

14.19 (a) This portion of the problem asks us to determine the ratio of butadiene to acrylonitrile repeat units in a copolymer having a weight-average molecular weight of 250,000 g/mol and a degree of polymerization of 4640. It first becomes necessary to calculate the average repeat unit molecular weight of the copolymer,  $\bar{m}$ , using Equation 14.6 as

$$\bar{m} = \frac{\bar{M}_n}{DP} = \frac{250,000 \text{ g/mol}}{4640} = 53.88 \text{ g/mol}$$

If we designate  $f_b$  as the chain fraction of butadiene repeat units, since the copolymer consists of only two repeat unit types, the chain fraction of acrylonitrile repeat units  $f_a$  is just  $1 - f_b$ . Now, Equation 14.7 for this copolymer may be written in the form

$$\bar{m} = f_b m_b + f_a m_a = f_b m_b + (1 - f_b) m_a$$

in which  $m_b$  and  $m_a$  are the repeat unit molecular weights for butadiene and acrylonitrile, respectively. These values are calculated as follows:

$$m_b = 4(A_C) + 6(A_H) = 4(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

$$m_a = 3(A_C) + 3(A_H) + (A_N) = 3(12.01 \text{ g/mol}) + 3(1.008 \text{ g/mol}) + (14.01 \text{ g/mol})$$

$$= 53.06 \text{ g/mol.}$$

Solving for  $f_b$  in the above expression yields

$$f_b = \frac{\bar{m} - m_a}{m_b - m_a} = \frac{53.88 \text{ g/mol} - 53.06 \text{ g/mol}}{54.09 \text{ g/mol} - 53.06 \text{ g/mol}} = 0.80$$

Furthermore,  $f_a = 1 - f_b = 1 - 0.80 = 0.20$ ; or the ratio is just

$$\frac{f_b}{f_a} = \frac{0.80}{0.20} = 4.0$$

(b) Of the possible copolymers, the only one for which there is a restriction on the ratio of repeat unit types is alternating; the ratio must be 1:1. Therefore, on the basis of the result in part (a), the possibilities for this copolymer are random, graft, and block.