Polymers of Intrinsic Microporosity derived from a carbocyclic analogue of Troger’s base

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a b s t r a c t
Troger’s base (TB) is often used as a building block for the synthesis of Polymers of Intrinsic Microporosity (PIMs) due to its rigid bicyclic V-shaped structure. In this study the TB component in the structure of a PIM is replaced by 2,3:6,7-dibenzobicyclo[3.3.1]nonane, a purely carbocyclic analogue of TB. This modification results in only a slightly reduced amount of microporosity as determined using nitrogen adsorption. Further comparisons with previously reported PIMs indicate that this building unit (and therefore TB) is significantly less effective for the generation of intrinsic microporosity than spirobisindane, a commonly used structural unit for PIM synthesis. It appears that the V-shape of the 2,3:6,7-dibenzobicyclo[3.3.1]nonane and TB units allows closer contact between polymer chains thereby enhancing packing efficiency.

1. Introduction

Over recent years there has been increasing interest in the preparation of new microporous materials using organic components [1]. For example, there are a number of different types of porous organic polymers including structurally ordered Covalent-Organic-Frameworks (COFs) [2] and amorphous network poly-mers such as Hypercrosslinked Polymers (HCPs) [3], Microporous Conjugated Polymers (MCPs) [4] and Porous Aromatic Frameworks (PAFs) [5]. Polymers of Intrinsic Microporosity (PIMs) differ in that they do not possess a network structure and, hence, are often so-lution processable materials [6]. PIMs generate porosity from their rigid and contorted macromolecular chains that do not pack effi-ciently in the solid state [7,8]. The solubility of PIMs allows them to be processed into self-standing films and coatings and, therefore, they are suitable for making devices such as sensors [9,10] or for the fabrication of polymer membranes, particularly for gas separations [11]. It is well established that increasing the rigidity of polymers used for gas separation membranes enhances their selectivity for one gas over another [12]. This prompted the recent development of PIMs derived from highly rigid bridged bicyclic structural units such as triptycene [13e16], ethanoanthracene [17] and the amine-based bicyclic system 6H, 12H-5,11-methanodibenzo[b,f][1,5]diazocine [17], which is more commonly known as Troger’s base (TB). The V-shaped TB unit is used in numerous applications including making components for supramolecular chemistry [18]. TB has been introduced into PIMs both by using polymerisation reactions that incorporate monomers that are TB derivatives, such as diamines suitable for PIM-polyimide synthesis [19e26], or by using TB formation as the polymerisation reaction [12,14,16,27e29]. The resulting TB-based PIMs have demonstrated excellent potential as gas separation membranes with high permeability and good selectivity for one gas over another, for which the latter can be partially attributed to the rigidity of TB.

Therefore, it is of interest to determine the structural contri-bution to the generation of intrinsic microporosity by the TB unit. With this objective, we report the synthesis of monomers and PIMs based on a purely hydrocarbon analogue of the TB unit i.e. 2,3:6,7-dibenzobicyclo[3.3.1]nonane [30e32]. Comparisons are made between these polymers, structurally related TB PIMs [21], and the more typical spirobisindane PIMs that have been described previously [33].
2. Experimental

2.1. Materials and methods

Commercially available reagents were used without further purification. Anhydrous dichloromethane was obtained by distillation over calcium hydride under a nitrogen atmosphere. Anhydrous N,N-dimethylformamide was bought from Aldrich. All reactions using air/moisture sensitive reagents were performed in oven-dried or flame-dried apparatus, under a nitrogen atmosphere. Flash chromatography was performed on silica gel 60A (35-70 flm) chromatography grade (Fisher Scientific). Melting points were recorded using a Gallenkamp Melting Point Apparatus and are uncorrected. Infrared spectra were recorded in the range 4000-600 cm⁻¹ using a Perkin-Elmer 1600 series FTIR instrument either as a thin film or as a nujol mull between sodium chloride plates. The positions of absorption bands are quoted in cm⁻¹. ¹H NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 instrument (400 MHz), with ¹³C NMR spectra recorded at 100 MHz. Chemical shifts (δH and δC) were recorded in parts per million (ppm) from tetramethylsilane (or chloroform) and are corrected to 0.00 (TMS) and 77.00 (CHCl₃), centre line, for ¹³C NMR. The abbreviations s, d, t, q, m and br. denote singlet, doublet, triplet, quartet, multiplet and broad-ended resonances; all coupling constants were recorded in Hertz (Hz). Low-resolution mass spectrometric data were obtained in electron impact ioniza-tion (EI) unless otherwise stated. High-resolution mass spectrometric data were determined using a Fisons VG Platform II quadrupole instrument using electron impact ionization (EI) unless otherwise stated. Low-resolution mass spectrometric data were determined using a Waters Q-TOF micromass spectrometer. HRMS Calc for C₁₇H₂₀O₆ 312.0634, found 312.0631. IR (DCM): 3200, 1653, 1596, 1517, 1428, 1299 cm⁻¹.

