Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage

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Received 28th February 2006
First published as an Advance Article on the web 17th March 2006
DOI: 10.1039/b600349d

This *tutorial review* describes recent research directed towards the synthesis of polymer-based organic microporous materials termed Polymers of Intrinsic Microporosity (PIMs). PIMs can be prepared either as insoluble networks or soluble polymers with both types giving solids that exhibit analogous behaviour to that of conventional microporous materials such as activated carbons. Soluble PIMs may be processed into thin films for use as highly selective gas separation membranes. Preliminary results also demonstrate the potential of PIMs for heterogeneous catalysis and hydrogen storage.

Microporous materials are defined as solids that contain interconnected pores of less than 2 nm in size, and consequently they possess large and accessible surface areas—typically 300–2000 m^2 g^{-1} as measured by gas adsorption.[1] Conventional microporous materials, such as zeolites (aluminosilicates) and activated carbons are widely used as adsorbents, heterogeneous catalysts and, if the micropores are of uniform size, for molecular separations on the basis of size and shape. Despite the success of these materials, it is recognised that the synthesis of entirely novel microporous materials would benefit fundamental research and provide new opportunities in emerging technological areas such as hydrogen storage.[2] Of particular interest is the construction of microporous materials from organic components. Such organic-based materials are expected to allow exquisite control over the chemical nature of the large accessible surface area and the introduction of specific molecular recognition or catalytic sites—thus facilitating chemo-selective adsorption and the design of efficient heterogeneous catalysts for industrial-scale synthesis.

For certain chemical separations and heterogeneous catalysed reactions it is desirable for the microporous material to be crystalline to provide uniform micropores. Hence the preparation of '*organic zeolites*', in which rigid organic units are assembled into a microporous, crystalline structure by metal–ligand[3] or hydrogen bonds,[4] has become a major research area in the past decade. Of particular note are the metal–organic frameworks (MOFs), prepared by Yaghi and co-workers, that possess vast accessible surface areas (>3000 m^2 g^{-1}).[5] However, crystalline order is not a requirement for microporosity nor, as demonstrated by activated carbon, is it always necessary for technological applications. This review will explore the synthesis and properties of amorphous microporous organic materials based on polymers, particularly the novel class of materials termed *Polymers of Intrinsic Microporosity* (PIMs).

Microporous network polymers

The ability of charcoal to adsorb contaminants from water has been known for thousands of years and today activated carbons are used in vast quantities as adsorbents, deodorizers

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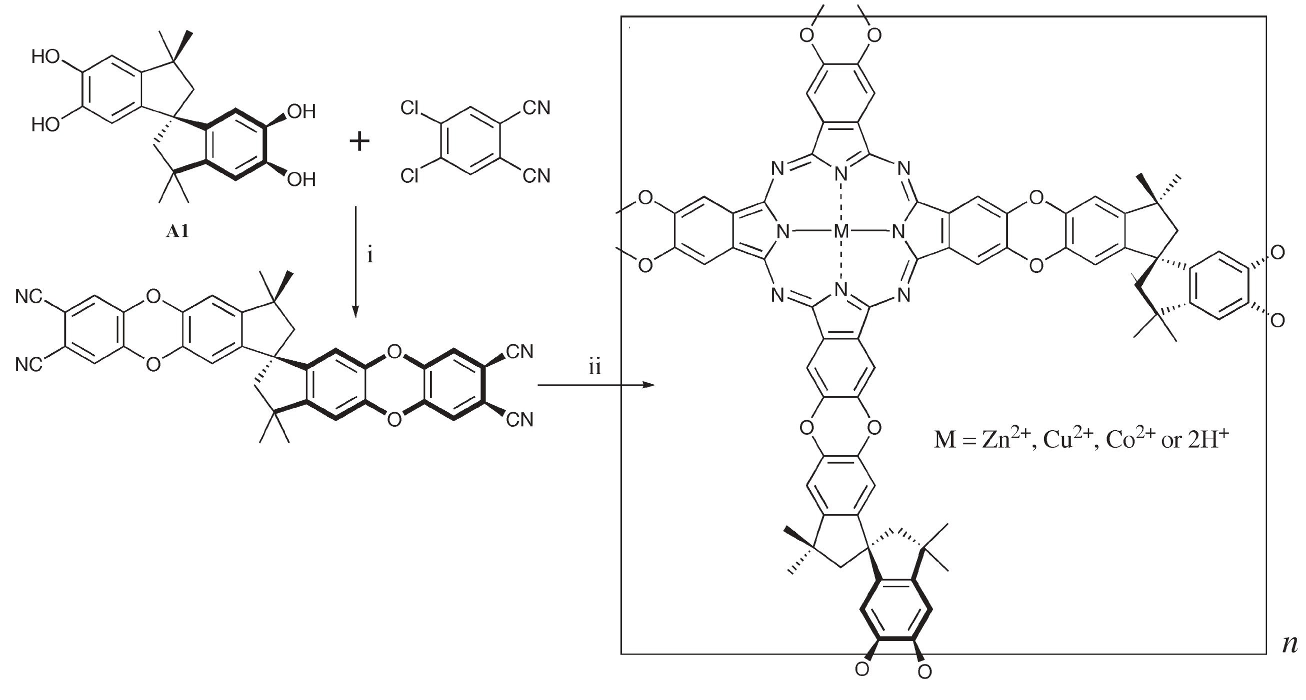
and catalyst supports. Activated carbons are network polymers composed of randomly arranged, inter-linked graphene sheets formed by the carbonisation of wood, nutshells and synthetic polymers.[6] Commercial carbons can offer surface areas in excess of 2000 $m^2 g^{-1}$ depending upon the precursor material and post-carbonisation treatment. Given the harsh method of preparation and complex nature of the starting materials, it is unsurprising that most activated carbons possess a wide distribution of pore sizes ranging from microporous to mesoporous (2–50 nm) to macroporous (>50 nm). Furthermore, the surface of activated carbons is chemically ill-defined with a large variety of oxygen- and nitrogen-containing functional groups present, in addition to the polycyclic aromatic units that form the graphene sheets. The heterogeneous structure and chemical nature of the exposed surface area explains the ability of activated carbons to adsorb a wide range of organic compounds and metal ions, but limits its potential for chemo-selective processes.

