<u>Porous inverse vulcanised polymers for mercury capture – electronic supplementary information</u>

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Materials: Sulfur (\geq 99.5 %), fumed silica (0.2-0.3 um average particle size), mercury chloride, and limonene (>93%) were purchased from Sigma Aldrich and used as received. Carbon black (Ketjen Black EC600 JD) was purchased from AkzoNobel. 1,3-diisopropenylbenzene (>97 %) was purchased from TCI and used as received. CO₂ was purchased from BOC (food grade). Kaolin (superfine china clay, 80 % <1 µm) was donated by Richard Baker Harrison LTD).

S-DIB synthesis: A 40 mL glass vial was equipped with a magnetic stir bar and sulfur added . This was then placed in an oil bath preheated 185 °C. The sulfur was left until it liquefied (orange solution) before adding 1,3-Diisopropenylbenzene (DIB) directly by pipette. The resulting mixture was stirred at T = 185 °C for 8-10 minutes, which resulted in vitrification of the reaction media. Recovery of the product required shattering of the glass vial and careful separation of the polymer and glass fragments. Two sulfur:DIB ratios were used in this study. 70 wt% Sulfur, and 50 wt% sulfur:

70 wt% sulfur: The copolymerization was carried out by following the general method written above with S8 (3.50 g, 13.7 mmol) and DIB (1.50 g, 9.48 mmol) to afford a red solid.

50 wt% sulfur: The copolymerization was carried out by following the general method written above with S8 (2.50 g, 9.69 mmol) and DIB (2.50 g, 15.8 mmol) to afford reddishbrown solid.

S-limonene synthesis: Closely following the procedure previously reported:¹ Sulfur (25.0 g, 97.5 mmol S8) was added to a 100 mL round bottom flask equipped with a stir bar. The flask was then placed in an oil bath pre-heated to 170 °C and stirred vigorously. After 30 minutes, limonene (25.0 g, 29.6 mL, 183 mmol) was added over 2 to 5 minutes. The flask was then equipped with distillation head and condenser. After another 60 minutes the temperature was increased 180 °C and volatile material was removed by vacuum distillation (~50 mm Hg). The non-volatile material remaining in the flask was then cooled and dried further under high vacuum (< 1 mm Hg) at 100 °C overnight. After cooling to room temperature, the final product vitrified and was obtained as a dark red material. H NMR is in agreement with previously published results (Fig. S17).¹ Some of the sulfur-limonene polysulfide was moulded into a shape by heating to 100 °C and pouring into a silicone mould before leaving to set in refrigerator overnight (4 °C).

Supercritical foaming: The process used to foam the co-polymers consists of two steps: soaking and expansion. The temperature of the fluid was at all times monitored directly via an in situ thermocouple. During soaking, the polymer substrate (~100 mg to 5 g, depending on sample) was placed inside a glass vial in a stainless steel autoclave which was then filled with ~5.5 MPa of CO₂. The autoclave was then heated to the desired temperature (usually 80 °C) and topped up to 10, 20, or 28 MPa. The scCO₂ was maintained under these conditions

for a duration (normally 3 hours) in order to allow the scCO₂ to infuse fully into the polymer. In the expansion step, the scCO₂ was then vented rapidly in less than one minute. The heating is then stopped, and the autoclave opened to remove the foamed sample. Reactions were conducted in a custom built high pressure, clamp sealed autoclave of 60 ml volume which contains a directly coupled magnetically driven agitator. The CO₂ was compressed using a PM-101 pump (New Ways of Analytics, Lörrach, Germany) and the temperature within the autoclave was regulated by means of an external heating jacket controlled to ± 1 °C using a Cal 3200 digital heating controller (RS, England).

Hg Capture: A stock solution of mercury was made by dissolving HgCl₂ in deionised water to a concentration of 2 ppm (1975 ppm by ICP-OES). 5 mL of this solution was placed in a series of glass sample vials along with 100 mg of sample (powder in the case of S-DIB, and foamed S-DIB, coalesced solid in the case of S-limonene). The sample vials were capped and stirred slowly by Teflon coated magnetic stirrer bars for 3 hours. The water was then decanted and filtered through a glass wool plug to remove any remaining solids, and analysed by ICP-OES. For the filtration experiment, 500 mg S-DIB polymer powder was loaded into a glass column (1 cm diameter) and held in place between small plugs of glass wool. HgCl₂ solution (5 mL, 2.37 ppm) was poured into the top. After approximately 5 minutes this had run through the column into a vial below, and was tested by ICP to have 1.40 ppm remaining.

Scanning Electron Microscopy (SEM): Imaging of the foamed polymer morphology was achieved using a Hitachi S-4800 cold Field Emission Scanning Electron Microscope (FE-SEM) operating in both scanning and transmission modes. The dry samples were prepared by dispersing the polymer powder directly onto adhesive carbon tabs. Imaging was conducted at a working distance of ~ 8 mm of 3 kV. Images were taken using a combination of both upper and lower detector signals.

Differential Scanning Calorimetry (DSC): DSC analysis was carried out using a DSC Q2000 at a heating/cooilng rate of 10 °C/min. Samples were heated from room temperature to 150 °C, before cooling to -90 °C, and heating back up to 150 °C.

