14.4 (a) Compute the repeat unit molecular weight of polystyrene.

(b) Compute the number-average molecular weight for a polystyrene for which the degree of polymerization is 25,000.

Solution

(a) The repeat unit molecular weight of polystyrene is called for in this portion of the problem. For polystyrene, from Table 14.3, each repeat unit has eight carbons and eight hydrogens. Thus,

\[ m = 8(A_C) + 8(A_H) \]

\[ = (8)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 104.14 \text{ g/mol} \]

(b) We are now asked to compute the number-average molecular weight. Since the degree of polymerization is 25,000, using Equation 14.6

\[ \bar{M}_n = (DP)m = (25,000)(104.14 \text{ g/mol}) = 2.60 \times 10^6 \text{ g/mol} \]
Below, molecular weight data for a polypropylene material are tabulated. Compute (a) the number-average molecular weight, (b) the weight-average molecular weight, and (c) the degree of polymerization.

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>x_i</th>
<th>w_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,000–16,000</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>16,000–24,000</td>
<td>0.16</td>
<td>0.10</td>
</tr>
<tr>
<td>24,000–32,000</td>
<td>0.24</td>
<td>0.20</td>
</tr>
<tr>
<td>32,000–40,000</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td>40,000–48,000</td>
<td>0.20</td>
<td>0.27</td>
</tr>
<tr>
<td>48,000–56,000</td>
<td>0.07</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**Solution**

(a) From the tabulated data, we are asked to compute $\bar{M}_n$, the number-average molecular weight.

This is carried out below.

<table>
<thead>
<tr>
<th>Molecular wt Range</th>
<th>Mean $M_i$</th>
<th>x_i</th>
<th>$x_i M_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,000-16,000</td>
<td>12,000</td>
<td>0.05</td>
<td>600</td>
</tr>
<tr>
<td>16,000-24,000</td>
<td>20,000</td>
<td>0.16</td>
<td>3200</td>
</tr>
<tr>
<td>24,000-32,000</td>
<td>28,000</td>
<td>0.24</td>
<td>6720</td>
</tr>
<tr>
<td>32,000-40,000</td>
<td>36,000</td>
<td>0.28</td>
<td>10,080</td>
</tr>
<tr>
<td>40,000-48,000</td>
<td>44,000</td>
<td>0.20</td>
<td>8800</td>
</tr>
<tr>
<td>48,000-56,000</td>
<td>52,000</td>
<td>0.07</td>
<td>3640</td>
</tr>
</tbody>
</table>

$$\bar{M}_n = \sum x_i M_i = 33,040 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\bar{M}_w$, the weight-average molecular weight.

<table>
<thead>
<tr>
<th>Molecular wt. Range</th>
<th>Mean $M_i$</th>
<th>w_i</th>
<th>$w_i M_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,000-16,000</td>
<td>12,000</td>
<td>0.02</td>
<td>240</td>
</tr>
<tr>
<td>16,000-24,000</td>
<td>20,000</td>
<td>0.10</td>
<td>2000</td>
</tr>
<tr>
<td>24,000-32,000</td>
<td>28,000</td>
<td>0.20</td>
<td>5600</td>
</tr>
<tr>
<td>32,000-40,000</td>
<td>36,000</td>
<td>0.30</td>
<td>10,800</td>
</tr>
</tbody>
</table>
(c) Now we are asked to compute the degree of polymerization, which is possible using Equation 14.6. For polypropylene, the repeat unit molecular weight is just

\[ m = 3(A_C) + 6(A_H) \]

\[ = (3)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 42.08 \text{ g/mol} \]

And

\[ DP = \frac{\bar{M}_n}{m} = \frac{33,040 \text{ g/mol}}{42.08 \text{ g/mol}} = 785 \]
14.8 High-density polyethylene may be chlorinated by inducing the random substitution of chlorine atoms for hydrogen.

(a) Determine the concentration of Cl (in wt%) that must be added if this substitution occurs for 5% of all the original hydrogen atoms.

(b) In what ways does this chlorinated polyethylene differ from poly(vinyl chloride)?

