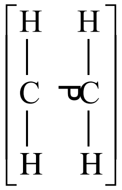
Solutions to Calculation Problems

7.1 A high-molecular-weight polyethylene has an average molecular weight of 410,000 g/mol. What is its average degree of polymerization?

To assess the average degree of polymerization (DP), the mass of the polyethylene mer is first calculated: (4 hydrogen atoms × 1 g/mol) + (2 carbon atoms × 12 g/mol) = 28 g/mol. The DP, defined in units of mers per mol, is:

$$\begin{aligned} \mathrm{DP} &= \frac{\text{molecular weight of polymer (g/mol)}}{\text{molecular weight of mer (g/mol/mer)}} \\ &= \frac{410{,}000\ \text{g/mol}}{28\ \text{g/mol/mer}} \\ &= \mathbf{14{,}643\ mers} \end{aligned}$$



Polyethylene

7.2 If a type of polyethylene has an average degree of polymerization of 10,000, what is its average molecular weight?

$$\begin{aligned} \mathrm{MW_{av}}(\text{polymer}) &= \mathrm{DP} \times \mathrm{MW_{av}}(\text{mer}) \\ &= (10{,}000\ \text{mers})(28\ \text{g/(mol}\cdot\text{mer))} \\ &= \mathbf{280{,}000\ g/mol} \end{aligned}$$

7.3 A nylon 6,6 has an average molecular weight of 12,000 g/mol. Calculate the average degree of polymerization. (See Sec. 7.7 for its mer structure.) M.W. (mer) = 226 g/mol

$$\mathrm{DP} = \frac{\text{molecular weight of polymer (g/mol)}}{\text{molecular weight of mer (g/mol/mer)}} = \frac{12{,}000\ \text{g/mol}}{226\ \text{g/mol/mer}} = \mathbf{53\ mers}$$

7.4 An injection–molding polycarbonate material has an average molecular weight of 25,000 g/mol. Calculate its degree of polymerization. (See Sec. 7.7 for the mer structure of polycarbonate.) M.W. (mer) = 254 g/mol

Molecular Weight Range (g/mol)	f_i	Molecular Weight Range(g/mol)	f_i
0-5000	0.01	20,000-25,000	0.19
5000-10,000	0.04	25,000-30,000	0.21
10,000-15,000	0.16	30,000-35,000	0.15
15,000-20,000	0.17	35,000-40,000	0.07

The average molecular weight is calculated as,

$$\bar{M}_m = \frac{\sum f_i M_i}{\sum f_i}$$

Based on the results of summing the products of the weight fractions and the average range weights,

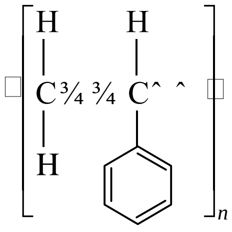
$$\bar{M}_m = \frac{22{,}850 \text{ g/mol}}{1.00}$$

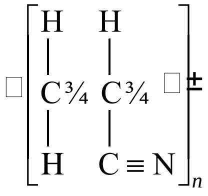
$$= \mathbf{22,850 \text{ g/mol}}$$

f_i	M_i	$\Sigma f_i M_i$ (g/mol)
0.01	2500	25.0
0.04	7500	300.0
0.16	12,500	2000.0
0.17	17,500	2975.0
0.19	22,500	4275.0
0.21	27,500	5775.0
0.15	32,500	4875.0
0.07	37,500	2625.0
1.00		22,850.0

7.6 A copolymer consists of 70 wt % polystyrene and 30 wt % polyacrylonitrile. Calculate the mole fraction of each component in this material.

Using a basis of 100 g of copolymer, we have 70 g of polystyrene and 30 g of polyacrylonitrile. The corresponding number of moles of each component is:





$$\text{No. of moles of polystyrene in 100 g of copolymer} = \frac{70\text{ g}}{105\text{ g/mol}} = 0.667\text{ mol}$$

Moles of polyacrylonitrile

$$\begin{aligned} MW_{PAN} &= 3\text{ H atoms} \times 1\text{ g/mol} + 3\text{ C atoms} \times 12\text{ g/mol} + 1\text{ N atom} \times 14\text{ g/mol} \\ &= 53\text{ g/mol} \end{aligned}$$

$$\text{No. of moles of polyacrylonitrile in 100 g of copolymer} = \frac{30\text{ g}}{53\text{ g/mol}} = 0.566\text{ mol}$$

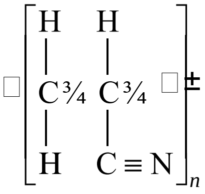
Thus, the mole fractions of the components are calculated as:

$$\text{Mole fraction of polystyrene} = \frac{0.667\text{ mol}}{0.667\text{ mol} + 0.566\text{ mol}} = \mathbf{0.541}$$

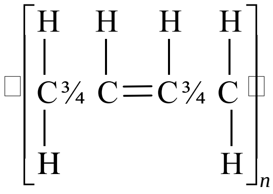
$$\text{Mole fraction of polyacrylonitrile} = \frac{0.566\text{ mol}}{0.667\text{ mol} + 0.566\text{ mol}} = \mathbf{0.459}$$

7.7 An ABS copolymer consists of 25 wt % polyacrylonitrile, 30 wt % polybutadiene, and 45 wt % polystyrene. Calculate the mole fraction of each component in this material.

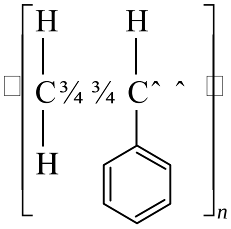
Using a basis of 100 g of copolymer, we have 25 g of polyacrylonitrile, 30 g of polybutadiene, and 45 g of polystyrene. The corresponding number of moles of each component is:



Polyacrylonitrile



Polybutadiene



Polystyrene

Moles of polyacrylonitrile

$$\text{MW}_{\text{polybutadiene}} = 6 \text{ H atoms} \times 1 \text{ g/mol} + 4 \text{ C atoms} \times 12 \text{ g/mol} = 54 \text{ g/mol}$$

$$\text{No. of moles of polybutadiene in 100 g of copolymer} = \frac{30 \text{ g}}{54 \text{ g/mol}} = 0.556 \text{ mol}$$

Moles of polystyrene

$$\text{MW}_{\text{polystyrene}} = 9 \text{ H atoms} \times 1 \text{ g/mol} + 8 \text{ C atoms} \times 12 \text{ g/mol} = 105 \text{ g/mol}$$

$$\text{No. of moles of polystyrene in 100 g of copolymer} = \frac{45 \text{ g}}{105 \text{ g/mol}} = 0.429 \text{ mol}$$

Thus, the total number of moles is 0.472 + 0.556 + 0.429 = 1.457 mol. Then the mole fractions of the components are:

$$\text{Mole fraction of polyacrylonitrile} = \frac{0.472 \text{ mol}}{1.457 \text{ mol}} = \mathbf{0.324}$$

$$\text{Mole fraction of polybutadiene} = \frac{0.556 \text{ mol}}{1.457 \text{ mol}} = \mathbf{0.382}$$

$$\text{Mole fraction of polystyrene} = \frac{0.429 \text{ mol}}{1.457 \text{ mol}} = \mathbf{0.294}$$

As a check, the mole fractions should add up to 1.00:

$$0.324 + 0.382 + 0.294 = 1.000 \ \ \text{checks}$$

7.8 Determine the mole fractions of polyvinyl chloride and polyvinyl acetate in a copolymer having a molecular weight of 11,000 g/mol and a degree of polymerization of 150.

From Example Problem 7.3, the molecular weights of PVC and PVA are 62.5 g/mol and 86.0 g/mol, respectively. The mole fractions of these polymers can be determined based upon the average molecular weight of the copolymer mer.

$$\text{MW}_{\text{av}}(\text{mer}) = f_{\text{PVC}}\text{MW}_{\text{PVC}} + f_{\text{PVA}}\text{MW}_{\text{PVA}} = f_{\text{PVC}}\text{MW}_{\text{PVC}} + (1 - f_{\text{PVC}})\text{MW}_{\text{PVA}}$$

where the average molecular weight of the copolymer mer is,

$$f_{\mathrm{PVC}}(62.5\ \mathrm{g/mol/mer}) + (1 - f_{\mathrm{PVC}})(86.0\ \mathrm{g/mol/mer}) = 73.33\ \mathrm{g/(mol \cdot mer)}$$

$$f_{\mathrm{PVC}} = \mathbf{0.539} \quad \text{and} \quad f_{\mathrm{PVA}} = 1 - f_{\mathrm{PVC}} = \mathbf{0.461}$$

7.9 How much sulfur must be added to 70 g of butadiene rubber to cross-link 3.0 percent of the mers? (Assume all sulfur is used to cross-link the mers and that only one sulfur atom is involved in each cross-linking bond.)

Assuming only one sulfur atom is involved in each cross-linking bond with butadiene, we know there is a one-to-one correspondence between the number of moles of sulfur and the number of moles of butadiene in the reaction. We are therefore able to assess the amount of sulfur required for 100% cross-linking.

$$\text{mass of S}\big|_{100\%} = \mathrm{MW_S} \times (\text{No. of moles of S}) \ = \ \mathrm{MW_S} \times (\text{No. of moles of butadiene})$$

$$= \mathrm{MW_S}\left(\frac{\text{mass of butadiene}}{\mathrm{MW_{butadiene}}(\text{mer})}\right)$$

The average molecular weight of the butadiene mer is:

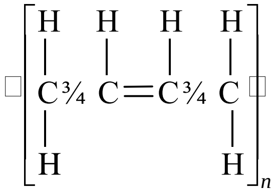
$$\mathrm{MW_{polybutadiene}} = 6\ \text{H atoms} \times 1\ \text{g/mol} + 4\ \text{C atoms} \times 12\ \text{g/mol} = 54\ \text{g/mol}$$

Substituting,

$$\text{mass of S}\big|_{100\%} = (32\ \mathrm{g/mol})\left(\frac{70\ \mathrm{g}}{54\ \mathrm{g/mol}}\right) = 41.48\ \mathrm{g\ S}$$

Thus for only 3 percent cross-linking,

$$\text{mass of S}\big|_{3\%} = 0.03 \times 41.48\ \mathrm{g\ S} = \mathbf{1.24\ g\ S}$$



Polybutadiene

7.10 If 5 g of sulfur is added to 90 g of butadiene rubber, what is the maximum fraction of the cross-link sites that can be connected?

Assuming one sulfur atom is involved in cross-linking each butadiene mer, the fraction of cross-link sites is simply the ratio of the moles of sulfur to the moles of butadiene.

$$\text{No. of moles of S} = \frac{5\ \mathrm{g}}{32\ \mathrm{g/mol}} = 0.156\ \text{mol S}$$

7.11 How much sulfur must be added to cross-link 10 percent of the cross-link sites in 90 g of polyisoprene rubber?

Since there is a one-to-one correspondence between the number of moles of sulfur and the number of moles of polyisoprene in the reaction, we can determine the amount of sulfur required for 100% cross-linking.

$$\text{mass of S}\big|_{100\%} = \text{MW}_\text{S} \times (\text{No. of moles of S}) \; = \; \text{MW}_\text{S} \times (\text{No. of moles of polyisoprene})$$

$$= \text{MW}_\text{S}\left(\frac{\text{mass of polyisoprene}}{\text{MW}_\text{polyisoprene}\,(\text{mer})}\right)$$

The average molecular weight of the polyisoprene mer is:

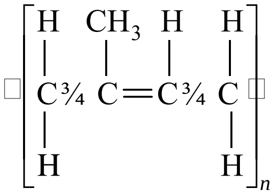
$$\text{MW}_\text{polyisoprene} = 8 \text{ H atoms} \times 1 \text{ g/mol} + 5 \text{ C atoms} \times 12 \text{ g/mol} = 68.0 \text{ g/mol}$$

Substituting,

$$\text{mass of S}\big|_{100\%} = (32 \text{ g/mol})\left(\frac{90.0 \text{ g}}{68.0 \text{ g/mol}}\right) = 42.35 \text{ g S}$$

Thus for only 10 percent cross-linking,

$$\text{mass of S}\big|_{10\%} = 0.10 \times 42.35 \text{ g S} = \mathbf{4.24\ g\ S}$$



$$\left[\begin{array}{cccc} \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} \\ | & | & | & | \\ \mathrm{C}¾ & \mathrm{C}= & \mathrm{C}¾ & \mathrm{C} \\ | & & & | \\ \mathrm{H} & & & \mathrm{H} \end{array}\right]_n$$

Polyisoprene

7.12 How many kilograms of sulfur are needed to cross-link 15 percent of the cross-link sites in 200 kg of polyisoprene rubber?

$$\text{mass of S}\big|_{100\%} = \text{MW}_\text{S} \times (\text{No. of moles of S}) \; = \; \text{MW}_\text{S} \times (\text{No. of moles of polyisoprene})$$

$$= \text{MW}_\text{S}\left(\frac{\text{mass of polyisoprene}}{\text{MW}_\text{polyisoprene}\,(\text{mer})}\right)$$

The average molecular weight of the polyisoprene mer is 68.0 g/mol. Substituting,

$$\text{mass of S}\big|_{100\%} = (32 \text{ g/mol})\left(\frac{200{,}000.0 \text{ g}}{68.0 \text{ g/mol}}\right) = 94{,}117.6 \text{ g S}$$

Thus for 15 percent cross-linking,

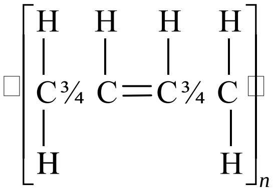
$$\text{No. of moles of S} = \frac{3000\text{ g}}{32\text{ g/mol}} = 93.75\text{ mol S}$$

$$\text{No. of moles of butadiene} = \frac{300{,}000\text{ g}}{54\text{ g/mol}} = 5555.56\text{ mol butadiene}$$

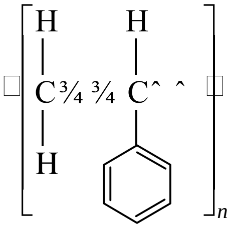
The fraction of cross-link sites is thus,

$$\text{Fraction of cross-link sites} = \frac{93.75}{5555.56} \times 100\% = \mathbf{1.69\%}$$

7.14 A butadiene-styrene rubber is made by polymerizing one monomer of styrene with seven monomers of butadiene. If 20 percent of the cross-link sites are to be bonded with sulfur, what weight percent sulfur is required? (See Ex. Problem 7.7.)



