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

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A simple approach to a high sulfur-content material from biomass-derived guaiacol and waste sulfur is introduced. This direct reaction of elemental sulfur with an anisole derivative lacking olefins or halogen leaving groups expands the monomer scope beyond existing routes to high sulfur-content materials.
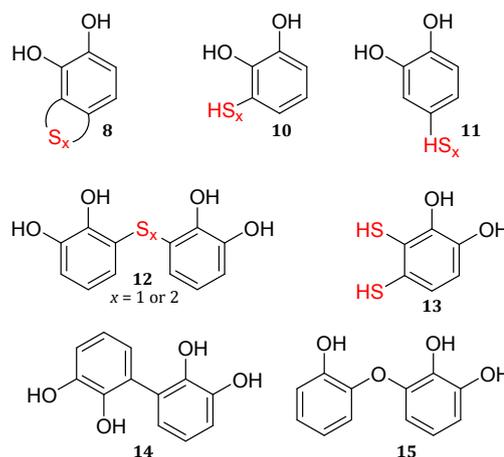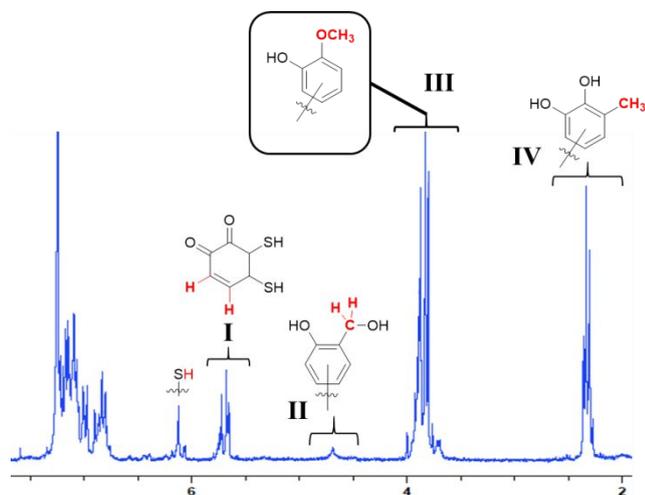
High sulfur-content materials (HSMs) have garnered significant interest recently as electrode materials,[1-5] elements of thermal imaging cameras,[6] adsorbents for water purification,[7-11] and as structural materials.[12-24] Advances in HSM preparation demonstrate that in many cases they can be readily processed,[25, 26] recycled[27] and prepared at relatively low temperatures.[28-31] HSMs are attainable when sulfur and an organic monomer are copolymerized in such a way as to yield a crosslinked network that stabilizes polymeric sulfur domains. In the absence of a stabilizing network, polymeric sulfur undergoes spontaneous homolysis of S–S bonds even at room temperature, eventually reverting back to the S_8 allotrope.[32] Current routes to high sulfur-content materials are inverse vulcanization (requiring an olefin monomer)[33-36] and radical-initiated aryl halide-sulfur polymerization (RASP, requiring an aryl halide monomer).