

Chapter 31 – Synthetic Polymers

Chapter Outline

- I. Chain-growth polymers (Sections 31.1 – 31.3).
 - A. General features of chain-growth polymerization reactions (Section 31.1).
 - 1. How polymerization occurs.
 - a. An initiator adds to a carbon–carbon double bond of a vinyl monomer.
 - b. The reactive intermediate adds to a second molecule of monomer.
 - c. The process is repeated.
 - 2. Types of polymerization.
 - a. A radical initiator leads to radical polymerization.
 - b. An acid causes cationic polymerization.
 - Acid-catalyzed polymerization is effective only if the vinyl monomers contain electron-donating groups.
 - c. Anionic polymerization can be brought about by anionic catalysts.
 - i. Vinyl monomers in anionic catalysis must have electron-withdrawing groups.
 - ii. Polymerization occurs by Michael addition to the monomer.
 - iii. Acrylonitrile, styrene and methyl methacrylate can be polymerized anionically.
 - iv. "Super glue" is an example of an anionic polymer.
 - B. Stereochemistry of polymerization (Section 31.2).
 - 1. There are three possible stereochemical outcomes of polymerization of a substituted vinyl monomer.
 - a. If the substituents all lie on the same side of the polymer backbone, the polymer is isotactic.
 - b. If the substituents alternate along the backbone, the polymer is syndiotactic.
 - c. If the substituents are randomly oriented, the polymer is atactic.
 - 2. The three types of polymers have different properties.
 - 3. Although radical polymerization can't control stereochemistry, Ziegler–Natta catalysts can yield polymers of desired stereochemical orientation.
 - a. Ziegler–Natta catalysts are organometallic-transition metal complexes.
 - b. Ziegler–Natta polymers have very little chain-branching.
 - c. Ziegler–Natta catalysts are stereochemically controllable.
 - d. Polymerization occurs by coordination of the alkene monomer to the complex, followed by insertion into the polymer chain.
 - 4. Common Ziegler–Natta polymers.
 - a. Polyethylene produced by the Ziegler–Natta process (high-density polyethylene) is linear, dense, strong, and heat-resistant.
 - b. Other high-molecular-weight polyethylenes have specialty uses.
 - C. Copolymers (Section 31.3).
 - 1. Copolymers are formed when two different monomers polymerize together.
 - 2. The properties of copolymers are different from those of the corresponding monomers.
 - 3. Types of copolymers.
 - a. Random copolymers.
 - b. Alternating copolymers.
 - c. Block copolymers.
 - Block copolymers are formed when an excess of a second monomer is added to a still-active mix.

d. Graft copolymers.

Graft copolymers are made by gamma irradiation of a completed homopolymer to generate a new radical initiation site for further growth of a chain.

II. Step-growth polymers (Section 31.4).

A. Step-growth polymers are formed by reactions in which each bond is formed independently of the others.

B. Most step-growth polymers result from reaction of two difunctional compounds.

Step-growth polymers can also result from polymerization of a single difunctional compound.

C. Types of step-growth polymers.

1. Polyamides and polyesters.

2. Polycarbonates (formed from carbonates and alcohols or phenols).

3. Polyurethanes.

a. A urethane has a carbonyl group bonded to both an -NR_2 group and an -OR group.

b. Most polyurethanes are formed from the reaction of a diisocyanate and a diol.

c. Polyurethanes are used as spandex fibers and insulating foam.

i. Foaming occurs when a small amount of water is added during polymerization, producing bubbles of CO_2 .

ii. Polyurethane foams often use a polyol, to increase the amount of cross-linking.

III. Polymer structure and physical properties (Section 31.5).

A. Physical properties of polymers.

1. Because of their large size, polymers experience large van der Waals forces.

These forces are strongest in linear polymers.

2. Many polymers have regions held together by van der Waals forces; these regions are known as crystallites.

a. Polymer crystallinity is affected by the substituents on the chains.

b. T_m is the temperature at which the crystalline regions of a polymer melt.