A few years ago, we initiated a research programme with the objective of preparing network polymers that possess amorphous microporous structures similar to that of activated carbon, but with a range of well-defined surface chemistries. Considering its enormous commercial importance and the limited scope for systematic chemical or structural modification that it offers, it is surprising that the structure of activated carbon had not previously inspired imitation. Indeed, with the exception of Webster's poly(arylcarbinol) network polymers[7,8] and Davankov's hypercrosslinked polystyrenes,[9,10] both of which demonstrate high surface areas (800–1200 $m^2 g^{-1}$), the concept of introducing robust microporosity within polymeric materials was largely unexplored—in contrast to the intense research efforts devoted to the control of polymer macro- and meso-porosity.[11,12]

Our initial strategy involved the incorporation of extended aromatic components, to mimic the graphene sheets of activated carbons, within a rigid polymer network. Initially, the phthalocyanine macrocycle was selected as the aromatic unit due to its extended planarity (diameter ~ 1.5 nm) and range of useful properties, which include oxidative catalysis if appropriate transition metal ions are placed in its central cavity.[13] Previously prepared phthalocyanine network polymers show a strong tendency of the aromatic components to aggregate into columnar stacks, due to strong non-covalent interactions (primarily π–π interactions), resulting in non-porous solids.[14] Therefore, it was deemed essential to use a highly rigid and nonlinear linking group between the phthalocyanine subunits that would ensure space-inefficient packing and prevent structural relaxation and loss of microporosity. Perfectly suited to fulfil these requirements is a linking group derived from the commercially available 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (monomer **A1**—Scheme 1). The spiro-centre (*i.e.* a single tetrahedral carbon atom shared by two rings) of **A1** provides the nonlinear shape, and the fused ring structure the required rigidity. Phthalocyanine network polymers are generally prepared from a bis(phthalonitrile) precursor *via* a cyclotetramerisation reaction which is usually facilitated by a metal ion template. Such a reaction using the bis(phthalonitrile), prepared from the dioxane-forming reaction between monomer **A1** and 4,5-dichlorophthalonitrile (an efficient double aromatic nucleophilic substitution reaction—S_NAr), gives network polymers as free-flowing, highly coloured powders (Scheme 1). Spectroscopic (ESR, UV/visible absorption) and X-ray diffraction analysis of the network polymers confirm that the spirocyclic cross-links prevent a close packing of the phthalocyanine components giving an amorphous microporous



Scheme 1 The preparation of phthalocyanine-based microporous network polymers (Pc-network-PIM) from the readily available spirocyclic monomer **A1**. Reagents and conditions: i. K_2CO_3, DMF, 80 °C; ii. metal salt, quinoline, 200 °C.

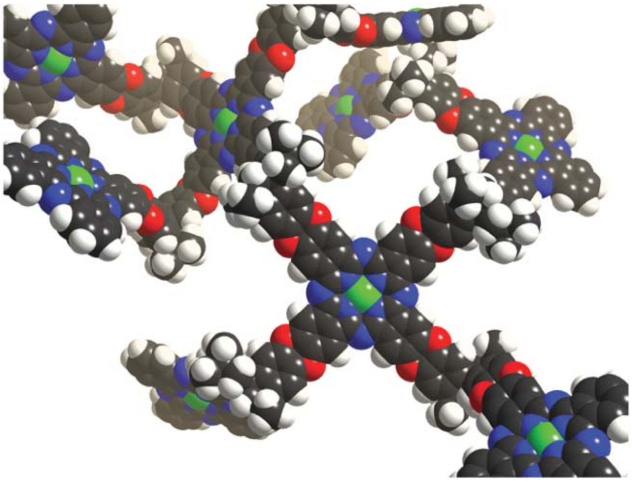


Fig. 1 A molecular model of the phthalocyanine-based PIM.