2.2. Synthetic procedures

2.2.1. General procedure for demethylation using BBr₃

Anhydrous solids were collected by suction filtration and dried under vacuum for 12 h at 30 °C to give the desired biscatechol product.

2.2.2. 2,3,8,9-Tetrahydroxy-6,12-methanodibenzo[a,e]cyclooctene-5,11(6H,12H)-dione [2]

Using the general procedure diketone 1 gave 2 (0.44 g, 80%) as a white solid, m.p. > 300 °C. ¹H NMR (400 MHz, MeOD) δ 7.27 (s, 2H), 6.76 (s, 2H), 3.65 (m, 2H), 2.87 (m, 2H). ¹³C NMR (100 MHz; MeOD) δ 197.1, 153.8, 147.6, 136.8, 122.5, 115.8, 115.2, 57.1, 35.3.

2.2.3. 5,6,11,12-Tetrahydro-2,3,8,9-tetrahydroxy-5,11-methanodibenzo[a,e]cyclooctene [3]

Using the general procedure diketone 5 gave 3 (0.4 g, 86%) as a white solid, m.p. > 300 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.56 (s, 2H), 6.31 (s, 2H), 3.05 (m, 4H), 2.54 (m, 2H), 1.98 (m, 2H). ¹³C NMR (125 MHz; MeOD) δ 144.1, 143.9, 133.4, 126.6, 116.0, 115.9, 39.8, 33.3, 26.0. HRMS Calc for C₁₇H₁₆O₄ 284.1049, found 284.1047. IR (DCM): 3386, 1630, 1520, 1266 cm⁻¹.

2.2.4. Tetracyclo[7.7.1.0³⁷.0⁹.15]heptadecane-16,9,9'-fluorene-2,3,9,9'-dione[6]

Using the general procedure diketone 6 gave 4 (0.43 g, 81%) as a light brown solid, m.p. > 300 °C. ¹H NMR (400 MHz, CDCl₃) δ 3.84 (3.2H), 8.18 (s, 2H), 7.00 (m, 16H), 5.44 (s, 2H), 5.39 (s, 2H), 2.09 (m, 2H), 2.79 (m, 2H). ¹³C NMR (100 MHz; CDCl₃) δ 156.7, 152.2, 144.2, 142.6, 140.3, 138.6, 130.8, 128.0, 127.9, 127.2, 127.1, 127.0, 125.9, 124.0, 120.0, 119.3, 119.1, 114.3, 60.0, 42.6, 25.8. HRMS Calc for C₄₁H₁₈O₄ 584.1988, found 584.1989. IR (DCM): 3523, 3046, 2914, 1612, 1516, 1443, 1267 cm⁻¹.

2.2.5. 2,3,8,9-Tetrahydroxy-6H,12H-5,11-methanodibenzo[1,5]-diazocine [7]

Using the general procedure diketone 8 gave 7 (2.57 mg, 88%). Mp > 300 °C. ¹H NMR (400 MHz; MeOD) δ 6.54 (s, 2H), 6.34 (s, 2H), 4.45 (d, 2H, 3.4 Hz), 4.21 (s, 2H), 0.89 (d, 2H, 16.5 Hz); ¹³C NMR (100 MHz; MeOD) δ 145.9, 144.0, 140.4, 139.9, 119.4, 113.6, 112.2, 111.4, 67.8, 58.9, 49.0. HRMS Calc for C₁₅H₁₅N₂O₄ 287.1032, found 287.1026.

