

CrossMark
click for updatesCite this: *J. Mater. Chem. A*, 2016, 4, 10110Received 19th April 2016
Accepted 13th June 2016

DOI: 10.1039/c6ta03257e

www.rsc.org/MaterialsA

Inexpensive polyphenylene network polymers with enhanced microporosity†

Kadhum J. Msayib and Neil B. McKeown*

Greatly enhanced microporosity is obtained for the amorphous porous polymers produced from the AlCl_3 -mediated coupling of aromatic hydrocarbons by using dichloromethane as the reaction solvent. A polymer of average BET surface area = $2435 \text{ m}^2 \text{ g}^{-1}$ was obtained reproducibly from 1,3,5-triphenylbenzene with the additional porosity being provided as ultramicroporosity as demonstrated by very high CO_2 adsorption at 273 K/1 bar.

The potential for applications in gas storage, carbon capture, adsorption, heterogeneous catalysis and molecular separations has inspired intensive research activity focused on the synthesis of microporous materials using molecular building units.¹ From a structural perspective, there is an important distinction between crystalline porous materials derived from molecular precursors, such as the much-studied Metal Organic Frameworks (MOFs), and amorphous materials that possess a broader range of pore size. However, amorphous porous materials are attractive because they can be prepared using a greater diversity of chemistry and may offer enhanced stability as they do not require crystallisation *via* reversible bond formation.² With a few notable exceptions,³ the generation of microporosity within amorphous polymers relies on the formation of a rigid and highly cross-linked network of covalent bonds. Among the rapidly growing number of reported porous network polymers, the Porous Aromatic Frameworks (*e.g.* PAF-1) and the structurally related Porous Polymer Networks (*e.g.* PPN-4) are particularly impressive with apparent Brunauer–Emmett–Teller (BET) surface areas rivalling those of the most porous MOFs ($\text{SA}_{\text{BET}} > 5000 \text{ m}^2 \text{ g}^{-1}$).⁴ PAFs and PPNs are prepared using the highly efficient Yamamoto aryl–aryl coupling reaction, which relies on the stoichiometric mediation of the expensive bis(1,5-cyclooctadiene)nickel(0) reagent. In addition, network polymer synthesis *via* Yamamoto coupling requires bromine-containing

monomers which are either expensive to purchase or are prepared using a multi-step synthesis, such as tetra-(4-bromophenyl) methane.⁵ However, for many of the proposed applications of porous polymers, such as gas storage, water purification or carbon capture, low-cost and large-scale manufacture are necessary to provide competition with conventional inexpensive microporous materials such as activated carbons.^{1,6} Therefore, network forming reactions that involve cheap monomers and reagents such as the Friedel–Craft reaction⁷ or direct oxidative aryl–aryl coupling⁸ (*i.e.* the Scholl reaction⁹) are of interest. Unfortunately, to date, these reactions have failed to provide highly porous network polymers. Here we report a simple modification to an aromatic coupling polymerisation that provides highly microporous polymers from readily available and inexpensive starting materials and reagent.

As part of our on-going research programme on triptycene-based porous polymers,¹⁰ we performed an acylation of triptycene, following a literature procedure using acetyl chloride and AlCl_3 in DCM.¹¹ An insoluble material was isolated from the reaction that proved to be a network polymer with a surprisingly high surface area ($\text{SA}_{\text{BET}} > 1000 \text{ m}^2 \text{ g}^{-1}$). Optimisation studies, without acetyl chloride, gave polymer with $\text{SA}_{\text{BET}} = 1750 \text{ m}^2 \text{ g}^{-1}$, which is a significantly higher value than previously obtained from polymers derived from triptycene using the Friedel–Craft reaction ($\text{SA}_{\text{BET}} = 1250\text{--}1430 \text{ m}^2 \text{ g}^{-1}$)^{6c,7d} and is comparable to results obtained using Yamamoto coupling of tribromo- or triiodo-triptycenes ($\text{SA}_{\text{BET}} = 1300\text{--}1990 \text{ m}^2 \text{ g}^{-1}$).¹²

This result encouraged the polymerisation of a range of readily available monomers, from which porous polymers had previously been prepared, using these reaction conditions (*i.e.* AlCl_3 , DCM at reflux). With the exception of tetraphenylmethane, highly porous polymers were obtained from each monomer (Table 1; Fig. 1). Indeed, for biphenyl, 1,3,5-triphenylbenzene (TPB), hexaphenylbenzene (HPB), spirobifluorene (SBF) and tetraphenylporphyrin (TPP) the SA_{BET} of the resulting polymer was greater than those reported for the polymers obtained previously from the same monomer using Friedel–Craft or Scholl reactions (ESI Table S1†). A particularly impressive result was obtained from the polymer derived from

