Supplementary Material (ESI) For Chemical Communications This Journal is © The Royal society of Chemistry 2020

# Mesoporous knitted Inverse Vulcanised Polymers

Samuel Petcher\*, Bowen Zhang, Thomas Hasell\*

Department of Chemistry, University of Liverpool, Crown Street, Liverpool, United Kingdom

## Supporting Information: Figures S1-SX

Method 1	Synthesis of poly[s-( <i>ran</i> )-styrene]		
Method 2	Post-synthetic 'knitting' of poly[s-(ran)-styrene] to produce SHCP-01		
Method 3	'One pot' synthesis of SHCP-01		
Figure S1	Summary report of N2 Isotherm as generated by Micrometrics Software		
Figure S2	N2 Uptake isotherm of generated porous polymer		
Figure S3	Micrographs of generated porous polymer powder (3.68 $\mu$ m FOV)		
Figure S4	Micrograph of generated porous polymer (500 $\mu$ m FOV)		
Figure S5	Micrograph of generated porous polymer (250 $\mu$ m FOV)		
Figure S6	Micrograph of generated porous polymer (50 µm FOV)		
Figure S7	Micrograph of generated porous polymer (10		
Figure S8	Powder X-Ray diffraction of SHCP-01 (pXRD)		
Figure S9	Fourier transform infra-red spectroscopy of SHCP-01.		
Figure S10	Thermogravimetric analysis of SHCP-01		
Figure S11	<sup>1</sup> H NMR of S-Styrene		
Figure S12	Elemental Analysis of SHCP-01		
Figure S13	Thermogram of SHCP-01 (DSC)		
Figure S14	S-Styrene thermogram (DSC)		
Table S1	Solubility study of SHCP-01		
Figure S15	EDS Spectra of SHCP-01		
Figure S16	EDS Spectra of SHCP-01		

### Method 1 Synthesis of poly[s-(*ran*)-styrene]

Sulfur (S<sub>8</sub>, 14.000 g, 0.05458 mol) and Styrene (C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>, 6 g, 0.057609 mol) were placed in a 250 mL round bottom flask with a cross shaped magnetic stirrer bar. The round bottom flask was equipped with a rubber septum and placed under nitrogen flow. The round bottom flask was then placed into a aluminium heating block thermostatted at 100 °C for 20 minutes. After the 20 minutes had passed the temperature was increased to 130 °C for 8 hours. Affording a viscous, insoluble yellow fluid. The sample was then allowed to cool and stored.

# Method 2 Post-synthetic 'knitting' of poly[s-(*ran*)-styrene] to produce SHCP-01

poly[s-(*ran*)-styrene] (2 g) was placed into a dry 250 mL round bottom flask and 50 mL of dry chloroform was added (an excess). The solution was heated to 50 °C to soften the poly[s-(*ran*)-styrene] and was stirred using a magnetic stirrer. After a suspension had formed AlCl<sub>3</sub> (2 g, 0.01499 mol) was added. Immediately a colour change was observed to a deep orange, which darkened with time. After 2 hours had passed the remaining AlCl<sub>3</sub> was quenched with MeOH and stirring. The resultant black powder was filtered and washed with MeOH once, then CHCl<sub>3</sub> once.

The resultant dark powder was then Soxhlet extracted with MeOH, and then  $CHCl_3$  to afford a brown powder. Yield was 56.4 %

### Method 3 'One pot' synthesis of SHCP-01

Sulfur (S<sub>8</sub>, 3.500 g, 0.01372 mol) and Styrene (C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>, 1.500 g, 0.01440 mol) were placed in a 100 mL round bottom flask with a cross shaped magnetic stirrer bar. The round bottom flask was equipped with a rubber septum and placed under nitrogen flow. The round bottom flask was then placed into a aluminium heating block thermostatted at 100 °C for 20 minutes. After the 20 minutes had passed the temperature was increased to 130 °C for 8 hours. The solution was cooled to 50 °C. To the round bottom flask 50 mL of CHCl<sub>3</sub> was added and stirred until a suspension formed. The solution was then chilled in an ice bath, with stirring. To the round bottom flask AlCl<sub>3</sub> (20 g, 0.1499 mol) was added. Immediately the suspension turned a deep orange, and darkened over time. After 2 hours had passed the remaining AlCl<sub>3</sub> was quenched with MeOH and stirring. The resultant black powder was filtered and washed with MeOH once, then CHCl<sub>3</sub> once. Yield was 45.6 %

Safety note: Reaction is highly exothermic, and heat generated can boil the CHCl<sub>3</sub>. To prevent this ensure mixture is cool before addition of AlCl<sub>3</sub>. Reaction was performed in a lab of temperature 11 °C.

