

Supporting Information for  
**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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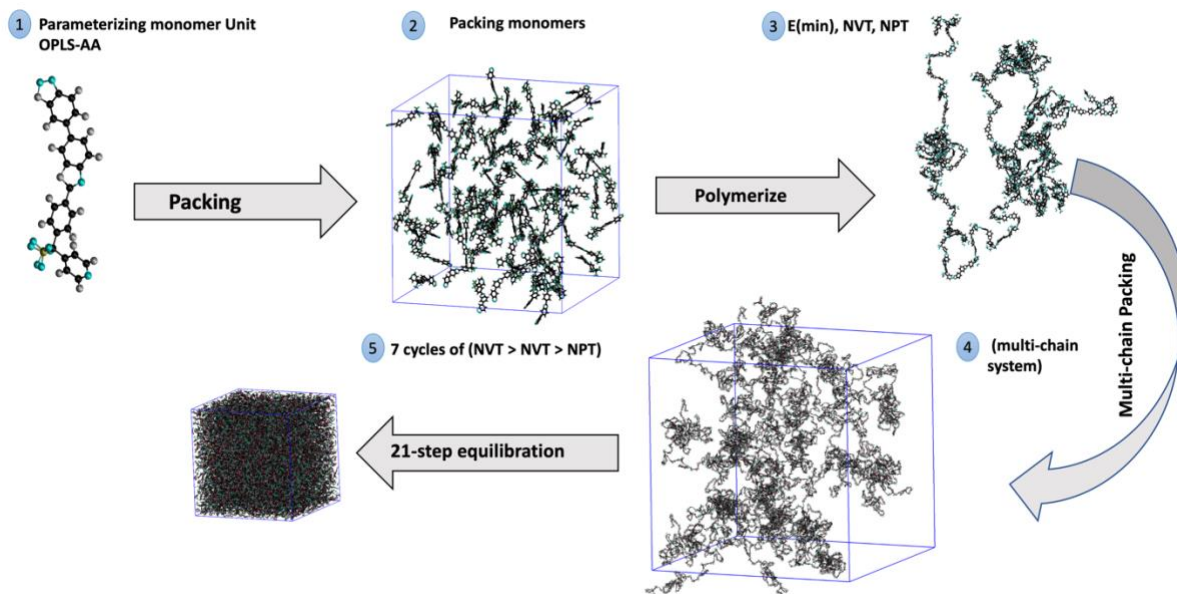
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### **Amorphous polymer generation**

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.<sup>1</sup> 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.<sup>2</sup> 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-rang 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<sup>3</sup> 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.



**Figure S1.** The overall workflow of constructing the polymer systems. OPLS-AA forcefield is used to parameterize the monomer unit. Monomer units are packed and polymerized as described above. 20 chains are packed into a large simulation box. An equilibration protocol that consists of 21 steps is performed to bring the system to the appropriate density.

## 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.<sup>3</sup> 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.<sup>4-6</sup>

System	Density before Polymatic equilibration protocol (g/cm <sup>3</sup> )	Density after Polymatic equilibration protocol (g/cm <sup>3</sup> )	Experimental density (g/cm <sup>3</sup> )
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.