EastChem School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, EH9 3JF, UK. E-mail: neil.mckeown@ed.ac.uk

† Electronic supplementary information (ESI) available: Information of synthesis and characterisation of porous polymers. See DOI: 10.1039/c6ta03257e



Table 1 Properties of porous polymers prepared from given monomer using AlCl₃ in refluxing DCM as solvent (alternatively CHCl₃ or DCE, if stated)

| Monomer ^a | S _{BET} (m ² g ⁻¹) | V _{total} ^b (cm ³ g ⁻¹) | V _{micro} ^c (cm ³ g ⁻¹) | CO ₂ uptake ^d (mmol g ⁻¹) |
|-------------------------------|--|--|--|---|
| Triptycene | 1750 | 1.0 | 0.6 | 5.8 [3.1] |
| TPB | 2435 | 1.6 | 1.0 | 5.9 [3.6] |
| TPB (CHCl ₃) | 1415 | 0.7 | 0.5 | 5.0 [3.2] |
| TPB (DCE) | 725 | 0.7 | 0.2 | 1.7 [1.1] |
| Spirobifluorene | 2035 | 1.0 | 0.7 | 5.8 [3.0] |
| HPB | 1790 | 0.9 | 0.6 | 4.5 [2.7] |
| Biphenyl | 1555 | 1.0 | 0.5 | 4.0 [2.7] |
| Biphenyl (CHCl ₃) | 800 | 0.5 | 0.2 | 3.3 [2.4] |
| Biphenyl (DCE) | 453 | 0.3 | 0.1 | 1.7 [1.1] |
| Triphenylene | 1180 | 0.7 | 0.4 | 4.0 [2.9] |
| DPA | 1020 | 0.6 | 0.3 | 3.2 [2.0] |
| TPP | 905 | 0.4 | 0.3 | 2.5 [2.0] |
| TPM | 125 | 0.2 | 0.0 | 2.0 [1.3] |

^a TPB = 1,3,5-triphenylbenzene; HPB = hexaphenylbenzene; TPP = tetraphenyl porphyrin; DPA = 9,10-diphenylanthracene; TPM = tetraphenylmethane. ^b Pore volume estimated from N₂ uptake at 77 K and P/P₀ = 0.98. ^c Micropore volume estimated from N₂ uptake at 77 K and P/P₀ = 0.01. ^d At 1 bar/273 K [1 bar/298 K].

TPB that demonstrated reproducibly a S_{BET} in the range 2328–2520 m² g⁻¹ greater than that of the equivalent porous polymer prepared from tri-brominated TPB using Yamamoto coupling (S_{BET} = 1500–1870 m² g⁻¹; ESI Table S1†).¹³ This result allows access to an extremely porous polymer using cheap AlCl₃ as reagent and from a monomer that is both inexpensive to buy and easily prepared on a large scale from acetophenone.¹⁴ Initial scale-up attempts showed that a 10 g batch of the TPB polymer was readily obtained and demonstrated the same S_{BET} as polymers from smaller (1 g) batches. The lack of success from tetraphenylmethane is likely due its insolubility in DCM combined with low reactivity due to relatively poorly activated phenyl groups.

The greatly enhanced porosity of the TPB and biphenyl network polymers – twice the S_{BET} of those reported in previous studies of AlCl₃-mediated polymerisation – is surprising because the only difference is the use of DCM as solvent instead of CHCl₃ (ESI Table S1†).^{8a,8c} This prompted us to perform a direct comparison of the effect of DCM with commonly used CHCl₃ or dichloroethane (DCE) solvent on the porosity of the resulting polymers from these two monomers (Table 1). It was found that the S_{BET} values obtained from the TPB and biphenyl polymers prepared using CHCl₃ as solvent were similar to those from previous studies.^{8a,8c} Reactions using DCE as solvent produced polymer with only modest porosity. Therefore, it appears that the choice of DCM as solvent provides the dramatic enhancement of S_{BET}. Consequently, it was important to determine whether DCM acts only as a solvent or also provides methylene cross-links *via* a Friedel–Craft reaction. The ¹³C solid-state NMR spectrum of all the polymers prepared using DCM shows a small peak between 30 and 40 ppm that may indicate the presence of methylene cross-links, originating from the DCM (ESI†). However, this peak is much smaller than that found previously from a network polymer prepared from a formal Friedel–Craft reaction between TPB and formyl

