Review Article

Polymers of Intrinsic Microporosity

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This paper focuses on polymers that demonstrate microporosity without possessing a network of covalent bonds—the so-called polymers of intrinsic microporosity (PIM). PIMs combine solution processability and microporosity with structural diversity and have proven utility for making membranes and sensors. After a historical account of the development of PIMs, their synthesis is described along with a comprehensive review of the PIMs that have been prepared to date. The important methods of characterising intrinsic microporosity, such as gas absorption, are outlined and structure-property relationships explained. Finally, the applications of PIMs as sensors and membranes for gas and vapour separations, organic nanofiltration, and pervaporation are described.

1. Introduction

The past decade has seen a revolution in the science of microporous materials, which are defined as solids that contain interconnected pores of less than 2 nm in diameter. Such materials are of general technological interest for heterogeneous catalysis, molecular separations, and gas storage [1]. In particular, there has been a rapid development of microporous materials that are prepared using organic components rather than the inorganic building blocks of conventional microporous materials such as the zeolites. These materials include the much studied crystalline metal organic frameworks (MOFs) [2–5] and purely organic but structurally similar covalent organic frameworks (COFs) [6–8]. In addition, there has been intense activity in the synthesis and study of amorphous polymer networks with a wide variety of structures such as the hyperCrosslinked polymers (HCPs) [9–12] and microporous conjugated polymers (MCPs) [13–18]. The rapid recent progress in the synthesis of microporous network polymers has been reviewed extensively [19, 20]. In contrast, this present paper will focus on polymers that do not require a network of covalent bonds in order to demonstrate microporosity—the so-called polymers of intrinsic microporosity (PIM).

Intrinsic microporosity in polymers is defined as "a continuous network of interconnected intermolecular voids, which forms as a direct consequence of the shape and rigidity of the component macromolecules" [21, 22]. In general, polymers pack space so as to maximize attractive interactions between the constituent macromolecules and, hence, minimize the amount of void space (from a molecule's point of view "empty space is wasted space") [23]. Most polymers have sufficient conformational flexibility to allow them to rearrange their shape so as to maximize intermolecular cohesive interactions and pack space efficiently. Our approach to maximizing intrinsic microporosity has been to design polymers with highly rigid and contorted molecular structures to provide "awkward" macromolecular shapes that cannot pack space efficiently. In particular due to their fused ring structures, PIMs do not possess rotational freedom along the polymer backbone, which ensures that the macromolecular components cannot rearrange their conformation, so that their highly contorted shape is fixed during synthesis. This paper will cover the origin of the early work on PIMs, their synthesis and structural characterization, properties, and potential applications.

It should be noted that several members of well-established classes of nonnetwork polymers can possess significant intrinsic microporosity as demonstrated by very fast gas permeabilities (e.g., polyacetylenes [24–26], fluorinated polymers [27–29], polynorbornanes [30, 31], and polyimides [32]), and these are exploited in the polymer membrane field where they are more commonly described as high free volume or ultrapermeable polymers [33]. However,
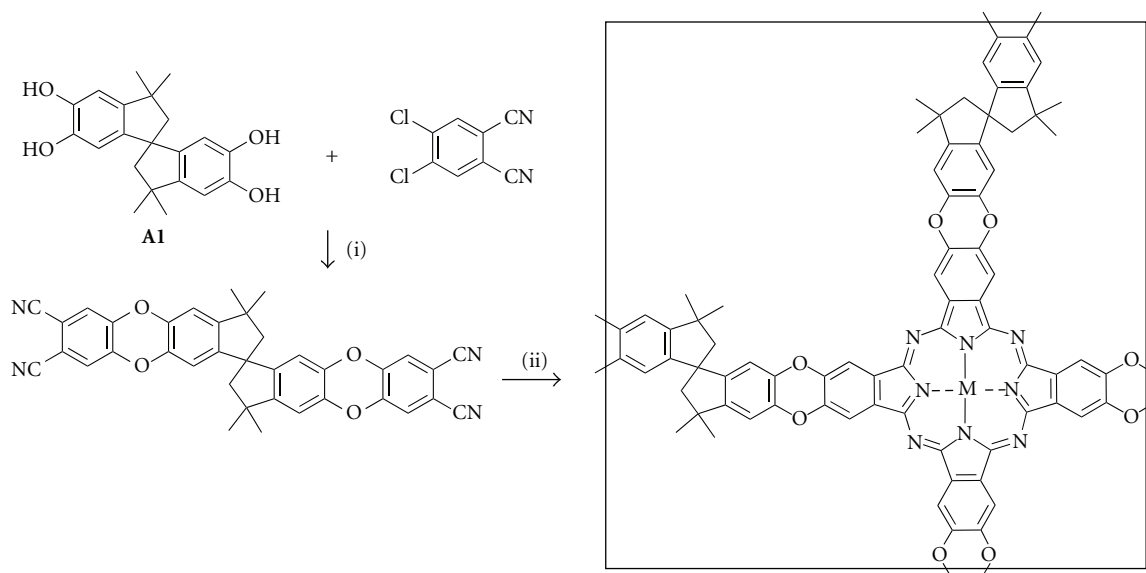
Scheme 1: The synthesis of phthalocyanine-based microporous polymer networks. Reagents and conditions. (i) 4,5-dichlorophthalonitrile, DMF, 100°C; (ii) metal cation (M) templated phthalocyanine formation at 200°C.

with the exception of some polyimides that have structural similarities to the PIMs (i.e., those termed PIM polyimides), these polymers will only be dealt with indirectly when comparisons of their properties with those of PIMs are instructive.

2. The Development of PIMs

The idea for PIMs developed from the author's work on phthalocyanine materials carried out at The University of Manchester during the 1990s. Phthalocyanines are large aromatic macrocycles related to the naturally occurring porphyrins, and metal-containing phthalocyanines can demonstrate useful catalytic activity, especially for oxidation reactions [34]. However in the solid state, the catalytic performance of phthalocyanines is hindered by the face-to-face aggregation of the macrocycles. In 1998 we designed a network polymer consisting of phthalocyanines fused together with spirocyclic groups that would produce a highly porous material in which each adjacent macrocycle would be orthogonal to its neighbor [35]. After several exploratory synthetic studies to devise a suitable polymerisation reaction that constructed the required spirocyclic framework, including the concept of using spiroketal polymerisations [36], it was found that the formation of a spirocyclic phthalocyanine network polymer was most easily achieved by the phthalocyanine-forming reaction of a spirocyclic bisphthalonitrile (Scheme 1). The important precursor to this bisphthalonitrile, 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (Table 1; monomer A1), a cheap commercial compound, reacts readily with 4,5-dichlorophthalonitrile to give the required bisphthalonitrile. Ultimately, this synthetic process gave phthalocyanine-network polymers with significant microporosity as demonstrated by nitrogen adsorption measurements from which

