Supporting Information


Bifunctionalized Intrinsically Microporous Polyimides with Simultaneously Enhanced Gas Permeability and Selectivity

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Bi-Functionalized Intrinsically Microporous Polyimides with Simultaneously Enhanced Permeability and Selectivity

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Experimental

Materials

4,4’-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99%), 3,5-diaminobenzoic acid (DABA) were obtained from Sigma-Aldrich and purified by sublimation before usage. m-Cresol, tetrahydrofuran, isoquinoline, and N, N’- dimethylformamide were obtained from Sigma-Aldrich and used as received. 3,3,3’,3’-Tetramethyl-1,1’-spirobisindane-5,5’-diamino-6,6’-diol (SBIDA), PIM-6FDA-OH and 6FDA-DABA were synthesized according a previously reported procedure.\textsuperscript{[1]}

Characterization and Methods

\textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of the newly synthesized monomer and polymers were recorded with a Bruker AVANCE-III spectrometer at a frequency of 400 MHz in either deuterated chloroform or deuterated dimethylsulfone with tetramethylsilane as an internal standard and recorded in ppm. Molecular weight (M\textsubscript{n}) and molecular weight distribution (PDI) of the polymers were obtained by gel permeation chromatography (Agilent GPC 1200) using THF as solvent and polystyrene as external standard. Thermal gravimetric analysis (TGA-QMS) was carried out in Netzsch TG 209 F1; the polymers were heated under N\textsubscript{2} atmosphere from room temperature to 800 °C at a heating rate of 3 °C/min. The BET surface area of the polymers was measured by N\textsubscript{2} sorption at -196 °C (Micrometrics ASAP 2020); each sample was degassed at 150 °C for 12 hrs before testing.
Polymer Synthesis

Synthesis of Co-80/20 polyimide. 3,3,3',3'-Tetramethyl-1,1'-spirobisindane-5,5'-diamino-6,6'-diol (338 mg, 0.800 mmol), 3,5-diaminobenzoic acid (30.0 mg, 0.200 mmol) and 4,4'-(hexafluoroisopropylidene)dipthalic anhydride (444.4 mg, 1.00 mmol) were added to 4.0 mL m-cresol (20% solid content). The solution was heated at 60 °C for 30 min, and thereafter one drop of isoquinoline was added. The system was then gradually heated to 180 °C and kept for 2 hrs. A viscous solution was formed and the polymer was obtained by precipitation in methanol/water (50/50, v/v) solution. The product was filtrated and dried under vacuum. The solid was re-precipitated in methanol/water twice to get the desired polymer as a light yellow filament (700 mg, yield: 90.9%). ¹H NMR (500 MHz, DMSO-d₆): 9.60 (s, 2H), 8.12-8.14 (m, 2.5H), 7.9 (s, 2H), 7.68-7.80 (m, 2.3H), 7.14 (s, 2H), 6.14 (s, 2H), 2.35 (s, 2H), 2.22 (s, 2H), 1.33 (s, 6H), 1.28 (s, 6H). FT-IR (polymer film, v, cm⁻¹): 3200 ~ 3500 (br, br, -OH and -COOH), 2920 (s, m, C-H), 1780, 1720 (s, str, imide), 1200 -1420 (m, str, ph). Molecular weight: Mn = 3.52 × 10⁴ g/mol, PDI = 1.65. S_BET = 300 m²/g.

Synthesis of Co-50/50 polyimide. The synthetic procedure was the same as the synthesis of Co-80/20 polyimide with a different monomer ratio of SBIDA (0.5) and DABA (0.5). The resulting polymer was obtained as a white powder with a yield of 90%. ¹H NMR (500 MHz, DMSO-d₆): 13.6 (s, 1H), 9.60 (s, 2H), 8.12-8.14 (m, 4H), 7.9 (s, 2H), 7.68-7.80 (m, 3H), 7.14 (s, 2H), 6.14 (s, 2H), 2.35 (s, 2H), 2.22 (s, 2H), 1.33 (s, 6H), 1.28 (s, 6H). FT-IR (polymer film, v, cm⁻¹): 3200 ~ 3500 (br, br, -OH and -COOH), 2920 (s, m, C-H), 1780, 1720 (s, str, imide), 1200 -1420 (m, str, ph). Molecular weight: Mn = 4.0 × 10⁴ g/mol; PDI = 1.68. S_BET = 9 m²/g.
Membrane Fabrication

PIM-6FDA-OH and Co-80/20 polyimides

The polymers were dissolved in THF (2-3% wt/v) to form a transparent solution and then purified using small 1.0 μm PTFE filter cartridges. The solution was carefully transferred into a flat glass Petri dish and the solvent was evaporated at room temperature for 2 days. Dry polymer films with a thickness of 80 to 100 μm were obtained. Each of the membranes was post-dried in vacuum oven at 250 °C for 24 hrs and 300 °C for 1 hr in a tube furnace under nitrogen atmosphere, respectively.

6FDA-DABA and Co-50/50 polyimides

The polymers were dissolved in DMF at a concentration of 3-5 (wt/v) and thereafter purified using small 1.0 μm PTFE filter cartridges. The solution was carefully transferred into a flat glass Petri dish and placed in an oven at 75 °C. The solvent was evaporated for 2 days and dry polymer films (~ 80 to 100 μm) were obtained. Each of the membranes was dried in a vacuum oven at 250 °C for 24 hrs and 300 °C for 1 hr in a tube furnace under nitrogen atmosphere, respectively.

