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The Synthesis of Polymers of Intrinsic Microporosity (PIMs)

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Polymers of Intrinsic Microporosity (PIMs) are a class of Porous Organic Polymer (POP) that form microporous solids due to the inefficient packing of their rigid and contorted macromolecular chains. In contrast to other types of POP, PIMs are not comprised of a network of cross-linked covalent bonds so that they can be dissolved in organic solvents and processed into robust films, coatings or fibres. Here, over twelve years accumulated research on the synthesis of PIMs is reviewed. To date, three types of polymerisation reaction have been used successfully to prepare PIMs of sufficient molecular mass to form robust self-standing films. These involve the formation of (i) dibenzodioxin, (ii) Tröger's base and (iii) imide linkages between monomeric units. This rapid development of synthetic methods for preparing PIMs has been driven by their rich potential for numerous diverse applications and this synergistic relationship between synthesis and functionality is set to continue.

Polymers of intrinsic microporosity, synthesis, Porous Organic Polymers

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1 Introduction

The Microporous materials contain free volume consisting of interconnected pores of diameter less than 2.0 nm. Over recent years there has been increasing interest in the preparation of new microporous materials using *organic* components.^[1] For example, there are numerous different types of porous organic polymers (POPs) including structurally ordered Covalent-Organic-Frameworks (COFs) and amorphous network polymers such as Hypercrosslinked Polymers (HCPs), Microporous Conjugated Polymers (MCPs) and Porous Aromatic Frameworks (PAFs). Polymers of Intrinsic Microporosity (PIMs) generate porosity from their rigid and contorted macromolecular chains that do not pack efficiently in the solid state.^[2–5] PIMs differ from other types of POPs in that they do not possess a network structure and, hence, are often freely soluble in organic solvents. The sol-

ubility of PIMs allows them to be processed into self-standing films and coatings and, therefore, they are suitable for making devices such as sensors^[6,7] or for the fabrication of polymer membranes,^[8] particularly for gas separations^[9] but also for electrochemical applications.^[10,11] To date, around 300 papers have been published dealing directly with the synthesis, modeling, physical properties and applications of PIMs. In addition, there have also been numerous patent applications related to the preparation of PIMs or for inventions for which they play a crucial role. Notably, an end-of-life-service-indicator for 3M's disposable respirator cartridge for organic vapours became the first commercial application of PIMs in 2015.^[7] Here we focus on the research relating to the synthesis of PIMs and review the literature up to the end of 2016.

2 How to design a PIM

As noted above the design concept of PIMs requires that the non-network macromolecular structure is both rigid and

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contorted (i.e. non-linear). To maintain permanent microporosity it is also crucial to ensure that rotation along the polymer chain is prohibited via a fused ring structure, or strongly hindered by steric inhibition to rotation, to avoid conformation changes that would help the polymer to pack more efficiently. This dictates the use of both conformationally locked monomers and a polymerisation reaction that provides a linkage about which rotation is either prohibited (e.g. a fused ring) or severely restricted via steric hindrance. The sites of contortion necessary to avoid a linear structure can be provided by the monomer (e.g. the spiro-centres of PIM-1), the linking group (e.g. Tröger's base), or both. In principle many step-growth polymerisation reactions could be used to prepare PIMs but in practise only a few are of proven utility for the preparation of solution processable materials, such as cast films, and these are based on forming (i) dibenzodioxin (Section 3), (ii) Tröger's base (Section 4) and (iii) imide linkages (Section 5). PIMs derived from these three types of reactions are described below and specific information and references provided in the accompanying tables. However, other polymerisation reactions show promise including cross-coupling reactions to make conjugated PIMs (C-PIMs),^[12, 13] triazine formation,^[14] palladium-catalysed annulation^[15] and stepwise nucleophilic substitution of octafluorocyclopentene.^[16] In addition, interfacial polymerisation using simple ester or amide linkages but using suitable monomers to induce intrinsic microporosity is a promising technique for making ultra-thin membranes.^[17]

3 PIM polymerisation using dibenzodioxane formation

The first successful polymerization reaction to produce a soluble PIM involved the aromatic nucleophilic substitution (S_NAr) mechanism between a bisphenol (**A**) and a tetrahalide-containing monomer (**B**) to form dibenzodioxin-linked polymers (Table 1). This reaction was initially used to prepare microporous network polymers^[18-20] but was subsequently found to be capable of forming a fused-ring linking group with sufficient efficiency to provide solution processable ladder polymers of high average molecular mass.^[2, 8, 21] Generally, aromatic nucleophilic substitutions require the halide-containing monomer to be activated by an electron-withdrawing substituent (e.g. $-CN$, F , etc.).^[22] For example PIM-1, the archetypal PIM, is readily prepared by the reaction between the commercially available monomers 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane (**A1**) and 2,3,5,6-tetrafluoroterephthalonitrile (**B1**).^[2, 8] The original method of making PIM-1 (sometimes called the "low temperature method") involves mixing the two monomers in equimolar quantity in a solution of anhydrous dimethyl formamide (DMF) with a two-fold excess of finely powdered dry potassium carbonate at 50-60 °C for 24-72 hours. This relatively low temperature avoids the decomposition of DMF to dimethylamine, which is a sufficiently strong nucleophile to interfere with the reaction. The con-

