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Highly permeable and aging resistant 3D architecture from polymers of intrinsic microporosity incorporated with beta-cyclodextrin

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ABSTRACT

The polymers of intrinsic microporosity (PIM) incorporated with beta-cyclodextrin (β-CD) (referred to as PIM-CD) are prepared to investigate the effects of unique 3-dimensional (3D) hollow bowl structure of β-CD on gas separation performance and physical aging behavior. Compared with the pristine PIM membrane, the permeability of PIM-CD membranes increases with an increase in β-CD loading. Pure gas permeation tests reveal that the incorporation of a very small amount of β-CD into the PIM matrix can significantly enhance the CO_2 permeability from 3368 to 8812 barrer, an increase of 162%, without too much sacrifice of gas selectivity. The gas separation performance of PIM-CD membranes can surpass the Robeson upper bound lines for almost all of the gases. Analyses from positron annihilation lifetime spectroscopy and wide angles x-ray diffraction confirm that the β-CD incorporation brings PIM-CD membranes with bigger micro-pores and higher fractional free volume, resulting in a higher gas permeability. In addition, the interactions between β-CD and PIM can restrict chain movement and make ultra-fine micro-pores difficult to collapse. Thus the PIM-CD membranes exhibit much greater resistance to physical aging than PIM membrane. These results may open up new avenues for molecular design of 3D architecture CD-based membranes for gas separation.

1. Introduction

Traditional processes for natural gas purification such as pressure swing adsorption and cryogenic distillation are energy intensive [1–4]. Membrane technology provides an alternative process to purify natural gas because it possesses advantages of low energy consumption, easy operation and maintenance, small footprint, and environmental friendliness [5–8]. However, the desirable polymeric membranes for industrial gas separation must have (1) high permeability and good selectivity since permeability and selectivity usually follow a trade-off relationship [9,10] and (2) long-term stability in separation performance without exhibiting physical aging [11–13].

These requirements make a big challenge for the commercial application of glassy polymers, especially for rigid kinked polymers of intrinsic microporosity (PIM) [14,15], because glassy polymer chains tend to gradually relax and approach a more thermodynamically stable state at the sacrifice of fractional free volume (FFV) [11–13]. As the FFV contracts, the paths for gas transport shrink, leading to a great loss of permeability. Therefore, a large body of research has been devoted to circumvent the trade-off relationship and physical aging issues in the past decades. Two strategies show promising to solve these problems; one is by post treatments, while the other is by adding inorganic or organic fillers. Some post treatments have successfully reduced physical aging, but often accompanied with a large loss in permeability [16–21].

Inorganic fillers, such as zeolite and metal organic framework, can be incorporated into the polymer matrix to form mixed matrix membranes (MMMs) [22–27]. Some MMMs exhibit good gas separation performance and even surpass the Robeson upper bound line. However, poor compatibility between inorganic fillers and polymer matrices often results in particle agglomeration and defective membranes. Alternatively, purely organic additives have better compatibility with polymer matrices than inorganic fillers. For example, porous aromatic frameworks display effectiveness as organic additives to enhance MMMs with higher permeability and resistance to physical aging [28–32]. However, their synthesis routes render it complex and expensive for commercialization.

β-CD consisting of seven α-D-glucose units bound together in a ring is one of the attractive commercially available organic additives. The geometry of β-CD is a unique 3D hollow bowl with an inner cavity diameter of about 6.0–7.8 Å. The incorporation of cyclodextrin into the polymer matrix for separation has received intensified attention recently owing to its unique 3D structure and molecular size [33–38]. However, the addition of CD into the polymeric matrix by simply

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physical blending encounters the problem of phase separation because of CD agglomeration especially in high CD loadings. In addition, CD grafted on the side chain of the polymer may partially fill the spaces among polymer chains and result in reductions of free volume and gas permeability.

Since β-CD contains reactive hydroxyl groups that can be easily modified [33–39], the incorporation of CD into the polymer main chain via chemical bonds would be an effective way to mitigate the problems of phase separation and free volume reduction. Therefore, the first objectives of this work are to incorporate 3D β-CD into the main chain of PIM via reactive hydroxyl groups and to generate lightly cross-linked 3D PIM-CD copolymer materials. Then, we aim to explore the science on how 3D β-CD (1) restructures the architecture of the PIM matrix, (2) regulates the packing of polymer chains, (3) manipulates the free volume and affects the gas separation performance, and (4) improves resistance to physical aging. This work may provide useful insights to design 3-dimensional CD-based membranes with enhanced gas separation performance.

2. Experimental

2.1. Materials

The monomer 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI, 97%) was purchased from Alfa Aesar and purified via re-crystallization from methanol. The spirocentre within TTSBI is a kinked and shape-persistent ladder structure, with a dihedral angle of 90°. The 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN, 99%) was purchased from Matrix Scientic and purified from sublimation under vacuum prior to use. β-Cyclodextrin (β-CD) was purchased from Cyclolab Ltd and dried overnight at 100 °C under vacuum prior to be used. The molecular weight of dehydrated β-CD (formula: $(C_6H_{10}O_5)_7$) is 1134 g/mol. The outer diameter of the larger opening of the β-CD toroid is 15.3 Å, the side rim depth is 7.8 Å and the inner cavity diameter of β-CD is 6.0–7.8 Å [38]. N, N′-Dimethylformamide (DMF, > 99.5%) from Merck (Germany) was further purified via vacuum distillation at 65 °C before being used as the solvent for the polymer synthesis. Anhydrous potassium carbonate (K_2CO_3, > 99.5%) from Sigma Aldrich and methanol (MeOH, ≥99.9%) from Merck were used without further purification. Dichloromethane (DCM, 99.99%) and hydrochloric acid (HCl, 37.5%) from Fisher Scientific (UK) were used as received. All purified gases (at least 99.95%), such as H_2, O_2, N_2, CH_4, CO_2, were supplied by SOXAL Pte. Ltd. (Singapore).