apparent BET surface areas of over $750 \, \text{m}^2 \, \text{g}^{-1}$ were calculated [37–39]. Subsequently, these materials were found to have useful catalytic activity in oxidations reactions as originally predicted [40, 41]. It was logical to extend this concept to the preparation of microporous polymer networks that contain catalytically active porphyrins. This aim was achieved with ease by the direct reaction between commercially available tetrakis-*meso*-(pentafluorophenyl)porphyrin and the spirocyclic monomer A1 to give materials with apparent BET surface areas of up to $1000 \, \text{m}^2 \, \text{g}^{-1}$ [42]. At this point, it became apparent that a wide variety of microporous organic network polymers could be prepared by the general strategy of reacting appropriate fluorinated or chlorinated monomers with complementary monomers that contain multiple catechol units (i.e., 1,2-dihydroxybenzene) such as A1. Hence, a wide range of microporous network polymers have been prepared including those containing hexaazatrinaphthylene units for efficient metal-cation binding [43], bowl shaped cyclotricatechylene [44], and tribenzotriquinacene [45] units and triptycene units that provided high and controllable surface areas (up to $1730 \, \text{m}^2 \, \text{g}^{-1}$) [46, 47]. These networks have been studied as potential hydrogen storage materials [44, 48–51] and as heterogeneous catalysts [20, 22, 52–54].

The parallel development of nonnetwork PIMs originated serendipitously from some simple control experiments to determine the efficiency of network formation during the synthesis of the microporous networks, described above, as this was difficult to determine directly due to their insolubility. Therefore, the efficiency of the dibenzodioxin-forming polymerization reaction used for the network formation had to be investigated by other means. One realistic method was to prepare a soluble (i.e., nonnetwork) polymer using the same reaction, whose average molecular mass could be determined by solution techniques such as

TABLE 1: Nonnetwork microporous polymers based on dibenzodioxin formation (i).
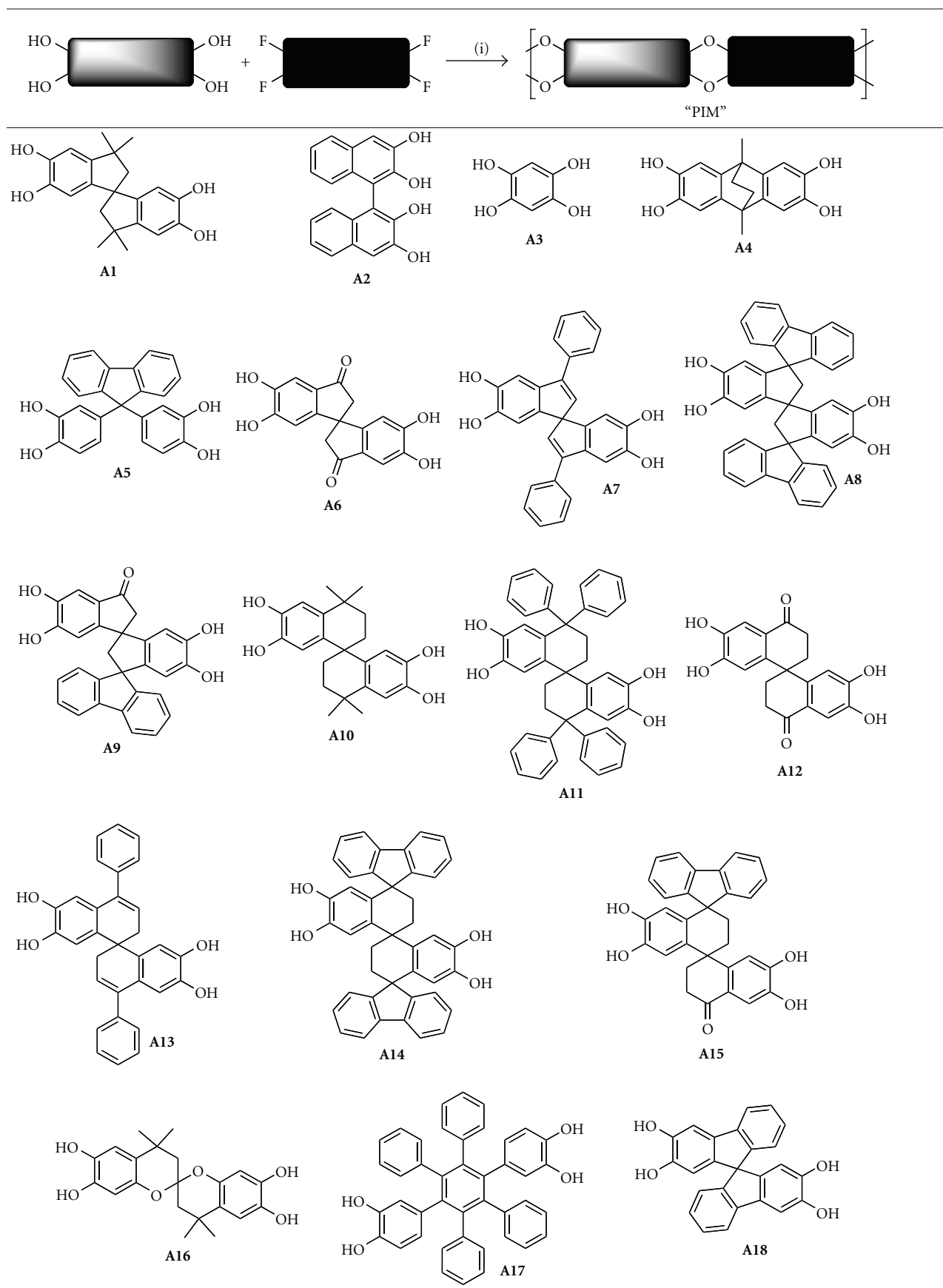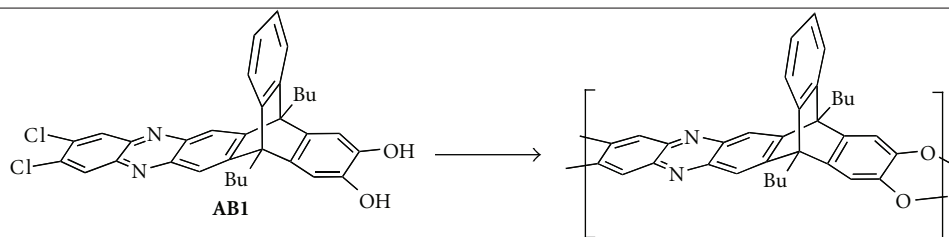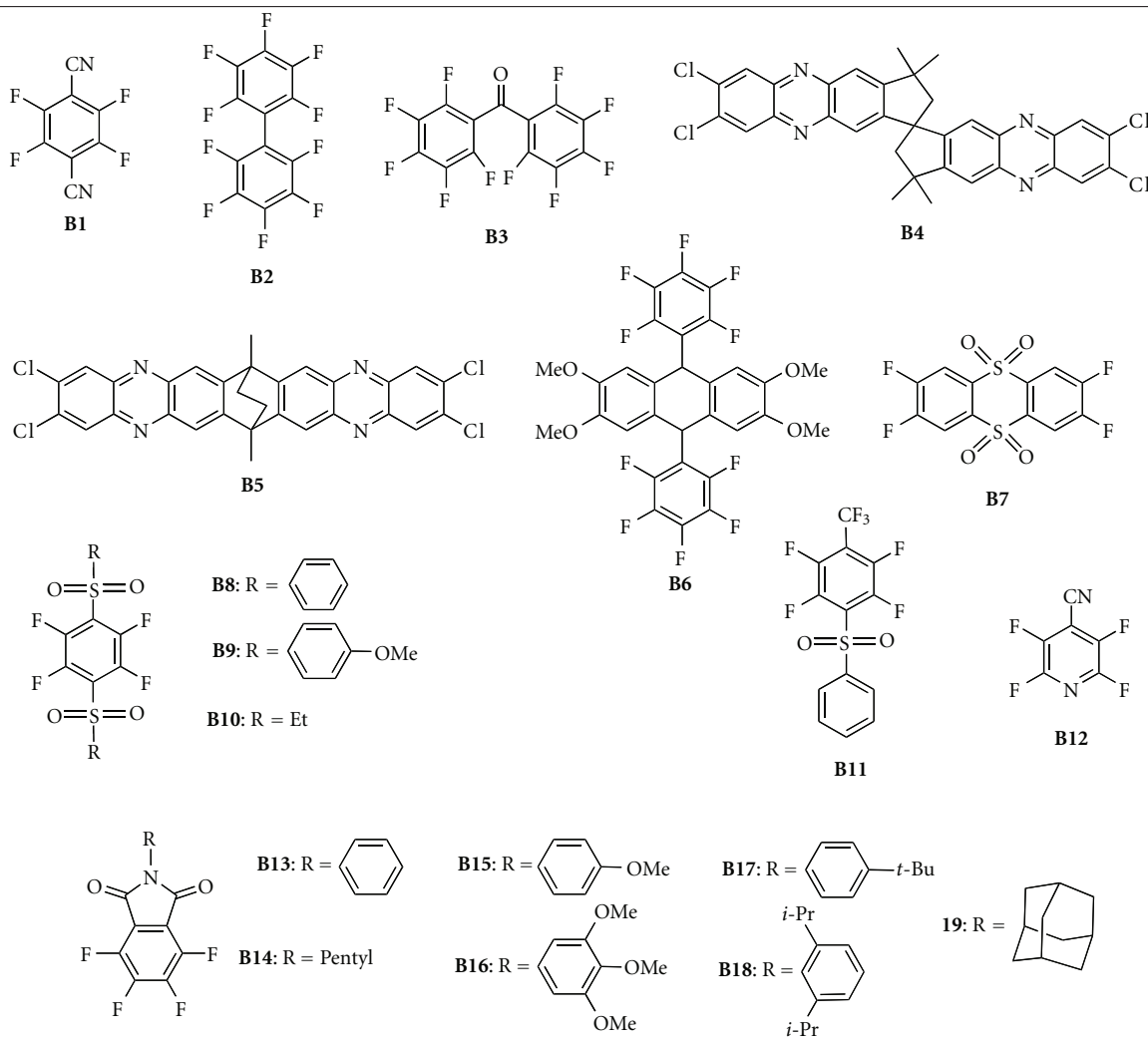
TABLE 1: Continued.

