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DYNAMIC MONTE CARLO SIMULATION OF 12-ARM STAR CHINS

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Star polymers show significant peculiarities in their conformational properties in solution, due to differences in the local polymer bead density at different distances from the star center, and also because of the impenetrability of the star cores. Computer simulations of the dynamic properties of these systems are scarce, due to difficulties in preparing equilibrated samples. Furthermore, explicit dynamic methods cannot easily handle enough number of beads to characterize properties as self-diffusion coefficient for non-dilute chains. On the other hand, the more efficient conventional lattice models for "dynamic" Monte Carlo require an adequate choice of complex move steps for the center of the star, in addition to the conventional set of "bead-jumps" consistent in crankshafts, bents and end moves for other units. The latter difficulty can, however, be circumvented through the use of the bond fluctuation model, where a bead jump can be defined a simple displacement of any unit. In previous work, we have successfully devised a method to equilibrate systems mimicking semidilute solutions of 12-arm self-avoiding walk stars. This has allowed us to characterize the structure of these systems.

We report here results for dynamic properties corresponding to these systems. Namely, we have obtained self-diffusion coefficients and the relaxation times of three different relaxation processes: the elastic deformation on the end-to-center length of an arm, the rotation of an arm (also describing the star overall rotation) and the disentanglement of a couple of arms. Our results correspond to different values of the total number of units (ranging between 73 and 289) and concentration (we study single chains, and also solutions with polymer volume fraction ranging from 0.075 to 0.3 (which correspond to the semidilute and concentrated regimes). The diffusion coefficient strongly decreases with concentration in the overlapping region, but this decrease is slow in the concentrated regime. The different relaxation times, however, show a moderate increase with concentration for the whole range of volume fractions. The ratio between the diffusion coefficient of the star and that of a homologous linear chain increases with the degree of overlapping. The star chains, however, always diffuse slower than the corresponding linear chains of the same span length (i.e. same number of beads than a couple of arms). Although the length of arms is not long enough to exhibit full intermolecular entanglements, these features are interesting since, in addition to entanglement, the presence of big impenetrable cores is surely a very important characteristic of the non-dilute star systems. It should also be considered that many real samples of stars might have relatively short arms, which cannot fully entangle with neighboring molecules.