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Mesoporous Poly(phenylenevinylene) Networks

Robert Dawson, Fabing Su, Hongjun Niu,
Colin D. Wood, James T. A. Jones,
Yaroslav Z. Khimyak, and Andrew I. Cooper*

Department of Chemistry and Centre for Materials
Discovery, University of Liverpool, Crown Street, Liverpool
L69 3BX, United Kingdom

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Microporous organic polymers such as polymers of intrinsic microporosity (PIMs),[1−7] hyper-cross-linked polymers (HCPs),[8−12] covalent organic frameworks (COFs),[13,14] and, recently, conjugated microporous polymers (CMPs)[15] have been the focus of much research for applications such as hydrogen storage.[6,7,9−11] There are currently relatively few methods available to synthesize microporous and mesoporous organic polymers with high surface areas (>750 m^2/g). Macroporous resins[16,17] can exhibit apparent Brunauer−Emmett−Teller (BET) surface areas of this order, but these materials usually exhibit a broad pore size distribution which, unlike PIMs,[1−7,18] COFs,[13,14] and CMPs,[15] is controlled more by the phase separation process than the molecular structure of the polymers.[16] There is a need to develop new routes to microporous and mesoporous organic polymers and to broaden the range of materials that can be produced in this way, for example, to extend beyond polystyrene-based systems which still constitute the majority of examples in this class of materials.[12,15−17,19] In addition, the introduction of new chemical functionalities should produce materials with unprecedented combined physical properties such as the combination of high physical surface areas with attributes such as electrical conductivity, superconductivity, light emission, and specific UV−vis absorption spectra. The production of conjugated polymer networks in highly porous forms is of particular interest in this regard. We have recently demonstrated this for the first time in the direct synthesis of microporous poly(aryleneethynylene) (PAE) and poly(phenylenebutadiynylene) (PPB) networks with high surface areas (up to ∼1000 m^2/g).[15]

Poly(*p*-phenylenevinylene)s (PPVs) have received much attention as materials in organic light-emitting diodes (OLEDs).[20,21] There have been no reports to our knowledge of the direct synthesis of porous PPV networks. In this Communication, we demonstrate a direct synthetic route to mesoporous PPV networks with high surface areas (>750 m^2/g) based on Gilch coupling polymer reactions.[22]

Self-condensation of 1,2,4,5-tetrakis(bromomethyl)benzene (TBMB) using potassium *tert*-butoxide in anhydrous THF gave rise to a brown powdered precipitate that was totally insoluble in all solvents tested. This material was characterized by ^{13}C solid-state NMR, N_2 and H_2 gas sorption, scanning electron microscopy (SEM), FT-IR, UV−vis spectroscopy, and elemental analysis.

The UV−vis spectrum showed a wide absorption maximum between 250 and 400 nm and fluorescence between 500 and 525 nm, similar to many PPVs. The N_2 adsorption/desorption isotherms collected at 77.3 K are shown in Figure 1. The adsorption isotherm is type IV according to IUPAC classifications and shows a significant H2 hysteresis loop in the desorption branch, consistent with a predominantly mesoporous structure. The pore size distribution curve derived from the Barrett−Joyner−Halenda (BJH) method[23] using the adsorption branch is depicted in the inset of Figure 1, showing that the pores are mainly located in the mesopore range (2.0−50.0 nm) and that the mesopore distribution is centered around 5.6 nm. The Brunauer−Emmett−Teller (BET) surface area for the material was calculated to be 761 m^2/g in the relative pressure range 0.05−0.20. The total pore volume at a relative pressure of 0.99 was calculated to be 0.63 cm^3/g. The micropore volume was 0.07 cm^3/g calculated using the *t*-plot method. Thus, the microporosity (micropore volume/total pore volume) is around 11%, further indicating that the PPV network is predominantly mesoporous. This suggests perhaps that the pore structure in these materials is determined more by the details of phase separation[16] than by the molecular framework structure. This contrasts with our PAE materials,[15] for example, where type I N_2 isotherms and high-percentage microporosity was observed, as well as a direct correlation between average pore size and molecular strut length. The H_2 isotherm of the polymer showed a maximum adsorption of 71.9 cm^3/g at 77.3 K, corresponding to a gravimetric H_2 uptake of 0.63 wt %; this is modest but consistent with the surface area and predominantly mesoporous nature of the material.

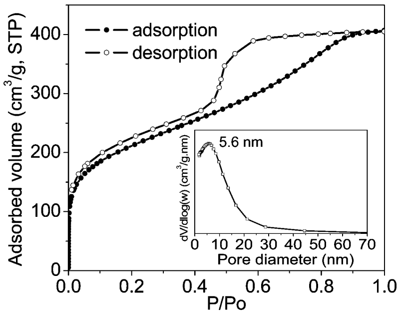

Figure 1. Nitrogen adsorption/desorption isotherms at 77.3 K.

Condensation of the 1,3,5-tris(bromomethyl)benzene monomer did not result in an insoluble porous polymer and formed a soluble hyperbranched oligomer.[19] This lower degree of condensation could be ascribed to the lower degree of functionality in this monomer and might also be explained in part by the coupling mechanism presented by Rehahn et al.,[24] which requires a diradical with a para geometry.

