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CROSS-LINKING OF INTRINSICALLY MICROPOROUS POLYMER MEMBRANES

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Introduction

The term 'Polymers of Intrinsic Microporosity' (PIMs) is commonly used to describe high-free-volume microporous materials having rigid ladder-type, predominately aromatic, polymeric structures incorporating contorted centers. These ladder polymers have characteristically high surface areas, and are considered as promising materials for membrane-based gas separation. In their original papers, Budd et al. and McKeown et al. reported 'PIM-1' and other related polymeric structures, as the first high molecular weight microporous ladder polymers in this class (Figure 1) (1-3). PIM-1 is the first reported and most studied material of this polymer class for several reasons: (a) it can be readily prepared from commercial monomers, (b) it has relatively high molecular weight and low polydispersity, and (c) good mechanical properties compared with many other PIMs. PIMs exhibit very high gas permeabilities, though lower than poly(trimethylsilyl propyne) (PTMSP). However, PTMSP membranes are prone to rapid and significant reductions in permeability, resulting from a collapse in free volume. One advantage of PIM-1 is that its aromatic ladder-type structure linked by a highly contorted spirobisindane centre has no rotational freedom, possibly making it less prone to free volume collapse.

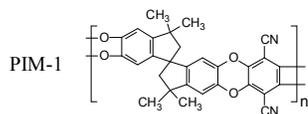


Figure 1. Structure of ladder polymer PIM-1

Since the initial reports on PIM-1 by McKeown and Budd, other structurally new, solvent-processable PIMs, having sufficiently high MW to enable membrane fabrication for the study of gas transport properties, have been developed. The PIMs have been typically prepared either from novel monomers or by post-polymerization modification. The particular molecular structures of PIMs have a strong influence on gas permeability and selectivity, such that the design of new PIMs allows the tuning of properties such as gas permeability and selectivity. Structural variables we have investigated to date include changes in the segmental distance between contorted centers, changes in the angle of contortion, incorporation of pendant groups, and the incorporation of strongly CO₂-philic groups that greatly enhance CO₂ permeability and CO₂ / N₂ selectivity, especially for mixed gases (4-7).

Results and Discussion

In membrane gas separations, exposure of membranes to CO₂ and other condensable gases affects CO₂/N₂ and CO₂/CH₄ separation performance, especially at high pressure, due to swelling-induced plasticization. Plasticization increases local segmental mobility, which leads to an increase in membrane permeability and a decrease in selectivity. In our investigations on PIM membranes, we observed that PIMs did not appear to suffer typical plasticization, but rather a phenomenon that could be more accurately described as 'swelling-induced densification'. With increasing CO₂ pressure, the microporous structures were affected by sorbed CO₂, resulting in a decrease in permeability. With progressively higher CO₂ pressures, the intrinsically microporous structure began to collapse, possibly caused by a slight overall increase in segmental mobility, though no rotational chain mobility is possible in ladder-type polymers.

Traditional methods for stabilizing polymeric membranes are either annealing or cross-linking. We have investigated two approaches to cross-link PIM-1 membranes, so that their gas transport properties would be more stable to condensable gases under high pressures. One approach has been to add a diazide cross-linking agent to PIM-1, which, when thermally activated, decomposes to a highly reactive dinitrene and cross-links the ladder polymer (8). A second approach involves controlled hydrolysis of nitrile groups to

carboxylic acid groups by treating PIM-1 membranes with NaOH (9). Thermal treatment of the resulting carboxylic acid-containing PIM (C-PIM) membranes led to decarboxylation and cross-linking (DC-PIM) of the polymer. This approach has been successfully employed to cross-link carboxyl-substituted polyimides (10). Recently, a new method for cross-linking PIM-1 was also reported, based on thermal treatment of the membrane to trimerize nitrile groups to form triazines (11).

In the present work, an investigation of the decarboxylation cross-linking by a combination of techniques suggests a mechanism involving aryl radicals is likely. The gas transport properties of the cross-linked DC-PIM membranes were dependant on the amount of the cross-linkable sites present in the precursors. In comparison with PIM-1, DC-PIM exhibited higher O₂/N₂, CO₂/N₂ and CO₂/CH₄ selectivities, coupled with expected reductions in pure gas permeabilities. The results of pure gas CO₂ and N₂ permeability, and mixed gas CO₂/N₂ normalized selectivity under the higher pressure indicate that DC-PIMs exhibit a reduction of swelling-induced densification for CO₂.

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