# Conjugated microporous poly(phenylene butadiynylene)s†

**Jia-Xing Jiang, Fabing Su, Hongjun Niu, Colin D. Wood, Neil L. Campbell, Yaroslav Z. Khimyak and Andrew I. Cooper***

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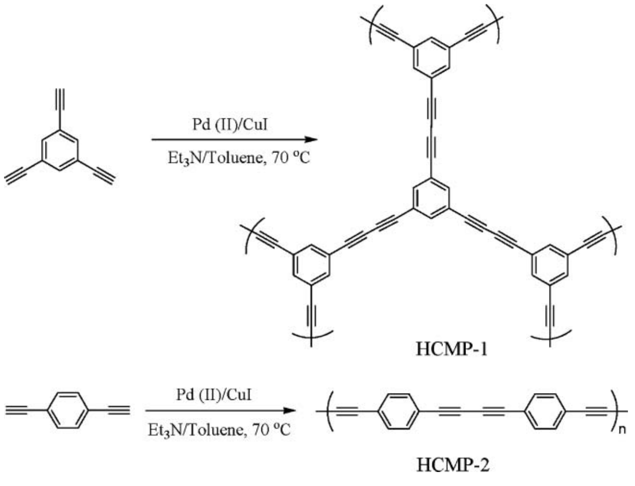
**High surface area porous poly(phenylene butadiynylene) networks were obtained (BET surface area up to 842 $m^2$ $g^{-1}$) by the palladium-catalyzed homocoupling of 1,3,5-triethynylbenzene and 1,4-diethynylbenzene.**

Micro- and mesoporous materials have attracted much attention recently because of their potential applications in areas such as gas storage, separations and heterogeneous catalysis.[1–3] Significant advances have been made in the preparation of microporous crystalline metal–organic[4,5] and covalent organic[6] frameworks. However, there are relatively few approaches for the direct synthesis of micro- and mesoporous organic polymers with high specific surface areas (>1000 $m^2$ $g^{-1}$). Polymers of intrinsic microporosity (PIMs) are a class of microporous organic polymer that can exhibit apparent Brunauer–Emmet–Teller (BET) surface areas in the range 500–1065 $m^2$ $g^{-1}$.[7–9] Hypercross-linked polymers represent another class of microporous organic materials that can exhibit surface areas as high as 2000 $m^2$ $g^{-1}$.[10–13] Recently, we have synthesized amorphous conjugated microporous polymers (CMPs) that display apparent BET surface areas in the range 500–800 $m^2$ $g^{-1}$ by using palladium-catalyzed Sonogashira–Hagihara cross-coupling chemistry.[14] These poly(arylene ethynylene) materials represent the first examples of conjugated microporous polymer networks with high surface areas. We also showed that the micropore size distribution was controlled in CMPs by the rigid node-strut topology, in particular by the average strut length.[14]

Poly(phenylene butadiynylene)s (PPBs)[15] may be synthesized by the oxidative coupling of terminal alkynes in the presence of $CuCl_2$ and $O_2$.[16] To our knowledge, there have been no reports on the synthesis of highly porous PPB-type polymers. We report here the synthesis of two porous PPB materials using Pd(II)/Cu(I)-catalyzed homocoupling polymerization[17,18] under mild conditions and in the absence of an additional oxidant (see ESI† full synthetic and characterization details). The synthetic routes to these polymers are shown in Scheme 1. The homocoupled conjugated microporous polymer (HCMP) produced from 1,3,5-triethynylbenzene (**HCMP-1**) was designed to have a three-dimensional net structure arising from the three-pronged butadiynylene linkages, while the polymer derived from 1,4-diethynylbenzene (**HCMP-2**) is notionally linear (Scheme 1) but, in fact, also incorporates cross-links that arise from the formation of head-to-tail 1,3-disubstituted enyenes under these polymerization conditions (Scheme 2),[17,18] as confirmed by $^1H$–$^{13}C$ CP/MAS solid-state NMR. These HCMPs are amorphous and show no evidence of long range molecular order, as found previously for cross-coupled CMP networks.[14]

The polymers precipitated from solution as brown-coloured powders that were totally insoluble in all the organic solvents tested as a result of there highly rigid macromolecular network structures. At higher monomer concentrations (>800 mmol $L^{-1}$), macroscopic gelation of the solutions was observed, but these gels fragmented into powders upon washing and drying rather than forming stable, coherent monoliths. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of both **HCMP-1** and **HCMP-2** showed no evidence of any glass transition or melting below the thermal decomposition temperature of the materials (>300 °C, see ESI Fig. S1–S3†). Both materials were also chemically stable, for example, to dilute solutions of acids and bases such as HCl and NaOH.