centration of monomers is critical as at very high concentrations insoluble cross-linked material is produced whereas at low concentrations a large amount of cyclic oligomers of modest molecular mass are formed. The optimal concentration appears to be around 3 mmol of each monomer per 10-15 ml DMF. Alternatively, the very rapid "high temperature method", described by Guiver *et al.* involves the high-speed stirring of the monomer mixture in dimethyl acetamide at 155 °C with the addition of toluene to enable the continuation of stirring.^[23, 24] A recent report suggests dimethylsulfoxide as a non-toxic and more environmentally benign solvent for PIM synthesis with 120 °C suggested as the optimum reaction temperature.^[25] These polymerisation methods all provide PIM-1 with sufficiently high average molecular mass to provide mechanically robust solvent cast films (typically $M_n > 30 \times 10^3 \text{ g mol}^{-1}$ and $M_w > 100 \times 10^3 \text{ g mol}^{-1}$) and have been adapted for the synthesis of many PIMs using a wide range of bisphenols (**A1-A24**) and halide-based monomers (**B1-20**) (Table 1).

A modified "high temperature" method of continuous production of PIM-1 using a flow reactor has been patented, although the average molecular mass of the resulting polymer was modest ($M_n \approx 6 \times 10^3 \text{ g mol}^{-1}$).^[26] An intriguing report of a very rapid mechanochemical synthesis of PIM-1 requires further investigation due to the extraordinarily high molecular mass of the product, as measured by gel permeation chromatography ($M_n > 300 \times 10^3 \text{ g mol}^{-1}$), which suggests the formation of cross-linked nanogels.^[27] The film-forming properties of this material were not reported.

Alternative precursors for making PIM-1 have been used. For example, the tetra-silyl ether of bisphenol **A1**, gives PIM-1 via a fluoride-mediated reaction but the synthesis of the precursor appears to be an unnecessary additional synthetic step.^[28, 29] PIM-1 has also been prepared using an AB monomer (**AB4**), which avoids potential complications arising from non-equivalent stoichiometry during the conventional AA-BB monomer mixture but also involves an additional synthetic step.^[30] However, the use of AB monomers has been successfully used for making triptycene-based PIMs (**AB1-3**).^[31, 32] An elegant method of preparing PIMs with alternating bisphenol monomeric units involves the synthesis of a tetrafluoro monomer (**B20**) via the reaction between a bisphenol **A1** with an excess of **B1**.

Despite the remarkable solubility of many PIMs some combinations of monomers result in insoluble material.^[33] One example of such an insoluble PIM is that formed from monomers **A4** and **B1**.^[34] A partial solution to this problem can be the synthesis of copolymers using the monomer that results in an insoluble polymer in combination with a monomer that results in a PIM with good solubility (e.g. **A1**).^{[34] [34, 35]}

[Insert Table 1 here]

4 PIM polymerisation using Tröger's base formation

Tröger's base (TB), more formally named as 2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine, is readily formed by an electrophilic aromatic substitution reaction between an aromatic amine and formaldehyde or a formaldehyde proxy (e.g. dimethoxy methane). The reaction is remarkable in that six new covalent bonds are formed in a single high-yielding step. TB has proven to be an excellent linking group for PIM synthesis due to its bridged bicyclic structure that provides *both* high rigidity and a site of contortion. Despite its long history^[53, 54] and proven efficiency,^[55] the use of TB formation in PIM synthesis was the first report of a successful polymerization using this reaction.^[56, 57] In general, TB polymerisations are performed readily by simply mixing a suitable aromatic diamine monomer and five molar excess of dimethoxymethane in trifluoroacetic acid at 0 °C and leaving under ambient conditions until the solution becomes viscous (Table 2).^[58] The need for only one type of aromatic monomer is an attractive feature of this step-growth polymerisation. For aromatic diamine monomers that possess more sites activated towards aromatic electrophilic substitution than the two required for TB polymerisation, gel formation due to cross-linking can be problematic. However, gel-formation can be avoided by using monomers within which methyl groups block these sites (e.g. **C8**, Table 2). With the exception of monomers **C6** and **C7** (Table 2), TB polymerisation provides polymers of good film-forming quality by casting from chloroform.

[Insert Table 2 here]

5 PIM polymerisation from imide formation: PIM-polyimides

Polyimides constitute one of the most important classes of polymer for commercial applications and are prepared via the efficient formation of imide linkages between diamine and dianhydride monomers. PIMs based on polyimide formation (PIM-PIs) can be obtained from monomers that are rigid with at least one of the monomers providing a site of contortion (Table 3).^[63, 64] In addition, to obtain PIM-PIs with a high degree of intrinsic microporosity, it is important to restrict rotation about the C-N bond of the imide linkage by choosing diamine monomers with two bulky substituents adjacent to both amine groups (Fig. 1).

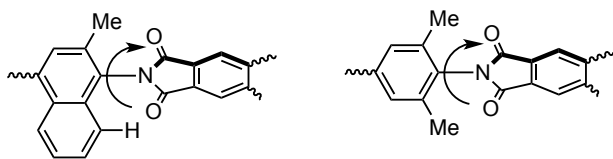


Figure 1 Restricted rotation around sterically crowded imide bonds.