[16, 17, 37, 38] In both of these mechanisms C–S bond formation is initiated by the thermal generation of radicals. In inverse vulcanization S_8 rings undergo homolysis followed by an equilibration to polymeric sulfur diradicals that subsequently react with olefins. In RASP, thermal homolysis of aryl halide C–X bonds creates aryl radicals that react with sulfur to facilitate C–S bond formation. We hypothesized that elemental sulfur could likewise undergo facile reaction with any number of organic molecules that degrade to radicals or radical-reactive species upon heating. This strategy could thus open up routes to HSMs using previously-inaccessible organic monomers. Guaiacol is an especially attractive molecule to test this hypothesis because 1) it is abundant and renewably-sourced from biomass lignin, and 2) the formation of radical-reactive species in the course of its thermal decomposition has
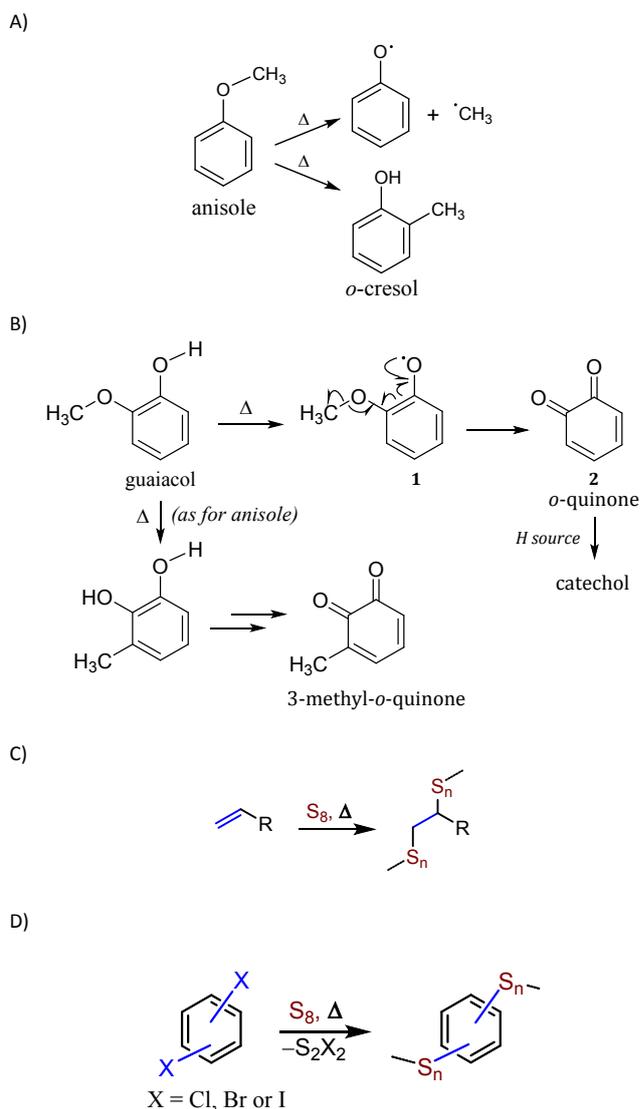
Scheme 1. Established thermal decomposition of anisole (A) and guaiacol (B) and established inverse vulcanization (A) and RASP (B) routes to HSMs
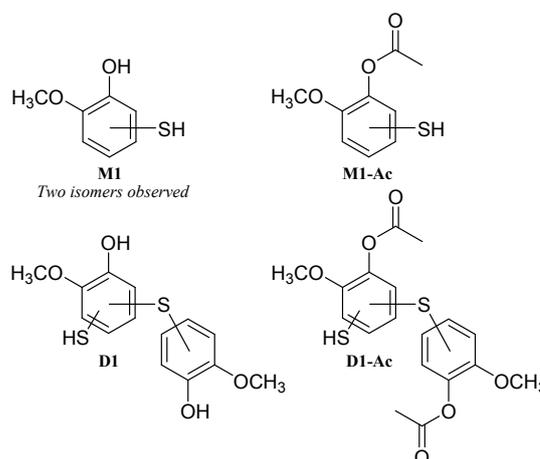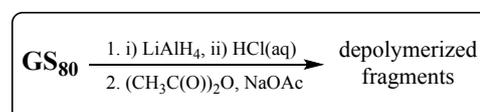
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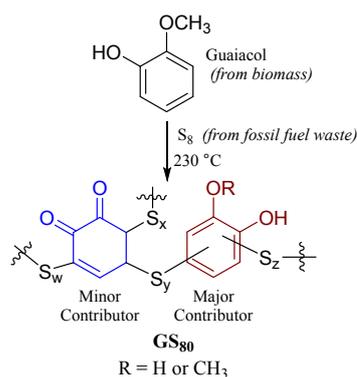
Scheme 2. Preparation of **GS$_{80}$**.