Monomers[a]	Solubility	Name[b]	Surface area (BET; m^2 g^{-1})	Reference
A1 + **B1**	THF, CHCl$_3$	PIM-1	760–850	[55, 57]
A1 + **B2**	THF	PIM-2	600	[55]
A1 + **B3**	THF	PIM-3	560	[55]
A2 + **B1**	THF	PIM-4	440	[55]
A2 + **B2**	THF	PIM-5	540	[55]
A3 + **B2**	THF	PIM-6	430	[55]
A1 + **B4**	CHCl$_3$	PIM-7	680	[74]
A4 + **B4**	CHCl$_3$	PIM-8	677	[74]
A1 + **B5**	CHCl$_3$	PIM-9	661	[74]
A4 + **B5**	m-cresol	PIM-10	680	[74]
A5 + **B4**	CHCl$_3$	Cardo-PIM-1	621	[74]

TABLE 1: Continued.

A5 + B5	CHCl$_3$ (partial)	Cardo-PIM-2	580	[74]
A4 + B1	Not soluble	PIM-CO-100	630	[75]
A6 + B1	Quinoline	"Polymer from 5"	501	[76]
A7 + B1	Quinoline	Polymer from 6	560	[76]
A8 + B1	THF	Polymer from 7	895	[76]
A9 + B1	DMF, quinoline	Polymer from 10	656	[76]
A10 + B1	THF	Polymer from 5	432	[77]
A11 + B1	THF	Polymer from 8	395	[77]
A12 + B1	Insoluble^c	Polymer from 10	713	[77]
A13 + B1	Insoluble^c	Polymer from 14	203	[77]
A14 + B1	THF	Polymer from 15	590	[77]
A15 + B1	Insoluble^c	Polymer from 16	300	[77]
A1 + B6	CHCl$_3$	MP-1	679	[51]
A16 + B1	Quinoline	PIM-CO15	518	[78]
A17 + B1	CHCl$_3$	PIM-HPB	527	[79]
A18 + B1	CHCl$_3$	PIM-SBF	803	[80]
A1 + B7	CHCl$_3$	TOT-PIM-100	560	[81, 82]
A1 + B1$_{0.5}$B7$_{0.5}$	CHCl$_3$	TOT-PIM-50	601	[81]
A1A2B1B7	CHCl$_3$	DNTOT-PIM-50	407	[81]
A1$_{0.5}$A2$_{0.5}$ + B1	CHCl$_3$	DN-PIM-50	709	[81]
A1 + B8	CHCl$_3$	DSPIM1-100	—	[82, 83]
A1 + B9	CHCl$_3$	DSPIM2-100	—	[83]
A1 + B10	CHCl$_3$	DSPIM3-100	—	[83]
A1 + B11	CHCl$_3$	PSTFPIM1	—	[82, 84]
A1 + B12	CHCl$_3$	—	—	[66]
A1 + B13	CHCl$_3$	PIM-R1	702	[85]
A1 + B14	CHCl$_3$	PIM-R2	595	[85]
A1 + B15	CHCl$_3$	PIM-R3	628	[85]
A1 + B16	CHCl$_3$	PIM-R4	889	[85]
A1 + B17	CHCl$_3$	PIM-R5	636	[85]
A1 + B18	CHCl$_3$	PIM-R6	714	[85]
A1 + B19	CHCl$_3$	PIM-R7	680	[85]
AB1	CHCl$_3$	—	523	[68]

^{a}See structures above.

