HW#3

Due Feb 7,2008

4.2 Mer weights for several polymers are asked for in this problem.

(a) For polytetrafluoroethylene, each mer unit consists of two carbons and four fluorines (Table 4.3). If A_C and A_F represent the atomic weights of carbon and fluorine, respectively, then

$$m = 2(A_C) + 4(A_F)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

(c) For nylon 6,6, from Table 4.3, each mer unit has twelve carbons, twenty-two hydrogens, two nitrogens, and two oxygens. Thus,

$$m = 12(A_C) + 22(A_H) + 2(A_N) + 2(A_O)$$

$$= (12)(12.01 \text{ g/mol}) + (22)(1.008 \text{ g/mol}) + (2)(14.01 \text{ g/mol}) + (2)(16.00 \text{ g/mol})$$

$$= 226.32 \text{ g/mol}$$

4.6 (a) From the tabulated data, we are asked to compute $\overline{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt. Range	Mean M_i	x_i	x_iM_i
8,000-20,000	14,000	0.05	700
20,000-32,000	26,000	0.15	3900
32,000-44,000	38,000	0.21	7980
44,000-56,000	50,000	0.28	14,000
56,000-68,000	62,000	0.18	11,160
68,000-80,000	74,000	0.10	7400
80,000-92,000	86,000	0.03	2580

$$\overline{M}_n = \sum x_i M_i = 47,720 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\overline{M}_w$, the weight-average molecular weight. This determination is performed as follows:

Molecular wt. Range	Mean M_i	w_i	w_iM_i
8,000-20,000	14,000	0.02	280
20,000-32,000	26,000	0.08	2080
32,000-44,000	38,000	0.17	6460
44,000-56,000	50,000	0.29	14,500
56,000-68,000	62,000	0.23	14,260
68,000-80,000	74,000	0.16	11,840
80,000-92,000	86,000	0.05	4300

$$\overline{M}_w = \sum w_i M_i = 53,720 \text{ g/mol}$$

(c) We are now asked if the number-average degree of polymerization is 477, which of the polymers in Table 4.3 is this material? It is necessary to compute $\overline{m}$ in Equation 4.4a as

$$\overline{m} = \frac{\overline{M}_n}{n_n} = \frac{47,720 \text{ g/mol}}{477} = 100.04 \text{ g/mol}$$

The mer molecular weights of the polymers listed in Table 4.3 are as follows:

Polyethylene--28.05 g/mol
Poly(vinyl chloride)--62.49 g/mol
Polytetrafluoroethylene--100.02 g/mol
Polypropylene--42.08 g/mol
Polystyrene--104.14 g/mol
Poly(methyl methacrylate)--100.11 g/mol
Phenol-formaldehyde--133.16 g/mol
Nylon 6,6--226.32 g/mol

PET--192.16 g/mol
Polycarbonate--254.27 g/mol

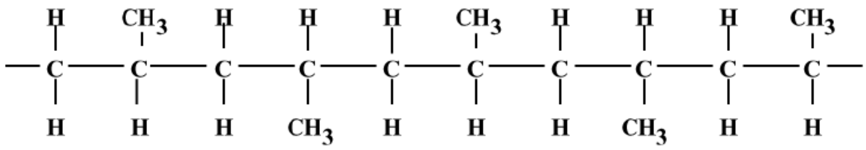
Therefore, polytetrafluoroethylene is the material since its mer molecular weight is closest to that calculated above.

(d) The weight-average degree of polymerization may be calculated using Equation 4.4b, since $\overline{M}_w$ and $\overline{m}$ were computed in portions (b) and (c) of this problem. Thus

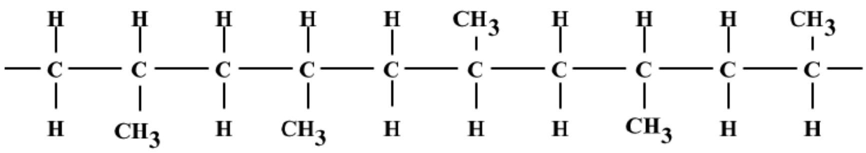
$$n_w = \frac{\overline{M}_w}{\overline{m}} = \frac{53,720 \text{ g/mol}}{100.04 \text{ g/mol}} = 537$$

4.11 We are asked to sketch portions of a linear polypropylene molecule for different configurations (using two-dimensional schematic sketches).