Figure 1. Proton NMR spectroscopic analysis of **GS$_{80}$** depolymerization products. Resonance groups are attributed to the red-highlighted protons within each attendant structure.

Chart 1. Products previously observed from reaction of polymeric sulfur radicals and *o*-quinone.

Chart 2. Depolymerization products from **GS$_{80}$** observed by GC-MS. Mass spectra for these species are provided in ESI Figures S5–8.

been well-studied (Scheme 1).[39-46] Lignin, of which guaiacol is a primary derivative, is a bountifully abundant yet remarkably underutilized resource, while sulfur is the primary underutilized by-product of petroleum and natural gas refining.[47] Accessing useful polymers by direct reaction of guaiacol and sulfur could thus be a notable accomplishment in sustainability science. Herein we demonstrate the formation of an HSM, **GS$_{80}$** (80 wt% sulfur in the monomer feed, Scheme 2), via the direct reaction of guaiacol and elemental sulfur. Insight into microstructures and potential mechanistic pathways by which this HSM forms are provided by ^{1}H NMR and GC-MS analysis.

When guaiacol and sulfur are heated together in a 1:4 mass ratio at 230 °C under nitrogen in a sealed pressure tube for 24 h followed by cooling to room temperature, the product is a remeltable brown solid, **GS$_{80}$** (Scheme 1 and ESI Figure S9). Differential scanning calorimetry (DSC) of **GS$_{80}$** confirms the presence of polymeric sulfur from observation of the diagnostic glass transition temperature (T_g) at −30 °C. The presence of some orthorhombic sulfur in **GS$_{80}$** was also indicated by the observation of melting and cold crystallization transitions in the DSC data (ESI Figure S1). Thermogravimetric analysis (TGA)

showed that **GS$_{80}$** also has good thermal stability, with a decomposition temperature (T_d) of 264 °C (onset temperature of the major mass loss by TGA). For comparison, the T_d of sulfur is 228 °C and the T_d for guaiacol is 105 °C (TGA curves for all the materials are provided in ESI Figure S2). Scanning electron microscopy (SEM) imaging with element mapping by energy dispersive X-ray analysis (EDX) confirm that bulk **GS$_{80}$** appears homogeneous with a uniform distribution of its elemental components (ESI Figure S4). In terms of mechanical strength, **GS$_{80}$** exhibited an ultimate tensile strength of 2.32±0.02 MPa with an elongation at break = 10.9±2.1%. The tensile strength of **GS$_{80}$** lies within the range of 1.5–4.5 MPa observed for other HSMs prepared by the established inverse vulcanization of sulfur (50 wt%) and dicyclopentadiene with either linseed oil, ethylene glycol dimethyl acrylate or limonene (photos of tensile measurements are shown in ESI Figure S9).[48] Another guaiacol-sulfur composite (**GS$_{90}$**) was prepared following the route for

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GS90, but comprising 90 wt% sulfur. Although the thermal stability of **GS90** (T_d = 252 °C) is similar to that of **GS80**, the higher percentage of sulfur in **GS90** led to it having ≤50% the tensile strength (1.16±0.53 MPa) and elongation at break (4.3±1.8%) of **GS80**, making it an inferior candidate as a structural material. Further investigation thus centred on **GS80**.

Having established the presence of polymeric sulfur domains and thermal/mechanical properties consistent with other HSMs prepared by established routes, additional investigation was undertaken to elucidate the microstructure of **GS80**. Being comprised in part by a crosslinked network, composite **GS80** is only partially soluble in organic solvents like CS_2 (80 wt% soluble), and the elemental composition of the soluble and insoluble fractions are not identical (see the ESI for details). In order to obtain information on microstructures present in the bulk, depolymerization of **GS80** was thus affected by its reaction with $LiAlH_4$ (followed by partial acetylation of OH and SH to facilitate travel in the GC column). Analysis of these soluble depolymerization products by ^{1}H NMR spectrometry (Figure 1) and GC-MS (Chart 2) revealed several structural units of **GS80**.

Established thermal decomposition pathways for anisole derivatives in general and guaiacol in particular (Scheme 1) serve as the starting point for understanding the formulation of the structural units observed in **GS80** and for unravelling potential mechanistic pathways by which these micro-structures form. The major thermal decomposition pathways shown for guaiacol in Scheme 1B lead to *o*-quinone derivatives. An insightful study[49] on the reaction between *o*-quinone and *in situ*-generated polymeric H–S_x–H thus provides significant insight into possible mechanisms for the formation of microstructures observed in **GS80**. That study revealed that *o*-quinone reacts with polymeric sulfur radicals formed from the spontaneous homolysis of the S–S bonds in H–S_x–H. These sulfur radicals facilitate C–S bond-formation with *o*-quinone to form species such as compounds **3–5** (Scheme 3). GC-MS analysis was used to characterize several products resulting from further reaction of **4** and **5**. Products observed included oligosulfanes **8** and species **10–15** resulting from typical *o*-quinone self-coupling motifs (Scheme 4 and Chart 1). Analogous reactions between *o*-quinone derivatives and sulfur radicals generated during preparation of **GS80** (Scheme 4) provide reasonable mechanisms for formation of the microstructures observed from ^{1}H NMR and GC-MS analysis of **GS80** depolymerization products.