The $^1H-^{13}C$ CP/MAS NMR spectrum for the porous network with assignment of the resonances is shown in Figure 2. The broad resonance at ca. 130−136 ppm corresponds to the main polymer backbone structure. The other lines correspond to terminal functionalities. The broad resonance at 130−136 ppm represents a combined line due to aromatic −**C**H−, −**C**H═CH−, and quaternary aromatic groups in the polymer backbone. This was confirmed by the unusual CP kinetics for this site where, at short CP contact times, the resonance maximum was observed at 130 ppm (Figure 3): this is due to the fast CP buildup of the aromatic −CH− and −CH═CH− groups, where two components with different T_{IS} and $T^{H}_{1\rho}$ times are identified depending on the mobility of the CP-determining ^1H source spins. As the CP contact time was increased, the main resonance maximum shifted downfield to 136 ppm where quaternary aromatic carbon sites are observed as a result of a slower CP “buildup” for the latter. The dipolar dephasing

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* Corresponding author. E-mail: aicooper@liv.ac.uk.

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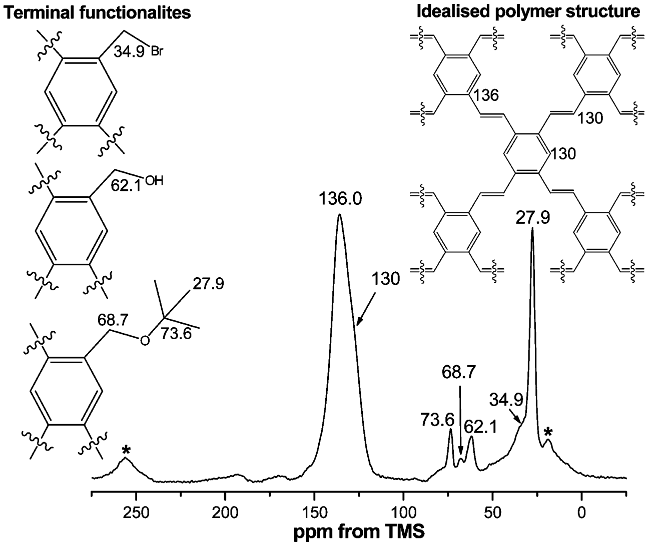

Figure 2. CP/MAS NMR spectrum for mesoporous PPVs network.

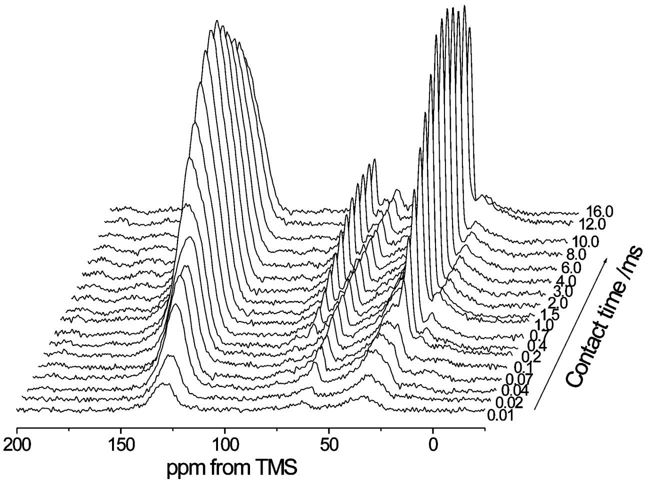

Figure 3. $^1H-^{13}C$ VCT CP/MAS NMR spectra plotted as a function of CP contact time.

experiments also confirmed the presence of aromatic −CH− and −CH═CH− functionalities at 130−136 ppm as the peak width at half-maximum (pwhm) was reduced as dephasing time increases.

The terminal functionalities were assigned as follows: the resonance at 27.9 ppm results from the *tert*-butyl $-CH_3$ groups (Figure 2), as confirmed by the dipolar dephasing experiments where the signal failed to dephase even after 200 μs. The CP kinetics of this site showed slow CP build and long $T_{1\rho}^{H}$ times. The resonances at 34.9, 62.1, and 68.7 ppm were attributed to $-\mathbf{C}H_2-Br$, $-\mathbf{C}H_2-OH$, and $Ar-\mathbf{C}H_2O-$ functionalities, respectively, as confirmed by fast CP "buildup" and fast dephasing after 10 μs − this is a typical behavior for methylene sites in polymer composites. The resonance at 73.8 ppm was assigned to the quaternary *tert*-butyl carbon $-\mathbf{C}(CH_3)_3$ based on the CP kinetics; this resonance displayed long T_{cp} times of 2.58 ms and did not dephase in the dipolar dephasing experiments. The presence of a substantial number of *tert*-butyl ether end groups in the network is consistent with a competitive nucleophilic substitution pathway which probably occurs in the solid precipitated network after the polymer is condensed to the point that further reactions between chain ends has ceased. The exponential growth in the number of chain ends with degree of reaction in branching polymerizations such as this will tend to exaggerate competitive side reactions, even if these pathways are of marginal importance for analogous linear polymers.

In summary, permanently mesoporous PPV-type materials with high BET surface areas (>750 m^2/g) were obtained by Gilch coupling chemistry, and these polymers have good chemical stability. There is a wealth of opportunity for producing porous materials with useful combined properties—for example, to introduce high-energy "binding sites" for H_2 storage applications.[25] For example, metal-decorated polyacetylene has been invoked as a material for ambient temperature H_2 storage,[26] but no strategy was proposed to produce alkene-containing conjugated polymers of this type in a porous state. The new route presented here represents a promising strategy for producing such C═C bond-containing conjugated polymers in a highly porous form.

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Supporting Information Available: Experimental procedures and sorption and solid-state NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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