

Supporting Information

Polyimides Containing Phosphaphenanthrene Skeleton: Gas Transport Properties and Molecular Dynamics Simulations

Rimpa Chatterjee^{a)}, SoumenduBisoi^{a)}, Anaparthi Ganesh Kumar^{a)}, Venkat Padmanabhan^{b)} and Susanta Banerjee^{a),*}

^{a)}Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur – 721302, India

^{b)}Department of Chemical Engineering, Tennessee Technological University, Cookeville, TN 38505, USA

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1. Molecular Dynamics (MD) Simulations. Atomistic molecular Dynamics (MD) simulations of PI s were performed by using the LAMMPS molecular simulation package to understand the structure-property relationships of the polymer membranes for gas separation applications.¹⁻⁷ The OPLS-AA (Optimized Potentials for Liquid Simulations - All Atom) force field was used to model all bonded and non-bonded interactions between explicit atoms of the system. An amorphous cell containing 20 polymer chains with 10 repeat units was first prepared for the individual PI systems using the Avogadro molecular editing package. Once the amorphous cell was constructed and all the force field parameters applied, the total energy of the system was minimized using the conjugate gradient method, with maximum distance of line search set at 0.1 Å. The structures were then equilibrated under isobaric-isothermal thermodynamic conditions (NPT ensemble) with the temperature and pressure fixed at 300 °C and 1 atm, respectively, for 5 ns, with a time step of 1 fs, until the conformational distribution, the box side length, and the potential energy fluctuated around constant values. Subsequently, all systems were compressed using the method of shrinking boxes to achieve system densities equal to the experimental values, as given in Table 1. To relax the systems at these densities, the systems were equilibrated further at a constant temperature of $T = 300$ °C, which is above the glass transition temperature (T_g) of all PIs, in a canonical (NVT) ensemble for 10 ns with a time step of 1 fs. The temperature was controlled using a direct velocity rescaling procedure with a temperature window of 10 °C. Under these conditions, greater temperature fluctuations are allowed, but the disturbance in the trajectory is insignificant. After equilibrating the polymers in the melt state, the temperature was lowered to 30 °C followed by another equilibration run at the same conditions in an NVT ensemble for 5 ns to release the residual stresses due to the rapid cooling of the system. The data

for the analysis were collected from additional production runs of 1 ns duration with a time step of 1 fs and a sample collection frequency of 1 ps.

The free-volume regions within the simulation box were determined by the general method of grid scanning. A grid with a spacing of 0.3 Å between the neighboring nodes was established within the simulation domain. The location of each grid point was then optimized to maximize its distance from all the atoms of the polymer chains. If the distance of the node from surrounding atoms is greater than their atomic radii, it indicates that the grid point is present in a void space within the box. The coordinates of such grid points were saved, together with the shortest distance from an atom, according to the algorithm described by Voorintholt et al.⁵ The saved data with the optimized locations of grid points along with the shortest distance allows determination of accessible positions for probes with different radii, with the shortest distance being the maximum radius of the probe molecule. The total free volume can then be calculated by setting the probe radius to 0. The fractional free volume (FFV) was calculated as the ratio of the total free volume to the total volume of the simulation box. The fractional free volume for all systems was obtained as average values calculated over 1000 samples collected from production runs to prevent redundant correlations. The fractional accessible volume (FAV) was estimated by considering various sizes of the (spherical) probe molecule. The free volume distribution (FVD) of the polymers was analyzed to get a better insight into the distribution of free volume elements, which affect gas diffusivity.

To estimate the diffusivity of various gas molecules through the different PI membranes, 5 molecules of each gas randomly inserted into the simulation box such that they do not overlap with the existing atoms of the polymer and then running a canonical ensemble MD simulation for 10 ns at a constant temperature of 30 °C. All gas molecules were represented by explicit

atoms with the OPLS-AA force field to monitor the mobility of gas molecules within these systems. The diffusion coefficients were obtained as the average of all five molecules. The mean-squared displacement (MSD) of the center of mass was plotted for each gas molecule in all the PI membranes as a function of time. The diffusion coefficient of all the gases in each type of PI membrane was then calculated from the MSD using Einstein's relation (S1):

$$\langle \text{MSD} \rangle = 6Dt \quad (\text{S1})$$

The angle brackets indicate the ensemble average. The diffusion coefficients were obtained as the average of all the five molecules.

