THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Centrotriindane- and triptindane-based polymers of intrinsic microporosity

Citation for published version:

Vile, J, Carta, M, Bezzu, CG, Kariuki, BM & McKeown, NB 2014, 'Centrotriindane- and triptindane-based polymers of intrinsic microporosity', *Polymer*, vol. 55, no. 1, pp. 326-329.
<https://doi.org/10.1016/j.polymer.2013.07.035>

Digital Object Identifier (DOI):

[10.1016/j.polymer.2013.07.035](https://doi.org/10.1016/j.polymer.2013.07.035)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Polymer

Publisher Rights Statement:

Copyright © 2013 Elsevier Ltd. All rights reserved. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the publisher.

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

This is the peer-reviewed author's version of a work that was accepted for publication in *Polymer*. Changes resulting from the publishing process, such as editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version is available at: <http://dx.doi.org/10.1016/j.polymer.2013.07.035>

Cite as:

Vile, J., Carta, M., Bezzu, C. G., Kariuki, B. M., & McKeown, N. B. (2014). Centrotriindane- and triptindane-based polymers of intrinsic microporosity. *Polymer (United Kingdom)*, 55(1), 326-329.

Manuscript received: 13.06.2013; Accepted: 12.07.2013; Article published: 01.08.2013

Centrotriindane- and triptindane-based polymers of intrinsic microporosity**

James Vile, Mariolino Carta, C. Grazia Bezzu, Benson M. Kariuki and Neil B. McKeown*

^[1]School of Chemistry, Cardiff University, Cardiff, UK

^[*]Current address: EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3FJ, UK; e-mail: neil.mckeown@ed.ac.uk

^[**]We acknowledge funding from EPSRC grants EP/G01244X (MC) and EP/H024034/1 (CGB) and thank the EPSRC National Solid State NMR Research Service (Durham University).

Supporting information:

Supplementary information including, synthetic procedures, physical methodology, crystallographic data and ¹³C solid state NMR spectra, can be found at <http://dx.doi.org/10.1016/j.polymer.2013.07.035>

Graphical abstract:

Keywords:

Intrinsic microporosity; Triptycene; Network polymers

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Centrotriindane- and triptindane-based polymers of intrinsic microporosity.

James Vile, Mariolino Carta, C. Grazia Bezzu, Benson M. Kariuki and Neil B. McKeown*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Hydroxyl containing Bowl-shaped “centrotriindane” and propellane-type “triptindane” derivatives, containing peripheral hydroxyl groups, are successful monomers for the preparation of network and non-network polymers of intrinsic microporosity (PIMs). Nitrogen adsorption measurements reveal apparent BET surface areas in the range of 555–1039 m² g⁻¹ which can be related to the distinct shape of the monomeric units.

Introduction

Recently, considerable efforts have been made in the synthesis of novel microporous materials which possess high internal surface areas and therefore can have applications in technologies such as hydrogen storage,³⁻⁴ CO₂ capture⁵⁻⁶ and gas separations.⁷⁻⁸ Typical examples include metal-organic frameworks (MOFs),⁹⁻¹⁰ zeolites¹¹⁻¹² and activated carbons.¹³⁻¹⁴ Increasingly, polymeric microporous materials built from purely organic components such as hypercrosslinked polymer networks,¹⁵⁻¹⁶ covalent-organic-frameworks (COFs)[REF] and polymers of intrinsic microporosity (PIMs) have attracted much interest.¹⁷ Generally, polymers lack microporosity because they have enough conformational and rotational freedom to pack space efficiently. However, PIMs are composed of highly rigid and contorted macromolecules which cannot pack space efficiently, leaving molecular sized interconnected voids.¹⁸ The rigidity is caused by the polymers being composed of fused ring units and the contorted structures arises from the incorporation of non-planar sites of contortion such as spiro-centres¹⁹ or triptycene units.²⁰ PIMs have attracted interest for applications in hydrogen storage,² membrane-based gas separations,⁷⁻⁸ sensors²¹ and

heterogeneous catalysis.²² An attractive feature is that their structure and properties can be tailored by the appropriate choice of monomer precursors. In the past we have shown that concave shaped monomers such as cyclotricatechylene (CTC)² or hydroxylated tribenzotriquinacenes (TBTQ)¹ and propeller-shaped triptycenes are suitable structural units for the preparation of PIMs by reaction with 2,3,5,6-tetrafluoroterephthalonitrile (Figure 1).

