

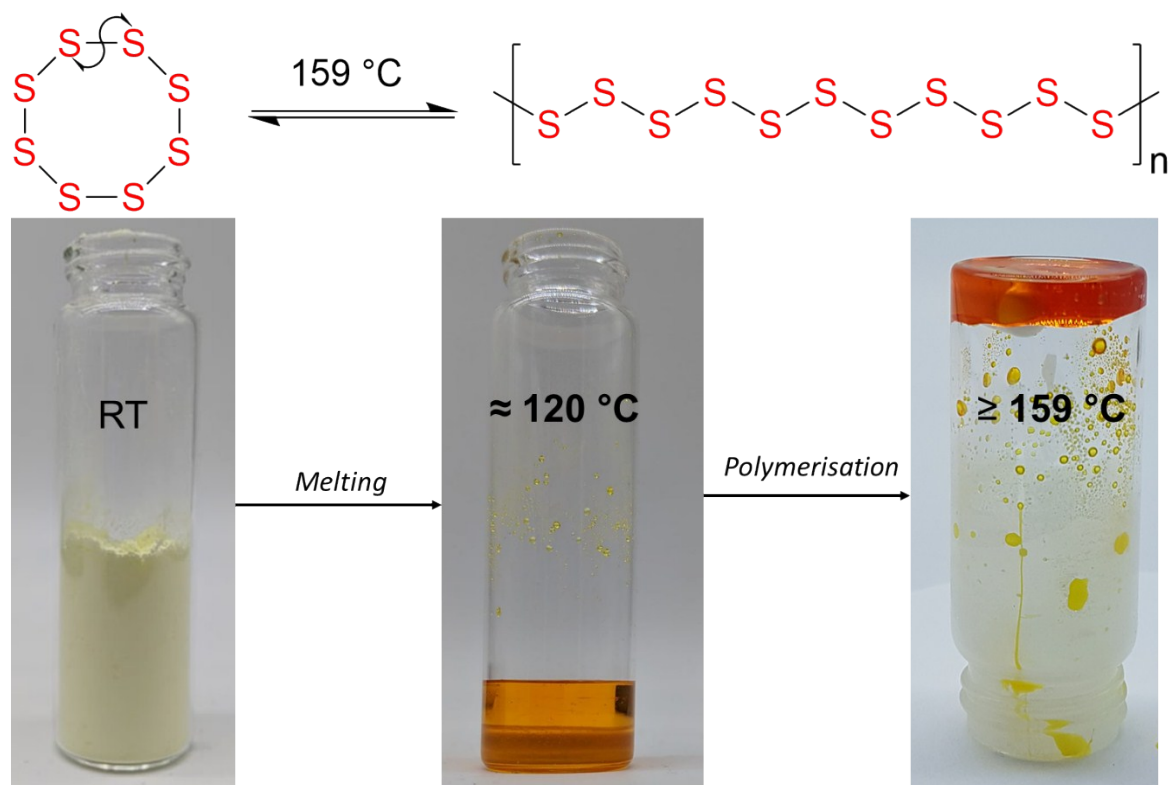
## Supporting Information

**Macroporous sulfur polymers from a sodium chloride porogen — a low cost, versatile remediation material**

Samuel Petcher, Douglas Parker, Thomas Hasell

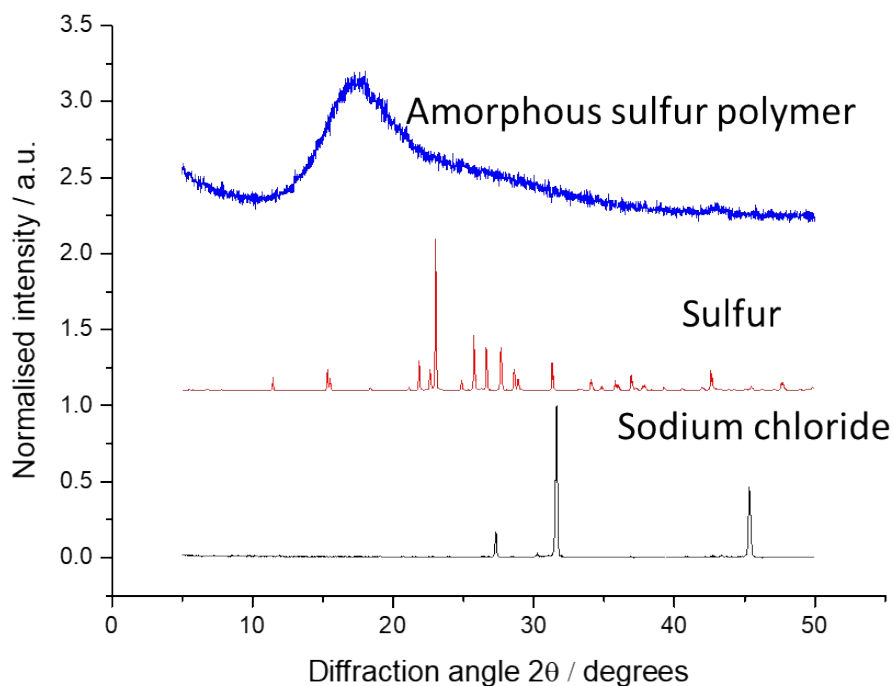
**Number of pages: 15**

S1 – Schematic showing the polymerisation of the elemental sulfur to the polymeric sulfur



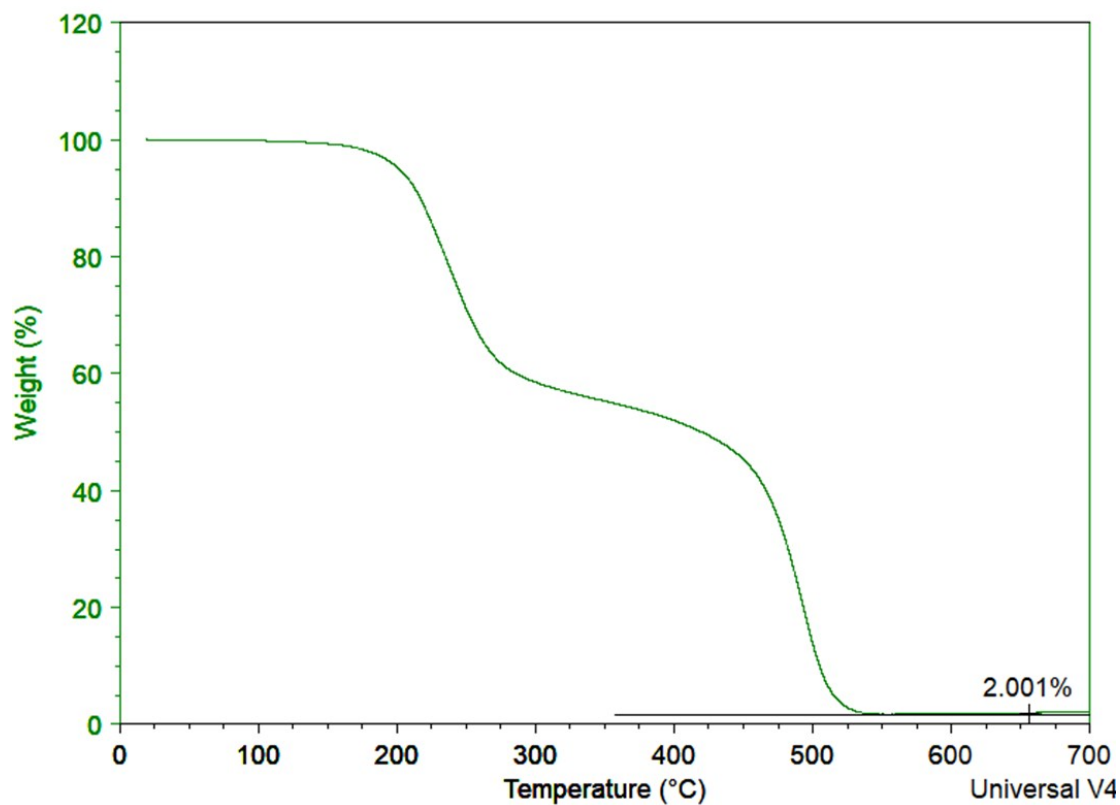
Shown above is the process that leads to the formation of polymeric sulfur. When heated the sulfur initially turn a clear yellow that darken upon the formation of sulfur. This process is however reversible and will revert to elemental sulfur via a backbiting mechanism. For more information see: <https://doi.org/10.1021/cr60301a003>

