line), **GS$_{80}$**-BDT (3:1) (purple solid line), **GS$_{80}$**-BDT (4:1) (pink solid line), **GS$_{80}$**-BDT (5:1) (blue solid line), and **GS$_{80}$**-BDT (10:1) (red solid line).

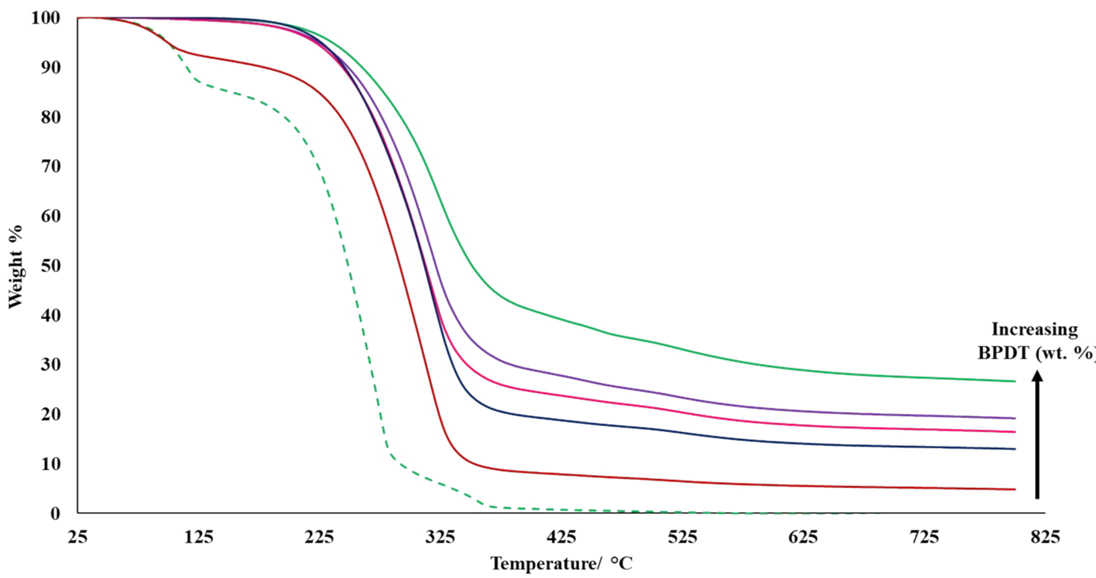

Figure S19. Thermogravimetric analysis (TGA) curves for **GS$_{80}$** (green dash line), **GS$_{80}$**-BPDT (2:1) (green solid line), **GS$_{80}$**-BPDT (3:1) (purple solid line), **GS$_{80}$**-BPDT (4:1) (pink solid line), **GS$_{80}$**-BPDT (5:1) (blue solid line), and **GS$_{80}$**-BPDT (10:1) (red solid line).

