15.1 From Figure 15.3, the elastic modulus is the slope in the elastic linear region of the 20°C curve, which is

$$E = \frac{\Delta\,(\text{stress})}{\Delta\,(\text{strain})} = \frac{30\ \text{MPa} - 0\ \text{MPa}}{9\ \text{x}\ 10^{-3} - 0} = 3.3\ \text{GPa}\quad(483{,}000\ \text{psi})$$

The value range cited in Table 15.1 is 2.24 to 3.24 GPa (325,000 to 470,000 psi). Thus, the plotted value is a little on the high side.

The tensile strength corresponds to the stress at which the curve ends, which is 52 MPa (7500 psi). This value lies within the range cited in Table 15.1—48.3 to 72.4 MPa (7000 to 10,500 psi).

15.2 The explanation of viscoelasticity is given in Section 15.4.

15.4 Below is plotted the logarithm of $E_r(10)$ versus temperature.
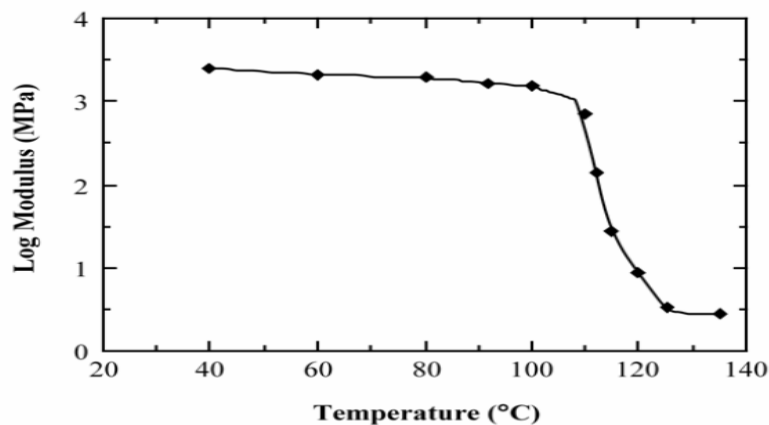
The glass-transition temperature is that temperature corresponding to the abrupt decrease in log $E_r(10)$, which for this PMMA material is about 115°C.

15.5 We are asked to make schematic strain-time plots for various polystyrene materials and at several temperatures.

(a) Crystalline polystyrene at 70°C behaves in a glassy manner (Figure 15.8, curve A); therefore, the strain-time behavior would be as Figure 15.5(b).

(b) Amorphous polystyrene at 180°C behaves as a viscous liquid (Figure 15.8, curve C); therefore, the strain-time behavior will be as Figure 15.5(d).

(c) Crosslinked polystyrene at 180°C behaves as a rubbery material (Figure 15.8, curve B); therefore, the strain-time behavior will be as Figure 15.5(c).

(d) Amorphous polystyrene at 100°C behaves as a leathery material (Figure 15.7); therefore, the strain-time behavior will be as Figure 15.5(c).

15.6 (a) Stress relaxation tests are conducted by rapidly straining the material elastically in tension, holding the strain level constant, and then measuring the stress as a function of time. For viscoelastic creep tests, a stress (usually tensile) is applied instantaneously and maintained constant while strain is measured as a function of time.

(b) The experimental parameters of interest from the stress relaxation and viscoelastic creep tests are the relaxation modulus and creep modulus (or creep compliance), respectively. The relaxation modulus is the ratio of stress measured after 10 s and strain (Equation 15.1); creep modulus is the ratio of stress and strain taken at a specific time (Equation 15.2).