**S2 – Powder patterns of the amorphous sulfur polymers, elemental sulfur and sodium chloride**



Shown above is a typical powder pattern obtained from within our lab for the diffraction of an amorphous sulfur polymer, elemental sulfur and then sodium chloride. Despite the fact the sodium chloride is not visible in the powder pattern thermogravimetric analysis has demonstrated there can be up to 5% w/w sodium chloride still trapped within the materials that cannot be removed by simply soaking the polymer in water.

S3 – Thermogravimetric analysis of sulfur polymers – residual sodium chloride

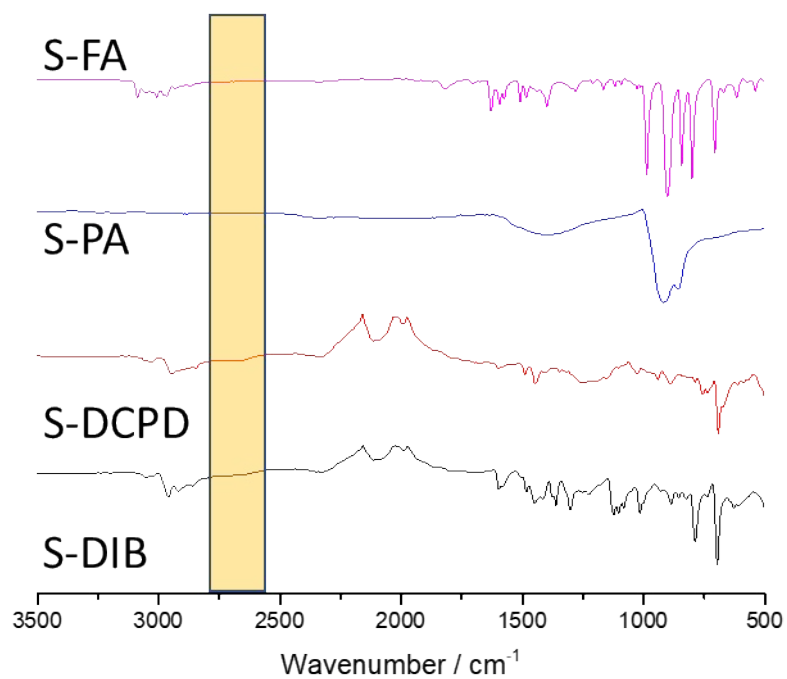


Shown above is a typical thermogram for the thermal decomposition of S-PA produced as a porous polymer. Residual mass is sodium chloride, operating under air flow to remove all sulfur and carbon/hydrogen. Remaining is NaCl – checked *via* pXRD.

Sample	Residual mass (%)
PA	2.001
DIB	0.9807
FA	7.430
DCPD	4.565

S4 – Thermogravimetric analysis of sulfur polymers – residual sodium chloride

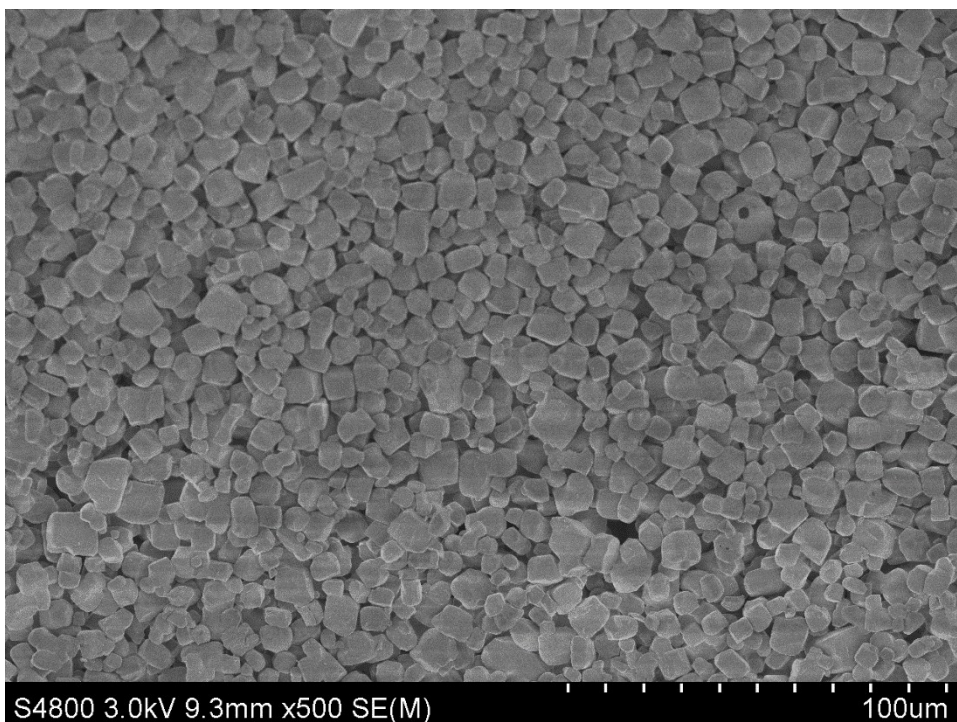
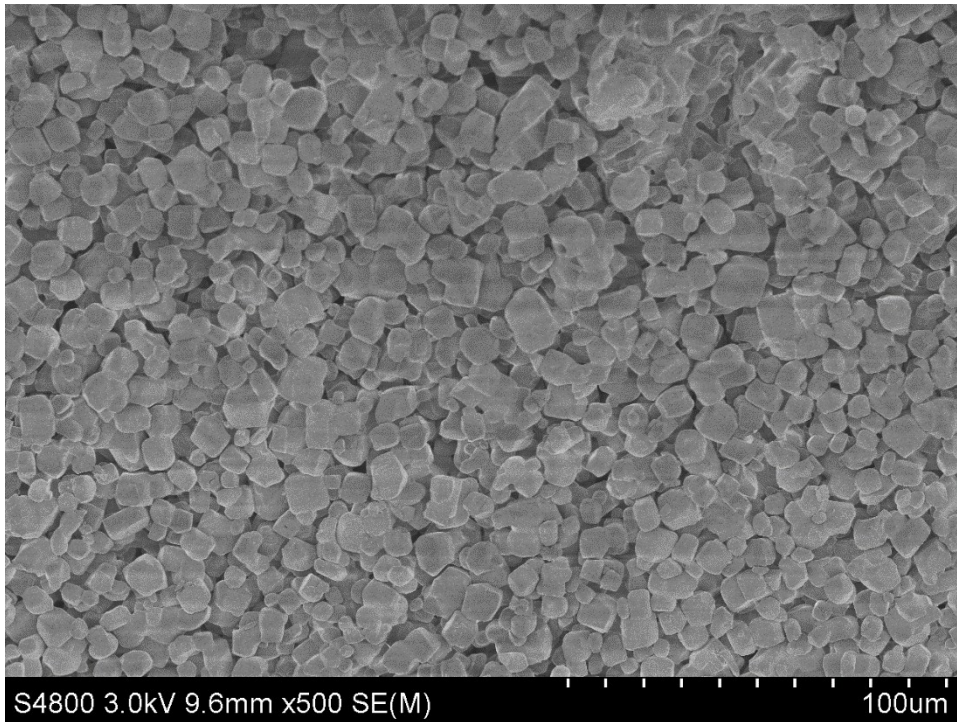
Region thiols would be expected