Solution

(a) For chlorinated polyethylene, we are asked to determine the weight percent of chlorine added for 5% Cl substitution of all original hydrogen atoms. Consider 50 carbon atoms; there are 100 possible side-bonding sites. Ninety-five are occupied by hydrogen and five are occupied by Cl. Thus, the mass of these 50 carbon atoms, \( m_C \), is just

\[
m_C = 50(A_C) = (50)(12.01 \text{ g/mol}) = 600.5 \text{ g}
\]

Likewise, for hydrogen and chlorine,

\[
m_H = 95(A_H) = (95)(1.008 \text{ g/mol}) = 95.76 \text{ g}
\]

\[
m_{\text{Cl}} = 5(A_{\text{Cl}}) = (5)(35.45 \text{ g/mol}) = 177.25 \text{ g}
\]

Thus, the concentration of chlorine, \( C_{\text{Cl}} \), is determined using a modified form of Equation 4.3 as

\[
C_{\text{Cl}} = \frac{m_{\text{Cl}}}{m_C + m_H + m_{\text{Cl}}} \times 100
\]

\[
= \frac{177.25 \text{ g}}{600.5 \text{ g} + 95.76 \text{ g} + 177.25 \text{ g}} \times 100 = 20.3 \text{ wt%}
\]

(b) Chlorinated polyethylene differs from poly(vinyl chloride), in that, for PVC, (1) 25% of the side-bonding sites are substituted with Cl, and (2) the substitution is probably much less random.
14.13 Make comparisons of thermoplastic and thermosetting polymers (a) on the basis of mechanical characteristics upon heating, and (b) according to possible molecular structures.

Solution

(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.
14.14 (a) Is it possible to grind up and reuse phenol-formaldehyde? Why or why not?

(b) Is it possible to grind up and reuse polypropylene? Why or why not?

Solution

(a) It is not possible to grind up and reuse phenol-formaldehyde because it is a network thermoset polymer and, therefore, is not amenable to remolding.

(b) Yes, it is possible to grind up and reuse polypropylene since it is a thermoplastic polymer, will soften when reheated, and, thus, may be remolded.
14.22 Explain briefly why the tendency of a polymer to crystallize decreases with increasing molecular weight.

Solution

The tendency of a polymer to crystallize decreases with increasing molecular weight because as the chains become longer it is more difficult for all regions along adjacent chains to align so as to produce the ordered atomic array.
15.2 Compute the elastic moduli for the following polymers, whose stress-strain behaviors may be observed in the “Tensile Tests” module of Virtual Materials Science and Engineering (VMSE): (a) high-density polyethylene, (b) nylon, and (c) phenol-formaldehyde (bakelite). How do these values compare with those presented in Table 15.1 for the same polymers?

Solution

The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

\[
E = \frac{\Delta \sigma}{\Delta \varepsilon} = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}
\]

Since all the stress-strain curves pass through the origin, we make take \(\sigma_1 = 0\) and \(\varepsilon_1 = 0\). Determinations of \(\sigma_2\) and \(\varepsilon_2\) are possible by moving the cursor to some arbitrary point in the linear region of the curve and then reading corresponding values in the “Stress” and “Strain” windows that are located below the plot.

(a) For high-density polyethylene, we selected \(\sigma_2 = 6.0\) MPa with its corresponding \(\varepsilon_2 = 0.0152\). Therefore,

\[
E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{6.0\ \text{MPa} - 0\ \text{MPa}}{0.0152 - 0} = 395\ \text{MPa} = 0.395\ \text{GPa}
\]

The elastic modulus (average) for high-density polyethylene given in Table 15.1 is 1.08 GPa, which is significantly higher than this value.

