Quiz 3 Polymer Properties 10/02/01

1) The Einstein equation for viscosity reflects the volumetric displacement of a fluid by colloidal particles.

a) Give the Einstein relationship.

b) Write the governing equation for a Newtonian fluid.

c) Sketch a 2d laminar flow between two planes showing force, area, and x and y directions. Then expand b) in terms of force, area, change in x, change in y and change in time.

d) Consider a colloid suspension of perfect cubes perfectly aligned in the xyz coordinate system with a volume fraction ϕ on your 2d diagram and write an expression for the viscosity in terms of ϕ based on this system. Show that this is equivalent to a).

e) How would your answer to d) differ if the cubes settled to the bottom and partially blocked the flowing volume?

f) What are the assumptions of a)? Would it work for a sugar solution?

(Pulvermacher O Zeitschrift für Anorganische und Allgemeine Chemie cxiii 147 (1920).)

2) Polymers in dilute solution display two main measures of size, the length of chain persistence and the overall coil size.

a) List 5 ways to quantify the overall coil size, and comment on their ability to describe linear, branched chains and cyclics.

b) Calculate the density of a polymer coil based on the molar mass, z, and the mass-fractal dimension, d_f . (d_f is 2 for a random walk.)

c) How would the intrinsic viscosity, $[\eta]$, scale with molar mass for a polymer coil?

d) How would the intrinsic viscosity, $[\eta]$, scale with molar mass of platelets for blood (a colloidal suspension of disk particles)?

- 3) The energy associated with deformation of an isolated polymer coil can be obtained from the Gaussian probability distribution.
 - a) Obtain an expression for the energy of an isolated chain using the Arrhenius function.

b) For mechanical systems the change in energy is the force times the change in distance. Calculate the force needed to deform a polymer chain of size R a distance dR (a perturbation) using the energy expression from a).

c) For an elastomer (rubber) the chain length between crosslink's, M_c , governs the modulus. Write an expression for the modulus of a rubber in terms of M_c and the absolute temperature, T.

d) Explain what might happen if a balloon was placed in an oven and the temperature rose (before it burns).

e) How is the plateau modulus for a polymer melt related to the modulus of an elastomer?

4) Entanglements are responsible for many of the physical features we associate with plastics.

a) Explain how entanglements effect the viscosity of a plastic (for example, viscosity as a function of rate of strain or velocity gradient).

b) Consider wax (no entanglements) and polyethylene (milk jug, grocery store bag, garbage bag). (You could also compare polystyrene (CD case) and napthlene (moth balls) or benzene (gasoline).) Explain how entanglements affect the mechanical strength of plastics.

c) Give two structural models (cartoon of structure with description) for entanglements in polymers based on what we discussed in class with respect to the packing length.

 The following text is from Advanced Monte Carlo Algorithm for Atomistic Simulation of Shot- and Long-Chain Branched Polymers. Baig C, Alexiadis O, Mavrantzas VG Macromolecules 43 986-1002 (2010).

a,b,c,d) Glance at the presentation and look at the third to the last line. Comment on the comparison with Ramachandran. (Worth 4 parts a, b, c, d).

e) m_b in equations 6 and 7 is not defined in the paper. Comment on what you think m_b

is. That is what molecular feature might the packing length scale with in short chain branched polyethylene's with variable branch content and branch length.

Packing Length. The packing length is an important measure of chain structure, since it is linked with its rheological behavior (i.e., its response to an applied flow field).^{49,50} It is defined as the ratio between the apparent volume per molecule in the system and the effective chain dimension; it takes therefore smaller and smaller values as the effective space occupied by a chain increases. As discussed by Lohse,⁵⁰ if we use the mean-square chain end-to-end distance to quantify chain dimensions, then the packing length is denoted by *p* and is mathematically defined as

$$p = \frac{V_{\rm occ}}{\langle R^2 \rangle} \tag{4}$$

If, on the other hand, the mean-square chain radius-ofgyration is chosen to quantify chain dimensions, then the packing length is denoted by l_p and is mathematically defined as

$$l_{\rm p} = \frac{V_{\rm occ}}{\langle R_{\rm g}^2 \rangle} \tag{5}$$

Ramos et al.⁴⁰ have analyzed in detail the dependence of the packing length l_p for ethylene–1-hexene copolymers and have found that to a very good approximation

$$l_{\rm p}$$
 (Å) = 0.27 $m_{\rm b}^{1.34}$ (simulation, $T = 450$ K) (6)

This agrees very well with experimental data which are in favor of the following relationship between l_p and m_b :

$$l_{\rm p}$$
 (Å) = 0.33 $m_{\rm b}^{1.29}$ (experiment, $T = 463$ K) (7)

The results obtained for the two SCB melts discussed here using eq 5 in the form

$$l_{\rm p} = \frac{M}{\rho N_{\rm A} \langle R_{\rm g}^2 \rangle} \tag{8}$$

where M is the chain molecular weight and N_A Avogadro's number, are $l_p = 11.6$ Å for SCB_48 × 16.5_47 × 6 PE and 11.2 Å for SCB_36 \times 22_35 \times 8 PE; these are slightly more consistent with eq 6 than with eq 7. We further note that for the L_1072 PE system the present MC simulations predict an l_p value equal to 8.4 Å. The predictions of our MC simulations for the packing length of all six PE systems simulated here are reported in the last column of Table 3. We see that at the conditions of the simulation (T = 450 K and P = 1 atm), the H-shaped and A₃AA₃ PE systems are characterized by l_p values that are approximately 10-20%higher than that of strictly linear PE, while the two SCB PE systems exhibit even higher (up to 40%) l_p values. These results compare very favorably with the measurements of Ramachandran et al.54 based on small-angle neutron scattering data according to which the value of l_p ranges from 6.5 ± 0.8 Å for linear polyethylene to 9.0 ± 0.6 Å for polyethylene with 12.1 branches per 1000 carbon atoms. Ramachandran et al.⁵⁴ have further suggested a relationship between number of SCBs and l_p , which indicates a maximum enhancement of persistence length to 9.1 Å for fully branched PE (i.e., when all carbon atoms in the backbone are branched).

Quit 3 Answerg

a) $\eta = \eta_0 (1 + 2.5 \phi) \eta_c = solvent linesity$ d= colume hachen of spheres q= solation circosity

6) $C_{12} = \binom{d}{d} \binom{X_1}{dX_2} = \binom{d}{d} \binom{X_1}{X_1}$

 $C) \qquad \underbrace{\frac{1}{1}}_{I} \qquad \underbrace{F_{I}}_{d_{X_{2}}} \qquad \underbrace{f_{X_{2}}}_{d_{X_{2}}} \qquad \underbrace{f_{X_{2}}}_{X_{1}}$ $\mathcal{T}_{12} = \frac{dF_{1}}{dA_{1}} = \mathcal{N}_{12} \frac{d(dx_{1})}{dF_{2}}$

d) when the fluid is compised of & cubes them dry is only (- 4) and of the arisinal x2 change so the gradientis stepper for the same Tiz or Tris layer for the some scadient. If The & Shace Vept the some Min Mult be large by $\frac{1}{(1-\phi)} = \mathcal{E}\phi^{h} = 1 + \phi^{2} + \phi^{3} + \phi^{3}$ at low of we have (1+ \$ [n]) when En J= 1 for the cabo, doscubed. depending a permetri de ve can propert di Pleiert Valus for LyJ.

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