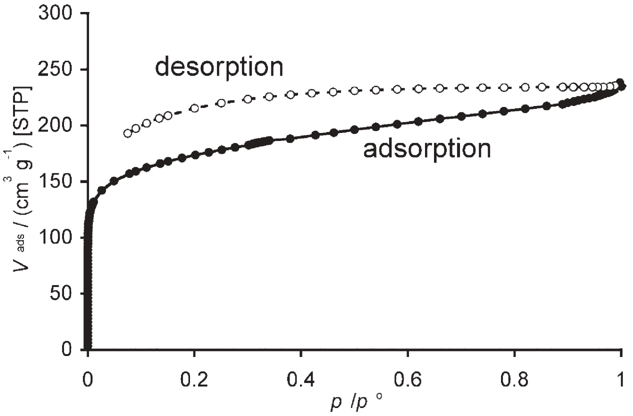
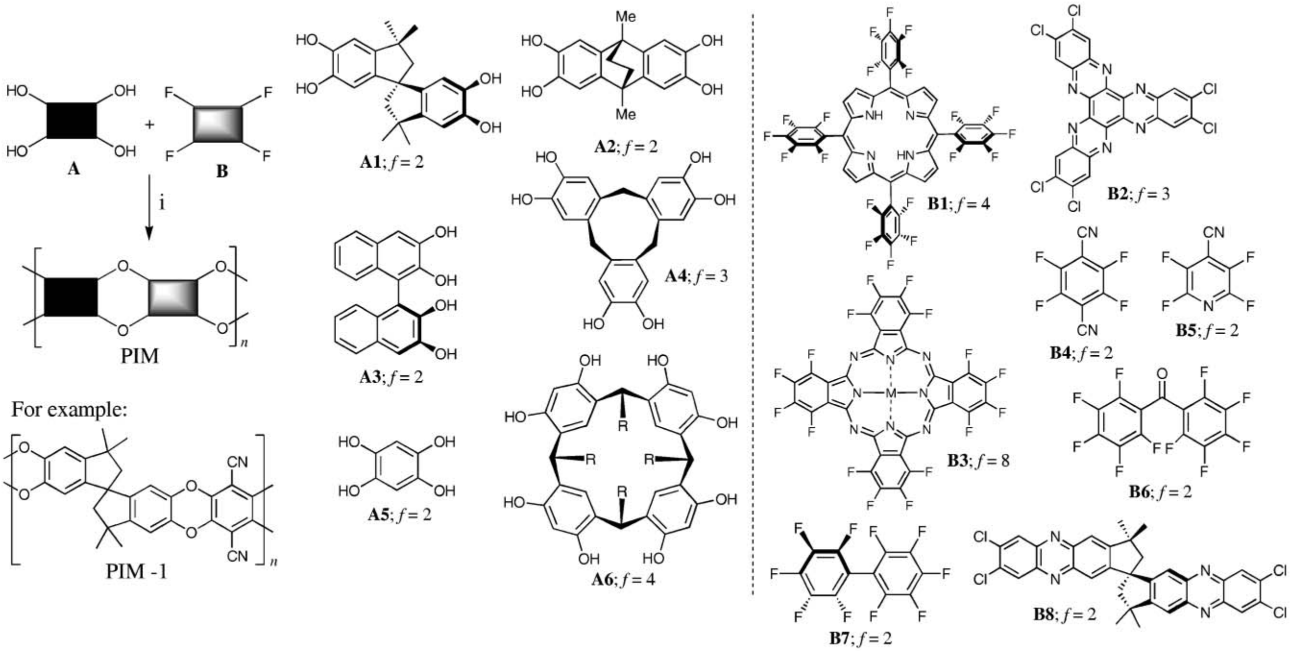


Fig. 2 The nitrogen adsorption isotherm at 77K for Pc-network-PIM (with M = Co^{2+}). The equivalent volume of adsorbed nitrogen at STP *versus* the relative pressure is plotted. From the isotherm a BET surface area of 650 m^2 g^{-1} can be calculated. The shape of the isotherm and the large volume of nitrogen adsorbed at low relative pressure indicates microporosity.

structure—as depicted by the model shown in Fig. 1. Nitrogen adsorption measurements (*e.g.*, Fig. 2) show that the materials have high surface areas (in the range 500–1000 m^2 g^{-1}) with very significant adsorption at low relative pressure ($p/p° < 0.01$) indicating microporosity.[15]

Following on from the successful preparation of these phthalocyanine-based network polymers of intrinsic microporosity (Pc-Network-PIMs), other rigid structures were investigated as components suitable for maintaining microporosity. For example, metal-containing porphyrins are an important family of catalysts and can display similar activity to that of the cytochrome P450 enzymes, such as alkene epoxidations and hydrocarbon hydroxylations.[23] These synthetic transformations are achieved using environmentally benign oxidants such as oxygen or hydrogen peroxide, therefore the possibility of useful heterogeneous catalysis make porphyrins desirable components of a microporous material. In this context, the type of metal cluster chemistry used by Yaghi has been exploited to prepare microporous MOFs that incorporate catalytically active porphyrin units.[24] However, porphyrin synthesis, unlike phthalocyanine formation, is a low-yielding reaction that is unsuitable for polymer network assembly. Instead, rigid spirocyclic linking groups were introduced directly between preformed porphyrin subunits *via* the efficient dioxane-forming reaction between the meso-tetrakis(pentafluorophenyl)porphyrin (monomer **B1**; Scheme 2) and the spirocyclic monomer **A1**. Although the resulting polymer is not wholly composed of fused rings, the restricted rotation about the single carbon–carbon bond at the meso-positions of the porphyrin prevents structural



Scheme 2 Synthesis and properties of PIMs. *Reagents and conditions*, i. Monomer **A**, Monomer **B**, K_2CO_3, DMF.

Table 1 Synthesis and properties of PIMs. *Reagents and conditions*, i. Monomer **A**, Monomer **B**, K_2CO_3, DMF

Monomers			Insoluble network/Soluble polymer	[a]Molecular mass M_w (g mole^{-1})	Surface area (BET; m^2 g^{-1})	Abbreviation	Analysed properties	Ref.
A	B	f_{av}						
A1	**B1**	3	Network	—	1000	Por-network-PIM	Catalysis	16
A1	**B2**	2.5	Network	—	820	HATN-network-PIM	Catalysis; adsorption	17,21
A1	**B3**	3	Network	—	500	Mpc-network-PIM	Catalysis	—
A1	**B4**	2	Soluble	$>200 \times 10^3$	760	PIM-1	Membranes; H_2-adsorption	18–21
A1	**B5**	2	Soluble	$>100 \times 10^3$	750	—	—	—
A1	**B6**	2	Soluble	170×10^3	560	PIM-3	—	19
A1	**B7**	2	Soluble	36×10^3	600	PIM-2	—	19
A1	**B8**	2	Soluble	$>100 \times 10^3$	750	PIM-7	Membranes	20,22
A2	**B2**	2.5	Network	—	750	HATN-Network-PIM-2	Catalysis	—
A3	**B4**	2	Soluble	5×10^3	450	PIM-4	—	19
A4	**B4**	3	Network	—	830	CTC-network-PIM	H_2-adsorption	21
A5	**B7**	2	Soluble	[b]	550	PIM-6	—	19
A6	**B4**	3	Network	—	800	Calix-network-PIM	—	—
A6	**B4**	2	Insoluble	—	2	—	—	19

