Conjugated Microporous Poly(phenylene butadiynylene)s

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SUPPORTING INFORMATION

Synthesis of PPB networks by alkyne homocoupling:

Both polymers were synthesized at a monomer concentration of 500 mmol/L and a reaction temperature of 70 °C / 36 h. HCMP-1: 1,3,5-triethynylbenzene (600 mg, 4.0 mmol), bis-(triphenylphosphine)palladium(II) dichloride (85 mg, 3 mmol%), and copper iodide (22 mg, 3 mmol%) were dissolved in the mixture of THF (4.0 ml) and Et_3N (4.0 ml). The reaction mixture was heated to 70 °C and stirred for 36 h under a dry nitrogen atmosphere. The mixture was cooled to room temperature and the precipitated homocoupled polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any unreacted monomer or catalyst residues. Further purification of the polymer was achieved by Soxhlet extraction (methanol) for 48 h. The product was dried in vacuum for 24 h at 70 °C. (Yield, 85.3%).; HCMP-2: This polymer was synthesized by the same method as used for HCMP-1. 1,4-diethynylbenzene (500 mg, 3.96 mmol), bis-(triphenylphosphine)palladium(II) dichloride (83 mg, 3 mol%), and copper iodide (22 mg, 3 mmol%) were used in this case. (Yield, 89.4%).

The porous properties of the polymers were investigated by nitrogen adsorption and desorption at 77.3 K using an ASAP2020 volumetric adsorption analyzer (Micromeritics Instrument Corporation). Hydrogen adsorption was measured at 77.3 K up to 1.13 bar using a Micromeritics ASAP2420 volumetric sorption analyzer.

Thermogravimetric Analysis (TGA)

The thermal properties of the polymer networks were evaluated by thermogravimetric analysis (TGA) using a differential thermal analysis instrument (EXSTAR6000) over the temperature range 50 to 700 °C under a nitrogen atmosphere with a heating rate of 5 °C/min.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on a Perkin Elmer Diamond HyperDSC under a helium atmosphere with a heating rate of 5 °C/min in the range +30 °C to 200 °C, calibrated using an indium primary standard.

SEM – full experimental protocol

High resolution imaging of the polymer morphology was achieved using a Hitachi S-4800 cold Field Emission Scanning Electron Microscope (FE-SEM). The dry polymers samples were prepared on 15 mm Hitachi M4 aluminium stubs using either silver dag or an adhesive high purity carbon spectro tab. The samples were then coated with a 2 nm layer of gold using an Emitech K550X automated sputter coater. The FE-SEM measurement scale bar was first calibrated using certified SIRA calibration standards and elemental quantification standards were also used to calibrate the Oxford Instruments EDX detector. Imaging was conducted at a working distance of 8 mm and a landing voltage of 3 kV using a mix of upper and lower secondary electron detectors. An Oxford Instruments 7200 EDX detector was used to conduct elemental analysis of polymer composition. EDX analysis for these samples showed atomic percentage contents for copper and iodine of < 0.2%.

Solid State NMR – full experimental protocol

Solid-state NMR spectra were measured on a Bruker Avance 400 DSX spectrometer operating at 100.61 MHz for ^{13}C and 400.13 MHz for ^{1}H. ^{1}H-^{13}C Cross Polarisation Magic Angle Spinning (CP/MAS) NMR experiments were carried out at MAS of 10.0 kHz using zirconia rotors of 4 mm in diameter. The ^{1}H $\pi/2$ pulse was 3.3 µs and TPPM decoupling[35] was used during the acquisition. The Hartmann-Hahn condition was set using hexamethylbenzene. The spectra were measured using contact time of 2.0 ms and relaxation delay of 10.0 s. Typically 2048 scans were accumulated. The ^{1}H-^{13}C dipolar dephasing spectra were recorded at the MAS rate of 10 kHz and using depasing delays of 20, 50, 100 and 200 µs. The variable contact time ^{1}H-^{13}C CP/MAS NMR spectra were measured using t_m= 0.02 – 12.0 ms. The ^{13}C{^{1}H} MAS NMR spectra were measured at MAS rate of 10.0 kHz using TPPM decoupling. The ^{13}C $\pi/2$ pulse was 3.5 µs. The spectra were measured using the recycle delay of 30.0 s. Typically 1024 scans were accumulated. The values of chemical shift are referred to TMS. The analysis of the spectra (deconvolution and integration) was carried out using Bruker TOPSPIN software.