2. Gas permeability measurements. The gas transport properties of CO₂, O₂, N₂, and CH₄ through PI membranes were performed at 3.5 bars of applied gas pressure and at 35 °C. The representative output pressure versus time plots for 6FDA based polyimide (PI A) are shown below (Figure S1 to S5). The slope of the individual plots (Figure S2 to S5) at the steady-state $[(dp/dt)_s]$ was used to calculate the gas permeability values of the membranes.^{6,7}

2.1. Output pressure versus time plots

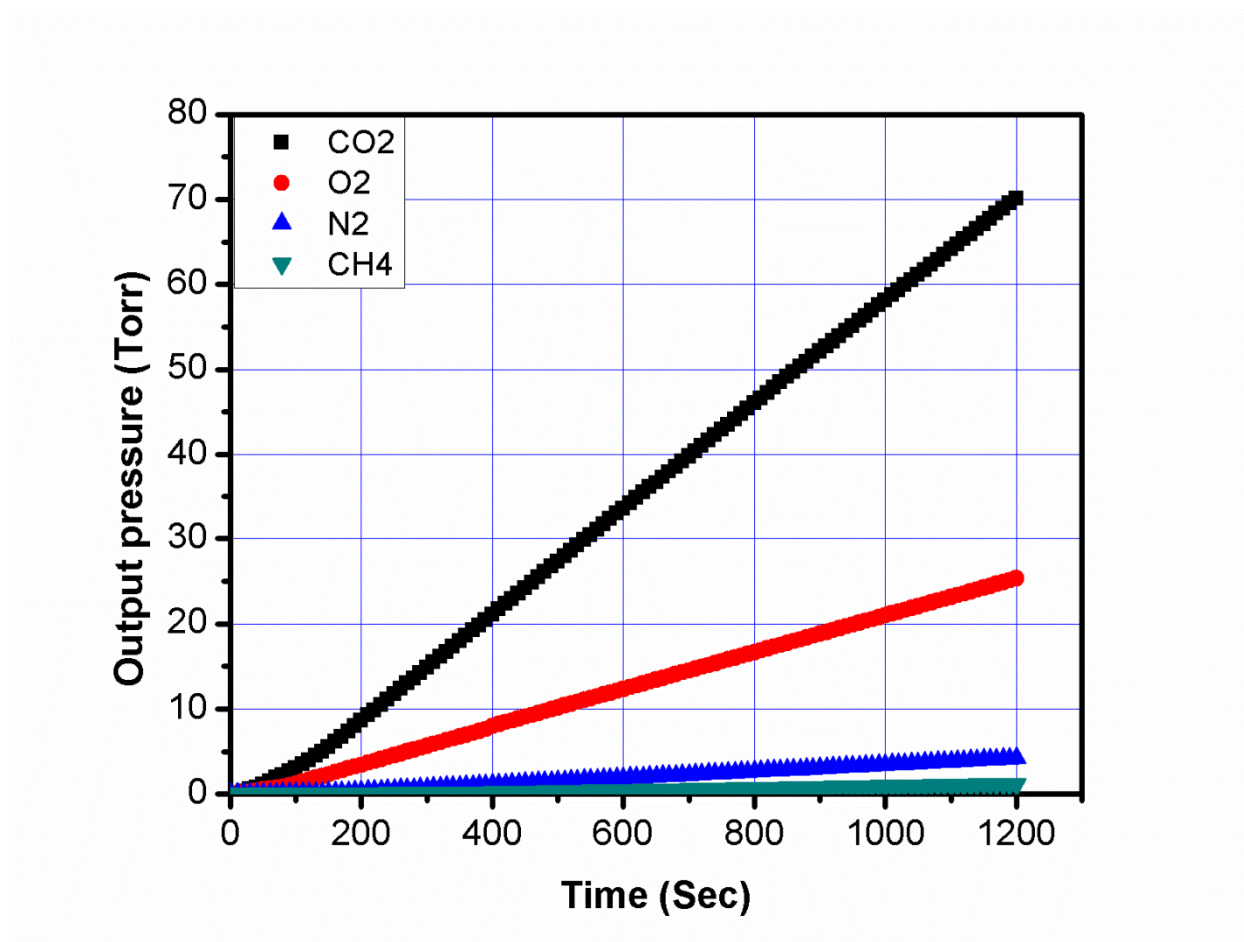


Figure S1. Combined plot of the output pressure in the downstream chamber of all four gases (CO₂, O₂, N₂, CH₄) versus time plot for PI A membrane.