In order to investigate how further changes in the structure can affect the properties of PIMs, our attention was drawn to the recent work of Kuck and coworkers²⁵ in which they describe the synthesis of the C₂-symmetrical 2,3,6,7,10,11-hexamethoxy-4b,8b,13,14-tetrahydrodiindeno[1,2-*a*:2',1'-*b*]indene the hydrocarbon core of which was termed “centrotriindane” and the C_{3v}-symmetrical 2,3,6,7,13,14-hexamethoxytriptindane the core of which was called “triptindane”. These rigid structural units appeared attractive for the synthesis of novel PIMs. Here we describe the synthesis of both propellane-type “triptindane” and “centrotriindane” monomers **C1**, **C2** and **C3** containing peripheral hydroxyl substituents, and their subsequent polymerisation with 2,3,5,6-tetrafluoroterephthalonitrile to give the network polymer **POL-A** and the non-network polymers **POL-B** and **POL-C** (Figure 2).

Figure 1. The structures of (a) the TBTQ1 network polymers and (b) the TBTQ non-network polymers.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Figure 2. The structure of propellane-type “triptindane” polymers **POL-A** and **POL-B** and the “centrotriindane” ladder polymer **POL-C**.

Experimental

Full experimental details for the multi-step synthesis of monomers **C1** - **C3** and **POL A** - **C** are given in the supplemental information along with solid state NMR spectra and nitrogen isotherms of the polymers.

Results and discussion

1. Synthesis

The original preparations of 2,3,6,7,10,11-hexamethoxy-4b,8b,13,14-tetrahydroindeno[1,2-*a*:2',1'-*b*]indene and 2,3,6,7,13,14-hexamethoxytriptindane reported by Kuck *et al.*²⁵ were modified to give monomers **C1**-**C3** suitable for forming network polymer **POL-A** and non-network polymers **POL-B** and **POL-C** (Scheme 2). The key intermediates used for preparing monomers **C1** – **C3** are the diketones **X** and **X**, which could be prepared directly in low yield by a two-fold benzylation of 5,6-dimethoxy-1H-indene-1,3(2H)-dione (**X** R = OMe) or the commercial available 1H-indene-1,3(2H)-dione (**X** R = H), respectively, using 3,4-dimethoxybenzyl bromide. However, better overall yields of diketones **X** and **X** were obtained using a multi-step synthetic procedure starting with the condensation between veratraldehyde and the diketones **X** and **X**, followed by reduction of the resulting benzylidenes and then a single benzylation using 3,4-dimethoxybenzyl chloride. Direct bicyclization of the resulting bis-ketones **8** and **9** with orthophosphoric acid in refluxing toluene gave the hexa- and

tetramethoxy-substituted triptindanones **10** and **11** in good yield. Reduction of triptindanones **10** and **11** was achieved by ionic hydrogenation using sodium borohydride in trifluoroacetic acid to form the desired hexa- and tetramethoxy “triptindanes” **12** and **13**. Demethylation of **12** and **13** with BBr₃ was successful and yielded the desired novel monomers **C1** and **C2**.

To gain access to the desired centrotriindane monomers, bis-ketones **8** and **9** were reduced with diisobutylaluminium hydride (DIBAL-H) to give **14** and **15** in quantitative yields (Scheme 2). Cyclization of **14** and **15** were performed readily in Eaton's reagent,²⁶ to provide a good yield of **16** and **17**. Demethylation of **17** with BBr₃ afforded the target novel monomer **C3**, whereas, demethylation of **16** produced an unstable compound, so, unfortunately, its isolation and its use as a PIM precursor proved impossible.

To assess the structural characteristics of these monomers, crystals suitable for XRD analysis of monomer **C1** and **C3** were grown by slow diffusion of hexane into THF solutions of the monomers. Their solid state molecular structures are shown in Figure 3. Both crystals are clathrates, with THF found as included solvent, a typical feature of catechol-containing molecules²⁷ (in Figure 3 the included THF is omitted for clarity). It is worth noticing that crystal structures of similar molecules are very rare in the Cambridge Structural Database (CSD). These new monomers appear significantly different from previously reported TBTQ¹ and CTC² structures. In fact, in the “triptindane” **C1** (Figure 3 a) the hydroxo groups of the catechol lay in an

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Scheme 2. Reagents and conditions. i. orthophosphoric acid, toluene, 125 °C, 16 h. ii. NaBH₄, DCM, trifluoroacetic acid, 48 h. iii. BBr₃, DCM, 0 °C 12–16 h. iv. K₂CO₃, DMF, 80 °C, 16 h. v. K₂CO₃, DMF, 65 °C, 96 h. vi. DIBAL-H, DCM, 4–16 h, 0 °C. vii. Eaton's reagent, 2–3 h, RT. iii. BBr₃, DCM, 4–12 h, 0 °C.

almost perpendicular direction compared to the plane of the "bowl", whereas in the TBTQ (Figure 3 c) they are disposed along the same plane. This will give a completely different polymerization pattern, making the "triptindane" monomer much more similar to a proper triptycene. The "centrotriindane" **C3**, instead, seems representing a sort of compromise between the two (Figure 3 b).

