Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information for

Evolution of Free Volume Elements in Amorphous Polymers Undergoing Uniaxial Deformation: A Molecular Dynamics Simulations Study

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Constructing Polymer Systems

The construction of the model is detailed in prior literature; however, briefly, we provide a brief overview here. Three distinct polymers were synthesized from unpolymerized monomer units, with the monomers being parameterized employing the all-atom OPLS forcefield. The monomers were incorporated as components of three contiguous monomer fragments to ensure the faithful representation of partial charges, mirroring their configuration within the polymer. Subsequently, the central monomer was isolated through the removal of excess atoms, and the 1.14 CM1A-LBCC charge model was applied for further characterization. Following the parameterization of the monomer unit, a total of 200 monomer units were assembled within a simulation box, and a simulated polymerization algorithm was implemented to generate a polymer chain. To assemble the system for simulation, 20 polymer chains were placed within a sizeable simulation box. Subsequently, a 21-step annealing protocol was executed, which involved a series of NPT (constant number of particles, pressure, and temperature) and NVT (constant number of particles, volume, and temperature) steps. This annealing process was carried out with the objective of equilibrating the system and attaining the experimental density.

Chain Length Effect on the FVE Distribution

Two models of TRP were constructed, differing in chain length: one model consisted of 100 monomers, while the other contained 200 monomers. We adjusted the size of the simulation box before polymerization to ensure an initial density of 0.3 g/cm^3. Following the polymerization of monomers using Polymatic, 20 chains are packed into a larger simulation box and subjected to annealing procedures as outlined in the manuscripts. Upon achieving system equilibration, we utilized VACUUMMS to obtain and compare the Free Volume Element (FVE) distribution

between the two models, investigating the impact of chain length on FVE distribution. Figure S1 shows a subtle shift in the FVE distribution towards higher diameter values as chain length increases. This observation aligns with prior research on the influence of chain length on polymer

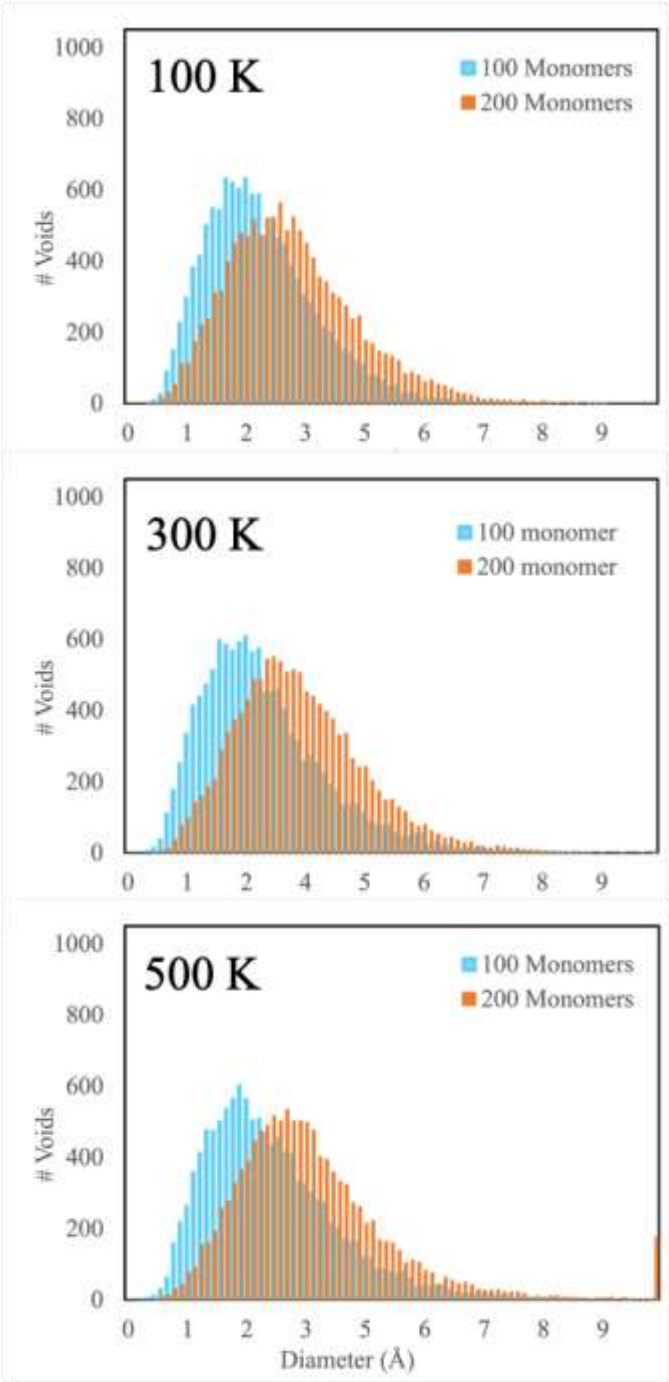

Figure S1: The chain length effect on the FVE distribution in TRP. The FVE distribution of polymer with higher chain length shift toward larger diameters.

structure, such as studies indicating an increase in accessible area with longer PVC chains. While the effect of chain length can be significant, particularly in deformation studies, it is essential to emphasize that the primary focus of this study lies in examining the individual effects of chemistry, temperature, and strain rate on each system. To maintain consistency throughout these investigations, the number of repeating units remained constant across the three systems. Figure S1 shows the difference in FVE distribution for TRP with 100 and 200 monomer units at three different temperatures.

FVE Distribution at 300 K

In the manuscripts, we present the FVE distribution at both 100 K and 500 K, as these temperatures exhibit the most significant contrast in data, allowing us to effectively capture the temperature-dependent effects within each system. Figure S2 shows the FVE distribution of the three systems at 300 K. We observe the formation of large cavities in TRP as the deformation progresses. A bimodal distribution starts forming at 20% stain in TRP. As the TRP structure gets deformed, some of the pores open and coalesce forming free volume pores with large diameter.

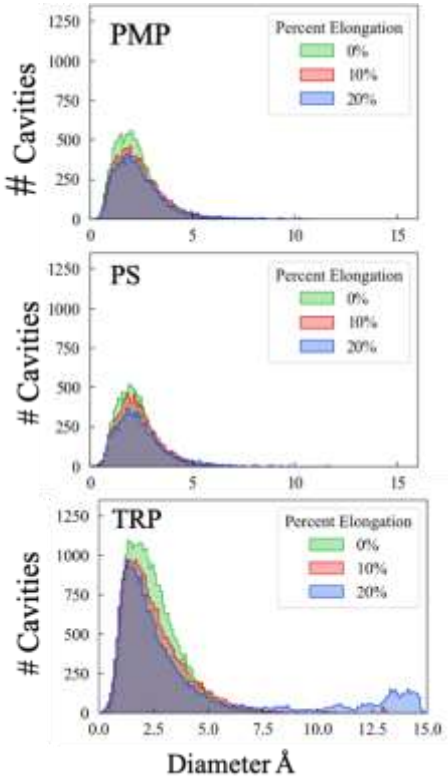

Figure 2: The chain length effect on the FVE distribution in TRP. The FVE distribution of polymer with higher chain length shift toward larger diameters.