^{b}As given in reference.

^{c}It is thought that this molecule is cross-linked due to an additional Aldol reaction, which takes place during polymerization.

gel permeation chromatography (GPC). The monomers chosen to prepare the soluble control polymer were the commercially available spirocyclic biscatechol **A1** and 2,3,5,6-tetrafluoroterephthalonitrile **B1** (Table 1). Optimised reaction conditions enabled a fluorescent yellow polymer to be prepared in a high yield with a very high apparent average molecular mass determined by GPC relative to polystyrene standards ($M_w > 100000$ g moL^{-1}). This polymer, subsequently known as PIM-1, aroused some initial interest due to its distinct green fluorescence and was sent for testing to Covion, a company specialising in organic light emitting diodes (OLEDs). These results were disappointing, and the polymer was then neglected for a number of months. However, eventually the polymer was characterised by nitrogen adsorption at 77 K, and a very respectable apparent

BET surface area of around 800 m^2 g^{-1} was calculated from this data. At this time it was realised that a covalent network was not necessary for obtaining microporosity in polymers and that we had developed a solution-processable microporous material. Our collaborator within the School of Chemistry, University of Manchester, Peter Budd, had research interests in the formation of zeolite membranes, which are notoriously difficult to process into usable forms. He immediately saw the potential of what we then termed PIM-1 for making membranes and devised some initial experiments based on the extraction of phenol from water using pervaporation [55]. In late 2003, a patent application [56] based on the preparation and applications of solution processable microporous polymers was submitted by the knowledge transfer office of the University of Manchester

prior to the publication of the initial communications on the synthesis of several examples of PIMs and membrane pervaporation experiments using films of PIM-1 [55, 57].

3. Synthesis of PIMs

PIMs are prepared by a polymerization reaction based on a double-aromatic nucleophilic substitution mechanism to form the dibenzodioxin linkage. This reaction is one of the few capable of forming two covalent bonds simultaneously and with sufficient efficiency to provide a linking group composed of fused rings and thus able to form ladder polymers of high average molecular mass [58, 59]. Generally, aromatic nucleophilic substitutions are known to proceed readily especially if the halide-containing monomer is activated by an electron-withdrawing substituent (e.g., –CN, F, etc.) [60]. This reaction was used previously by the author's research group to prepare phthalocyanine oligomers [61] and extended planar molecules and oligomers for discotic liquid crystals [62].

A number of variations of PIM synthesis all using the dibenzodioxin-forming reaction have been described in the literature. The original method (sometimes called the "low temperature method") involves mixing the two monomers (e.g., **A1** and **B1** for PIM-1) in equimolar quantities in a solution of anhydrous dimethyl formamide (DMF) with a twofold excess of finely powdered dry potassium carbonate at 50–60°C for 24–72 hours [55, 57]. Alternatively, the "high temperature" method, developed by Michael Guiver's group at the Canadian NRC laboratories, involves high-speed stirring of the mixture in dimethyl acetamide at 155°C for only 8 minutes with the addition of toluene to enable the continuation of stirring [63]. Both methods provide PIM-1 with sufficiently high average molecular mass to provide mechanically robust solvent cast films but generally the low temperature method is favoured as it is easier to control and more suitable to scale up [64]. A modified "high temperature" method of continuous production of PIM-1 using flow reactors has been patented, although the average molecular mass of the resulting polymer was modest [65]. An alternative preparation method involves the initial formation of the silyl ether of the biscatechol monomer **A1**; although successful, this appears to be an unnecessary additional synthetic step [66]. The concentration of the monomers in the standard "low-temperature" polymerisation is important as at very high concentrations insoluble crosslinked material is produced [64] whereas at low concentrations a large amount of cyclic oligomers of modest molecular mass is formed [66, 67]. The optimal concentration appears to be around 3 mmol of each monomer per 10–15 mL DMF. The "low temperature" method has been applied to a large combination of catechol-based monomers (**A1–A18**) and halide-based monomers (**B1–19**) resulting in PIMs with a wide range of structures as shown in Table 1. In addition, a triptycene-based AB-monomer (monomer **AB1**, Table 1) has been successfully polymerised [68].

Due to the interest in PIM-1 as a membrane material (see Section 6.1), several studies have sought to modify the structure of the preformed polymer by postsynthesis reactions centred on the nitrile group. These include simple hydrolysis groups to provide carboxylic acids [69, 70], reaction with P_2S_5 to provide thioamines [71], reaction of hydroxylamine to give amidoximes [72], and the reaction of sodium nitride to provide tetrazole functionality (Scheme 2) [73].

In addition to the dibenzodioxin reaction, the more classical polymerisation reaction of imide formation has been used to form PIMs termed PIM-PIs (Table 2). Although the imide link is not composed of fused ring units, if suitable diamine aromatic monomers (e.g., **D1**, **D6** or **D9**) are used that contain methyl groups adjacent to the amine group, rotation about the C–N single bond is sufficiently restricted to prohibit conformation rearrangement and generation of significant intrinsic microporosity.

4. Characterisation of PIMs

4.1. Structural Characterization. PIMs can be structurally characterized in the same way as other soluble polymers using solution ^1H and ^{13}C NMR and gel permeation chromatography (GPC). GPC gives an estimate of number average (M_n) and weight average (M_n) molecular mass from which the polydispersity (M_w/M_n) can be calculated. The figures obtained from GPC should be treated with some caution as they are calculated from calibrations against standard polymers of known molecular mass (e.g., polystyrene), which are structurally dissimilar. However, as both PIMs and polystyrene are random coil polymers, albeit with a fixed random coil in the case of PIMs, any discrepancy should be relatively small. Matrix-assisted laser desorption ionization mass spectrometry can be useful for determining the presence of cyclic oligomers and the nature of the end-groups [66, 67].