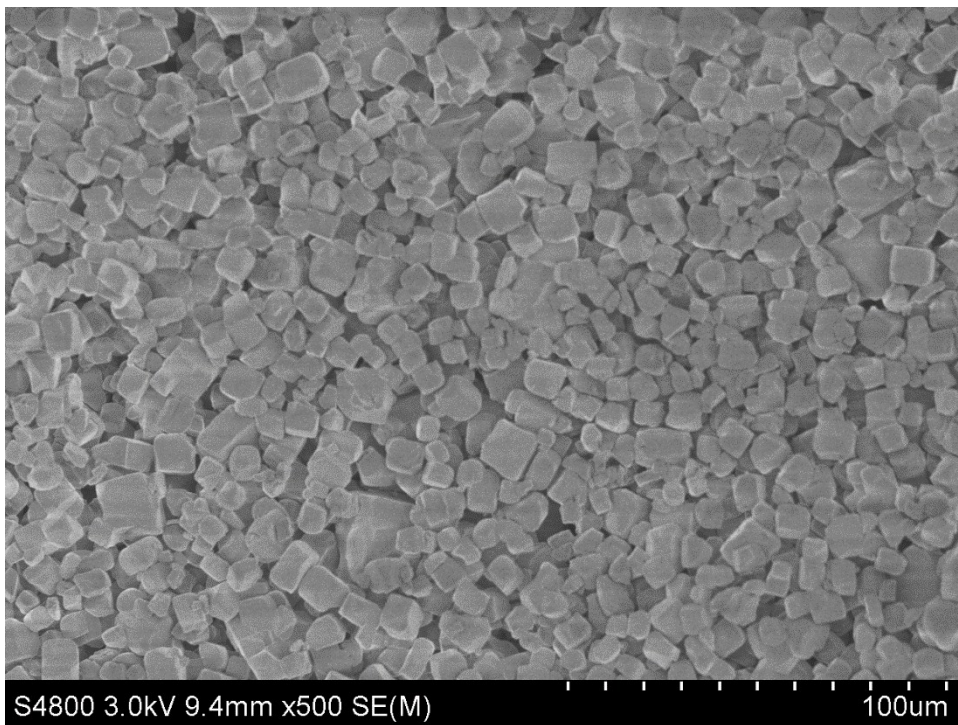
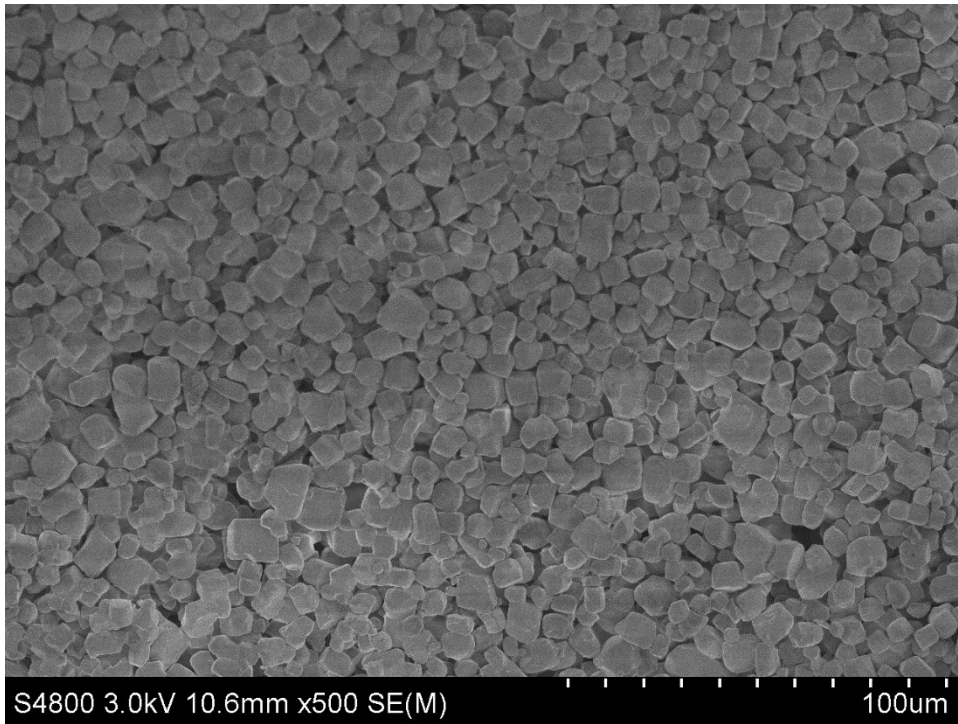
FTIR has revealed that there is no peak where the thiol peak would be expected. However, this is not conclusive as the resolution of the spectrum is relatively poor and the peak may be obscured by the background as it is a weak stretch.

**S5 – Micrographs demonstrating the size increase when increasing the proportion of ethanol in the antisolvent precipitation process**

