Effect of Local Chain Dynamics on the Structure of Free Volume Elements in Glassy Polymer Membranes from All-Atom Molecular Dynamics Simulations

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Abstract
Polymers are attractive membrane materials owing to their mechanical robustness and relatively inexpensive fabrication. An important dictator of membrane performance are free volume elements (FVEs) – microporous void spaces created by the inefficient packing of bulky groups along the polymer chain. FVEs tend to degrade over time as polymer chains reorganize irreversibly; relating local chain dynamics to the distribution of FVEs can help control phenomena like plasticization and aging. In this work, we implement all-atom molecular dynamics (MD) simulations to study three polymers with different glass transition temperatures ($T_g$)—polymethylpentene (PMP), polystyrene (PS), and HAB-6FDA thermally rearranged polymer (TRP). We observe that chain segments near FVEs have higher mobility compared to the atoms in the bulk; the extent of this difference is a function of $T_g$. To capture penetrant diffusion through the polymer matrix, hydrogen is inserted, and the mean squared displacement is calculated; penetrant mobility is dependent on both FVE distribution and polymer chain dynamics.
Traditional hydrocarbon separation is carried out through cryogenic distillation, which requires a large amount of energy.\(^1\) Integrating membrane-based separation with distillation is a promising alternative to reduce the energy consumption in the separation industry. The performance of a membrane is characterized by the amount of penetrant flux or permeability, as well as the efficiency of separation or selectivity. For gas separation membranes, these factors are inversely correlated, as illustrated by the permeability-selectivity plot developed by Robeson.\(^2\)

Amongst the different membrane-based technologies that are available today, polymers are attractive materials due to their mechanical robustness, controllable properties, and inexpensive means of fabrication.\(^3\)–\(^5\) Despite their many benefits, polymer membranes are limited in their application due to the inherent flexibility that arises from the molecular conformation of the chains in the matrix. This flexibility leads to irreversible structural rearrangement that causes membranes to lose their efficiency over time, leading to plasticization and aging.\(^5\)–\(^7\) A grand challenge is to develop polymers that are tailored to separate gases while maintaining a high level of selectivity with long lifetimes.\(^1\)

Glassy, amorphous polymers with rigid chains are ideal membrane materials compared to rubbery polymers.\(^4\),\(^8\) An important feature of glassy polymers are free volume elements (FVEs) – the distribution of highly microporous void spaces created by the inefficient packing of bulky groups on the polymer chain backbone.\(^9\),\(^10\) Due to this network of voids, the primary driving force for separation in glassy polymers is penetrant diffusivity, with solubility playing a smaller role in the transport of penetrants through the membrane.\(^11\),\(^12\) The upper bound of the Robeson plot is populated with highly glassy polymers mainly due to their superior diffusion selectivity.\(^13\)–\(^15\) According to the free volume theory, a penetrant will diffuse through the polymer matrix by a series of jumps between voids that are large enough to accommodate it, making FVE distribution an important parameter that dictates penetrant transport in glassy polymers.\(^12\),\(^16\),\(^17\)

Although polymers have restricted dynamics below their glass transition temperature (\(T_g\)), they are not completely immobile.\(^18\),\(^19\) Under certain operating conditions (high pressures and high penetrant concentrations), their chains are susceptible to irreversible rearrangements which alter the polymer morphology and FVE size and distribution. Local segmental motions, including translational, vibrational, and rotational motions of the chains, influence the FVE structure. Common FVE characterization techniques such as positron annihilation lifetime spectroscopy (PALS), NMR spectroscopy, and photochromic probing have been used to obtain the average FVE distribution in a polymer membrane at a given point in time.\(^20\)–\(^22\) These methods cannot capture the transient nature of FVEs that arise due to segmental motions of the chains. Recently, restricted orientation anisotropy method (ROAM) has been shown to provide a measure of the dynamics of FVE by correlating the orientational confinement experienced by the probe molecule to the local structural environment.\(^9\),\(^10\)

Relating chain dynamics to FVE distribution will enable us to address challenges like plasticization and physical aging in glassy polymer membranes, which have prevented polymer membranes from being widely implemented in the industry.\(^5\),\(^23\) Both these phenomena arise from irreversible chain reorganization in the polymer matrix, which causes membrane performance to decline over time.\(^24\),\(^25\) Elucidating the molecular underpinnings of chain rearrangement and its relation to the structure and chemistry of the polymer will enable the rational design of durable, high-performance membranes. To this end, we utilize all-atom molecular dynamics (MD)
simulations to elucidate the impact of local chain dynamics on FVEs by highlighting the translational and orientational relaxation dynamics of the polymer segments as a function of their distance from the voids. We offer novel insights on the glassy polymer dynamics at different length scales and illustrate the interplay between these dynamics and FVE distribution in three chemically distinct polymers. We also compare the dynamics of these polymer chains before and after penetrant insertion.

