Supplementary Materials: A Facile Synthesis of (PIM-Polyimide)-(6FDA-Durene-Polyimide) Copolymer as Novel Polymer Membranes for CO\textsubscript{2} Separation

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S-1. Materials

4,4’-(Hexafluoropropylidene) di-phthalic anhydride (6FDA), 2,3,5,6-tetramethyl benzene-1,4-diamine (durene), and 4,5-dichloro phthalonitrile (98%), were purchased from Tokyo Chemical Industry (TCI) Co. Ltd. (Tokyo, Japan) and were used as obtained. 5,5’,6,6’-Tetrahydroxy-3,3’,3’-tetramethyl-1,10-spirobisindane (97%) was obtained from Alfa Aesar. Acetic anhydride, toluene, and triethylamine were obtained from Sigma Aldrich. Methanol, ethanol, dimethylformamide, dimethylacetamide, potassium carbonate, and potassium hydroxide were purchased from DaeJung Chemicals & Metals Co. Ltd. in South Korea. 6FDA, durene, and K\textsubscript{2}CO\textsubscript{3} were dried under a vacuum at 60 °C for 24 h prior to use. Anhydride monomer of PIM (An) was synthesized following the literature method [22]. All chemicals, unless otherwise noted, were obtained from commercial sources and were used as received.

S-2. Characterization and Measurements

The \textsuperscript{1}H NMR spectra were obtained on an Agilent 400-MR (400 MHz) instrument using \textit{d}\textsubscript{6}-DMSO or CDCl\textsubscript{3} as a reference or an internal deuterium lock.

The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded using a Bruker Vertex 80v Hyperion 2000 ATR-FTIR spectrometer.

Molar masses were determined by gel permeation chromatography (GPC) using two PL Gel 30 cm × 5 µm mixed C columns at 30 °C running in DMF and calibrated against polystyrene (M\textsubscript{n} = 600×10\textsuperscript{6} g mol\textsuperscript{-1}) standards using a Knauer refractive index detector.

The thermal stability of the membranes was analyzed by thermogravimetric analysis (TGA) measurements conducted on a Shimadzu TGA-2950 instrument at a heating rate of 10 °C min\textsuperscript{-1} under a nitrogen flow.

The tensile properties were measured on a Shimadzu EZ-TEST EZ-L instrument benchtop tensile tester using a crosshead speed of 5 mm min\textsuperscript{-1} at 25 °C under 50% relative humidity. The engineering stress was calculated from the initial cross-sectional area of the sample and Young’s modulus (E) was determined from the initial slope of the stress-strain curve. The membrane samples were cut into rectangular shapes 40 mm × 10 mm (total) and 20 mm × 10 mm (test area) in size.

The densities of the membranes (g cm\textsuperscript{-3}) were determined experimentally using a top-loading electronic Mettler Toledo balance (XP205, Mettler-Toledo, Switzerland) coupled with a density kit based on the Archimedes principle. The samples were weighed in air and in a known-density liquid, high-purity heptane. The measurements were performed at room temperature using the buoyancy method, and the density was calculated as follows:

\[
\rho_{\text{polymer}} = \frac{W_0}{W_0 - W_1} \cdot \rho_{\text{liquid}} \tag{S1}\]
where \( W_0 \) and \( W_1 \) are the membrane weights in air and in heptane respectively. Heptane sorption of the membranes was not considered due to their extremely low absorption properties.

The X-ray diffraction patterns of the membranes were measured using a Rigaku DMAX-2200H diffractometer operated at a scanning rate of 4° min\(^{-1}\) in a 20 range from 5° to 30° with Cu Kα1 X-ray radiation (\( \lambda = 0.1540598 \)). The \( d \)-spacings were calculated using Bragg’s law (\( d = \lambda / 2 \sin \theta \)).

Tapping-mode AFM was conducted using a Bruker MultiMode instrument. A silicone cantilever with an end radius of <10 nm and a force constant of 40 Nm\(^{-1}\) (NCHR, nanosensors, \( f = 300 \) kHz) was used to image the samples at an ambient temperature.

S-3. Gas Permeation Procedure

Permeation measurements of pure gas were taken using a high-vacuum time-lag measurement unit based on a constant-volume/variable-pressure method. All of the experiments were performed at a feed pressure of 2 bar (except for the pressure effect experiments which were carried out in the range of 100 mbar to 2 bar feed pressure) and a feed temperature of 30 °C. Before taking these measurements, both the feed and the permeate sides were thoroughly evacuated to below 10\(^{-5}\) Torr (1.33×10\(^{-8}\) bar) until the readout showed zero values for the removal of any residual gases. The downstream volume was calibrated using a Kapton membrane and was found to be 50 cm\(^3\). The upstream and downstream pressures were measured using a Baraton transducer (MKS; Model No. 626B02TBE) with a full scale of 10,000 and 2 Torr (13.3 and 2.7×10\(^{-3}\) bar), respectively. The pressure on the permeate side was recorded as a function of time using a pressure transducer and passed to a desktop computer through a shielded data cable. The permeability coefficient was determined from the linear slope of the downstream pressure versus a time plot (\( dp/dt \)) according to the following equation:

\[
P = \frac{273}{76} \times \frac{V l}{ATp_0} \times \frac{dp}{dt}
\]  

(S2)

where, \( P \) is the permeability expressed in Barrer (1 Barrer = 10\(^{-10}\) [cm\(^3\) (STP) cm.cm\(^{-2}\).s\(^{-1}\).cm\(^{-1}\).Hg\(^{-1}\)], \( V \) (cm\(^3\)) is the downstream volume, \( l \) (cm) is the membrane thickness, \( A \) (cm\(^2\)) is the effective area of the membrane, \( T \) (K) is the measurement temperature, \( p_0 \) (Torr) is the pressure of the feed gas in the upstream chamber, and \( dp/dt \) is the rate of the pressure change under a steady state. For each gas, the permeation tests were repeated more than three times, and the standard deviation from the mean values of the permeabilities was within ca. ± 3%. Sample-to-sample reproducibility was high and within ± 3%. The effective membrane areas were 15.9 cm\(^2\). The ideal permselectivity, \( \alpha_{A/B} \), of the membrane for a pair of gases (A and B) is defined as the ratio of the individual gas permeability coefficients:

\[
\alpha_{A/B} = \frac{P_A}{P_B}
\]  

(S3)

The diffusivity and solubility were obtained from the time-lag (\( \theta \)) value according to the equations:

\[
D = \frac{l^2}{6\theta}
\]  

(S4)

\[
S = \frac{P}{D}
\]  

(S5)

where, \( D \) (cm\(^2\) s\(^{-1}\)) is the diffusivity coefficient, \( l \) is the membrane thickness (cm) and \( \theta \) is the time lag (s), as obtained from the intercept of the linear steady-state part of the downstream pressure versus a time plot. The solubility, \( S \), was calculated from Equation. (S5) with the permeability and diffusivity obtained from Equation. (S3) and (S4).
Figure S1. TGA graph (a) and S-S curve (b) of the copolymer [(PIM-PI)-(6FDA-durene-PI)] membranes.

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