Polybutadiene



Polystyrene

Since the copolymer has 1 mole of styrene for every 7 moles of polybutadiene, we have

$$7\text{ moles polybutadiene} \times 54\text{ g/mol} = 378\text{ g}$$
$$1\text{ mole polystyrene} \times 105\text{ g/mol} = \underline{105\text{ g}}$$
$$\text{Copolymer total mass} = 483\text{ g}$$

However, in this reaction, only the butadiene can participate in the cross-linking with sulfur. We thus need the mass fraction of butadiene: 378 g / 483 g = 0.783. Using a basis of 100 g of copolymer, the number of moles of butadiene is,

$$\text{moles butadiene} = \frac{\text{mass of butadiene}}{\text{MW(mer)}} = \frac{100\text{ g} \times 0.783}{54\text{ g/mol}} = 1.45\text{ mol}$$

The mass of sulfur required for 20 percent cross-linking is therefore,

$$\text{Weight percent S} = \frac{9.28\text{ g}}{100\text{ g} + 9.28\text{ g}} \times 100\% = \mathbf{8.49\%}$$

7.15 What weight percent sulfur must be added to polybutadiene to cross-link 20 percent of the possible cross-link sites?

Using a basis of 100 g and recalling that the molecular weight of polybutadiene is 54.0 g/mol, the number of moles of rubber is

$$\text{No. of moles of polybutadiene} = \frac{100\text{ g}}{54.0\text{ g/mol}} = 1.85\text{ mol}$$

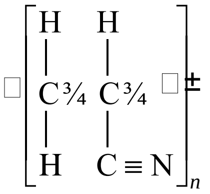
For 20 percent cross-linking, the mass of sulfur required is,

$$\text{mass of S}\big|_{20\%} = (0.20)(1.85\text{ mol})(32\text{ g/mol}) = 11.84\text{ g}$$

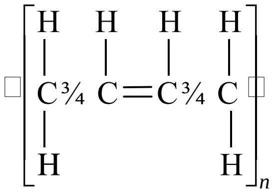
And the weight percent of sulfur required for this reaction is

$$\text{Wt \% S} = \frac{11.84\text{ g}}{100\text{ g} + 11.84\text{ g}} \times 100\% = \mathbf{10.59\%}$$

7.16 A butadiene-acrylonitrile rubber is made by polymerizing one acrylonitrile monomer with five butadiene monomers. How much sulfur is required to react with 200 kg of this rubber to cross-link 22 percent of the cross-link sites? (See Ex. Problem 7.8)



Polyacrylonitrile



Polybutadiene

First, note that only the polybutadiene cross-links with the sulfur in this reaction and recall that the molecular weights for butadiene and acrylonitrile are, respectively, 54 g/mol and 53 g/mol. Then, copolymer total mass based on a 5:1 mole ratio is, The mass fraction of butadiene is thus: 270 g / 323 g = 0.836. Thus in 200 kg of copolymer, the number of moles of polybutadiene is,

$$\text{moles of butadiene} = \frac{\text{mass of butadiene}}{\text{MW(mer)}} = \frac{200{,}000\ \text{g} \times 0.836}{54\ \text{g/mol}} = 3096.3\ \text{mol}$$

The mass of sulfur required for 22 percent cross-linking is therefore,

$$\text{mass of S}\big|_{22\%} = (0.22)(3096.3\ \text{mol})(32\ \text{g/mol}) = 21{,}798\ \text{g} = 21.8\ \text{kg}$$

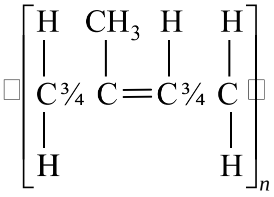
And the weight percent of sulfur required for this reaction is

$$\text{Wt \% S} = \frac{21{,}798\ \text{g}}{200{,}000\ \text{g} + 21{,}798\ \text{g}} \times 100\% = \mathbf{9.83\%}$$

7.17 If 15 percent of the cross-link sites in isoprene rubber are to be bonded, what weight percent sulfur must the rubber contain?

Using a basis of 100 g and recalling that the molecular weight of isoprene is 68.0 g/mol, the number of moles of isoprene is

$$\text{No. of moles of isoprene} = \frac{100\ \text{g}}{68.0\ \text{g/mol}} = 1.47\ \text{mol}$$



$$\left[-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}_3}{\text{C}}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}- \right]_n$$

Polyisoprene

For 15 percent cross-linking, the mass of sulfur required is,

$$\text{mass of S}\big|_{15\%} = (0.15)(1.47\ \text{mol})(32\ \text{g/mol}) = 7.06\ \text{g S}$$

Thus the weight percent of sulfur required for this reaction is

$$\text{Wt \% S} = \frac{7.06\ \text{g}}{100\ \text{g} + 7.06\ \text{g}} \times 100\% = \mathbf{6.56\%}$$

7.18 A stress of 9.0 MPa is applied to an elastomeric material at a constant stress at 20ºC. After 25 days, the stress decreases to 6.0 MPa. (a) What is the relaxation time τ for this material? (b) What will be the stress after 50 days?

$$\sigma = (9.0\text{ MPa})e^{-(50\text{ days}/61.7\text{ days})} = \mathbf{4.0\ MPa}$$

7.19 A polymeric material has a relaxation time of 60 days at 27ºC when a stress of 7.0 MPa is applied. How many days will be required to decrease the stress to 6.0 MPa?

The decrease in stress is given by $\sigma = \sigma_0 e^{-t/\tau}$. Thus,

$$t = -\tau\left[\ln(\sigma/\sigma_0)\right] = -(60\text{ days})\left[\ln(6\text{ MPa}/7\text{ MPa})\right] = \mathbf{9.25\ days}$$

7.20 A stress of 1000 psi is applied to an elastomer at 27ºC, and after 25 days the stress is reduced to 750 by stress relaxation. When the temperature is raised to 50ºC, the stress is reduced from 1100 to 400 psi in 30 days. Calculate the activation energy for this relaxation process using an Arrhenius-type rate equation.

First, the relaxation time must be calculated for each set of conditions:

$$\tau_1 = \frac{-t}{\ln(\sigma/\sigma_0)} = \frac{-25\text{ days}}{\ln(750\text{ psi}/1000\text{ psi})} = 86.90\text{ days}$$

$$\tau_2 = \frac{-t}{\ln(\sigma/\sigma_0)} = \frac{-30\text{ days}}{\ln(400\text{ psi}/1100\text{ psi})} = 29.66\text{ days}$$

Since the Arrhenius-type equation uses absolute temperature, we must next convert the temperatures to Kelvin: $T_1 = 27° + 273° = 300\text{ K};\ T_2 = 50° + 273° = 323\text{ K}$. Applying the Arrhenius-type rate equation, $1/\tau = Ce^{-Q/RT}$, we obtain two equations in two unknowns.

$$\frac{1}{\tau_1} = Ce^{-Q/RT_1} \quad \text{and} \quad \frac{1}{\tau_2} = Ce^{-Q/RT_2}$$

Dividing these equations, we obtain a single equation with one unknown – Q

$$\frac{\tau_2}{\tau_1} = \exp\left[\frac{-Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$\frac{29.66}{86.90}=\exp\left[\frac{-Q}{8.314\text{ J/mol}\cdot\text{K}}\left(\frac{1}{300\text{ K}}-\frac{1}{323\text{ K}}\right)\right]$$

$$Q=\left(\frac{-8.314\text{ J/mol}\cdot\text{K}}{2.3736\times10^{-4}\text{ / K}}\right)\ln\left(\frac{29.66}{86.90}\right)=37{,}653\text{ J/mol}=\mathbf{37.65\ kJ/mol}$$

7.21 The stress on a sample of a rubber material at constant strain at 27ºC decreases from 6.0 to 4.0 MPa in three days. (a) What is the relaxation time τ for this material? (b) What will be the stress on this material after (i) 15 days and (ii) after 40 days?

(a) The decrease in stress is given by $\sigma=\sigma_0 e^{-t/\tau}$. Thus,

$$\tau=\frac{-t}{\ln(\sigma/\sigma_0)}=\frac{-3\text{ days}}{\ln(4\text{ MPa}/6\text{ MPa})}=\mathbf{7.4\ days}$$

(b) For a relaxation time constant of 7.4 days, the stress will be,

$$(i)\quad \sigma=(6.0\text{ MPa})e^{-(15\text{ days}/7.4\text{ days})}=0.79\text{ MPa}=\mathbf{790.4\ kPa}$$

$$(ii)\quad \sigma=(6.0\text{ MPa})e^{-(40\text{ days}/7.4\text{ days})}=0.02695\text{ MPa}=\mathbf{26.95\ kPa}$$

7.22 A polymeric material has a relaxation time of 100 days at 27ºC when a stress of 6.0 MPa is applied. (a) How many days will be required to decrease the stress to 4.2 MPa? (b) What is the relaxation time at 40ºC if the activation energy for this process is 25 kJ/mol?

(a) The decrease in stress is given by $\sigma=\sigma_0 e^{-t/\tau}$. Thus,

$$t=-\tau\left[\ln(\sigma/\sigma_0)\right]=-(100\text{ days})\left[\ln(4.2\text{ MPa}/6\text{ MPa})\right]=\mathbf{35.7\ days}$$

(b) By applying the Arrhenius-type rate equation, $1/\tau=Ce^{-Q/RT}$, for two sets of general conditions and dividing the resulting equations, we obtain

$$\frac{\tau_2}{\tau_1}=\exp\left[\frac{-Q}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right]$$

$$\frac{\tau_2}{100} = \exp\left[-\frac{25{,}000\ \text{J}}{8.314\ \text{J/mol}\cdot\text{K}}\left(\frac{1}{300\ \text{K}} - \frac{1}{313\ \text{K}}\right)\right]$$

$$\tau_2 = \mathbf{65.95\ days}$$

Answers to Study Problems

7.23 Define the polymeric materials (a) plastics and (b) elastomers.

Plastics are a large and varied group of synthetic materials which are produced through forming and molding processes and are classified as either thermoplastic or thermosetting. Elastomers (rubbers) are highly flexible plastics: when subjected to stress, they are capable of withstanding large elastic deformation; once the stress is removed, these plastics regain, or nearly regain, their original shape and dimensions.

7.24 Define a thermoplastic plastic.

Thermoplastics are a class of plastics which can be repeatedly melted and reformed into different shapes and are thus used for recycling products. Upon cooling, these plastics retain their shape and exhibit insignificant changes to their original properties.

7.25 Describe the atomic structural arrangement of thermoplastics.

Thermoplastics consist of very long molecular chains of covalently bonded carbon atoms.

7.26 What types of atoms are bonded together in thermoplastic molecular chains? What are the valences of these atoms in the molecular chains?

The main molecular chains of thermoplastics are comprised of carbon, nitrogen, oxygen and sulfur atoms. The valences of these atoms are: C (+4); N (-3); S (+2); O (-2).

7.27 What is a pendant atom or group of atoms?

7.29 What type of bonding exists between the molecular chains of thermoplastics?

Between thermoplastic chains, permanent dipole bonds provide weak secondary bonding.

7.30 Define thermosetting plastics.

Thermosetting plastics are plastics which can be formed into a shape and permanently cured or "set" by a chemical reaction. The cured product can not be melted and reused because these materials degrade at high temperatures.

7.31 Describe the atomic structural arrangement of thermosetting plastics.

Most thermosetting plastics consist of three-dimensional networks of covalently bonded atoms, as compared to the long chain-like molecules of thermoplastics.

7.32 What are some of the reasons for the great increase in the use of plastics in engineering designs over the past years?

The surge in the application of plastics is attributed to their low cost and unique set of properties; plastics are light, corrosion resistant, easily formed, and excellent insulators.

7.33 What are some of the advantages of plastics for use in mechanical engineering designs?

The incorporation of plastics in engineering designs often allows for the elimination of many parts and finishing operations, the reduction of weight and noise, and the simplification of assembly processes. In some cases, plastics eliminate the need for lubrication of parts.

7.34 What are some of the advantages of plastics for use in electrical engineering designs?

Plastics are used extensively in electrical designs primarily because of their outstanding insulating properties and low cost. However, their low density and facilitation of assembly processes are also important to electronic applications.

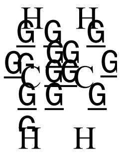
7.35 What are some of the advantages of plastics for use in chemical engineering designs?

Chemical engineering designs take advantage of the corrosion resistant and thermal insulating properties of plastics.

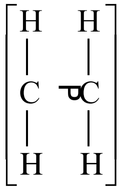
7.36 Define the following terms: chain polymerization, monomer, and polymer.