[Insert Table 3 here]

6 Post synthetic modification of PIMs.

[Insert Fig. 2 here]

It is also possible to modify the structure of PIMs by post-synthesis reactions, which have mainly focused on performing chemistry on the nitrile group of PIM-1 (Fig. 2). Simple hydrolysis of the CN groups was reported to provide carboxylic acids,^[83] although a later report suggests that simple hydrolysis under basic conditions mainly results in amide functionality.^[86] Similarly, reaction of the nitrile group with P₂S₅ gives thioamides,^[85] hydroxylamine gives amidoximes,^[84] borane gives benzyl amine,^[89] amines give amides,^[90] and the reaction of sodium nitride gives tetrazole functionality.^[87] Generally, such modifications result in a reduction in intrinsic microporosity, presumably due to the additional inter-chain cohesive interactions from hydrogen bonding. Attempted post-synthesis modifications to the biscatechol monomeric units such as sulfonation has been less successful due to polymer degradation, insolubility and embrittlement.^[91] Structural modifications from thermal,^[92, 93] and photooxidative^[70, 94, 95] processes generally reduce intrinsic microporosity, as shown by a reduction in gas permeability but can greatly enhance selectivity for one gas over another. An interesting approach to polymers for membrane applications has been to combine the concept of intrinsic microporosity with that of the so-called Thermally Rearranged (TR) polymers. For example, PIM-PIs with reactive -OH substituents next to the imide linking group form benzoxazole units on heating.^[65, 75, 96-98] These PIMs, like all TR polymers become insoluble on thermal processing. Post-synthetic cross-linking using a variety of reactions such as those of azides,^[99] nitrenes,^[100] decarboxylation of hydrolysed PIM-1,^[101] has also been investigated due to its importance for membrane stability. Post-synthesis modification of PIM-TB polymers to give positively charged polyelectrolytes, suitable for highly efficient anion transport, has been achieved by quaternisation of the tertiary amine functionality of the TB unit.^[10]

7 Conclusions

Described above is the accumulation of over 12 years work on the synthesis of PIMs. The simple design concept of constructing highly rigid, conformationally locked, and contorted polymer chains is often challenging to achieve with conventional polymerisations. Nevertheless, three distinct types of reactions based on the formation of dibenzodioxin, Tröger's base and imide linkages reliably provide PIMs of sufficient molecular mass to form robust self-standing films by simple solution casting. It is anti-

pated that the many potential applications of PIMs, as solution processable microporous materials, will provide increasing impetus for the further design and synthesis of PIMs using these three proven synthetic methodologies and also the development of new PIM-forming polymerisation reactions.

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Conflict of interest The author declares that they have no conflict of interest.