2.2. Syntheses of polymers

The typical procedure to synthesize PIM-CD-0.1% was carried out as follows: β-CD (0.011 g, 0.010 mmol), TTSBI (3.40 g, 9.99 mmol), TFTPN (2.00 g, 10.0 mmol), and K_2CO_3 (5.53 g, 40.0 mmol), and freshly distilled DMF (60 mL) were added into a 100 mL round-bottom flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser. The system was purged with N_2, then the N_2 inlet was removed and the mixture was placed on a hot stirring plate. The mixture was heated and maintained at 80 °C for 24 h and then a yellowish suspension was gradually obtained. The solution was cooled down to room temperature and carefully poured into 300 mL deionized water with a vigorously stirred magnetic stirrer to yield a powder-like precipitate. The residual K_2CO_3 was removed by adding 1 N HCl until CO_2 evolution stopped and pH was about 5. The recovered precipitate was filtered, then washed thoroughly with deionized water for several times until pH was about 7. After that, the orange precipitate was washed with methanol at 60 °C to remove the organic solvent and unreacted monomers. Finally, the orange solid dried at 120 °C under high vacuum for 12 h. Other PIM-CD-0.5%~2.0% and PIM polymers were synthesized under a similar procedure.

2.3. Fabrication of membranes

A 4 wt% solution in DCM was prepared to fabricate dense membranes in petri dishes by the solution casting method. Typically, 0.4 g polymer power was dissolved in 9.6 g DCM overnight to prepare a fully dissolved polymer solution. Then, the polymer solution was pre-filtered by a 1.0 µm PTFE filter and cast in petri dishes at ambient temperature

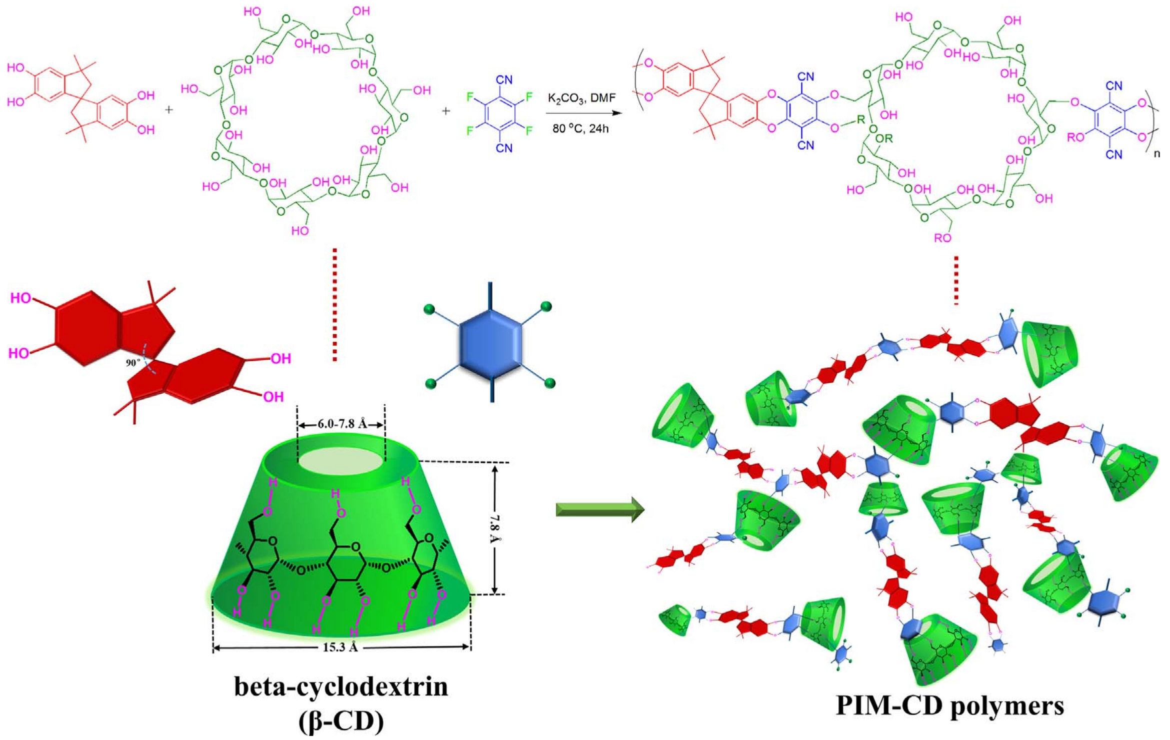

Fig. 1. Synthesis of the PIM and PIM-CD polymers via aromatic nucleophilic substitution polymerization of β-CD, TTSBI and TFTPN.