Molecular Dynamics Investigation into the High Permeability and High Selectivity of Nano-Porous Polyimide Membranes for the “Green” Separation of Natural Gas

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Molecular modeling techniques were used to investigate the permeability and selectivity of various natural gas components through nano-porous polyimide membranes for the environmentally-friendly “green” separation of natural gas. The polyimide membranes showed the ability of creating nano-scale channels within the polymeric matrix during the molecular mobility of the polymeric chains through which specific gas molecules can penetrate the membrane surface. The four natural gas components investigated in this study were methane, ethane, propane and butane, all hydrocarbon materials of similar basic chemical structures. The self-diffusion coefficients of the gas molecules were thus used to express the permeability of the various gases through the membranes since the solubility of the gas molecules in the polymeric substances were assumed to be constant. Methane showed a noticeably high self-diffusion coefficient calculated from the application of Einstein relation to the generated molecular dynamics trajectories. All other gases had similar values for the self-diffusion coefficients, which indicate the ability of the methane molecules to penetrate the polymeric membrane in a much larger speed due to a possible matching between the methane molecular size and the size of the interconnected nano-channels within the membranes. The results also showed that the polymer molecules had lower self-diffusion coefficients than the gas ones due to the large size of the polymeric segments. Other structural parameters such as the radial distribution function in direct relationship to the local packing of the polymeric segments and penetrant molecules are also illustrated.

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I. INTRODUCTION

Natural gas is of a great importance to both the petrochemical industry and power-producing plants [1]. It supplies petrochemical precursors such as ethane, propane, butane, etc., which will be converted later to plastics, rubbers, paints, adhesives, coatings and medicines as well as, of course, methane, which is an excellent energy source. Gas separation of mixtures of natural gases for the production of these petrochemicals is a key task to the petrochemical industries. The same is also true for greenhouse gases such as CH₄, CO₂ and CFCs or mixtures of exhaust gases such as NO₂, SO₂ and CO₂ known as acid-rain gases. Normally, cryogenic separation involving liquefaction and distillation of the gas mixture is used extensively [1]. However, recently this energy-intensive process has forced the industry to explore other environmentally friendly routes for the separation of gases through selective membranes, which allow the permeation of one gas type only through the membrane on the expense of other types of gases. Consequently, there is an increasing demand to develop new and more powerful membrane materials for the various gas separation applications.

Recent strategies on membrane development are centered around the synthesis of new polymeric substances with specific structural parameters such as bulkiness, presence of electronegative atoms, alternating double bond, out-of-plane kinks, etc. that can create nano-voids or nano-scale channels within the polymeric matrix during the molecular mobility of the polymeric chains [2–6]. One main property to be optimized is the permeability, which is commonly expressed as product of diffusivity and solubility. Whereas the diffusivity is affected by the free volume, i.e. the unoccupied space in the polymeric matrix, the solubility is influenced by the physical and chemical interactions between the gas molecules and the polymer [5, 6].

Free volume in a polymeric membrane is generally considered a major factor for gas transport. Studies relating polymer properties and free volume have been carried out by many authors in order to understand the transport mechanism of gases through the membranes [3, 6–11]. The total free volume in a polymer is, as a first approach, defined as the unoccupied volume in the polymer. More precisely it consists of complex interconnected nano-spaces between the polymeric chains [12–14]. The term fractional free volume (FFV) for the total fraction of unoccupied space in the polymer is thus used frequently. This fractional free volume consists of many isolated spaces of variable volume and size, which can be determined experimentally by Positron annihilation lifetime spectroscopy (PALS). Detailed information on the particulars of the free volume can be provided by applying computational modeling and molecular dynamics simulations [15–17]. By manipulating the polymeric chains and the size, shape and distribution of the nano-channels, the free volume in the polymeric matrix can be tuned to provide variations in the membrane permeability and selectivity [2, 4, 5, 18–22].