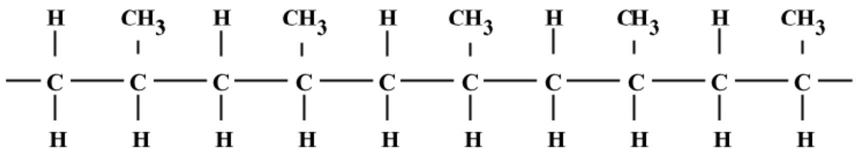
(a) Syndiotactic polypropylene



(b) Atactic polypropylene



(c) Isotactic polypropylene



4.13 This question asks for comparisons of thermoplastic and thermosetting polymers.

(a) Thermoplastic polymers soften when heated and harden when cooled, whereas thermosetting polymers, harden upon heating, while further heating will not lead to softening.

(b) Thermoplastic polymers have linear and branched structures, while for thermosetting polymers, the structures will normally be network or crosslinked.

4.16 For a poly(styrene-butadiene) alternating copolymer with a number-average molecular weight of 1,350,000 g/mol, we are asked to determine the average number of styrene and butadiene mer units per molecule.

Since it is an alternating copolymer, the number of both types of mer units will be the same. Therefore, consider them as a single mer unit, and determine the number-average degree of polymerization. For the styrene mer, there are eight carbon atoms and eight hydrogen atoms, while the butadiene mer consists of four carbon atoms and six hydrogen atoms. Therefore, the styrene-butadiene combined mer weight is just

$$m = 12(A_C) + 14(A_H)$$

$$= (12)(12.01 \text{ g/mol}) + (14)(1.008 \text{ g/mol}) = 158.23 \text{ g/mol}$$

From Equation 4.4a, the number-average degree of polymerization is just

$$n_n = \frac{\overline{M}_n}{m} = \frac{135,000 \text{ g/mol}}{158.23 \text{ g/mol}} = 8530$$

Thus, there is an average of 8530 of both mer types per molecule.

4.27 (a) We are asked to compute the densities of totally crystalline and totally amorphous polypropylene (ρ_c and ρ_a from Equation 4.6). From Equation 4.6 let $C = \frac{\% \text{ crystallinity}}{100}$, such that

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$$

Rearrangement of this expression leads to

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are specified in the problem, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which ρ_{s1} = 0.904 g/cm^3, ρ_{s2} = 0.895 g/cm^3, C_1 = 0.628, and C_2 = 0.544. Solving the above two equations for ρ_a and ρ_c leads to

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

$$= \frac{(0.904 \text{ g/cm}^3)(0.895 \text{ g/cm}^3)(0.628 - 0.544)}{(0.628)(0.904 \text{ g/cm}^3) - (0.544)(0.895 \text{ g/cm}^3)} = 0.841 \text{ g/cm}^3$$

And

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)}$$

$$= \frac{(0.904 \text{ g/cm}^3)(0.895 \text{ g/cm}^3)(0.544 - 0.628)}{(0.895 \text{ g/cm}^3)(0.544 - 1.0) - (0.904 \text{ g/cm}^3)(0.628 - 1.0)} = 0.946 \text{ g/cm}^3$$

(b) Now we are asked to determine the density of a specimen having 74.6% crystallinity. Solving for ρ_s from Equation 4.6 and substitution for ρ_a and ρ_c which were computed in part (a) yields

$$\rho_s = \frac{-\rho_c \rho_a}{C(\rho_c - \rho_a) - \rho_c}$$

$$= \frac{-(0.946 \text{ g/cm}^3)(0.841 \text{ g/cm}^3)}{(0.746)(0.946 \text{ g/cm}^3 - 0.841 \text{ g/cm}^3) - 0.946 \text{ g/cm}^3}$$

$$= 0.917 \text{ g/cm}^3$$