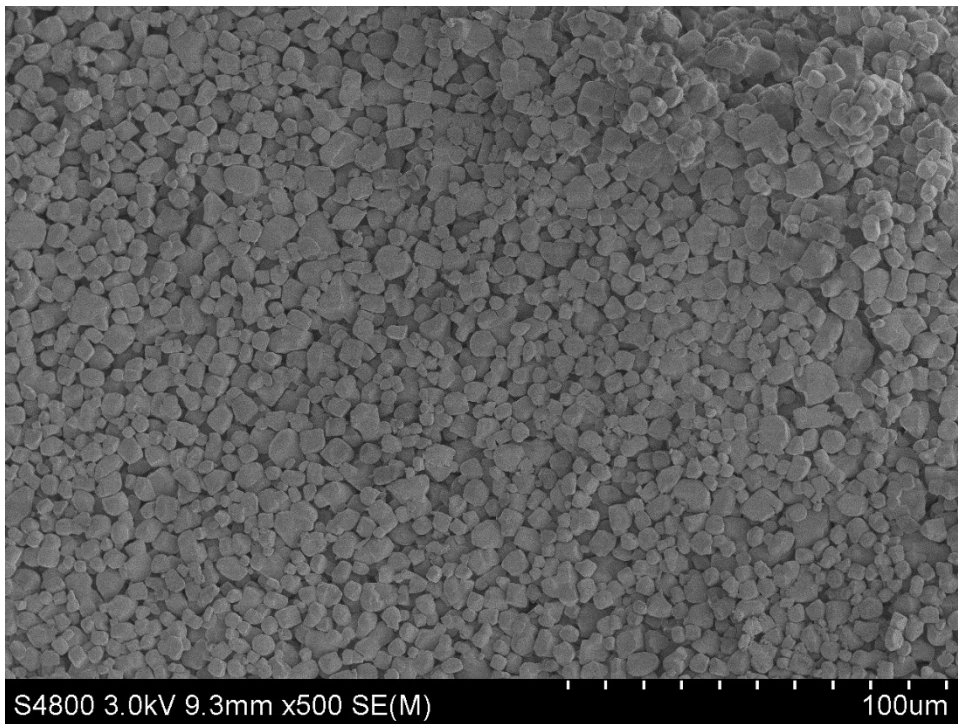
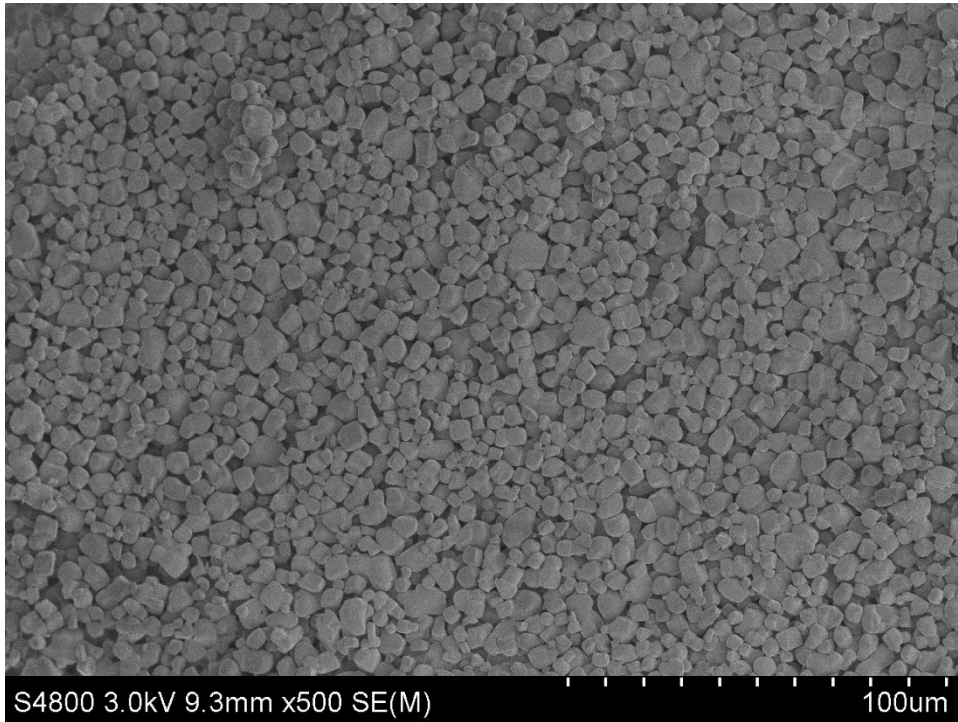
50% Ethanol



75% Ethanol



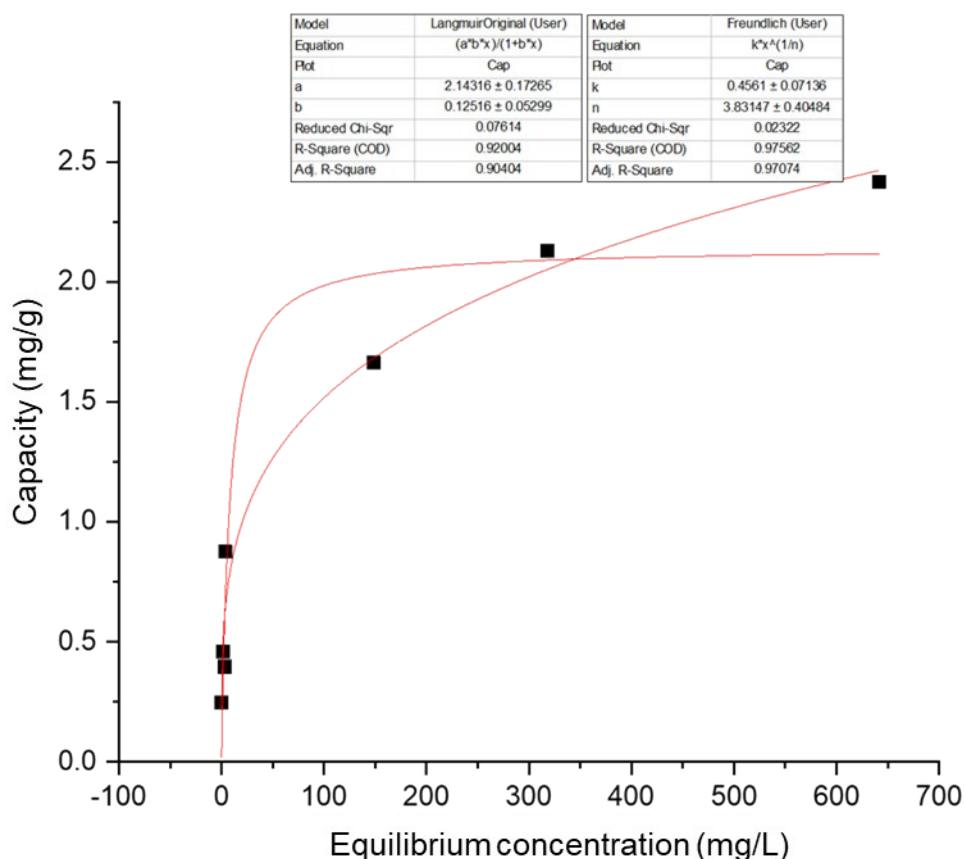
90% Ethanol



Note: It seems the most noticeable decrease is from 75%->90% rather than 50%->75%



## S6 – Mercury absorption experiments



While we note that the Freundlich has a lower regression we feel that the Langmuir fit is good enough to be used and has more extractable data than the Freundlich.

## S7 – Effect of NaCl on mercury removal from a 64 ppm solution

A 64 ppm stock solution of mercury chloride was prepared from a 2000 ppm stock by dilution. Aliquots of the 64 ppm stock solution (50 mL) were taken and the appropriate amount of NaCl was dissolved into the solution to achieve the concentration required. The porous polymer was then added to the solution and stirred for 48 hours. Upon removal the solution was filtered and analysed *via* ICP-OES.

