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Rheology modification with ring polymers

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It is now established that experimental unconcatenated ring polymers can be purified effectively by means of fractionation at the critical condition. For molecular weights well above the entanglement threshold, purified rings relax stress via power-law (with an exponent of about -0.4), sharply departing from their linear counterparts. Experimental results are in harmony with modeling predictions and simulations. Here, we present results from recent interdisciplinary efforts and discuss two challenges: (i) the nonlinear shear rheology of purified ring melts is also very different from that of unlinked chains. Whereas the latter exhibit features that can be explained, to a first approach, in the framework in the tube model, the former behave akin to unentangled chains with finite extensibility and exhibit much small deformation at steady state. (ii) blends of rings and linear polymers exhibit unique features in different regimes: The addition of minute amounts of linear chains drastically affects ring dynamics. This relates to ring purity and the ability of unlinked linear chains to thread rings. With the help of simulations, it is possible to rationalize the observed surprisingly slow viscoelastic relaxation, which is attributed to ring-linear and ring-ring penetrations. On the other hand, adding small amounts of rings to linear polymers of different molecular weights influences their linear and nonlinear rheology in an unprecedented way. The blend viscosity exceeds that of the slower component (linear) in this non-interacting mixture, and its dependencies on composition and molecular weight ratio are examined, whereas the role of molecular architecture is also addressed. Consequently, closing the ends of a linear chain can serve as a powerful means for molecular manipulation of its rheology. This presentation reflects collaborative efforts with S. Costanzo, Z-C. Yan, R. Pasquino, M. Kaliva, S. Kamble, Y. Jeong, P. Lutz, J. Allgaier, T. Chang, D. Talikis, V. Mavrantzas and M. Rubinstein.