Polymerisation of monomer **C1**, **C2** and **C3** with the commercially available 2,3,5,6-tetrafluoroterephthalonitrile, by a nucleophilic aromatic substitution reaction commonly used for

PIM synthesis, gave **POL-A**, **POL-B** and **POL-C** (Figure 2). Despite **POL-B** and **POL-C** possessing non-network structures, all three polymers proved to be insoluble in all solvents tested, which precluded characterisation techniques such as Gel Permeation Chromatography (GPC) and solution based NMR. However, characterisation was achieved by use of solid state ¹³C NMR which gave spectra consistent with the ideal structures of the polymer (see ESI for spectra).

Figure 3. Single crystal XRD data of monomer **C1** (a) and **C3** (b) and the TBTQ1 (c).

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

2. Microporosity

Nitrogen adsorption measurements at 77K of powdered samples of POL A - C confirmed their microporosity by demonstrating significant adsorption at low relative pressures (see ESI for isotherms). The apparent BET surface areas and pore volumes of the polymers are shown in Table 1 along with those of the related TBTQ¹ and CTC² PIMs. (Trip-PIM??)

Table 1. Summary of polymer properties.

Monomer	Polymer	BET surface area (m ² g ⁻¹)	Pore volume (ml g ⁻¹) ^a
C1	POL-A	1039	0.79
C2	POL-B	653	0.46
C3	POL-C	555	0.43
n/a	CTC-network-PIM 2	830	0.39
n/a	TBTQ-PIM-11	565	0.36
n/a	TBTQ-PIM-21	673	0.41
n/a	TBTQ-PIM-31	511	0.37
n/a	TBTQ-PIM-41	568	0.37

^aCalculated from amount of nitrogen adsorbed at 77K and relative pressure P/P₀ = 0.98)

The network polymer **POL-A** which is derived from the “triptindane” structural unit demonstrates greater microporosity than the non-network polymer **POL-B** which is derived from the same structural unit. This is in agreement with previous research¹ which suggests that a network rather than a non-network structure favours porosity. **POL-A** demonstrates also greater microporosity than the CTC-network-PIM² and all of the previously reported TBTQ PIMs.¹ This suggests that the “triptindane” structural unit is more rigid than TBTQ and CTC and packs less efficiently, making it more suitable for forming microporous materials. It is notable that the surface area of PIM-triptindane is between that of bowl-shaped PIM-CTC (830 m² g⁻¹) and trigonal-planar PIM-trip (1300 m² g⁻¹). In addition, it is possible to predict from the crystal structure of C2 (Figure 3a) that the shape of the developing polymer network more closely resemble that of PIM-trip than PIM-CTC with the monomer promoting the formation of a more regular networked structure during polymerisation.

Conclusions

Novel “centrotriindane” and “triptindane” monomers were successfully synthesised, their structural units were incorporated into polymers and these materials demonstrated microporosity. The network “triptindane” polymer (**POL-A**) had a BET surface area of 1039 m² g⁻¹, which was significantly higher than the previously reported CTC-network-PIM² and TBTQ PIMs,¹ which suggests that the rigid and contorted “triptindane” structural unit frustrates packing in the solid state and leads to enhanced microporosity relative to CTC and TBTQ. The synthetic route used did allow the formation of tetrahydroxylated monomers useful for the synthesis of non-network polymers

(**POL-B** and **POL-C**) which unfortunately proved to be insoluble in all tested solvents. Unfortunately, the hexahydroxylated “centrotriindane” monomer **18** was highly prone to oxidation, making it unsuitable for forming PIMs. The microporosity and solubility of the non-network polymer **POL-C** is comparable to that of the non-network TBTQ polymers which suggests than no benefit is gained from using the “centrotriindane” structural unit.

More recently we have reported the synthesis of a new series of concave shape monomers based on the Four novel TBTQ monomers suitable for forming both network and non-network PIMs were prepared and polymerized. They showed apparent BET surface areas ranging from 511 – 673 m² g⁻¹. The microporosity of the TBTQ polymers is believed to arise from the highly rigid bowl-shape of their monomer units.¹ Despite their high surface areas, all of the TBTQ polymers failed to match the microporosity of the similarly shaped CTC-network-PIM.² This observation was rationalized analysing the single crystal XRD patterns of the respective monomers²³⁻²⁴ which showed that, in all cases, the TBTQ unit was less concave relative to CTC, as demonstrated by the greater angle between the neighbouring benzene rings.

Acknowledgements

We acknowledge funding from EPSRC grants EP/G01244X (MC) and EP/H024034/1 (CGB) and thank the EPSRC National Solid State NMR Research Service (Durham University).