The gas solubility parameter expresses the nature and magnitude of the interaction between the pene-
trant molecules and the membrane polymeric chains. For instance, organic molecules have smaller diffusion coefficients than those of oxygen molecules, yet they have higher permeability rates because of their much higher solubility in polymer membranes such as poly(dimethylsiloxane) and polyimides. Other properties that play a critical role in the performance of various membranes are van der Waals interactions, hydrogen bonding, electrostatic effects, charge transfer effects, and dipole moments. Several attempts for the improvement of gas permeability beyond the realm of current conventional membranes were done [22, 23]. While polyimides, for instance, are known for their exceptional chemical and thermal stability, mechanical robustness, processability, and structural diversity, current research efforts are focusing on the intrinsic nanoporosity and high gas permeability of these membranes [23].

Gas molecules permeate through rubbery polymers faster than they do in glassy polymers since the binding force between the molecular segments of the polymer is not strong, and segments can move relatively easily to open nano-channels through which even large molecules can pass. Since the chain segment motions in glassy polymers are more restricted than in rubbery polymers, polymers above their glass transition temperatures (T_g) can discriminate between extremely small differences in the dimensions of common gases (0.2-0.5 Å). It was shown that in most cases of practical interest, the rate of gas permeation through the polymer membranes is controlled by the diffusion of the penetrant gas in the polymer matrix. Many theoretical models have been proposed in the literature to describe the mechanisms of gas diffusion in polymers on a molecular level [24]. Such models provide expressions for gas diffusion coefficients, and sometimes also for permeability coefficients, derived from free-volume, statistical-mechanical, energetic, structural or other considerations. Based on solubility, permeability and other data, it was concluded that fast diffusion (and not a large solubility) is responsible for the large gas permeability observed for the nano-porous polymeric membranes. The fast diffusion was reported to depend on the presence of nano-voids in the polymer and on the high connectivity among the voids. It is thus expected that these nano-voids form the dispersed phase as the dense region forms the continuous phase, which renders the membranes as a loosely packed network of polymer chains with continuous channels or pores for diffusion. The formulation of the diffusion coefficients in various nano-porous membranes is complicated by the fact that gas transport occurs through markedly different mechanisms in rubbery and glassy polymers at temperatures above and below the T_g of the polymers, respectively. Additional complications are due to polymer plasticization (swelling) by the penetrant gas, polymer crystallinity, pretreatment (particularly of glassy polymers), and other factors. It has also been shown that crystalline polymers have high chemical and thermal stability but difficult to process since they are insoluble in most solvents [22]. In order to (i) facilitate the development of new and novel gas-selective polymer membranes, (ii) provide a better understanding of the gas transport mechanisms in nano-porous polymers, and (iii) employ experimental observations into the validation of the theoretical findings, molecular modeling techniques are frequently used in conjunction with experimental investigations [25].

Recent advances in the development of very fast computers used for the computer simulation of polymer nanostructures may provide much more realistic molecular models of gas diffusion in nano-porous polymers. A number of investigators have already shown that diffusion coefficients for light gases in nonporous rubbery polymers can be estimated from molecular dynamics simulations [25]. The estimated diffusion coefficients are generally consistent with experimental values. The estimation of diffusion coefficients of gases in nano-porous polymers is a more difficult task, however, since such polymers exhibit the aforementioned voids or channels. The influence of the molecular structural parameters on the creation of the nano-voids will also provide very valuable information for the design of new nano-porous membranes with exceptional properties. This is evident by considering the various structural parameters, which forces the polymer to create these channels or nano-voids. For example, high torsional energy barriers for rotation about a backbone single bond may cause the rotation around the single bond extremely unlikely and render the polymeric chains to be viewed as inflexible coils. Gas permeation occurs probably through large interchain regions formed by rigid polymeric chains which could be well described by the dual-mode model for sorption (S) of gasses in glassy polymers, given by:

\[
S = C = K_d a + C_H \left( \frac{ba}{T} + ba \right)
\]  

where \( a \) is the relative penetrant pressure \((p/p^*)\). The concentration of penetrant molecules in the polymer \((C)\) has the units of mass of vapor sorbed per mass of polymer. Henry law parameter, \( K_d \), is identified with penetrant sorption into the densified equilibrium matrix of the polymer, whereas the Langmuir capacity parameter, \( C_H \), characterizes the sorption capacity of the non-equilibrium excess free-volume associated with the glassy state of the polymer. Finally, the Langmuir affinity, \( b \), is an equilibrium constant characterizing the affinity for the Langmuir site in the polymer.
II. THEORETICAL METHODOLOGY

