Homework 3
February 3, 2025
Polymer Physics

Over the past 20 years significant advances have been made in the connection between the local "Kuhn" structure of polymers, the entanglement network in melts and semi-dilute solutions, and the dynamic mechanical properties of polymers based on work from Exxon Central Research in Annandale (named after two ducks) NJ and their various collaborators including Colby at Penn State who also worked with de Gennes etc (something of a cabal). In this context, in 2008 Everaers (Uchida N, Grest GS (mr. "LAMMPS"), Everaers R *Viscoelasticity and primitive path analysis of entangled polymer liquids: From F-actin to polyethylene* J. Chem. Phys **128** 044902 (2008) produced the "Everaers plot" which presents a general rule on how to design a polymer with a desired modulus (very useful to a company like Exxon). The E-plot showed two regimes, flexible chains at large l_K^3/v_0 (where l_K is the Kuhn length, v_0 is the volume of a Kuhn unit) and stiff chains at small l_K^3/v_0, in this plot the transition regime was largely missing from the available experimental data. In 2022, Colby and Gomez with a group of synthetic chemists, and analytic chemists designed polymers that could bridge this gap by adjusting the monomer mass while maintaining constant l_K using conjugated polymers, Fenton AM, Xie R, Aplan MP, Lee Y, Gill MG, Fair R, Kempe F, Sommer M, Snyder CR, Gomez ED, Colby RH *Predicting the Plateau Modulus from Molecular Parameters of Conjugated Polymers* ACS Cent. Sci. **8** 268-274 (2022).

a) The Everaers plot seeks to predict the plateau modulus G^0_N which for monodisperse polymers is a plateau in G' but for polydisperse polymers needs to be estimated from a slope, Colby's Figure 3. What is G^0_N and how can it be measured (describe the experimental setup/instrument). Derive a function for G^0_N using the Gaussian end-to-end distance, the Boltzmann equation, and a model for an entangled melt in terms of T, l_K, and $N_{K,e}$. Colby's equation 2 is missing a factor from your equation, explain this. Colby's equation 1 is missing a different factor from your equation, explain this. (Does equation 3 solve this problem? Explain equation 3.)

b) Explain how varying the monomer mass (figure 1) while maintaining a fixed l_K allows for exploration of "a large area of the Everears plot".

c) Explain what is the "nematic to isotropic transition". How can it be observed in rheology, DSC, birefringence, scattering or diffraction, microscopy? Why is this transition present in Colby's materials?

d) Colby mentions the time-temperature superposition (TTSP) for his SAOS (small-angle oscillatory shear) measurements. Explain TTSP using the Arrhenius dependence of viscosity on temperature. Replace the activation energy by $\Delta H - T\,\Delta S$, and T by the Vogel expression $(T - T_0)$ to obtain a three-parameter function for viscosity, or relaxation time (~1/viscosity).

e) Figure 2 of Colby shows how they determined the Kuhn length using neutron scattering. Compare this with reference 29 Figures 1, 2, and 5 which they cite as the method they use. Is it possible to observe the persistence length in the figure shown by Colby knowing what you know about scaling laws in scattering? (Should there be a flat portion at high-q?)