Polymer 55 (2014) 326-329

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Centrotriindane- and triptindane-based polymers of intrinsic microporosity

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

School of Chemistry, Cardiff University, Cardiff, UK

A R T I C L E I N F O

Article history: Received 13 June 2013 Accepted 12 July 2013 Available online 2 August 2013

Keywords: Intrinsic microporosity Triptycene Network polymers

1. 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 [1,2], CO₂ capture [3,4] and gas separations [5–7]. Typical examples include metal-organic frameworks (MOFs) [8,9], zeolites [10,11] and activated carbons [12,13]. Increasingly, polymeric microporous materials built from purely organic components such as hypercrosslinked polymer networks, covalent-organic-frameworks (COFs) [14] and polymers of intrinsic microporosity (PIMs) have attracted much interest [15]. 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 [16]. 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-centres [17] or triptycene units [18]. PIMs have attracted interest for applications in hydrogen storage [19] membrane-based gas separations [6,7], sensors [20] and heterogeneous catalysis [21]. An attractive feature is that their structure and properties can be tailored by the appropriate choice of monomer precursors. Previously we have shown that concave shaped monomers such as cyclotricatechylene (CTC) [19] or

ABSTRACT

In this paper we describe the synthesis and physical characterisation of polymers derived from hydroxyl containing bowl-shaped "centrotriindane" and propellane-type "triptindane" monomers using the dibenzodioxin-forming polymerisation reaction with 2,3,5,6-tetrafluoroterephthalonitrile. Evaluation of the microporosity of the resulting polymers via nitrogen adsorption measurements revealed apparent Brunauer-Emmett-Teller (BET) surface areas in the range of 555–1039 m² g⁻¹ which can be related to the distinct shape of the monomeric units. An evaluation of the shape of the monomers, using X-ray crystallography, helps to explain the degree of microporosity of the polymers from which they are made. © 2013 Elsevier Ltd. All rights reserved.

hydroxylated tribenzotriquinacenes (TBTQ) [22] and propellershaped triptycenes [23] are suitable structural units for the preparation of PIMs by reaction with 2,3,5,6-tetrafluoroterep hthalonitrile (Fig. 1).

In order to investigate how further changes in the monomer structure can affect the properties of PIMs, our attention was drawn to the recent work of Kuck and co-workers [24] in which they describe the synthesis of the C2-symmetrical 2,3,6,7,10,11hexamethoxy-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 propellane-type "triptindane" monomers M1, M2 and "centrotriindane" monomer M3 all of which contain the required peripheral hydroxyl substituents, and their subsequent polymerisation with 2,3,5,6-tetrafluoroterephthalonitrile to give the network polymer Triptindane-PIM A and the nonnetwork polymers Triptindane-PIM B and Centrotriindane-PIM (Fig. 2).

2. Experimental

Full experimental details for the multi-step synthesis of monomers and polymers are given in the Supplemental information along with ¹³C solid-state NMR spectra. Crystallographic data for **M1** and **M3** are also summarised and full data for these compounds are available on request from the Cambridge Crystallographic Data centre (CCDC 868321 and 868322).







^{*} Corresponding author. Tel.: +44 2920 875850. *E-mail address:* mckeownnb@cardiff.ac.uk (N.B. McKeown).

^{0032-3861/\$ –} see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2013.07.035



Fig. 1. The structures of network PIMs (a) TBTQ [22] (b) CTC [19] and (c) Triptycene [23].

3. Results and discussion

3.1. Monomer synthesis and structural characterisation

The previous syntheses of 2,3,6,7,10,11-hexamethoxy-4b,8b,13,14-tetrahydrodiindeno[1,2-a:2',1'-b]indene and 2,3,6, 7.13.14-hexamethoxytriptindane reported by Kuck et al. [24] were modified to give hexahydroxy monomer M1 suitable for forming network polymer **Triptindane-PIM A** and tetrahydroxy monomers M2 and M3 precursors for the non-network polymers Triptindane-PIM B and Centrotriindane-PIM, respectively (Scheme 1). The key intermediates used for preparing monomers M1–M3 are the bis-ketones 1 and 2, the synthesis of which are described in detail in the Supplemental information (see Scheme SI.1) Briefly, the bis-ketones 1 and 2 were prepared directly, albeit in low yield, by a two-fold benzylation of 5,6-dimethoxy-1H-indene-1,3(2H)-dione or the commercial available 1Hindene-1,3(2H)-dione, respectively, using 3,4-dimethoxybenzyl. Alternatively, better overall yields of bisketones 1 and 2 were obtained using a multi-step synthetic procedure starting with the Aldol condensation between veratraldehyde and the appropriate diones followed by reduction of the resulting benzylidenes and then a single benzylation using 3,4-dimethoxybenzyl chloride. Direct bicyclization of the resulting bis-ketones 1 and 2 with orthophosphoric acid in refluxing toluene gave the hexa- and tetramethoxy-substituted triptindanones 3 and 4. Reduction of triptindanones **3** and **4** was achieved by ionic hydrogenation using sodium borohydride in trifluoroacetic acid to form the desired hexa- and tetramethoxy "triptindanes" 5 and 6. Demethylation of 5 and 6 with BBr₃ was successful and yielded the desired novel monomers M1 and M2.