15.7 (a) This portion of the problem calls for a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased molecular weight. Such a plot is given below. Increasing molecular weight increases both glass-transition and melting temperatures.
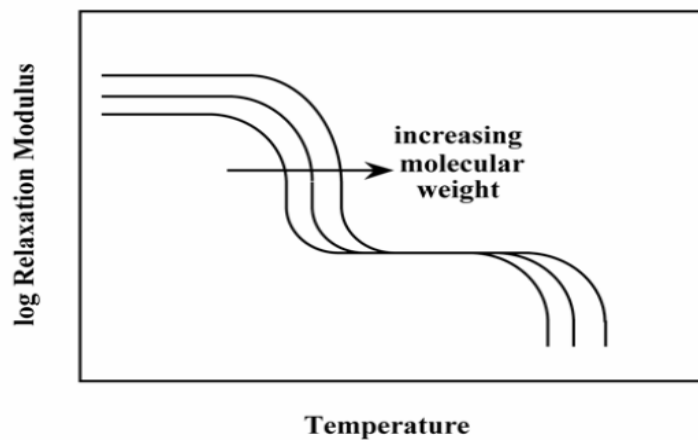
(b) We are now called upon to make a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased crosslinking. Such a plot is given below. Increasing the degree of crosslinking will increase the modulus in both glassy and rubbery regions.
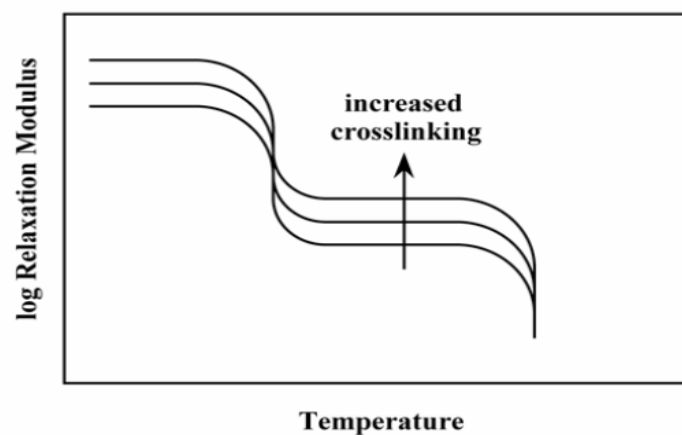
15.8 For thermoplastic polymers, five factors that favor brittle fracture are as follows: (1) a reduction in temperature, (2) an increase in strain rate, (3) the presence of a sharp notch, (4) increased specimen thickness, and (5) modifications of the polymer structure.

15.10 (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.

(a) Stages in the elastic deformation of a semicrystalline polymer. (a) Two adjacent chain-folded lamellae and interlamellar amorphous material before deformation. (b) Elongation of amorphous tie chains during the first stage of deformation. (c) Increase in lamellar crystallite thickness (which is reversible) due to bending and stretching of chains in crystallite regions.

(b) Stages in the plastic deformation of a semicrystalline polymer. (a) Two adjacent chain-folded lamellae and interlamellar amorphous material after elastic deformation. (b) Tilting of lamellar chain folds. (c) Separation of crystalline block segments. (d) Orientation of block segments and tie chains with the tensile axis in the final plastic deformation stage.

(c) Elastomers have the ability to be deformed to quite large deformations, and then elastically spring back to their original form. Elastomeric behavior was probably first observed in natural rubber;

15.11 (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.

15.12 (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.

15.14   This problem gives us the tensile strengths and associated number-average molecular weights for two poly(methyl methacrylate) materials and then asks that we estimate the tensile strength for $\overline{M}_n = 40{,}000$ g/mol. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$50 \text{ MPa} = TS_\infty - \frac{A}{30{,}000 \text{ g/mol}}$$

$$150 \text{ MPa} = TS_\infty - \frac{A}{50{,}000 \text{ g/mol}}$$

Thus, the values of the two constants are: $TS_\infty = 300$ MPa and $A = 7.50 \times 10^6$ MPa-g/mol. Substituting these values into Equation 15.3 for $\overline{M}_n = 40{,}000$ g/mol leads to

$$TS = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

$$= 300 \text{ MPa} - \frac{7.50 \times 10^6 \text{ MPa - g/mol}}{40{,}000 \text{ g/mol}}$$

$$= 112.5 \text{ MPa}$$

15.15   This problem gives us the tensile strengths and associated number-average molecular weights for two polyethylene materials and then asks that we estimate the $\overline{M}_n$ that is required for a tensile strength of 140 MPa. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$90 \text{ MPa} = TS_\infty - \frac{A}{20{,}000 \text{ g/mol}}$$

$$180 \text{ MPa} = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

Thus, the values of the two constants are: $TS_\infty = 270$ MPa and $A = 3.6 \times 10^6$ MPa-g/mol. Solving for $\overline{M}_n$ in Equation 15.3 and substituting $TS = 140$ MPa as well as the above values for TS_∞ and A leads to

$$\overline{M}_n = \frac{A}{TS_\infty - TS}$$

$$= \frac{3.6 \times 10^6 \text{ MPa - g/mol}}{270 \text{ MPa} - 140 \text{ MPa}} = 27{,}700 \text{ g/mol}$$