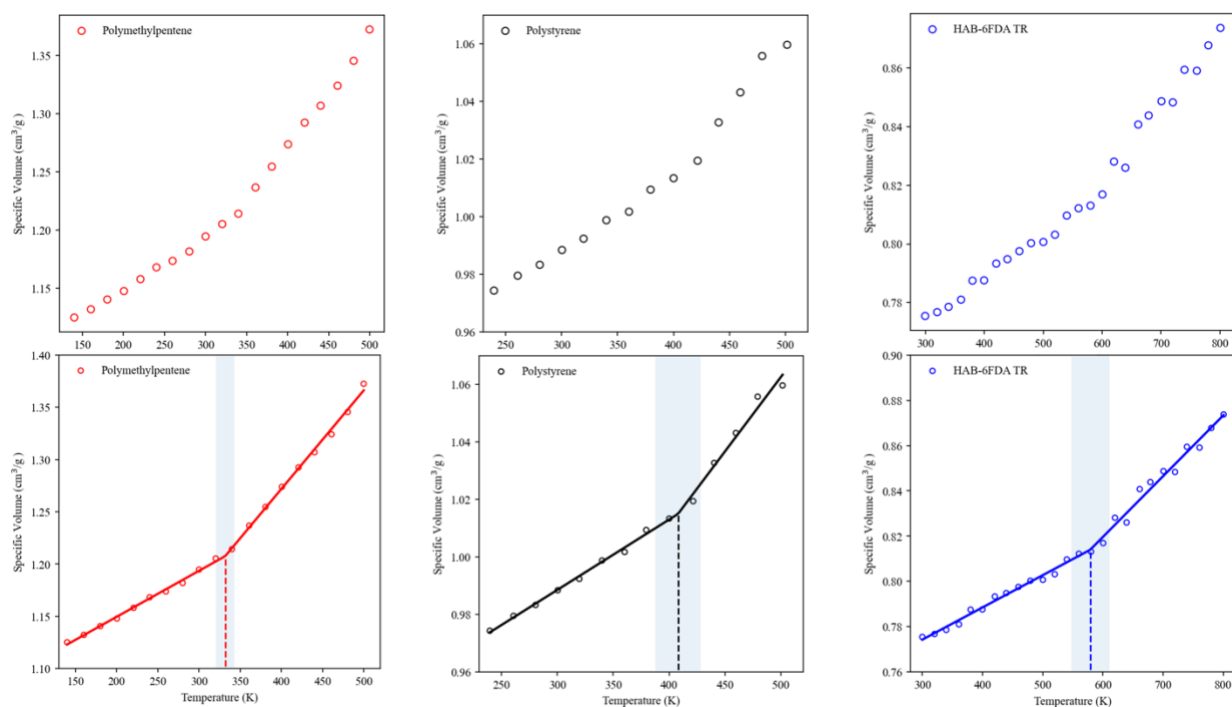
## Glass Transition Temperature

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  $T_g$ .<sup>7</sup>

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.



**Figure S2.** The annealing procedure used to obtain  $T_g$ . The polymers are cooled at 20K/ns rate and specific volume data are obtained every 1 ns. Piecewise regression is used to fit the data and find  $T_g$ .

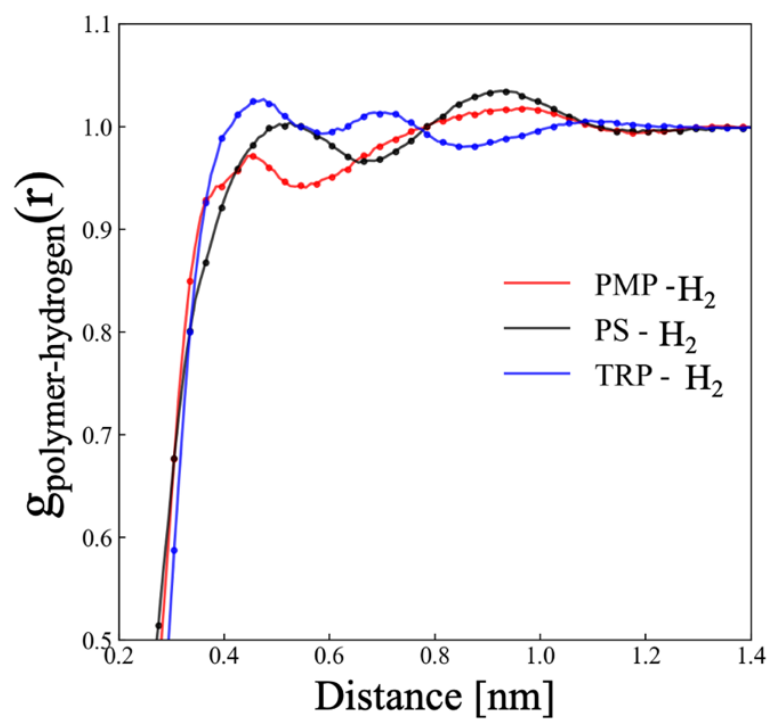
System	$T_g$ (simulation) (K)	$T_g$ (Experiment) (K)
PMP	331	300
PS	408	364 - 401
TRP	579	578

**Table S2.** The glass transition temperature of the three systems obtained using the quenching protocol compared to the experimental glass transition. Experimental  $T_g$  is 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.

## Bibliography

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