ChE 531 Polymer Engineering University of Rhode Island
Professor Greenfield Spring 2008

Homework 1
due February 13, 2008

If you find yourself without enough information, make and justify a reasonable approximation. Also notice that sometimes the question contains an additional part at the end (e.g. problem 2). Be sure to answer it!

1. Textbook, chapter 1, problem 15 (molecular weight distribution). For the same mixture, also calculate the z-average molecular weight, $\overline{M_z} = \dfrac{\sum_i n_i {M_i}^3}{\sum_i n_i {M_i}^2}$, and the polydispersity, $\overline{M_w}/\overline{M_n}$.

   (n_i is the number of moles that have the i'th size.)

2. Calculate the crystal densities as described in the text, problems

   (a) 2.1 (subsection 2 only)

   (b) 2.2 (subsection 2 only)
   Hint (or reminder from class): the volume of a parallelepiped is base $\times$ height. To calculate the base and height, draw a picture of the unit cell and try adding some lines to make triangles. See, you will use math from geometry class after all.

   How do the densities and geometries compare to those listed in the table distributed in class?

3. Tadokoro (*Structure of Noncrystalline Polymers*, **1979**, 375) reported orthorhombic polyethylene lattice constants as a function of temperature:

T (K)	a (Å)	b (Å)	c (Å)
4	7.121	4.851	2.548
77	7.155	4.899	2.5473
293	7.399	4.946	2.543
303	7.414	4.942	2.5473

   (a) What is the theoretical thermal expansion coefficient $\alpha = \frac{1}{V}\left(\partial V/\partial T\right)_P$ for crystalline domains of this phase of polyethylene?

   (b) Why are the c axis parameters independent of temperature?

   (c) How would you compare the expansion in different directions of a partially crystalline sample of polyethylene that was processed isotropically?

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4. Textbook, chapter 2, problem 7, part 2 only (percent crystallinity).

5. The web page provides data for the fraction crystallinity x as function of time (minutes) for a polymer crystallization process at multiple temperatures (in $^\circ$C).

   (a) Use a plot to estimate the Avrami exponent n and rate constant k at the two temperatures assigned to you (see web page and/or email).

   (b) Over what time(s) does the Avrami equation apply for these data?

   (c) During polymer processing, different parts of a polymer sample can be at different temperatures. Use the Avrami model parameters you determined in part a to compare the fraction crystallinity at the two temperatures assigned, for the amount of time listed in the web page/email.

6. Textbook, chapter 2, problem 8

7. Fox and Flory (*J. Polym. Sci.*, **1954**, *14*, 315) (Fox-Flory equation)
   measured the glass transition temperature of polystyrene as a function of molecular weight, finding

M (g/mol)	85,000	19,300	13,300	6,650	4,980	3,590	3,041	2,600	2,085	1,675
T_g ($^\circ$C)	100	89	86	77	78	75	65	62	53	40

   What would be the T_g of a theoretically infinite molecular weight sample?

8. Textbook, chapter 2, problem 11 (copolymer or mixture T_g)
   Repeat the problem for both copolymer compositions defined in problem 10 (i.e. both the “4 methyls per 100” and “20 methyls per 100” compositions). Then sketch (all on one plot) the qualitative results that you would expect from dilatometry experiments for each sample.
   Note: The equation used in this problem is sometimes called the inverse rule of mixtures. It can sometimes be applied to a mixture of compounds, not just a mixture of monomers.