

Polymer Physics
Homework 2
January 21, 2022 (Due January 25)

Parisi D, Costanzo S, Jeong Y, Ahn J, Chang T, Vlassopoulos D, Halverson JD, Kremer K, Ge T, Rubinstein M, Grest GS, Srinin W, Grosberg AY *Nonlinear Shear Rheology of Entangled Polymer Rings* *Macromolecules* **54** 2811-2827 (2021) studied the viscoelastic behavior of un-concatenated ring polymer melts by experiment, simulation, and theory. Concatenation involves topological connections of rings such as in the Olympic rings. Un-concatenated rings are not topologically connected but can entangle in the melt. Interest in ring polymers was originally for their use to approximate high molecular weight polymers in dynamic models and simulations where end-group effects became a problem. Long rings do not have end groups but are otherwise similar to long polymers. In some polymers rings naturally form such as in polydimethyl siloxane (PDMS or silicone). Parisi synthesized un-concatenated rings of polystyrene (PS) as well as linear PS of similar molecular weights. Both linear and ring melts display shear thinning behavior as shown in Figure 3 but with different power-law decays. The viscosity at the highest strain rates approach the same value for all of the PSs.

- a) Figure 2 shows two rheological measurements, a) an oscillatory shear experiment and b) a creep experiment. The creep experiment involves application of a fixed and constant torque to the fluid and observation of the rotational strain response as a function of time. At long times the fluid reaches steady flow and there is no storage modulus but at first it displays a resistance as indicated by a decaying modulus in time. Explain how the oscillatory shear experiment from a) is conducted. Indicate where the polymer behaves as a fluid, and where it behaves as an elastic solid. To what does the cross-over frequencies correspond? Explain to what the arrows at the top axis refer in the two plots.
- b) Figure 4 is a plot with the shear viscosity reduced by the plateau viscosity and the strain rates converted to Wissenberg numbers, Wi , and the frequencies to Deborah numbers, De from Figures 3 and 2a. The comparison is based on the Cox-Merz Rule which is verified by the observed universal behavior (all of the curves fall onto each other). Define the Wissenberg and Deborah numbers and explain how they relate to each other under the Cox-Merz Rule.
- c) Figure 1 depicts the model used to explain a difference between ring and linear polymers for the power-law fluid exponent α from equation 1, a difference that is observed in both experimental and simulation results, Figures 3, 4 and 5, 6. α is about 0.57 for rings and about 0.85 for linear chains. The model involves two size scales, ξ_s and ξ_t , the shear and tensile blob sizes. A blob is a subsection of a chain that displays a different mass-fractal scaling behavior (size \sim mass^{df}) above and below the blob size. Explain the origin of these two size scales.
- d) Parisi indicates in the introduction that “... rings in the melt of other long rings adopt a compact state with gyration radius scaling as $N^{1/3}$ as a function of the number of monomers N compared to $\sim N^{1/2}$ for linear chains.” Is this this statement consistent with the cartoon shown in Figure 1? (The radius of gyration is a measure of the size of the chain and N is the mass of the chain.) Note that on page 2823 Parisi states, “The next open question is about the fractal structure of the chain inside the shear slit. We assumed, based on our computational data (see specifically Figure 14) that chains retain compact fractal globule

statistics in the y direction ($y_k \sim k^{1/3}$) despite the fact that stretching in the x direction could be thought to ease topological constraints.”

- e) Parisi also notes at the end of page 2823 that shear thinning is observed in shear flow, but during extensional flow, such as when a fiber is drawn from the spinneret, thickening is observed with increasing strain rate for ring polymer melts. Consider Parisi’s explanation. Does this make sense? Is there another explanation for thickening with increased strain rate for extensional flow of ring polymers? (Such behavior is not observed for linear polymers.) Consider that non-Newtonian behavior (shear thickening or thinning) always has a structural basis.