2.2.6. 5,6,11,12-Tetrahydro-2,3,8,9-tetrahydroxy-5,11-methanodibenzo[a,e]cyclooctene [5][32]

Potassium hydroxide (3.04 g, 54.4 mmol) and ethylene glycol (75 ml) were heated to 80°C and to this mixture hydrazine mon-oxide (2.72 g, 54.4 mmol) and diketone 1 (2.50 g, 6.8 mmol) were added and the mixture was refluxed at 200°C for 16 h. The mixture was cooled to room temperature, quenched with water (200 ml) and acidified slowly with aqueous hydrochloric acid until neutral. The solid was collected by suction filtration and purified by column chromatography (hexane/EtOAc, 7:3) and recrystallized from MeOH to give the desired product (0.92 g, 40%) as a white solid, m.p. 206±208 C (209±210 C) [32]. ¹H NMR (400 MHz, CDCl₃) δ 6.68 (s, 2H), 6.44 (s, 2H), 3.86 (s, 6H), 3.77 (s, 6H), 3.17 (m, 4H), 2.72 (m, 2H), 2.07 (m, 2H). ¹³C NMR (125 MHz; CDCl₃) δ 147.7, 147.4, 133.0, 126.5, 112.0, 111.9, 56.0, 55.6, 38.9, 32.7, 29.2. HRMS Calc for C₂₁H₂₂O₄ 340.1675, found 340.1664. IR (DCM): 2907, 1609, 1514, 1464, 1355, 1258, 1216, 1125, 1033 cm⁻¹. Crystals were pre pared by slow diffusion of hexane into THF solution of monomer. Crystal size: 0.4 ± 0.02 mm, orthorhombic, space group P 2₁2₁2₁. reflections measured, 1828 unique reflections (Rint 0.0000), 1596 reflections with I > 2σI, R1 = 0.057 and wR2 = 0.01179 (observed data), R1 = 0.0706 and wR2 = 0.1127 (all data). Crystallographic data was deposited in the Cambridge Structural Database (CCDC 1529467).

2.2.7. 4,7,10,15-tetrahydroxydipyrop-[9H,9'-fluorene]-2,3,9,9'-dione[6]

In a two-necked round bottom flask was added diketone 1 (2.00 g, 5.4 mmol) and dry THF (60 ml). 2-Biphenyl magnesium bromide (5.54 g, 21.6 mmol) in dry THF (60 ml) was added slowly at...
0 C under vigorous stirring and the mixture was refluxed for 48 h. The reaction was quenched with water (150 ml) and the THF was evaporated under reduced pressure. The precipitate was filtered under suction and dried.

The crude product was stirred in Eaton’s reagent (50 ml) for 16 h, quenched carefully with water (150 ml) and extracted with DCM (2 x 150 ml). The organic layers were evaporated under reduced pressure to give the crude product. Purification by column chromatography (hexane/EtOAc) yielded 6 (1.04 g, 30%) as a white solid. Mp. 175±180 C.

2H, 16.3 Hz), 3.85 (s, 6H), 3.77 (s, 6H); 6.65 (s, 2H), 6.37 (s, 2H), 4.60 (d, 2H, J 13C NMR (100 MHz; CDCl3) δ 156.1, 152.1, 148.1, 145.8, 140.8, 139.0, 132.4, 129.4, 128.3, 127.2, 127.1, 127.0, 126.2, 124.3, 120.0, 119.4, 114.9, 110.5, 61.5, 55.6, 55.0, 43.9, 25.5.

Crystal NMR (100 MHz; CDCl3) δ 156.1, 152.1, 148.1, 145.8, 140.8, 139.0, 132.4, 129.4, 128.3, 127.2, 127.1, 127.0, 126.2, 124.3, 120.0, 119.4, 114.9, 110.5, 61.5, 55.6, 55.0, 43.9, 25.5.

CRMS Calc. for C19H23O7N2 343.1658, found 343.1669.

2.3. General procedure for polymer synthesis

In a two-necked round bottom flask was added, under inert atmosphere, equimolar amount of the bis-catechol monomer (2, 3, 4 or 5) and 2,3,5,6-tetrafluoroterephthalonitrile, were added to anhydrous dimethylformamide (25 ml per g of catechol). The mixture was heated to 65 C, until the two starting materials were completely dissolved, then dry potassium carbonate (8 equivalents) was added and the mixture kept to stirring for 96 h. The solution was quenched with water (80 ml per g of catechol), filtered and washed repeatedly with water and acetone. For the insoluble polymers P1, P2 and P4, the crude polymer was washed under reflux using solvent in the following sequence: THF, CHC3, acetone and methanol. The product was then refluxed overnight in methanol, filtered off and dried under vacuum. For soluble polymer P3, the solid was dissolved in CHC3 (15 ml per g of solid), the solution filtered through cotton wool and poured into a mixture of acetone/methanol (2/1, 40 ml/g). The product was dried and refluxed with methanol overnight, collected and dried under vacuum.

