Quiz 10   Polymer Properties
April 12, 2019

Chain overlap and chain entanglement are related concepts but display distinct behavior as a function of concentration for uncharged polymers in theta and good solvents and for polyelectrolytes, the three universal classes for flexible polymers in solution, Figure 1.

a) Figure 2 shows the behavior of c^* and c_e,
    -top circles c_e for uncharged polymers following $M^{-0.8}$,
    -next circles down c_e for polyelectrolytes $M^{-0.8}$,
    -middle stars c^* for uncharged polymers in good solvent following $M^{-0.8}$ and
    -bottom stars etc. c^* for polyelectrolytes following M^{-2}.
    Explain the origin of the dependence of c^* on molecular weight for the polyelectrolytes (bottom stars) and noncharged polymers in a good solvent (middle stars).
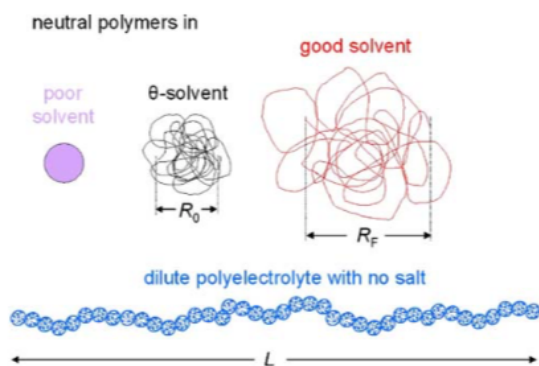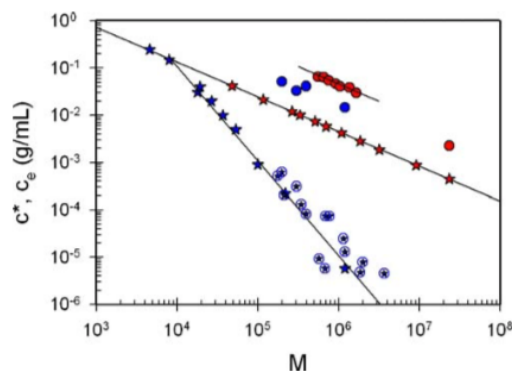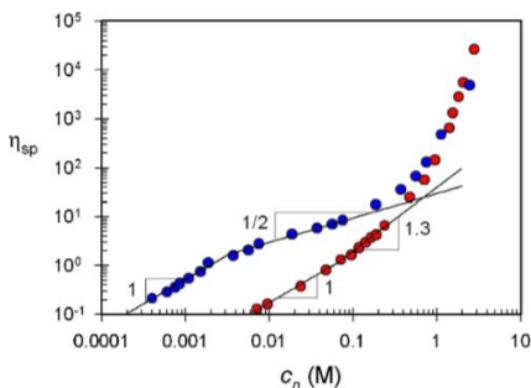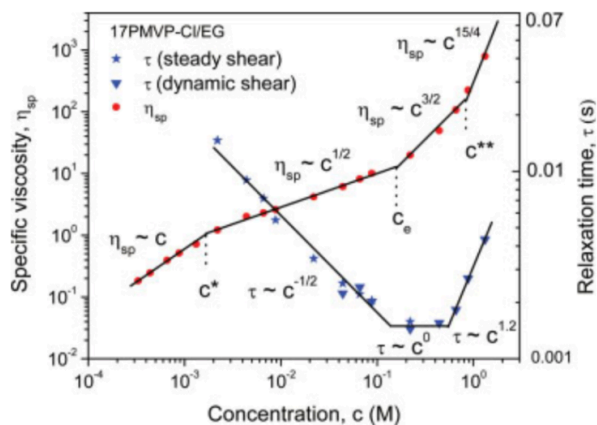

Figure 1*

Figure 2*

Figure 10*

Figure 5**

*Colby RH *Structure and linear viscoelasticity of flexible polymer solutions: comparison of Polyelectrolyte and neutral polymer solutions.* Rheol. Acta **49** 425-42 (2010)
Dou S and Colby RH *Charge Density Effects in Salt-Free Polyelectrolyte Solution Rheology* J. Polym. Sci. Polym. Phys. **44 2001-2013 (2006).

b) The entanglement concentration (top circles), c_e, is larger than the overlap concentration, c^*, by a factor of 10 for uncharged polymers and by a factor of up to 10,000 for polyelectrolytes. **Why do you think the entanglement concentration follows $M^{-0.8}$ for**

both the polyelectrolytes and for the uncharged polymers in good solvents noting the differences in c^* behavior from part "a"?