15.16 For each of four pairs of polymers, we are to do the following: (1) determine whether or not it is possible to decide which has the higher tensile modulus; (2) if so, note which has the higher tensile modulus and then state the reasons for this choice; and (3) if it is not possible to decide, then state why.

(a) Yes, it is possible. The linear and isotactic poly(vinyl chloride) will display a greater tensile modulus. Linear polymers are more likely to crystallize that branched ones. In addition, polymers having isotactic structures will normally have a higher degree of crystallinity that those having atactic structures. Increasing a polymer's crystallinity leads to an increase in its tensile modulus. In addition, tensile modulus is independent of molecular weight--the atactic/branched material has the higher molecular weight.

(b) Yes, it is possible. The block styrene-butadiene copolymer with 10% of possible sites crosslinked will have the higher modulus. Block copolymers normally have higher degrees of crystallinity than random copolymers of the same material. A higher degree of crystallinity favors larger moduli. In addition, the block copolymer also has a higher degree of crosslinking; increasing the amount of crosslinking also enhances the tensile modulus.

(c) No, it is not possible. Branched polyethylene will tend to have a low degree of crystallinity since branched polymers don't normally crystallize. The atactic polypropylene probably also has a relatively low degree of crystallinity; atactic structures also don't tend to crystallize, and polypropylene has a more complex repeat unit structure than does polyethylene. Tensile modulus increases with degree of crystallinity, and it is not possible to determine which polymer is more crystalline. Furthermore, tensile modulus is independent of molecular weight.
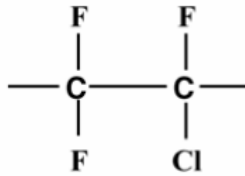

15.17 For each of four pairs of polymers, we are to do the following: (1) determine whether or not it is possible to decide which has the higher tensile strength; (2) if it is possible, then note which has the higher tensile strength and then state the reasons for this choice; and (3) if it is not possible to decide, to state why.

(a) Yes, it is possible. The linear and isotactic material will have the higher tensile strength. Both linearity and isotacticity favor a higher degree of crystallinity than do branching and atacticity; and tensile strength increases with increasing degree of crystallinity. Furthermore, the molecular weight of the linear/isotactic material is higher (100,000 g/mol versus 75,000 g/mol), and tensile strength increases with increasing molecular weight.

(b) No, it is not possible. Alternating copolymers tend to be more crystalline than graft copolymers, and tensile strength increases with degree of crystallinity. However, the graft material has a higher degree of crosslinking, and tensile strength increases with the percentage of crosslinks.

(c) Yes, it is possible. The network polyester will display a greater tensile strength. Relative chain motion is much more restricted than for the lightly branched polytetrafluoroethylene since there are many more of the strong covalent bonds for the network structure.

15.18 The strength of a polychlorotrifluoroethylene having the repeat unit structure

$$\text{—}\underset{\underset{\displaystyle F}{|}}{\overset{\overset{\displaystyle F}{|}}{C}}\text{—}\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle F}{|}}{C}}\text{—}$$

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.