dimethyl acetal as the methylene source.^{7a} In addition, the non-aromatic peaks observed for the TPB polymer are of a similar size, relative to that of the much larger peak of the aromatic carbons, to those previously observed from a TPB network obtained using CHCl₃.^{8a,8c} Therefore, it appears that network formation is predominately based on direct aryl–aryl coupling *via* the Scholl reaction, however, it seems likely that the DCM may contribute some cross-links to the network but

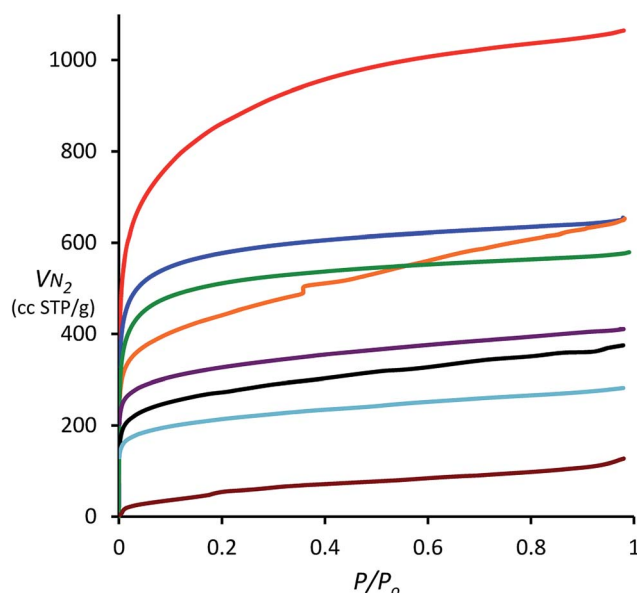


Fig. 1 N₂ adsorption isotherms obtained at 77 K for porous polymers derived from 1,3,5-triphenylbenzene (TPB, red), spirobifluorene (blue), triptycene (green), biphenyl (orange), triphenylene (purple), 9,10-diphenylanthracene (DPA, black), tetraphenylporphyrin (TPP, light blue) and tetraphenylmethane (TPM, brown) using DCM and AlCl₃. Note that the isotherm of hexaphenylbenzene (HPB) is superimposable on that of triptycene and has been omitted for clarity (see ESI†).



only to a similar extent as CHCl_3 or DCE. Therefore, the effect of DCM in enhancing SA_{BET} is predominately related to its role as a solvent ensuring a more efficient network formation and/or facilitating the generation of a more microporous structure by behaving as a better porogen.¹⁵ Similarly large solvent effects on SA_{BET} have been reported for other types of reactions to make porous network polymers.^{7e,16}

The N_2 adsorption isotherms also provide information about the pore size distribution within the porous polymers. For the polymers derived from TPB, spirobifluorene and triptycene, the relatively large uptake of N_2 at 77 K at low relative pressure ($P/P_0 < 0.01$), demonstrates that micropores (<2 nm) contribute a large portion (>60%) of the total pore volume (Table 1). The absence of significant hysteresis between the adsorption and desorption isotherms (ESI†) for all polymers, with the exception of that from biphenyl, indicates both low degree of mesoporosity and that the pore structure appears fixed on adsorption of N_2 with no significant swelling.

CO_2 adsorption isotherms obtained at 273 K (ESI and Table S1†) also provide information on pore size distribution. Such data are also useful as an indicator of the suitability of a polymer for use in carbon capture using pressure-swing adsorption.^{6a,b} CO_2 uptake for the triptycene, SBF and TPB network polymers are all approximately 5.8 mmol g^{-1} at 1 bar/273 K ($3.0\text{--}3.6 \text{ mmol g}^{-1}$ at 1 bar/295 K), which is impressive in comparison with other polymers derived from these building units (ESI Table S1†) and are similar to the best performing network polymers ($\sim 6.0 \text{ mmol g}^{-1}$ at 1 bar/273 K and 3.6 mmol g^{-1} at 1 bar/295 K).¹⁷ The high uptake of CO_2 suggests that the use of DCM provides additional porosity in the form of ultramicropores (*i.e.* pores of diameter less than 0.7 nm), which are the physisorption sites for CO_2 at 273 K/1 bar. The porosity and gas adsorption of the polymer derived from TPB is strikingly similar to that of one of the best performing activated carbons for CO_2 capture.¹⁸

