



High-productivity gas separation membranes derived from pyromellitic dianhydride and nonlinear diamines



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ARTICLE INFO

Article history:

Received 29 September 2015

Received in revised form

20 November 2015

Accepted 26 November 2015

Available online 28 November 2015

Keywords:

Polyimides

Gas separation

Rigidity

Fractional free volume

ABSTRACT

Two new polyimides have been obtained from commercial and inexpensive pyromellitic dianhydride and two affordable *meta*-substituted diamines bearing *ortho* methyl substituents (i.e., 2,4,6-trimethyl-1,3-phenylene diamine (TMPD) and 5,7-diamino-1,1,4,6-tetramethylindane (TMID)). Due to a combination of dianhydride rigidity and *meta* substitution, in addition to the influence of the *ortho* substituents on the orthogonal placement of the amine and imide planes, the two polyimides exhibited a high fractional free volume and a high rigidity. Therefore, these polyimides were able to produce gas separation membranes with an excellent balance between permeability and selectivity, and these membranes performed similar to many polymers with intrinsic microporosity (PIMs) and surpassed the 1991 Robeson upper bound for all gas pairs. The behavior is more favorable than that for similar polyimides based on 6FDA, which is considered to be the best dianhydride for gas separation polyimides.

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1. Introduction

Polyimides are among the more efficient polymers for gas separation membranes due to a good combination of high fractional free volume, high rigidity and good thermal and mechanical properties [1–7]. Therefore, more than two hundred different structures with a large variety of dianhydrides and diamines have been investigated for use in gas separation [8–11]. Among these dianhydrides, 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA) has been preferred, and more than eighty polyimides derived from 6FDA have been developed [12–14]. However, the very rigid pyromellitic dianhydride (PMDA) has been studied less than twenty times, which is most likely due to the membranes that are obtained in combination with conventional diamines exhibiting very low permeability. Therefore, most of the studied structures combine PMDA with flexible diamines in an attempt to overcome the high rigidity provided by the dianhydride.

However, in a recent study [6] we demonstrated that the combination of a rigid planar dianhydride (i.e., 3,8-diphenylpyrene-1,2,6,7-tetracarboxylic dianhydride) and diamines bearing *ortho* substituents yielded polyimides with a very rigid and conformed structure, which resulted in an important restriction on the packing and yielded gas separation membranes with an excellent combination of permeability and selectivity. This balanced effect

was particularly important when using *meta*-diamines, such as 2,4,6-trimethyl-1,3-phenylene diamine (TMPD).

The effect of the substituents placed *ortho* to the amino groups has been studied in other cases, especially in combinations consisting of TMPD with biphenyl dianhydride (BPDA) [15], benzophenone tetracarboxylic dianhydride (BKDA) [15,16] and 6FDA [15,17–20]. In these cases, the permeability values were significantly higher than those obtained for the corresponding unsubstituted 1,3-phenylene diamine (MPD) in the few cases where the last diamine had been tested in membranes.

The positive effect of *ortho*-methyl groups has also been demonstrated for 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene diamine) combined with 6FDA (i.e., dianhydride bearing a spirobisindane group [21], several polyimides derived from 5,7-diamino-1,1,4,6-tetramethylindane (TMID), and 6FDA, BKDA and 4,4'-oxydiphthalic dianhydride [22]).

Recently, this hypothesis was confirmed by Pinnau et al. by combining several dianhydrides with *ortho*-bromo substituted spirobifluorene diamine [1]. In this study, we studied the use of the planar, very rigid and very cheap PMDA (i.e., between 10 and 15 times cheaper than 6FDA), which has been combined with two of the previously mentioned *ortho*-substituted *meta*-diamines (i.e., TMPD and TMID). Both diamines, especially TMPD, are relatively affordable monomers that could yield cost-efficient polymeric materials that have the potential to be employed in industrial gas separation applications. Moreover, the differences between polyimides derived from dianhydrides (i.e., PMDA and 6FDA) and similar diamines have been investigated to determine the permeability/selectivity trade-off.

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2. Experimental

2.1. Materials

m-Xylene, isoprene, fuming sulfuric and nitric acids, concentrated sulfuric acid (95–98%), hydrazine monohydrate (64–65%), Pd/C (10% Pd basis), pyridine (anhydrous, 99.8%), 4-(dimethylamino)pyridine (>99%), trimethylchlorosilane, 1,2-dichloroethane, and *N*-methylpyrrolidone, (NMP) (99%) (Sigma-Aldrich) were used as received. 2,4,6-Trimethyl-1,3-phenylene diamine (TMPD) and pyromellitic dianhydride (PMDA) (Sigma-Aldrich) were purified by sublimation immediately prior to use.

2.2. Synthesis of 5,7-diamino-1,1,4,6-tetramethylindane (TMID)

The diamine was synthesized in three steps by modifying a previously reported method [23]. According to this method, the first step involves the preparation of 1,1,4,6-tetramethylindane by reacting isoprene and *m*-xylene in the presence of concentrated sulfuric acid at 10 °C for 7 h. Then, the organic layer was separated, washed with an aqueous sodium chloride solution and neutralized with aqueous ammonia. After removal of the aqueous layer, the organic layer was heated to remove the excess *m*-xylene, and the final product was purified by vacuum distillation (Yield: 65%).

