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Polymers of Intrinsic Microporosity (PIMs): High Free Volume Polymers for Membrane Applications

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Summary: We are developing new types of polymer – termed polymers of intrinsic microporosity (PIMs) – which in the solid state behave like molecular sieves. As pervaporation membranes, they show selectivity for organics over water. As gas separation membranes, they exhibit a remarkable combination of high permeability and good selectivity for gas pairs such as O_2/N_2.

Keywords: gas separation; membrane; microporous polymer; pervaporation

Polymers of Intrinsic Microporosity

Polymers with no single bonds in the backbone about which free rotation can occur, but which incorporate sites of contortion giving the backbone an irregular, kinked shape, are unable to pack efficiently in the solid state and so trap sufficient free volume that they behave like molecular sieves (i.e., they are microporous according to the IUPAC definition,[1] with effective pore dimensions <2 nm). We are developing a range of polymers of intrinsic microporosity (PIMs),[2–5] including both insoluble network-PIMs containing catalytic centres or specific binding sites,[6–9] and soluble PIMs that can be cast from solution to form membranes.[10–12]

PIM-1 (Fig. 1) and PIM-7 (Fig. 2) are examples of membrane-forming PIMs. In both these polymers, the site of contortion is a spiro-centre (a single tetrahedral carbon atom shared by two rings). They are thermally stable, amorphous, glassy polymers. Analysis of N_2 adsorption data by the BET method gives apparent surface areas >700 m^2 g^{-1}. PIM-1 is soluble in tetrahydrofuran, chloroform, dichloromethane, *o*-dichlorobenzene and benzyl alcohol. PIM-7 is soluble in chloroform, o-dichlorobenzene and m-cresol. Membrane samples have a density in the range 1.06–1.09 g cm^{-3}, as determined by measurements of the weight in air and in the fluorocarbon fluid Fluorinert FC-77. In PIM-7, the phenazine unit acts as a ligand for the coordination of metal ions and a PIM-7 membrane is readily crosslinked with Pd(II) salts.

PIM Membranes

PIM membranes are being investigated for a variety of applications, including pervaporation and gas separation. In pervaporation, they preferentially transport organic compounds rather than water.[11] In gas permeation they exhibit high permeability coupled with a selectivity that breaks Robeson's[13] upper bound for important gas pairs such as CO_2/CH_4 and O_2/N_2 (Fig. 3).[12] The exceptional performance in gas separation is linked to very high apparent solubility coefficients, which boost the permeability whilst maintaining selectivity.

Preparation of PIMs

PIM-1 (Fig. 1) and PIM-7 (Fig. 2) are formed by a step polymerization involving a

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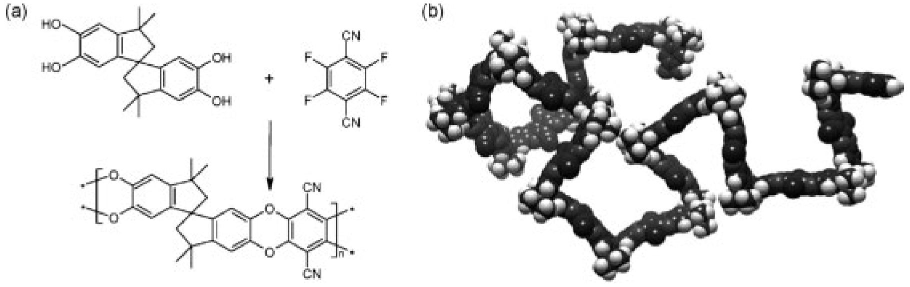

Figure 1.
(a) Preparation of polymer PIM-1. *Reagents and conditions:* K_2CO_3, DMF, 65 °C. (b) Molecular model of a fragment of PIM-1 showing its irregular, kinked shape.