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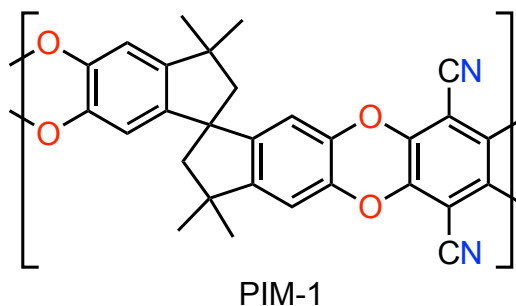
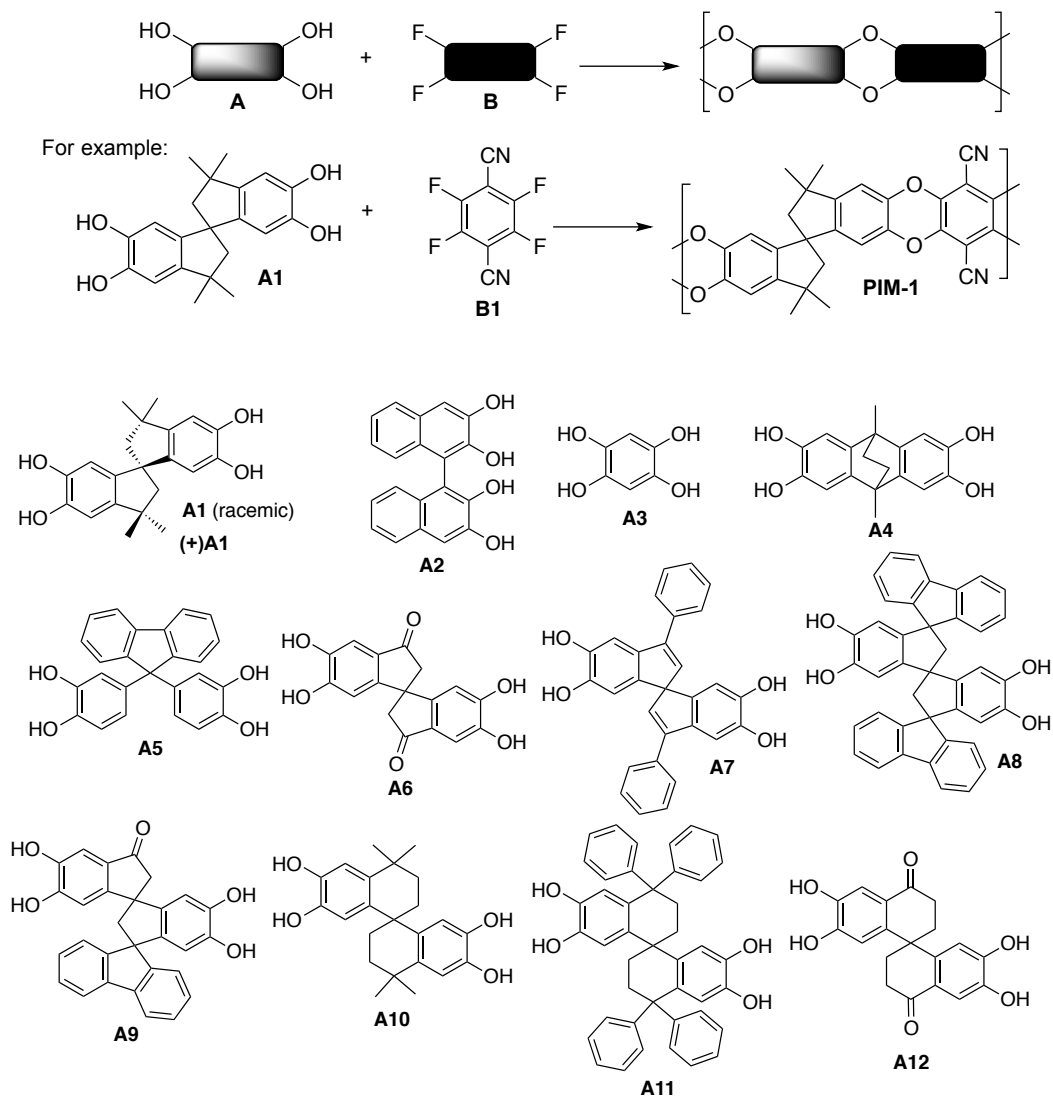
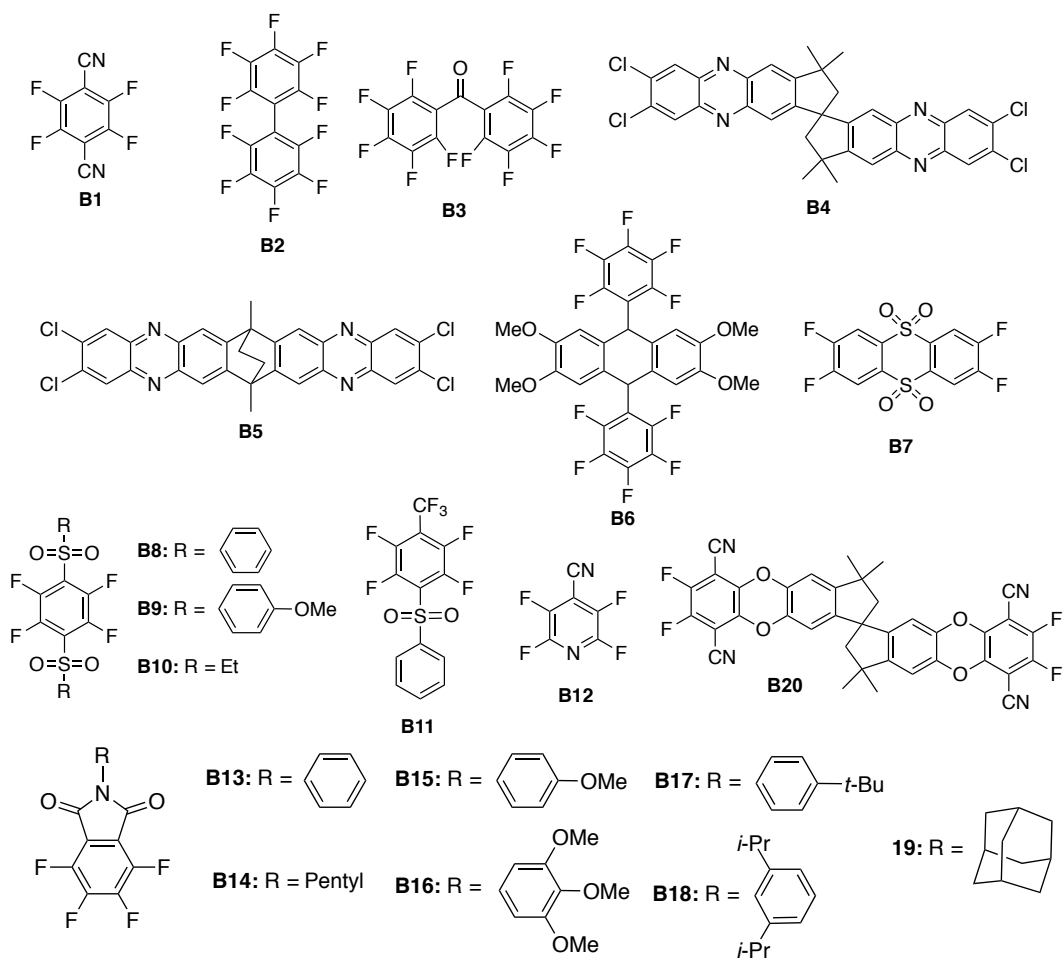
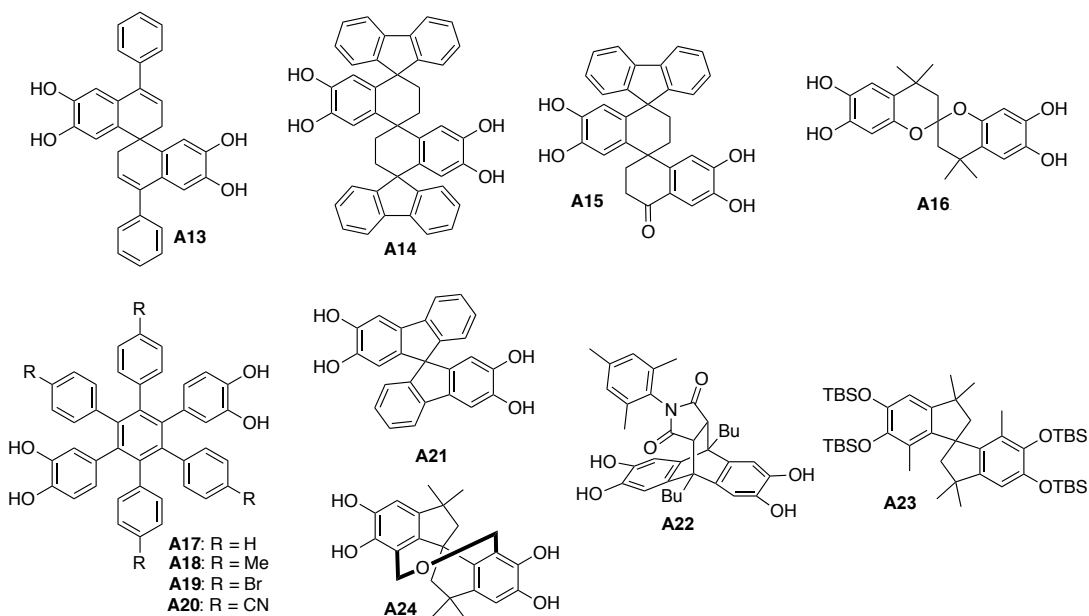
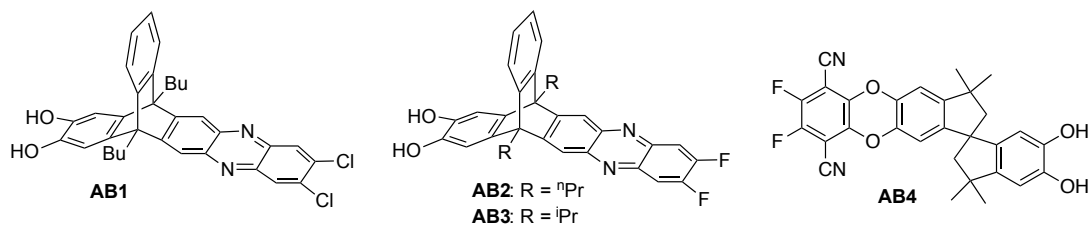