7.37 Describe the bonding structure within an ethylene molecule by using (a) the electron-dot-cross notation and (b) straight-line notation for the bonding electrons.

(a) Electron-dot-cross notation of ethylene



(b) Straight-line notation for ethylene

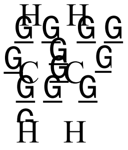


7.38 What is the difference between a saturated and an unsaturated carbon-containing molecule?

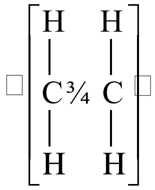
A saturated carbon-containing organic molecule has only single covalent bonds in its main chain. An unsaturated carbon-containing molecule has one or more double or triple bonds in its main chain.

7.39 Describe the bonding structure of an activated ethylene molecule that is ready for covalent bonding with another activated molecule by using (a) the electron-dot-cross notation and (b) straight-line notation for the bonding electrons.

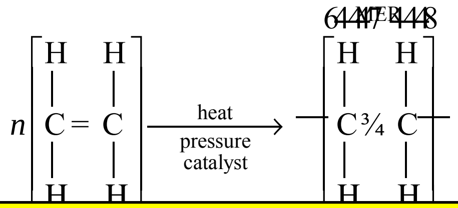
(a) Electron-dot-cross notation of activated ethylene



(b) Straight-line notation for activated ethylene



7.40 Write a general chemical reaction for the chain polymerization of ethylene monomer into the linear polymer polyethylene.



The repeating chemical unit of a polymer chain is called a mer. The mer for polyethylene is shown above, in the solution to Prob. 7.40.

7.42 Define the degree of polymerization for a polymer chain.

The degree of polymerization is equal to the number of subunits or mers within the polymer molecule.

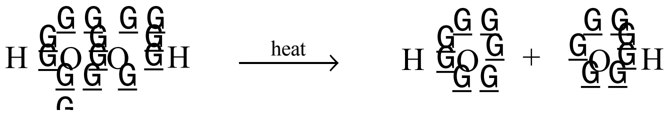
7.43 What are the three major reactions that occur during chain polymerization?

The three major reactions that occur during chain polymerization are: initiation, propagation, and termination.

7.44 What is a free radical? Write a chemical equation for the formation of two free radicals from a hydrogen peroxide molecule by using (a) the electron-dot-cross notation and (b) straight-line notation for the bonding electrons.

A free radical is a group of atoms having an unpaired (free) electron that can covalently bond to an unpaired (free) electron of another molecule.

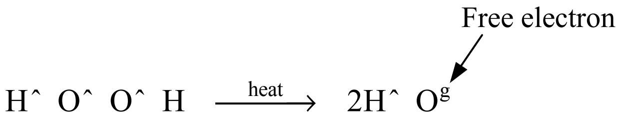
(a)



Hydrogen Peroxide

Free radicals

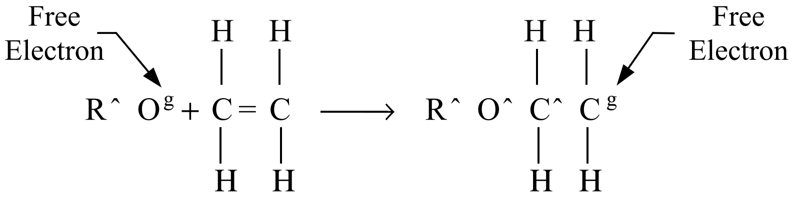
(b)



Hydrogen Peroxide

Free Radicals

7.45 Write an equation for the formation of two free radicals from a molecule of benzoyl peroxide by using straight-line notation for the bonding electrons.



$$R\hat{}\;O^{g} + \overset{H}{C} = \overset{H}{C}_{\;} \longrightarrow R\hat{}\;O\hat{}\;\overset{H}{C}\hat{}\;\overset{H}{C}^{g}$$

7.47 What is the function of the initiator catalyst for chain polymerization?

The initiator catalyst provides a free radical to a monomer and thus activates the monomer and allows the propagation stage of chain polymerization to begin.

7.48 Write a reaction for the free radical $R\hat{}\;CH_2\hat{}\;CH_2$ with an ethylene molecule to extend the free radical. What type of reaction is this?

$$R\hat{}\;CH_2\hat{}\;CH_2^{g} + CH_2 = CH_2 \longrightarrow R\hat{}\;CH_2\hat{}\;CH_2\hat{}\;CH_2\hat{}\;CH_2^{g}$$

This reaction is a polymerization process of degree two.

7.49 How is it possible for a polymer chain such as a polyethylene one to keep growing spontaneously during polymerization?

The polymer chains in chain polymerization keep growing spontaneously because the energy of the chemical system is lowered by the chain polymerization process; the total energy of newly created polymers is lower than the total energy of the monomers that have reacted to form them.

7.50 What are two methods by which a linear chain polymerization reaction can be terminated?

A linear chain polymerization reaction can be terminated by reacting with a terminator free radical or by combining with another polymer chain.

7.51 Why must one consider the *average* degree of polymerization and the *average* molecular weight of a thermoplastic material?

Since thermoplastics consist of polymer chains of varying lengths, and thus different molecular weights, an average molecular mass must be assessed based upon the average degree of polymerization for the material.

where

M_i = mean molecular weight for each molecular weight range selected

f_i = weight fraction of the material for a selected molecular weight range representative of the material

The average molecular weight is thus a weighted average based upon mean molecular weights, of weight ranges representative of the material, and the weight fractions of the respective ranges.

7.53 What is the functionality of a monomer? Distinguish between a bifunctional and trifunctional monomer.
The functionality of a monomer is the number of active bonds the monomer has. A bifunctional monomer uses two active bonds for long-chain polymerization while a trifunctional monomer utilizes three active bonds.

7.54 What causes a polyethylene molecular chain to have a zigzag configuration?

A polyethylene molecular chain has a zigzag configuration because, at the microscopic level, the single carbon-carbon covalent bonds form an angle of approximately 109º.

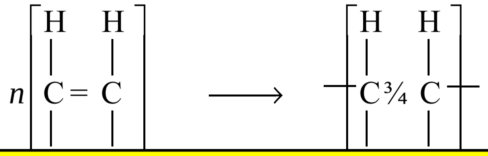
7.55 What type of chemical bonding is there between the polymer chains in polyethylene?

Between the polymer chains of polyethylene, permanent dipoles bonds provide weak secondary bonding.

7.56 How do side branches on polyethylene main chains affect the packing of the molecular chains in a solid polymer? How does branching of the polymer chains affect the tensile strength of solid bulk polyethylene?

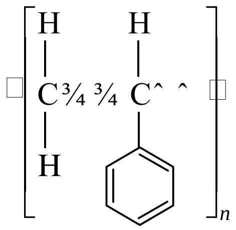
Side branches on polyethylene main chains reduce the packing of the molecular chains. As a result of loose packing, the secondary bonds between chains are weakened and thus, the tensile strength of the solid bulk polyethylene is lowered.

7.57 Write a general reaction for the polymerization of a vinyl-type polymer.



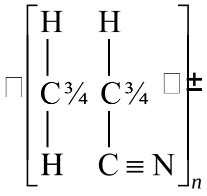
$$n\left[\begin{matrix}\mathrm{H} & \mathrm{H}\\ | & |\\ \mathrm{C}= & \mathrm{C}\\ | & |\end{matrix}\right]\longrightarrow -\!\left[\begin{matrix}\mathrm{H} & \mathrm{H}\\ | & |\\ \mathrm{C}\text{¾} & \mathrm{C}\\ | & |\end{matrix}\right]\!-$$

(d) Polystyrene



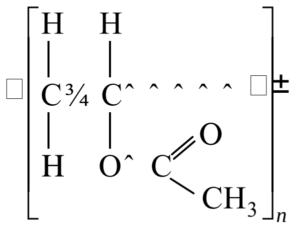
mp: 150-243ºC
(330-470ºF)

(e) Polyacrylonitrile



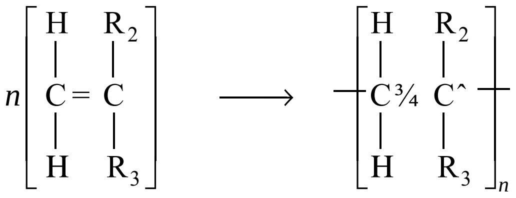
does not melt

(f) Polyvinyl Acetate



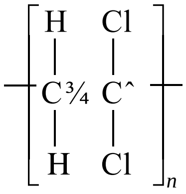
mp: 177ºC
(350ºF)

7.59 Write a general reaction for the polymerization of a vinylidene polymer.

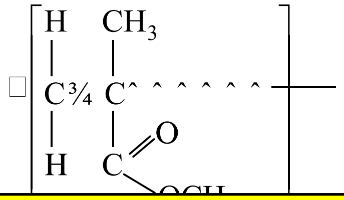


7.60 Write structural formulas for the mers of the following vinylidene polymers: (a) polyvinylidene chloride and (b) polymethyl methacrylate.

(a) Polyvinylidene Chloride



(b) Polymethyl Methacrylate

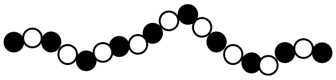


A homopolymer consists of polymer chains made up of a single repeating unit; whereas a copolymer consists of polymer chains containing two or more repeating units, of dissimilar chemical structure, that can form a variety of sequences.

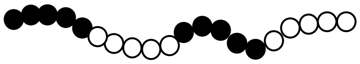
7.62 Illustrate the following types of copolymers by using filled and open circles for their mers: (a) random, (b) alternating, (c) block, and (d) graft.

(a) Random Distributed Units

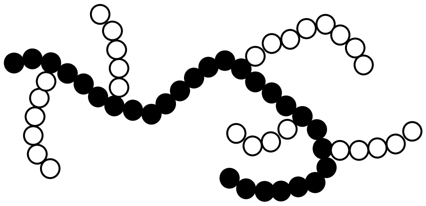
(b) Alternating Units



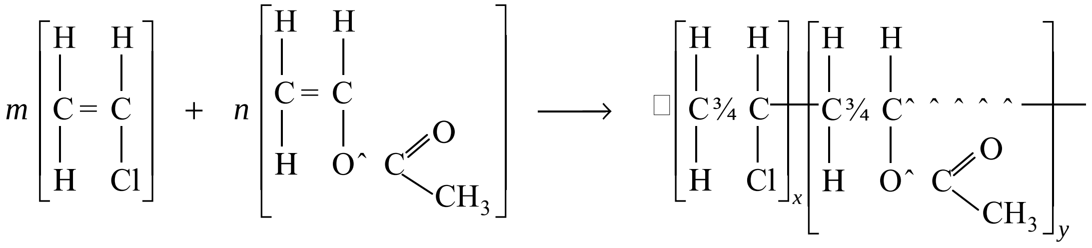
(c) Block Copolymer



(d) Graft Copolymer



7.63 Write a general polymerization reaction for the formation of a vinyl chloride and vinyl acetate copolymer.



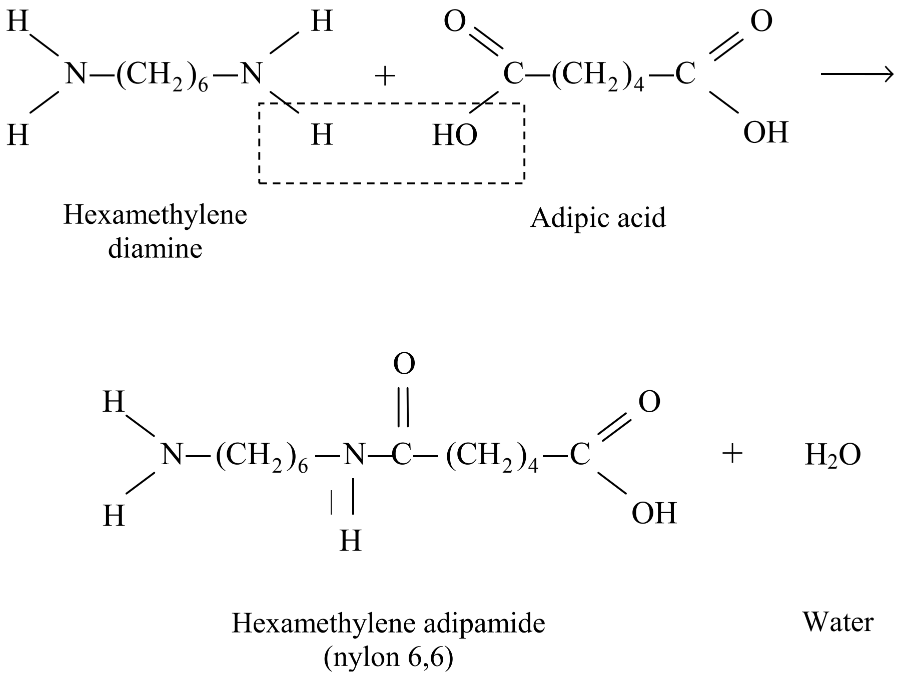
Vinyl chloride monomer

Vinyl acetate monomer

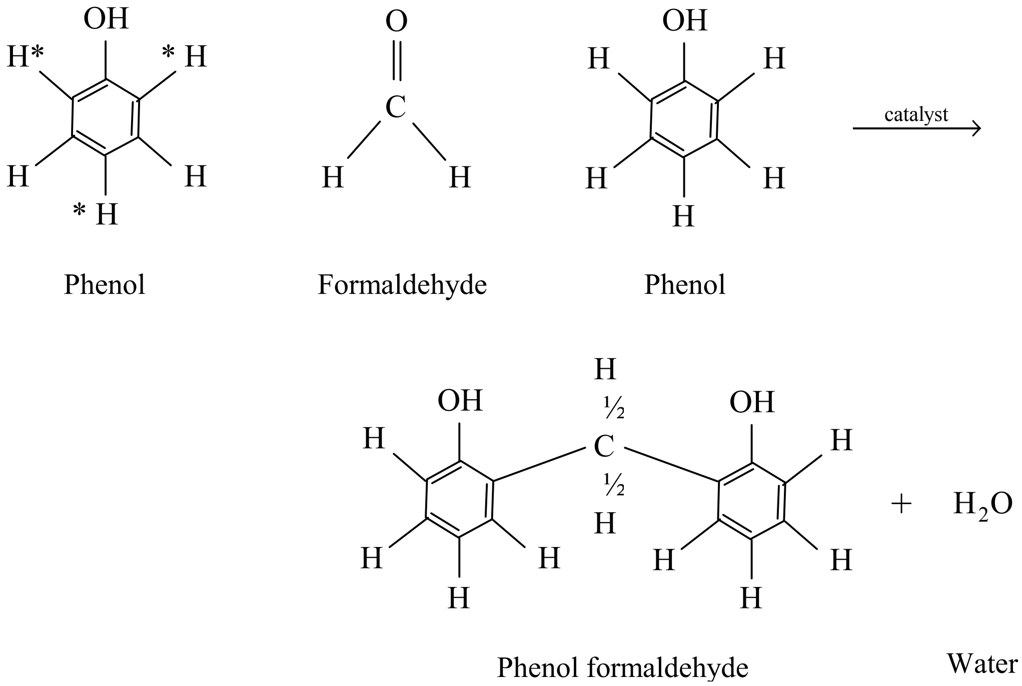
Polyvinyl chloride-polyvinyl acetate copolymer

7.64 Define stepwise polymerization of linear polymers. What by-products are commonly

7.65 Write the equation for the reaction of a molecule of hexamethylene diamine with one of adipic acid to produce a molecule of nylon 6,6. What is the by-product of this reaction?