Notes and references

School of Chemistry, Cardiff University, Cardiff, UK. E-mail: mckeownnb@cardiff.ac.uk; Tel: +44 2920 875850

† Electronic supplementary information (ESI) available: Synthetic procedures, physical methodology, nitrogen isotherms and ¹³C solid state NMR spectra. For ESI see DOI: 10.1039/c0xx00000x

1. J. Vile, M. Carta, C. G. Bezzu and N. B. McKeown, *Polym. Chem.*, 2011, **2**, 2257-2260.
2. N. B. McKeown, B. Gahnem, K. J. Msayib, P. M. Budd, C. E. Tattershall, K. Mahmood, S. Tan, D. Book, H. W. Langmi and A. Walton, *Angew. Chem.*, 2006, **118**, 1836-1839.
3. L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294-1314.
4. L. L. Zhang, T. Lin, X. Pan, W. Wang and T.-X. Liu, *J. Mater. Chem.*, 2012, **22**, 9861-9869.
5. S. Ren, M. J. Bojdys, R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Adv. Mater.*, 2012, **24**, 2357-2361.
6. Q. Chen, M. Luo, P. Hammershoej, D. Zhou, Y. Han, B. W. Laursen, C.-G. Yan and B.-H. Han, *J. Am. Chem. Soc.*, 2012, **134**, 6084-6087.
7. D. Fritsch, G. Bengtson, M. Carta and N. B. McKeown, *Macromol. Chem. Phys.*, 2011, **212**, 1137-1146.
8. C. G. Bezzu, M. Carta, A. Tonkins, J. C. Jansen, P. Bernardo, F. Bazzarelli and N. B. McKeown, *Adv. Mater.*, Ahead of Print.

-
9. D. Laessig, J. Lincke, J. Moellmer, C. Reichenbach, A. Moeller, R. Glaeser, G. Kalies, K. A. Cychosz, M. Thommes, R. Staudt and H. Krautscheid, *Angew. Chem., Int. Ed.*, 2011, **50**, 10344-10348.
10. L. T. L. Nguyen, K. K. A. Le, H. X. Truong and N. T. S. Phan, *Catal. Sci. Technol.*, 2012, **2**, 521-528.
11. A. Corma, M. J. Diaz-Cabanas, J. Martinez-Triguero, F. Rey and J. Rius, *Nature* 2002, **418**, 514-517.
12. E. Alvarez-Ayuso, A. Garcia-Sanchez and X. Querol, *Water Res.*, 2003, **37**, 4855-4862.
13. M. Jorda-Beneyto, F. Suarez-Garcia, D. Lozano-Castello, D. Cazorla-Amoros and A. Linares-Solano, *Carbon*, 2007, **45**, 293-303.
14. W. Xing, C. Liu, Z. Zhou, L. Zhang, J. Zhou, S. Zhuo, Z. Yan, H. Gao, G. Wang and S. Z. Qiao, *Energy Environ. Sci.*, 2012, **5**, 7323-7327.
15. R. Dawson, E. Stockel, J. R. Holst, D. J. Adams and A. I. Cooper, *Energy Environ. Sci.*, 2011, **4**, 4239-4245.
16. B. Li, F. Su, H.-K. Luo, L. Liang and B. Tan, *Microporous Mesoporous Mater.*, 2010, **138**, 207-214.
17. E. Preis, C. Widling, U. Scherf, S. Patil, G. Brunklaus, J. Schmidt and A. Thomas, *Polym. Chem.*, 2011, **2**, 2186-2189.
18. N. B. McKeown and P. M. Budd, *Macromolecules*, 2010, **43**, 5163-5176.
19. M. Carta, K. J. Msayib and N. B. McKeown, *Tetrahedron Lett.*, 2009, **50**, 5954-5957.
20. M. Hashem, C. G. Bezzu, B. M. Kariuki and N. B. McKeown, *Polym. Chem.*, 2011, **2**, 2190-2192.
21. Y. Wang, N. B. McKeown, K. J. Msayib, G. A. Turnbull and I. D. W. Samuel, *Sensors*, 2011, **11**, 2478-2487.
22. H. J. Mackintosh, P. M. Budd and N. B. McKeown, *J. Mater. Chem.*, 2008, **18**, 573-578.
23. J. A. Hyatt, E. N. Duesler, D. Y. Curtin and I. C. Paul, *J. Org. Chem.*, 1980, **45**, 5074-5079.
24. M. Harig, B. Neumann, H.-G. Stammer and D. Kuck, *Eur. J. Org. Chem.*, 2004, 2381-2397.
25. M. Harig and D. Kuck, *Eur. J. Org. Chem.*, 2006, **2006**, 1647-1655.
26. P. E. Eaton, G. R. Carlson and J. T. Lee, *J. Org. Chem.*, 1973, **38**, 4071-4073.
27. J. A. Bjork, M. L. Brostrom and D. R. Whitcomb, *J. Chem. Crystallogr.*, 1997, **27**, 223-230.