(b) For nylon, we selected \(\sigma_2 = 24.3\) MPa with its corresponding \(\varepsilon_2 = 0.0085\). Therefore,

\[
E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{24.3\ \text{MPa} - 0\ \text{MPa}}{0.0085 - 0} = 2860\ \text{MPa} = 2.86\ \text{GPa}
\]

The elastic modulus range for nylon 6,6 given in Table 15.1 is 1.58 GPa to 3.80 GPa; therefore, the value for the VMSE nylon lies within this range.
(c) For phenol-formaldehyde (bakelite), we selected $\sigma_2 = 33.0 \text{ MPa}$ with its corresponding $\varepsilon_2 = 0.0068$. Therefore,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{33.0 \text{ MPa} - 0 \text{ MPa}}{0.0068 - 0} = 4850 \text{ MPa} = 4.85 \text{ GPa}$$

The elastic modulus range for the phenol-formaldehyde given in Table 15.1 is 2.76 GPa to 4.83 GPa; therefore, this value for the VMSE phenol-formaldehyde lies just above the maximum value for this range.
15.3 For the nylon polymer, whose stress strain behavior may be observed in the “Tensile Tests” module of Virtual Materials Science and Engineering (VMSE), determine the following:

(a) the yield strength, and
(b) the approximate ductility, in percent elongation.

How do these values compare with those for the nylon material presented in Table 15.1?

Solution

(a) The yield strength corresponds to the first maximum (just beyond the initial linear-elastic region) of the stress-strain curve. This reading in the stress window located below the plot as the cursor point is dragged along the stress-strain curve is 84 MPa.

(b) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 44.5%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 4%); this gives a value of about 40%EL.

For nylon 6,6, the range of values of yield strength presented in Table 15.1 is 44.8 MPa to 82.8 MPa; therefore, the value for the VMSE nylon lies slightly above the upper value. The ductility range for nylon 6,6 is 15%EL to 300%EL; therefore, our value (40%EL) lies within this range.
15.8 On the basis of the curves in Figure 15.5, sketch schematic strain–time plots for the following polystyrene materials at the specified temperatures:

(a) Amorphous at 120°C
(b) Crosslinked at 150°C
(c) Crystalline at 230°C
(d) Crosslinked at 50°C

Solution

(a) Amorphous polystyrene at 120°C behaves a rubbery material (Figure 15.8, curve C); therefore, the strain-time behavior would be as Figure 15.5c.

(b) Crosslinked polystyrene at 150°C behaves as a viscoelastic material (Figure 15.8, curve B); therefore, the strain-time behavior will be as Figure 15.5c.

(c) Crystalline polystyrene at 230°C behaves as a viscous liquid (Figure 15.8, curve A); therefore, the strain-time behavior will be as Figure 15.5d.

(d) Crosslinked polystyrene at 50°C behaves in a glassy manner (Figure 15.8, curve B); therefore, the strain-time behavior will be as Figure 15.5b.
For thermoplastic polymers, cite five factors that favor brittle fracture.

Solution

For thermoplastic polymers, five factors that favor brittle fracture are as follows: (1) a reduction in temperature, (2) an increase in strain rate, (3) the presence of a sharp notch, (4) increased specimen thickness, and (5) modifications of the polymer structure
15.13 In your own words, describe the mechanisms by which semicrystalline polymers (a) elastically deform and (b) plastically deform, and (c) by which elastomers elastically deform.

(a) and (b) The mechanisms by which semicrystalline polymers elastically and plastically deform are described in Section 15.7.

(c) The explanation of the mechanism by which elastomers elastically deform is provided in Section 15.9.
15.14 *Briefly explain how each of the following influences the tensile modulus of a semicrystalline polymer and why:*

(a) **Molecular weight**

(b) **Degree of crystallinity**

(c) **Deformation by drawing**

(d) **Annealing of an undeformed material**

(e) **Annealing of a drawn material**

**Solution**

(a) The tensile modulus is not directly influenced by a polymer's molecular weight.

(b) Tensile modulus increases with increasing degree of crystallinity for semicrystalline polymers. This is due to enhanced secondary interchain bonding which results from adjacent aligned chain segments as percent crystallinity increases. This enhanced interchain bonding inhibits relative interchain motion.

(c) Deformation by drawing also increases the tensile modulus. The reason for this is that drawing produces a highly oriented molecular structure, and a relatively high degree of interchain secondary bonding.

(d) When an undeformed semicrystalline polymer is annealed below its melting temperature, the tensile modulus increases.

