

1. For a polyethylene chain of the molecular weight of 14000 with the characteristic ratio of 6.8, the bond angle of 112° , and the C-C bond length of 1.53 \AA :

(a) How many conformations are available to this chain?

$$\text{The number of bonds, } n = (14000/14) - 1 = 999$$

$$\text{The number of conformations} = 3^{n-2} = 3^{997}$$

(b) Calculate the unperturbed **root-mean-square** end-to-end distance.

$$\langle r^2 \rangle_0^{1/2} = \sqrt{C} \sqrt{n l} = (6.8)^{1/2} (999)^{1/2} (1.53 \text{ \AA}) = 126.1 \text{ \AA}$$

(c) Calculate the length of Kuhn chain. Take the extended chain with the bond angle maintained as the contour length.

$$n_e l_e^2 = \langle r^2 \rangle_0$$

$$n_e l_e = \text{contour length} = (999)(1.53 \text{ \AA})(\cos 34^\circ) = 1267 \text{ \AA}$$

$$l_e = \langle r^2 \rangle_0 / \text{contour length} = 12.5 \text{ \AA}$$

(d) Suppose that this chain is freely rotating with a bond angle of 90° , what is the **root-mean-square** end-to-end distance?

$$\langle r^2 \rangle_{\text{FRC}}^{1/2} = [(1 - \cos 90^\circ) / (1 + \cos 90^\circ)]^{1/2} \sqrt{n l} = (999)^{1/2} (1.53 \text{ \AA}) = 48.3 \text{ \AA}$$

(e) How much larger is the chain of (d) than if it were freely jointed?

Since the bond angle is 90° , the dimension of FRC is the same to that of FJC.

2. (a) Explain in your own words why do you expect the dimension of a chain in amorphous bulk state is the same to that in a theta condition.

As the magnitude of solvent-polymer interaction in a theta condition is supposed to be the same to that of polymer-polymer interaction in amorphous bulk state, chain dimension remains the same.

(b) Explain in your own words why do you expect the dimension of a chain in semicrystalline state is the same to that in a theta condition.

Upon crystallization from melt, only parts of the chain participate in the crystallization without the motion of whole chain. As a result chain dimension remains the same to that in melt state, which is again the same to that in a theta condition.

3. [Fill the blanks. No need to explain. Each right answer counts 3 points, plus 1 point when you get all eight correct.]

By slowly lowering the temperature of a polyethylene solution, plate-like single crystal, called (a) lamella, is formed. The typical unit cell crystallographic structure of this crystal is (b) orthorhombic or orthogonal, in which the c-axis (chain axis) is perpendicular to the a-b plane. The crystal grows by crystallization of the chains on (c) (110) plane (write down the Miller index). By the discovery of this polyethylene single crystal, the idea of folded-chain model, in contrast to the earlier (d) fringed-micelle model, of polymer semicrystalline state was developed.

By lowering the temperature of a polyethylene melt, ball-like crystal, called (e) spherulite, is formed. In this type of crystal chain axis is (f) tangential to the ball surface. The crystallization proceeds by (g) nucleation-and-growth mechanism, in which the two processes have different temperature dependences. As a result, size of the ball is smaller when the crystallization occurs at a temperature closer to (h) glass transition temperature of the polymer.

4. (a) How is physical aging distinguished from annealing?
Physical aging occurs at a temperature below T_g in the amorphous region. Annealing occurs at a temperature between T_g and T_m in the crystalline and the amorphous regions.
- (b) How is nematic mesophase distinguished from smectic mesophase?
In nematic mesophase mesogens are ordered in one dimension (directional order) only. In smectic mesophase mesogens are ordered in two dimensions (positional and directional order).
- (c) Arrange the followings in the order of increasing permeability, and explain. (A) N_2 through natural rubber, (B) O_2 through natural rubber, (C) N_2 through PVC, (D) O_2 through PVC, all at room temperature.
 $C < D < A < B$
PVC is in its glassy state and natural rubber is in rubbery state at room temperature. O_2 is only slightly smaller than N_2 . See Figure 4.19 textbook.
- (d) How would you determine the equilibrium melting temperature of a polymer?
[Explain Hoffman-Weeks plot. Explain in words, not by drawings only.]
Quench melt to a few different temperatures below T_m and allow crystallization isothermally at those temperatures. Determine the T_m 's of the samples and plot them against respective T_c 's. T_m^0 is where the extrapolation of the data intersects the $T_m = T_c$ line.
- (e) Why is the dielectric constant of a polymer related to its solubility parameter?
Both of dielectric constant and solubility parameter depend on the intermolecular interactions including dipole-dipole interaction.
5. A thin sheet of polyethylene ($E = 1.0$ GPa, $\nu = 0.4$) is subjected to a tensile load of 2.0 kN in the x-direction. The dimension of the sheet is 150 mm long (x), 100 mm wide (y), and 1.0 mm thick (z).
- (a) Calculate σ_x .
 $\sigma_x = F/A = (2000 \text{ N}) / (1E-3 \text{ m})(100E-3 \text{ m}) = 2E7 \text{ N/m}^2 = 20 \text{ MPa}$
- (b) Since it is a thin sheet, the specimen does not contract in y-direction, i.e., $\epsilon_y = 0$. Since it is on a free surface, there is no stress in z-direction, i.e., $\sigma_z = 0$. Calculate σ_y .
 $\epsilon_y = 0 = (1/E)[\sigma_y - \nu(\sigma_x + \sigma_z)] = (1/E)[\sigma_y - \nu\sigma_x]$
 $\sigma_y = \nu\sigma_x = (20)(0.4) = 8 \text{ MPa}$
- (c) Estimate the final thickness of the specimen.
 $\epsilon_z = (1/E)[\sigma_z - \nu(\sigma_x + \sigma_y)] = (1/1000)[0 - (0.4)(20+8)] = -0.0112 = (T - T_0)/T_0$
 $T = 0.9888 \text{ mm}$