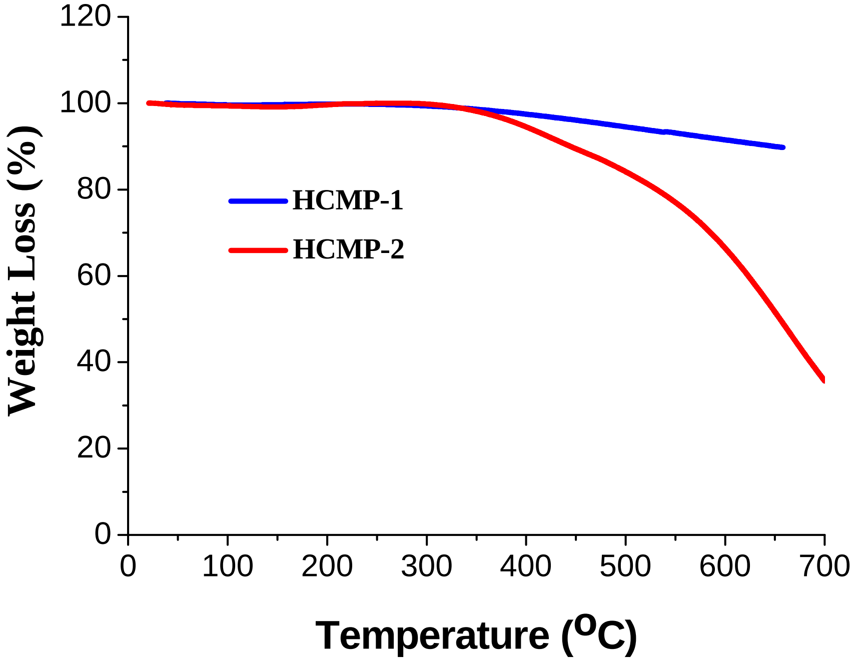


Figure S1. Thermogravimetric analysis for polymers HCMP-1 and HCMP-2.