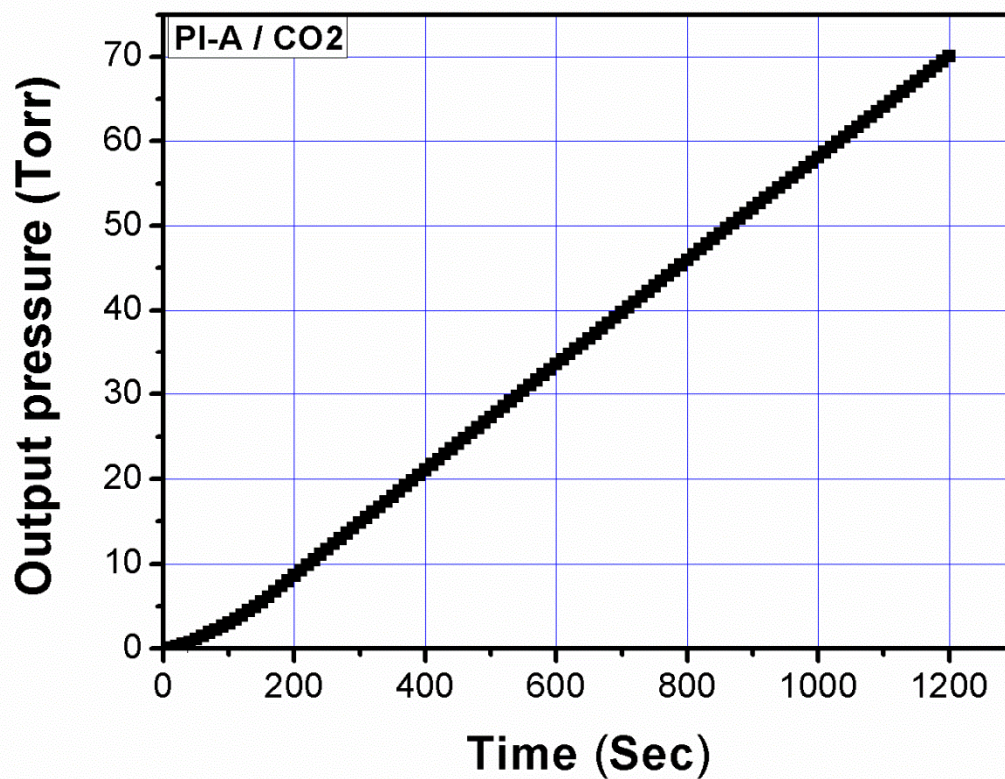


Figure S2. The output pressure of CO₂ at the downstream chamber versus time for PI A membrane.