4.2. Characterisation of Microporosity. Several methods can be used to gain information on the microporous structure obtained from the packing of the PIM macromolecules in the solid state. However, it should be noted that the resulting amorphous structure and the lack of a covalent network means that all methods are dependent on the form (e.g., powder, thin film, etc.) and previous history of the solid (solvent of solid fabrication, exposure to vacuum, exposure to heat, ageing, etc.). The micropore structure may even be changed during analysis by, for example, the adsorption of gas molecules resulting in swelling of the material.

4.2.1. Gas Sorption Analysis. Microporous materials are commonly characterized by N_2 adsorption/desorption at liquid nitrogen temperature (77 K). At the lowest pressures, the very smallest pores accessible to N_2 are filled, because multiwall interactions give rise to enhanced adsorption. On increasing the pressure, progressively larger pores are filled. Above a certain size (in practice around 2 nm), the mechanism of pore filling changes, with condensate building from the walls towards the centre. This represents the transition from micropores to mesopores.
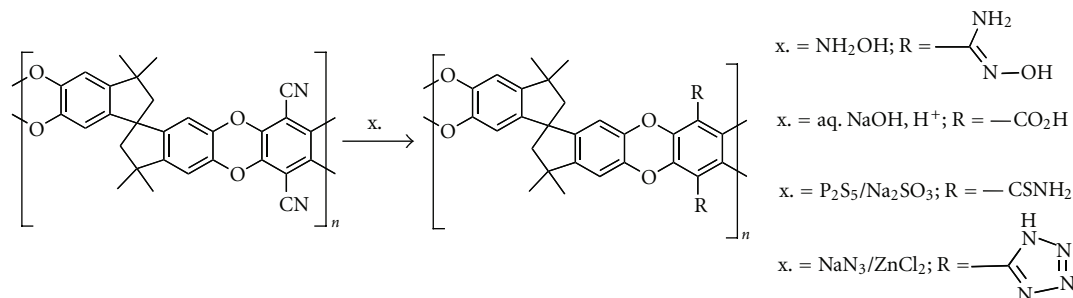
SCHEME 2: Postsynthetic modification of PIM-1.

Significant N_2 uptake at low values of relative pressure (p/p^o) is the primary indicator of microporosity in PIMs. Figure 1 shows a typical N_2 adsorption/desorption isotherm for PIM-1 showing features common with all PIMs including increasing uptake with increasing relative pressure and a hysteresis that extends down to low relative pressures. These features have been attributed to either swelling of the polymer and/or to the tortuosity of the micropore structure that results from the packing of the macromolecules in the solid state. From the isotherm a value for the apparent Brunauer, Emmett, and Teller (BET) surface area of the PIM can be calculated [90]. Although the value of this figure when compared to those of other porous materials is highly debatable, it is a useful parameter for indicating the relative amount of intrinsic microporosity in one PIM compared to another. In addition, the apparent distribution of micropore size can be calculated from the very low pressure region of a N_2 adsorption isotherm by the Horvath-Kawazoe (HK) method, which assumes that all pores of a certain size will fill at a particular relative pressure [91]. This method generally shows a smooth distribution with a peak at maximum 0.6 nm extending to 2.0 nm, although the apparent maximum at 0.6 nm is contributed to by micropores of smaller diameter for which analysis is limited by the difficulty in obtaining N_2 adsorption data at sufficiently low pressure. In order to probe smaller pores the HK method can be applied to data obtained from CO_2 absorption at 303 K [20] or Xenon at 298 K [75]. In addition, ^{129}Xe NMR can be used to demonstrate gas adsorption within PIMs [75].

4.2.2. Positron Annihilation Lifetime Spectroscopy (PALS).

Ortho-positronium (*o*-Ps), a metastable particle produced by the reaction of a positron with an electron, can act as a probe of free volume in a material. In a vacuum, *o*-Ps has an average lifetime of 142 ns, but within matter this is reduced, because the *o*-Ps encounters electrons and is annihilated. In a polymer, *o*-Ps tends to be localised in free volume elements or holes, in which case its lifetime decreases with decreasing hole size. If assumptions are made about the shape of the hole (e.g., spherical or cylindrical), the hole size can be calculated using the Tao-Eldrup model [92]. In high free volume polymers, such as PIM-1, more than one *o*-Ps lifetime may be measured, which can be interpreted in terms of either a broad or a bimodal distribution of hole size [93]. However,

there seems little evidence from other techniques to support the formation of a bimodal distribution in microporous polymers. PALS has been used to investigate the pore size distribution of PIM-1 and closely related PIMs, under a range of environments, relative to other high free volume polymers [75, 94, 95]. An unusual reduction in the apparent size of free volume elements is noted from PALS above 100°C for PIM-1 [75, 94]. The use of X-ray scattering to characterise the amorphous structure of PIMs is also of value, especially in combination with computer simulations (see below) [96].

4.2.3. Computer Simulation.

Computer simulations can give an insight and provide graphical representations of the packing of PIM macromolecules in the solid state. Early work required the accurate experimental measurement of the density of the PIM, which is difficult to achieve as a film and almost impossible as a powder [97]. However, subsequent studies using a series of simulated high pressure compression and relaxation achieve a realistic packing without the need for density measurements [98, 99]. Validation of the resulting packing structure was performed by comparison with X-ray scattering measurements on thin films of the polymer [96]. An interesting observation that can be made from the simulated packing is the distortion of the macromolecule due to the energetically disfavoured formation of intrinsic microporosity and the attempt of the polymer to minimise surface area and maximise intermolecular interactions. In particular there are a wide variety of dihedral angles adopted about the spirocentres and dibenzodioxin units within PIM-1 indicating a surprising degree of flexibility.

The application of packing simulation to understand and predict the performance of PIMs as gas separation membranes (see below) is also an active area of research [100–102]. However, it should be noted that, at present, simulations of PIM packing do not take into account polymer dynamics, which are important for the accurate prediction of gas diffusivities, nor do they give information on possible swelling effects due to gas adsorption. Nevertheless, simulations will have a major role to play in the design of new polymers and will be of increasing importance for the prediction of the performance of PIMs for gas adsorption and membrane separations.

TABLE 2: Nonnetwork microporous polymers based on imide formation (ii).