NaCl concentration (ppm)	Percentage removal from 64 ppm solution (%)
10	30.12
100	32.93
1000	29.07

## S8 – Effect of pH on mercury removal from a 64 ppm solution

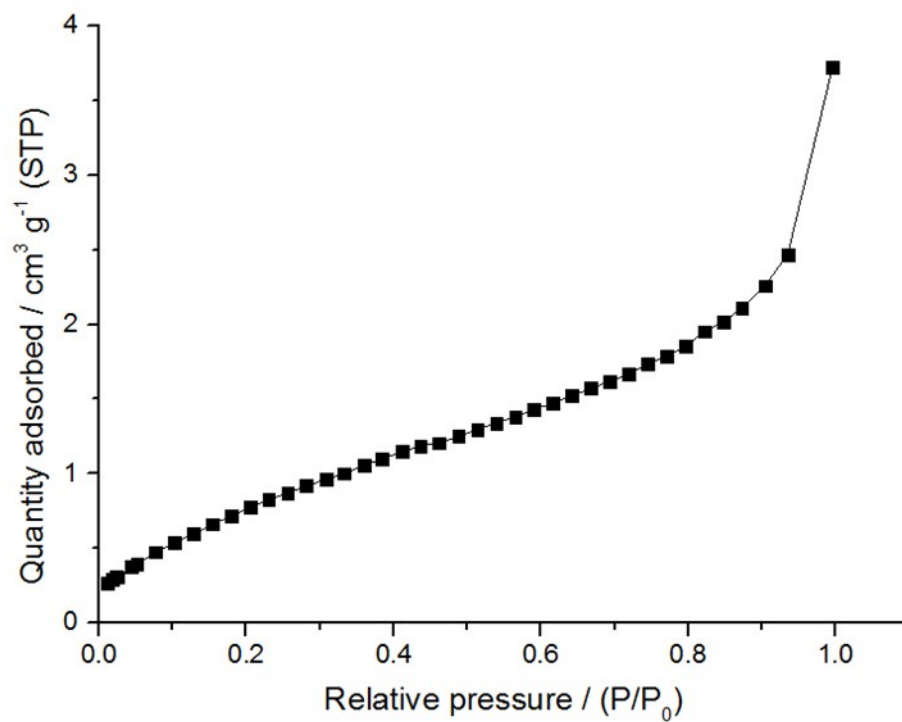
3 100 mL buffer solutions were prepared for a basic, neutral and acidic condition. The concentration of buffer was maintained at 10 mmol. To the buffer solutions 1.6 mL of stock was added to achieve a concentration of 63 ppm.

pH (phosphate buffer)	Percentage removal from 64
-----------------------	----------------------------

**ppm solution**

4.9	10.70264633
7	55.93794812
9.1	55.32959632

**S9 – N2 Isotherm of porous polymer**



Sample ID: SAMPLE SCP-01  
Operator: DPL  
Submitter: LIVERPOOL UNI / S PETCHER / 5652/1  
File: C:\MicroActive AutoPore V 9600\data\Cl...\MCA-8283.SMP

LP Analysis Time: 14-Aug-19 11:59:31 AM	Sample Mass: 0.2286 g
HP Analysis Time: 14-Aug-19 02:04:50 PM	Stem Volume Used: 67 %
Report Time: 14-Aug-19 02:18:44 PM	Show Neg. Int: No
Report Range: 0.10 to 61,000.00 psia	Correction Type: Blank
Adv. Contact Angle: 140.000 °	Mercury Temperature: 22.31 °C
Rec. Contact Angle: 140.000 °	

### Summary Report

#### Intrusion Data Summary

Total intrusion volume at 59,944.50 psia: 1.2085 mL/g  
Total pore area at 59,944.50 psia: 15.891 m<sup>2</sup>/g  
Median pore diameter (volume) at 40.41 psia and 0.604 mL/g: 5.27879 µm  
Median pore diameter (area) at 45,755.64 psia and 7.946 m<sup>2</sup>/g: 0.00466 µm  
Average pore diameter (4V/A): 0.30420 µm  
Bulk density at 0.34 psia: 0.5092 g/mL  
Apparent (skeletal) density at 59,944.50 psia: 1.3258 g/mL  
Porosity: 61.5930 %

#### Physical Properties

Linear coefficient: 3.2540e-007 1/psia  
Quadratic coefficient: -9.3682e-012 1/psia<sup>2</sup>

### S10 – Mercury porosimetry of porous polymer

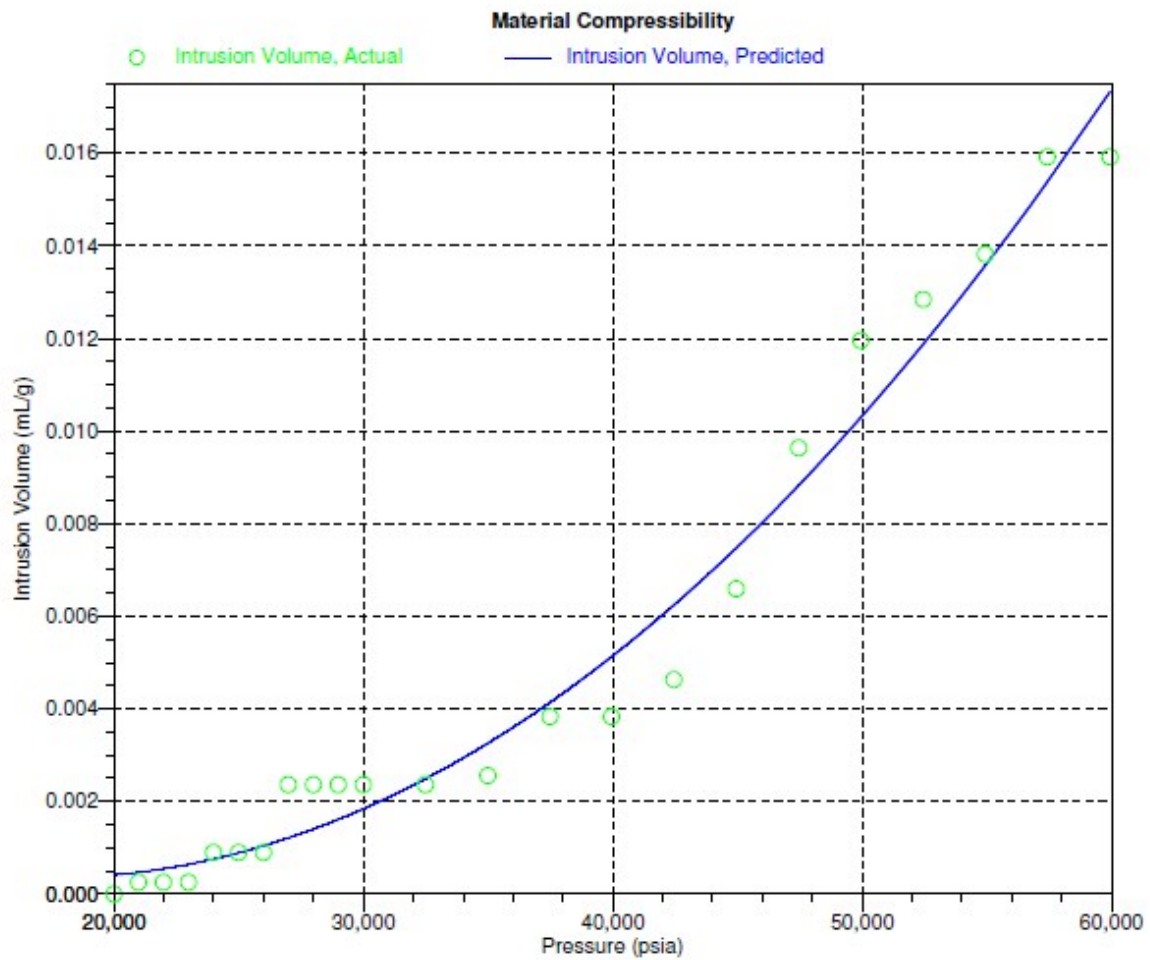
### S11 – Material compressability from mercury porosimetry

