Fine-Tuned Intrinsically Ultramicroporous Polymers Redefine the Permeability/Selectivity Upper Bounds of Membrane-Based Air and Hydrogen Separations

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Experimental

Polymer Film Preparation and Storage

Solutions containing 3-5 wt% polymer in chloroform were syringe-filtered with 0.45 μm PTFE filters and cast onto clean, flat-bottomed glass dishes. Clear, isotropic polymer films were obtained by covering the dishes to induce slow evaporation of the casting solvent. All films were dried at 120 ^{o}C under vacuum for 12 h, soaked in methanol for 24 h to "reset" their thermal histories and exchange any residual casting solvent, and finally dried at 120 ^{o}C under vacuum for 24 h – except those of PIM-EA-TB, PIM-Trip-TB and SBFDA-DMN, which were air-dried after the methanol soak. Removal of the casting solvent was confirmed with thermal gravimetric analysis (TGA, TA Q-5000). Effective areas and thicknesses of the films were determined by calibrated scanning software and a digital micrometer, respectively. During the first 15 days, all films (except those of PIM-EA-TB, PIM-Trip-TB and SBFDA-DMN) were aged *in-vacuo* at 35 ^{o}C and then kept in plastic bags under ambient conditions thereafter during physical aging. PIM-EA-TB, PIM-Trip-TB and SBFDA-DMN were stored under ambient conditions during the physical aging.

Pure-gas Permeation Measurements

The pure-gas permeabilities of the films were determined using the constant-volume/variable-pressure method. Films dried after the methanol soak were immediately masked between two aluminum-tape donuts. On one side, the interface between the film and tape was lightly epoxied using a two-part potting epoxy (GC Electronics) which showed excellent durability over long times. The masked film was degassed in the permeation test apparatus on both sides under high vacuum at 35 ^{o}C. Pure gases (grade 5 and above) were fed to the epoxied side at 35 ^{o}C and 2 bar.

Data for PIM-EA-TB, PIM-Trip-TB and PIM-PI-EA were previously reported and collected at 25 ^{o}C after *ambient* drying of the methanol-soaked films. The increase in permeate pressure with time was measured by an MKS Baratron transducer. The pure-gas permeabilities were calculated by

$$P = DS = 10^{10} \frac{V_d l}{p_{up} ART} \frac{dp}{dt}$$

where P is the gas permeability (Barrer) (1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}), p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg s^{-1}), V_d is the calibrated permeate volume (cm^3), l is the membrane thickness (cm), A is the effective membrane area (cm^2), T is the operating temperature (K), and R is the gas constant (0.278 cm^3 cmHg cm^{-3}(STP) K^{-1}). The ideal permselectivity ($\alpha_{A/B}$) for separation of A/B was calculated by:

$$\alpha_B^A = \frac{P_A}{P_B}$$

Low-Pressure Physisorption Measurements

Powder polymer samples were degassed under high vacuum at 120 ^{o}C for 15 hours in the degas port of a Micromeritics ASAP-2020 equipped with the "micropore option." The nitrogen sorption isotherms were measured using low-pressure dosing at 77 K. Analysis of the pore-size distributions was performed using the NLDFT (Non-Local Density Functional Theory) model, assuming carbon slit-pore geometry in the version 4.02 software provided by Micromeritics.
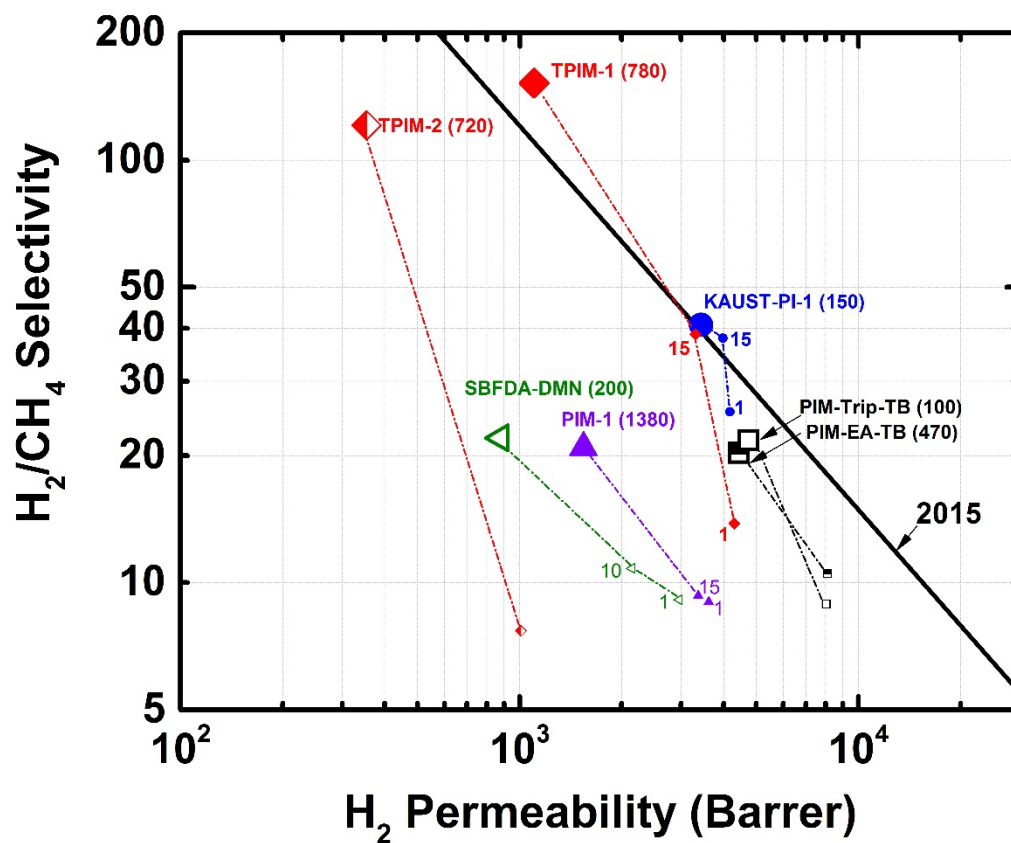