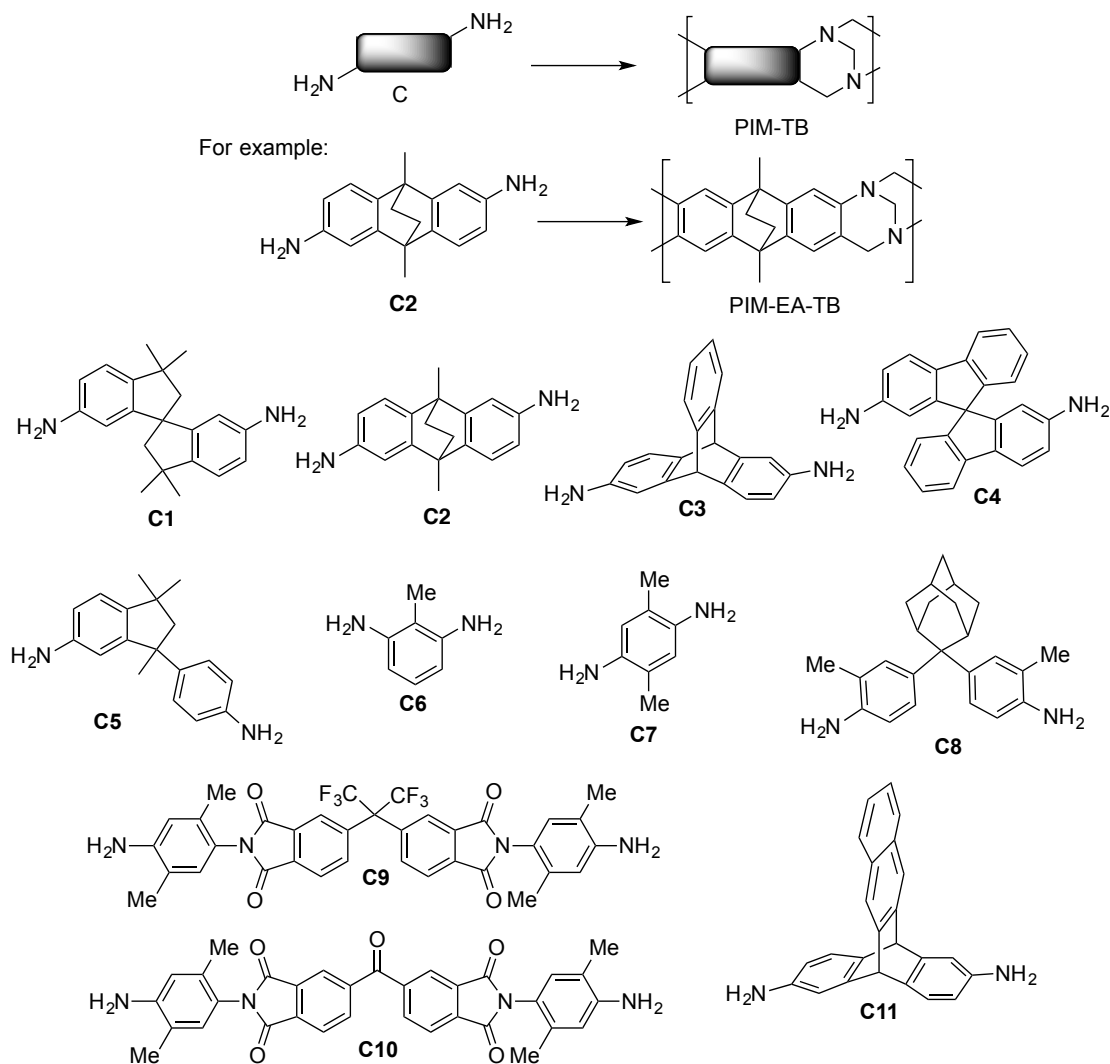
Table 1. PIMs prepared via dibenzodioxane polymerisation.