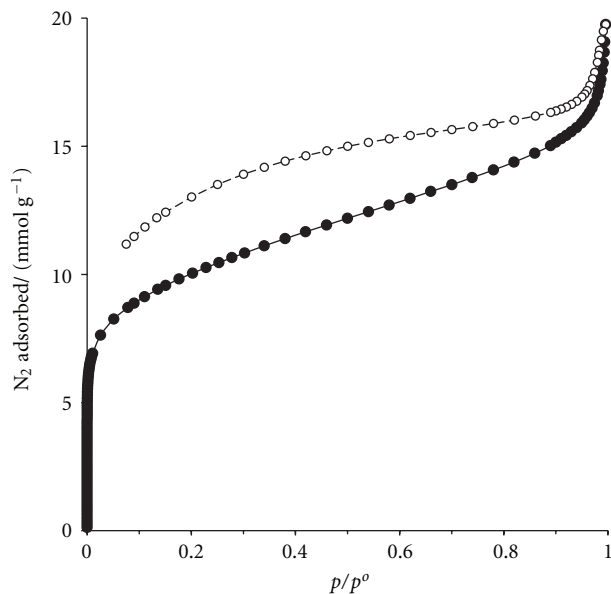| Monomers	Solubility	Name[b]	Surface area (BET; m² g⁻¹)	Reference
C1 + D1	CHCl₃	PIM-PI-1	680	[86, 87]
C1 + D2	CHCl₃	PIM-PI-2	500	[87]
C1 + D3	CHCl₃	PIM-PI-3	471	[86, 87]
C1 + D4	CHCl₃	PIM-PI-4	486	[87]
C1 + D5	CHCl₃	PIM-PI-7	485	[87]
C1 + D6	CHCl₃	PIM-PI-8	683	[86, 87]
C2 + D7	CHCl₃	P4	551	[88]
C3 + D1	THF	6FDA-m4	—	[32]
C4 + D9	THF	6FDA-m3	—	[32]
C2 + D10	THF	PIM-6FDA-OH	225	[89]
C3 + D10	THF	PIM-PMDA-OH	190	[89]

FIGURE 1: The nitrogen adsorption (filled circles) and desorption (empty circles) for PIM-1 measured at 77 K.

5. Structure-Property Relationships of PIMs

5.1. Solubility. One of the characteristic properties of a PIM is high solubility in common organic solvents (Table 1). Generally ladder polymers are notoriously insoluble [58], and often long alkyl chains substituents are required in order to induce solubility. However, for PIMs it appears that the rigid and contorted macromolecular structures help to reduce intermolecular cohesive interactions by limiting the amount of close contacts between polymer chains. The relative flexibility of the spirobisindane unit may also assist in solubility [97]. It is notable that the PIM prepared from the ethanoanthracene monomer **A4** and tetrafluorotereph-thalonitrile **B1** is insoluble [75], and this may be due to the greater rigidity of the bridged bicyclic ethanoanthracene unit. It may also be attributed to the fact that the polymer chain is contorted only within two dimensions allowing the polar nitrile groups to interact more fully thus increasing polymer cohesion, whereas soluble PIMs form random coils in all three dimensions.

5.2. Mechanical, Chemical, and Thermal Properties. Thermal analysis of PIM-1, including differential thermal calorimetry (DSC) and thermal dynamic mechanical analysis (DMTA), shows no glass transition temperature or other thermal transition below its decomposition at around 450°C [57]. A tensile storage modulus of ~1 GPa [57], a tensile strength of 45–47 MPa, and a strain of 10%-11% at breakage have been reported for PIM-1 [64, 81]. Interestingly, copolymers prepared using monomers **A1** and a 50 : 50 mixture of **B1** and **B7** give a higher strain at breakage of 20% [81].

5.3. Microporosity. Values for the apparent BET surface area of PIMs are given in Table 1. The quoted values of

PIM-1 lie within the range of 720–875 $m^2 g^{-1}$ with the variance presumably arising from different sample history or measurement technique [44, 55, 103]. Only a few PIMs match or demonstrate higher apparent surface area than PIM-1, and these are prepared from monomers containing highly rigid aromatic substituents such as **A8**, **A18**, and **B16** [76, 80, 85]. It is clear from direct comparisons that PIMs based on more flexible structures, such as those derived from the tetrahydronaphthalene unit (e.g., from **A10** and **B1**), are significantly less microporous than the equivalent spirobisindane-based polymers [77]. In general, it is difficult to predict the effect on microporosity by adding substituents to a PIM. For some rigid substituents, such as fused fluorenes (e.g., **A8**), some modest enhancement has been noted [76] but in most cases it appears that the substituents fill the microporosity generated by the packing of the polymer chains. Modifications to the nitrile substituents of PIM-1 to introduce carboxylic acid, thioamide, and tetrazole groups all significantly reduce the apparent surface area presumably due to the hydrogen bonding properties of these groups increasing polymer cohesion and improving packing [69, 71, 73]. However, the introduction of amidoxime substituents does not reduce significantly the apparent surface area and has thus been termed a "non-invasive" modification [72].

6. Applications of PIMs

PIMs uniquely combine some of the advantages of a microporous material, in that they can selectively take up and transport molecular species, with the solution processability of a polymer. Hence they are of interest for a number of applications.

6.1. Membranes. Membrane technology can provide energy-efficient, cost-effective separations for a wide range of industries [27, 33, 104–107]. For membrane separations, there is a balance between the separation that is achievable (i.e., selectivity) and the productivity (i.e., flux or permeance). In general, it is desirable to maximize the permeance, so as to minimize the membrane area required; therefore, the important challenge is to develop highly permeable membrane materials that show improved separation. This will enable their application to large-scale separations for which current polymer membranes would require too large a surface area to be practical.

