

**Polymer Physics**  
**Homework 4**  
**February 4, 2022 (Due February 8)**

Simon, Schneck, Noirez, Rahn, Davidovich, Talmon, and Gradzielski *Effect of Polymer Architecture on the Phase Behavior and Structure of Polyelectrolyte/Microemulsion Complexes (PEMECs)* *Macromolecules* **53** 4055-4067 (2020) studied the impact of polyelectrolyte (PE) chain persistence on a grapevine structure of PE/microemulsion complexes (PEMECs). Simon used cationic surfactants, oil, and anionic polyelectrolytes in an aqueous system. The persistence of the PE structure was reflected in the structure of the resulting PEMECs, Figure 8.

- a) Figure 2 shows the phase diagram for the three PEs used in this study which are shown in Figure 1, NaHA (high persistence length, 9 nm), NaPA (low persistence length, 1.3 nm), NaCMC ( $l_p = 6-16$  nm but with flexible anionic groups). In all three cases the miscibility limit occurs at  $z \sim 0.7 = [-]/([-]+[+])$  meaning an excess of anionic groups on the PE compared to the cationic surfactant charge groups. Explain why you would need more anionic PE groups using the sketch shown in the inset to Figure 8 as the basis of your logic for  $z \sim 0.7$  as the point where the system reaches miscibility, presumably where anions and cations are paired perfectly.
- b) Figure 7b shows the dependence of the number of spheres in an aggregate, presumably the aggregates seen in Figure 5, as a function of the molecular weight of the PE. From the inset to Figure 8 what dependence would you expect? The observed power-law dependence seems to be close to (number of spheres in an aggregate)  $\sim MW^3$ . Can you make a cartoon that would agree with this scaling law? Does this model explain the  $z \sim 0.7$  value from question “a”? (Keep in mind that the number of spheres per aggregate is always less than 10 so a scaling law is probably not appropriate, that is, you usually expect at least one full decade on each axis for a scaling law.)
- c) Dynamic light scattering measures the diffusion of nanoparticles through a time term  $\Gamma$ , and an inverse size term  $q$ . At the end of page 4058 Simon indicates that some NaHA samples had two  $\Gamma$ s reflecting two different molecular translation processes. For one, time scales with (distance)<sup>2</sup>, while for the other time scales with (distance)<sup>3</sup>. Explain these two behaviors. A third option would be time scaling with size. What would that indicate?
- d) Figure 8 shows log intensity versus log of  $q$  for small-angle neutron scattering where the intensity scales with the mass and  $q$  scales with the inverse size. Explain what a power law of -1 indicates in this plot, that is mass  $\sim$  size. How do the two power-laws compare with the cartoon in the inset? The persistence length for NaHA is 9 nm, for NaPA is 1.3 nm, and for NaCMC is 6-16 nm. Calculate  $q = 2\pi/\text{size}$  and compare with the extent of the -1 power-laws in this plot. Comment on the agreement or disagreement.
- e) On page 4064 Simon uses the following equation to calculate the persistence length:

$$\langle h^2 \rangle = 2L_c l_p - 2l_p^2 (1 - e^{-L_c/l_p})$$

Explain the origin of this equation. How can this be used to determine the relationship between the Kuhn length and the persistence length. Is that comparison appropriate in this case? Why or why not?