Gas Sorption Analysis: Nitrogen adsorption and desorption isotherms were measured at 77.3 K using a Micromeritics ASAP2420 volumetric adsorption analyzer. Samples were degassed by heating to 60 °C at 10 °C/min and holding for 15 h under dynamic vacuum (10⁻⁵ mbar) before analysis.



Figure S1. Photographs of a sample of sulfur-limonene polysulfide. a) After removing from a mould. b) After 2 hours at room temperature. c) After 24 hours at room temperature.



scCO₂ foaming

80 °C, 28 Mpa, 3 hr



Figure S2. Photographs of a sample of S-DIB polymer (30 % DIB) as it appears directly before and after supercritical foaming in CO_2 .



Figure S3. Photographs of a 1 g sample S-DIB polymer (30 % DIB) coarsely ground (left), and the same mass of coarsely ground S-DIB polymer after CO₂ foaming (right).



Figure S4. Photographs of cut cross sections of pieced of Sulfur-DIB polymer (30 % DIB). a) before $scCO_2$ processing. b) After a 40 °C soak in 28 MPa CO₂ for 30 minutes. c) After a 60 °C soak in 28 MPa CO₂ for 30 minutes. d) After an 80 °C soak in 28 MPa CO₂ for 30 minutes. e) After an 80 °C soak in 28 MPa CO₂ for 30 minutes. e) After an 80 °C soak in 28 MPa CO₂ for 3 hours. A five pence piece is shown in the upper image for scale. The lower right image indicates the approximate depth of CO₂ infusion into sample (d). Samples (b) and (c) showed only superficial surface modification. Sample (e) was foamed all the way through the sample.



Figure S5. SEM imaging of several areas of a $scCO_2$ foamed sulfur-DIB crosslinked polymer sample (50 wt% sulfur). There is an inhomogeneity of pore size across different areas of the sample.



Figure S6. SEM imaging of several areas of a scCO₂ foamed sulfur-DIB crosslinked polymer sample (70 wt% sulfur). The higher sulfur content results in smaller pores.



Figure S7. SEM imaging of scCO₂ foamed sulfur-DIB (50 wt% sulfur, 50 wt% DIB) polymer sample at 80 °C, and variable pressure: a) and b) 28 MPa, c) and d), 20 MPa, e) and f), 10 MPa. The size of the voids produced can be seen to decrease with increasing pressure.



Figure S8. Photograph of samples with common fillers, after $scCO_2$ foaming at 80 °C, 28 MPa, 3 hours. All 30 wt % DIB, 70 wt% sulfur, before addition of fillers. From left to right: with an additional 5 wt% silica, with 5 wt% carbon black, and with 5 wt% kaolin. Note the kaolin sample, while it increases in volume during foaming, retains more of the original particle shape, not 'ballooning' as much as the other samples.



Figure S9. SEM imaging of several areas of a scCO₂ foamed sulfur-DIB (70 wt% sulfur, 30 wt% DIB) polymer sample with fumed silica filler (5 wt% of original polymer mass added).



Figure S10. SEM imaging of several areas of a scCO₂ foamed sulfur-DIB (70 wt% sulfur, 30 wt% DIB) polymer sample with carbon black filler (5 wt% of original polymer mass added).



Figure S11. SEM imaging of several areas of a scCO₂ foamed sulfur-DIB (70 wt% sulfur, 30 wt% DIB) polymer sample with kaolin filler (5 wt% of original polymer mass added).



Figure S12. SEM imaging of a) kaolin particles – note platelet morphology, and b) 70 wt% sulfur, 30 wt% DIB polymer sample with kaolin filler (5 wt% of original polymer mass added).



Figure S13. Representative DSC trace. Shown is a 50 wt% DIB, 50 wt% Sulfur co-polymer, with T_g at 25 °C.



Figure S14. SEM imaging of 50 wt% sulfur, 50 wt% DIB polymer sample a) as made, b) after 24 hours at 50 °C, and c) after a further 24 hours at 100 °C. 70 wt% sulfur, 30 wt% DIB polymer sample with kaolin filler (5 wt% of original polymer mass added), d) as made, e) after 24 hours at 50 °C, and c) after a further 24 hours at 100 °C. After incubation at 50 °C there is some reduction in pore size. After incubation at 100 °C, original pores have completely disappeared. For the kaolin sample treated at high temperature larger pores are seen within cross sectioned material – presumably as the higher temperature allows gas in closed cells to coalesce.



Figure S15. The percentage mercury remaining in solution after 3 hours of exposure to a 2 ppm solution of $HgCl_2$ (100 mg sample, 5 mL solution). Samples are 50% DIB, 50% Sulfur copolymers foamed at 80 °C and different pressures of $scCO_2$. Values are given as a mean of three repeats with standard deviation shown as error bars.



Figure S16. Photograph of filtration setup. The S-DIB polymer is help in place by small amounts of glass wool, and the aqueous $HgCl_2$ solution allowed to flow through under gravity. This took approximately 5 minutes.



Figure S17. ¹H NMR spectrum of the sulfur-limonene polysulfide produced.

1 Crockett, M. P. *et al.* Sulfur-Limonene Polysulfide: A Material Synthesized Entirely from Industrial By-Products and Its Use in Removing Toxic Metals from Water and Soil. *Angewandte Chemie International Edition* **55**, 1714-1718, doi:10.1002/anie.201508708 (2016).