Exercise 29-1 Write a reasonable mechanism for the thermal *depolymerization* of 1,3-cyclopentadiene tetramer. How could one chemically alter the tetramer to make thermal breakdown more difficult? Explain.

Exercise 29-2 Suppose a bottle of 1,3-cyclopentadiene were held at a temperature at which polymerization is rapid but depolymerization is insignificant. Would the polymerization result in conversion of all the 1,3-cyclopentadiene into essentially one gigantic molecule? Why or why not? How would you carry on the polymerization so as to favor formation of polymer molecules with high molecular weights?

Exercise 29-3* Calculate a number-average and a weight-average molecular weight for a low-molecular-weight sample of poly-1,3-cyclopentadiene having the following composition:

<table>
<thead>
<tr>
<th>(n)</th>
<th>(n')</th>
<th>Weight %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>12</td>
<td>8</td>
<td>(\geq) 0</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Under what circumstances would you expect \(\overline{M_n}\) to be equal to \(\overline{M_w}\)? Suppose one were to determine a molecular weight for a sample of poly-1,3-cyclopentadiene by quantitative hydrogenation of the terminal double bonds. Would the resulting molecular weight be equal to \(\overline{M_n}\), \(\overline{M_w}\), or neither of these?

Exercise 29-4 Show how each of the following polymer structures may be obtained from suitable monomers either by addition or condensation. More than one step may be required.

- \(\ce{-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-}\) (three ways)
- \(\ce{-N(CH_3)-CH_2-CH_2-N(CH_3)-CH_2-CH_2-N(CH_3)-CH_2-CH_2-}\)
- \(\ce{-CH(CH_3)-CH(CH_3)-CH(CH_3)-CH(CH_3)-CH(CH_3)-CH(CH_3)-}\)
- \(\ce{-O-CH_2-CH_2-C(=O)-O-CH_2-CH_2-C(=O)-O-CH_2-CH_2-C(=O)-}\)
- \(\ce{-CH_2-CH(OCOCH_3)-CH_2-CH(OCOCH_3)-CH_2-CH(OCOCH_3)-}\)
- \(\ce{-CH_2-CH(OH)-CH_2-CH(OH)-CH_2-CH(OH)-}\)
- \(\ce{-CH_2-C_6H_4-CH_2-C_6H_4-CH_2-C_6H_4-CH_2-C_6H_4-CH_2-}\)
- \(\ce{-}\)
Exercise 29-5 High-pressure polyethene (Section 10-8C) differs from polyethene made with the aid of Ziegler catalysts (Section 10-8D) in having a lower density and lower $(T_m)$. It has been suggested that this is due to branches in the chains of the high-pressure material. Explain how such branches may arise in the polymerization process and how they would affect the density and $(T_m)$.

Exercise 29-6 Radical-induced chlorination of polyethene in the presence of sulfur dioxide produces a polymer with many chlorine and a few sulfonyl chloride $\text{SO}_2\text{Cl}$ groups, substituted more or less randomly along the chains. Write suitable mechanisms for these substitution reactions. What kind of physical properties would you expect the chlorosulfonated polymer to have if substitution is carried to the point of having one substituent group to every 25 to 100 $\text{CH}_2$ groups? How may this polymer be cross-linked? (A useful product of this general type is marketed under the name Hypalon.)

Exercise 29-7 When polyethene (and other polymers) are irradiated with x rays, cross-links are formed between the chains. What changes in physical properties would you expect to accompany such cross-linking? Would the polyethene become more flexible? Explain.

Suppose polyethene were cross-linked by irradiation at a temperature above $(T_m)$. What would happen if it were then cooled?

Exercise 29-8 Answer the following questions in as much detail as you can, showing your reasoning:

a. Why is atactic polymethyl 2-methylpropenoate not an elastomer?

b. How may one make a polyamide that is an elastomer?

c. What kind of physical properties are to be expected for isotactic polyethenylbenzene (polystyrene)?

d. What would you expect to happen if a piece of high-molecular-weight polypropenoic acid, $\text{CO}_2\text{H}$, were placed in a solution of sodium hydroxide?

e. What kind of properties would you expect for high-molecular-weight "poly-para-phenylene"?
f. Are the properties, listed in Table 29-1, of polychloroprene produced by radical polymerization of 2-chloro-1,3-butadiene such as to make it likely that trans-1,4-addition occurs exclusively?