7.66 Write the reaction for the stepwise polymerization of two phenol molecules with one of formaldehyde to produce a phenol formaldehyde molecule.



7.67 What type of by-product is produced by this reaction?

The by-product for this reaction is water.

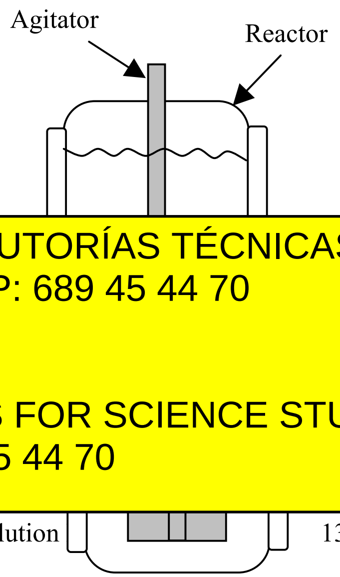
7.68 What are three basic raw materials used to produce the basic chemicals needed for the polymerization of plastic materials?

Natural gas, petroleum and coal are the three basic raw materials used to produce the basic chemicals needed for the polymerization of plastic materials.

7.69 Describe and illustrate the following polymerization processes: (a) bulk, (b) solution, (c) suspension, and (d) emulsion.

(a) Bulk Polymerization:

As shown schematically in Fig. P7.68*a*, bulk polymerization is accomplished by mixing the monomer and activator in a reactor that allows for heating and



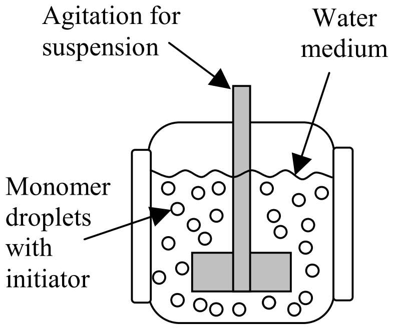
(b) Solution

(b) Solution Polymerization:

In solution polymerization, a monomer is dissolved in a non-reactive solvent that contains a catalyst. Since the solvent absorbs the heat released by the reaction, the reaction rate is reduced. A schematic of this reaction is provided in Fig. P7.69*b*.

(c) Suspension Polymerization:

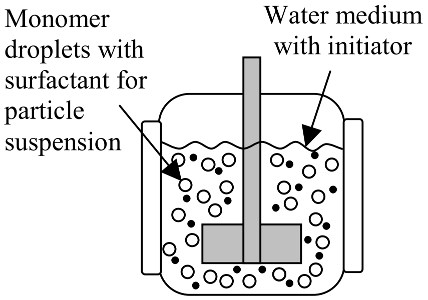
In this process (Fig. P7.69*c*), the monomer is mixed with a catalyst and then dispersed as a suspension in water. The particles are maintained in suspension through agitation while the water absorbs the heat released by the reaction. At the conclusion of polymerization, the product, typically a vinyl-type polymer, is separated and dried.



(c) Suspension

(d) Emulsion Polymerization:

The emulsion polymerization process is similar to the suspension process in that it is carried out in water and uses an initiator. However, an emulsifier is also added to the suspension in order to disperse the monomer into very small particles. Fig. P7.69*d* schematically illustrates the emulsion process.



(d) Emulsion

7.70 In which polymerization process is the heat released by the reaction absorbed by water? In which is the heat absorbed by the solvent? Which process is used when the polymerization heat of reaction is low?

In the suspension process the heat of reaction is absorbed by water; whereas, the heat is absorbed by the solvent in the solution polymerization process. When the polymerization heat of reaction is low, the bulk polymerization process is used.

7.71 Describe the Unipol process for producing low-density polyethylene. What are the

7.72 During the solidification of thermoplastics, how does the specific volume versus temperature plots differ for noncrystalline and partly crystalline thermoplastics?

A noncrystalline thermoplastic experiences a gradual change in specific volume as the material is cooled from its melting point to its glass transition temperature. Conversely, partly crystalline thermoplastics display an abrupt decrease in specific volume as it solidifies. This sudden reduction is attributed to the increased packing of polymer chains into crystalline regions.

7.73 Define the glass transition temperature T_g for a thermoplastic?

A glassy material like a thermoplastic has no sharp freezing point; the plastic liquid gradually transitions from a viscous liquid to a soft plastic and finally becomes hard and brittle. The glass transition temperature is therefore defined as the average temperature at which the specific volume versus temperature curve changes slope. This change in gradient indicates the onset of solidification.

7.74 What are measured T_g values for (a) polyethylene, (b) polyvinyl chloride, and (c) polymethyl methacrylate? Are T_g values material constants?

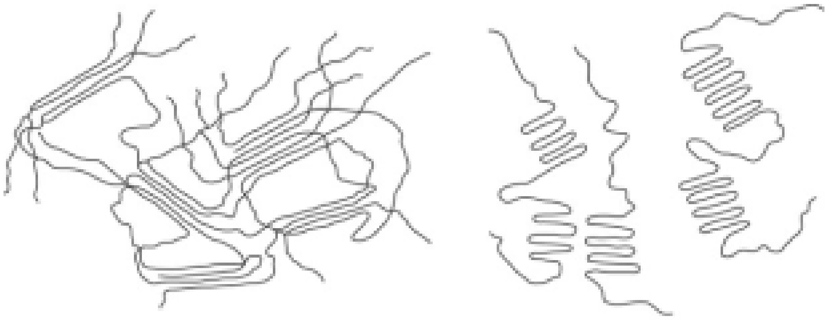
The measured T_g values are:

(a) -110ºC for polyethylene;
(b) 82ºC for polyvinyl chloride;
(c) 72ºC for polymethyl methacrylate.

Glass transition temperatures are not material constants since they depend upon variables such as degree of crystallinity, rate of cooling of the thermoplastic, and the average molecular weight of the polymer chains.

7.75 Describe and illustrate the fringed-micelle and folded-chain models for the structure of partly crystalline thermoplastics.

According to the fringed-micelle model, long polymer chains, approximately 5000 nm in length, pass through ordered and disordered regions along the molecule’s length. These regions correspond to the areas of crystalline and noncrystalline thermoplastic material. A more recent model, the folded-chain model, predicts that sections of the molecular chains fold upon themselves and thus allow the formation of crystalline and noncrystalline regions.



(a) Fringed-micelle model (b) Folded-chain model

7.76 Describe the spherulitic structure found in some partly crystalline thermoplastics.

The spherulitic structure is observed in some partly crystalline thermoplastics having the folded-chain type of structure. The spherulitic regions consist of crystalline lamellae which represent individual layers of the folded-chain structure. The spherulites grow within an otherwise noncrystalline structure and appear roughly spherical in shape.

7.77 Why is complete crystallinity in thermoplastics impossible?

Complete crystallinity is impossible in thermoplastics because of molecular entanglements and crossovers which exist in all linear polymeric materials.

7.78 How does the amount of crystallinity in a thermoplastic affect (a) its density and (b) its tensile strength? Explain.

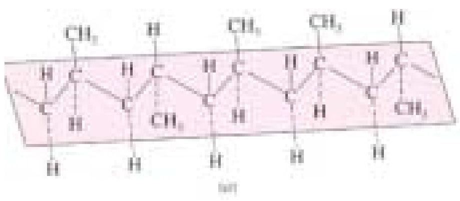
(a) As the degree of crystallinity increases in a thermoplastic, the packing of polymer chains increases and thus the material density also increases.
(b) Similarly, since the polymer chains become closer with increased crystallinity, the bonding forces between polymers increase and thus the tensile strength of the material increases.

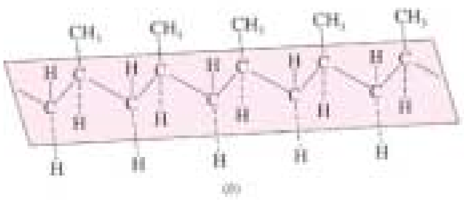
7.79 What are stereoisomers with respect to chemical molecules?

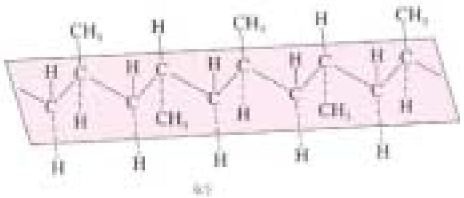
Stereoisomers have identical chemical formulas but different structural arrangements.

7.80 Describe and draw structural models for the following stereoisomers of polypropylene: (a) atactic, (b) isotactic, and (c) syndiotactic.

(c) The syndiotactic stereoisomer has an alternating arrangement of the pendant group, from one side of the main chain to the other.







7.81 What is a stereospecific catalyst? How did the development of a stereospecific catalyst for the polymerization of polypropylene affect the usefulness of commercial polypropylene?

A stereospecific catalyst is one that enables a polymer to be polymerized such that it consists of an individual stereoisomeric structure. The development of a stereospecific catalyst for the polymerization of isotactic polypropylene significantly affected the polymer's usefulness commercially; the catalyst provided a cost-effective method of mass production.

7.82 In general how does the processing of thermoplastics into the desired shape differ from the processing of thermosetting plastics?

In general, thermoplastics are heated to a softened state and then reshaped prior to cooling; whereas, thermosetting plastics are shaped prior to a final polymerization process in which the polymer chains are cross-linked into a polymeric network.

7.83 Describe the injection-molding process for thermoplastics.

In the injection-molding process, thermoplastics material, in either powder or pellet form, The reciprocating-screw injection-molding machine is a modern design which incorporates a reciprocating-screw mechanism for melting and injecting the plastic and a water-cooled mold for rapid solidification of the part.

7.85 What are some advantages and disadvantages of the injection-molding process for molding thermoplastics?

Advantages of the injection-molding process include: potential for creating high quality parts at a high production rate; low labor costs; good surface finishes; capability for a highly automated process; ease of producing intricate shapes. The primary disadvantages of injection molding are: the large initial investment required to purchase the machine necessitates a large volume of production; the process must be closely controlled to produce a high quality part.

7.86 What are the advantages of the reciprocating-screw injection-molding machine over the old plunger type?

Compared to its predecessor, the plunger-type machine, the reciprocating-screw machine is more efficient and delivers a more homogeneous melt for injection.

7.87 Describe the extrusion process for processing thermoplastics.

In the extrusion process, thermoplastic resin is fed into a heated cylinder that contains a rotating screw mechanism. As the screw propels the material along the cylinder, the plastic is melted and then forced through a small opening into an accurately machined die where it is cooled below its glass transition temperature. This process is capable of forming a variety of continuous shapes such as pipes, rods, films, and sheets.

7.88 Describe the blow molding and thermoforming processes for forming thermoplastics.

In blow molding, a cylinder or tube of heated plastic (a parison) is placed between the jaws of a mold. The mold is then closed to pinch off the cylinder ends, and compressed air is blown into the mold, forcing the plastic against the mold walls. The result is a hollow part such as a bottle.

In thermoforming, a heated plastic sheet is forced into the contours of a mold by applying pressure – either mechanical, positive air pressure, or vacuum.

7.89 Describe the compression-molding process for thermosetting plastics.

In compression molding, preheated or room temperature plastic resin is placed between

7.90 What are some of the advantages and disadvantages of the compression-molding process?

Advantages of the compression-molding process include: low initial mold costs; minimal wear and abrasion of molds due to relatively short material flow; ease of producing large parts; simplicity of mold design allows for more compact molds; means for expulsion of reaction gases during the molding process. The main disadvantages of this process are: difficulty in producing complicated part configurations; inability to achieve close tolerances on inserts; increased cost associated with trimming flash from molded parts.