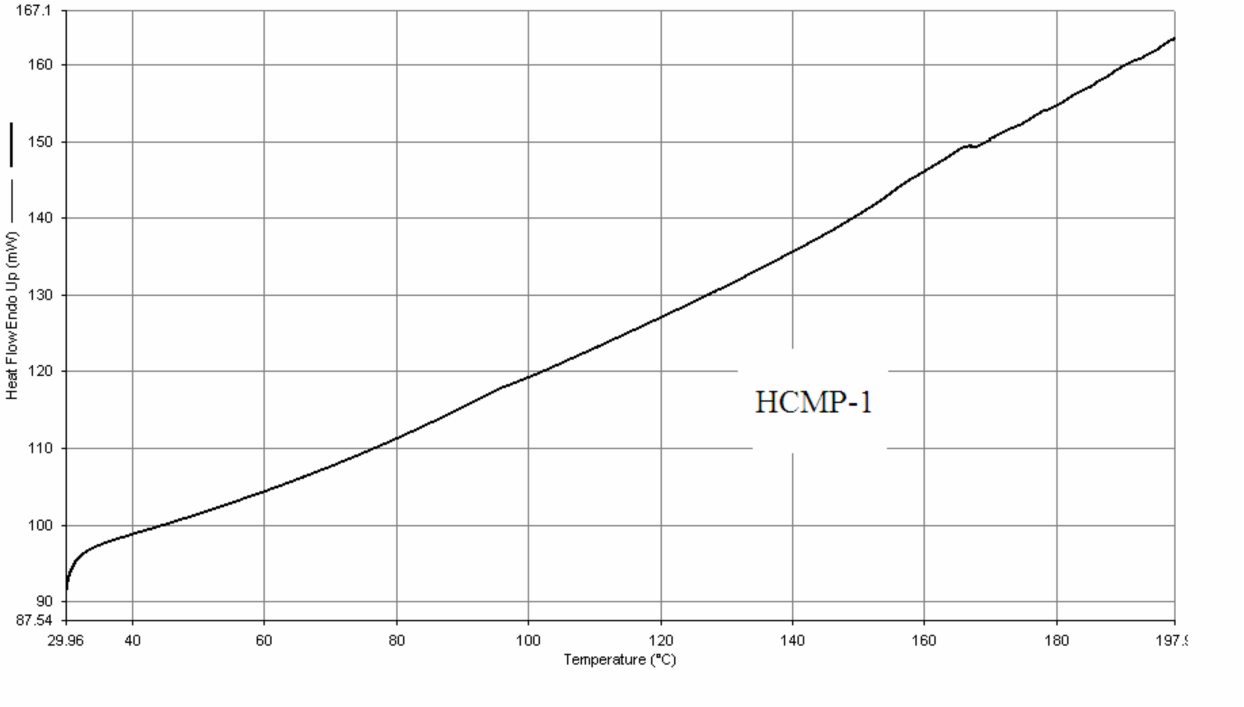


Figure S2. DSC measurement for polymer HCMP-1 (30–200 °C, 5 °C/min).