The molecular level structure of both polymers was assessed by $^1H$–$^{13}C$ CP/MAS solid-state NMR (Fig. 1). These spectra show significantly broader lines in comparison to those observed for the aligned linear PPB prepared in silica pore channels.[15] The spectrum of **HCMP-2** is dominated by a broad line corresponding to $sp^2$ carbon sites, which is consistent with our previous report on CMP networks.[14] The peaks at *ca.* 123 and *ca.* 131 ppm correspond to $\mathbf{C}_{ar}$–C and $\mathbf{C}_{ar}$–H sites. This is in agreement with the reported spectrum for the aligned linear PPB.[15] The peaks at *ca.* 90 and 82 ppm can be ascribed to sp-hybridised –$C_{ar}$–$\mathbf{C}$≡C– and –C≡$\mathbf{C}$–$\mathbf{C}$≡C– sites, respectively. The shoulder at *ca.* 78 ppm



**Scheme 1** Route to homocoupled conjugated polymers, showing a network structure for **HCMP-1** and a notionally linear structure for **HCMP-2**.

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*Department of Chemistry and Centre for Materials Discovery, University of Liverpool, Crown Street, Liverpool, L69 3BX, UK. E-mail: aicooper@liv.ac.uk*

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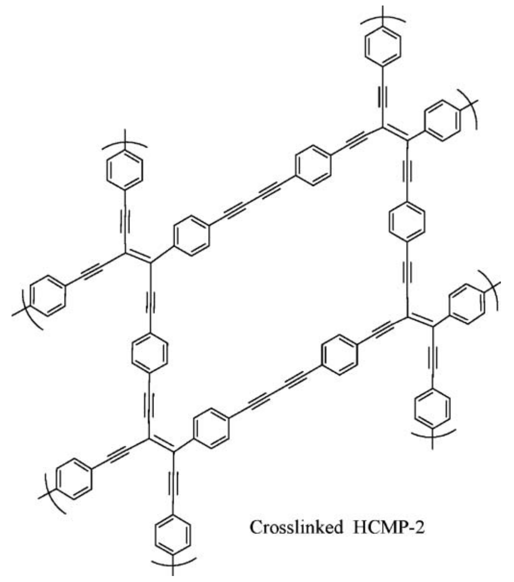

**Scheme 2** Representation of the cross-linked 1,3-disubstituted enyene polymer structure for **HCMP-2**.

can be assigned to the –C≡**C**–H end groups. The broad lines in the lower field range with respect to the $C_{ar}$–H sites indicate the presence of other types of $sp^2$ carbons in the structure. Most probably, these originate from the C=C bonds formed during cross-linking (Scheme 2). Indeed, similar spectra were reported for the PPB formed within the pores of mesoporous silica.[15] The NMR spectrum of **HCMP-1** is comparable with that of **HCMP-2**; the main difference is the increased population of carbon resonances with a chemical shift above 135 ppm. The broader resonances and the complexity of the NMR spectrum for these HCMP samples relative to our previously reported CMP networks[14] is consistent with a higher degree of disorder and a more complex mechanism of cross-linking that involves the formation of C=C bonds.