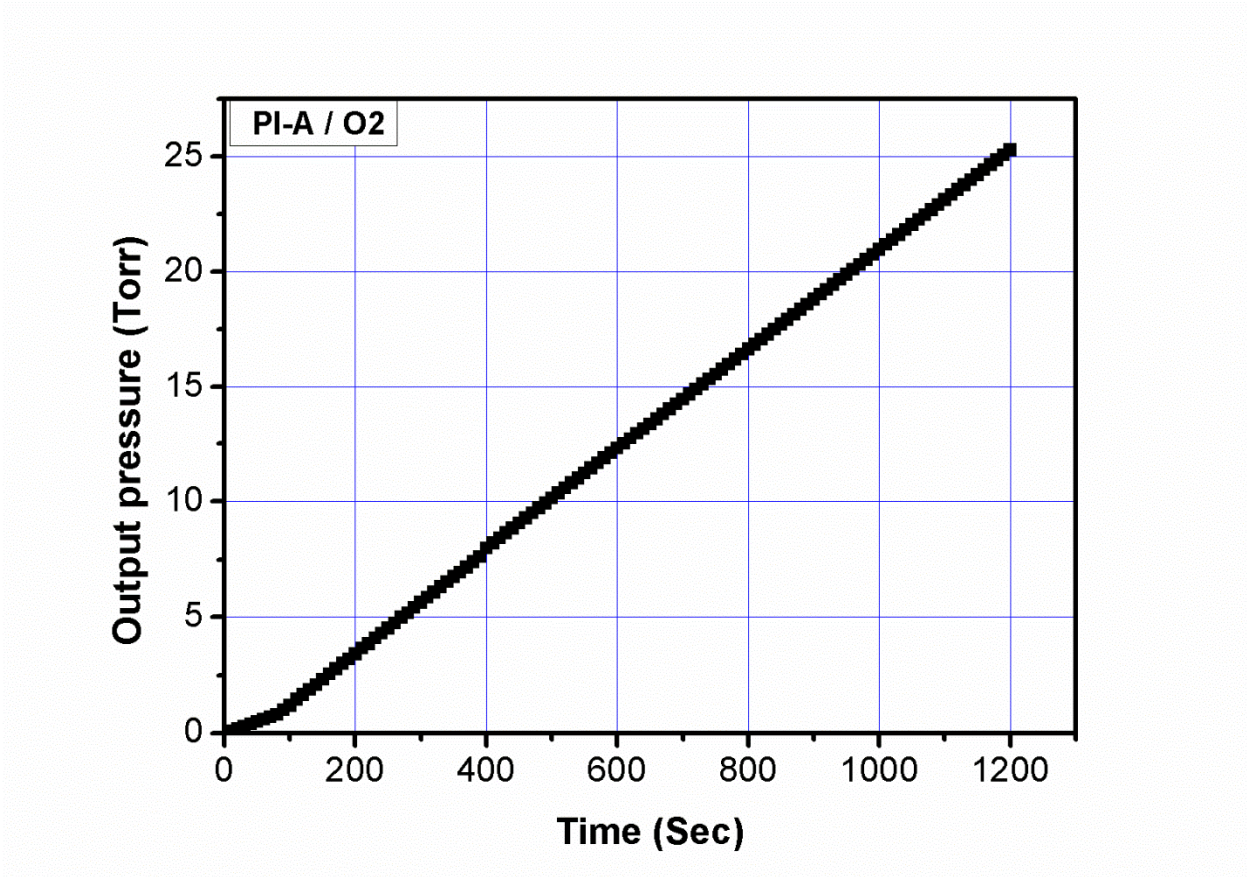


Figure S3. The output pressure of O₂ at the downstream chamber versus time for PI A membrane.