2.3.1. Polymer P1

Monomer 2 (0.503 g, 1.61 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.322 g, 1.61 mmol) and dry potassium carbonate (1.78 g, 12.90 mmol) were reacted according to the general procedure to give a yellow solid (521 mg, 75% based on the molecular weight of the repeated unit). Apparent BET surface area ¼ 437 m² g⁻¹; total pore volume ¼ 0.36 cm³ g⁻¹ estimated from nitrogen adsorption at P/0 K ¼ 0.98; TGA analysis (nitrogen): 5.51% loss of weight occurred at ~ 100 C. Initial weight loss due to thermal degradation commences at ~416 C. IR (DCM): 3200, 2250 (CN), 1653, 1596, 1517, 1348, 1299.

2.3.2. Polymer P2

Monomer 3 (0.304 g, 1.07 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.214 g, 1.07 mmol) and dry potas-sium carbonate (1.78 g, 12.90 mmol) were reacted according to the general procedure to give a yellow solid (367 mg, 85% based on the molecular weight of the repeated unit). Apparent BET surface area ¼ 437 m² g⁻¹; total pore volume ¼ 0.36 cm³ g⁻¹ estimated from nitrogen adsorption at P/0 K ¼ 0.98; TGA analysis (nitrogen): 5.51% loss of weight occurred at ~ 100 C. Initial weight loss due to thermal degradation commences at ~505 C. IR (Nujol): 2924, 2238 (CN), 1600 cm⁻¹; SS 13C NMR (100 MHz): δ ¼ 138.3, 133.9, 94.0, 67.8, 39.1, 32.3, 25.7.

2.3.3. Polymer P3

Monomer 4 (0.338 g, 0.58 mmol), 2,3,5,6-tetrafluoroterephthalonitrile (0.116 g, 0.58 mmol) and dry potas-sium carbonate (0.64 g, 4.62 mmol) were reacted according to the general procedure to give a yellow solid (0.224 g, 55% based on the molecular weight of the repeat unit). Apparent BET surface area ¼ 684 m² g⁻¹; total pore volume ¼ 0.63 cm³ g⁻¹ estimated from nitrogen adsorption at P/0 K ¼ 0.98; TGA analysis (nitrogen): 0.80% loss of weight occurred at ~ 100 C. Initial weight loss due to thermal degradation commences at ~477 C. IR (1H NMR (400 MHz, CDCl3); δ ¼ 6.66 1H, 3.82 (br m, 6H), 1.34 (br s, 6H); 13C NMR (100 MHz, CDCl3) δ 148.3, 146.1, 140.4, 118.8, 108.8, 107.9, 67.1, 57.9, 55.9; HRMS Calc. for C19H23O7N2 343.1658, found 343.1669.

3. Results and discussion

3.1. Monomer synthesis

Following the work of Ogura et al. [32], the key intermediate diketone 1 was conveniently prepared from commercially available (3,4-dimethoxyphenyl)acetoinitile in three steps in a good overall yield of 40% (Scheme 1; Supplementary Data).

Bisatechol monomers 264, which are suitable for PIM syn-thesis via polymerisation using dibenzodioxine formation, were prepared from diketone 1 as outlined in Scheme 2. Simple removal of the methyl groups from boron tribromide gave the diketone monomer 2. Wolff-Kishner reduction was successfully performed on 1 to give 5 followed by methyl group removal (BrBr1) to give bisatechol monomer 3, which contains the simplest carbocyclic analogue to the TB unit. Fused fluorene substituents were introduced by the reaction of 1 with the Grignard reagent derived from 2-bromobiphenyl to give 6, which was demethylated.
to give monomer 4.

To allow the direct comparison between a TB PIM and a PIM derived from a carbocyclic TB analogue, the biscatechol-containing TB monomer 7 was prepared using a previously reported procedure (Scheme 3) via tetramethoxy-substituted TB derivative 8 [19,21,34].

The structure of the 2,3,6,7-dibenzo[3,3.1]nonane units within the novel monomers was confirmed by growing crystals suitable for x-ray diffraction analysis from intermediates 5 and 6 and this was compared with the structure reported by Bu et al. [34] of the related tetramethoxy derivative of Troger’s base 8 (Fig. 1).