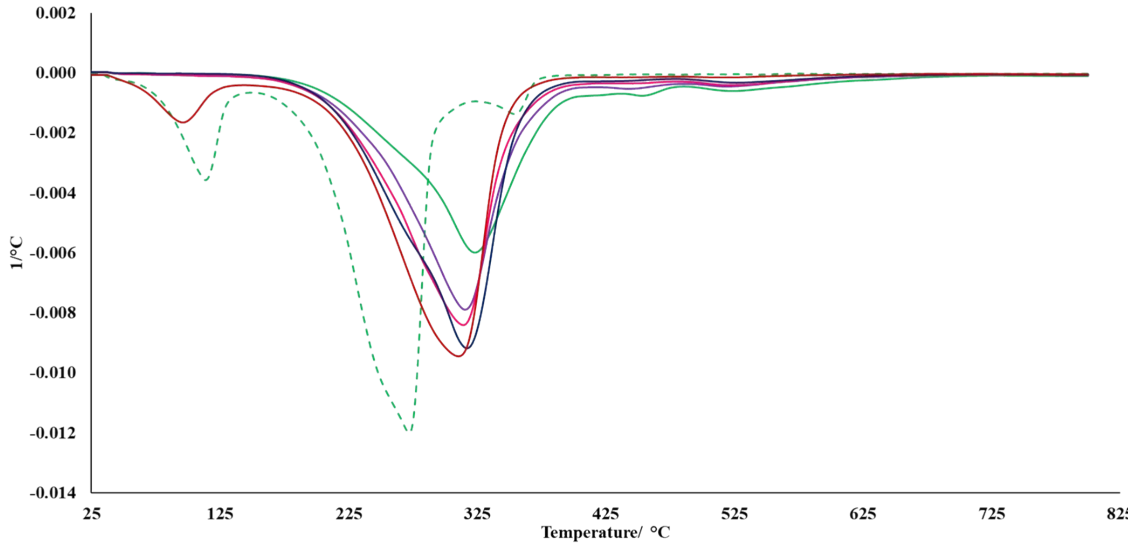

Figure S20. Thermogravimetric analysis–first derivative (DTG) curves for **GS$_{80}$** (green dash line), **GS$_{80}$**-BPDT (2:1) (green solid line), **GS$_{80}$**-BPDT (3:1) (purple solid line), **GS$_{80}$**-BPDT (4:1) (pink solid line), **GS$_{80}$**-BPDT (5:1) (blue solid line), and **GS$_{80}$**-BPDT (10:1) (red solid line).

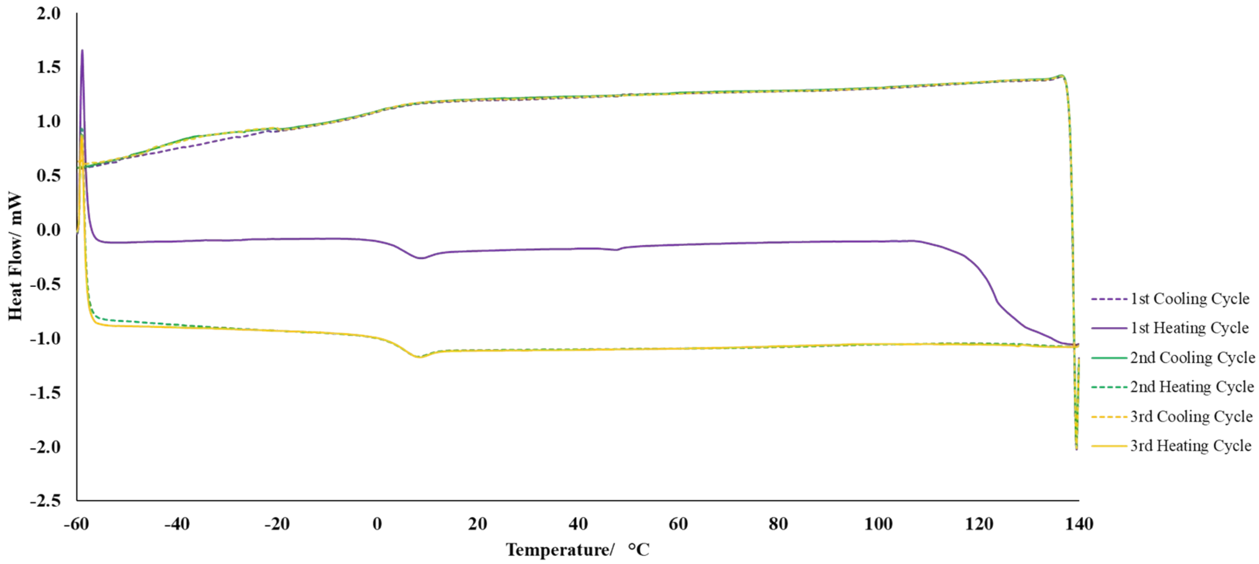

Figure S21. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BDT (2:1). Endothermic features are downward.