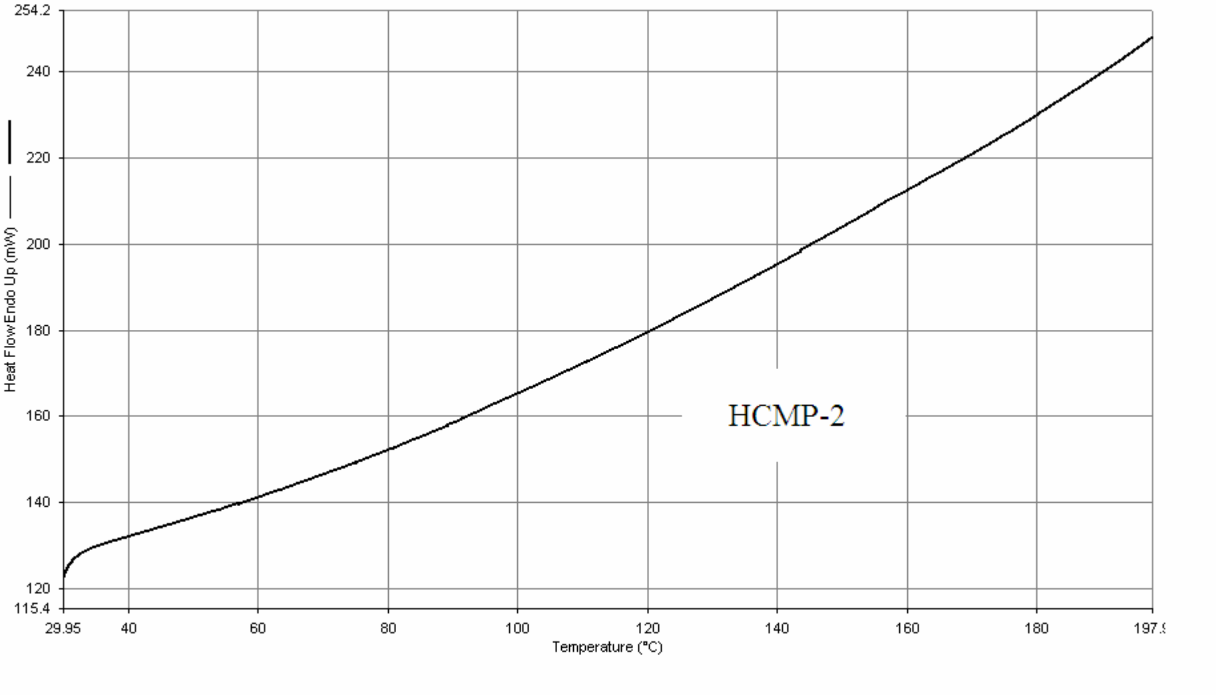
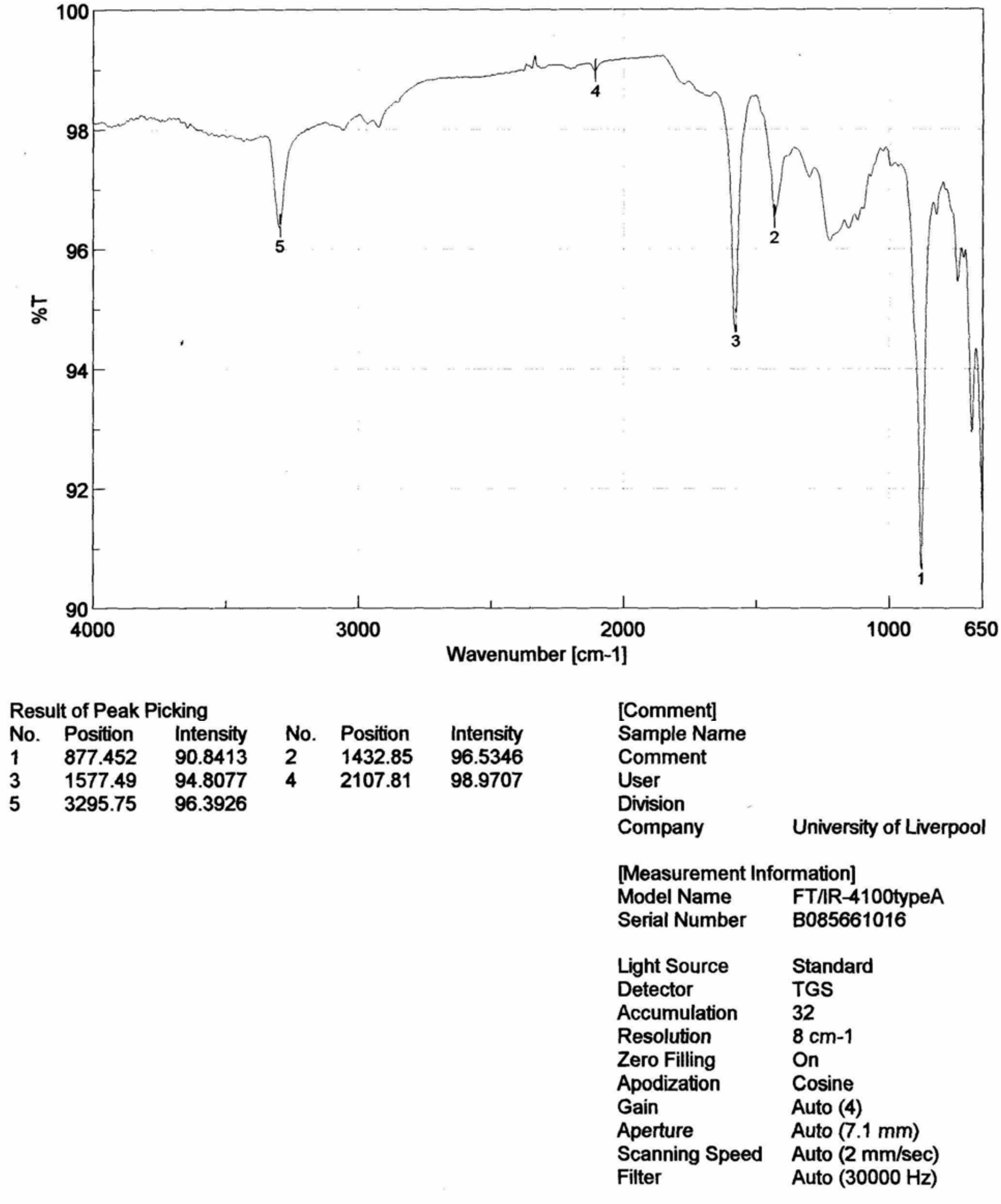


Figure S3. DSC measurement for polymer HCMP-2 (30–200 °C, 5 °C/min).



Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity
1	877.452	90.8413	2	1432.85	96.5346
3	1577.49	94.8077	4	2107.81	98.9707
5	3295.75	96.3926			

[Comment]

Sample Name	
Comment	
User	
Division	
Company	University of Liverpool

[Measurement Information]

Model Name	FT/IR-4100typeA
Serial Number	B085661016
Light Source	Standard
Detector	TGS
Accumulation	32
Resolution	8 cm-1
Zero Filling	On
Apodization	Cosine
Gain	Auto (4)
Aperture	Auto (7.1 mm)
Scanning Speed	Auto (2 mm/sec)
Filter	Auto (30000 Hz)

Figure S4. FT-IR spectrum, HCMP-1.

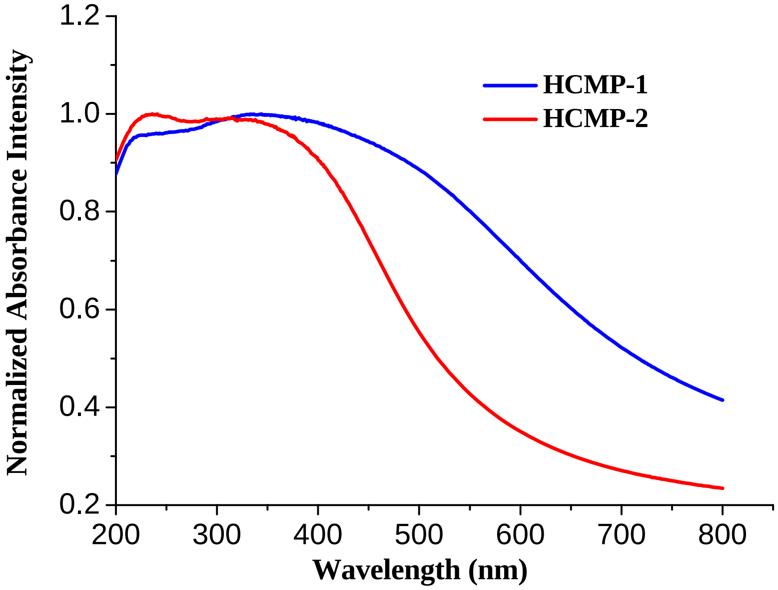


Figure S5. Solid state UV-visible adsorption spectra for polymers HCMP-1 and HCMP-2.

