SELF-ASSOCIATING COPOLYMERS WITH DIFFERENT MOLECULAR ARCHITECTURES: MOLECULAR DYNAMICS STUDIES

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Using nonequilibrium molecular dynamics simulation technique (NEMD) we study the aggregation process in the solution of self-associating copolymers depending on their molecular architectures and solvent composition under the influence of a planar Couette flow. We considered three systems of self-associating copolymers with different molecular architectures. The first system contained linear copolymer chains with strongly attracting groups equidistantly distributed along the chain. The second system contained comblike copolymers with short end-functionalized side chains. Both copolymers were immersed in a neutral low-molecular-weight solvent. The third one consisted of linear associating chains in the presence of complex solvent involved besides apolar solvent a small amount of polar solvent. In real systems such situation corresponds to three-component system containing associating copolymers, low-molecular-weight polar solvent and external solvent medium (apolar organic solvent). During computer simulation the following system parameters were changed: interaction energy between associating groups ε, linear density of these groups δ (for liner chains), linear grafting density m (for polymer brushes), temperature, polymer concentration, volume fraction of small associative molecules (Φ_S), and shear rate γ. The main aim was to find optimal parameters which can be recommended for the formation of synthetic polymer fibers via the elongation of the gels in the process of fiber spinning. It was found that the external shear field causes additional aggregation in the systems under investigation, when the energy parameter ε is above some critical value ε^*. The growth of shear rate γ dramatically changes the spatial structure of associative networks. These structural reorganizations lead to changes in the shear dependent steady-state viscosity. When the γ values approaches the critical value γ^*, the associative network falls to pieces and forms dense fibrils which are oriented just along the flow direction and separated from each other. The similar state is known as a string phase. We observed dramatic shear thinning when continuous network transits to the fibrous textures, then the shear viscosity becomes lower. These fundamental flow-induced changes are observed for both linear and comblike copolymers. Consequently the string phase provides more oriented and well-ordered structures with the lowest values of shear viscosity. Therefore this state should be the most optimal for the formation of synthetic polymer fibers. The similar phenomenon has been observed experimentally for copolymers synthesized on the basis of poly(acrylonitrile-co-acrylic acid) in the Scientific Institute for Synthetic Fibers (Tver). Also it was found that the inclusion even small amount of polar solvent reduces values of molecular orientation and leads to destruction of string phase.

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