#### Summary Report

Su	face Area	
Single point surface area at P/Po = 0.290707079:	161.1134 m²/g	
BET Surface Are	ea: 236.0425 m²/g	
t-Plot external surface area	a: 353.5279 m²/g	
BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius:	219.1382 m²/g	
BJH Desorption cumulative surface area of pores		
between 0.8500 nm and 150.0000 nm radius:	228.0329 m²/g	
Po	re Volume	
Single point adsorption total pore volume of pores		
less than 101.4713 nm radius at P/Po = 0.990473218:	0.472236 cm <sup>3</sup> /g	
t-Plot micropore volume	e: -0.094615 cm³/g	
B IH Adsorption cumulative volume of pores		
between 0.8500 nm and 150.0000 nm radius:	0.478265 cm <sup>3</sup> /g	
BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius:	0.479740 cm³/g	
F	Pore Size	
BJH Adsorption average pore radius (2V/A):	4.3650 nm	
BJH Desorption average pore radius (2V/A):	4.2076 nm	
DET	Pore Size	
Volume in Pores	1 666 nm	0 00000 cm <sup>3</sup> /a
Total Volume in Pores	= 38 734 nm	0.26536 cm <sup>3</sup> /g
Area in Pores	38.734 nm	39.352 m²/a
Total Area in Pores >	= 1.666 nm	142.937 m <sup>2</sup> /g
Horva	th-Kawazoe	
Maximum pore volume at P/Po = 0.179967880:	0.054802 cm <sup>3</sup> /g	
Median pore widt	h: 1.1486 nm	

Figure S1 Summary report generated for the  $N_2$  isotherm. BET specific surface area was calculated to be 236.04 m<sup>2</sup> g<sup>-1</sup>.



**Figure S2** The nitrogen absorption isotherm for sample SHC1. The shape of the curve is indicative of a type V isotherm,<sup>1</sup> with the convex curve, and hysteresis that results from the capillary filling of the mesopores.



Figure S3 Micrograph with a field of view of 3.62  $\mu$ m. Imaging was performed with a beam current of 28 pA and 2 keV acceleration voltage.



**Figure S4** Micrograph of the polymer with a field of view of 500  $\mu$ m. Imaging was performed at a working distance of 6.38 mm with an acceleration voltage of 2 keV and a beam current of 28 pA.



**Figure S5** Micrograph of the polymer with a field of view of 250  $\mu$ m. Imaging was performed at a working distance of 6.38 mm with an acceleration voltage of 2 keV and a beam current of 28 pA.



**Figure S6** Micrograph of the polymer with a field of view of 50  $\mu$ m. Imaging was performed at a working distance of 6.38 mm with an acceleration voltage of 2 keV and a beam current of 28 pA.



**Figure S7** Micrograph of the polymer with a field of view of 10  $\mu$ m. Imaging was performed at a working distance of 6.38 mm with an acceleration voltage of 2 keV and a beam current of 28 pA.



**Figure S8** pXRD of SHC1, demonstrating the lack of crystallinity, and hence elemental sulfur. The amorphous nature of the produced samples is also good evidence that the polymer is a crosslinked material.



Figure S9 The FTIR of SHCP-01 prodcued the spectrum shown above. There were several peaks that unveiled characteristics of the produced material. Firstly, the strong and broad band present at ~600-830 cm<sup>-1-</sup> is characteristic of a C-Cl stretch. This is likely to be result of the formed bridges between styrenics, which will have a remaining Cl. (green) There is also the aromatic C-H stretch highlighted. (purple)



**Figure S10** Thermogravimetric analysis (TGA) demonstrated the thermal stability of the material. The thermogram demonstrated that the material had a sharp decomposition at around 200 °C. This type of decomposition is characteristic of polymer with high sulfur content



**Figure S11** 1H NMR of the sample of S-Styrene, in deuterated chloroform. The NMR experiment confirmed the consumption of alkene within the polymer, indicating a successful synthesis. (~ 5.6 ppm) Previous work has indicated that the polymerisation mechanism of S-Styrene is complex, and likely proceeds via several different mechanism.

Sample Name	Concentration (ppm)
Blank	0.02
SHCP-01 Filtered	0.02
Control	11.45

**Table S12** demonstrates the concentrations of mercury resulting from the dissolution of methylmercury chloride in solution (Control) vs a blank solution of distilled water (Blank), and the control filtered by SHCP-01.



**Figure S13** is the thermogram obtained when SHCP-01 is analysed *via* differential scanning calorimetry. The resultant thermogram is featureless. This is common for highly crosslinked materials, and it may be that a 'theoretical' glass transition exists beyond the decomposition temperature of the sample. The absence of melting peak ~120 °C indicates the absence of crystalline S<sub>8</sub>. Ran under nitrogen at 10 °C per minute. The separate colours allow the heat/cool/heat cycles to be differentiated. Green = first heating step. Orange = first cooling step. Blue = second heating step.



**Figure S14** – DSC of poly[S-(*ran*)-styrene] demonstrating a  $T_g$  of -25.6 °C that is not present in the hypercrosslinked sample SHCP-01. Ran under nitrogen at 10 °C per minute. The separate colours allow the heat/cool/heat cycles to be differentiated. Green = first heating step. Orange = first cooling step. Blue = second heating step.

Solvent	Solubility
Chloroform	Insoluble
Toluene	Insoluble
Dichloromethane	Insoluble
Tetrahydrofuran	Insoluble
DMSO	Insoluble
Water	Insoluble
Methanol	Insoluble
Ethanol	Insoluble

 Table S1 – Results of a solubility study for SHCP-01.



**Figure S15** – EDS Spectra of SHCP-01, not quantitative but demonstrates the inclusion of Cl, and complete removal of Al from the polymer produced. The Ag is an artefact from sample preparation.

**Figure S16** – EDS Spectra of SHCP-01, not quantitative but demonstrates the inclusion of Cl, and complete removal of Al from the polymer produced. The Ag is an artefact from sample preparation.

References:

1. Michal Kruk and Mietek Jaroniec, Chem. Mater. 2001, 13, 10, 3169–3183