To model glassy polymer membranes, we utilize the all-atom forcefield OPLS-AA\textsuperscript{26} to represent three polymer chemistries – polymethylpentene (PMP), polystyrene (PS), and HAB-6FDA thermally rearranged polymer (TRP), as shown in Figure 1. These polymers exhibit diverse chemical structures and $T_g$, allowing us to examine the interplay between polymer structure and membrane function. Importantly, TRPs belong to a class of novel polymers with tunable pore distributions that are very promising as hydrocarbon separation membranes. Generating initial structures with the correct bulk density is challenging for amorphous polymers. We use the open-source package Polymatic, which has been used to generate a wide variety of polymers in the past.\textsuperscript{27} Polymatic uses simulated polymerization algorithm to construct the polymer matrix; details can be found in the Supporting Information. Briefly, multiple monomers are first packed in a box and polymerized to form a chain, following which twenty chains are packed into a large simulation box followed by a 21-step equilibration protocol to bring the systems to the appropriate density at 300 K and 1 atm.\textsuperscript{28} PMP and PS consist of 200 monomers per chain while TRP consists of 100 monomers per chain. Next, we run the systems in the isothermal-isobaric ensemble at 300 K and 1 atm for 3 ns to ensure that the systems fluctuate within their set densities.\textsuperscript{29,30} Following this, production runs are performed under the same conditions for additional 20 ns, over which data is collected. Nose-Hoover thermostat and barostat are employed, with a timestep of 1 fs. To study penetrant diffusion, hydrogen gas molecules are randomly inserted into the three equilibrated polymer structures such that it corresponds to a gas concentration of 1.18 mol/L, equivalent to hydrogen molecular density at 29.6 atm and 300 K. After this, a short equilibration of 1 ns followed by a 20 ns production run was performed in NVT, similar to the method outlined in prior work.\textsuperscript{31,32} This insertion protocol bypasses the time needed to achieve a penetrant-saturated configuration. All simulations are carried out using the LAMMPS package.\textsuperscript{33} Long range interactions are calculated using particle-particle particle mesh algorithm (PPPM) with a 1.5 nm cutoff.
We first computed $T_g$ of the three systems using a gradual quenching protocol. The details and results of the protocol are presented in the Supporting Information. We find that PMP has the lowest $T_g$ of 331K, while the $T_g$ of PS and TRP have $T_g$ of 407K and 579K, respectively. To probe the structure of the polymers, we assess the microporosity by calculating the ratio of the voids in the polymer matrix. There are different methods to measure voids (or porosity) from molecular simulations. We have chosen to use the alpha-shape method in this work because it allows for the classification of atoms as a function of their distance from FVEs. Moreover, it allows us to identify regions within a surface manifold, bound by the intersection between empty regions (pores) and filled regions (bulk polymer). In this way, we classify polymer atoms as belonging to the surface or in the bulk depending on their atomic positions in the first frame. This allows us to capture the structural heterogeneities of the polymer and compare the dynamics between surface and bulk regions. We utilize the software package Ovito to view and analyze the FVE structure and distribution. The probe size that we use is 0.25 nm (approximately the kinetic diameter of ethane) across all systems. As seen in Figure 2, we find that the percentage of void space (ratio of free to total volume) in the three systems increases as a function of $T_g$, with PMP having the lowest void volume and TRP having the highest void.

Figure 1. The structures and snapshots of the three polymer systems – (a) Polymethylpentene (PMP), (b) Polystyrene (PS), and (c) HAB-6FDA TR (TRP). Chains are constructed using Polymatic. Each system has 20 chains, and each chain contains 200 monomers for PMP and PS and 100 monomers for TRP. Heavy atoms are shown in blue, and hydrogens are in pink. Snapshots depict 2.5 nm slices in the z direction.
This correlates with the structure of the monomers; PMP is the most flexible of the three polymers with the no cyclic groups along the chain while TRP has a rigid monomer unit with cyclic groups and bulky moieties.\cite{44-47}

