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# The structure-property relationships of Polymers of Intrinsic Microporosity (PIMs)

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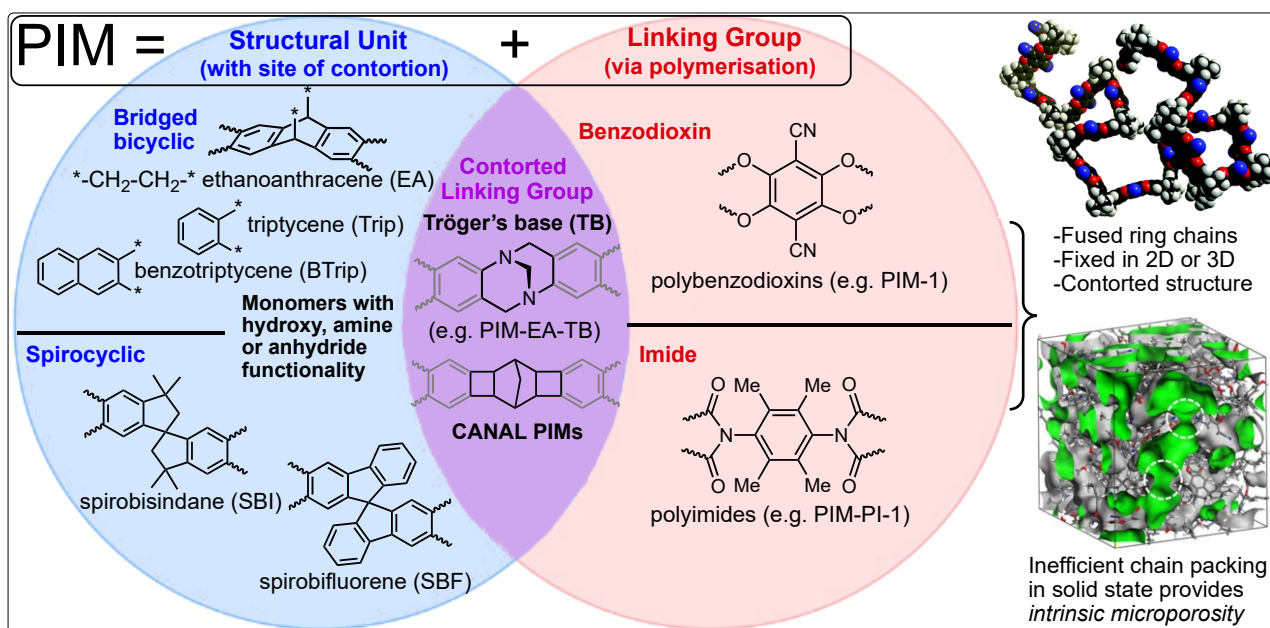
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## Abstract

Based on almost 20 years of published research, the structure-property relationships of Polymers of Intrinsic Microporosity (PIMs) are considered. Following an analysis of the structure of the archetypal PIM-1 and how it contributes to its now well-understood properties, the key properties of solubility, thermal properties, gas adsorption and gas permeability are related to the structures of more recently prepared PIMs. In order to deliver their technological potential, it is recommended that further synthetic effort should focus both on broadening the structural diversity of PIMs and providing synthetically accessible variants.

## 1. Introduction

Polymers of Intrinsic Microporosity (PIMs) comprise a unique class of macromolecule which developed from work on porous polymer networks published nearly 20 years ago[1]. A recently revised definition of a PIM is a “*Polymer that is composed of a fully (or predominantly) fused-ring macromolecular chain that is fixed in a 2D or 3D random coil conformation due to sites of contortion, such as bridged bicyclic or spirocyclic units, so that they pack space inefficiently in the solid state*” (Fig. 1) [1]. The concept of PIMs provides organic materials with a unique combination of properties including good solubility, exceptional chain rigidity, and high free volume. As reviewed in the articles within this special issue, the synthesis, properties and applications of PIMs have been the subject of over 900 publications and 80 patents with research activity accelerating in recent years. Importantly, PIMs are directly solution-processable into useful forms suitable for the fabrication of separation membranes and these can act as efficient molecular sieves due to the rapid and selective transport of small molecules. Several types of step-growth polymerisation may be used to prepared PIMs, predominately those based on the formation of dibenzodioxin[2], Trögers Base (TB)[3] and imide linkages (Fig. 1) [4]. The more recently developed Catalytic Arene Norbornene Annulation (CANAL) polymerization provides another valuable method of preparing ladder polymers which can be defined as PIMs[5]. This short article will examine the relationship between the molecular structure of PIMs resulting and their key properties of solubility, microporosity, and gas permeability.