To gain access to the desired centrotriindane monomers, bisketones **1** and **2** were reduced with diisobutylaluminium hydride (DIBAL-H) to give **7** and **8** in quantitative yields (Scheme 1). Cyclization reactions of the resulting diols **7** and **8** were performed readily in Eaton's reagent [25], to provide a good yield of centrotriindanes **9** and **10**. Demethylation of **10** with BBr₃ afforded the target novel monomer **M3**, whereas, demethylation of **9** produced an unstable compound prone to oxidation, so unfortunately, the isolation of the desired monomer hexahydroxy-centrotriindane and its use as a PIM precursor proved impossible.

To fully characterise the structure of these monomers, crystals suitable for XRD analysis of monomer M1 and M3 were grown by slow diffusion of hexane into THF solutions. Their solid-state molecular structures are shown in Fig. 3(a and b). Both crystals proved to be clathrates, with THF found as the included solvent (in Fig. 3 the included THF is omitted for clarity). Clathrate formation is a typical feature of catechol-containing monomers that prove suitable for PIM synthesis, presumably due to their awkward shapes that cannot form crystals with efficient molecular packing without the incorporation of solvent molecules [26]. The structures of these new monomers are significantly different from those of TBTQ [22] and CTC [19] structures (Fig. 3). For the "triptindane" M1 (Fig. 3a), the aromatic planes of the catechol units are parallel to the threefold molecular axis, as they are in triptycene (Fig. 3d) [27], whereas in the bowl-shaped TBTQ monomer they are at an angle of roughly 120° to the three-fold axis (Fig. 3c). For the "centrotriindane" M3, the planes of the catechol units are approximately perpendicular to each other as they are on opposites side of the spirocentre.

3.2. Polymer synthesis and characterisation

Polymerisation of monomers **M1**, **M2** and **M3** with the commercially available 2,3,5,6-tetrafluoroterephthalonitrile, by a nucleophilic aromatic substitution reaction commonly used for PIM synthesis [19,23], gave **Triptindane-PIM A** and the non-network polymers **Triptindane-PIM B** and **Centrotriindane-PIM** (Fig. 2)



Fig. 2. The structure of propellane-type "triptindane" and "centrotriindane" polymers.



Scheme 1. 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.

in good yields. Despite the anticipated lack of a network structure for **Triptindane-PIM B** and **Centrotriindane-PIM**, all three polymers proved to be insoluble in all solvents tested, which precluded solution-based 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 SI for spectra). Thermogravimetric analysis of the three polymers shows that they all demonstrate excellent thermal stability with no mass loss below 350 °C.

Nitrogen adsorption measurements at 77 K (Fig. 4) of powdered samples of the polymer derived from **M1–M3** confirmed their



Fig. 3. Single crystal XRD data of monomer M1 (a) and M3 (b), TBTQ [22] (c) and Triptycene (d) [27].



Fig. 4. Nitrogen adsorption isotherms of Triptindane-PIM A (♦), Triptindane-PIM B (■) and Centrotriindane-PIM (▲) measured at 77 K. Desorption isotherms are shown in gray.

Table 1

Summary of polymer properties.

Monomer	Polymer	BET surface area $(m^2 g^{-1})$	Pore volume $(ml g^{-1})^a$
M1	Triptindane-PIM A	1039	0.79
M2	Triptindane-PIM B	653	0.46
M3	Centrotriindane-PIM	555	0.43
n/a	CTC-PIM [19]	830	0.39
n/a	TBTQ-PIM-1 [22]	565	0.36
n/a	TBTQ-PIM-3 [22]	511	0.37
n/a	Tript-PIM [23]	1318	0.89

^a Calculated from amount of nitrogen adsorbed at 77 K and relative pressure $P/P_0 = 0.9814$.

microporosity by demonstrating significant adsorption at low relative pressures. The apparent BET surface areas and pore volumes of the polymers calculated from these isotherms are shown in Table 1 along with those of the related PIM networks based on TBTQ [22], CTC [19] and triptycene units [23].

The network polymer Triptindane-PIM A, demonstrates greater microporosity, both in terms of apparent BET surface area and pore volume, than the non-network polymer Triptindane-PIM B. This finding is consistent with previous observations that polymer networks are more efficient at generating intrinsic microporosity as compared to non-network polymers assembled using the same structural units [16,22]. In addition, Triptindane-PIM A demonstrates greater microporosity than the related network PIMs derived from tri-catechol components such as CTC [19] and TBTQ [22] but less than that from triptycene [23] (Fig. 1). It is possible to predict from the molecular structure of monomer M1 (Fig. 3a), as characterised by single crystal X-ray diffraction analysis, that the shape of the developing polymer network would more closely resemble that of Tript-PIM than CTC-PIM. In contrast, consideration of the structure of monomer M3 (Fig. 2) suggests that the Centrotriindane-PIM would form almost linear chains with the microporosity presumably resulting from the rigid aromatic ring protruding from the chains blocking efficient packing.

