Non-linear shear and elongational flows of ring and linear melts

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Shear Flows: In the melt state at equilibrium, entangled non-concatenated ring macromolecules adapt more compact conformations than linear chains, do not form an entanglement network, and have a much lower Newtonian viscosity than linear melts of similar molecular weight. We study the steady-state shear viscosity η of non-concatenated ring polymer melts as a function of the shear rate $\dot{\gamma}$ by combining experiments, simulations, and theory. Experiments with polystyrenes having molar masses 84 kg/mol and 185 kg/mol, which correspond respectively to $Z \approx 5$ and $Z \approx 11$ entanglements (for linear polymers), indicate weak shear thinning for rings compared to linear polymers, with a scaling $\eta \sim \dot{\gamma}^{-0.56}$. Non-equilibrium molecular dynamics simulations using the generic bead-spring model of polymers reveal a universal shear thinning behavior of entangled non-concatenated rings with $\eta \sim \dot{\gamma}^{-0.62\pm0.02}$ for $4 \leq Z \leq 57$. The experimental and simulation power-law thinning exponents for linear melts are -0.82 and -0.89±0.04, respectively. Obtaining pure non-concatenated ring polymers remains an experimental challenge and the presently measured number of entanglements of about 11 is the largest so far. On the other hand, non-equilibrium molecular dynamics simulations using the bead-spring model extend to Z=57. The empirical Cox-Merz rule is essentially validated experimentally and by computer simulations. To describe the shear thinning of ring polymers, we develop a scaling model for their response under non-linear shear flow. The model is based on the concept of "shear blobs", which refer to polymer sections with relaxation times of the order of $\dot{\gamma}^{-1}$ that are able to relax and dissipate energy at $\dot{\gamma}$. This model considers that under shear the ring is composed of elastically independent shear blobs, i.e., sections with a relaxation time of the order of $\dot{\gamma}^{-1}$ (smaller than the relaxation time of the ring) and being able to relax and dissipate energy at a rate $\dot{\gamma}$. Larger sections follow the flow and get aligned, whereas smaller sections remain in equilibrium and their dynamics can be described by the fractal loopy globule model. Hence, the shear thinning viscosity emerges from the estimation of the viscosity of a shear blob. The prediction of the model $\eta \sim \dot{\gamma}^{-0.57}$, agrees well with both experimental and simulation results.

Extensional Flows: Ring polymers subjected to uniaxial stretching, exhibit a unique response, which sets them apart from any other polymer. Melts of entangled non-concatenated ring polymers are extraordinarily sensitive to extensional flow, exhibiting a large rise in viscosity even for Weissenberg numbers Wi well below unity. We explain the origin of this massive rise in viscosity through molecular dynamics simulations of non-concatenated ring melts in uniaxial extensional flows. Ring melts of three molecular weights are elongated for constant Rouse time from 0.1 to 25 and compared to analogous data for linear melts. Simulations confirm that strong extension-rate thickening occurs for all Wi and we find it coincides with the extreme elongation of a minority population of rings that grows with Wi. The large susceptibility of rings to extension is due to a flow-induce formation of "tight-links" that connect two or more rings into supramolecular daisy-chains while flow persists. Links are pulled tight and stabilized by flow and can form spontaneously after the flow begins. Once linked, the composite rings act like much larger molecules and experience much larger drag forces than individual rings, driving their strong elongation. At high rates, stretching leads to viscosity thinning similar to that of entangled linear polymers, albeit with subtle differences.