Gravimetric sorption

Gas sorption of the polymers was obtained by a gravimetric technique using an IGA instrument (Hiden Isochema) at 2 bar and 35°C. All polymer samples (30 - 50 mg) were degassed for 24 hrs prior to starting the sorption experiments. Each of the samples was tested three times to ensure good data reproducibility (± 5%). The density of the polymers was measured by weighting the
sample in air and \textit{iso}-octane. The density of the polymers were then calculated using the following equation:

\[ \rho = \frac{A}{A-B} (\rho_0 - \rho_{\text{air}}) + \rho_{\text{air}} \]

where, \( A \) is the weight of polymer in the air, \( B \) is the weight of the polymer in the solution of \textit{iso}-octane, \( \rho_0 \) is the density of \textit{iso}-octane (0.688 cm\(^3\)/g), \( \rho_{\text{air}} \) is the density of air, which is 0.00122 cm\(^3\)/g. The density values of the PIM-6FDA-OH, Co-80/20 polyimide and Co-50/50 polyimide are shown in Table S1.

\begin{table}[h]
\centering
\begin{tabular}{lcc}
\hline
Polymer & 250 °C treated (g/cm\(^3\)) & 300 °C treated (g/cm\(^3\)) \\
\hline
PIM-6FDA-OH & 1.300 & 1.245 \\
Co-80/20 & 1.312 & 1.250 \\
Co-50/50 & 1.362 & 1.329 \\
\hline
\end{tabular}
\caption{Density of PIM-6FDA-OH and co-polyimides heat-treated under different conditions.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{lcccccccc}
\hline
Polymer & CHCl\(_3\) & THF & DMF & Acetone & NMP & DMAc & m-cresol \\
\hline
PIM-6FDA-OH & -- & ++ & ++ & ++ & ++ & ++ & ++ \\
Co-80/20 & -- & ++ & ++ & ++ & ++ & + & -- \\
Co-50/50 & -- & ++ & ++ & ++ & ++ & ++ & + \\
6FDA-DABA & -- & ++ & ++ & ++ & ++ & ++ & ++ \\
PIM-6FDA-OH & -- & ++ & ++ & ++ & ++ & ++ & ++ \\
Co-80/20 & -- & -- & -- & -- & -- & -- & -- \\
Co-50/50 & -- & -- & -- & -- & -- & -- & -- \\
\hline
\end{tabular}
\caption{Solubility of PIM-6FDA-OH, 6FDA-DABA and co-polyimides heat-treated under different conditions.}
\end{table}

\textsuperscript{a} The polymers were heated to 250 °C and kept for 24 hrs under vacuum. \textsuperscript{b} The polymers were heated to 300 °C and kept for 1 hr. Quantitative solubility: 1 mg of the polymer in 1 mL solvent. ++, completely dissolved; +, partial dissolved; --, not dissolved.
Table S3. Permeability and ideal selectivity of Co-80/20 and Co-50/50 copolymer membranes heat-treated at 300 °C after aging for one month.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Permeability (Barrer)</th>
<th>Ideal selectivity (α_{XY})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>N₂</td>
</tr>
<tr>
<td>Co-80/20</td>
<td>380</td>
<td>10.2</td>
</tr>
<tr>
<td>Co-50/50</td>
<td>155</td>
<td>2.5</td>
</tr>
<tr>
<td>Co-80/20</td>
<td>322</td>
<td>7.7</td>
</tr>
<tr>
<td>Co-50/50</td>
<td>144</td>
<td>2.3</td>
</tr>
</tbody>
</table>

a The membranes were heated to 300 °C and kept for 1 hr under N₂; fresh samples.

Table S4. Diffusion coefficient (D), solubility coefficient (S), diffusion selectivity (α_D) and solubility selectivity (α_S) of PIM-6FDA-OH and co-polyimide films.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>D (10^{-8} \text{ cm}^2/\text{s})</th>
<th>S (10^{-2} \text{ cm}^3/\text{cm}^3 \text{ cmHg})</th>
<th>α_D</th>
<th>α_S</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPIM-6FDA-OH</td>
<td>0.58</td>
<td>5.56</td>
<td>5.87</td>
<td>21.4</td>
</tr>
<tr>
<td>Co-80/20</td>
<td>0.77</td>
<td>8.69</td>
<td>5.33</td>
<td>19.9</td>
</tr>
<tr>
<td>Co-50/50</td>
<td>0.25</td>
<td>3.87</td>
<td>5.82</td>
<td>19.9</td>
</tr>
<tr>
<td>PIM-6FDA-OH</td>
<td>1.06</td>
<td>8.62</td>
<td>4.99</td>
<td>19.5</td>
</tr>
<tr>
<td>Co-80/20</td>
<td>1.62</td>
<td>15.2</td>
<td>4.13</td>
<td>17.2</td>
</tr>
<tr>
<td>Co-50/50</td>
<td>0.30</td>
<td>3.85</td>
<td>4.38</td>
<td>17.4</td>
</tr>
</tbody>
</table>

a) The membranes were heated to 250 °C under vacuum oven for 24 hrs. b) The membranes were heated to 300 °C under N₂ and kept for 1 hr. c) The solubility data were obtained by IGA sorption of polymer powders at 2 bar and 35 °C.
Figure S1. CO$_2$/CH$_4$ and H$_2$/CH$_4$ separation performance of the polyimide membranes annealed at 250 °C under vacuum for 24 hrs and thermally treated at 300 °C under N$_2$ atmosphere for 1 hr.

References