Material compressibility is material property that is most commonly used in fluid dynamics, but also in thermodynamics. The most simple explanation of the value is the intrinsic property of material volume change in response to an external pressure. Why this property is useful in the discussion of porous materials for sequestration is that the end goal is the use of the material in a flow type situation wherein a pressure will be exerted on the material. To bring the material we have produced into context we have provided a doi below that investigates the compressibility of various coals. From this paper we can see that the compressibility is of the same order but slightly more compressible than coal.

[https://doi.org/10.1016/0016-2361\(88\)90069-5](https://doi.org/10.1016/0016-2361(88)90069-5)

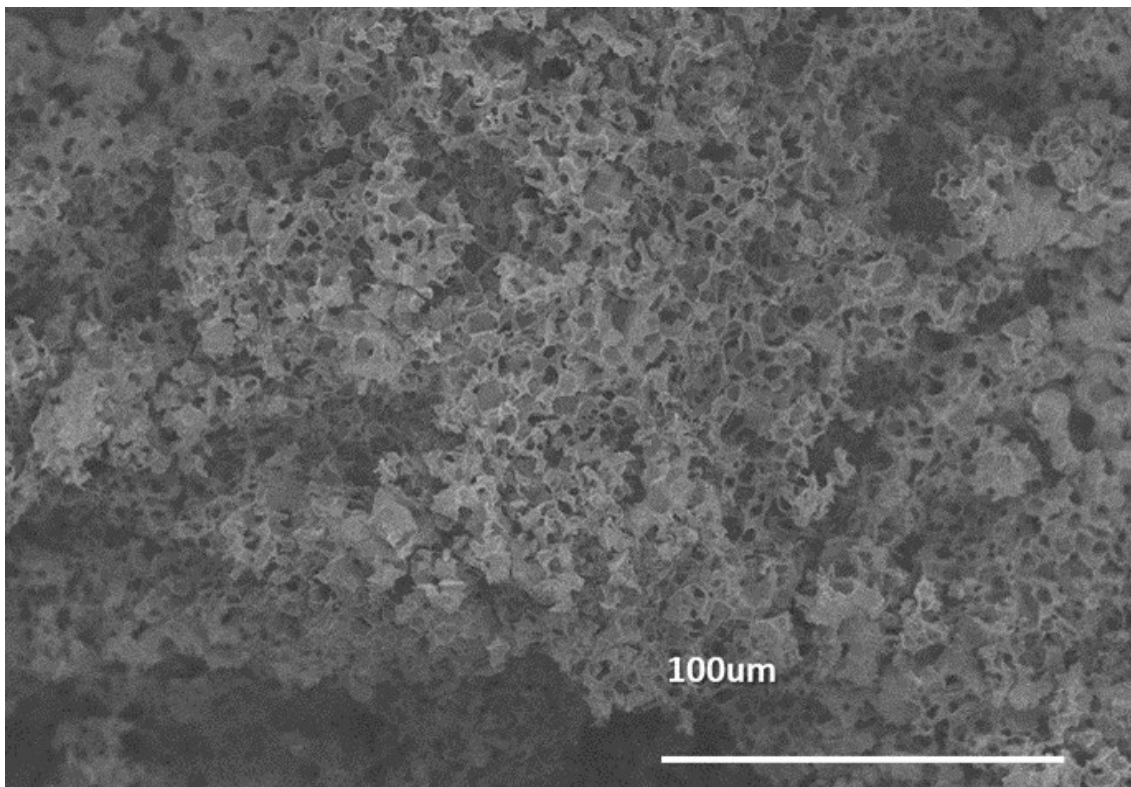
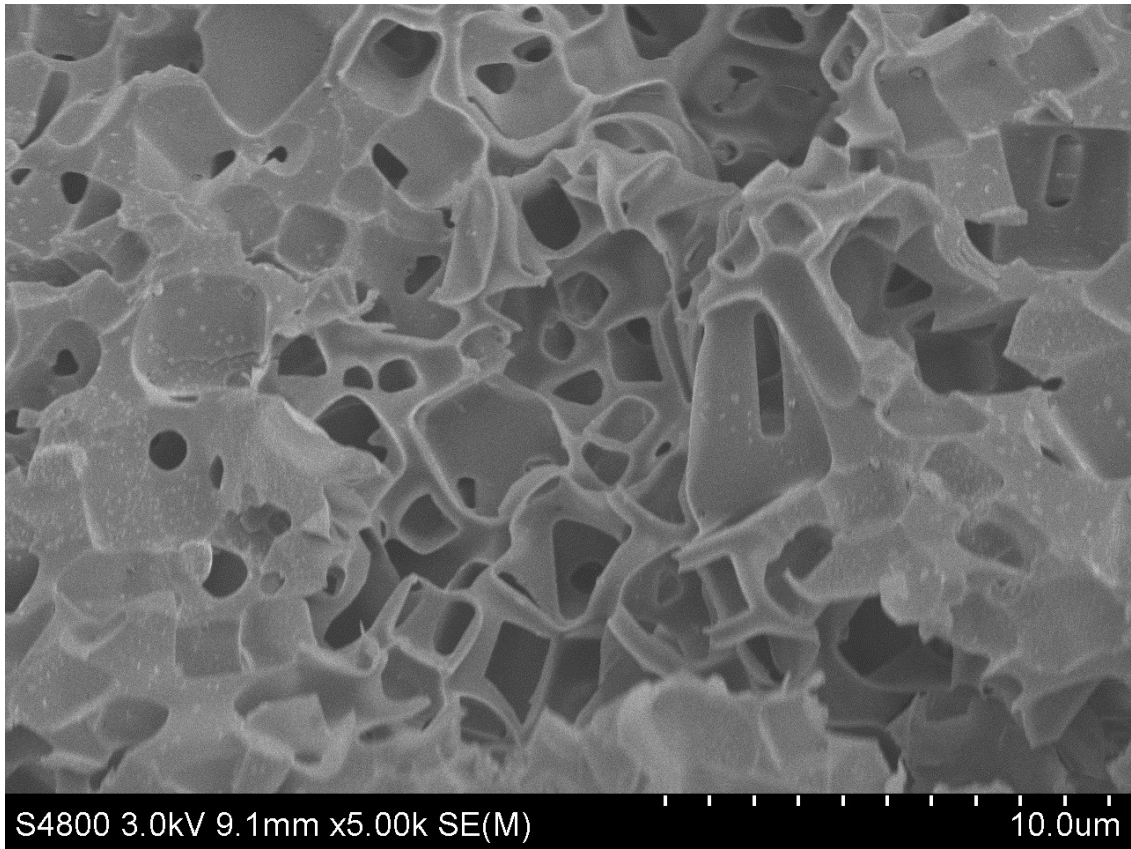
### Compressibility Summary