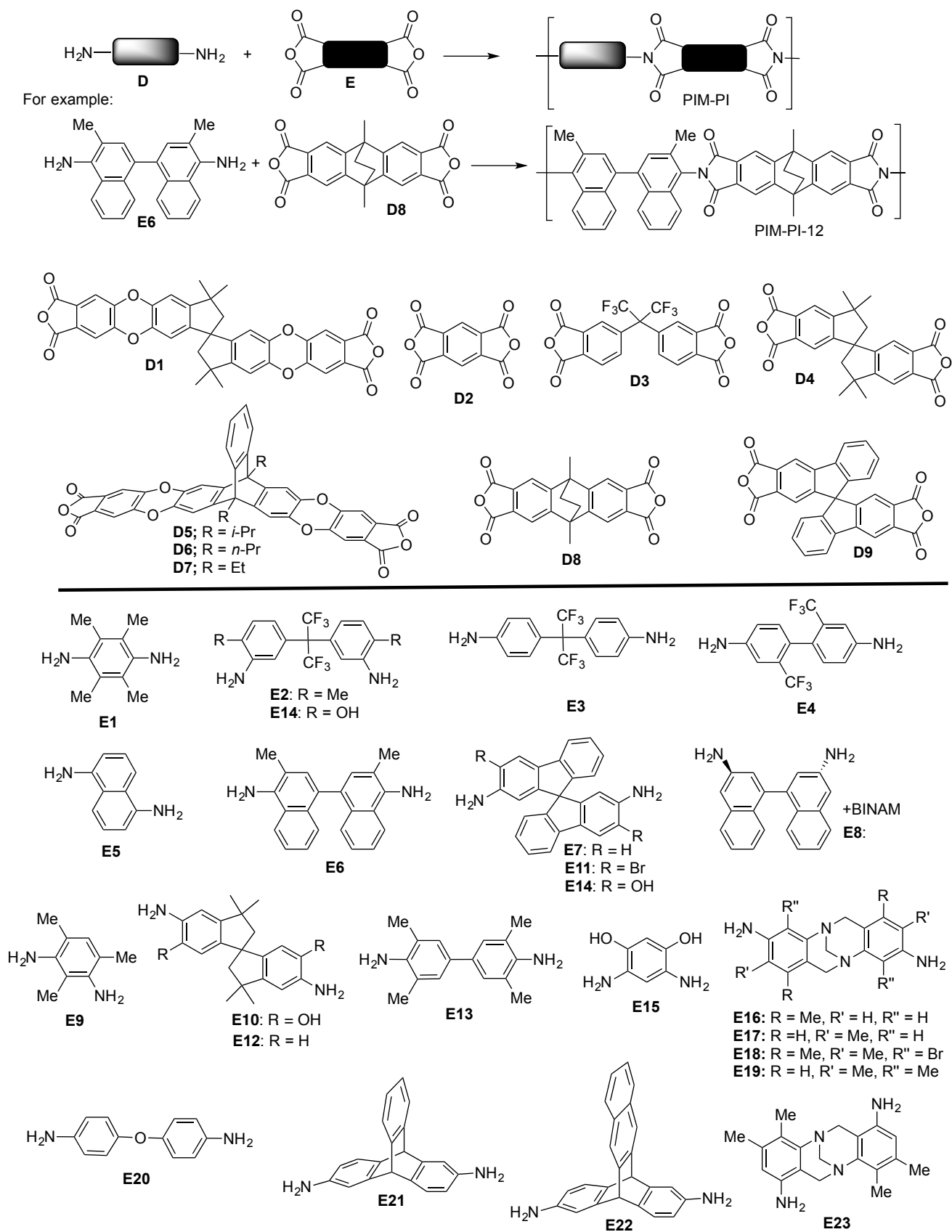
Monomers	Solubility	Name ^a	Surface area (BET; m ² g ⁻¹)	Ref.
A1 + B1	THF, CHCl ₃	PIM-1	760-850	[2, 8, 23]
(+)A1 + B1	THF, CHCl ₃	(+)PIM-1	740	[36]
A1 + B2	THF	PIM-2	600	[2]
A1 + B3	THF	PIM-3	560	[2]
A2 + B1	THF	PIM-4	440	[2]
A2 + B2	THF	PIM-5	540	[2]
A3 + B2	THF	PIM-6	430	[2]
A1 + B4	CHCl ₃	PIM-7	680	[37]
A4 + B4	CHCl ₃	PIM-8	677	[37]
A1 + B5	CHCl ₃	PIM-9	661	[37]
A4 + B5	<i>m</i> -cresol	PIM-10	680	[37]
A5 + B4	CHCl ₃	Cardo-PIM-1	621	[37]
A5 + B5	CHCl ₃ (partial)	Cardo-PIM-2	580	[37]
A4 + B1	Not soluble	PIM-CO-100	630	[34]
A6 + B1	quinoline	"Polymer from 5"	501	[38]
A7 + B1	quinoline	Polymer from 6	560	[38]
A8 + B1	THF	Polymer from 7	895	[38]
A9 + B1	DMF, quinoline	Polymer from 10	656	[38]
A10 + B1	THF	Polymer from 5	432	[39]
A11 + B1	THF	Polymer from 8	395	[39]
A12 + B1	Insoluble ^b	Polymer from 10	713	[39]
A13 + B1	Insoluble ^b	Polymer from 14	203	[39]
A14 + B1	THF	Polymer from 15	590	[39]
A15 + B1	Insoluble ^b	Polymer from 16	300	[39]
A1 + B6	CHCl ₃	MP-1	679	[40]
A16 + B1	quinoline	PIM-CO15	518	[41]
A17 + B1	CHCl ₃	PIM-HPB	527	[42, 43]
A18 + B1	CHCl ₃	PIM-CH ₃ -HPB	560	[43]
A19 + B1	CHCl ₃ , THF	PIM-Br-HPB	410	[43]
A20 + B1	THF	PIM-CN-HPB	440	[43]
A21 + B1	CHCl ₃	PIM-SBF	803	[44]
A22 + B1	CHCl ₃ , THF	PIM-4bIII	660	[45, 46]
A1 + B7	CHCl ₃	TOT-PIM-100	560	[35]
A1 + B1 _{0.5} B7 _{0.5}	CHCl ₃	TOT-PIM-50	601	[35]
A1A2B1B7	CHCl ₃	DNTOT-PIM-50	407	[35]
A1 _{0.5} A2 _{0.5} + B1	CHCl ₃	DN-PIM-50	709	[35]
A1 + B8	CHCl ₃	DSPIM1-100	-	[47]
A1 + B9	CHCl ₃	DSPIM2-100	-	[47]
A1 + B10	CHCl ₃	DSPIM3-100	-	[47]
A1 + B11	CHCl ₃	PSTFPIM1	-	[48]
A1 + B12	CHCl ₃	-	-	[49]
A1 + B13	CHCl ₃	PIM-R1	702	[50]
A1 + B14	CHCl ₃	PIM-R2	595	[50]
A1 + B15	CHCl ₃	PIM-R3	628	[50]
A1 + B16	CHCl ₃	PIM-R4	889	[50]
A1 + B17	CHCl ₃	PIM-R5	636	[50]
A1 + B18	CHCl ₃	PIM-R6	714	[50]
A1 + B19	CHCl ₃	PIM-R7	680	[50]
A4 + B20	CHCl ₃	PIM-A1	-	[51]
A23 + B1	CHCl ₃	Polymer 4	-	[29]
A24 + B1	CHCl ₃	PIM-c1	818	[52]
AB1	CHCl ₃	-	523	[31]
AB2	CHCl ₃	TPIM-1	862	[32]
AB3	CHCl ₃	TPIM-2	612	[32]
AB4	CHCl ₃	PIM-1	-	[30]