6.1.1. Pervaporation Membranes. In pervaporation, the feed is a liquid mixture and the permeate is removed as a vapour, which can then be condensed into a liquid or solid at lower temperature. The driving force for transport comes from application of a vacuum or sweep gas to the permeate side of the membrane. An advantage of pervaporation is that it can be used to break an azeotrope. Commercial pervaporation plants, for example, for dehydration of ethanol/water mixtures, commonly employ hydrophilic membranes. However, there is increasing interest in hydrophobic membranes for waste-water treatment and for the separation of organic-organic mixtures. Pervaporation was the first application
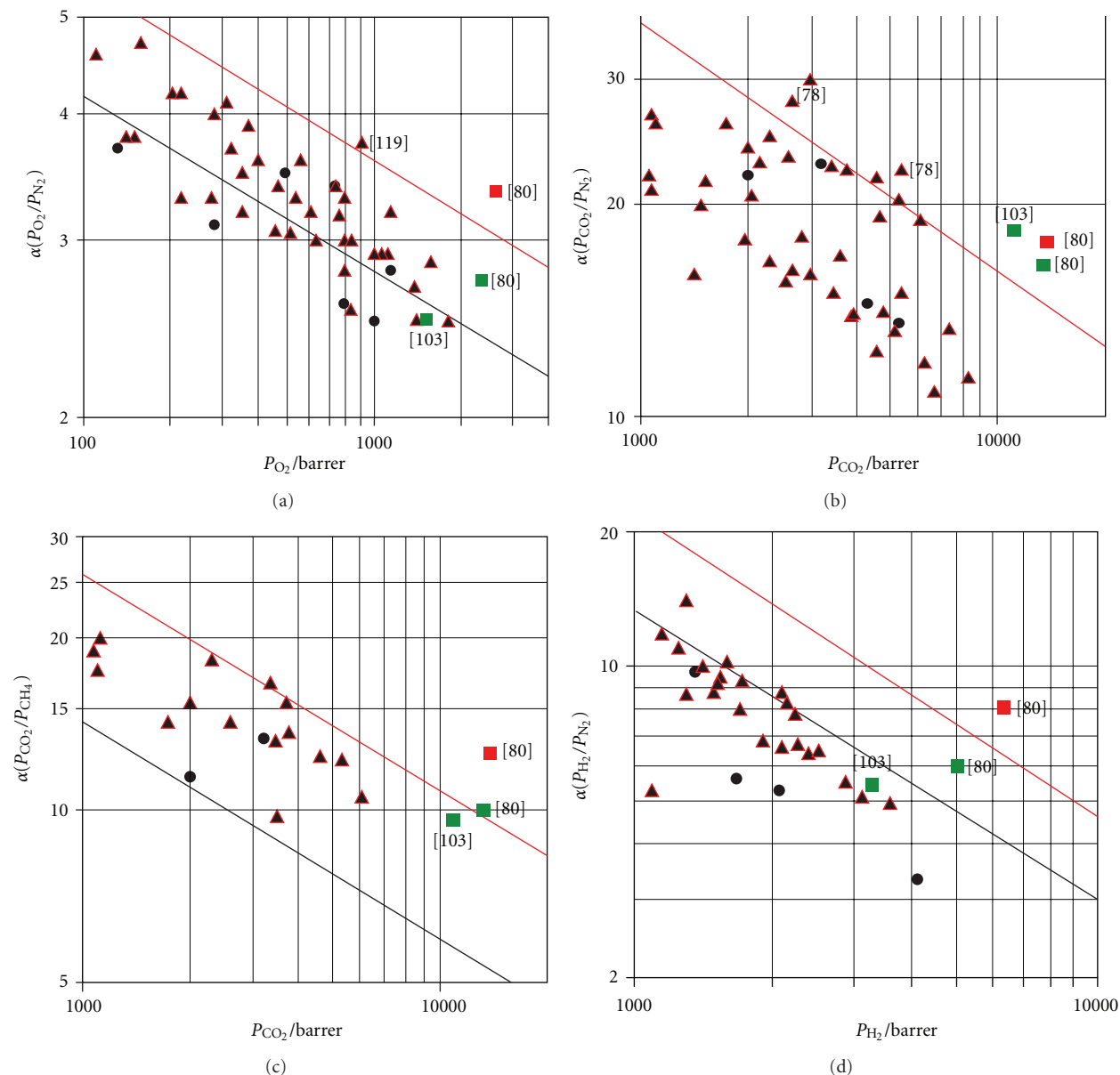
FIGURE 2: Robeson plots for (a) O_2/N_2, (b) CO_2/N_2, (c) CO_2/CH_4, and (d) H_2/N_2 gas pairs showing the data for PIMs. The black and red lines represent the 1991 and 2008 upper bounds, respectively. References for notable data points are given in square brackets. Data for methanol treated films of PIM-1 are given as green squares whereas the data for a methanol treated film of spirobisfluorene-based PIM, prepared from monomer **A18**, is given as a red square. Data for other PIMs are given as black triangles and for PIM polyimides as black circles.

of PIM membranes to be investigated. PIM-1 was shown to form a hydrophobic membrane, selectively transporting organics, such as phenol [57] and aliphatic alcohols (i.e., ethanol and butanol), from mixtures with water [57, 108]. High flux, coupled with good separation factor and stability, makes this a promising area for further development.

6.1.2. Organic Solvent Nanofiltration (OSN) Membranes. Nanofiltration is now a well-established technology for treating aqueous solutions by retaining molecules above a certain size. Unlike pervaporation, there is no phase change on permeation. An area of particular interest for new polymers

such as PIMs is that of solvent-resistant nanofiltration for the treatment of organic mixtures, where the aim is to operate a continuous reaction whilst extracting products but retaining a large molecular catalyst [109]. Membranes of PIM-1 and PIM copolymers show real promise in this respect [110, 111]. Cross-linking methodologies (see below) may play an important role to enhance the stability of PIM OSN membranes especially for those organic solvents for which the PIM demonstrates solubility.

6.1.3. Gas Separation Membranes. Polymer membranes offer an energy-efficient method for many gas separations as they

do not require thermal regeneration, a phase change, or active moving parts in their operation [112]. In membrane gas separation, the driving force comes from a pressure difference across the membrane [33, 113]. Commercially important membrane-based gas separations include O_2 and N_2 enrichment of air, hydrogen recovery from ammonia production (predominately H_2 from N_2) or hydrocarbon processing (e.g., H_2 from CH_4), and the purification of natural gas (predominantly CO_2 from CH_4). However, polymers suffer from a well-defined trade-off between the desirable properties of permeability and selectivity for the required gas component. Presently, commercial gas separation membranes are based on a few well-established polymers with low permeability and high selectivity; therefore, large membrane areas are required to compensate for lack of permeance. This means that existing polymer membranes are not currently competitive with other technologies for large-scale gas separations. For any given gas pair, the trade-off between permeability (i.e., permeance multiplied by membrane thickness) and selectivity [108] (expressed as a ratio of permeabilities) may be represented by a double-logarithmic plot of selectivity against the permeability of the fastest species (Figure 2). In 1991, Robeson delineated an empirical upper bound in such plots that represented the state-of-the-art performance against which the gas permeability data of new polymers could be compared [114]. The originally published data for PIM-1 and PIM-7 were well above the 1991 upper bound for important gas pairs such as O_2/N_2 and CO_2/CH_4 [115]. This data contributed to Robeson's revision of the upper bounds in 2008 [116]. Subsequently, it was found that the permeability of PIM-1 could be enhanced further by the simple treatment of solvent cast films by methanol, which helps flush out residual solvent and allows relaxation of the polymer chains [103]. Methanol-treated PIM-1 provides data just above the 2008 upper bounds for the CO_2/N_2 and CO_2/CH_4 gas pairs [103]. In common with other glassy polymers, the transport properties of PIMs are strongly dependent on their processing history. This accounts for the large variation in reported gas permeation data for PIM-1 [93, 103, 117]. In particular, residual solvent from casting and ageing of films, the latter a phenomenon shown by all glassy polymers especially those with high free volume [118], cause a reduction in permeability. Therefore, in order to allow a fair comparison between PIMs, it is best to use methanol treatment of the polymer film to ensure removal of casting solvent and to "reset" the ageing clock.