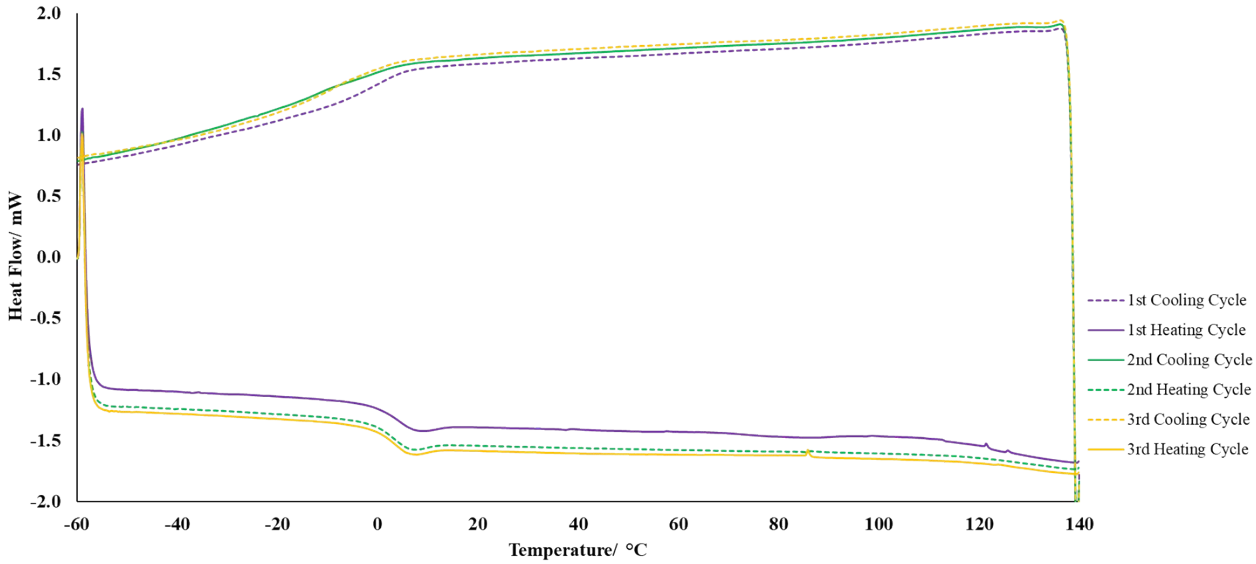

Figure S22. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BDT (3:1). Endothermic features are downward.

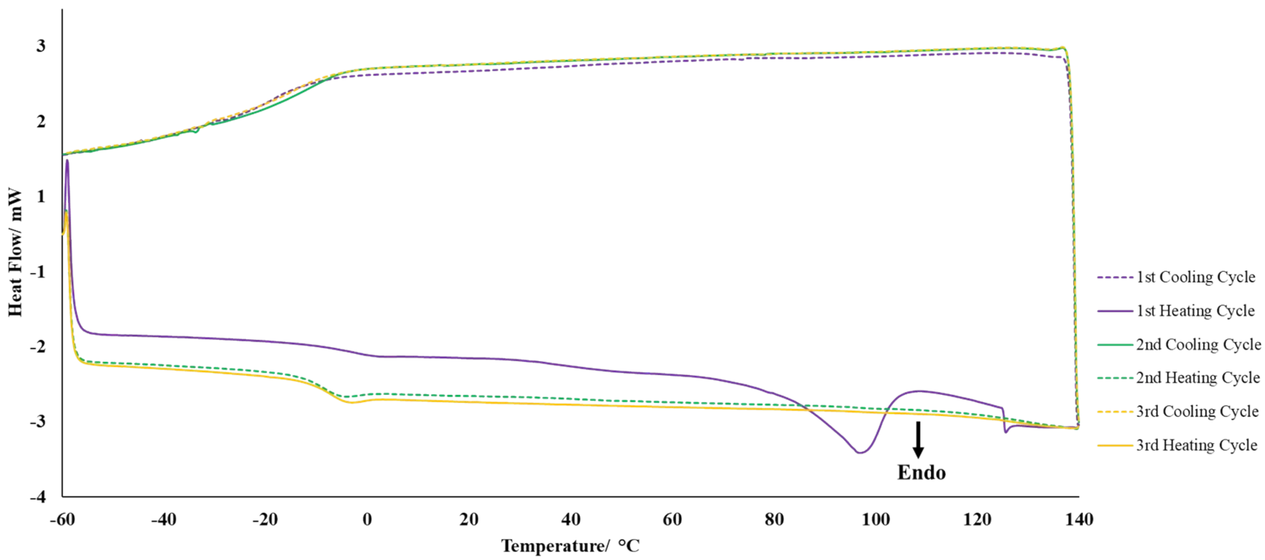

Figure S23. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BDT (4:1).