Despite the large number of reported porous polymers, prepared using a wide variety of monomers and network-forming reactions,² only a few demonstrate SA_{BET} in excess of $2000 \text{ m}^2 \text{ g}^{-1}$ and all of these require preparation from monomers that need a multistep synthesis or expensive precursors.^{4a,b,5,13b,17a,19} This work now allows access to highly microporous network polymers, of surface areas in excess of those of commercial activated carbons, from readily obtained starting materials.

Acknowledgements

We thank the EPSRC for funding (EP/K008102/2 & EP/M01486X/1) and the EPSRC UK Solid State NMR Service at Durham University.

Notes and references

- 1 A. G. Slater and A. I. Cooper, *Science*, 2015, **348**, 988.
- 2 (a) N. B. McKeown and P. M. Budd, *Macromolecules*, 2010, **43**, 5163–5176; (b) R. Dawson, A. I. Cooper and D. J. Adams, *Prog. Polym. Sci.*, 2012, **37**, 530–563; (c) D. Wu, F. Xu, B. Sun, R. Fu,

- H. He and K. Matyjaszewski, *Chem. Rev.*, 2012, **112**, 3959–4015; (d) Y. Zhang and S. N. Riduan, *Chem. Soc. Rev.*, 2012, **41**, 2083–2094; (e) Z. Chang, D.-S. Zhang, Q. Chen and X.-H. Bu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5430–5442; (f) Z. Xiang and D. Cao, *J. Mater. Chem. A*, 2013, **1**, 2691–2718; (g) M. Rose, *ChemCatChem*, 2014, **6**, 1166–1182.

- 3 Polymers of intrinsic microporosity and some other high free volume polymers exhibit microporosity without a network structure – see N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675–683.
- 4 (a) T. Ben, H. Ren, S. Q. Ma, D. P. Cao, J. H. Lan, X. F. Jing, W. C. Wang, J. Xu, F. Deng, J. M. Simmons, S. L. Qiu and G. S. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9457–9460; (b) D. Yuan, W. Lu, D. Zhao and H.-C. Zhou, *Adv. Mater.*, 2011, **23**, 3723–3725; (c) C. Pei, T. Ben and S. Qiu, *Mater. Horiz.*, 2015, **2**, 11–21.
- 5 W. Lu, D. Yuan, D. Zhao, C. I. Schilling, O. Plietzsch, T. Muller, S. Braese, J. Guenther, J. Bluemel, R. Krishna, Z. Li and H.-C. Zhou, *Chem. Mater.*, 2010, **22**, 5964–5972.
- 6 (a) R. Dawson, E. Stoeckel, J. R. Holst, D. J. Adams and A. I. Cooper, *Energy Environ. Sci.*, 2011, **4**, 4239–4245; (b) C. F. Martin, E. Stockel, R. Clowes, D. J. Adams, A. I. Cooper, J. J. Pis, F. Rubiera and C. Pevida, *J. Mater. Chem.*, 2011, **21**, 5475–5483; (c) R. T. Woodward, L. A. Stevens, R. Dawson, M. Vijayaraghavan, T. Hasell, I. P. Silverwood, A. V. Ewing, T. Ratvijitvech, J. D. Exley, S. Y. Chong, F. Blanc, D. J. Adams, S. G. Kazarian, C. E. Snape, T. C. Drage and A. I. Cooper, *J. Am. Chem. Soc.*, 2014, **136**, 9028–9035; (d) H. A. Patel, F. Karadas, A. Canlier, J. Park, E. Deniz, Y. Jung, M. Atilhan and C. T. Yavuz, *J. Mater. Chem.*, 2012, **22**, 8431–8437.
- 7 (a) B. Li, R. Gong, W. Wang, X. Huang, W. Zhang, H. Li, C. Hu and B. Tan, *Macromolecules*, 2011, **44**, 2410–2414; (b) G. Liu, Y. Wang, C. Shen, Z. Ju and D. Yuan, *J. Mater. Chem. A*, 2015, **3**, 3051–3058; (c) K. Schute and M. Rose, *ChemSusChem*, 2015, **8**, 3419–3423; (d) C. Zhang, P.-C. Zhu, L. Tan, J.-M. Liu, B. Tan, X.-L. Yang and H.-B. Xu, *Macromolecules*, 2015, **48**, 8509–8514; (e) N. Fontanals, R. M. Marce, F. Borrull and P. A. G. Cormack, *Polym. Chem.*, 2015, **6**, 7231–7244.
- 8 (a) B. Li, Z. Guan, X. Yang, W. D. Wang, W. Wang, I. Hussain, K. Song, B. Tan and T. Li, *J. Mater. Chem. A*, 2014, **2**, 11930–11939; (b) L. Li, H. Ren, Y. Yuan, G. Yu and G. Zhu, *J. Mater. Chem. A*, 2014, **2**, 11091–11098; (c) L. Li, K. Cai, P. Wang, H. Ren and G. Zhu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 201–208.
- 9 M. Grzybowski, K. Skonieczny, H. Butenschoen and D. T. Gryko, *Angew. Chem., Int. Ed.*, 2013, **52**, 9900–9930.
- 10 (a) B. S. Ghanem, M. Hashem, K. D. M. Harris, K. J. Msayib, M. Xu, P. M. Budd, N. Chaukura, D. Book, S. Tedds, A. Walton and N. B. McKeown, *Macromolecules*, 2010, **43**, 5287–5294; (b) M. Carta, M. Croad, R. Malpass-Evans, J. C. Jansen, P. Bernardo, G. Clarizia, K. Friess, M. Lanc and N. B. McKeown, *Adv. Mater.*, 2014, **26**, 3526–3531; (c) R. G. D. Taylor, C. G. Bezzu, M. Carta, K. J. Msayib, J. Walker, R. Short, B. M. Kariuki and N. B. McKeown, *Chem.–Eur. J.*, 2016, **22**, 2466–2472.