[a] As measured by GPC *versus* polystyrene standards. [b] Insoluble in GPC solvents.

relaxation and maintains an open structure—as demonstrated by the high surface areas of the resulting Network-PIM ($\sim$1000 m^2 g^{-1}).[16]

It became clear that the dioxane formation reaction used for the synthesis of porphyrin-network-PIM offers a general reaction for the preparation of PIMs from appropriate rigid monomers (*e.g.* **A1**–**A6**) and fluorinated (or chlorinated) aromatic monomers (*e.g.* **B1**–**B8**) as shown in Scheme 2 and Table 1.[22] For microporosity, at least one of the rigid monomers must contain a site of contortion, which may be a spiro-centre (*e.g.* **A1** and **B8**), a single covalent bond around which rotation is hindered (*e.g.* **A7**, **B1** and **B7**) or a non-planar rigid skeleton (*e.g.* **A2**, **A4** and **A6**). If two planar monomers are reacted (*e.g.* **A5** with **B4**) a non-porous material results. To obtain an insoluble network polymer, the average functionality (f_{av}) of the monomer combination should be greater than two ($f_{av} > 2$)—for dioxane formation each pair of adjacent hydroxyl or fluorine substituents count as a single functional group. The non-exhaustive 'pick-and-mix' range of successful monomers includes pre-formed, fluorinated phthalocyanine **B3**, the tridentate ligand hexachlorohexaazatrinaphthylene (HATN; **B2**) and rigid hydroxylated monomers, such as cyclotricatechylene (CTC; **A4**) or calixresorcarene **A6**, that possess cavities for hosting molecules.

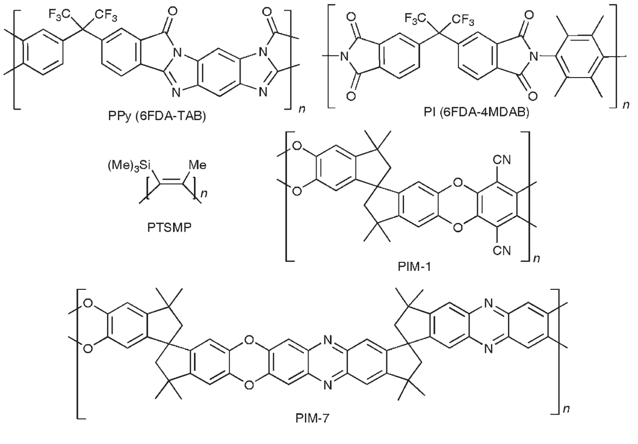
Soluble polymers of intrinsic microporosity

The microporosity within Network-PIMs, like that of other microporous materials, is maintained by a robust network of covalent bonds. Generally, non-network polymers pack space efficiently because the macromolecules can bend and twist to maximise intermolecular interactions. However, it has long been recognised that some polymers can possess large amounts of void space, which is usually referred to as free volume. It is reasonable to anticipate that above a certain amount of free volume, the voids would be interconnected and therefore the polymer will behave as a conventional microporous material despite the lack of a network structure.[25] Such a material could be soluble like an ordinary polymer, which would facilitate solution-based processing and which would provide an advantage over other microporous materials.

Therefore, it was of interest to prepare non-network polymers, using the same dioxane-forming polymerisation reaction, from various combinations of the bifunctional monomers (Scheme 2; f_{av} = 2), which had proved successful in forming Network-PIMs. It was found that if at least one of the two precursor monomers contains a 'site of contortion' (*e.g.* **A1**, **A3**, **B7** or **B8**), the resulting polymer is microporous as a powdered solid (surface areas 500–850 m^2 g^{-1}; Table 2).[19] These PIMs confirm that a network structure is not necessary for the generation and maintenance of microporosity within an organic material. Instead microporosity can arise simply from a polymer whose molecular structure is highly rigid and

Table 2 Structures and gas permeability data for a range of glassy polymers of interest for gas separation membranes

Polymer	$P(O_2)$ (Barrer)[a]	$\alpha(O_2/N_2)$	$D(O_2) \times 10^8$ (cm^2 s^{-1})	$S(O_2) \times 10^3$ (cm^3(STP)/cmHg	Ref.
PPy (6FDA-TAB)	15	5.9	7	21	30
PI (6FDA-4MDAB)	122	3.4	66	19	31
PTMSP	9000	1.4	5200	15	27
PIM-1	380	4.0	82	46	20
PIM-7	190	4.5	62	30	20



