Structural and Dynamical behavior of Star-shaped Polystyrene and Poly(ethylene-oxide) Melts through Atomistic Molecular Dynamics Simulations

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ABSTRACT

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.[1,2] In more detail, the functionality (number of arms) of the stars plays a significant role in the determination of the dynamical behavior of these systems, affecting properties like the degree of penetrability of these molecules. 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. Our model 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.[3,4] Moreover, we implement a challenging grid-based algorithm for the estimation of the free volume in the system, a quantity which is difficult to be measured experimentally or estimated by more generic models.

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.[5]

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