Next, we evaluate the translational dynamics of the three polymers by calculating the mean squared displacement (MSD). MSD measures the change in the position of the particles from their initial positions, defined as:

$$\text{MSD} (t) = \langle \Delta r^2(t) \rangle = \langle (r(t_0 + t) - r(t_0))^2 \rangle$$

where $r (t_0 + t)$ is the position of a particle at time $t$. We do not examine the center of mass dynamics of each chain, but instead compare the dynamics of all atoms across the three systems to improve statistics. We also compute the MSD of the surface and bulk atoms separately to evaluate the difference in dynamics between different regions in each of the three systems as shown in Figure 3. MSD has three distinct regions for a polymeric system.\cite{18,19,48} At short times, all three systems follow ballistic dynamics. After about 1 ps, the dynamics of the three systems move into the sub-diffusive regime. A distinct plateau regime develops after 1 ps which is more prominent in PS and TRP, presumably due to the time-scale separation between vibrational and relaxational degrees of freedom.\cite{18,19} Between 10 and 20 ns, we find that the slopes of the MSD curves are 0.20, 0.42, 0.31 for PMP, PS, and TRP, respectively. At long times, polymer melts and rubbers attain diffusive behavior; however, none of the three glassy systems reach diffusive regime due to the slow dynamics and constrained nature of the chains.\cite{18,19} PMP shows the highest MSD at 20 ns, followed by PS, and finally, TRP. Interestingly, we observe higher translational dynamics in the atoms that are at the surface, compared to atoms in the bulk. This is because surface atoms have more translational degrees of freedom as a result of being close to a free interface. We also find that the

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**Figure 2.** Void volume as a function of the three polymer systems studied in this work. Voids are obtained by constructing a surface mesh on Ovito using the alpha-shape method, with a spherical probe of 0.25 nm radius. Insets are snapshots of the three systems, with white space representing filled polymer, and voids depicted in cyan.
difference in the dynamics between surface and bulk atoms is more pronounced in PMP compared to PS and TRP, because the chains of TRP are inherently rigid, whether it is near the bulk or at the surface. For flexible chains in PMP, atoms in the bulk region have significantly slower dynamics due to higher number of neighboring atoms that constrain atom movement significantly.

To study the orientational dynamics, we calculate the bond vector autocorrelation function (BACF). BACF is defined by

$$\text{BACF} = \frac{\langle B(t) \cdot B(0) \rangle}{B(0) \cdot B(0)}$$

where B(t) is bond vector at time t. Calculating the bond vector enables us to capture local orientational fluctuations in these glassy systems, as shown in Figure 4. As expected, BACF in the moderately glassy PMP decorrelates faster compared to the glassy PS and highly glassy TRP, which relax much slower. Similar to the MSD, BACF is calculated separately for bonds near the void (surface bonds) and bonds in the bulk that do not neighbor a void. Surface bonds decorrelate faster compared to the bulk bonds, and the difference in dynamics is more pronounced in PMP compared to PS and TRP, in agreement with what was observed previously for MSD. Overall, atoms near the surface have more translational and orientational degrees of freedom compared to bulk atoms.
As polymer FVEs are transient, the dynamics of surface segments are a measure of how susceptible FVEs are to rearrangement. The slow dynamics in TRP compared to PMP indicates a more stable FVE distribution, which is less likely to age and plasticize when used as a membrane under the same operating conditions. To explore the effect of penetrant loading on transport through the three polymers, we insert hydrogen as described earlier; the mean-squared displacement of the hydrogen molecules is calculated and shown in Figure 5. We see that at short times, the diffusion of H₂ is highest in TRP, followed by PS and PMP; the early high diffusion in TRP is likely driven by its high microporosity. However, at around 0.2 ns, the hydrogen MSD in PMP overtakes that of TRP. The increase in hydrogen transport in PMP at long time can be attributed to two factors. The first is chain rearrangement, which causes the FVE pores to dilate, allowing the penetrant to jump more easily between the newly formed dilated channels. This is in line with the diffusion theories, which state that penetrant diffusion consists of series of jumps between FVEs in the polymer matrix.12,49,50 The second factor is that the PMP chains are inherently more mobile compared to TRP and PS, this mobility contributes to the penetrant motion. In addition to the hopping motion between different FVEs, the motion of the polymer enables the penetrant to follow the dynamics of the PMP chains. This coupling between penetrant motion and polymer local dynamics has also been observed in other systems, such as phenol diffusion in bisphenol-A-polycarbonate and helium diffusion in polypropylene.51,52