[a] Barrer = $\times 10^{-10}$ cm^3(STP) cm^{-1} s^{-1} cmHg^{-1}

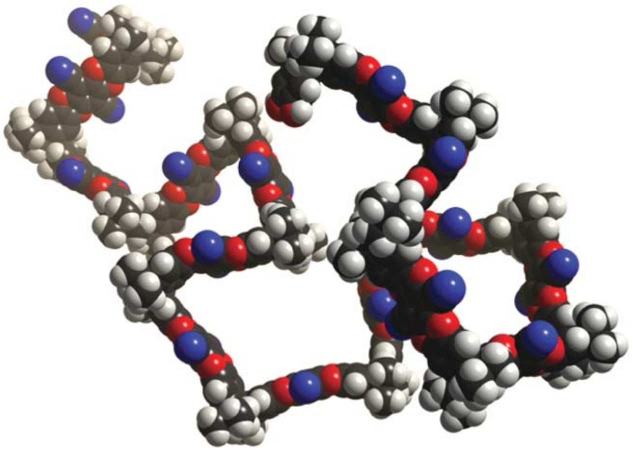


Fig. 3 A molecular model of a small fragment of PIM-1 showing its rigid and contorted structure.

contorted so that space-efficient packing in the solid state is frustrated (Fig. 3). In particular, the lack of rotational freedom along the polymer backbone ensures that the macromolecules cannot rearrange their conformation to collapse the open structure of the material. Differential scanning calorimetry shows no glass transition or melting point for each of the polymers and samples of powdered material heated to below their decomposition temperatures (300 °C for 24 h), or left for prolonged periods of time (>1 year) under ambient conditions, display similar surface areas to freshly precipitated samples. Thus, so long as the polymer's molecular structure remains intact, its intrinsic microporosity is maintained.

Despite their rigid structures, these PIMs are freely soluble in some organic solvents, which allow an estimation of their average molecular mass by gel permeation chromatography. The highly fluorescent spiropolymer, denoted PIM-1, derived from monomers **A1** and **B4**, which consists of a completely fused ring structure, proved to be of particularly high molecular mass (Table 1), which confirms the exceptional efficiency of the dioxane-forming polymerisation reaction. The high molar mass and good solubility of PIM-1 and PIM-7 (from monomers **A1** and **B8**), allow conventional solution-based polymer processing techniques to be applied. For example, robust, self-standing films of high optical clarity and high surface area (650 m^2 g^{-1}) can be prepared by simply casting from solution (Fig. 4).[18] Dynamic mechanical thermal analysis of a cast film of PIM-1 shows a tensile storage modulus, E', of about 1 GPa, in the range expected for a glassy polymer; a value that hardly decreases as the temperature is increased up to 350 °C in air. As described below, these free-standing films are useful as membranes for various separation processes.

Gas permeability and separations

The study of the gas permeability of polymers is a well-established technological field due to the extensive commercial interest in using polymer-derived membranes for gas separations. Over the past four decades an enormous volume of data has been compiled on the two main performance indicators of a polymer: the permeability coefficient P(x) (units: Barrer = 10^{-10} cm^3(STP) cm^{-1} s^{-1} $cmHg^{-1}$) for a particular gas (x) and the selectivity of one gas (x) over another (y), which in most cases is ideal selectivity, α(x/y) = P(x)/P(y), derived from single gas permeability measurements. For a useful polymer membrane it is desirable to have both high permeability and high selectivity.[26]

Fig. 4 A self-standing film of PIM-1 cast from a solution of THF.

Gas permeation through polymer membranes is frequently discussed in terms of a simple solution-diffusion model, for which P(x), is the product of a diffusion coefficient, D(x), and a solubility coefficient, S(x). In terms of the solution-diffusion model, selectivity may arise either through the solution term (solubility selectivity) or through the diffusion term (mobility selectivity). A polymer held above its glass transition temperature (*e.g.* polydimethylsiloxane—PDMS) exists in a rubbery state and has a large amount of free volume due to transient voids existing between the highly mobile polymer chains, therefore, values of D are relatively high and the mobility selectivity is low. On the other hand, most polymers held below their glass transition temperatures possess only small amounts of free volume and consequently exhibit low values of D and show a high mobility selectivity, smaller gas molecules diffusing more rapidly than larger ones. For gas separations, most attention has been paid to membranes derived from such glassy polymers, due to their higher selectivities. However, there are a few examples of 'ultrapermeable' glassy polymers, best represented by the much studied polyacetylene derivative poly(1-trimethylsilyl-1-propyne) (PTMSP) which has been the focus of considerable fundamental and applied interest, especially for membrane applications.[27]

Unfortunately, highly permeable polymers such as PTMSP are generally of low selectivity and *vice versa.* Robeson has quantified this trade-off by developing the idea of an upper bound in double logarithmic plots of selectivity against permeability.[28] Robeson's 1991 upper bound for O_2/N_2 is shown in Fig. 5, together with more recent data for polymers that perform close to, or exceed, this upper bound. The data for PIM-1 and PIM-7 are also plotted. As might be expected for microporous materials, films of PIM-1 ($P(O_2)$ = 380 Barrer) and PIM-7 ($P(O_2)$ = 180 Barrer) are highly gas permeable with only PDMS and the 'ultrapermeable' polymers such as PTMSP demonstrating higher overall gas permeabilities.[20] In addition, PIM-1 and PIM-7 show substantially higher selectivities ($\alpha(O_2/N_2)>3.0$) than other polymers of similar

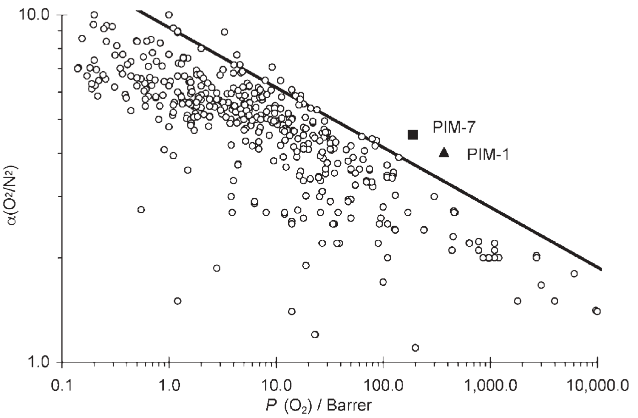


Fig. 5 The Robeson plot showing the trade-off between polymer gas permeability and ideal selectivity for oxygen *versus* nitrogen. The empirical upper bound line is shown and is based upon the polymers that demonstrated the best selectivity for a given permeability in 1991. For separation membranes it is desirable to obtain polymers whose data points lies above the upper bound line and towards the top right-hand side of the plot.