A. Molecular simulation of the polyimide-penetrant systems

Molecular representation of the polyimide and different penetrant gas molecules will be constructed and evaluated for their permeability and selectivity characteristics using molecular dynamics simulation modules in Materials Studio® simulation package available from Accelrys, Inc, UK [26]. The simulation study will be used to investigate the self diffusion of the various components of natural gas such as methane, ethane, propane and butane through a polyimide membrane known as PIM [27]. Figure 1 illustrates the molecular structure of the polyimide, PIM, employed in this study. The MS amorphous cell module was used to construct the four individual simulation cells consisting of 3 PIM chains of 1,600 g mol$^{-1}$ each along with 10 penetrant molecules representing each one of the four gases under study, respectively. Figure 2 represents one of the simulation cells used to study the self-diffusion of propane through the PIM polymer. The simulations cells in the four case studies were all cubic cells having densities 1.0 g/cc. The cells were all constructed using COMPASS forcefield assigned charges and Ewald summation method. After the construction is complete, the simulation cell was minimized using the MS Discover module till complete convergence. Once the simulation cells were minimized, they were all subjected to molecular dynamics runs using NVT ensemble for 300 ps with 1 fs time step at the temperature of 298K. Recent studies showed that running the simulations for 300 ps produces meaningful trajectories with reproducible results and allows for better sampling averages over the whole course of the simulation [26, 27]. Full trajectories were saved every 100 steps. During the simulation, the temperature was controlled using Anderson thermostat.

B. Determination of the mean square displacement and self-diffusion coefficients

In order to enhance the sampling efficiency in calculating the diffusion coefficients, ten gaseous molecules of each type were inserted into the cells. This was done to ensure a reliable representation of the trajectories. The self-diffusion coefficients of the gas molecules were calculated from the Einstein relation:

$$D_0 = \frac{1}{6N} \lim_{x \to \infty} \frac{d}{dt} \sum_{i=1}^{N} \langle [r_i(t) - r_i(0)]^2 \rangle$$

where $r_i$ is the position vector of atom $i$ and $N$ is the number of all atoms in the chain. The angular brackets denote averaging over all choices of time origin and over all particles and expressed in all the figures as error bars referring to the standard errors. The diffusion coefficients of the penetrant molecules will be considered in evaluating the permeability of the four gases through the PIM membranes. This is possible since the permeability of gases through polymers depends on both the diffusion of gases through the polymeric material and the solubility of the gas molecules in the polymer. Since the four gases under study, namely, methane, ethane, propane and butane have similar structural characteristics, their solubility in the polymeric material is expected to be comparable and their permeability will therefore depend only on their diffusivity through the polymeric membrane.

III. RESULTS AND DISCUSSION

Results of the molecular dynamics study are all shown in Figs. 3 through 8 and in Table I. Figures 3-6 clearly show the evolution of the mean square displacement for the different gases under study and the polymer molecules as a function of time for the various PIM/gas systems. It should be obvious from the figures that the polymeric
FIG. 4: The evolution of the mean square displacement of ethane gas molecules and PIM polymer.

FIG. 5: The evolution of the mean square displacement of propane gas molecules and PIM polymer.

FIG. 6: The evolution of the mean square displacement of butane gas molecules and PIM polymer.

FIG. 7: The radial distribution function of the PIM polymer in the four simulated systems.

FIG. 8: The radial distribution function of the various gases in the four simulated systems.

segments show much lower mean square displacements as compared to those of the different gases at the different systems. This is because the polymer molecules are much larger than the gas ones and as such have more hindered mobility and a lower diffusivity. The gas molecules, however, are small enough to penetrate the polymeric materials through the voids on its surface and are able to jump from one unoccupied site to another through the nanochannels created within the polymeric matrix during the molecular mobility of the polymeric chains.