Figure 4. Bond vector autocorrelation function (BACF) for atoms in the three polymer systems, as labeled. Solid lines, dotted lines, and dashed lines correspond to the BACF for all atoms, atoms at the interface (surface atoms), and atoms in the bulk (bulk atoms), respectively.
To confirm this, we first analyzed the structure of the polymer systems after the insertion of hydrogen. Upon calculating the FVE distribution at 5 ns after insertion, we find that the void percentages are 21%, 27%, and 44%, for PMP, PS, and TRP, respectively, corresponding to an increase of 5%, 3%, and 1% in the void percentages. Then, we investigated the dynamics of the chains post H\textsubscript{2} insertion, this is shown in Figure 6. We find the chains in both PMP and PS are slightly more mobile after insertion, as seen by the difference in the long-time behavior of MSD and BACF. TRP chains on the other hand do not show a change in dynamics in the timescales considered in this work, indicating the least rearrangement and the most robust FVE structure. The change in dynamics after insertion is more pronounced in PS than PMP. This is because PS is initially rigid and thus experiences a larger increase in mobility after the penetrant is introduced.

Figure 5. Mean squared displacement of H\textsubscript{2} in the three systems, as labeled. Between 15 and 20 ns, the slopes of the curves are 0.98 for PMP, 1.14 for PS, and 0.90 for TRP.
In summary, we implemented MD simulations to study how local chain dynamics influence free volume element distribution and penetrant transport in glassy polymers. By using the alpha-shape method for calculating FVEs, we were able to isolate polymer segments adjacent to voids (surface segments), from the bulk segments. Translational dynamics in surface and bulk segments were examined using MSD, and the orientational dynamics are captured using bond vector ACF. As polymer segments near the surface have more degrees of translational and orientational freedom, they exhibit higher MSD and a faster bond decorrelation compared to bulk segments. The mobility of surface segments is directly correlated with the FVE redistribution in the polymer matrix during separation. Upon the introduction of hydrogen penetrant, polymer rearrangement is most pronounced in PMP and PS as translational and orientational mobility are maximized. For the highly glassy TRP, surface segments show a slow relaxation and a small FVE redistribution. This work suggests that the relaxation of polymer segments near the voids can be used to reveal the stability of FVE distribution across different polymer membranes. This in turn can guide the design of superior membrane materials to address challenges such as plasticization and physical aging which are closely linked to chain dynamics. Future studies will be carried out to understand

![Figure 6. Mean squared displacement (top) and bond vector ACF (bottom) of all polymer atoms before insertion (solid lines) and after insertion (dashed lines), for the three systems as labeled.](image-url)
how tunable parameters such as polymer chemistry, polydispersity, and crosslinking influence the chain mobility and FVE distribution.

Acknowledgement
This research was financially supported by Prof. Sampath’s startup funds provided by the Department of Chemical Engineering and Herbert Wertheim College of Engineering at the University of Florida. [https://www.che.ufl.edu](https://www.che.ufl.edu) The authors acknowledge University of Florida Research Computing for providing computational resources and support that have contributed to the research results reported in this publication. [http://researchcomputing.ufl.edu](http://researchcomputing.ufl.edu)

Supporting Information
Details related to polymer parameterization and structure generation, glass transition temperature calculation, and hydrogen-polymer radial distribution function.

Data availability
Analysis codes, input scripts, and data file containing forcefield parameters and structures can be found here - [https://github.com/UFSRG/published-work/tree/main/2022-Otmi-Macroletters](https://github.com/UFSRG/published-work/tree/main/2022-Otmi-Macroletters).
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Amorphous polymer generation

OPLS-AA forcefield is used to parameterize all the polymer structures. A segment of three connected monomers is submitted into the LigParGen to ensure bonded and non-bonded parameters and atomic charges are appropriately calculated. The middle monomer unit is isolated to be used for the simulated polymerization step. Simulated polymerization is achieved using the open-source package Polymatic, which uses a general methodology to construct amorphous polymers. Polymatic consists of multiple Perl scripts and python codes. First, a simulation box is packed with the parameterized monomer units at low density (Figure S1). Neighboring monomers that satisfy polymerization criteria are then connected. Energy minimization using steepest descent and conjugated gradient is performed to relax the newly formed bonds. Short simulations are performed in the microcanonical ensemble (NVT) and isothermal-isobaric ensemble (NPT) to allow different polymerized fragments to find each other. All simulations within the Polymatic framework use Nose-Hoover thermostat and barostat, velocity Verlet integrator, particle-particle/particle-mesh (PPPM) for long-range interactions, and a 1fs timestep.