permeability, and represent a significant advance across Robeson's upper bound plot for O_2/N_2. PIMs also lie near to or above the upper bound line for several other commercially important gas combinations including CO_2/CH_4, H_2/N_2 and H_2/CH_4. This behaviour indicates that PIMs are different to the many hundreds of polymers that have been investigated for gas permeability and it is of interest to establish the cause of this difference.[22]

It has been noted that polymers which lie on or close to Robeson's upper bound all possess very rigid molecular structures (Table 2).[29] These include PTMSP,[27] polypyrrolones (*e.g.* 6FDA-TAP)[30] and certain polyimides (*e.g.* 6FDA-4MDAB)[31] within which rigidity is engineered by the use of trifluoromethyl and methyl substituents to restrict rotation within the polymer backbone. In contrast rubbery polymers with flexible backbones (*e.g.* PDMS) lie well below the upper bound. Polymers that function well with one pair of gases usually also perform well with other pairs of gases. The slope of the upper bound plot relates to the kinetic diameters of the gases involved. Freeman has developed a theory to rationalize these observations and justify an empirical principle that to obtain the best permeability/selectivity properties one needs to create a polymer structure with a stiff backbone (which enhances mobility selectivity at the expense of diffusivity) whilst also disrupting interchain packing (to improve permeability).[29] This design principle is taken to the extreme with PIM-1 and PIM-7, for which rigidity and the prohibition of rotation are ensured by their fused ring structures whilst the spirocyclic sites of contortion disrupt inter-chain packing.

For the separation of O_2 and N_2 the most important factor is the mobility selectivity, which favours the smaller oxygen molecule (diameter = 0.346 nm) rather than the larger nitrogen molecule (diameter = 0.364 nm) and, for a microporous polymer, is primarily dependent on the size distribution of the micropores. For PIM-1 and PIM-7 it is evident that the pore size is smaller than that found in the microporous ultrapermeable polymers such as PTMSP for which the high permeability arises from very large diffusion coefficients. PTMSP also exhibits microporous character in low temperature N_2 sorption analysis, but there are differences in the sorption behaviour at very low relative pressures that suggest a larger pore size for PTMSP (7–12 nm) as compared to the PIMs (5–7 nm). For PIM-1 and PIM-7 the contribution of solubility selectivity in favour of oxygen is small, but the overall values of solubility are extraordinarily high ($S(O_2) > 0.03$ cm^3 cm^{-3} cmHg^{-1}), significantly higher than the values typically encountered with other polymers ($S(O_2) < 0.02$ cm^3 cm^{-3} cmHg^{-1}).

Adsorption of organics

Being organic microporous materials with amorphous structures related to that of activated carbon, it was anticipated that the Network-PIMs should be suitable for the adsorption and separation of organic compounds and this was confirmed by measuring the adsorption of phenol from aqueous solution. This process is of environmental relevance as phenols are common contaminants of wastewater streams from industrial processes. The HATN-network-PIM, of surface area 830 m^2 g^{-1}, derived from the spiro-monomer **A1** and HATN **B2**, adsorbs up to 5 mmol g^{-1} of phenol from solutions of initial concentration of 0.2 mol L^{-1} (*i.e.* 0.5 g of phenol for 1 g of Network-PIM).[17] In addition, this material can be used for the efficient removal of phenol from water at low concentration (5–20 × 10^{-4} mol L^{-1}). Similar results (*e.g.* ~3 mmol g^{-1} of phenol is adsorbed from solutions of initial concentration of 0.1 mol L^{-1}) are obtained from PcCo-network-PIM. These results are comparable to those obtained from activated carbons. Interestingly, the adsorption of dyes from aqueous solution by PcCo-network-PIM shows a distinct size exclusion effect with no significant adsorption of the large dye Napthol Green B (diameter ~ 1.0 nm). In contrast activated carbons can adsorb this dye efficiently. The enhanced size-selectivity of the PIM is due to its relatively narrow micropore size distribution.

The removal of phenol from aqueous solution has also been achieved by pervaporation using the robust self-standing films derived from soluble PIM-1 or PIM-7 as membranes.[18] Pervaporation is a separation process in which the feed is a liquid mixture and a vacuum is applied to the opposite side of the membrane to remove permeate as a vapour, which is then condensed and collected. In Fig. 6 it can be seen that, with the PIM-1 membrane, the permeate was enriched in phenol up to tenfold, which demonstrates that the membrane is strongly organophilic (*i.e.* selective for organic compounds over water) which is unusual for a polymer membrane derived from a glassy polymer. Membranes derived from PIM-7 behave similarly.