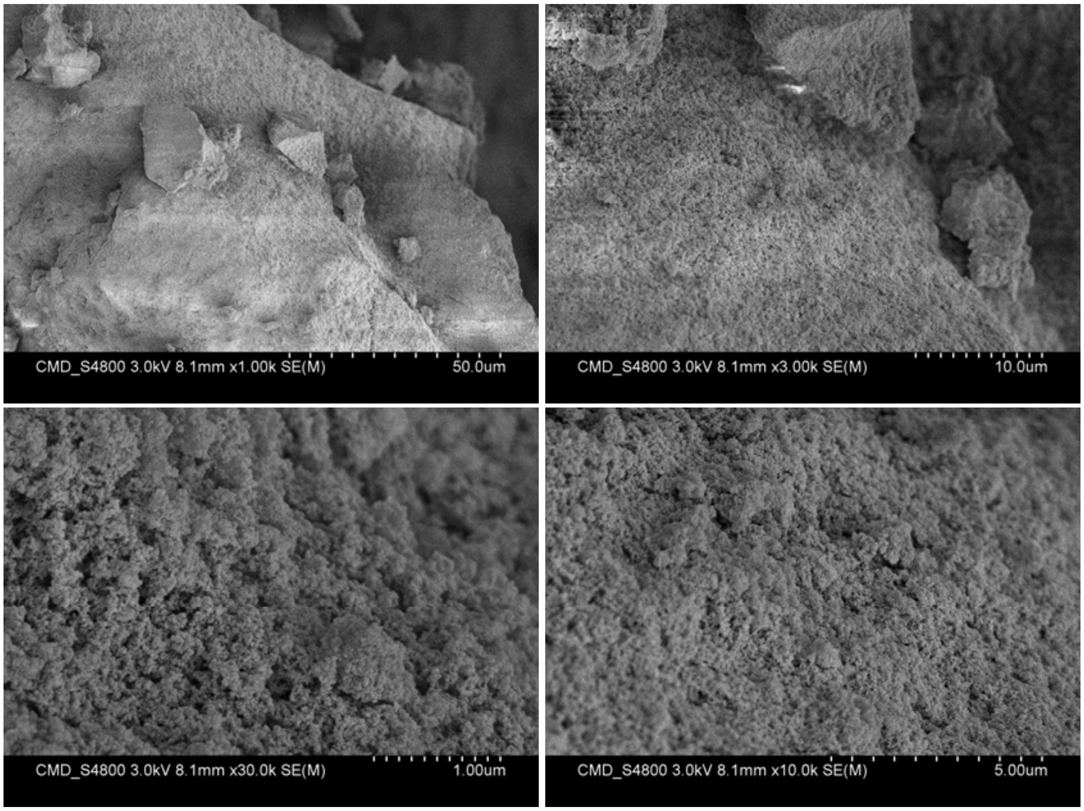


Figure S6. Scanning electron microscope images for polymer HCMP-1 at various magnifications. The sample was sputter-coated with gold before analysis.