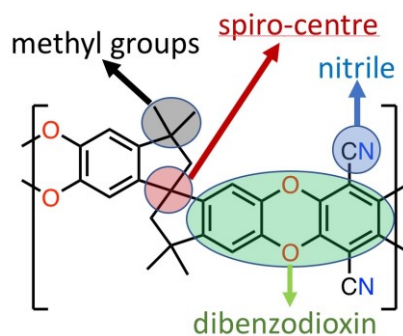


**Figure 1.** The modular concept of PIMs in which structural units are fused together via linking groups to produce a rigid and contorted macromolecule which cannot fill space efficiently[1].

## 2. Structure property relationship of PIMs

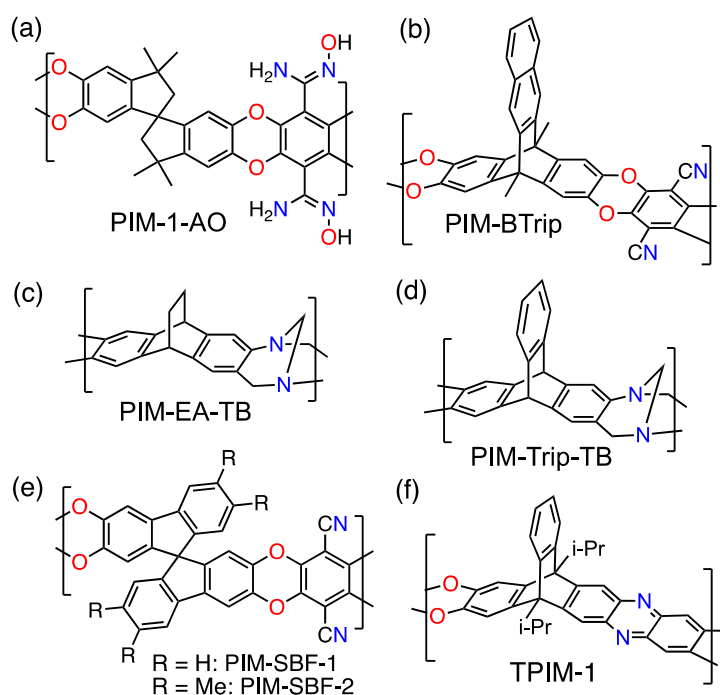
**2.1. How the properties of PIM-1 arise from its structure.** PIM-1, the archetypal PIM, was originally the outcome of curiosity-driven synthesis[2], however, its ease of preparation from two commercially available precursors has resulted in it being the focus of over half of the published studies on PIMs. Hence, it is of interest to analyse the structural features of PIM-1 (Fig. 2) to understand how they contribute to its properties. The fused-ring structure of the dibenzodioxin linkage and the spiro-centre provide the defining features of rigidity and contorted back-bone, respectively, which result in the generation of intrinsic microporosity. The methyl and nitrile groups are consequences of synthetic convenience, with the former resulting from the use of the cheaply available 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1-spirobisindane (the condensation product between catechol and acetone) and the latter from the commercial 2,3,5,6-tetrafluoroterephthalonitrile co-monomer. The nitrile groups provide the necessary activation for the efficient aromatic nucleophilic substitution reaction that forms the dibenzodioxin linking groups during the step-growth polymerisation. The four methyl groups per repeat unit of PIM-1 increase inter-chain distances and provide high solubility (the equivalent PIM without these methyl groups is insoluble in common organic solvents)[6]. In addition, the methyl groups occupy the benzylic sites of the polymer thereby greatly enhancing thermal oxidative stability by preventing facile free-radical hydrogen abstraction. In contrast, the strong dipole-dipole interactions between nitrile groups will enhance inter-chain cohesion. The nitrile group is also useful for a variety of post-synthetic modifications of PIM-1[7] via hydrolysis to give

amide[8] or carboxylic acid[9], reduction to give amine[7], or reaction with hydroxylamine to give amidoxime (e.g. PIM-1-AO; Fig. 3a)[10]. The latter modification is useful in providing inter-chain cohesion via hydrogen bonding, which has proven useful for suppressing plasticisation at high pressure of CO<sub>2</sub> during natural gas purification[11], but without sacrificing good solubility in organic solvents. Two very obvious properties of PIM-1 are its yellow colour ( $\lambda_{max}$ = 420 nm) and strong green fluorescence at ~480 nm, which arise from the benzodioxin unit[12], as shown by the loss of colour on modification of the nitrile group (e.g., PIM-1-AO is colourless). PIM-1 is also fluorescent as a solid although this property appears to be lost from films over time as a consequence of physical ageing causing greater self-quenching.