7.91 Describe the transfer-molding process for thermosetting plastics.

In transfer molding, the plastic resin is fed into a chamber outside the mold cavities and forced, by a plunger, through a system of runners and gates into the closed mold. Once the resin has had time to cure into a rigid network polymeric material, the formed part is ejected from the mold.

7.92 What are some of the advantages of the transfer-molding process?

Advantages of transfer molding are: the molded part requires less finishing since no flash is created; the runner system allows for molding many parts simultaneously; small intricate parts can be produced.

7.93 What are the four major thermoplastic materials that account for about 60 percent of the sales tonnage of plastic materials in the United States? What were their prices per pound in 1988? in the year 2000?

The four major types of thermoplastic materials that account for approximately sixty percent of the sales tonnage of plastics in the U.S. are polyethylene, polyvinyl chloride, polypropylene, and polystyrene.

7.94 How does the molecular-chain structure differ for the following types of polyethylene: (a) low-density, (b) high-density, and (c) linear-low-density?

(a) Low-density polyethylene (LDPE) has a fully branched-chain structure.
(b) High-density polyethylene (HDPE) has a straight-chain structure.
(c) Linear-low-density polyethylene (LLDPE) has a linear-chain structure with short, slanting side branches.

7.95 How does chain branching affect the following properties of polyethylene: (a) amount of crystallinity, (b) strength, and (c) elongation?

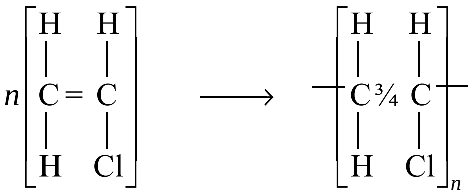
7.96 What are some of the properties that make polyethylene such an industrially important plastic material?

Some of the properties of that make polyethylene industrially important are: toughness at room temperature and low temperature, good flexibility over a wide temperature range, excellent corrosion resistance, excellent insulating properties, odorless, tasteless, and low water-vapor transmission.

7.97 What are some of the industrial applications for polyethylene?

Polyethylene is used to make containers, electrical insulation, chemical tubing, housewares, and blow-molded bottles.

7.98 Write the general reaction for the polymerization of polyvinyl chloride.



$$n\left[\begin{array}{cc} H & H \\ | & | \\ C = & C \\ | & | \\ H & Cl \end{array}\right] \longrightarrow \left[\begin{array}{cc} H & H \\ | & | \\ C\text{¾} & C \\ | & | \\ H & Cl \end{array}\right]_n$$

7.99 How can the higher strength of polyvinyl chloride as compared to polyethylene be explained?

Polyvinyl chloride has a higher strength than polyethylene because the chlorine atoms, in the PVC chain, create strong dipole moments which produce strong cohesive forces between the polymer chains.

7.100 How is the flexibility of bulk polyvinyl chloride increased?

The flexibility of bulk polyvinyl chloride is increased through the addition of a plasticizer.

7.101 What are some of the properties of polyvinyl chloride that make it an important industrial material?

Polyvinyl chloride is important to industry primarily because of its high chemical resistance and its distinct ability to serve as the base material for a large number of compounds having a wide range of physical and chemical properties.

Plasticizers are high-molecular-weight compounds selected to be completely miscible and compatible with the base material. They are used to impart flexibility, softness and extensibility to polymeric materials and consequently decrease tensile strength. Phthalate esters are commonly used in the production of PVC.

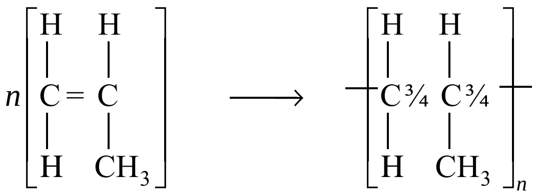
7.103 How is the processibility of PVC improved to produce rigid PVC?

In the production of rigid PVC, rubbery resins, added to the PVC, improve the melt flow by forming a dispersion of small, soft rubbery particles.

7.104 What are some of the applications for plasticized PVC?

Plasticized PVC is used in a wide range of applications which include: furniture, interior wall coverings, rainwear, shoes, electrical wire insulation, garden hoses, refrigerator gaskets, appliance components, housewares and automobile upholstery, floor mats, and top coverings.

7.105 Write the general reaction for the polymerization of polypropylene from propylene gas.



$$n\left[\begin{array}{cc} H & H \\ | & | \\ C = & C \\ | & | \\ H & CH_3 \end{array}\right] \longrightarrow \left[\begin{array}{cc} H & H \\ | & | \\ -C- & C- \\ | & | \\ H & CH_3 \end{array}\right]_n$$

7.106 Why is the use of a stereospecific catalyst in the polymerization of polypropylene so important?

The use of a stereospecific catalyst is important to the polymerization of polypropylene because the catalyst allows for the control of the distribution of the pendant methyl group. Specifically, the atactic form of polypropylene is wax-like and softens at approximately 74ºC. By introducing a stereospecific catalyst, the more useful isotactic structure can be mass produced with high crystallinity, and thus high strength, and with a melting point of approximately 175ºC.

7.107 How does the presence of a methyl group on every other carbon atom of the main polymer chain affect the glass transition temperature of this material when compared to polyethylene?

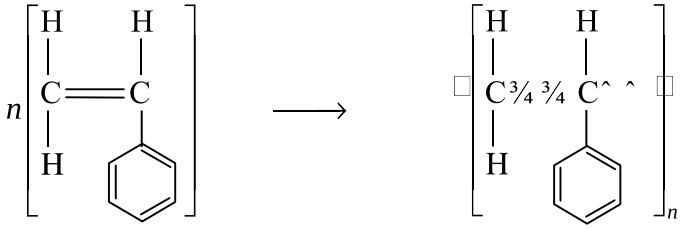
The substitution of hydrogen atoms with methyl groups increases the bond strengths by

Polypropylene has numerous valuable properties including: low cost, light weight, outstanding flex life, good surface hardness, and good chemical, heat, and moisture resistance.

7.109 What are some of the applications for polypropylene?

Polypropylene is primarily used in housewares, appliance parts, packaging (screw closures, cases, and containers), laboratory ware and bottles. However, polypropylene copolymers have replaced hard rubber in applications like automobile battery housings, fender liners and splash shrouds. Also, polypropylene homopolymer is used for carpet backing and woven to produce shipping sacks.

7.110 Write the general reaction for the polymerization of polystyrene from styrene.



Styrene Polystyrene

7.111 What effect does the presence of the phenyl group on every other carbon of the main chain have on the impact properties of polystyrene?

The presence of the phenylene ring, on alternating carbon atoms of the main polystyrene chain, results in a rigid bulky steric configuration and thus an inflexible polymeric material having low-impact resistance.

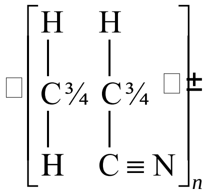
7.112 How can the low-impact resistance of polystyrene be improved by copolymerization?

Polystyrene's low-impact resistance can be improved through the addition of a copolymer with a rubber level between 3 and 12 percent. An example is the polybutadiene elastomer.

7.113 What are some of the applications for polystyrene?

Polystyrene is typically used in automobile interior parts, appliance housings, dials and knobs, and housewares.

Polyacrylonitrile
(does not melt)



$$\left[\begin{array}{cc} H & H \\ | & | \\ -C- & C- \\ | & | \\ H & C\equiv N \end{array}\right]_n$$

7.115 What effect does the presence of the nitrile group on every other carbon of the main polymer chains have on the molecular structure of polyacrylonitrile?

The highly electronegative nitrile group, present on alternating main-chain carbon atoms, induces mutual electrical repulsion which causes the molecular chains to form extended, stiff, rodlike structures.

7.116 What special properties do polyacrylonitrile fibers have? What are some applications for polyacrylonitrile?

Due to hydrogen bonding between the polymer's chains, polyacrylonitrile fibers have high strength and good resistance to moisture and solvents.

7.117 What are SAN resins? What desirable properties do SAN thermoplastics have? What are some of the applications for SAN thermoplastics?

SAN (styrene-acrylonitrile) resins are random, amorphous copolymers of styrene and acrylonitrile. SAN thermoplastics are high performance members of the styrene family which possess improved chemical resistance, heat-deflection temperatures, toughness and load-bearing characteristics than standard polystyrene. But like polystyrene, these plastics are rigid, hard, easily processed, and exceptionally clear. SANS are used in automotive instrument lenses, dash board components, glass-filled support panels, appliance knobs, blender and mixer bowls, medical syringes, blood aspirators, construction safety glazing, and houseware mugs.

7.118 What do the letters A, B, and S stand for in the ABS thermoplastic?

The letters A, B, and S of the ABS acronym stand for the monomers *a*crylonitrile, *b*utadiene, and *s*tyrene.

7.119 Why is ABS sometimes referred to as a terpolymer?

7.121 Describe the structure of ABS. How can the impact properties of ABS be improved?

ABS is not a random terpolymer but a blend of a glassy copolymer (styrene-acrylonitrile) and rubbery domains created from a butadiene polymer or copolymer. The impact properties can be further improved by grafting the styrene-acrylonitrile copolymer matrix to the rubber domains. This technique produces a two-phase structure.

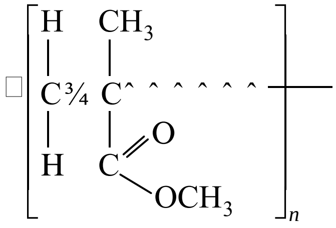
7.122 What are some of the applications for ABS plastics?

The primary applications for ABS plastic are pipe and fittings for building construction. However, ABS is also used in automotive parts, appliance parts, business machines, computer and telephone housings, and electrical conduits.

7.123 What is the repeating chemical structural unit for polymethyl methacrylate? By what trade names is PMMA commonly known?

Polymethyl methacrylate, commonly called Plexiglas and Lucite, has the following mer:

Polymethyl methacrylate
mp: 160ºC (320ºF)

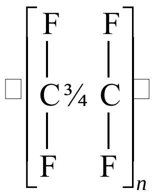


7.124 What are some of the important properties of PMMA that make it an important industrial plastic?

PMMA is hard, rigid and transparent and has good chemical resistance to outdoor environments.

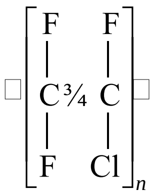
7.125 What are the fluoroplastics? What are the repeating chemical structural units for polytetrafluoroethylene and polychlorotrifluoroethylene?

Fluroplastics are plastics made from monomers having one or more fluorine atoms. Polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE), the two most



$\left[-\mathrm{CF_2}-\mathrm{CF_2}- \right]_n$

Polytetrafluoroethylene
Softens at 370 ºC (700ºF)



$\left[-\mathrm{CF_2}-\mathrm{CFCl}- \right]_n$

Polychlorotrifluoroethylene
Melting Point: 218ºC (420ºF)

7.126 What are some of the important properties and applications of polytetrafluoroethylene?

PTFE is a high density crystalline polymer with exceptional chemical resistance, high impact strength and a low coefficient of friction. It can be used over a wide range of temperatures (-200ºC to 260ºC) and can be strengthened by fillers. Applications of PTFE include: chemically resistant pipe and pump parts, high temperature cable insulation, molded electrical components, tape, and non-stick coatings. Filled PTFE compounds are used for bushings, bearings, O-rings, seals, packings and gaskets.

7.127 How does the presence of the chlorine atom on every other carbon atom of the main chain of polychlorotrifluoroethylene modify the crystallinity and moldability of polytetrafluoroethylene?

The substitution of every fourth fluorine atom with a chlorine atom introduces irregularity in the polymer chains' structure. As a result, PCTFE is less crystalline and has a lower melting temperature and melt viscosity. Thus, unlike PTFE, PCTFE can be molded and extruded using conventional molding processes.

7.128 What are some of the important applications of polychlorotrifluoroethylene?

Important applications of extruded, molded and machined products of PCTFE are chemical processing equipment, electrical applications, gaskets, O-rings, seals, and electrical components.

7.129 Define an engineering thermoplastic. Why is this definition arbitrary?

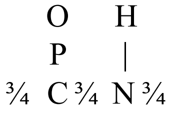
In the current text, an engineering thermoplastic is defined as a thermoplastic having a set of properties that makes it especially useful for engineering applications. However, this is an arbitrary definition; virtually every plastic could be classified as an engineering plastic.

7.131 How do the densities and tensile strengths of engineering thermoplastics compare with those of polyethylene and polyvinyl chloride?

The densities of engineering thermoplastics range from approximately 1.0 – 1.5 g/cm^3, and are thus higher than those of polyethylene (0.92–0.96 g/cm^3) but lower than rigid PVC (1.49–1.58 g/cm^3). The tensile strengths of engineering plastics are significantly higher than either high density or low density polyethylene and approximately equal to or greater than the strength of rigid PVC.

7.132 What is the structural formula for the amide linkage in thermoplastics? What is the general name for polyamide thermoplastics?

The general name for polyamide thermoplastics is *polyamides* or *nylons*. The structural formula for the amide linkage, present in all nylon thermoplastics, is shown to the right.