^aAs denoted in reference. ^bIt is thought that this molecule is cross-linked due to an additional Aldol reaction, which takes place during polymerization.

Table 2. PIMs prepared using Tröger's base polymerisation.

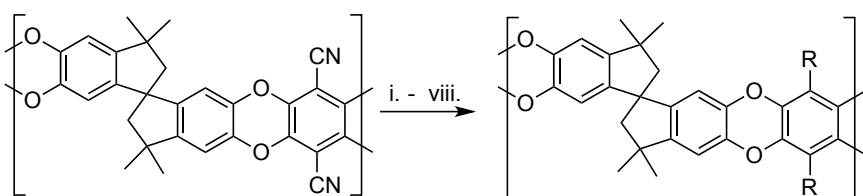
Monomer	Solubility	Name	Surface area (BET; m ² g ⁻¹)	Ref.
C1	CHCl ₃	PIM-SBI-TB	745	[57] [58]
C2	CHCl ₃	PIM-EA-TB	1028	[57] [58]
C3	CHCl ₃	PIM-Trip-TB	899	[59] [58]
C4	CHCl ₃	PIM-SBF-TB	566	[58] [58]
C5	CHCl ₃	Polymer 5	536	[58]
C6	CHCl ₃	Polymer 8	504	[58]
C7	CHCl ₃	Polymer 9	677	[58]
C8	CHCl ₃	TB-Ad-Me	605	[60]
C9	CHCl ₃	PI-TB-1	544	[61]
C10	CHCl ₃	PI-TB-2	270	[61]
C11	CHCl ₃	PIM-BTrip-TB	870	[62]

Table 3. PIMs prepared using polyimide formation.