g. A very useful oil-resistant commercial polymer called "Hytrel" is a block copolymer, having repeating units of the following basic structure:

![Hytrel Structure]

The length of the blocks is determined by \((m)\) and \((n)\), and the overall molecular weight by \((m + n)\). With appropriate average values, the material is a "thermoplastic elastomer", which means that it is elastic and can be stretched without plastic flow at ordinary temperatures but when heated becomes fluid enough to be easily molded. What physical properties would you expect for polymers of this type having \((m + n)\) large, but with \((m = 1)\), \((m = 200)\); \((n = 30)\), \((n = 200)\); \((n = 200)\); \((m = 200)\); \((n = 200)\); and \((m = 200)\), \((n = 1)\)? Which composition would you expect to correspond to Hytrel?

h. Millions of light, strong soft-drink bottles were made from a recyclable \((75\%)\) ethenylbenzene-\((25\%)\) propenenitrile copolymer. The mechanical strength of the polymer is increased significantly in the operation of blowing a polymer bubble to fit the mold. Why should this be so?

Exercise 29-9 The material popularly known as "Silly Putty" is a polymer having an \([\text{-O-Si(R)\text{-2-O-Si(R)\text{-2-O}}\text{-}]\) backbone. It is elastic in that it bounces and snaps back when given a quick jerk, but it rapidly loses any shape it is given when allowed to stand. Which of the polymers listed in Table 29-1 is likely to be the best candidate to have anything like similar properties? Explain. What changes would you expect to take place in the properties of Silly Putty as a function of time if it were irradiated with x rays (see Exercise 29-7)?

Exercise 29-10* Suppose one had a sample of completely isotactic polypropene prepared from nonoptically active substances with the structure \([\text{H-[CH(CH\text{-3})-CH\text{-2]-(499)-C(CH\text{-3)}=CH\text{-2}}}]\).

a. Would the material theoretically cause a net rotation of the plane of polarized light? Explain.

b. Suppose one could make this polypropene with all \((D)\) orientations of the \((CH\text{-3})\) groups. Would the resulting material have an optical rotation theoretically? Practically?

Exercise 29-11 What kind of polymer would you expect to be formed if 4-methylbenzenol were used in place of benzenol in the Bakelite process?

Exercise 29-12 Write a reasonable mechanism for the base-catalyzed condensation of urea with methanal to give bis-methyleneurea, \([\text{NH\text{-2CONHC\text{-2NHCONH\text{-2}}}]})\).

Exercise 29-13 Show the reaction whereby butenedioic anhydride would be able to cross-link an epoxy prepolymer with
\( n = 1 \).

**Exercise 29-14** The terminal carbon of the epoxide ring of epichlorohydrin generally is quite a bit more reactive toward nucleophilic agents than is the carbon bonded to chlorine. Work out a mechanism for the following reaction that takes account of this fact (review Section 15-11D):

\[ 
\begin{align*}
\text{\( \text{O} \)} & \quad \text{\( \text{O} \)} \\
\text{\( \text{O} \)} & \quad \text{\( \text{O} \)} \\
\text{\( \text{O} \)} & \quad \text{\( \text{O} \)} \\
\text{\( \text{O} \)} & \quad \text{\( \text{O} \)}
\end{align*}
\]

**Exercise 29-15** Polymerization of methyl 2-methylpropenoate with benzoyl peroxide labeled with \( ^{14}\text{C} \) in the aromatic ring gives a polymer from which only \( 57\% \) of the \( ^{14}\text{C} \) can be removed by vigorous alkaline hydrolysis. Correlation of the \( ^{14}\text{C} \) content of the original polymer with its molecular weight shows that, on the average, there are 1.27 initiator fragments per polymer molecule. Write mechanism(s) for this polymerization that are in accord with the experimental data, and calculate the ratios of the different initiation and termination reactions.

**Exercise 29-16** The radical polymerization of ethenylbenzene gives atactic polymer. Explain what this means in terms of the mode of addition of monomer units to the growing-chain radical.

**Exercise 29-17** Polyvinyl alcohol prepared by hydrolysis of polyethenyl ethanoate (polyvinyl acetate; Table 29-1) does not react with measurable amounts of periodic acid or lead tetraethanoate (Sections 16-9A and 20-4A). However, periodic acid or lead tetraethanoate treatment of the polymer does decrease the number-average molecular weight, for a typical sample from 25,000 to 5000. Explain what these results mean in terms of the polymer structures and the mechanism of the polymerization.