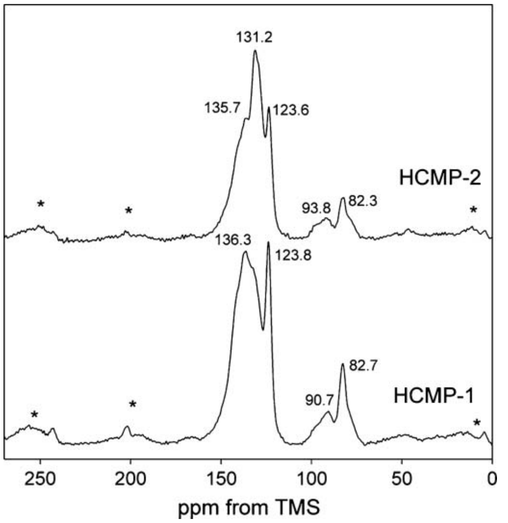

**Fig. 1** Solid-state NMR spectra for the homocoupling polymers. $^1H$–$^{13}C$ CP/MAS spectra were recorded at a MAS rate of 12.0 kHz and reported relative to $Me_4Si$. Asterisks denote spinning sidebands.

The porous properties of the polymers were investigated by nitrogen adsorption analyses at 77.3 K (see ESI†). Fig. 2(a) shows the nitrogen adsorption and desorption isotherms for the polymers. According to the IUPAC classification,[19] both polymers gave rise to Type I nitrogen gas sorption isotherms with H3 hysteresis loops, indicating that the materials consist of micro- and mesopores. Fig. 2(b) shows the pore size distribution (PSD) curves for the two polymers, as calculated using non-local density functional theory (NLDFT). **HCMP-1** exhibited a median pore diameter of 1.6 nm with a shoulder peak centered at 1.1 nm, while **HCMP-2** showed two comparable peaks located at around 0.9 and 1.6 nm, respectively. The relatively broad PSD curves for both polymers suggest the presence of both micropores and mesopores. Plots of the cumulative NLDFT pore volume for the polymers (Fig. 2(a) inset) show that **HCMP-2** has an increased ultra-micropore volume (<1 nm) relative to **HCMP-1**. The apparent BET surface areas were found to be 842 and 827 $m^2 g^{-1}$ for **HCMP-1** and **HCMP-2**, respectively. The micropore surface areas, derived using the t-plot method, were 177 and 324 $m^2 g^{-1}$ for **HCMP-1** and **HCMP-2**, respectively. The total pore volumes, estimated from the amount of gas adsorbed at $P/P_o$ = 0.99, were 1.16 and 1.35 $cm^3 g^{-1}$, while the micropore volumes derived from the cumulative pore volume graph (NLDFT) were 0.23 and 0.26 $cm^3 g^{-1}$ for **HCMP-1** and **HCMP-2**, respectively. These results demonstrate that there is a significant proportion of mesopores in both polymers, unlike our CMP cross-coupled networks, which were found to be totally microporous in nature.[14]

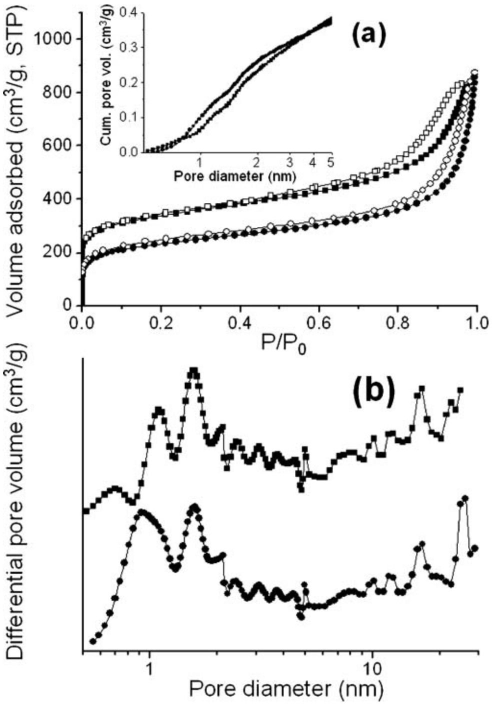

**Fig. 2** (a) $N_2$ adsorption–desorption isotherms measured at 77.3 K (adsorption branch is labelled with filled symbols) for **HCMP-1** (squares) and **HCMP-2** (circles). For clarity, the isotherms of **HCMP-1** were shifted vertically by 100 $cm^3 g^{-1}$. The BET surface areas are 842 (**HCMP-1**) and 827 (**HCMP-2**) $m^2 g^{-1}$. The inset shows the cumulative pore volume curves calculated by NLDFT. (b) Pore size distribution for **HCMP-1** (■) and HCMP-2 (●). For clarity, the curve of **HCMP-1** is shifted vertically.