Monomers	Solubility	Name ^a	Surface area (BET; m ² g ⁻¹)	Ref.
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D1 + E1	CHCl ₃	PIM-PI-1	680	[63, 64]
D1 + E2	CHCl ₃	PIM-PI-2	500	[64]
D1 + E3	CHCl ₃	PIM-PI-3	471	[63, 64]
D1 + E4	CHCl ₃	PIM-PI-4	486	[64]
D1 + E5	CHCl ₃	PIM-PI-7	485	[64]
D1 + E6	CHCl ₃	PIM-PI-8	683	[63, 64]
D1 + E14	THF	SPDA-HSBF	400	[65]
D2 + E7	CHCl ₃	P4	551	[66]
D2 + E8(+)	CHCl ₃	(+)BINAM-PMDA	500	[67]
D3 + E1	THF	6FDA-m4	-	[68]
D4 + E9	THF	6FDA-m3	-	[68]
D2 + E10	THF	PIM-6FDA-OH	225	[69]
D3 + E10	THF	PIM-PMDA-OH	190	[69]
D3 + E7	CHCl ₃ , THF	6FDA-SBF	240	[70]
D2 + E7	CHCl ₃ , THF	PMDA-SBF	320	[70]
D1 + E7	CHCl ₃ , THF	SPDA-SBF	460	[70]
D3 + E11	CHCl ₃ , THF	6FDA-BSBF	440	[70]
D2 + E11	CHCl ₃ , THF	PMDA-BSBF	450	[70]
D2 + E11	CHCl ₃ , THF	SPDA-BSBF	510	[70]
D4 + E1	CHCl ₃	PIM-PI-9	700	[71]
D4 + E6	CHCl ₃	PIM-PI-10	700	[71]
D4 + E12	CHCl ₃	PIM-PI-11	200	[71]
D5 + E1	CHCl ₃	KAUST-PI-1	752	[72, 73]
D5 + E12	CHCl ₃	KAUST-PI-2	737	[72, 73]
D5 + E9	CHCl ₃	KAUST-PI-3	760	[73]
D5 + E20	CHCl ₃	KAUST-PI-4	420	[73]
D5 + E3	CHCl ₃	KAUST-PI-5	650	[73]
D5 + E2	CHCl ₃	KAUST-PI-6	500	[73]
D5 + E6	CHCl ₃	KAUST-PI-7	840	[73]
D6 + E1	CHCl ₃	KAUST-PI-1'	610	[73]
D6 + E3	CHCl ₃	KAUST-PI-5'	430	[73]
D7 + E5	CHCl ₃	KAUST-PI-5''	430	[73]
D8 + E6	THF	PIM-PI-12	699	[74]
D1 + E14	THF	PIM-PI-OH-1	360	[75]
D4 + E14	DMAc	PIM-PI-OH-2	-	[75]
D1 + E15	THF(p), DMA	PIM-PI-OH-3	430	[75]
D1 + E16	CHCl ₃	TBDAI-SBI-PI	560	[76]
D1 + E17	CHCl ₃	TBDA2-SBI-PI	615	[76]
D3 + E17	CHCl ₃	TBDA2-6FDA-PI	320	[77]
D3 + E21	CHCl ₃	6FDA-DAT1	320	[78]
D3 + E22	CHCl ₃	6FDA-DAT2	450	[78]
D9 + E6	CHCl ₃	SBFDA-DMN	686	[79]
D5 + E2	CHCl ₃	TBDA-ATAF	-	[80]
D5 + E14	THF	TPDA-APAF	-	[80]
D3 + E18	CHCl ₃ , THF	PIM-PI-TB-1	440	[81]
D3 + E23	CHCl ₃ , THF	PIM-PI-TB-2	580	[81]
D2 + E19	CHCl ₃ ,	4MTBDA-PMDA	650	[82]
D3 + E19	CHCl ₃ ,	4MTBDA-6FDA	584	[82]
D4 + E19	CHCl ₃ ,	4MTBDA-SBIDA	733	[82]
D9 + E19	CHCl ₃ ,	4MTBDA-SBFDA	739	[82]

i. R = -CO₂Hiv. R = -CONH₂

ii. R =

v.; vi. R =

iii. R = -CSNH₂vii. R = -CH₂NH₂viii. R = -CONHCH₂CH₂NHCH₂CH₂OH

Figure 2. Post-synthetic modification of PIM-1. *Reactions and conditions.* i. NaOH (aq), reflux; acidic work-up.^[83] ii. NH₂OH, THF, reflux.^[84] iii. P₂S₅, NaSO₃, dioxane, ethanol, reflux.^[85] iv. NaOH (aq), reflux; acidic work-up.^[86] v. NaN₃, ZnCl₂.^[87, 88] vi. NaN₃, ZnCl₂, K₂CO₃, MeI.^[88] vii. Borane-THF, THF, reflux.^[89] viii. Ethanolamine, Reflux.^[90]