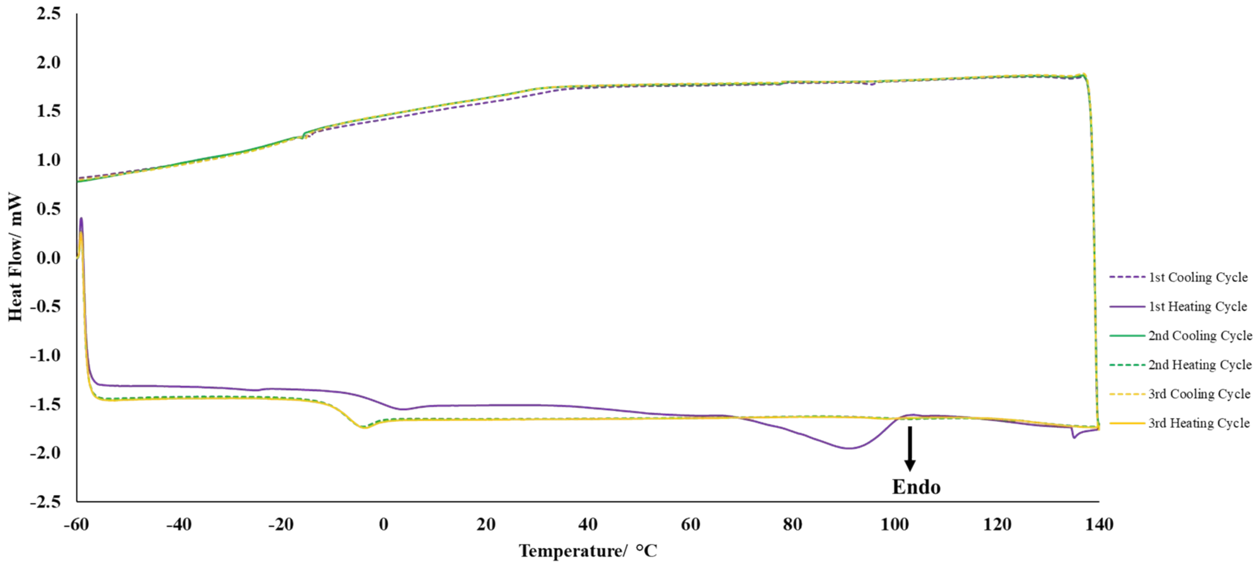

Figure S24. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BDT (5:1).

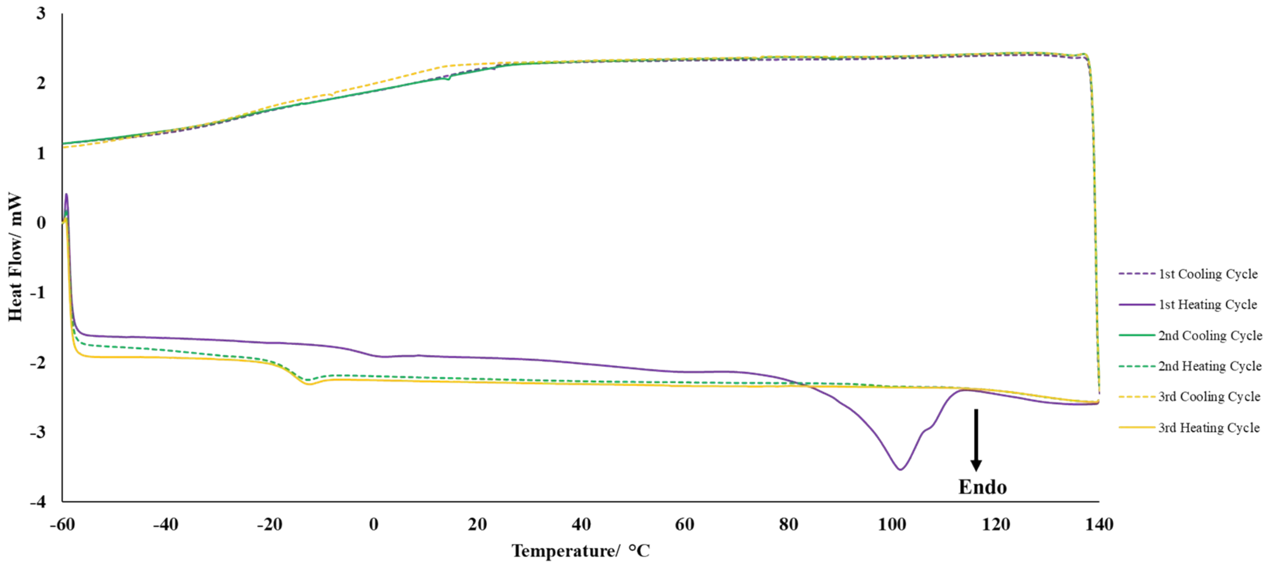

Figure S25. Differential scanning calorimetry (DSC) traces for $\mathbf{GS_{80}}$-BDT (10:1).