Linear compressibility:  $3.2540 \times 10^{-7}$  1/psia  
Quadratic compressibility:  $-9.3682 \times 10^{-12}$  1/psia<sup>2</sup>  
RMS Error: 0.0008 mL/g

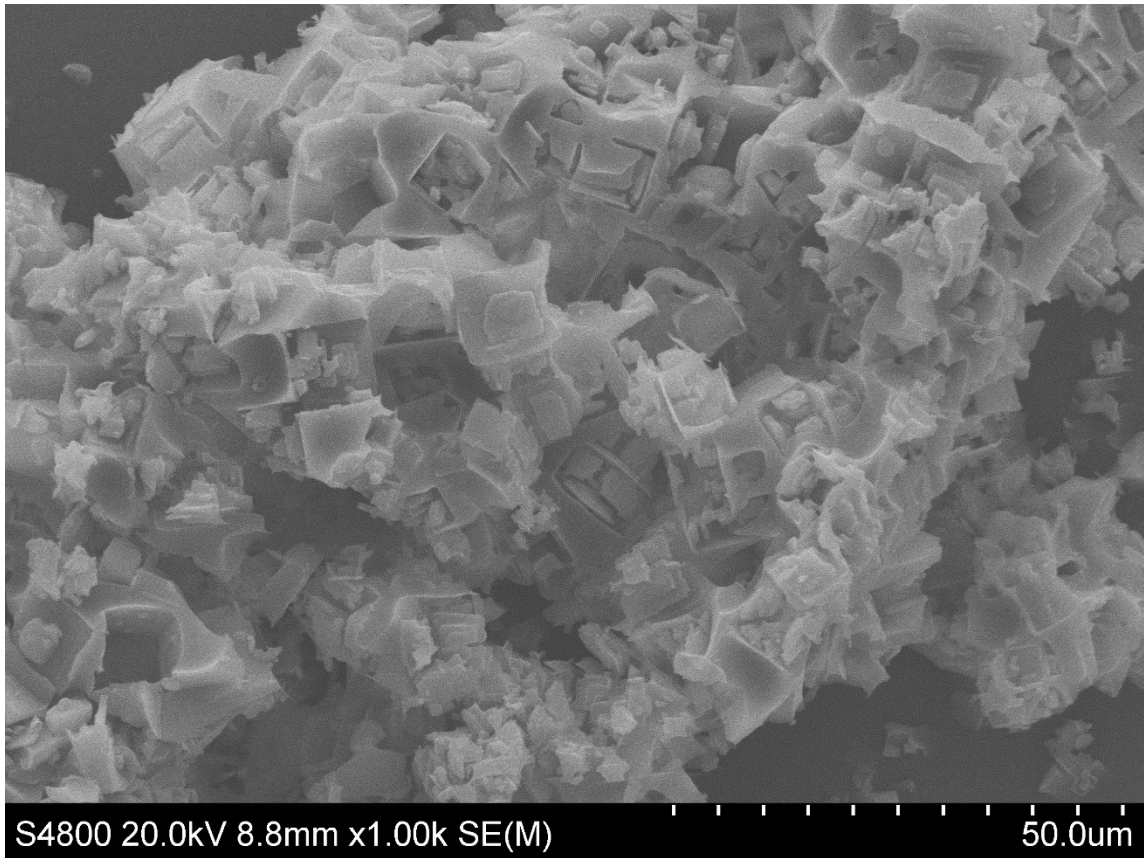


S12 - Micrographs of macroporous polymer

BELOW: S-DCPD porous polymer

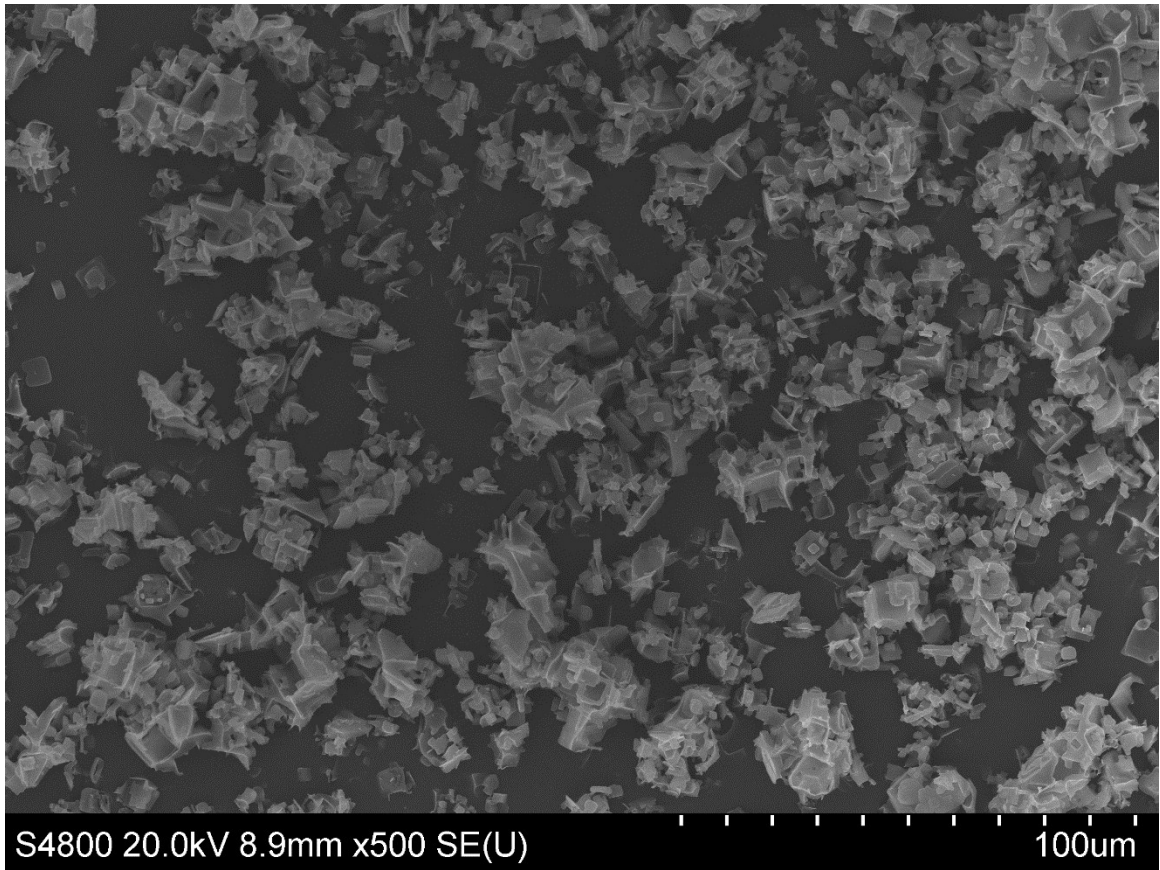


S-DIB Copolymer

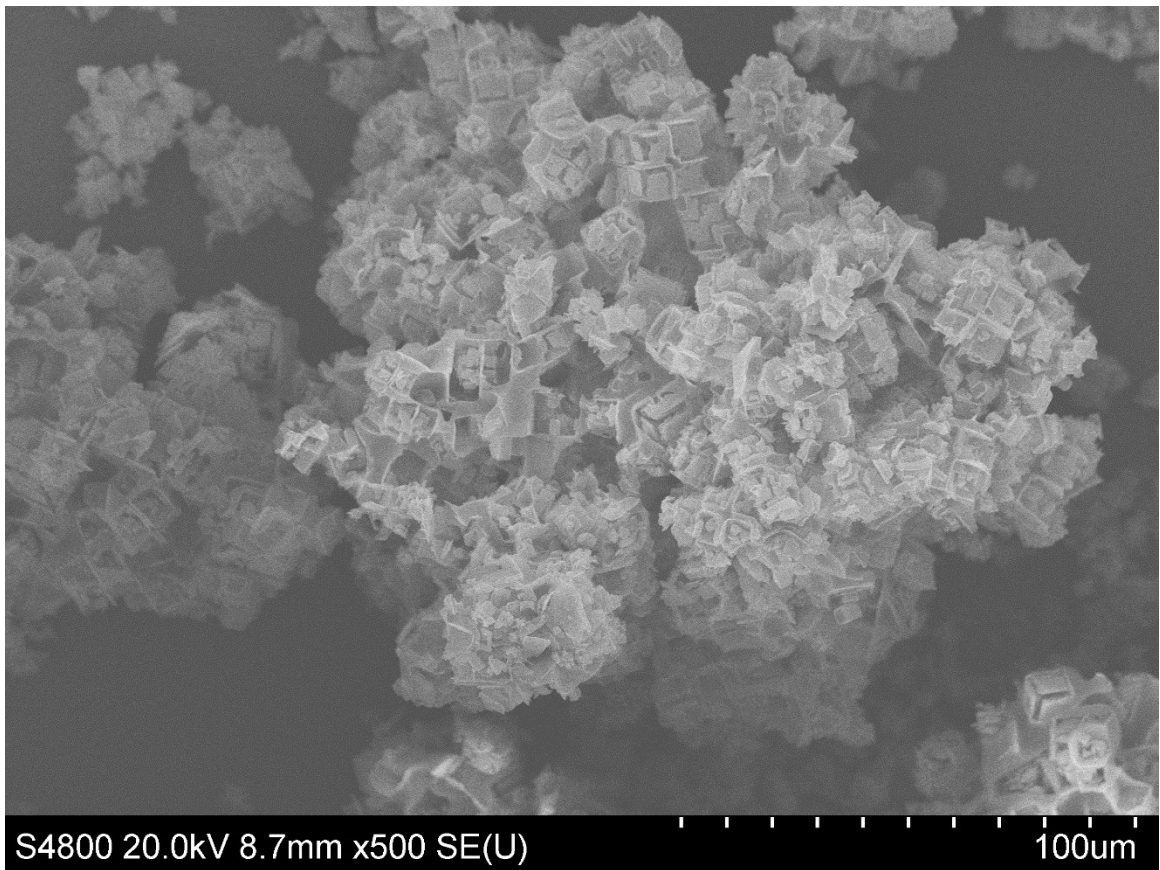


