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Self-associating hybrid polymers under shear

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Abstract:

Star block-copolymers (SBCs) have been demonstrated to constitute self-assembling building blocks with specific softness, functionalization, shape, and flexibility. In this work, we study the behavior of an isolated SBC and suspensions of SBCs under shear flow by means of particlebased multi-scale simulations. We systematically analyze the conformational properties of lowfunctionality stars as well as the formation of attractive patches on their corona as a function of the shear rate. We cover a wide range of system parameters, including functionality, amphiphilicity, and solvent quality. Three mechanisms of patch reorganization under shear were identified, which determine the dependence of the patch numbers and orientations on the shear rate, namely, free arms joining existing patches, a fusion of medium-sized patches into bigger ones, and fission of large patches into two smaller ones at high shear rates. As well as, the dynamics of the SBC was investigated by means of the so-called Eckart's frame, which allows separating pure rotational and vibrational motions. It is shown that SBCs display a richer structural and dynamical behavior than athermal star polymers in a shear flow. We also investigated the behavior of dilute and semidilute suspensions of SBCs under linear shear flow for a wide range of parameters of the system; the latter include the monomer packing fraction. Our analysis focus on the dynamical behavior of the network structures formed at equilibrium as a consequence of the patch reorganization induced by the shear flow. The obtained results have interesting implications on the system's rheological properties and viscoelastic response in dilute and semidilute bulk phases because the SBCs are able to form a variety of different intermolecular transient bonds involving rather weak ones between individual arms and much stronger ones between multiarm patches. In the final part of this work, we propose two generalizations of the Multi-Particle Collision Dynamics (MPCD) numerical method, in the first we use the density profile information to obtain a polymer system with effective monomers in which we eliminate the monomer-monomer interaction, in the second we use a more advanced model called penetrable soft colloid, we design new collision rules for the interaction between the solvent and the penetrable soft colloid. We apply these two generalizations for linear polymers and star polymers, we compare the results of the mean square displacement, we find that our first approach is consistent with linear polymers while the second is consistent with polymer stars. Our approaches can be extended to more complex polymer systems.