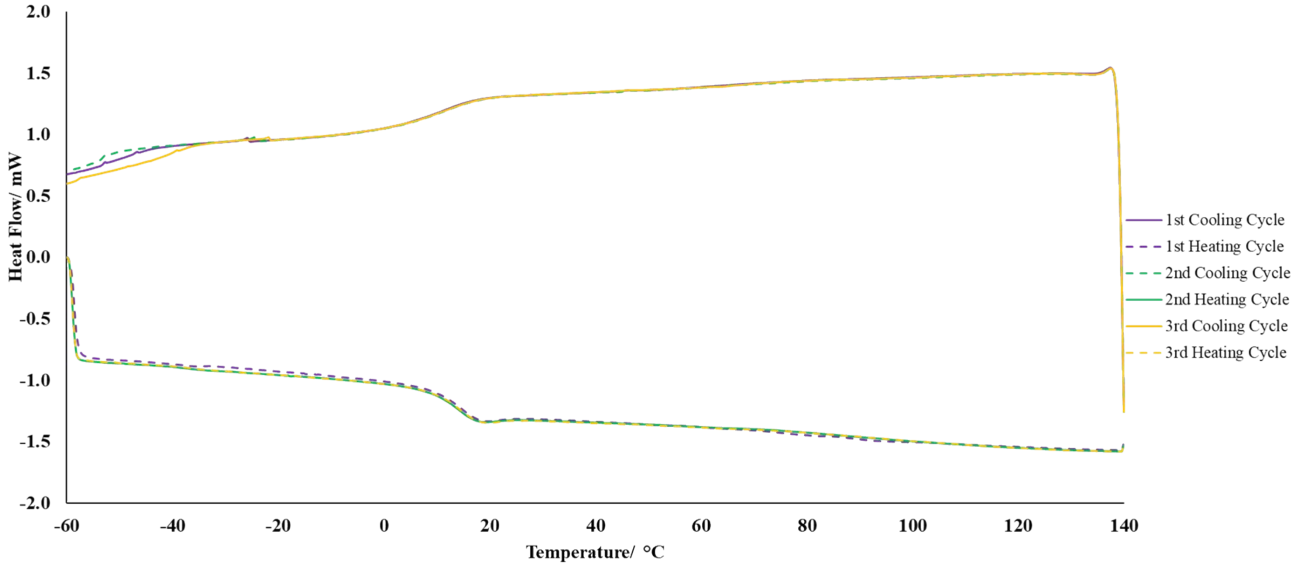

Figure S26. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BPDT (2:1). Endothermic features are downward.