**Figure 2.** The key structural features of PIM-1 which contribute to its properties.

**2.2. Solubility.** Rigid fused-ring polymers have a reputation for insolubility, however, solubility is a defining property of a PIM. Solubility of PIMs is promoted by the same design features that ensure inefficient packing and the generation of intrinsic microporosity, with the rigid and contorted chain structure also reducing inter-chain cohesion and encouraging the absorption of solvent to aid dissolution. PIM-1 is readily soluble in the standard organic solvents, tetrahydrofuran and chloroform, at ambient temperature. Most other benzodioxin-based PIMs are less soluble, such as those derived from bridged bicyclic components (e.g. PIM-BTrip; Fig. 3b) but can be dissolved in a high boiling aromatic solvent such as quinoline, from which then can be processed into films. TB-based PIMs, such as PIM-EA-TB (Fig. 3c) and PIM-Trip-TB (Fig. 3d), tend to have good solubility only in chloroform and dichloromethane, likely due to strong H-bonding interaction between the tertiary amine and the solvent[13]. A mixed solvent system of chloroform and *n*-propyl lactate was successfully used to prepare electrospun fibres of PIM-EA-TB[14]. Amidoxime-modified PIM-1 (PIM-1-AO) is soluble in polar aprotic solvents such as DMF and DMSO, which is useful for the fabrication of self-standing films and electrospun fibres[15].



**Figure 3.** The structure of PIMs used to illustrate structure-property relationships.

**2.3. Thermal and mechanical properties.** In general, PIMs are thermo-oxidatively stable polymers degrading at temperatures greater than 250 °C in air. Exception are PIMs derived from ethanoanthracene components (e.g. PIM-EA-TB) for which the retro-Diels-Alder fragmentation of ethene occurs at ~200 °C leading to linear anthracene units within the polymer.[3] Glass transition temperatures ( $T_g$ ) are also very high for PIMs and the glass transition can be very difficult to locate prior to thermal decomposition. However, the use of fast-scanning differential scanning calorimetry was used to establish that PIM-1 and PIM-EA-TB have a  $T_g$  of 371 °C and 390 °C, respectively[16]. These are some of the highest values for a solution-processable material. An additional sub- $T_g$  transition at ~200 °C has been suggested for PIM-1 based on dielectric spectroscopy, which was attributed to enhanced interactions between the dibenzodioxin units and results in loss of fluorescence via self-quenching.[17] It is notable that dibenzodioxin-based PIM derived from benzotriptycenes (e.g. PIM-BTrip) do not show strong fluorescence from their films, perhaps also indicating strong interchain interactions.

Insufficient data is available for a rigorous analysis of the structure-property relationship for the mechanical properties of PIMs, although it is likely that the flexibility of the spiro-centres contributes to the robustness of PIM-1[18] and that Young's modulus is enhanced by the use of more rigid components such as those found in PIM-EA-TB[3]. Similar conclusions were reached for the analysis of highly rigid PIM-BTrip using the nanoindentation mode of atomic force microscopy, which is a useful technique for obtaining mechanical data for PIMs when the scarcity of sample due

to synthetic complexity makes traditional stress-strain analysis difficult[19]. Nanoindentation can also be used for tracking the change in mechanical properties during physical ageing.

**2.3 Gas adsorption.** The significant adsorption of gases, particularly at low relative pressure ( $P/P_0 < 0.01$ ), is a defining feature of PIMs arising from the presence of free volume elements acting as micropores. Typically, the adsorption of nitrogen ( $N_2$ ) at 77 K and carbon dioxide ( $CO_2$ ) at 273 K are used to probe porosity with the resulting isotherm providing information on apparent internal surface area, pore size distribution and pore volume.[20] PIMs which possess high rigidity and components that result in larger inter-chain distances (e.g. structural units such as triptycene[21], benzotriptycene[22,23] or suitably placed methyl groups[24]) tend to demonstrate greater gas adsorption at low relative pressure. Also characteristic of PIMs is the continuous uptake of  $N_2$  on increasing relative pressure with a large hysteresis between the adsorption and desorption isotherms. These isotherm features are associated with swelling of the polymer during  $N_2$  uptake (i.e. *absorption*) and give information on the inter-chain cohesion within the PIM. For example, PIMs modified to possess amidoxime substituents (e.g. PIM-1-AO) show less  $N_2$  uptake at higher relative pressure and less hysteresis due to strong inter-chain hydrogen-bonding [10]. Such isotherms more closely resemble the classical Type-1  $N_2$  isotherm characteristic of microporous materials[20]. The modulation of swelling may be of particular importance for the use of PIM membranes in natural gas upgrading at high pressures where plasticization (i.e. swelling following absorption) reduces selectivity[11,25].