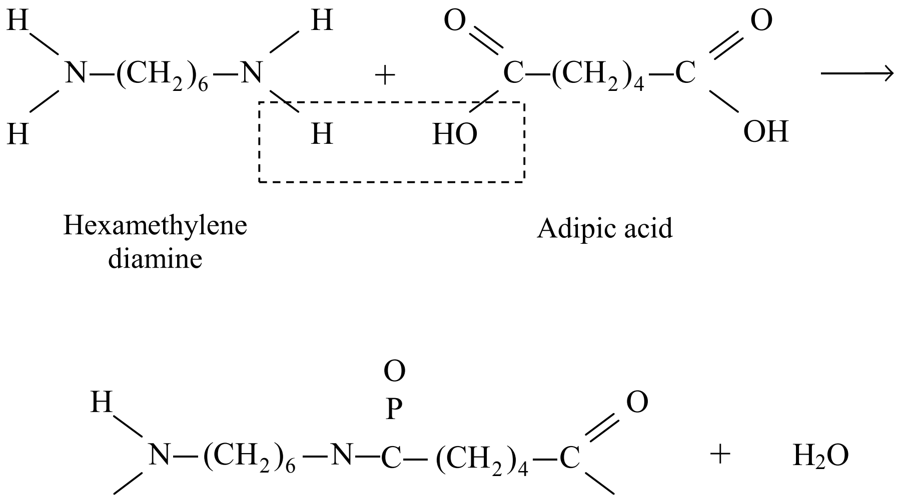


$-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$

Amide linkage

7.133 Write a chemical reaction for one molecule of a dibasic acid with a diamine to form an amide linkage. What is the by-product of this reaction?

An example of a reaction involving one molecule of a dibasic acid with a diamine is polymerization of hexamethylene diamine and adipic acid which produces the most important nylon, Nylon 6,6, with water as the by-product.



7.134 In the designation nylon 6,6 what does the 6,6 stand for?

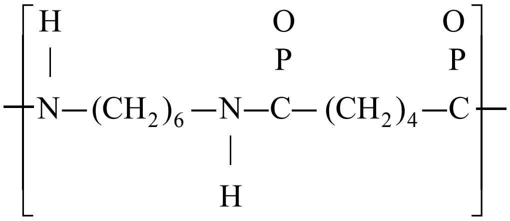
The 6,6 of nylon 6,6 refers to the fact that there are six carbon atoms in the reacting diamine, hexamethylene diamine, and six carbon atoms in the reacting organic acid, adipic acid.

7.135 Write a chemical reaction for one molecule of adipic acid and one molecule of hexamethylene diamine to form an amide linkage.

See the solution to problem 7.133.

7.136 What is the repeating structural unit for nylon 6,6?

The repeating structure for nylon 6,6 is:

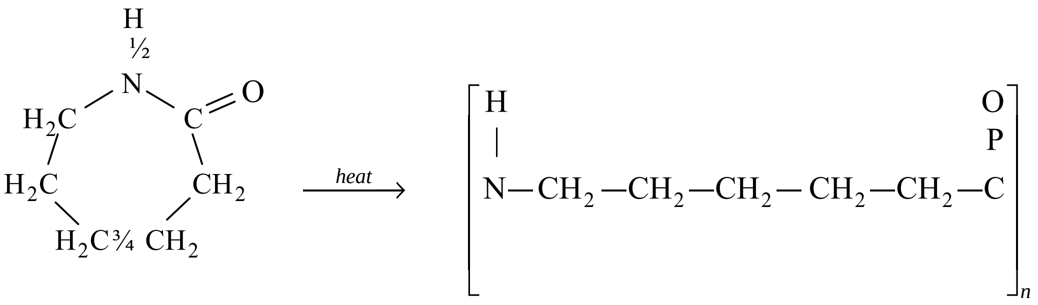


$$-\!\!\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{P}{C}}-(CH_2)_4-\overset{O}{\overset{P}{C}}\right]\!\!-$$

7.137 How can nylons 6,9, 6,10 and 6,12 be synthesized?

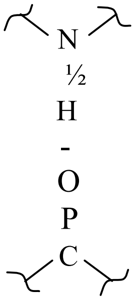
Nylons 6,9, 6,10, and 6,12 can be synthesized using the same stepwise polymerization reaction as nylon 6,6 by replacing the adipic acid with azelaic acid (9 carbons), sebacic acid (10 carbons), and dodecanedioic acid (12 carbons), respectively.

7.138 Write the reaction for the polymerization of nylon 6 from ∫-caprolactam.



7.139 Illustrate the bonding between polymer chains of nylon 6,6. Why is this bonding particularly strong? (See Fig. 7.35)

The bonding between the nylon 6,6 chains is particularly strong because of the —NHO hydrogen bonds as shown schematically to the right.



7.140 What properties do nylons have that make them useful for engineering applications? What is an important undesirable property of nylon?

Nylons have high strength and heat-deflection temperatures. The flexibility of the main chain leads to low melt viscosity, and thus ease of processing, as well as high lubricity, low surface friction and good abrasion resistance. The polyamides also have good chemical resistance. However, nylon also exhibits high water absorption which results in dimensional changes with increasing moisture content.

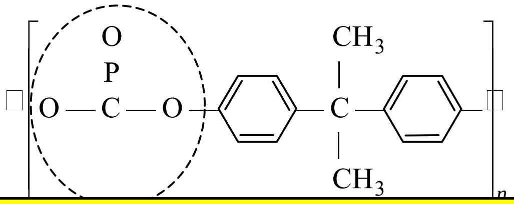
7.141 What are some of the engineering applications for nylons?

Nylons are used throughout industry. Their high lubricity provides for use in applications such as unlubricated gears, bearings, and antifriction parts while their high temperature endurance, in conjunction with their chemical resistance, permits them to be used in mechanical and electrical parts designed for severe thermal-chemical environments. In addition, nylons are utilized in high-impact parts, and when reinforced with glass, in engine fan blades, valve covers, and steering column housings.

7.142 What is the basic repeating chemical structural unit for polycarbonates? What is the carbonate linkage? What are the common trade names for polycarbonate?

Polycarbonates, manufactured under the trade names of Lexan and Merlon, have a carbonate linkage consisting of carbon-oxygen bonds as identified in below in the schematic of their repeating chemical structural unit.

Polycarbonate
mp: 270ºC (520ºF)



7.143 What part of the polycarbonate structure makes the molecule stiff? What part of the polycarbonate molecule provides molecular flexibility?

The attachment of the two phenol groups and the two methyl groups to the same carbon atom makes the molecular structure very stiff. However, flexibility is provided by the single C—O bonds.

7.144 What are some of the properties of polycarbonates that make them useful engineering thermoplastics?

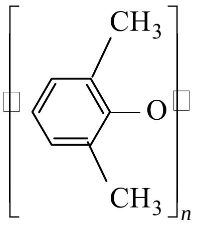
Properties of polycarbonate that make them useful engineering thermoplastics include relatively high impact and tensile strengths, thermal resistance, good electrical insulation, and transparency.

7.145 What are some engineering applications for polycarbonates?

Some engineering applications for polycarbonates are safety shields, cams and gears, helmets, electrical relay covers, aircraft components, boat propellers, traffic light housings and lenses, window glazings, and housings for handheld power tools, small appliances, and computers terminals.

7.146 What is the basic repeating chemical structural unit for the polyphenylene oxide-based resins? What are the trade names for these resins?

Polyphenylene oxide-based resins, produced under the trade name Noryl, have the repeating chemical structural unit shown diagramed to the right.



7.147 What part of the structure of polyphenylene oxide provides its relatively high strength? What part of its structure provides its molecular flexibility?

The repeating phenylene rings provide for relatively high strength and rigidity while the oxygen linkage contributes to the molecular flexibility of the structure.

7.148 What are some of the properties that make polyphenylene oxide resins important engineering thermoplastics?

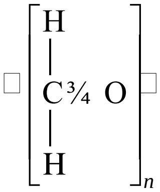
Polyphenylene oxide-based resins are important to engineering applications because of

Common applications of polyphenylene oxide resins are electrical connectors, television tuners and deflection yoke components, small appliance and business machine housings, and automobile dashboards, grills and exterior body parts.

7.150 What is the repeating chemical structural unit for the acetal high-performance engineering thermoplastics? What are the two main types of acetals and what are their trade names?

The two primary types of acetals are a homopolymer with trade name Delrin, and a copolymer with trade name Celcon. The repeating chemical structural unit for the high-performance acetals is diagramed to the right.

Polyoxymethylene
mp: 175ºC (347ºF)



$$\left[-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{O}- \right]_n$$

7.151 What part of the structure of the acetals provides high strength?

High strength is provided through the regularity, symmetry and flexibility of the acetal polymer molecules; high bonding strengths are thus achieved between the molecular chains with hydrogen and oxygen interaction.

7.152 What are some of the properties of acetals that make them important engineering thermoplastics?

Acetals have exceptionally high melting points, long-term load carrying properties (low wear and friction and exceptional fatigue resistance) and dimensional stability. The homopolymer is particularly hard and rigid with high tensile and flexural strengths, as compared to the copolymer. In contrast, the copolymer is more stable for long-term, high-temperature applications and has a higher elongation.

7.153 What outstanding property advantage do the acetals have over nylons?

Unlike nylons, homopolymer acetals have low moisture absorption and thus good dimensional stability.

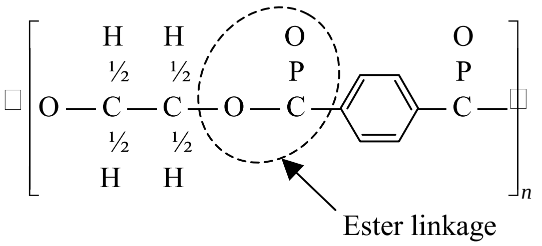
7.154 What are some of the engineering applications for acetals?

Acetals have replaced many metal castings and stampings, where high strength is not required in such applications as automobile seat belt, fuel system and window handle components and in such machinery applications as mechanical couplings, pump

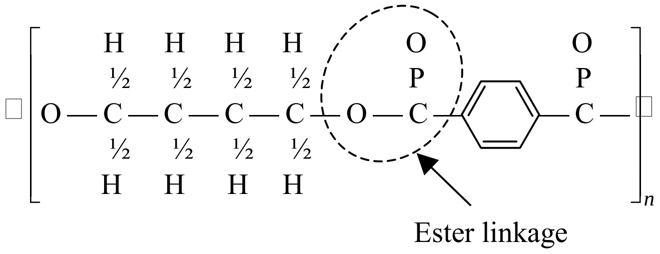
Acetals have replaced metal zinc, brass and aluminum castings and steel stampings due to their manufacturing cost-effectiveness; finishing and assembly operations costs have been reduced or eliminated in many applications.

7.156 What are the two most important engineering thermoplastic polyesters? What are their repeating chemical structural units?

The two most important engineering thermoplastic polyesters are polybutylene terephthalate (PBT) and polyethylene terephthalate (PET). The repeating mers of these plastics are shown below.



Polyethylene terephthalate (PET)



Polybutylene terephthalate (PBT)

7.157 What is the chemical structure of the ester linkage?

The ester linkage consists of a carbon atom with a double bond to one oxygen atom and a single bond to a second oxygen atom. This linkage is depicted above in Prob. 7.156.

7.158 What part of the structure of the thermoplastic polyesters provides rigidity? What part provides molecular mobility?

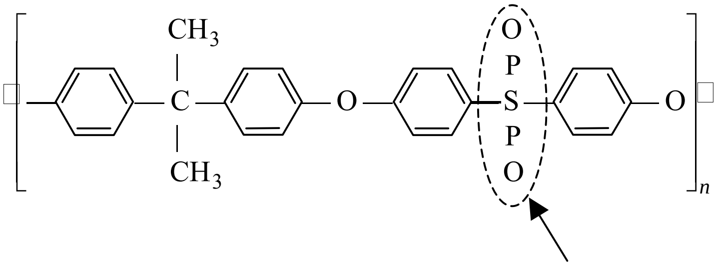
Thermoplastic polyesters crystallize readily, have good strength, chemical resistance and electrical insulation properties, and have low moisture-absorption characteristics.

7.160 What are some engineering applications for PBT thermoplastics?

PBT is used in electrical applications such as connectors, switches, relays, TV tuner components, high-voltage components, terminal boards, integrated circuit boards, motor brush holders and housings. In industry, pump impellers, housings and support brackets, irrigation valves and bodies, and water meter components are made of PBT. Automotive applications include large exterior-body components, high-energy ignition caps and rotors, ignition coil caps, coil bobbins, and speedometer frames and gears.

7.161 What is the repeating chemical structural unit for polysulfone?

Polysulfone
mp: 315ºC (600ºF)



Sulfone linkage

7.162 What part of the polysulfone structure provides its high strength? What part provides chain flexibility and impact strength? What part provides high-oxidation stability?

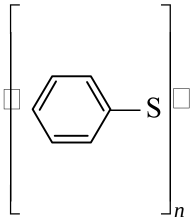
High strength and rigidity is provided through the phenylene rings of the polysulfone; these rings create rigidity and strong intermolecular attraction between polymer chains. The oxygen atom between the phenylene rings (ether linkage) imparts chain flexibility and impact strength. The para positions of the two oxygen atoms, with respect to the phenylene rings and the sulfone group, provide high-oxidation stability.

7.163 What are some of the properties of polysulfone that are important for engineering designs?

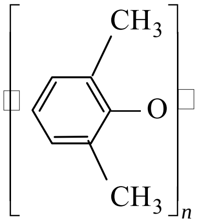
Significant properties of polysulfone are its high heat-deflection temperature of 174ºC at 1.68 MPa and its endurance at temperatures of 150ºC to 174ºC. In addition, polysulfone has excellent tensile strengths for a thermoplastic 70 MPa (10.2 ksi), a relatively low creep rate, and hydrolysis resistance in both aqueous acid and alkaline environments due polyester is also used for corrosion-resistant piping, pumps, tower packing and filter modules and plates.

7.165 What is the repeating chemical structural unit for polyphenylene sulfide? What engineering thermoplastic has a similar structure?