(e) A drawn semicrystalline polymer that is annealed experiences a decrease in tensile modulus as a result of a reduction in chain-induced crystallinity, and a reduction in interchain bonding forces.
15.15 Briefly explain how each of the following influences the tensile or yield strength of a semicrystalline polymer and why:

(a) Molecular weight
(b) Degree of crystallinity
(c) Deformation by drawing
(d) Annealing of an undeformed material

Solution

(a) The tensile strength of a semicrystalline polymer increases with increasing molecular weight. This effect is explained by increased chain entanglements at higher molecular weights.

(b) Increasing the degree of crystallinity of a semicrystalline polymer leads to an enhancement of the tensile strength. Again, this is due to enhanced interchain bonding and forces; in response to applied stresses, interchain motions are thus inhibited.

(c) Deformation by drawing increases the tensile strength of a semicrystalline polymer. This effect is due to the highly oriented chain structure that is produced by drawing, which gives rise to higher interchain secondary bonding forces.

(d) Annealing an undeformed semicrystalline polymer produces an increase in its tensile strength.
15.21 Would you expect the tensile strength of polychlorotrifluoroethylene to be greater than, the same as, or less than that of a polytetrafluoroethylene specimen having the same molecular weight and degree of crystallinity? Why?

Solution

The strength of a polychlorotrifluoroethylene having the repeat unit structure

\[
\begin{array}{c}
\text{F} \\
\hline
\text{C} \\
\hline
\text{C} \\
\text{F} \\
\text{Cl}
\end{array}
\]

will be greater than for a polytetrafluoroethylene having the same molecular weight and degree of crystallinity. The replacement of one fluorine atom within the PTFE repeat unit with a chlorine atom leads to a higher interchain attraction, and, thus, a stronger polymer. Furthermore, poly(vinyl chloride) is stronger than polyethylene (Table 15.1) for the same reason.

15.22 For each of the following pairs of polymers, plot and label schematic stress-strain curves on the same graph [i.e., make separate plots for parts (a), (b), and (c)].

(a) Isotactic and linear polypropylene having a weight-average molecular weight of 120,000 g/mol; atactic and linear polypropylene having a weight-average molecular weight of 100,000 g/mol

(b) Branched poly(vinyl chloride) having a degree of polymerization of 2000; heavily crosslinked poly(vinyl chloride) having a degree of polymerization of 2000

(c) Poly(styrene-butadiene) random copolymer having a number-average molecular weight of 100,000 g/mol and 10% of the available sites crosslinked and tested at 20°C; poly(styrene-butadiene) random copolymer having a number-average molecular weight of 120,000 g/mol and 15% of the available sites crosslinked and tested at -85°C. Hint: poly(styrene-butadiene) copolymers may exhibit elastomeric behavior.

Solution

(a) Shown below are the stress-strain curves for the two polypropylene materials. These materials will display the stress-strain behavior of a normal plastic, curve B in Figure 15.1. However, the isotactic/linear will have a higher degree of crystallinity (since isotactic are more likely to crystallize than atactic/linear), and therefore, will have a higher tensile modulus and strength. Furthermore, the isotactic/linear also has a higher molecular weight which also leads to an increase in strength.
(b) Shown below are the stress-strain curves for the two polyvinyl chloride materials. The branched PVC will probably display the stress-strain behavior of a plastic, curve \( B \) in Figure 15.1. However, the heavily crosslinked PVC will undoubtedly have a higher tensile modulus, and, also a higher strength, and will most likely fail in a brittle manner--as curve \( A \), Figure 15.1; these are the typical characteristics of a heavily crosslinked polymer.

(c) Shown below are the stress-strain curves for the two poly(styrene-butadiene) random copolymers. The copolymer tested at 20°C will display elastomeric behavior (curve \( C \) of Figure 15.1) inasmuch as it is a random copolymer that is lightly crosslinked; furthermore, the temperature of testing is above its glass transition temperature. On the other hand, since -85°C is below the glass transition temperature of the poly(styrene-butadiene) copolymer, the stress-strain behavior under these conditions is as curve \( A \) of Figure 15.1.