In theory, the structural diversity afforded by the range of potential monomers for PIM synthesis (Table 1) and postsynthetic modification (Scheme 2) should allow for the transport properties of PIMs to be optimised. However, very few of the many PIMs that have been studied have demonstrated gas permeability data that is significantly improved as compared to that of methanol-treated PIM-1 or that lies above the 2008 Robeson upper bound (Figure 2). Some copolymers of PIM-1 that incorporate monomers **A2** [119] or **A4** [78] do appear to enhance performance to give data at the 2008 upper bound for certain gas pairs. Also, modification of PIM-1 by the introduction of

triazole units via reaction of the nitrile group gives a less permeable polymer but with data above the CO_2/N_2 upper bound (TZ-PIMs; Scheme 2) [73]. However, one of the few significant improvements is afforded by the PIM using the spirobifluorene monomer **A18**, recently prepared by the author's group, that has gas permeability data well above the 2008 Robeson upper bounds for most important gas pairs (e.g., O_2/N_2, CO_2/CH_4, CO_2/N_2, and H_2/N_2) [80]. We attributed the improved performance to the increased rigidity about the spirocentre of the spirobifluorene as compared to that of spirobisindane. This conclusion is in accordance with an excellent theoretical study on the position of the upper bounds that suggests that improvements in diffusivity selectivity can be achieved by enhancing the rigidity of the polymer to suppress local motion and optimise the molecular sieve behaviour of the polymer [120, 121].

Generally PIM polyimides such as those shown in Table 2 demonstrate high gas permeability (similar to many other PIMs and higher than any other of the many polyimides studies for gas separations) [32] but lower selectivity than PIM-1 [86, 87, 89].

A different approach to improving membrane performance for gas separations is the formation of mixed-matrix membranes using fused silica nanoparticles [122] zeolites and related inorganic microporous materials [123], or metal organic frameworks (MOFs) [27]. To date such membranes have demonstrated enhanced permeability but at the expense of selectivity and suggest that poor interaction between polymer and inorganic particle produces enhanced free volume that is poorly size selective. Nevertheless, further research in this area should result in improved performance. Composite membranes consisting of PIMs and other polymers also represent a promising strategy for tailoring membrane properties [27, 124].

In addition to gas separations, PIMs show promise for the separation of vapours from gases [125]. For example, excellent performance for the separation of butane from hydrogen was demonstrated for PIM-1 based upon the far greater solubility of the larger butane molecule and a pronounced pore-blocking effect slowing the transport of hydrogen [126]. Interestingly, a similar pore-blocking effect has been observed for the tetrazine-modified PIM for mixed gas CO_2/N_2 separations of interest for carbon capture [73, 107].

PIMs are now recognized as one member of the third generation of polymer materials for membranes (along with thermally rearranged polymers) [127–130] following on from the commercially useful but low performance cellulose-based polymers and better performing polymers such as polyimides, which are now becoming commercially exploited. The intense activity on PIMs for gas separations should result in better materials and optimized membrane fabrication. Of particular importance is the challenge of physical ageing whereby the remarkably high gas permeability is lost over time. This phenomenon is particularly relevant to very thin films (submicron thickness) such as those used for membrane fabrication, which allow

high fluxes to be achieved. It is possible that cross-linking may help to solve this problem and produce membranes that can function reliably over their expected lifetime (3–5 years). Cross-linking of PIM-1 has been achieved by thermal processing [131], UV treatment [132], and the reaction of azides [133]. In addition to enhancing mechanical robustness and reducing ageing, cross-linking [131, 132] has been shown to provide gas permeabilities that lie above the Robeson upper bound (although formally the Robeson plot is only for solution processable polymers).

6.2. Sensors. The combination of solution processability, porosity, and optical clarity makes PIMs useful for sensor applications. For example, the incorporation of the fluorescent dye Nile Red into solvent cast films of PIM-3 (formed from monomers **A1** and **B3**, see Table 1) produced an optical sensor for ethanol [134, 135]. The intrinsic fluorescence of PIM-1 has also been exploited in sensors described in patents and enabled the fabrication of a laser sensor with great sensitivity for the detection of nitrated aromatics [136]. A colorimetric optical sensor based on the rapid change in refractive index of a thin film of PIM-1 on adsorption of organic vapor provides a dramatic green-to-red color change, which can be visualised for sensing concentrations in air down to 50 ppm or, if using a fibre-optic spectrometer, down to 50 ppb [137, 138]. The optical response is general for all organic vapors but the hydrophobic nature of PIM-1 ensures the lack of interference by humidity. The fabrication and performance of this device both benefit from the unique combination of solvent processability and microporosity of the PIM component.

In a related application, PIM-1 has been used as a preconcentrator medium for adsorbing organics from air which can then be desorbed by heating into a conventional sensor [139, 140]. For this application, the thermal stability of PIMs is of importance.

7. Conclusions

As this paper demonstrates, in less than ten years, PIMs have established themselves as an important class of microporous materials with over seventy academic papers dealing directly with some aspect of PIMs and more than thirty patent applications. Many groups are now engaged on research involving PIMs both in industry and academia so that the rate of progress is likely to increase further. This activity will lead to new ways of making PIMs beyond the dibenzodioxin and imide forming reactions described in Section 3, and work in the author's group at Cardiff is concentrating on this strategy. Equally important will be new and simple ways to cross-link PIMs that are applicable to *in situ* reactions in thin films and thus useful for membrane stabilisation. The ease of making PIM-1 from commercial starting materials also allows groups with only limited expertise in polymer synthesis to engage in research to fully explore the properties and applications of this material. Hence, it can be expected that the next decade in PIM research will be at least as exciting as the last.
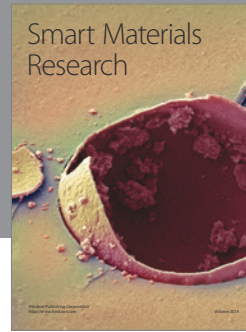
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