In the presence of a large excess of sulfur (80 wt%) during the preparation of **GS80**, dilution should preclude significant production of *o*-quinone self-coupling products, and none of these self-coupling products were observed in the GC-MS analysis. With an excess of sulfur, species like **4**, **5** and **8** also have the potential to be appended with polymeric sulfur that could be stabilized by the crosslinked network. The presence of such polymeric sulfur chains in **GS80** is supported by the observation of a pronounced T_g at −30 °C in the DSC. Olefin functionalities in **5** are subject to reaction with sulfur radicals by
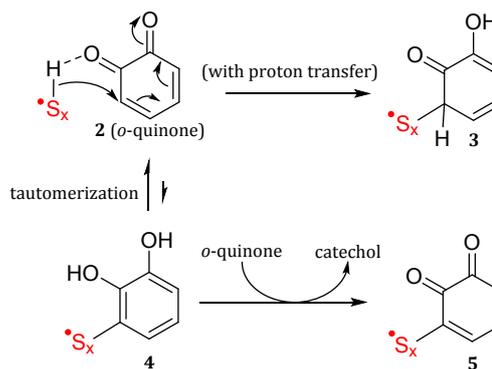
Scheme 3. Reaction of *o*-quinone with sulfur radicals.
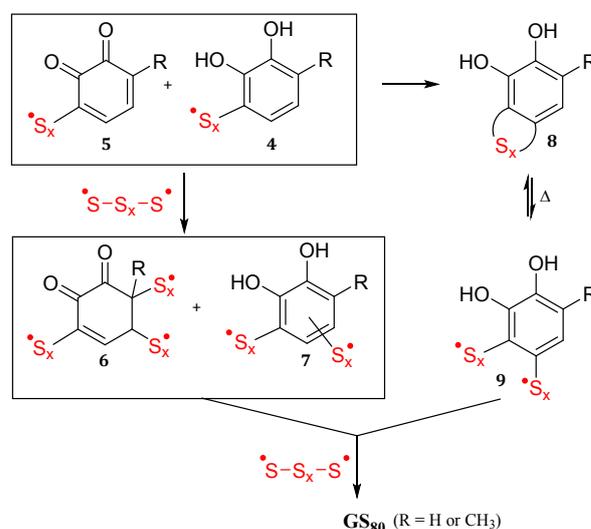
Scheme 4. Formation of **GS80** from compounds **4**, **5** and **8**

the usual inverse vulcanization pathway to give species such as **6**, and formation of C–S bonds at sites *o*- or *p*- to hydroxyl groups on catechol derivatives continues in a manner analogous to the mechanism for formation of **8**. Equilibration of poly- and oligosulfur chains allows the formation of the crosslinked network necessary to stabilize these extended sulfur catenates in **GS80** with the bonding motifs shown in Scheme 2.

Although one pathway for thermal degradation of anisole derivatives is loss of the methyl fragment from the methoxy substituent, the observation of resonance groups III and IV in the ^{1}H NMR spectrum of **GS80** depolymerization products confirms that some methoxy groups are retained in the composite, while methyl migration typical for thermal degradation of anisoles occurs for some of the rings as well. The decrease in the integration of aromatic signals relative to the methyl resonances also confirms the expected loss of aryl H atoms as C–S bonds are formed. Unfortunately, it cannot be assumed that all methyl groups are retained in **GS80** – methyl radicals could react with sulfur directly or aryl methyl groups

may form benzylic species as discussed below – so the absolute number of C–S bonds formed cannot be quantified from these data. Resonance group I is consistent with non-aromatic olefinic protons on structural subunits resulting from the addition of sulfur radicals across an unsaturated unit of transiently-formed *o*-quinone species such as **5**. These quinone derivatives would also be intermediates to access subunits **D1** and **D1-Ac** observed by GC-MS analysis (Chart 2).

In addition to functional units shown for the representation of **GS$_{80}$** in Scheme 1, a very small (2–3%) contribution of a species having resonances around 4.6 ppm (peak II in Figure 1) is also observed. This is tentatively assigned as a unit containing a benzylic alcohol unit. The formation of benzylic alcohols from *o*-methoxy phenol derivatives is well-known, for example as a key intermediate step in the thermal production of vanillin from syringol (a close structural analogue of guaiacol).[50]

Conclusions

In conclusion, we report a new strategy for preparing organosulfur composites by the reaction of elemental sulfur with an anisole derivative. Polymerization exploits reactivity between radical-reactive thermal degradation products of guaiacol with majority component elemental sulfur. This approach thus provides a remarkably simple method to prepare a composite (**GS$_{80}$**) from two abundant, low-value materials – biomass-derived guaiacol and fossil fuel waste sulfur. The functionalities observed in the microstructure are consistent with a mechanism wherein established thermal degradation products of guaiacol react with sulfur radicals. Work is ongoing to establish structure-property relationships in these and related terpolymers of sulfur, guaiacol and other crosslinkers to establish optimal monomer ratios to accomplish desired mechanical and thermal properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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