**2.4. Gas permeability and performance as gas separation membranes.** The gas permeability of PIMs is of interest due to their potential as membranes for gas separations.[26] For this application the performance of polymers is limited by the trade-off between gas permeability and the selectivity for one gas over another. This trade-off is best demonstrated by the standard Robeson plots of the permeability for gas  $x$  ( $\log P_x$ ) versus the selectivity for gas  $x$  over gas  $y$  ( $\log P_x/P_y$ ), with the best performing polymers defining the upper bound for each gas pair.[27] Overall, the development of PIMs has resulted in several revisions of the Robeson upper bounds with the 2008 revisions for multiple gas pairs using data from PIM-1.[28] The permeability-selectivity trade-off is a direct consequence of the continuum of size distribution of elements of free volume within polymers, which provide the transport paths for gases.[29,30] Hence, loosely chain-packed polymers, such as some polyacetylenes (e.g. poly(trimethylsilylpropyne), provide high permeability but low selectivity, whereas, polymers with tight chain-packing provide high selectivity but low permeability. For PIMs, a very neat illustration of the structure-property relationship for gas permselectivity comes from

comparison between the data from PIM-1, containing a spirobisindane (SBI) unit, with that from spirobifluorene-based PIMs (PIM-SBF-1; Fig. 3e)[24]. Simple molecular dynamic modelling, or the analysis of bond deformations in packing simulations[31], revealed that the spiro-linkage of the SBI unit is the most flexible part of PIM-1. Similar modelling showed that fusing a benzo group to the spiro-centre, to give an SBF unit, enhances rigidity.[32] Furthermore, polymer chain packing simulations predicted that placing four methyl groups on this benzo-unit (i.e. PIM-SBF-2; Fig. 3e) would result in greater free volume inter-chain distances and this was verified by enhanced gas permeability relative to unsubstituted PIM-SBF-1[24,33]. The resulting PIMs based on the more rigid SBF component provide data significantly above the 2008 upper bounds for most gas pairs. PIMs with even greater chain rigidity are obtained from using bridged bicyclic components both as structural building units and, in the case of TB, as the linking group for the polymerisation (Fig. 1) [3]. In particular, data obtained from PIMs based on triptycene units, such as PIM-Trip-TB[34] and TPIM-1 (Fig. 3f)[35], show enhanced selectivity and were used to redefined the 2015 upper bounds for O<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub>. [36] In 2019 the upper bounds for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>, of relevance to post-combustion carbon capture and natural gas upgrading, respectively, were redefined based on the data from a series of ultrapermeable benzotriptycene-based PIMs with rigid 2D chains, which were shown by chain packing simulations to pack space less efficiently than similar PIMs with 3D contorted chains.[23,37] The success of increasing selectivity via enhanced PIM chain rigidity results from the greater thermal activation required to open sufficiently large apertures to allow larger gas molecules (CH<sub>4</sub> or N<sub>2</sub>) to move from one element of free volume to another, relative to that required for smaller gas molecules (He, H<sub>2</sub>, O<sub>2</sub> or CO<sub>2</sub>).[38,39] As a consequence of this thermally activated mechanism, very impressive separation performances can be obtained from PIM membranes at sub-ambient temperatures.[40-42]

### 3. Conclusions and Outlook.

The above concise analysis of PIM structure-property relationships focusses on the defining properties of solubility, thermal properties, gas adsorption and gas permeability. The assumption has been made that the PIM structure is close to its ideal structure, as represented in Fig.1 and Fig. 2, however for PIM-1, a closer analysis shows that cyclic formation, branching and cross-linking can have a strong influence over the resulting properties[43]. It is anticipated that a greater understanding of PIM structure-property relationships will result in the design and synthesis of polymers with enhanced performance that can be tailored to the requirements for a particular use. For example, emerging applications for PIMs in fuel cell[44] and battery technologies are driving intense current research activity.[45,46] Of particular interest is the use of PIMs as separators in redox flow batteries,

which are a potential solution to the large-scale storage of energy. PIMs have demonstrated that they allow the high permeability of small charge-carrying cations (e.g. Na<sup>+</sup> or K<sup>+</sup>) whilst blocking large redox-active molecules.[47,48] Satisfying these criteria require similar structural features to those of gas separation membranes so as to provide both rigidity and the generation of free volume but, additionally, the PIM design must also introduce charged and/or hydrophilic components to promote cation solubility and transport. Similarly, a recent study on developing PIMs as anode-stabilising interlayers within lithium batteries demonstrated the potential of diversity-oriented synthesis for the optimisations of structure-property relationships.[49] Clearly, for PIMs to realise their full technological potential, it is important for synthetic chemists to broaden their structural diversity. However just as important, is to learn the lesson taught to us by the many published studies on the properties and applications of our old friend PIM-1 (>450) that synthetic accessibility to these structurally diverse PIMs is required if they are to be fully investigated and exploited.

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A recent review on the importance field of PIM application in electrochemistry, fuel cells and batteries.

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Important paper showing the potential of diversity-oriented strategy in the synthesis of PIMs for an importance application.