5,7-Dinitro-1,1,4,6-tetramethylindane was obtained by the dropwise addition of 1,1,4,6-tetramethylindane to a mixture of fuming nitric and sulfuric acids and 1,2-dichloroethane. After the reaction was complete, water was added, the organic layer was separated, and 1,2-dichloroethane was distilled off as an azeotrope. The remaining product was dissolved in toluene and passed through a silica column to remove any impurities. The solvent was evaporated, and the dinitro compound was recrystallized from ethanol–water (1/1) with a yielding of 93%. Finally, the diamine was obtained by reduction of the purified dinitro compound catalyzed by Pd/C. In this case, hydrazine hydrate (dropwise addition) was used instead of hydrogen. After refluxing in an ethanolic solution for 15 h, the solution was filtered on Celite[®], the ethanol and residual hydrazine were evaporated, and the diamine was recrystallized from ethanol–water (1/1) to afford white crystals with mp.: 77.0 °C and 99.8% purity (determined by DSC using the van't Hoff method) in 85% yield.

¹H-NMR (300 MHz, CDCl₃) δ, ppm: 1.16 (s, 6 H, CH₃), 1.83 (t, 2 H, CH₂), 2.14 (s, 3 H, CH₃), 2.23 (s, 3 H, CH₃), 2.68 (t, 2 H, CH₂), 3.72 (s, NH₂).

2.3. Polyimide synthesis

Both polyimides were synthesized using *in situ* silylation of aromatic diamines, which is a very efficient activation method to afford polyimides with much higher molecular weights than those obtained from conventional polyimidation methods [24,25]. Moreover, an azeotropic method was used to remove the water released during the imidization step [26].

For example, the synthesis of PMDA-TMPD is as follows: a three-neck flask, which was equipped with a mechanical stirrer as well as a gas inlet and outlet, was charged with 10.0 mmol of 2,4,6-trimethyl-1,3-phenylenediamine and 10.0 mL of NMP. The mixture was stirred at room temperature under a blanket of nitrogen until the solid was completely dissolved. Then, the solution was cooled to 0 °C, and 20.0 mmol of pyridine, 2.0 mmol of dimethylaminopyridine (10% molar of pyridine) and 20.0 mmol of trimethylchlorosilane were slowly added. The solution was allowed to warm to room temperature and stirred for 15 min to ensure formation of the silylated diamine. Next, the solution was cooled again to 0 °C, and 10.0 mmol of pyromellitic dianhydride were added followed by 10.0 mL of NMP. The reaction mixture was

stirred for 15 min at 0 °C, and then, the temperature was increased to room temperature and maintained overnight. Subsequently, 20 mL of *m*-xylene, which was used as an azeotropic agent, were added to the solution, which was stirred vigorously and heated for 6 h at 190 °C to promote imidization. During this step, the water released by the ring-closure reaction was separated as a xylene azeotrope along with silanol and other siloxane by-products, and an extraordinary increase in the viscosity was observed. Excess *m*-xylene was distilled from the flask, which was subsequently cooled to room temperature. Due to the high viscosity, the reaction bulk had to be cut and redissolved in NMP overnight followed by precipitation in distilled water. The polymer was repeatedly washed with water and methanol and dried in an oven at 120 °C for 24 h under vacuum.

2.4. Preparation of membranes

Dense homogeneous membranes were prepared using a solution-casting method. 0.500 g of polymer were dissolved in 10 mL of NMP, and the solution was filtered through a 3.1 μm fiberglass Symta[®] syringe filter, poured onto a glass ring placed on a leveled glass plate and maintained at 60 °C overnight to remove most of the solvent. The membranes were peeled off of the glass and placed into a vacuum oven at 100 °C for 24 h, 120 °C for 1 h, 150 °C for 1 h, 180 °C for 1 h and 200 °C for 30 min. Finally, these membranes were warmed to 250 °C and slowly cooled in the oven. The absence of residual solvent was confirmed using thermogravimetric analysis. The thickness of the membranes ranged from 70 to 80 μm. The percent uncertainty in the thickness of a membrane was between 3 and 4%.

2.5. Techniques

The Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer RX-1 spectrometer using an ATR accessory. The ¹H-NMR spectra of the intermediates, diamine TMID and polyimide PMDA-TMID were recorded on a Bruker Avance-300 in CDCl₃. The inherent viscosities (η_{inh}) of all of the polymers were measured using an Ubbelohde viscometer at a polymer concentration of 0.5 g dL⁻¹ in NMP at 30 °C. The molecular weight and intrinsic viscosity of PMDA-TMID were determined by size exclusion chromatography using a system with an isocratic pump Perkin-Elmer 250 and RI detector Viscotek VE 3580 in parallel with a dual detector Viscotek 270, which was composed of a differential viscometer and right angle light scattering (RALS). Three Polymer Labs PL-gel[™] columns with a 10³, 10⁴ and 10⁵ Å pore diameter were used. The eluent consisted of DMF containing 0.1% LiBr at 70 °C, with a flow rate of 1 mL min⁻¹. The instrument constants were determined with a narrow polystyrene standard (Mp: 66,000 Da. Mw/Mn: 1.03, Polymer Labs). The density (ρ) of the films was determined from the Archimedes' principle using a top-loading electronic XS105 Dual Range Mettler Toledo balance and a density kit. The samples were sequentially weighed in air and in high purity isooctane at 25 °C. Five density measurements were carried out on at least three samples for each membrane. Wide-angle X-ray diffraction (WAXS) patterns were recorded in reflection mode at room temperature using a Bruker D8 Advance diffractometer with a Goebel mirror and a PSD Vantec detector. CuKα radiation (wavelength λ = 1.542 Å) was used. The step-scanning mode was employed for the detector with a 2θ step of 0.0241 ° and 0.5 s per step, where θ is the scattering angle. The *d*-spacing was calculated using Bragg's law ($d = \lambda / 2 \sin \theta$) and θ of the broad peak maximum. The thermogravimetric analysis (TGA) data were recorded on a TA Q-500 analyzer. The scans were run at 10 °C min⁻¹ under a nitrogen atmosphere (60 mL min⁻¹) in a temperature range from 50 to 800 °C. The sample mass was

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