There is a clear similarity between the TB unit (Fig. 1a) and the TB analogous structures (Fig. 1b and c). For example, for 5 and 8 the angle between the two planes formed by the dimethoxy benzene moieties was found to be 88 for both structures. For monomer 6, instead, the same angle was found of 114 presumably due to the bulky fluorene substituents.

### 3.2. Polymer synthesis

Monomers 2e4 and 7 where polymerised using the typical conditions optimised previously for PIM preparation using dibenzo-dioxin formation to give polymers P1eP4, respectively (Scheme 4) [6,35]. With the exception of P3, all of the polymers proved to be insoluble in common organic solvents preventing their structural characterisation via solution-based techniques such as Gel Permeation Chromatography (GPC). In contrast, P3 is fully soluble in THF and chloroform, presumably due to the bulky fused fluorene groups enhancing solubility. Hence P3 was readily characterised by $^1$H NMR and GPC (THF), which revealed a value for $M_w$ of 10,300 g mol$^{-1}$ relative to polystyrene standards (Table 1). This modest molecular mass was insufficient for the formation of robust self-standing films.
**3.3. Analysis of microporosity**

Nitrogen adsorption isotherms obtained at 77 K from powdered samples of the polymers (Fig. 2; Supplementary Data) allowed apparent BET surface area and pore volumes to be estimated (Table 1). Isotherms from polymers P2, P3 and P4 all show significant nitrogen adsorption at low relative pressure ($P/P_0 < 0.01$), which indicates the presence of intrinsic microporosity. In contrast, polymer P1 proved non-porous, which may be attributed to the large cohesive interactions between polymer chains due to the polar ketone groups. Polymer P3 displays relatively high surface area, which suggests that the rigid, spiro-fused fluorene units increase free volume by maintaining a larger distance between polymer chains. The larger hysteresis between the nitrogen adsorption and desorption isotherms (Fig. 2; Supplemental data) suggests swelling during analysis that indicates weaker cohesion between chains, which is consistent with the solubility of Polymer P3 in organic solvents. A direct comparison of the nitrogen adsorption isotherms of the structurally related polymers P2 and P4, shows that 2,3,6,7-dibenzobicyclo[3.3.1]nonane of P2 appears to be only slightly less efficient at generating intrinsic microporosity than the TB unit of P4. In addition, previous work demonstrated that the equivalent spirobisindane-based PIMs to polymers P1 and P3, containing ketone and fused fluorene substituents, had apparent BET surface areas of 501 and 895 m$^2$ g$^{-1}$, respectively [33]. Therefore, it can be deduced that 2,3,6,7-dibenzobicyclo[3.3.1]nonane unit is significantly less efficient at inducing intrinsic microporosity than the spirobisindane unit, which is an often used component in the synthesis of PIMs.

**4. Conclusions**

Replacing the TB component in the structure of a PIM with 2,3,6,7-dibenzobicyclo[3.3.1]nonane, a purely carbocyclic analogue of TB, results in only a slightly reduced microporosity as determined using nitrogen adsorption. Indeed direct comparison with previously reported PIMs indicates that thus building unit (and therefore TB) is significantly less effective for the generation of intrinsic microporosity than spirobisindane, a common structural unit used in PIM synthesis. It appears likely that the shape of the 2,3,6,7-dibenzobicyclo[3.3.1]nonane unit allows closer contact between polymer chains thereby enhancing packing efficiency. Greater cohesive interaction between chains is apparent from the lack of solubility of the resulting polymers, although placing bulky fused fluorene substituents onto the polymer improves solubility and microporosity, presumably by increasing the distance between chains in the solid state.

![Scheme 4. Reagents and conditions. i. 2,3,5,6-tetrafluoroterephthalonitrile, K$_2$CO$_3$, DMF, 65 C, 3 days.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer</th>
<th>Solubility</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Pore Volume$^a$ (ml g$^{-1}$)</th>
<th>$M_w$</th>
<th>$PDI$</th>
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<td>P1</td>
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<td>0.15</td>
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<tr>
<td>P3</td>
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<td>0.63</td>
<td>10,300</td>
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</tr>
<tr>
<td>P4</td>
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<td>570$^b$</td>
<td>0.35</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

$^a$ Calculated from the amount of nitrogen adsorbed at 77 K and relative pressure $P/P_0 = 0.98$.

$^b$ This apparent BET surface area is in good agreement with the previously reported value of 565 m$^2$ g$^{-1}$ [21].
Acknowledgements

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References