15.19 (a) Shown below are the stress-strain curves for the two polyisoprene materials, both of which have a molecular weight of 100,000 g/mol. These two materials are elastomers and will have curves similar to curve *C* in Figure 15.1. However, the curve for the material having the greater number of crosslinks (20%) will have a higher elastic modulus at all strains.
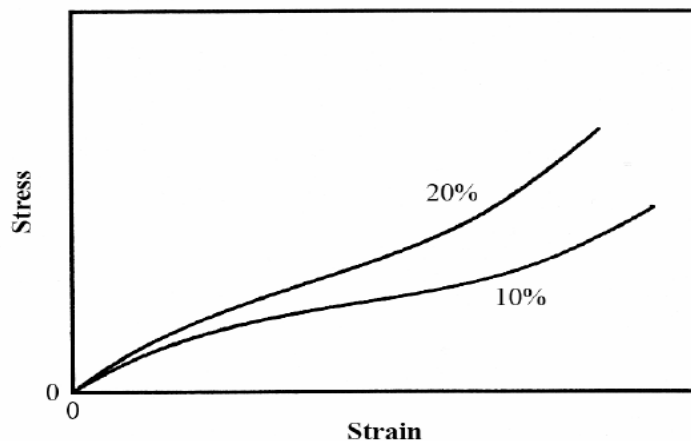
(b) Shown below are the stress-strain curves for the two polypropylene materials. These materials will most probably display the stress-strain behavior of a normal plastic, curve *B* in Figure 15.1. However, the syndiotactic polypropylene has a higher molecular weight and will also undoubtedly have a higher degree of crystallinity; therefore, it will have a higher strength.
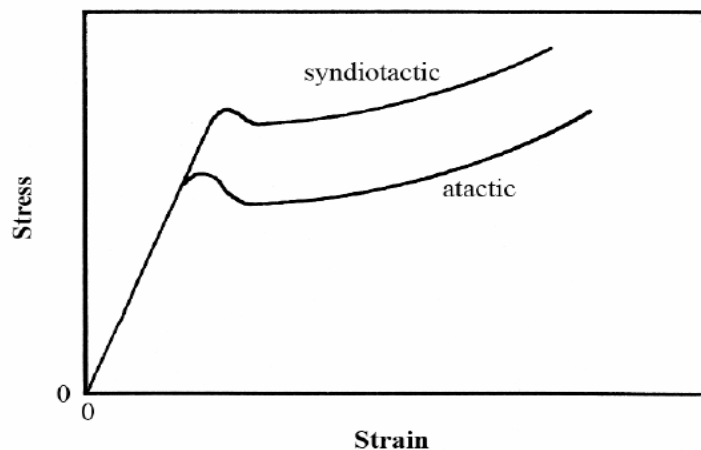
(c) Shown below are the stress-strain curves for the two polyethylene materials. The branched polyethylene will display the behavior of a normal plastic, curve *B* in Figure 15.1. On the other hand, the heavily crosslinked polyethylene will be stiffer, stronger, and more brittle (curve *A* of Figure 15.1).
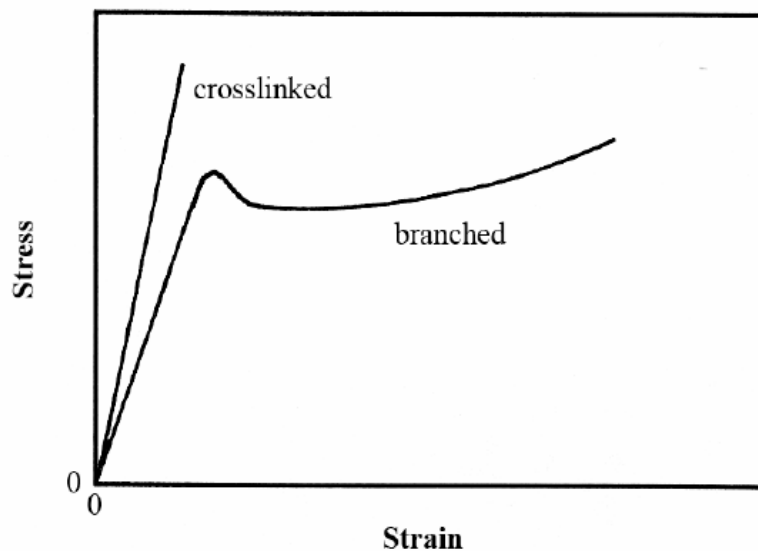
15.20 Two molecular characteristics essential for elastomers are: (1) they must be amorphous, having chains that are extensively coiled and kinked in the unstressed state; and (2) there must be some crosslinking.