Homework 1
January 21, 2025
Polymer Physics

Cyclics are of interest to polymer science and molecular biology for several reasons. Many synthetic polymer systems, in particular polydimethyl silioxane (PDMS, silicone, bathtub sealant, silicone lubricant, etc.) exists in a cyclic/linear equilibrium. Other polymers like polylethylene oxide (hand sanitizer) also naturally display cyclic/linear equilibrium and there are some synthetic oil additives that include cyclics. In molecular biology, messenger RNA can exist as cyclics and the study of the folding mechanisms of cyclic biopolymers such as RNA, DNA and proteins is of interest to certain diseases. In vivo polymers exist in a concentrated regime where there is significant entanglement of chains and the potential for "threading" of cyclics with linear molecules. If a single cyclic is threaded on a linear chain an "entropic motor" can be created. If multiple threads exist then the cyclic acts as a crosslink and can dramatically increase the viscosity by orders of magnitude depending on the extent of threading. In November, 2024 Wang W, Lu J, Sun R, *Effect of threading on static and dynamic properties of polymer chains in entangled linear-ring blend systems with different stiffness* Polymer **290** 126513 (2024) reported on the impact of the size of cyclics, Z_R, on the number of threads, N_T, in linear/cyclic blends using molecular dynamic simulations (MD) and "inner minimal surface penetration" (IMS) analysis of the MD results.

a) Wang uses molecular dynamics (MD) to study ring/linear polymer chain blends. Briefly explain the MD method. Why did they choose to use HOOMID Blue versus LAMMPS for their simulations?

b) In Table 3 the value of the scaling factor ν_R is close to 1 indicating Gaussian (random) chains, yet in Figure 6, $\langle\kappa\rangle$ has values near 0.25 indicating asymmetric chains. Does this make sense? Explain how this is possible or argue that it is not possible (i.e. what is the difference between a Gaussian (random) chain and a symmetric chain).

c) In equation (4), the radius of gyration, R_g, is defined. Why is this measure of size used? What alternatives might be used (end-to-end distance for instance)? In Figure 4 $\langle R_g^2\rangle$ is plotted for the rings. Why would it increase with the length of the rings and decrease with the stiffness, (a)? Why would it increase with the number of threaded linear chains, (b), (c), (d)? How is the value of $\langle\kappa\rangle$ related to $\langle R_g^2\rangle$ in this context?

d) In Figure 5, the surface area of the minimal surface is shown as a function of the ring size, number of threads, and chain stiffness. Explain what the minimal surface is and why it was used versus the method of Hagita et al. using the "Gauss linking number" (refs. 36-38). Why does the surface area, S, show the same dependencies as $\langle R_g^2\rangle$ in Figure 4?

e) Explain Figure 6. What is the asphericity? Why does it decrease with the size of the ring polymers and with the stiffness of the ring, Fig. 6 (a)? For small rings, (b), the asphericity doesn't depend on the number of threaded linear chains but for large rings, (d), there seems to be an exponential increase with number of threaded linear chains. Why is this so? What function could model this behavior and what parameter could you get from this function?