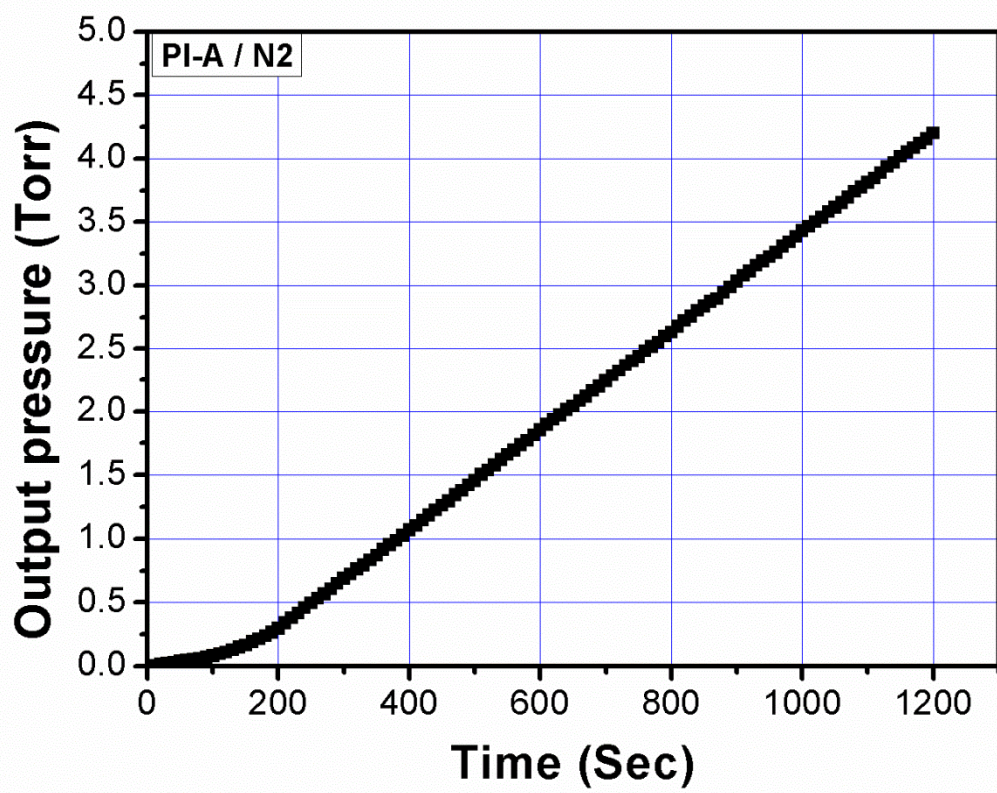


Figure S4. The output pressure of N₂ at the downstream chamber versus time for PI A membrane.

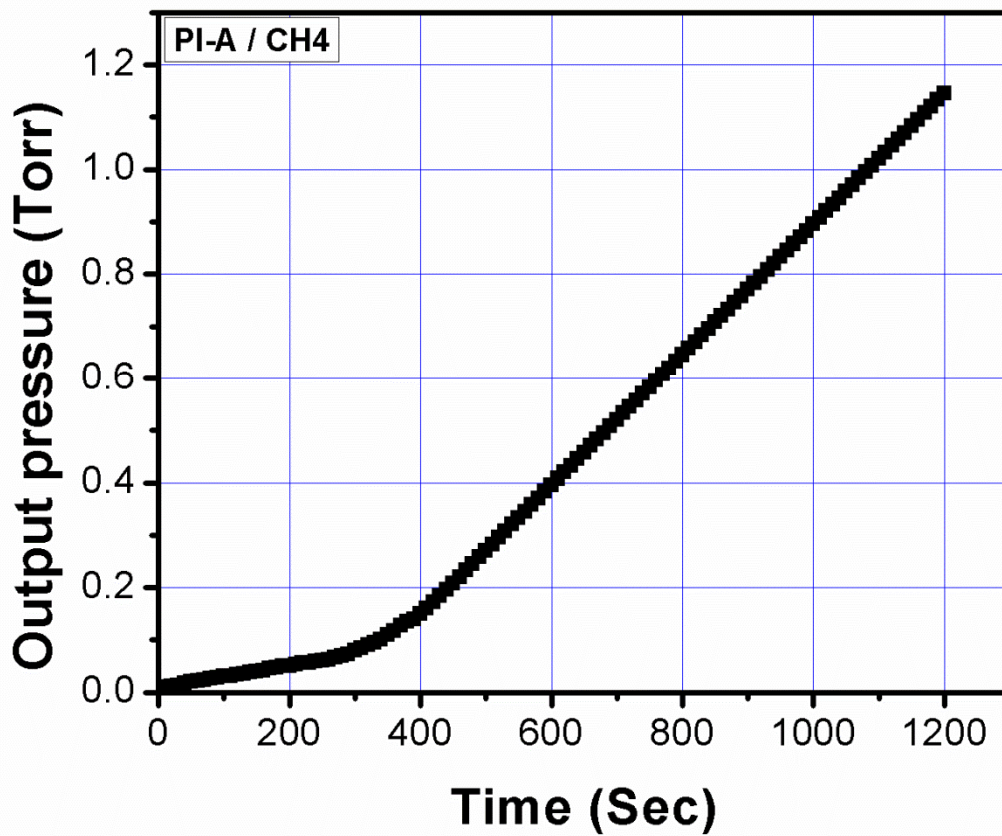


Figure S5. The output pressure of CH₄ at the downstream chamber versus time for PI A membrane.

3. References

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