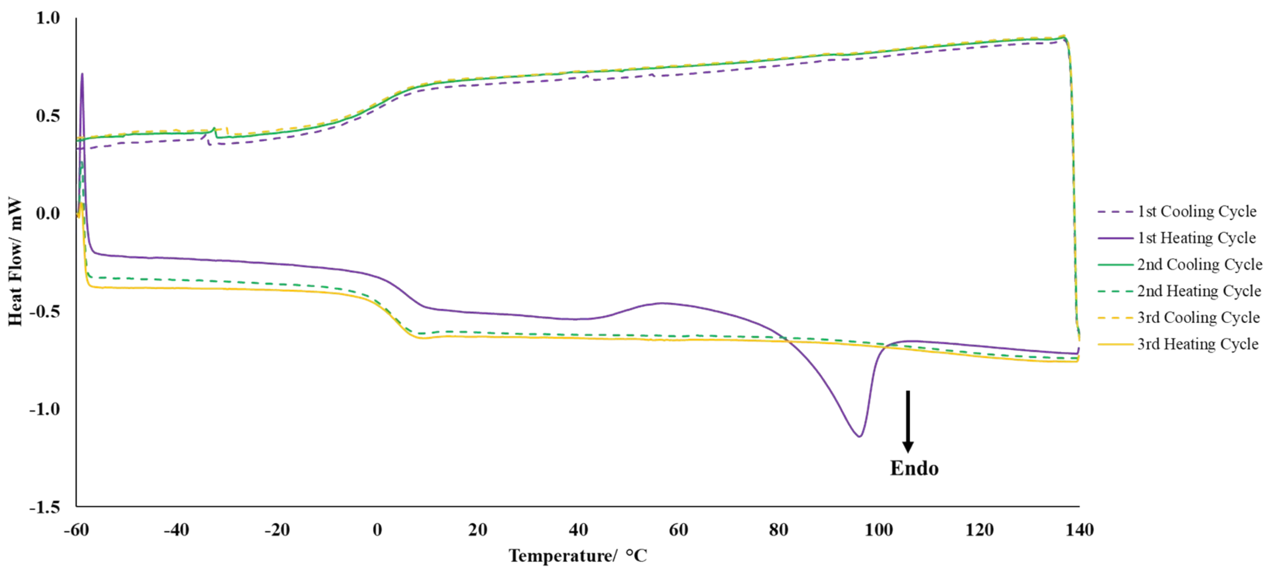

Figure S27. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BPDT (3:1).

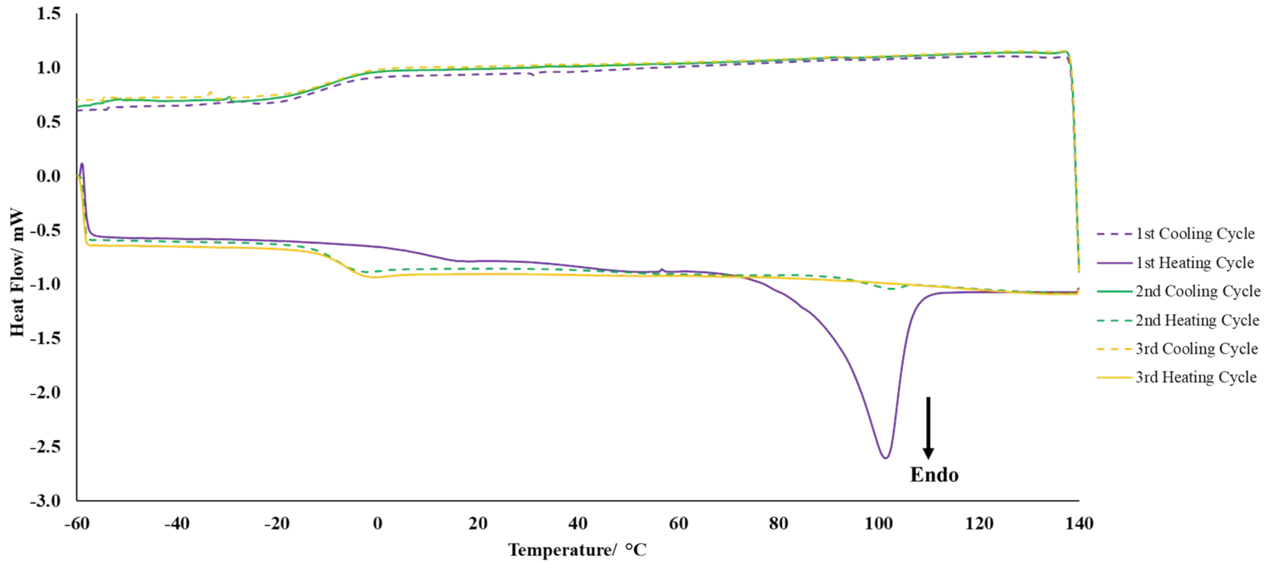

Figure S28. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BPDT (4:1).