Polymerization is performed at a relatively low density. If the density is too high, the system enters a frozen state. At the same time, the initial density should not be too low, or the monomer fragments will be far apart, preventing the formation of a high degree of polymerization. Densities of the three polymers before polymerization are 0.22, 0.16, 0.25 g/cm$^3$ for PMP, PS, TRP respectively.

Polymatic does not use a reactive forcefield to generate the polymer structure; although the process of building the polymer chain resembles the radical polymerization process, Polymatic simply connects monomer units and uses a classical forcefield to relax the structure after the addition of each monomer. Once a single chain is constructed, it is replicated by packing 20 identical chains into a larger simulation box. Figure S1 shows the overall workflow used in this work for constructing TRP.
Equilibration protocol

As Polymatic carries out the simulated polymerization at a low density, it is necessary to compress the system to a realistic density once the desirable degree of polymerization has been achieved. It was observed that the abrupt change in pressure generates inconsistent stress tensor. Thus, a multiple-step equilibration technique, which consists of mild compressions and decompressions to avoid any abrupt pressure changes, is adopted here. This protocol consists of seven cycles to gradually heat and compress the system to a maximum pressure. The structure is then decompressed gradually until it reaches the desirable conditions (1 atm and 300K). Each cycle consists of high temperature NVT followed by a room temperature NVT followed by a room temperature NPT. Density before and after equilibration are shown in Table S1. Table S1 shows the densities of the three systems before and after the equilibration compared to the experimental density. Experimental densities for PMP, PS, and TRP are obtained from references 4–6.
### Glass Transition Temperature

Thermal properties like glass transition temperature ($T_g$) are used to validate the simulation model against experiments. $T_g$ represents the temperature at which amorphous polymers experience a gradual transition from a glassy phase to rubbery phase or vice versa. Multiple experimental techniques have been developed including dynamic mechanical analysis and differential scanning calorimetry to capture $T_g$. In simulations, annealing protocol is commonly used to heat up the system to a maximum temperature followed by gradually decreasing the temperature using $\Delta T$ increments, to calculate $T_g$. The range and increment should be chosen carefully based on the system and the desired accuracy. Polymers should be heated to a temperature below their melting point to ensure an adequate sampling of the system in its rubbery phase. The $T_g$ data for the three systems is presented in Figure S2.

The specific volume data acquired during annealing for PMP, PS, and TRP are fitted using a bilinear fit, and the intersection of the two lines generated corresponds to $T_g$. Different fitting protocols have been developed specifically for $T_g$. Piecewise regression method, also known as broken-stick regression, is used in this paper to fit the two lines and obtain $T_g$. It is important to point out that glass transition is highly dependent on the chain length, and Flory-Fox relationship captures this dependence. $T_g$ obtained from MD simulations also depends on the annealing rate. Simulations will most likely overestimate $T_g$ due to the fast cooling and the breadth of relaxation implemented in the annealing protocol. A faster quenching rate can potentially cause higher deviation from experimental procedure. It is necessary to choose a moderately fast quenching rate to make the computation reasonable. The annealing rate adopted in this work is 20 K/ns.

| System | Density before Polymatic equilibration protocol (g/cm$^3$) | Density after Polymatic equilibration protocol (g/cm$^3$) | Experimental density (g/cm$^3$) |
|--------|----------------------------------------------------------|----------------------------------------------------------|---------------------------------|
| PMP    | 0.22                                                     | 0.83                                                     | 0.83                            |
| PS     | 0.16                                                     | 1.00                                                     | 1.05                            |
| TRP    | 0.25                                                     | 1.30                                                     | 1.36-1.45                       |

Table S1. The density of the three systems before and after the equilibration compared to the experimental density. Experimental densities are obtained from references 4-6.
Radial Distribution Function

To understand the local ordering of hydrogen near the polymer chains, we compute the radial distribution function of all hydrogen atoms to all polymer atoms (Figure S3). The resulting RDF shows that hydrogen has a higher probability to be close to TRP at short distance compared to PS and PMP. This might be due to the high microporosity that allow hydrogen molecule to exist in interstitial free sites between chains in TRP.

It is important to note that the structure of the polymers studied here are vastly different, making a direct comparison of the RDF across the three systems challenging. To understand structure and thermodynamics better, future work will include enhanced sampling methods to extract this information.
Figure S3: shows the polymer-hydrogen radial distribution function in the three polymer systems. Values are averaged over 500 hydrogen molecules in PS and PMP and 1000 in TRP.
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