Quiz 1 Polymer Properties August 30, 2013

1) It is observed that a bubble in shampoo takes the shape of a teardrop. Shampoo contains worm-like micelles that are long cylindrical structures about 10 μ m in contour length (path length along the chain) and about 4 nm in diameter that are convoluted and subject to thermally driven motion similar to a polymer in solution.

a) Explain why the bubble takes a tear drop shape rather than a spherical shape by sketching a drawing of the bubble and showing the forces acting on the bubble with arrows. Explain the origin of these forces.

b) A typical shampoo contains 30 volume percent worm-like micelles that display a Kuhn length of about 100 nm. Calculate the size $\langle R^2 \rangle^{1/2}$ for a worm-like micelle.

c) Calculate the volume fraction within an isolated coil of a worm-like micelle (occupied cylinder volume/(coil volume)). Comparing this with the shampoo volume fraction what can you say about the micelles?

d) If the concentration were reduced to below the isolated micelle concentration what shape would the bubbles take?

e) If the micelles were spherical micelles at 30 volume percent what shape would the bubbles take?

2) Polymers differ from metals and ceramics in that they are primarily defined by their dynamic behavior. For polymers in the melt the viscosity shows shear thinning behavior when polymers are above the entanglement molecular weight.

a) Using a sketch and laminar flow (deck of cards flow) define the shear stress, rate of strain (velocity gradient) and viscosity. Please make sure to indicate the relative directions of force, area, velocity and change in velocity.

b) Show a plot of log of viscosity versus log of shear rate (velocity gradient) for a polymer melt indicating the zero shear rate viscosity and the relaxation time (inverse shear rate characteristic of chain disentanglement).

c) How does the relaxation time change with molecular weight?

d) Show a plot of log of the zero shear rate viscosity versus molecular weight. Indicate the entanglement molecular weight.

e) Show a plot of log of the zero shear rate viscosity versus concentration. Indicate the overlap concentration.

1) a)



b) The chains contain $10^4/10^2 = 100$ Kuhn units $= N_k$. $\langle R^2 \rangle^{1/2} = N_k^{1/2} l_k \sim 1 \mu m$. c) $V_{coil} = 4/3 \pi R^3 = 4.2 \text{ e } 9 \text{ nm}^3$. $V_{occupied} = \pi R^2 L = 5.0 \text{ e } 5 \text{ nm}^3$. So $\phi_v = 0.01\%$. The micelles are highly overlapped and entangled at 30 %.

d) At extremely low concentration the bubbles would be spherical since the fluid would be Newtonian.

e) If the micelles were spherical the fluid would also be Newtonian and the bubbles would be spherical.

2) a)

b) Zero shear rate viscosity is the plateau at low shear rate. The time constant is the inverse of the shear rate where the viscosity begins to decay.



FIGURE 3.6-5. Composite plot of dimensionless viscosity $\eta_i \eta_0$ versus initial encoders and receipt for several different concentrated polystyrene-*n*-butyl benzene solutions. Molecular weights rated from 1.6 × 10⁵ to 2.4 × 10⁵, concentrations from 0.255 to 0.55 g/cm³, and temperatures from 305 to 333 K. [W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1–179 (1974).]

c) The relaxation time increases with increasing molecular weight so the decay in viscosity begins at lower shear rate for higher molecular weights.



d) Entanglement molecular weight is the molecular weight where there is a transition in the power laws from 1 to 3.4 slope.

FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is popurtional to concentration, which is constant for a given undiluted polymer. For each polymer the dopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. For, Adz. Polym. Sci., 5, 261-357 (1963).]

e) Overlape concentration is at the transition point between the two power law regimes. Power law 1 at low concentration and about 3 above the overlap concentration.



Figure 11.17. Concentration dependence of the specific viscosity of dilute and moderately concentrated solutions of cellulose acetate in dimethyl sulfoxide.³ The intersection of straight lines that are drawn through the dilute-solution (\bigcirc) and concentrated-solution (\bigcirc) data marks the critical concentration, c^* (ca. 3.7 g dL¹ is this case).