# ATOMISTIC MOLECULAR DYNAMICS SIMULATIONS AS A TOOL FOR PREDICTING THE STRUCTURE-DYNAMICS RELATIONS OF STAR-SHAPED POLYMER MELTS

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Star polymers are used as model systems to study more complex architectures of industrial relevance. Their dynamical behavior ranges from linear-like to coloidal-like and can be tuned by adjusting the star composition. The penetrability of the molecules plays a significant role in the determination of the dynamical behavior of these systems. A recent experimental evidence suggests that this property may depend not only on the number of arms but also on their internal packing specific for each polymer type[1].

To obtain an insight about the inner structure of star-shaped polymer melts, we perform atomistic molecular dynamics (MD) simulations of non-entangled poly(ethylene oxide) (PEO) and polystyrene (PS) stars. The used method captures all atomistic details, accounting for local packing and/or stiffness of the two chosen dissimilar polymers, which differ in flexibility and glass transition temperature. By varying the number of arms, we aim to tune the star penetrability and mutual star-star interactions. We quantified the shape and size characteristics and we discuss the differences in intramolecular and intermolecular packing for the two studied chemistries [2,3]. Moreover, we implement a challenging grid-based algorithm for the estimation of the free volume in the system. We focus on the distribution of the free volume around the stars and the differences between the two polymer types. Results are related to the permeability of the material and the glass transition temperature.

To the best of our knowledge, our study represents the first attempt to describe the star polymer melts in atomic detail. Our results, related to the packing and the cooperative motion of the molecules, provide information complementary to the experimental techniques or more generic models and can thus contribute to a better understanding of structure-dynamics relation in materials with branch-like architectures, such as those used in all-polymer nanocomposites or nanostructured electrolytes[4].

**KEYWORDS:** Star polymers, polymer melts, atomistic simulations, free volume, molecular dynamics simulations

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