**Exercise 29-18** Treatment of polychloroethylene with zinc in alcohol removed \( 85\% \) of the chlorine as zinc chloride without formation of unsaturated polymer. What does this result indicate about the polymer structure? Would you have expected that all of the chlorine would be removed by the zinc treatment? Explain. (See Section 14-10C.)

**Exercise 29-19** Ozonizations of natural rubber and gutta-percha, which are both poly-2-methyl-1,3-butadienes, give high yields of \( \text{\( \text{CH_3COCH_2CH_2CHO} \)} \) and no \( \text{\( \text{CH_3COCH_2CH_2COCH_3} \)} \). What are the structures of these polymers?

**Exercise 29-20** What conditions would you choose for producing the highest possible yield of (phenylmethylthiophenylethane by radical-induced addition of phenylmethanethiol to ethenylbenzene? What structure would you expect the product to have? Explain.

**Exercise 29-21** The rate of radical polymerization of ethenylbenzene, induced by benzoyl peroxide in mixtures of tetrachloromethane and benzene, is independent of the concentration of tetrachloromethane. At high concentrations of tetrachloromethane, the average molecular weight of the polymer is greatly reduced and chlorine is found in the polymer. Explain.

**Exercise 29-22** 2-Propenyl ethanoate with radical initiators gives a rather short-chain polymer in a relatively slow polymerization. Deuterated 2-propenyl ethanoate of the structure \( \text{\( \text{CH_2=CHCD_2C}O_2\text{CH_3} \)} \) gives higher-molecular-weight polymer at a faster rate. Explain.
Exercise 29-23 Devise a synthesis of polyethenamine, remembering that ethenamine (vinylamine) itself is unstable.

Exercise 29-24* Write an equation for the dimerization of sodium naphthalenide analogous to dimerization of the ethenylbenzene radical anion \((1)\) to give \((2)\). Show why you may expect that this dimerization would not be as energetically favorable as the dimerization of \((1)\).

Exercise 29-25* How could you use the living-polymer technique to synthesize \(\ce{HOCH_2CH_2[(C_6H_5)CHCH_2]_2-[CH_2CH(C_6H_5)]_2-CH_2CH_2OH}\)?

Exercise 29-26* What physical properties would you expect for a 2-methylpropene-butenedioic anhydride copolymer? (Review Section 29-3.)

Exercise 29-27* What would be the expected structure of a copolymer of ethenylbenzene and propene made by a Ziegler catalyst if the growing chain is transferred to the monomer as a radical? As an anion?

Exercise 29-28* Devise a synthesis of a block polymer with poly-1,2-ethanediol and nylon 66 segments. What kind of physical properties would you expect such a polymer to have?

Exercise 29-29* Suppose one were to synthesize two block copolymers with the following structures:

\[
\ce{H-[CH(C_6H_5)-CH_2]_{10}-[CH_2CH\_\text{cis}CHCH_2)_{100}-[CH(C_6H_5)-CH_2]_{10}-H}\}
\]

\[
\ce{H-[CH_2CH\_\text{cis}CHCH_2)_{50}-[CH(C_6H_5)-CH_2]_{20}-[CH_2CH\_\text{cis}CH-CH_2)_{50}-H}\}
\]

What difference in physical properties would you expect for these two materials? (Review Sections 29-3 and 13-4.)

Exercise 29-30* What would you expect for the physical and chemical properties of the following ladder polymer?

Exercise 29-31* Fibers made from aromatic polyamides such as from 1,4-benzenedicarboxylic acid and 1,4-benzenediamine are at least as strong as steel wire with the same ratio of weight to length. What are the structural features of this kind of polyamide that contribute to the strength?

Exercise 29-32 The economically important chain reaction, wool \(\rightarrow\) moths \(\rightarrow\) holes \(\rightarrow\) more moths, has, as a key step, scission of the disulfide linkages of cystine in the polypeptide chains by the digestive enzymes of the moth larva. Devise a method of mothproofing wool that would involve chemically altering the disulfide linkages in such a way as to make it unlikely that they would be attacked by the moth enzymes.

Contributors
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