BELOW: Porous S-Perrilyl alcohol copolymer

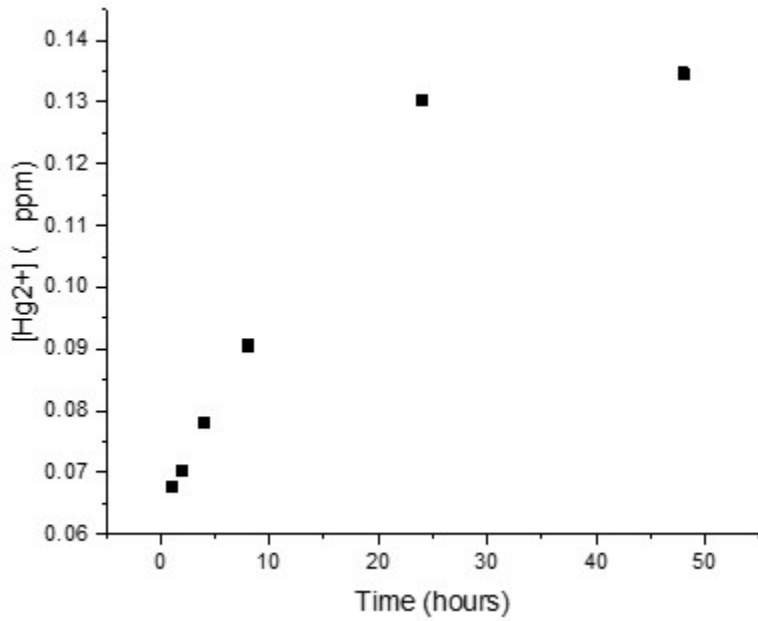
Interesting feature is the lack of a monolithic structure. Becomes a powder when the salt is removed.



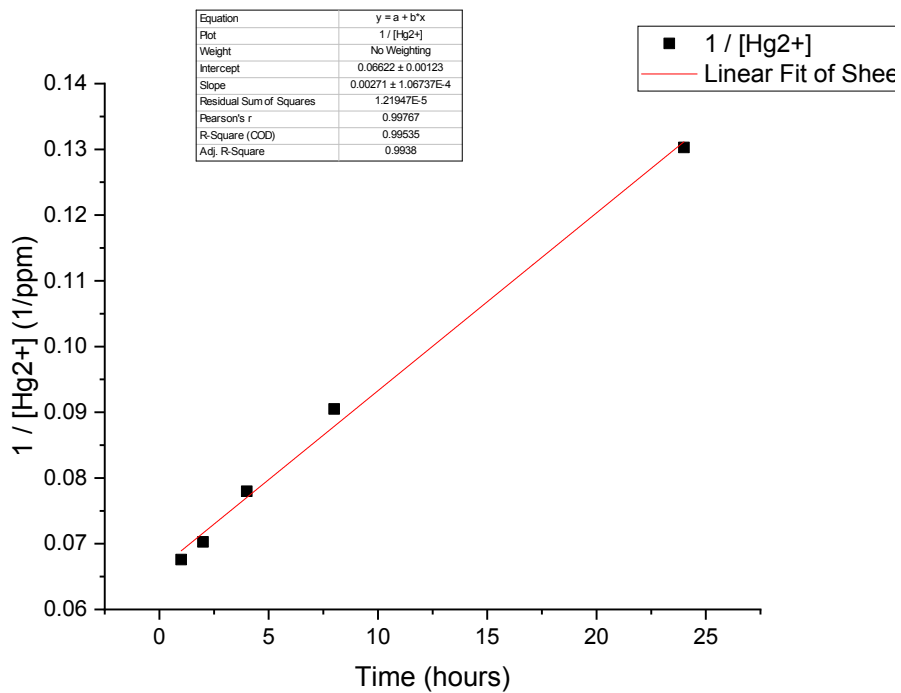
BELOW: S-Farnesol copolymer



S13 – Kinetics experiment



Plot is indicative of a second order absorption kinetics mechanism. Indicative of chemisorption.



Plot with line fitting.