PIM gas transport properties post methanol treatment
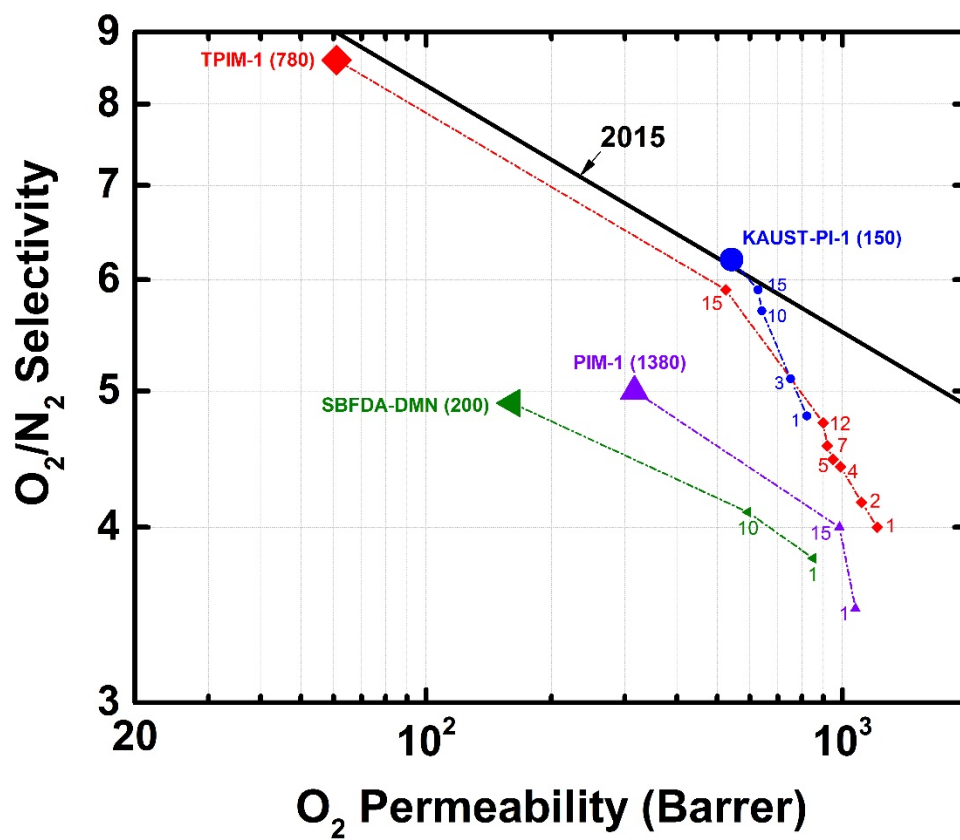
Figure S1. Evolution of the O_2/N_2 gas transport properties of several PIMs over time after methanol treatment. The numeric labels indicate days elapsed.
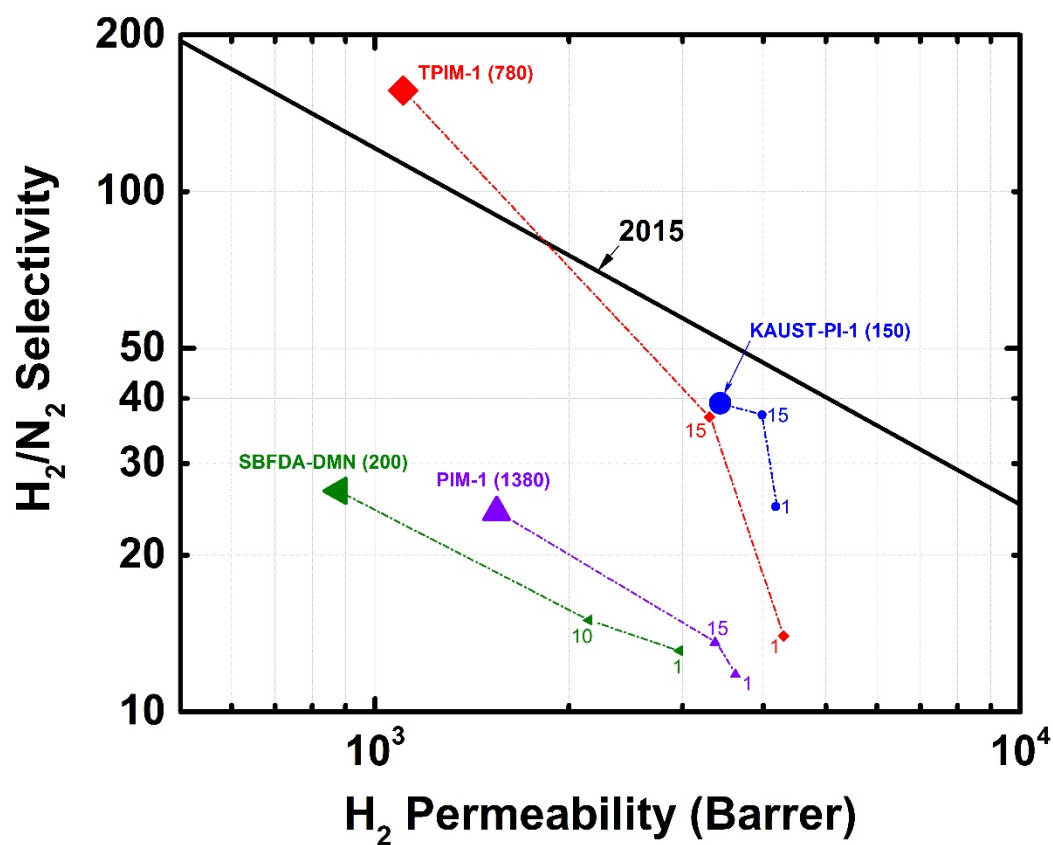
Figure S2. Evolution of the H_2/N_2 gas transport properties of several PIMs over time after methanol treatment. The numeric labels indicate days elapsed.

Figure S3. Evolution of the H_2/CH_4 gas transport properties of several PIMs over time after methanol treatment. The numeric labels indicate days elapsed.