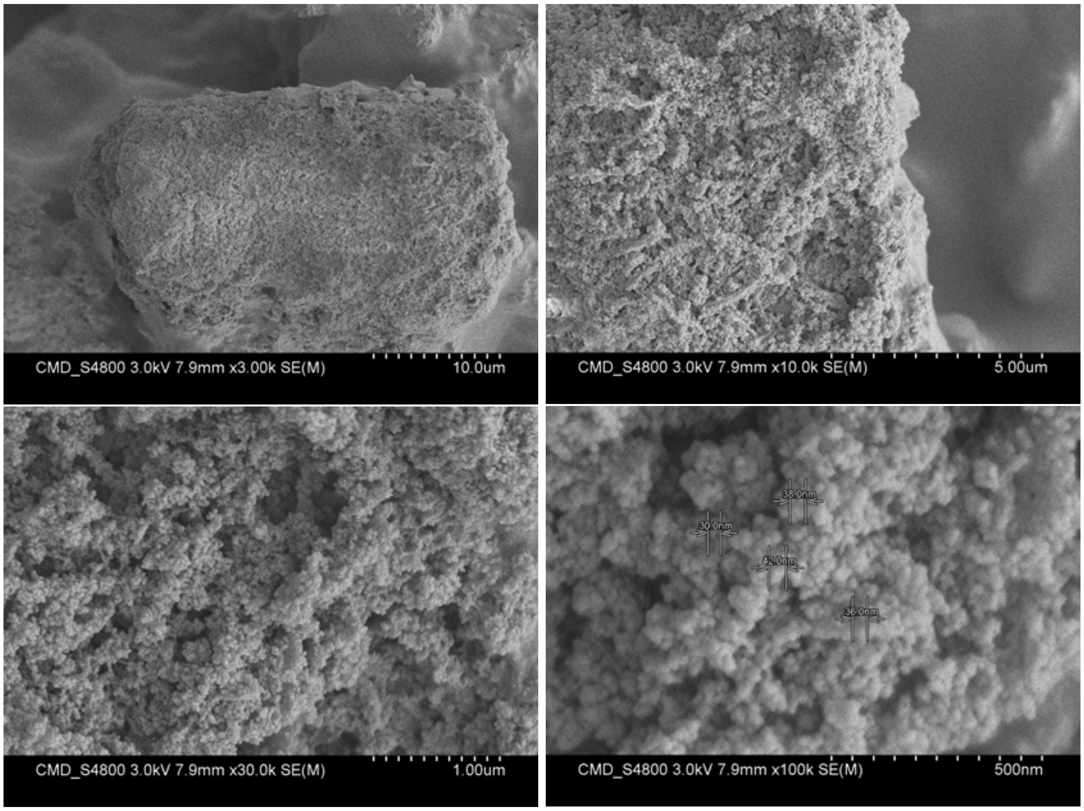


Figure S7. Scanning electron microscope images for polymer HCMP-2 at various magnifications. The sample was sputter-coated with gold before analysis.

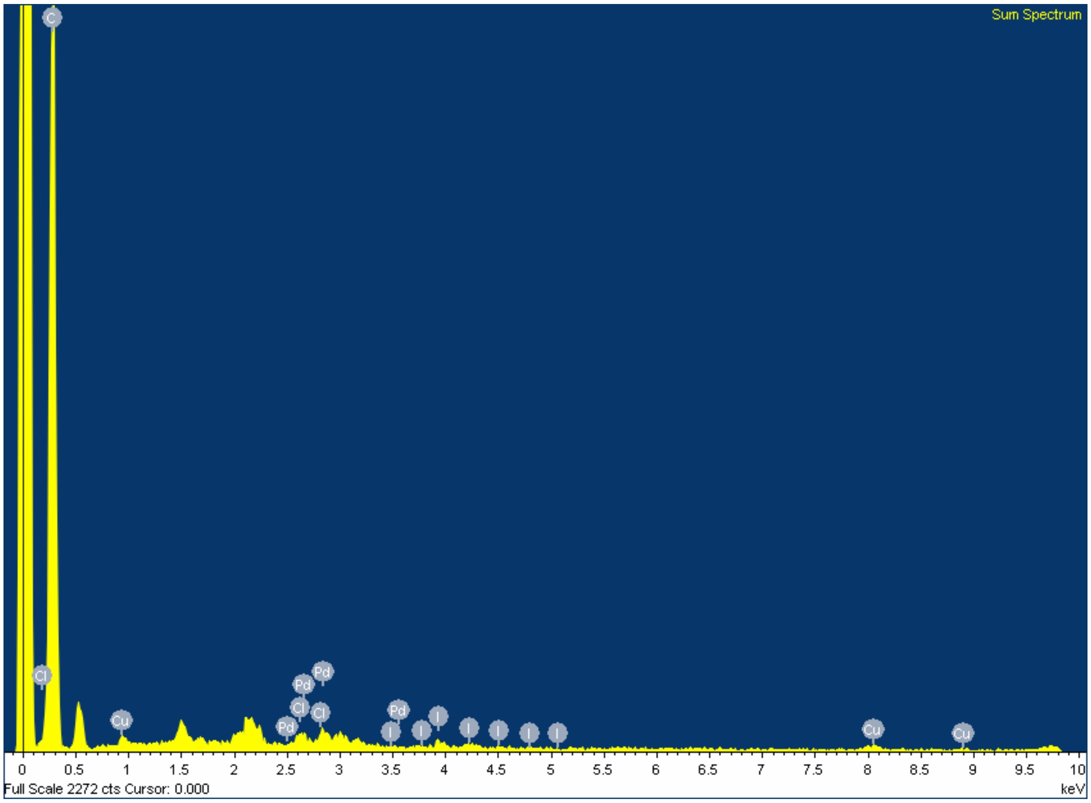


Figure S8. EDX spectrum for HCMP-1.