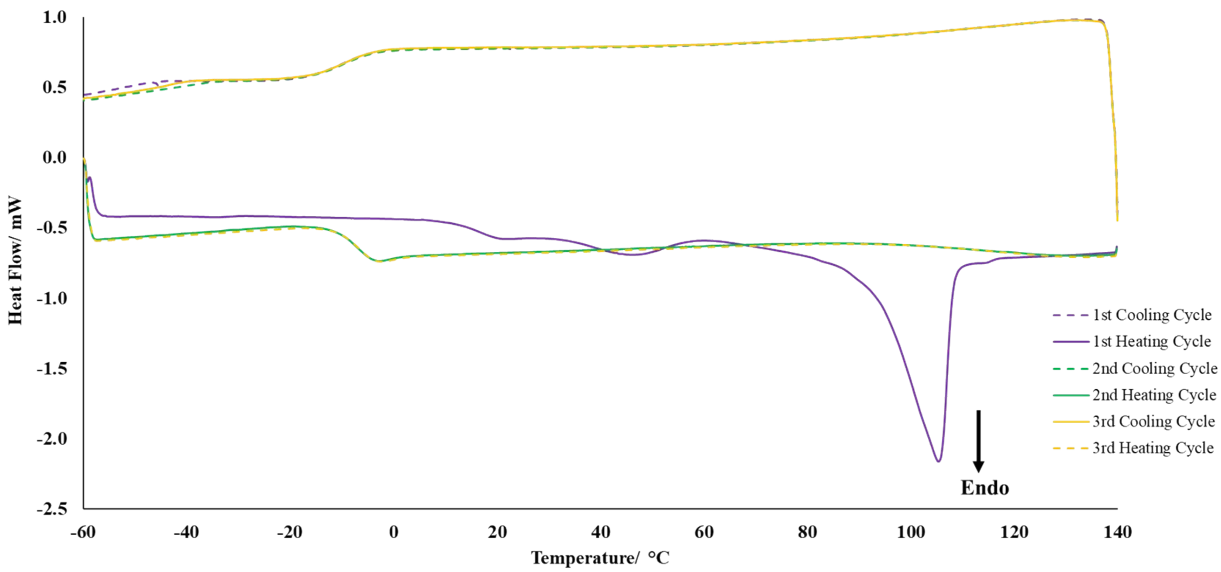

Figure S29. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BPDT (5:1).

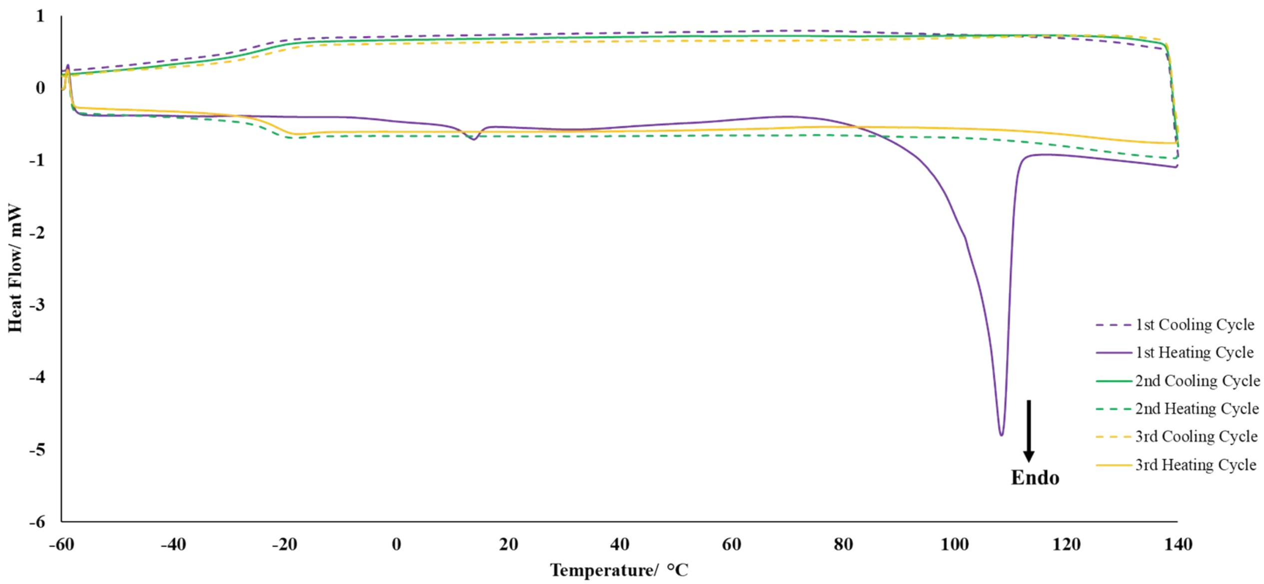

Figure S30. Differential scanning calorimetry (DSC) traces for **GS$_{80}$**-BPDT (10:1).

References

1. M. S. Karunarathna, M. K. Lauer and R. C. Smith, *Journal of Materials Chemistry A*, 2020, **8**, 20318-20322.
2. J. J. Dale, J. Stanley, R. A. Dop, G. Chronowska-Bojczuk, A. J. Fielding, D. R. Neill and T. Hasell, *European Polymer Journal*, 2023, **195**, 112198.