4. Conclusions

Microporous polymers were prepared from novel "centrotriindane" and "triptindane" monomers. The network "triptindane" polymer (**Triptindane-PIM A**) has a large apparent BET surface area of 1039 m² g⁻¹, which suggests that the rigid and contorted "triptindane" structural unit frustrates packing in the solid state and leads to enhanced microporosity similar to that of the structurally related triptycene unit. By appropriate modifications of the established synthetic route, tetrahydroxylated monomers of "centrotriindane" and "triptindane" were prepared that proved successful for the synthesis of non-network PIMs (**Triptindane-PIM B** and **Centrotriindane-PIM**) but, unfortunately, these proved to be insoluble in all solvents. The microporosity and insolubility of the non-network polymer **Centrotriindane-PIM** is comparable to that of the related TBTQ polymers. A network polymer based on "centroindane" could not be prepared due to the extreme instability of its hexahydroxy precursor.

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).

Appendix A. Supplementary information

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.07.035.

References

- [1] Murray LJ, Dinca M, Long JR. Chem Soc Rev 2009;38(5):1294-314.
- [2] Zhang LL, Lin T, Pan X, Wang W, Liu T-X. J Mater Chem 2012;22(19):9861-9.
 [3] Ren S, Bojdys MJ, Dawson R, Laybourn A, Khimyak YZ, Adams DJ, et al. Adv Mater 2012;24(17):2357-61.
- [4] Chen Q, Luo M, Hammershoej P, Zhou D, Han Y, Laursen BW, et al. J Am Chem Soc 2012:134(14):6084–7.
- [5] Carta M, Malpass-Evans R, Croad M, Rogan Y, Jansen JC, Bernardo P, et al. Science 2013;339(6117):303-7.
- [6] Fritsch D, Bengtson G, Carta M, McKeown NB. Macromol Chem Phys 2011;212(11):1137–46.
- [7] Bezzu CG, Carta M, Tonkins A, Jansen JC, Bernardo P, Bazzarelli F, et al. Adv Mater 2012;24(44):5930-3.
- [8] Laessig D, Lincke J, Moellmer J, Reichenbach C, Moeller A, Glaeser R, et al. Angew Chem Int Ed 2011;50(44):10344–8.
- [9] Nguyen LTL, Le KKA, Truong HX, Phan NTS. Catal Sci Technol 2012;2(3): 521-8.
- [10] Corma A, Diaz-Cabanas MJ, Martinez-Triguero J, Rey F, Rius J. Nature 2002;418(6897):514-7.
- [11] Alvarez-Ayuso E, Garcia-Sanchez A, Querol X. Water Res 2003;37(20): 4855–62.
- [12] Jorda-Beneyto M, Suarez-Garcia F, Lozano-Castello D, Cazorla-Amoros D, Linares-Solano A. Carbon 2007;45(2):293–303.
- [13] Xing W, Liu C, Zhou Z, Zhang L, Zhou J, Zhuo S, et al. Energy Environ Sci 2012;5(6):7323-7.
- [14] Ding S-Y, Wang W. Chem Soc Rev 2013;42(2):548-68.
- [15] Preis E, Widling C, Scherf U, Patil S, Brunklaus G, Schmidt J, et al. Polym Chem 2011;2(10):2186–9.
- [16] McKeown NB, Budd PM. Macromolecules 2010;43(12):5163-76.
- [17] Carta M, Msayib KJ, McKeown NB. Tetrahedron Lett 2009;50(43):5954-7.
 [18] Hashem M, Bezzu CG, Kariuki BM, McKeown NB. Polym Chem 2011;2(10):
- 2190–2.
- [19] McKeown NB, Gahnem B, Msayib KJ, Budd PM, Tattershall CE, Mahmood K, et al. Angew Chem 2006;118(11):1836–9.
- [20] Wang Y, McKeown NB, Msayib KJ, Turnbull GA, Samuel IDW. Sensors 2011;11(3):2478–87.
- [21] Mackintosh HJ, Budd PM, McKeown NB. J Mater Chem 2008;18(5):573-8.
- [22] Vile J, Carta M, Bezzu CG, McKeown NB. Polym Chem 2011;2(10):2257–60.
 [23] Ghanem BS, Hashem M, Harris KDM, Msayib KJ, Xu M, Budd PM, et al. Macromolecules 2010;43(12):5287–94.
- [24] Harig M, Kuck D. Eur J Org Chem 2006;2006(7):1647–55.
- [25] Eaton PE, Carlson GR, Lee JT. J Org Chem 1973;38(23):4071–3.
- [26] Bjork JA, Brostrom ML, Whitcomb DR. J Chem Crystallogr 1997;27(4): 223-30.
- [27] Anzenhofer K, De Boer JJZ. Kristallogr Kristallgeometrie Kristallphys Kristallchem 1970;131(1–2):103–13.