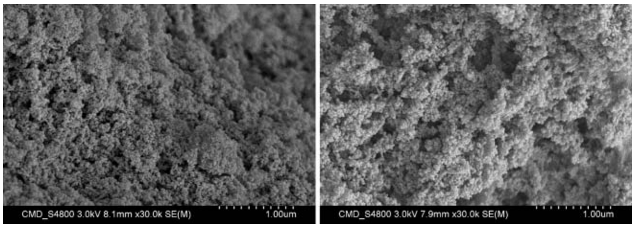

**Fig. 3** Scanning electron microscope images of homocoupling polymers **HCMP-1** (left) and **HCMP-2** (right) (scale bar = 1 μm).

The permanent porosity of both **HCMP-1** and **HCMP-2** results from the rigid butadiynylene-linked network, coupled in both cases with additional C=C cross-links, as shown by $^{1}H$–$^{13}C$ CP/MAS solid state NMR. The microporosity in these samples can therefore be rationalized in a similar fashion to the CMP networks reported previously,[14] albeit with a broader micropore distribution in this case, possibly because of the more diverse linking chemistry, as discussed above. By way of contrast, these HCMP structures exhibit a mesostructure that was absent in the CMP networks (Fig. 3).

Fig. 3 shows scanning electron microscope (SEM) images of these polymers. The samples consist of relatively uniform solid sub-micron spheres. The mesopores in both polymers can be ascribed mostly to the interparticulate porosity that exists between agglomerated primary microgel particles (Fig. 3). This kind of mesostructure was not observed for CMP networks prepared by cross-coupling—indeed, those samples were wholly microporous and featureless at this length scale when observed by SEM and TEM.[14] This suggests that the phase separation process differs significantly between HCMP and CMP processes.[20,21]

The hydrogen sorption properties of the polymers at 77.3 K were investigated by volumetric methods.[10,12] Fig. 4 shows the $H_2$ adsorption isotherms at 77.3 K up to a maximum $H_2$ pressure of 1.13 bar. The polymers were found to adsorb up to 107 and 131 $cm^3 g^{-1}$ $H_2$ under these conditions. Fig. 4 shows that **HCMP-2** exhibits a higher $H_2$ adsorption capacity than **HCMP-1**, even though the apparent BET surface area is slightly lower than that of **HCMP-1**. This can be assigned to the higher micropore surface area and ultramicropore volume observed for **HCMP-2**, since micropores, not mesopores, mostly contribute to the $H_2$ adsorption at these pressures and temperatures.

In summary, permanently porous polymers with high surface areas were obtained by the palladium-catalyzed homocoupling polymerization of 1,3,5-triethynylbenzene and 1,4-diethynylbenzene. These polymers have good chemical and thermal stability and are composed solely of carbon–carbon and carbon–hydrogen bonds. It is possible to produce activated carbons with much higher surface areas than these materials[22] but the synthetic scope for derivatizing carbon is relatively limited. These HCMPs are highly conjugated, and there is a wealth of opportunity for producing porous materials with specific functionalities; for example, by attaching metals to the alkyne and/or alkene bonds in the network to facilitate catalysis or to introduce high binding energy sites, such as metals[23,24] or transition metal complexes,[25] for $H_2$ storage.

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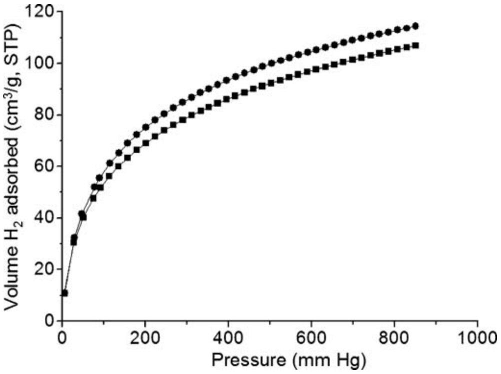

**Fig. 4** Volumetric $H_2$ sorption analysis for **HCMP-1** (squares) and **HCMP-2** (circles) at 77.3 K.

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