Heterogeneous catalysis

For Network-PIMs containing either phthalocyanine, porphyrin or hexaazatrinaphthylene subunits, it is possible to introduce appropriate transition metal-ions for catalytic activity. Preliminary studies on the degradation of hydrogen peroxide using PcCo-network-PIM show a greatly enhanced rate as compared to a non-porous microcrystalline model

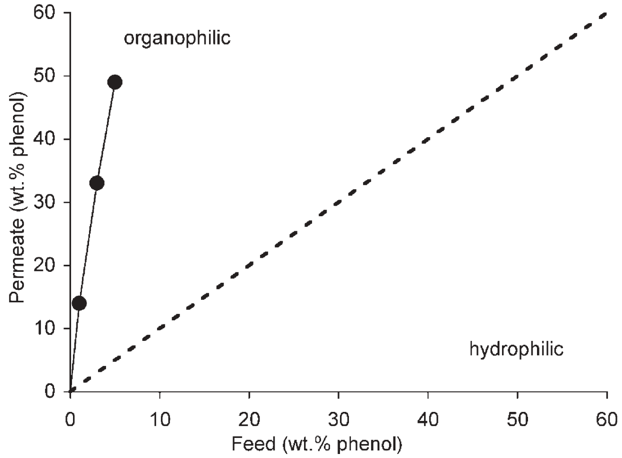


Fig. 6 Pervaporation-based separation of phenol from aqueous solution using a membrane derived from PIM-1. Generally, the efficiency of separation may be expressed as a separation factor, $\alpha = (Y_o/Y_w)/(X_o/X_w)$, where (Y_o/Y_w) is the weight ratio of organic compound to water in the permeate and (X_o/X_w) is the weight ratio of organic compound to water in the feed. Values of α of 16–18 were obtained at temperatures in the range 50–80 °C and feed compositions in the range 1–5 wt.% phenol.

compound (Fig. 7). In addition, this network-PIM is both efficient and selective for the catalysis of the oxidation of cyclohexene to 2-cyclohexene-1-one (78% yield after 48 h), even when compared to the activity of cobalt phthalocyanine-based homogeneous catalysts. The CoPc-network-PIM formed by the original phthalocyanine-forming reaction (of surface area = 650 $m^2\ g^{-1}$) proved to be a more efficient catalyst than that prepared *via* a dioxane formation using the pre-formed fluorinated phthalocyanine**3B** (surface area = 500 $m^2\ g^{-1}$).

The hexaazatrinaphthylene (HATN) subunit is a well-established ligand capable of forming a complex with up to three transition metal ions. Exposing the orange HATN-network-PIM to a chloroform solution containing bis(benzonitrile) palladium(II) dichloride gave a highly coloured material with a mass loading of palladium of 26%. Nitrogen adsorption analysis of the material subsequent to metal adsorption gave a specific surface area of 347 $m^2\ g^{-1}$. Much of the loss of specific surface area can be attributed to the gain in mass (65%) of the material rather than a loss of intrinsic microporosity. It was found that the initially prepared material catalysed a model Suzuki aryl–aryl coupling reaction very efficiently but that around 20% of the metal was leached from the PIM. Subsequent runs using the same material also efficiently catalysed the reaction (up to four runs) but without further loss of metal or reactivity. Fig. 8 shows the kinetics of these runs as compared to the standard homogeneous $Pd(Ph_3)_4$ catalyst and shows that, unlike the homogeneous catalyst high conversion can be achieved within 24 h without the need for the addition of fresh catalyst.

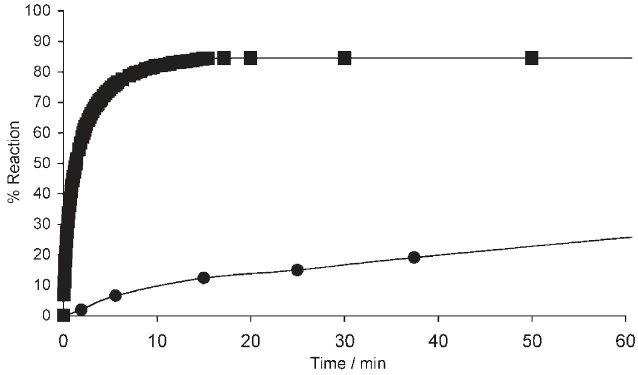


Fig. 7 Dependence of extent of reaction on time for the degradation of H_2O_2 (0.74 mol dm^{-3}, T = 30 °C) with (●) low molar mass cobalt phthalocyanine (CoPc) and (■) CoPc-network-PIM as catalyst. Oxygen evolution measured with a gas burette.

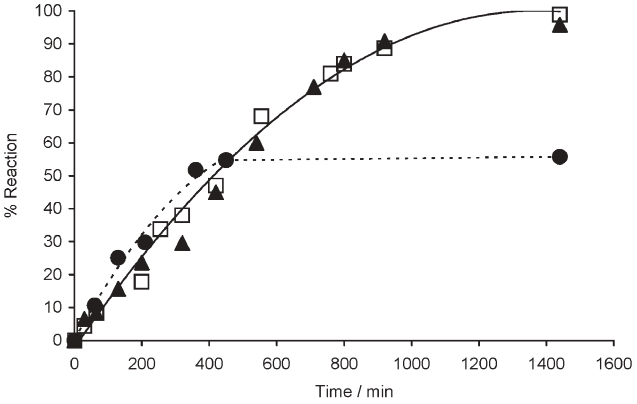


Fig. 8 Dependence of extent of reaction on time for the Suzuki aryl–aryl coupling reaction between 4-fluorobromobenzene and 4-methoxyphenylboronic acid catalysed homogeneously by (●) $Pd(PPh_3)_4$ and heterogeneously by palladium-containing HATN-network-PIM (▲) recycled twice and (□) recycled three times.