The repeating chemical structural unit for polyphenylene sulfide is similar to the polyphenylene oxide mer; the oxygen atom is replaced with sulfur and the two —CH_3 groups are removed from the benzene ring. The molecular structures of these units are compared below.



Polyphenylene sulfide
mp: 288ºC (550ºF)



Polyphenylene oxide

7.166 What is the trade name for polyphenylene sulfide?

The trade name for polyphenylene sulfide (PPS) is Ryton.

7.167 What part of the structure of PPS provides its rigidity and strength? What part provides it high resistance to chemicals?

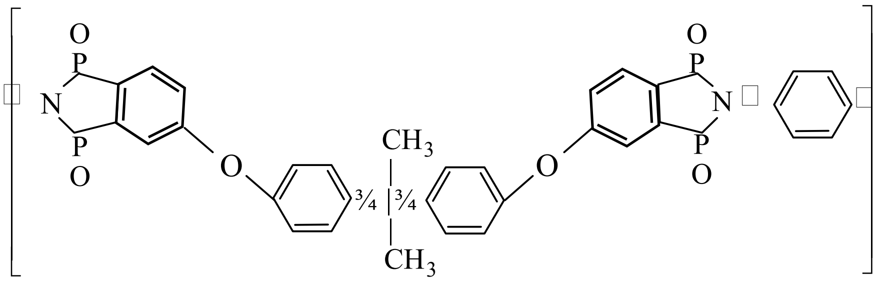
The compact structure of the phenylene rings separated by sulfur atoms produces the strong, rigid thermoplastic material. The sulfur atoms impart such high chemical resistance to PPS that no know chemical can dissolve this polymer.

7.168 What properties make PPS a useful engineering thermoplastic?

Additional properties which make PPS useful in engineering designs include: high degree of crystallinity which affords a gradual decrease in strength up to 200ºC; capability for nearly doubling of strength to 120 MPa (17 ksi) through glass filler.

7.169 What are some engineering applications for PPS?

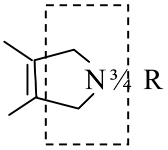
7.170 What is the chemical structure of polyetherimide? What is its trade name?



Polyetherimide

7.171 What is the imide linkage?

The imide linkage, shown to the right, gives polyetherimide high heat resistance, creep resistance and high rigidity.



Imide linkage

7.172 What is the function of the ether linkage in polyetherimide?

The ether linkage, between the phenyl rings in polyetherimide, imparts the chain flexibility required for good melt and flow characteristics.

7.173 What special properties does polyetherimide have for (a) electrical engineering designs and (b) mechanical engineering designs?

(a) Polyetherimide has good electrical insulation properties over a wide range of temperatures and frequencies.
(b) Properties of polyetherimide which are valuable to mechanical engineering designs are its high heat resistance, creep resistance and rigidity.

7.174 What are some applications for polyetherimide?

and bonds: alloys consist of different types of polymeric chains bonded by secondary intermolecular dipole forces; whereas copolymers consist of two different monomers bonded within a molecular chain by strong covalent bonds.

7.176 Why are polymer alloys of great importance for engineering applications?

Polymer alloys are particularly important to engineering applications because materials can now tailored to have specific properties and thus material performance and cost can be optimized.

7.177 What type of polymer alloy is (a) Xenoy 1000, (b) Valox 815, and (c) Bayblend MC2500?

(a) Xenoy 1000 is a polymer alloy made of polycarbonate, PBT and elastomer.
(b) Valox 815 is a thermoplastic polyester alloy made of PBT and PET.
(c) Bayblend MC2500 is an ABS/polycarbonate alloy.

7.178 What are some of the advantages of thermosetting plastics for engineering design applications? What is the major disadvantage of thermosets that thermoplastics do not have?

General advantages of thermosetting plastics include one or more of the following: high thermal stability; high rigidity; high dimensional stability; resistance to creep and deformation under load; light weight; and high electrical and thermal insulating properties.

7.179 What are the major processing methods used for thermosets?

Thermosets are typically processed using compression or transfer molding; however, special cases exist for which injection-molding techniques have been developed.

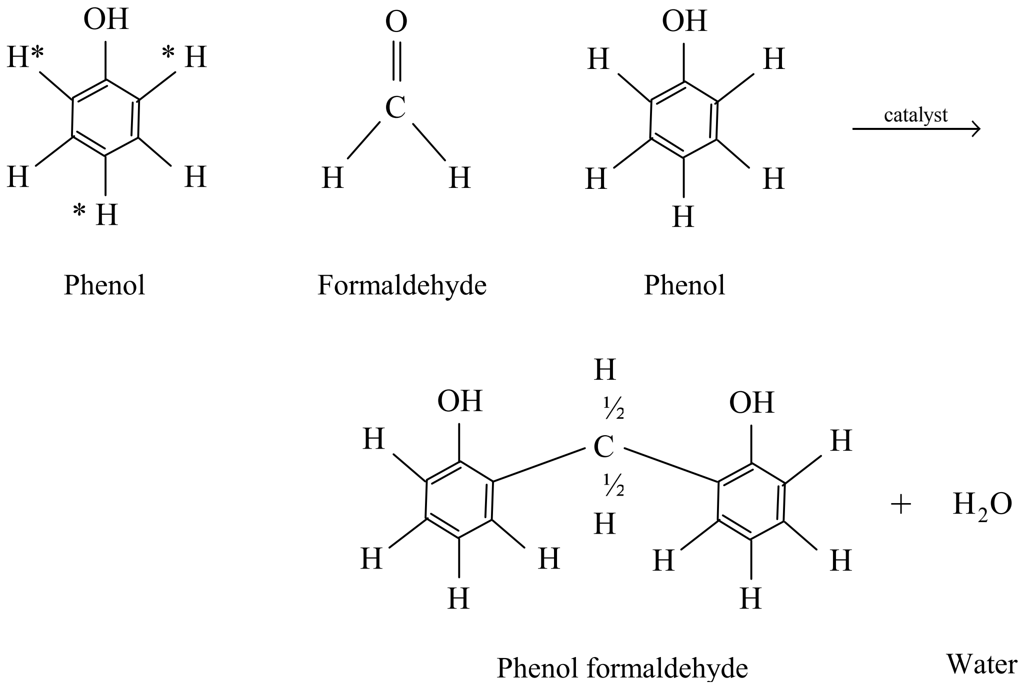
7.180 What are the two major ingredients of thermosetting molding compounds?

Two primary ingredients of thermosetting molding compounds are : a resin containing curing agents, hardeners, and plasticizers; and organic or inorganic fillers and/or reinforcing materials.

7.181 What are the major advantages of phenolic plastics for industrial applications?

Phenolic plastics are low cost materials with good electrical and heat insulating properties, as well as, good mechanical properties.

In the production of phenol-formaldehyde, water is formed as shown in the diagram below.

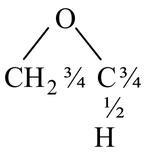


7.183 Why are large percentages of fillers used in phenolic molding compounds? What types of fillers are used and for what purposes?

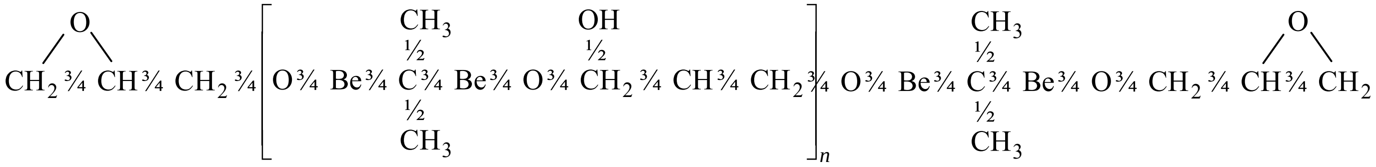
Phenolic molding compounds contain large percentages of fillers, as much as 50-80%, because the fillers reduce shrinkage during molding, lower cost and improve strength.

7.184 What are some of the applications for phenolic compounds?

Typical applications of phenolic compounds include wiring devices, electrical switchgear, connectors, telephone relay systems, and heat resistant parts for small appliances such as handles, knobs and end panels. They are also used for lamination of some plywood and particle boards and as a binder for sand in foundry and molding



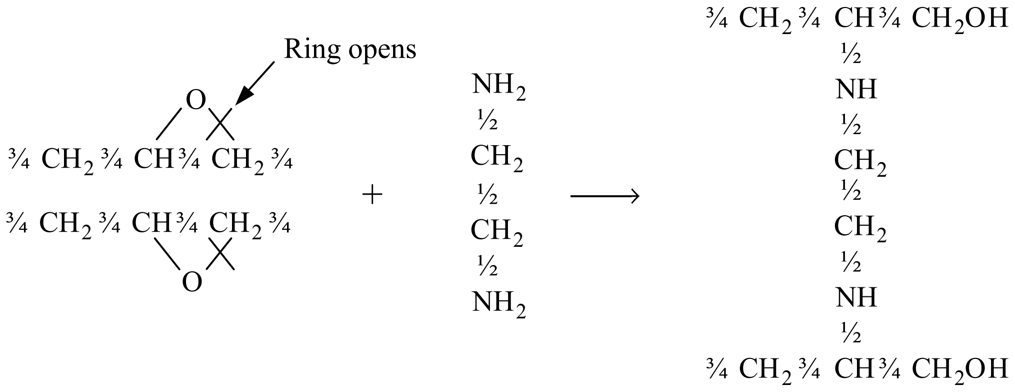
The general chemical structure of most commercial epoxy resins is:



7.186 What are two types of reaction sites that are active in the cross-linking of commercial epoxy resins?

The epoxy and hydroxyl (—OH) groups are the two active reaction sites in the cross-linking of commercial epoxy resins.

7.187 Write the reaction for the cross-linking of two epoxy molecules with ethylene diamine.



Epoxide rings at ends of two linear epoxy molecules

Ethylene diamine

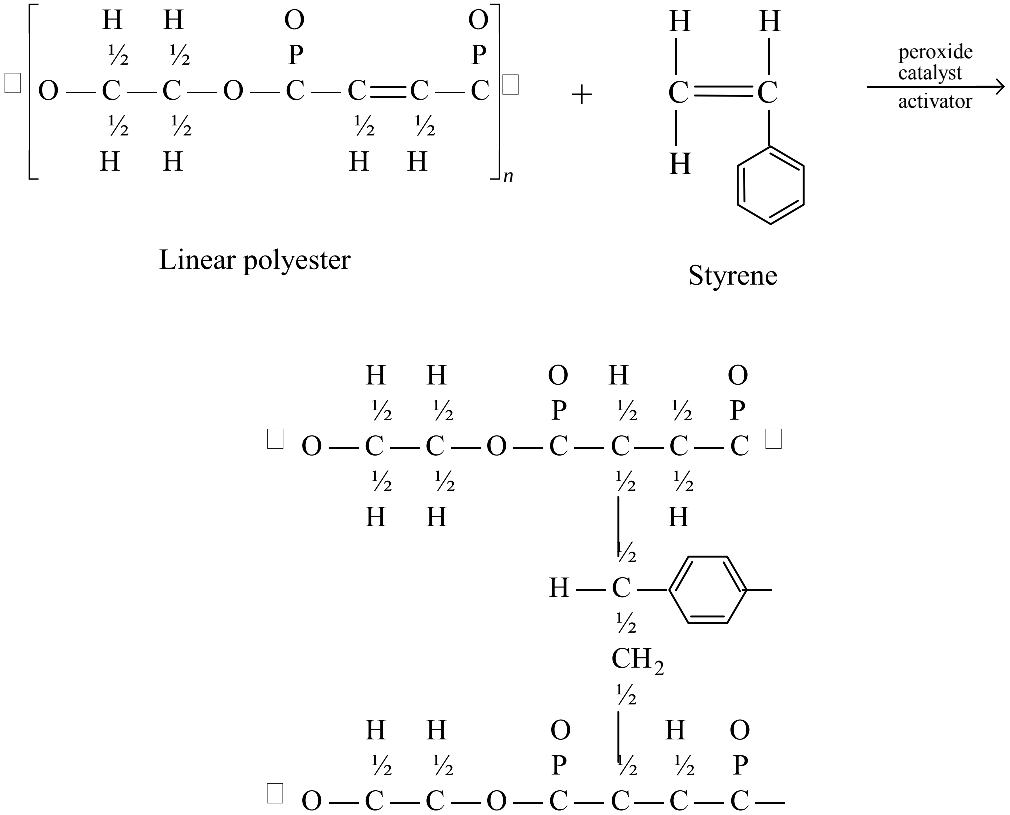
Cross-link formed between two linear epoxy molecules shrinkage, strong adhesive properties and exceptional wetting characteristics. This set of attributes makes epoxies a natural choice for a wide variety of protective and decorative coatings, adhesives, fiber-reinforced matrix materials, electrical potting and encapsulating applications.

7.189 What makes an unsaturated polyester resin "unsaturated"?

An unsaturated polyester resin is "unsaturated" because it has reactive double carbon-carbon bonds available for the cross-linking necessary to form thermosets.

7.190 How are linear unsaturated polyesters cross-linked? Write a structural formula chemical reaction to illustrate the cross-linking of an unsaturated polyester.

Linear unsaturated polyesters are usually cross-linked with vinyl-type molecules such as styrene in the presence of a free-radical curing agent.



Most unsaturated polyesters are reinforced with glass fibers; the content of glass-fiber reinforcement may be as high as 80 percent and the resulting strength up to 172 to 344 MPa (25 to 50 ksi).