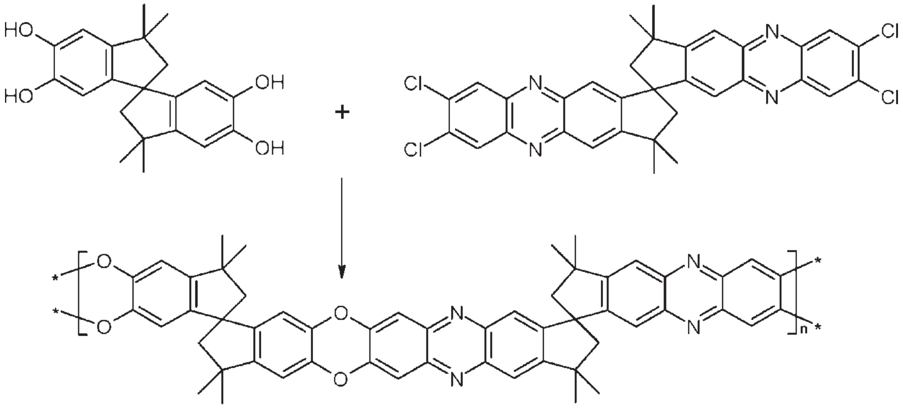

Figure 2.
Preparation of polymer PIM-7. *Reagents and conditions:* 18-crown-6, K_2CO_3, DMF, 150 °C.

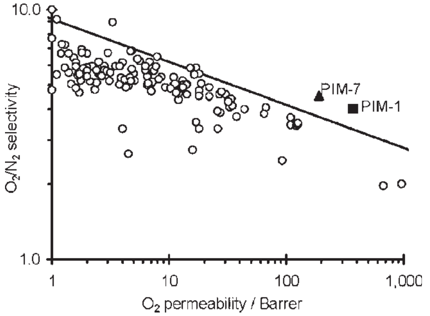

Figure 3.
Double logarithmic plot of O_2/N_2 selectivity against O_2 permeability, showing results for PIM-1 and PIM-7. The solid line is Robeson's 1991 upper bound.[13] The circles represent recent data from the literature for a variety of polymers.

double aromatic nucleophilic substitution reaction between 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane and an aromatic fluorinated or chlorinated monomer. In the case of PIM-1, high molar mass polymer is readily obtained at temperatures in the range 60–80 °C, but the molar mass is reduced at higher temperature. Fig. 4 indicates how the molar mass distribution for PIM-1 builds up over time. Oligomer is formed rapidly and polymer of moderate molar mass is obtained within a few minutes. Over a longer period of time, a high molar mass peak builds up, with a tail that extends to very high molar mass. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) provides

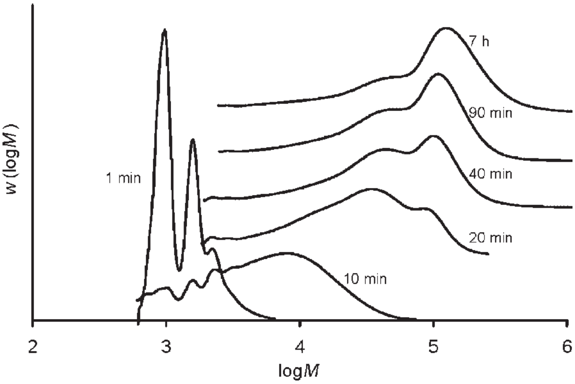

Figure 4.
Distribution of log(molar mass) (polystyrene equivalent) from Gel Permeation Chromatography for PIM-1 after various times of polymerization at 65 °C. Data obtained by Laura Grant (University of Manchester).

an insight into the oligomeric ($M < 10{,}000$ g mol^{-1}) species present. After 10 minutes of polymerization, the MALDI spectrum indicates a mixture of linear species with different combinations of end groups (both catechol, both fluoro-, or one catechol and one fluoro-). However, after a very long reaction time (96 h), the MALDI spectrum shows the low molar mass region of the distribution to consist predominately of cyclic species. Kricheldorf *et al.* have also observed cyclic species in PIM-1 prepared using a silylated tetrahydroxy monomer.[14] This may be attributed to competition between cyclization and propagation, as has been argued to occur commonly in step polymerizations.[15] However, it is also feasible in the case of PIM-1 that cyclics are generated through a back-biting reaction, in which a catechol end attacks an activated dibenzodioxane linkage within the same polymer chain. The details of the polymerization process are currently being investigated further.

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