CO_2 separation of fluorinated 6FDA-based polyimides, performance- improved ZIF-incorporated mixed matrix membranes and gas permeability model evaluations

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1. Introduction

The introduction of amorphous perfluorinated polymers was not too long time ago, but the materials caught on quickly in the membrane gas separation field due to their high gas permeability, high selectivity, large free volume, and the possibility to use in various fashions (thick or thin layer, flat sheet or hollow fiber) efficiently. Their other distinguished and valuable properties, such as high rigidity, mechanical strength, and high thermo-oxidative properties, make the materials more attractive [1]. Most of all, the fluorine atom is highly electronegative, making the C–F bond very strong (485 $kJ\cdot mol^{-1}$), which implies their high thermal stability and inertness [2]. Moreover, the bulkiness of these C-F bonds causes low chain packing, reflected by their lower polymer densities compared to the crystalline polymers. Also, some perfluorinated polymers have very large fractional free volume (FFV), as high as 32%, as demonstrated by the amorphous Teflon AF2400 [3].

2. Experimental

2.1. Materials

To discard any trapped moisture, the aromatic dianhydride monomer 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99%) was vacuum dried (<160 °C, 6 – 7 h). Other materials for polymer synthesis are aromatic diamine monomers; 4,4′-(1,4-phenylenediisopropylidene) bisaniline (bis-P, ≥99%, Mitsui Japan) and 4,4′-oxydianiline (ODA, 97%), dipolar aprotic solvent n-methyl-2-pyrrolidone (NMP, ≥99%, Merck) and n,n-dimethylformamide (DMF, anhydrous ≥99.9%). For ZIF-8 synthesis: zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$, ≥99%), 2-methylimidazole (Hmim, 99%), high purity methanol CHROMASOLV® (MeOH, ≥99.9%) and absolute methanol (>99.8%, Penta Czech Republic). Unless specified, the materials were obtained from Sigma Aldrich, Czech Republic and used as received

2.2. ZIF-8 synthesis

As previously reported [4], ZIF-8 was synthesized accordingly to the optimized Cravillon et al.'s rapid synthesis method [5]. The method successfully synthesized ZIF-8 nanoparticles without stabilizing agents or conventional activations at room temperature. Typically, the ZIF-8 synthesis was conducted at $Zn(NO_3)_2\cdot 6H_2O$: Hmin:MeOH molar ratio of 1:6:350. Under magnetic stirring, the 0.84 mmol $Zn(NO_3)_2\cdot 6H_2O$ (0.25 g) and 6.72 mmol Hmim (0.41 g) were each dissolved in 11.9 mL high purity MeOH. Once dissolved, the Hmim-MeOH solution was added into $Zn(NO_3)_2$-MeOH. The mixing was conducted for 60 min before the colloidal solution was centrifuged (~20,000 rpm). For each rinsing cycle, the nanoparticles were rinsed with fresh absolute MeOH (3×20 mL) and sonicated (~60 – 90 min or until no visible agglomerates) to separate the agglomerated particles. Once the rinsing cycle was completed, the nanoparticles were dried in an oven at 60 °C for 2 – 3 days, ready for characterization and use.

2.3. 6FDA-based polyimide synthesis

The 6FDA-polyimides were synthesized through a classic two-step polycondensation polymerization method by reacting dianhydride and diamine monomers (one-to-one stoichiometric amount) in a polar aprotic solvent (in NMP for 6FDA-bisP and DMF for 6FDA-ODA) under a N_2 atmosphere. The reaction produces a poly(amic) acid solution (PAA) and is thermally imidized into a polyimide. Firstly, a nucleophilic attack by the diamine's amino groups onto the anhydride carbonyl carbons occurs to form the intermediate PAA. In the second step, the intermediate was thermally imidized through a step-wise annealing profile (6FDA-bisP, 70 – 250 oC; 6FDA-ODA, 70 – 300 oC), followed by gradual cooling to 30 oC (remained for30 min). Their detailed synthesis reactions are as previously presented [4], [6], and the overall reaction scheme is presented in Fig. 1.

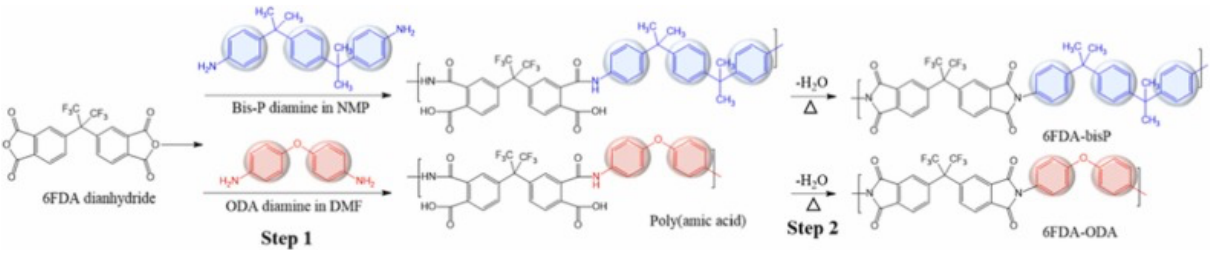

Fig. 1. The chemical structures of 6FDA dianhydride, aromatic diamines bis-P and ODA monomers, and the proposed schematic of two-step polymerization reaction to produce 6FDA-bisP and 6FDA-ODA polyimides, through Step 1: the synthesis of intermediate poly(amic acid), PAA, and Step 2: its thermal (cyclo-dehydration) imidization.

3. Conclusions

We report the successful synthesis of 6FDA-based perfluorinated polyimides, 6FDA-bisP (FFV = 0.214, P_{CO2} = 35.3 Barrer, $\alpha_{CO2/CH4}$ = 25.5) and 6FDA-ODA (FFV = 0.163, P_{CO2} = 25.9 Barrer, $\alpha_{CO2/CH4}$ = 20.6). This work demonstrates the effectiveness of the 6FDA-polyimides toward CO_2/CH_4 separation, and their gas transport properties were further improved by the addition of selective ZIF-8 nanoparticles (100 – 160 nm). An optimum loadings were achieved and presented superior performing membranes; 15 wt.% 6FDA-bisP MMM (FFV = 0.337, P_{CO2} = 81.2 Barrer, $\alpha_{CO2/CH4}$ = 35.0) and 10 wt.% 6FDA-ODA MMM (FFV = 0.214, P_{CO2} = 42.2 Barrer, $\alpha_{CO2/CH4}$ = 44.8). The study validates the effectiveness of adding the ZIF-8 nanoparticles, which directly contributes to the higher CO_2 diffusivity MMMs and CO_2/CH_4 selectivity improvements. The produced membranes also surpassed the separation performances of the industrially relevant polymers such as Matrimid®, TB-BisA-PC, PSF, CA, and PPO [7], [8], [9]. All gas permeability models (MM, MWS, HM, LNM) underestimate P_{CO2} and overestimate P_{CH4} for the studied 6FDA-polyimide MMMs. The trends could be attributed to several discussed factors, such as: (i) competitive sorption of CO_2 and CH_4 is not considered, (ii) the assumption of ideal morphology between both phases with homogeneous dispersion, and (iii) the model only assumes the particles are spherical. This under- and over- estimation directly contribute to the lower CO_2/CH_4 selectivity in all models. Furthermore, the enhanced free volume in MMMs was not included in the idealized models. We suggest that these factors should be considered when improving the gas permeability prediction model.

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