7.192 What are some applications for reinforced polyesters?

Applications for reinforced polyesters include automobile panels and body parts, small boat hulls, building panels, bathroom components, and pipes, tanks and ducts designed for corrosive environments.

7.193 What are elastomers? What are some elastomeric materials?

Elastomers (rubbers) are polymeric materials whose dimensions can be significantly altered under stress yet return to nearly or exactly their original dimensions once the stress is removed. Examples of elastomeric materials include natural rubber, synthetic polyisoprene, styrene-butadiene rubber, nitrile rubbers, polychloroprene, and the silicones.

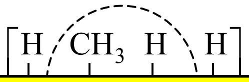
7.194 From what tree is most natural rubber obtained? What countries have large plantations of these trees?

Most natural rubber is obtained from the latex of the *Hevea brasiliensis* tree. Tropical regions of southeast Asia, particularly Malaysia and Indonesia, have large plantations of the *Hevea brasiliensis* tree

7.195 What is natural rubber latex? Briefly describe how natural rubber is produced in the bulk form?

Natural rubber latex is a milky liquid, collected from trees and diluted to approximately 15 percent rubber content. This mixture is coagulated with formic acid, and the material is then compressed into sheets by rollers and dried. Subsequently, milling between heavy rolls is performed to break up some of the long polymer chains and thus reduce their average molecular weight.

7.196 Write the formula for *cis*-1,4 polyisoprene. What does the prefix *cis*- stand for? What is the significance of the 1,4 in the name *cis*-1,4 polyisoprene.



The formula for the *cis*-1,4 polyisoprene is shown to the right. The prefix *cis*- indicates that the methyl

7.197 What is natural rubber mainly made of? What other components are present in natural rubber?

Natural rubber is mainly made of *cis*-1,4 polyisoprene mixed with small quantities of components such as proteins, lipids, inorganic salts.

7.198 To what structural arrangement is the coiling of the natural rubber polymer chains attributed? What is steric hindrance?

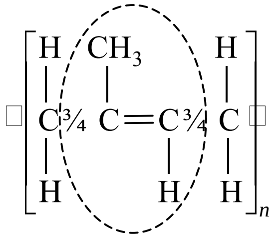
The coiling of the natural rubber polymer chains is attributed to the steric hindrance of the methyl group and the hydrogen atom. By definition, steric hindrance is the prevention or retardation of a chemical reaction, caused by the steric (spatial) arrangement of atoms. Here the term refers to the spatial interference of the methyl group and hydrogen atom, causing the molecule to coil.

7.199 What are chemical structural isomers?

Structural isomers are compounds having identical chemical compositions but different structural arrangement of their atoms.

7.200 What is gutta-percha? What is the repeating chemical structural unit for gutta-percha?

Gutta-percha is a structural isomer of polyisoprene also known as *trans*-1,4 polyisoprene. The repeating chemical structural unit for gutta-percha, shown to the right, is identical to the *cis*-1,4 except that the methyl group and hydrogen atom are on opposite sides of the carbon-carbon double bond. However, this material is not an elastomer.



gutta-percha
(*trans*-1,4 Polyisoprene)

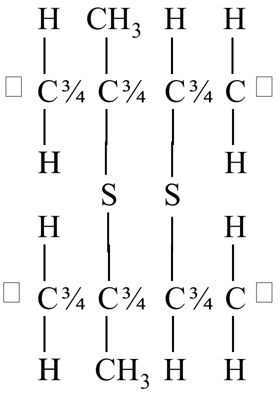
7.201 What does the *trans*- prefix in the name *trans*-1,4 polyisoprene refer to?

The *trans*- prefix refers to the fact that the methyl group and hydrogen atom are on opposite sides of the mer.

7.202 Why does the trans isomer lead to a higher degree of crystallinity than the cis isomer for polyisoprene?

In the vulcanization process for natural rubber, the rubber polymer chains are cross-linked with sulfur atoms to restrict molecular mobility and thus increase the material's strength. Charles Goodyear discovered this process, through which a thermoplastic material is converted to an elastomeric material, in 1839. The rigid structure obtained by cross-linking cis-1,4 polyisoprene with divalent sulfur atoms is illustrated below.

Schematic of *cis*-1,4 polyisoprene chain after cross-linking with sulfur at the active double-bond sites.



7.204 How does cross-linking with sulfur affect the tensile strength of natural rubber? Why is only about 3 wt % of sulfur used in the process?

The cross-linking of natural rubber with sulfur increases the material's tensile strength significantly. Only about 3 wt % sulfur is used in the process because larger amounts cause greater cross-linking, resulting in a harder, less-flexible material.

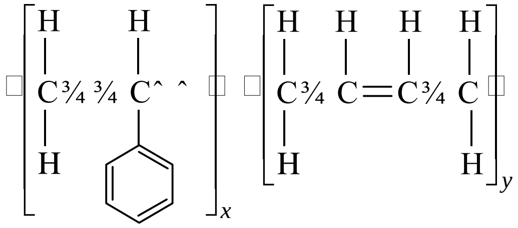
7.205 What materials are used in the compounding of rubber and what is the function of each?

Fillers, plasticizers, accelerators and antioxidants are used in the compounding of rubber. Fillers, such as carbon black and silicas, lower the cost of production and increase the material's strength. Plasticizers impart greater flexibility while accelerators shorten the cure time at elevated temperatures. Antioxidants are added to retard oxidation and thus reduce brittleness.

7.206 How can oxygen atoms cross-link the rubber molecules? How can the cross-linking of rubber molecules by oxygen atoms be retarded?

Similar to sulfur atoms in vulcanization, oxygen atoms can cross-link the rubber molecules by reacting with the carbon double bonds. This process can be retarded

Styrene-butadiene rubber, the most important synthetic rubber, is a copolymer containing approximately 20 to 23 percent styrene. The repeating chemical structural unit for SBR is shown to the right.



Polystyrene Polybutadiene

7.208 Can SBR be vulcanized? Explain.

SBR can be vulcanized through cross-linking of the carbon double bonds in the butadiene mer with sulfur.

7.209 What are some of the advantages and disadvantages of SBR? Natural rubber?

Advantages of SBR over natural rubber are lower cost, better wear resistance, and greater elasticity; however, SBR generates greater frictional heat. Both SBR and natural rubber have the disadvantage of absorbing organic solvents such as gasoline and oil.

7.210 What is the composition of nitrile rubbers? What effect does the nitrile group have on the main carbon chain in nitrile rubber?

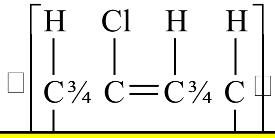
Nitrile rubber is composed of 55 to 82 percent butadiene and 45 to 18 percent acrylonitrile copolymers, respectively. The nitrile group imparts good resistance to oils and solvents and improves the abrasion and heat resistance of the rubber, but also reduces the flexibility of the main carbon chain.

7.211 What are some applications for nitrile rubbers?

Nitrile rubbers are costly and thus their applications are limited to parts such as fuel hoses and gaskets for which high resistance to oils and solvents are essential.

7.212 Write the repeating chemical structural unit for polychloroprene. What common name is given to polychloroprene rubber? How does the presence of the chlorine atom in polychloroprene affect some of its properties?

The repeating chemical structural unit for polychloroprene, better known as Neoprene, is shown schematically to the right. The presence of



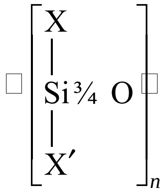
Polychloroprene elastomeric materials can be vulcanized using metallic oxides. Zinc oxide is typically used as a catalyst for vulcanization which produces zinc chloride. Magnesium oxide is thus used as a stabilizer to remove the zinc chloride.

7.214 What are some engineering applications for neoprene rubbers?

Neoprene rubbers are better strength than ordinary rubbers and fair fuel and oil resistance. However, they are costly and have poor low-temperature flexibility. Consequently, their application is restricted to parts such as wire and cable covering, industrial hoses and belts, and automotive seals and diaphragms.

7.215 What are the silicones? What is the general repeating chemical structural unit for the silicones?

The silicones are polymers which have repeating units of silicone and oxygen. Here, the X and X' may be hydrogen or groups such as methyl ($\pm CH_3$) or phenyl (C_6H_5—) as shown in the diagram to the right.

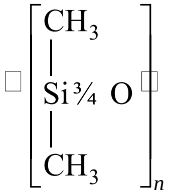


$$\square\left[\begin{array}{l} X \\ | \\ \text{Si¾ O} \\ | \\ X' \end{array}\right]_n\square$$

Silicone polymer

7.216 What is a silicone elastomer? What is the chemical structural repeating unit of the most common type of silicone rubber? What is its technical name?

A silicone elastomer is a silicone rubber based on the silicon-oxygen repeating structure main chain with side groups on the silicon. The most common type of silicone elastomer is Polydimethyl siloxane, shown in the diagram to the right, which has methyl side groups.



$$\square\left[\begin{array}{l} CH_3 \\ | \\ \text{Si¾ O} \\ | \\ CH_3 \end{array}\right]_n\square$$

Polydimethyl siloxane

7.217 How can a silicone rubber be cross-linked at room temperature?

Polydimethyl siloxane rubber can be cross-linked at room temperature through the addition of an initiator, such as benzoyl peroxide, which causes the methyl groups to react with each other. As a result, hydrogen gas is driven off and $Si\pm CH_2\pm CH_2\pm Si$ is formed.

7.219 Describe the general deformation behavior of a thermoplastic plastic above and below its glass transition temperature.

Below their glass transition temperatures, thermoplastics deform primarily by elastic deformation whereas above their glass transition temperatures, these plastics deform plastically.

7.220 What deformation mechanisms are involved during the elastic and plastic deformation of thermoplastics?

During elastic deformation, the covalent bonds of the molecular chains stretch. Subsequently, the chains uncoil in a process that involves both elastic and plastic deformation. Finally, plastic deformation occurs as secondary dipole bonds are broken, allowing the chains to slide relative to each other and establish new dipole bonding forces.

7.221 How does the average molecular mass of a thermoplastic affect its strength?

The average molecular mass of a thermoplastic directly affects its strength as it is indicative of the degree of polymerization of the solid; the plastic must attain a critical molecular mass to become a stable solid. However, increasing the mass beyond this minima does not appreciably increase the thermoplastic's strength.

7.222 How does the amount of crystallinity within a thermoplastic material affect (a) its strength, (b) its tensile modulus of elasticity, and (c) its density?

(a) As the amount of crystallinity increases, the polymer chains become more tightly packed and the tensile strength increases.
(b) The tensile modulus of elasticity is also directly related to crystallinity; the modulus increases with increasing crystallinity.
(c) Increased crystallinity corresponds to an increase in density.

7.223 Explain why low-density polyethylene is weaker than high-density polyethylene.

Low-density polyethylene is weaker than high-density because the molecular chains are more branched and farther apart from each other, causing weaker bonding forces and thus lower strength.

7.224 Explain why bulky side groups strengthen thermoplastics.

Highly polar pendant atoms of the main carbon chain greatly strengthen thermoplastics by increasing the molecular bonding forces between polymer chains.

7.226 Explain how oxygen atoms covalently bonded in the main carbon chain strengthen thermoplastics. Give an example.

The introduction of oxygen atoms in the main carbon chain strengthens a thermoplastic by increasing the rigidity and the permanent dipole bonds between polymer chains. Examples are polyoxy methylene (acetal) and polycarbonates.

7.227 Explain how phenylene rings covalently bonded in the main carbon chain strengthen thermoplastics. Give an example.

The covalent bonding of phenylene rings to the main carbon chain is an important means of producing high-strength engineering plastics such as polyphenylene oxide and polycarbonates. These rings increase the thermoplastic's strength by causing steric hindrance to rotation within the polymer chain and electronic attraction of resonating electrons between adjacent molecules.

7.228 Explain why thermosetting plastics have in general high strengths and low ductilities.

In general, thermosetting plastics have high strengths and low ductilities because their molecular structure is comprised of a covalently bonded network produced by chemical reaction within the material after casting or during pressing under heat and pressure.

7.229 How does increasing the temperature of thermoplastics affect their strength? What changes in bonding structure occur as thermoplastics are heated?

As the temperature of thermoplastics increases, the secondary bonding forces become weaker and the material softens.

7.230 Why don't cured thermoset plastics become viscous and flow at elevated temperatures?

As cured thermoset plastics are heated to elevated temperatures, the strong covalent bonds of their molecular network weaken but continue to prevent viscous flow; instead, the material degrades and chars.

7.231 How do increases in stress and temperature affect the creep resistance of thermoplastics?

An increase in applied stress or temperature will increase the creep experienced by a

Above their glass transition temperatures, plastic materials experience viscoelastic behavior – a combination of both elastic and plastic deformation in which molecular chains are able to slide relative to each other.

7.233 Define the creep modulus of a plastic material.

The creep modulus of a plastic material is the ratio of the initial applied stress, σ_0, at constant temperature to the resulting creep strain, $\varepsilon(t)$, after a specified time interval.

7.234 How can the creep modulus of a thermoplastic be increased?

The creep modulus of thermoplastics can be increased by reinforcing the material with glass fibers.

7.235 How can the extra energy required to fracture glassy thermoplastics, as compared to inorganic glasses, be explained?

The additional energy required to fracture glassy thermoplastics, as compared to inorganic glasses, is attributed to the energy required for the development of crazes in glassy plastics prior to fracture.

7.236 What is a craze in a glassy thermoplastic?

A craze is a highly stressed region consisting of aligned molecular chains with a high density of dispersed voids.

7.237 Describe the structure of a craze in a thermoplastic.

Refer to the answer above for Prob. 7.236.