

**Homework 7**  
**Polymer Physics 2023**  
**Due Tuesday February 28 at noon**

(Please send one email with a **pdf** attachment to [beaucag@uc.edu](mailto:beaucag@uc.edu))

The file should be called: **HW 3 Group x Last Name\_Name\_Name\_Name.pdf**)

Anilkumar P, Lawson TB, Abbina S, Mäkelä JTA, Sabatelle RC, Takeuchi LE, Snyder BD, Grinstaff MW, Kizhakkedathu JN *Mega macromolecules as single molecule lubricants for hard and soft surfaces* Nat. Comm. **11** 2139 (2020) describe a method to make molecular ball bearings that can mimic biological synovial fluid to lubricate joints. (This concept is not particularly new, as seen in the tribonet.org webpage <https://www.tribonet.org/nanolubricants-2/>). Tribology (the study of friction) is an important application area for polymers. Generally, we consider the shear thinning behavior of polymeric fluids (power-law fluids) as being advantageous to many applications such as engine oil, see Anilkumar's Supplemental Figure 12.

- a) Anilkumar used gel permeation chromatography with index of refraction, light scattering (dynamic and static) and Wheatstone bridge viscosity detectors to determine that there was a monomodal (one peak) distribution with a fairly narrow molecular weight distribution ( $\bar{M}_w/\bar{M}_n = PDI \sim 1.2$ ). Explain how a GPC MALS works {that is: 1) how would you build a GPC MALS (this has two parts, a GPC and a MALS) 2) what raw data does such an instrument produce 3) how do you convert that raw data to amount versus molecular weight}. What moment of molecular weight does MALS give? Why is GPC also called SEC (size exclusion chromatography)?
- b) Anilkumar's Table 1 lists the DOB (degree of branching), "Size", and intrinsic viscosity. DOB is obtained from the linear, branched and end groups that can be counted in an NMR spectra,  $DOB = (Br + EG)/(Br + EG + L)$ , does this equation seem reasonable? The "Size" is the hydrodynamic size,  $R_h$ , using a quasi-elastic light scattering detector on the MALS/GPC (<https://www.chromatographyonline.com/view/online-mals-qels-quasi-elastic-light-scattering>). Explain how the hydrodynamic radius is determined in QELS (that is: 1) how would you build a QELS 2) what raw data does such an instrument produce 3) how do you convert that raw data to diffusion coefficient and  $R_h$ )?
- c) The intrinsic viscosity is measured with a Wheatstone bridge attached to the GPC as explained in: Kainthan RK, Muliawan EB, Hatzikiriakos G, Brooks DE *Synthesis, Characterization, and Viscoelastic Properties of High Molecular Weight Hyperbranched Polyglycerols* *Macromolecules* **39** 7708-7717 (2006) equations 1–6. Explain the following statement by Anilkumar:

*...the size does not scale with molecular weight as with linear polymers<sup>28</sup> and low molecular weight HPG (Fig. 2a, Supplementary Table 1). The size of the mega HPGs lies between linear polymers (e.g., PEG) and dendrimers (e.g., PAMAM; Fig. 2a). The data further indicate that mega HPGs are more compact than linear polymers and less compact in comparison to dendrimers, and this might be advantageous in terms of offering more 'interior room' between branching units.*

*The mega HPGs possess very low intrinsic viscosity in comparison to other polymeric systems. The intrinsic viscosity,  $[\eta]$ , of the mega HPGs does not change considerably with molecular weight (Table 1); this small change in*

*intrinsic viscosity of mega HPGs also does not follow the Mark–Houwink–Sakurada equation and instead falls in line with the Einstein viscosity theory’s prediction of almost minimal change in  $[\eta]$  with molecular weight for “hard” globular-shaped polymers<sup>27</sup>. This result is in striking contrast to dendrimers (PAMAM, generation G1–G10), which show an unusual bell shape dependence of  $[\eta]$  with increasing molecular weight (Fig. 2b)<sup>29</sup>.*

Give the Einstein Equation and explain to what it pertains. In what way is this a displacement law? Give the Mark-Houwink equation and the expected values of “a” for Gaussian chain, expanded coil, spheres, and rods. Explain why dendrimers show a bell-shaped molecular weight dependence. Estimate the slope of the blue circles in Figure 2b (count the number of decades on the y (right) axis for one decade on the x-axis, the ratio is the power law slope, “a” from the Mark-Houwink equation). What type of structure does this correspond?

- d) Anilkumar makes Stribeck plots of the coefficient of friction (COF) versus the Hersey number. Describe the Hersey number and the three regimes in the Stribeck curve ([https://en.wikipedia.org/wiki/Stribeck\\_curve](https://en.wikipedia.org/wiki/Stribeck_curve)). How do Anilkumar’s curves (Figure 3b) compare with what is expected? How is this used to compare the mega HPGs to bio and synthetic lubricants?
- e) Figure 12 in Anilkumar’s supplemental material shows that only low molecular weight HPGs display shear thinning, a feature that is common to synthetic lubricants for applications such as in car engines where high viscosity at high engine speeds leads to heat and breakdown of the lubricant, while high viscosity at low speeds provide protection to the engine and prevents oil leakage. Anilkumar indicates that Newtonian behavior (constant viscosity with shear rate) is superior for lubrication of biomedical joints. Explain why this might be the case. What is the mechanism that Anilkumar proposes for lubrication using HPGs in joints?