- 11 P.-F. Li and C.-F. Chen, *J. Org. Chem.*, 2012, **77**, 9250–9259.
- 12 C. Zhang, Y. Liu, B. Li, B. Tan, C.-F. Chen, H.-B. Xu and X.-L. Yang, *ACS Macro Lett.*, 2012, **1**, 190–193.
- 13 (a) H. Ren, T. Ben, F. Sun, M. Guo, X. Jing, H. Ma, K. Cai, S. Qiu and G. Zhu, *J. Mater. Chem.*, 2011, **21**, 10348–10353; (b) Z. Xiang, X. Zhou, C. Zhou, S. Zhong, X. He, C. Qin and D. Cao, *J. Mater. Chem.*, 2012, **22**, 22663–22669.
- 14 (a) Y. Zhao, J. Li, C. Li, K. Yin, D. Ye and X. Jia, *Green Chem.*, 2010, **12**, 1370–1372; (b) S. Zhao, L. Kang, H. Ge, F. Yang, C. Wang, C. Li, Q. Wang and M. Zhao, *Synth. Commun.*, 2012, **42**, 3569–3578; (c) D. Prasad, A. Preetam and M. Nath, *C. R. Chim.*, 2013, **16**, 252–256; (d) H. R. Safaei, M. Davoodi and M. Shekouhy, *Synth. Commun.*, 2013, **43**, 2178–2190.
- 15 D. C. Sherrington, *Chem. Commun.*, 1998, 2275–2286.
- 16 R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Macromolecules*, 2010, **43**, 8524–8530.
- 17 (a) S. Hug, L. Stegbauer, H. Oh, M. Hirscher and B. V. Lotsch, *Chem. Mater.*, 2015, **27**, 8001–8010; (b) Y. Zhu, H. Long and W. Zhang, *Chem. Mater.*, 2013, **25**, 1630–1635.
- 18 M. Sevilla and A. B. Fuertes, *Energy Environ. Sci.*, 2011, **4**, 1765–1771.
- 19 (a) J. H. Ahn, J. E. Jang, C. G. Oh, S. K. Ihm, J. Cortez and D. C. Sherrington, *Macromolecules*, 2006, **39**, 627–632; (b) P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450–3453; (c) E. Preis, C. Widling, G. Bruncklaus, J. Schmidt, A. Thomas and U. Scherf, *ACS Macro Lett.*, 2013, **2**, 380–383; (d) Z. Xiang, R. Mercado, J. M. Huck, H. Wang, Z. Guo, W. Wang, D. Cao, M. Haranczyk and B. Smit, *J. Am. Chem. Soc.*, 2015, **137**, 13301–13307.