c) **Explain the behavior seen in Figure 10** for the specific viscosity, $\eta_{sp} = (\eta - \eta_0)/\eta_0$ based on your answers to parts a and b. The top curve is for a polyelectrolyte and the bottom curve for an uncharged polymer. Compare the concentration ranges in Figure 10 for the 1/2 and 1.3 power-law regimes with Figure 2.

d) Figure 5 shows four regimes for the specific viscosity of a polyelectrolyte. Write an expression that relates the specific viscosity to the intrinsic viscosity. **Show** that if $\phi^* = 1/[\eta]$ then η_{sp} must equal 1 at ϕ^*. **Does Figure 5 support this conjecture?**

e) For polyelectrolytes the tube diameter (entanglement spacing), d_t, is much larger than the spacing between chains or mesh size, ξ. This is because the tube diameter is defined in terms of the point where the kT energy of each monomer cannot overcome the constraint of surrounding chains, whereas ξ is defined as the distance of first contact between chains, a shorter distance. Within the tube the chain is a random walk of correlation blobs. For polyelectrolytes, as chain concentration increases the counterion concentration also increases until the charge is screened out at ϕ^{**} and the chains become neutral chains since all of the charge effects are screened. Figure 5 below (circles) shows this behavior. **Explain how you could change the three transition points, ϕ^*, ϕ_e, and ϕ^{**} for a given polymer.**

ANSWERS: **Quiz 10   Polymer Properties**
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a) Uncharged polymers are in a good solvent so $d_f = 5/3$ (or $1/0.588$). $c^* = M/V = M/M^{3/df}$. This has a value of $M^{-0.8}$ for good solvents. For rods $d_f = 1$, so $c^* \sim M^{-2}$

b) For both chains there is a transition at about η_{sp} of 1 from dilute to semi-dilute unentangled chains. Dilute chains follow Rouse behavior with $\eta_{sp} \sim c$. Above c^*, Fuoss behavior is seen for polyelectrolytes $\eta_{sp} \sim c^{1/2}$, and a power law of $c^{1.3}$ for noncharged good solvent chains. Then there is a gap until c_e is reached where a much stronger power-law dependence is observed on the order of c^3.
   The issue concerning the dependence of the entanglement concentration on M is not addressed in the papers as far as I saw. The reason is hinted at in Figure 1. The linear size of the polyelectrolyte follows $L \sim N$. But the lateral size follows $D \sim N^{0.588}$. The lateral size is what controls entanglements for polyelectrolytes, whereas the length controls c^*. There doesn't seem to be another explanation, though this explanation doesn't seem particularly believable. Nonetheless, the data that he presents clearly supports this argument.

c) For Figure 10 and the uncharged chain the transition from Rouse to unentangled overlap occurs at about $c_n = 0.1$. c_n is the number of monomers per liter. c_n is proportional to c^*/c_e which are in g/ml. We don't know the conversion factor. So say the conversion factor is $c^* \sim c_e \sim c_n/20$ so $c_n = 0.1$ becomes $c \sim 5e^{-3}$ g/ml and the gap between red stars and red circles is about a factor of 10 so $^*c_e \sim 5e^{-2}$ g/ml and the corresponding c_n is 1, which is about where the transition to the entangled regime occurs in Figure 10 for the red circles on the bottom. Similarly, the c^* transition for polyelectrolytes in Figure 10 occurs at $c_n \sim 3e^{-3}$ which might correspond to $c^* \sim 1.5\,e^{-4}$ at a molecular weight of 25,000 in Figure 2 with a corresponding c_e of $7e^{-2}$ g/ml or c_n of 1.4 which agrees fairly well with figure 10.

d) $\eta = \eta_0(1+\phi[\eta])$ so $\eta_{sp} = (\eta-\eta_0)/\eta_0 = \phi[\eta]$. If $\phi^* = 1/[\eta]$, then $\eta_{sp} = 1$ at ϕ^*. The data in Figure 5 and 10 support this conjecture more or less. The actual transition seems to happen at a slightly higher η_{sp}.

e) ϕ^{**} can be changed by adding salt which would lower the value due to Debye screening. ϕ^* can be changed with the molecular weight or solvent quality (changing d_f). ϕ_e can be changed with the temperature, at higher temperature the tube would be larger and ϕ_e would be higher since the tube would be larger.