By applying the Einstein relation, Eq. (2), the diffusion coefficients of the different gases and the PIM-polymide polymer could be calculated by evaluating the various slopes in Figs. 3 through 6. These are shown in Table I. The results shown in the table are quite interesting since for the four simulated systems, all the different gases showed similar diffusion coefficients except for methane.
This is quite interesting since the different gases have basically the same chemical structural characteristics and therefore their solubility through the PIM should be similar. The only variant in this case is the size of the gas molecules with the methane gas has the smallest molecular size among all gases under study. It could be deduced, therefore, that the small size of the methane gas molecule has a direct and simple relationship to its high diffusivity, which is apparently not the case since accordingly, an incremental trend for the self-diffusion coefficient should have been observed for the four gases in the order of methane > ethane > propane > butane. Therefore, a more complicated mechanism must exist to explain the high diffusion coefficient for methane alone with all other gases having similar gas diffusion coefficients. This is possible by considering the relationship between the methane molecular size and the size of the nano-pores created within the polymeric matrix during the molecular mobility of the polymeric chains through which the methane molecules may jump from one unoccupied site to another. For the other gases, the larger size of their molecules as compared to the size of the methane molecules and possibly to the size of the nano-pores doesn’t allow these gases to jump as such. In this case, the nano-pores act as a filter system, which allows the small-size methane molecules to pass through the channel system only but block all other larger gas types. The other gases diffuse rather slowly during the normal steady molecular mobility of the system.

To characterize the local packing and intermolecular structure in the simulated amorphous structures, the radial distribution functions were evaluated. The radial distribution function, \( g_{\alpha\beta}(r) \), is calculated from the average of the static relationship of every given pair of particles, \( \alpha\beta \), as:

\[
g_{\alpha\beta}(r) = \frac{\langle n_{\alpha\beta}(r) \rangle}{4\pi r^2 \Delta y \rho_{\alpha\beta}}, \tag{3}
\]

where \( \langle n_{\alpha\beta}(r) \rangle \) is the average number of atom pairs in the spherical shell between \( r \) and \( r + \Delta r \), and \( \rho_{\alpha\beta} \) is the density of atom pairs of type \( \alpha\beta \). In this investigation, \( g(r) \) is evaluated for either all pairs of carbon atoms in different chains and molecules or all pairs of carbon atoms in the same chain that are separated by at least four bonds. Figures 7 and 8 represent the radial distribution function, evaluated as an average value over the whole molecular dynamics trajectories, for the PIM polymer in the four different simulated systems and for the four gases, respectively. It is obvious from the figures that the PIM polymer showed similar packing patterns in all four simulated system. This is because of the stiff nature of the ring-fused backbone of the polyimide polymer, which hinders its conformational movement tremendously throughout the entire simulation time. The packing of the methane molecules, however, showed higher amplitudes than all others, which indicates a denser packing of the methane molecules into the polymer free volume when compared to the other gases. This is very interesting as it explains the ability of the methane molecules to diffuse quickly into the polymer in perfect agreement with the self-diffusion values indicated earlier.

### IV. CONCLUSIONS

The ability of various polymeric structures to manipulate the amount and distribution of the interconnecting channels within the polymeric matrix created during the molecular mobility of the polymeric chains allows for the production of specific membranes that combine the characteristic of conventional polymers and microporous solids. PIM, polymers of intrinsic microporosity, have stiff backbones that show no freedom to change conformation but with enough distortion to prevent chain alignment that may result in the polymer crystallization and thus hinders the penetrant gas molecules from diffusing through the polymeric membranes. Depending on their chemical nature, different polymeric materials may have interconnected nano-pores or channels of different size and distribution. Diffusing gas molecules of different sizes to these nano-pores may diffuse through this polymer in a different fashion. PIM-polyimide, under study here, showed remarkable self-diffusion characteristics to methane, ethane, propane and butane, all components of natural gas. The latter three gases showed almost similar gas diffusion coefficients whereas that of methane was four times the others in magnitude. This was attributed to the small size of the methane gas as compared to the other gases, which allowed its penetration to the nano-pores small size of the methane gas as compared to the other gases, which allowed its penetration to the nano-pores created within the polymeric matrix during the molecular mobility of the polymeric chains. The larger size of the other gases, apparently, was greater than the size of the nano-pores, which prohibited their molecules from jumping through the interconnecting channels. This is quite interesting since the purpose of this study is to identify polymeric membranes that could be used to separate the gas components of natural gas. By continuing to uncover polymeric structures that have the potential to separate a specific gas component, the rest of the natural gas mixture may be finally separated into its individual components.

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