

**3. 063 Polymer Physics**  
**Spring 2007**  
**Problem Set #5**  
**Due Thursday May 10, 2007**

**5.1 Kinetics of Crystallization**

(a). Describe the two factors that control the crystallization of a homopolymer. Sketch the temperature dependence of the crystallization rate,  $C(T_c)$ , over the interval  $T_g \leq T_c \leq T_m$  and give an explanation for why there is a maximum in  $C(T_c)$ .

(b). Explain why the crystallization rate at a particular crystallization temperature  $T_c$  in a blend of a crystallizable polymer A and a higher molecular weight non-crystallizable polymer B decreases by a factor of about 100 times when the content of B in the blend is increased from 0% to 50%. Note: polymers A and B form a miscible, single homogeneous melt at temperatures above the melting point of polymer A. Also note that the glass transition temperature of the B polymer is considerably higher than that of the A polymer.

A-B Polymer Blend	Relative $C(T_c)$
100% A, 0% B	1.0
50% A, 50% B	0.01

**5.2 Crystalline Morphology**

Polyethylene is orthorhombic with space group Pnam. At room temperature, the unit cell parameters are:

$$\begin{aligned}a &= 7.40 \text{ \AA} \\b &= 4.93 \text{ \AA} \\c &= 2.53 \text{ \AA} \text{ (the chain axis direction)}\end{aligned}$$

There are two  $\text{-(CH}_2\text{CH}_2\text{-)}$  monomer units per unit cell.

- (i) Calculate the crystal density at room temperature.

- (ii) If the density of the amorphous phase of PE is  $0.86 \text{ g/cm}^3$  at room temperature, calculate the percent crystallinity of a sample having a measured density of  $0.94 \text{ g/cm}^3$ .
- (iii) The small angle X-ray period for the lamellar sample of part (ii) was found to be  $340 \text{ \AA}$ . Assuming a lamellar morphology, estimate the average thickness of the crystal and noncrystalline regions. Hint: 1D period  $P = l_c + l_a$
- (iv) Estimate the melting point of this sample based on fold surface energy  $\sigma_e = 0.042 \text{ J/m}^2$  and equilibrium melting point of  $T_m^\circ = 141^\circ \text{ C}$ .
- (v) Hydrogenated 1,4 polybutadiene (PB) is essentially polyethylene except for some short branches due to the fact that the polymerization of butadiene always results in at least some 1,2 and 3,4 isomers. When hydrogenated, these monomeric units give rise to butyl branches. Draw a representative portion of a polyethylene chain with a branch unit. Explain why the percent crystallinity and melting point of hydrogenated PB is considerably lower ( $T_m = 98^\circ \text{ C}$ ) than PE.

### 5.3 Chain Folded Lamellae and Per Cent Crystallinity

(a). The melting points of polyethylene crystals whose thickness was varied by controlling the conditions of crystallization were investigated by DSC and by X-ray diffraction (SAXS). The following results were obtained:

$T_m (\text{°C})$	139.4	137.5	136.0	134.9	131.9	127.9	117.0
$l (\text{\AA})$	1750	758	481	392	258	177	100

Prepare a plot of  $T_m$  versus  $1/l$ , and from the slope and intercept, respectively, evaluate  $T_m^\circ$  and the fold surface energy from these data. Assume the heat of fusion of 100% crystalline polyethylene is  $\Delta H_V^\circ = 1.44 \times 10^8 \text{ J/m}^3$ .

(b). Crystallization can be thought of as a self organization process. Even in a simple, linear polymer, such as polyethylene, the material is never 100% crystalline. Discuss at least 3 factors why the material always exhibits a degree of crystallinity less than 100%.

## 5.4 CNTs and Polymers

(a). Argue the case that single wall carbon nanotubes can be well described as just another type of polymer, albeit with certain unique features. Discuss how the variation in rolling vector  $(n,m)$ , tube diameter and tube length are related to conventional polymer descriptors such as stereochemistry of the monomer repeat and polydispersity. Can you describe two different types of polydispersity index for CNT's?

(b). In the future, it may be possible to find synthetic conditions such that truly monodisperse tube types can be made in high yield. This should lead to outstanding physical properties. Describe your choice of optimum type of tube and state your reason why (SWNT vs MWNT and  $(n,m)$  value if appropriate) for the following properties: (in case cite the anticipated ideal value of the property and compare it to an existing material).

(i). Tensile modulus

(ii). Tensile strength

(iii). Thermal conductivity

(iv). Electrical conductivity