Similar palladium-containing materials of even higher specific surface area can be derived from PIM-7 by exploiting the ability of its phenazine subunits to act as a ligand for metal ion coordination. Thus, the addition of bis(benzonitrile) palladium(II) dichloride to a yellow solution of PIM-7 causes an immediate precipitation of a red solid which is insoluble in all organic solvents. This material contains over 20% by mass Pd^{2+} and has a surface area of 650 $m^2\ g^{-1}$. It can be deduced that the Pd^{2+} ion is acting as a cross-link between the PIM macromolecules to give a network material. Of interest is the observation that a solvent cast-film of PIM-7, swollen in methanol, can also be cross-linked by Pd^{2+} ions to give an insoluble network. This process has potential for the fabrication of reactive membranes.

Hydrogen storage

A major technical obstacle to the widespread use of hydrogen (H_2) as a non-polluting fuel for cars is the lack of a safe and efficient system for on-board storage. Of the many potential solutions being investigated,[32] an attractive possibility is a system based on the reversible adsorption of H_2 on the internal surface of a microporous material. At present the quantity of H_2 that can be adsorbed onto any type of microporous material falls below the requirements of a practical H_2 storage system. Hence, there is an urgency to develop materials which can be tailored to provide a structure and chemical composition suitable for the specific demands of H_2 physisorption.

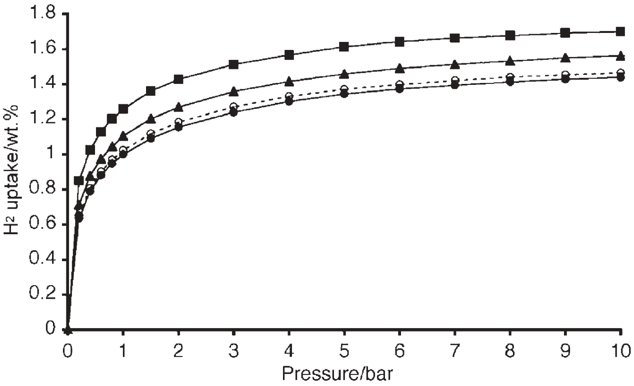


Fig. 9 The H_2 adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K for (●) PIM-1, (▲) HATN-network-PIM and (■) CTC-network PIM, obtained using gravimetric analysis.

The adsorption of H_2 was measured on three PIMs (PIM-1, HATN-network and CTC-network) at 77K using both volumetric and gravimetric techniques (Fig. 9) with consistent results for each sample. The adsorption isotherms show that the three PIMs each adsorb significant quantities of H_2 (maximum = 1.7% by mass) at relatively low pressures with saturation being reached at less than 10 bar pressure and with most of the adsorption taking place below 1 bar.[21] Calculations show that the maximum number of hydrogen molecules adsorbed per fused-ring of the polymeric repeat unit is approximately 0.5 H_2 per ring. However, the spread of values from 0.43 (HATN-network), 0.5 (PIM-1) to 0.56 (CTC-network) suggests that the greater predominance of smaller micropores (ultramicropores), resulting from the bowl-shaped CTC subunit, enhances H_2 adsorption.

The results show that these PIMs adsorb comparable amounts of H_2 to that of the best examples of zeolites[33] and MOFs[34] and, although their performance falls short of some very high surface area carbons, they adsorb comparable quantities of H_2 to carbons of similar surface area.[35] However, in order to attain practical hydrogen storage materials from PIMs, it will be necessary to engineer examples with larger *accessible* surface areas (>2000 m^2 g^{-1}) whilst maintaining the predominately ultramicroporous structure necessary to retain the beneficial multi-wall interactions with H_2 molecules. We are currently engaged in this interesting challenge.

Conclusions

The area between two established fields of technology is often a stimulating and rewarding research environment. We believe that PIMs effectively bridge the gap between conventional microporous materials and polymers because they possess properties common to both classes of material. The potential offered by the structural diversity of PIMs, which can be controlled simply by the choice of monomer precursors, remains largely unexplored. Nevertheless, the few examples that have been studied suggest an enticing prospect of readily processed, bespoke organic microporous materials designed to adsorb, or react with, target molecules using the principles of molecular recognition. It can be assumed that once a potentially useful material is recognised its performance can be tuned incrementally by synthesis. Ultimately, the concept of PIMs may be developed to provide materials to engage in highly specific processes that mimic the sophisticated 'lock-and-key' receptor sites found in enzymatic catalysis.

PIMs provide another example of the utility of amorphous organic materials. The fascinating and beautiful crystalline mimics of zeolites that increasingly grace the pages of chemistry journals will stimulate welcome interest in organic microporous materials. Ultimately however, commercial applications may result from materials that can be readily fabricated into useful forms. A lesson to be learned from the development of polymers and organic electronic materials is that it pays to play to the strengths of organic materials (*e.g.*, processability and the exquisite control over structure and function *via* synthesis). The PIMs concept is built upon the firm foundations of polymer technology and we believe that it offers a highly practical approach to organic microporous materials.

Acknowledgements

We thank the EPSRC for funding. We thank all the postdoctoral research assistants and students who contributed to this work including: Dr Saad Makhseed, Dr Kadhum Msayib, Dr Carin Tattershall, Dr Bader Ghanem, Dr Khalid Mahmood, Verena Maffei, Helen Kingston, Dong Wang, Kevin Reynolds, Laura Grant, Siren Tan, Alssalhen Elabas, Jia He, Bert Jones, Sarah Hall, Madeeha Iqbal, Nosheen Zahra and Catherine Kelly. We thank our collaborators, Dr David Book, Ms Henrietta W. Langmi and Dr Allan Walton (Department of Metallurgy and Materials, The University of Birmingham) for hydrogen adsorption measurements and Dr Detlev Fritsch (GKSS Research Centre, Geesthacht, Germany) for gas permeability data and useful discussions.

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