

Polymer Physics
Homework 5
February 11, 2022 (Due February 15)

Synthetic oil contains viscosity additives that can have thermally driven structural changes which impact viscosity. One example was studied by van Ravensteijn BGP, Zerdan RB, Hawker CJ, Helgeson ME *Role of Architecture on Thermorheological Properties of Poly(alkyl methacrylate)-Based Polymers* *Macromolecules* **54** 5473-5483 (2021). Van Ravensteijn studied random copolymers of stearyl methacrylate and methyl methacrylate (p(SMA-co-MMA)), two similar monomers one with a long alkyl chain and the other with a methyl group attached to a methacrylate monomer. The copolymer displays an upper critical solution temperature (UCST) with oil meaning that it phase separates on cooling. At high temperature the chains display expanded coils which contract on cooling. Since the viscosity of the oil follows an Arrhenius behavior the expansion of the copolymer and chain entanglements may lead to a leveling off the viscosity and viscosity enhancement at high temperatures. Van Ravensteijn studies three topologies of this copolymer, linear chains ($c = 1$), randomly branched chains ($c \sim 1.5$), and star polymers with 8 arms as shown in figure 1. Star polymers don't have a simple dimensional description since the arms correlate.

- a) Van Ravenstijn determines the overlap concentration to ensure his coil measurements are in dilute conditions. How does he determine c^* and why is it important? (This is described in the supplemental information)
- b) Figure 3 shows SANS data from linear, branched and star polymers as well as the radius of gyration as function of temperature. Compare the plot of R_g with that given for polystyrene in cyclohexane given in class. What functionality do you expect R_g to follow in temperature? Why did van Ravensteijn indicate a linear dependence?
- c) Figure 3a has been digitized and plotted in Igor Pro with lines of slope $-3/5$, -2 , and -4 . How do you expect the curves to behave as a function of temperature? Why is there a transition from $-3/5$ to -2 ? Estimate the size of this transition from $2\pi/q$ for the cross-over between $-3/5$ and -2 and plot that value as a function of temperature.
- d) Figure 1a indicates that the viscosity enhancement effects practical use. This enhancement of the viscosity in Figure 2d is from about 13 to 20 so the solution viscosity about doubles. How much will the oil viscosity decrease in this same temperature range due to Arrhenius behavior using $A = 0.007889$ and $B = 1456.2$ K. Will the impacts predicted in Figure 1a be possible under these conditions?
- e) Keane DP, Mellor MD, Poling-Skutvik R *Responsive Telechelic Block Copolymers for Enhancing the Elasticity of Nanoemulsions* *Appl. Nano Mat.* In press <https://doi.org/10.1021/acsnm.1c03666> discuss another approach to thermally controlled viscosity enhancement which also uses UCST phase behavior and vesicles similar to those in HW 4 last week. In this case PEO chains with PS ends (soluble in cyclohexane vesicles) assemble into a network as shown in Figure 2a which can be released on cooling due to phase separation of the PS/cyclohexane, dropping the viscosity. This transition occurs between 10 and 40 °C. Kean doesn't mention that both PEO and the non-ionic surfactant Tween 20 (which is based on ethylene oxide chains) have an LCST phase separation in water at about 60°C. What impact do you think this would have on the viscosity of the system?