3. Some polymers have little ordering but are hard at room temperature.

These polymers become soft at a temperature T_g .

B. Polymers can be classified by physical behavior.

1. Thermoplastics.

a. Thermoplastics have a high T_g and are hard at room temperature.

b. Because they become soft at higher temperatures, they can be molded.

c. Plasticizers such as dialkyl phthalates are often added to thermoplastics to keep them from becoming brittle at room temperature.

2. Fibers.

a. Fibers are produced by extrusion of a molten polymer.

b. On cooling, the crystallite regions orient along the axis of the fiber to add tensile strength.

3. Elastomers.

a. Elastomers are amorphous polymers that can stretch and return to their original shape.

b. These polymers have a low T_g and a small amount of cross-linking.

c. The randomly coiled chains straighten out in the direction of the pull, but they return to their random orientation when stretching is done.

d. Natural rubber is an elastomer, but gutta percha is highly crystalline.

4. Thermosetting resins.

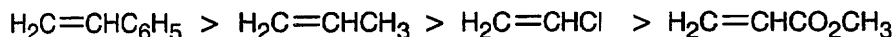
a. Thermosetting resins become highly cross-linked and solidify when heated.

b. Bakelite, a phenolic resin formed from phenol and formaldehyde, is the most familiar example.

Solutions to Problems

31.1

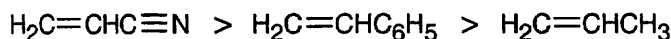
Most reactive \longrightarrow Least reactive



The alkenes most reactive to cationic polymerization contain electron-donating functional groups that can stabilize the carbocation intermediate. The reactivity order of substituents in cationic polymerization is similar to the reactivity order of substituted benzenes in electrophilic aromatic substitution reactions.

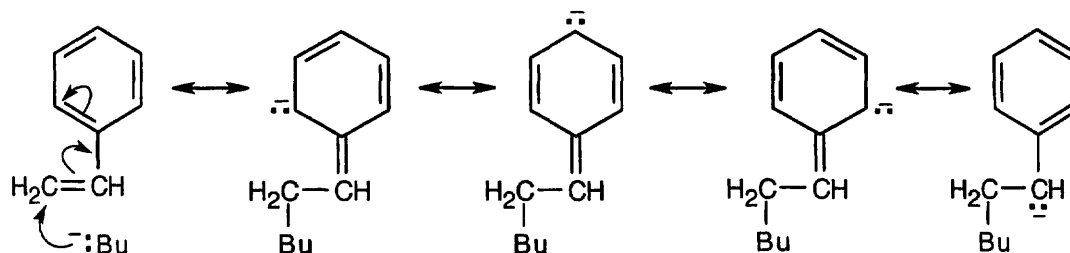
31.2

Most reactive \longrightarrow Least reactive



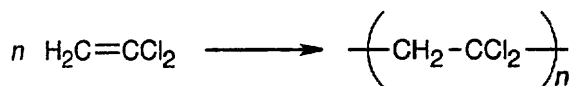
Anionic polymerization occurs most readily with alkenes having electron-withdrawing substituents.

31.3



The intermediate anion can be stabilized by resonance involving the phenyl ring.

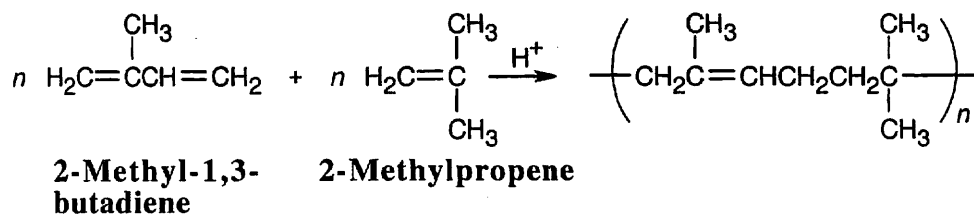
31.4



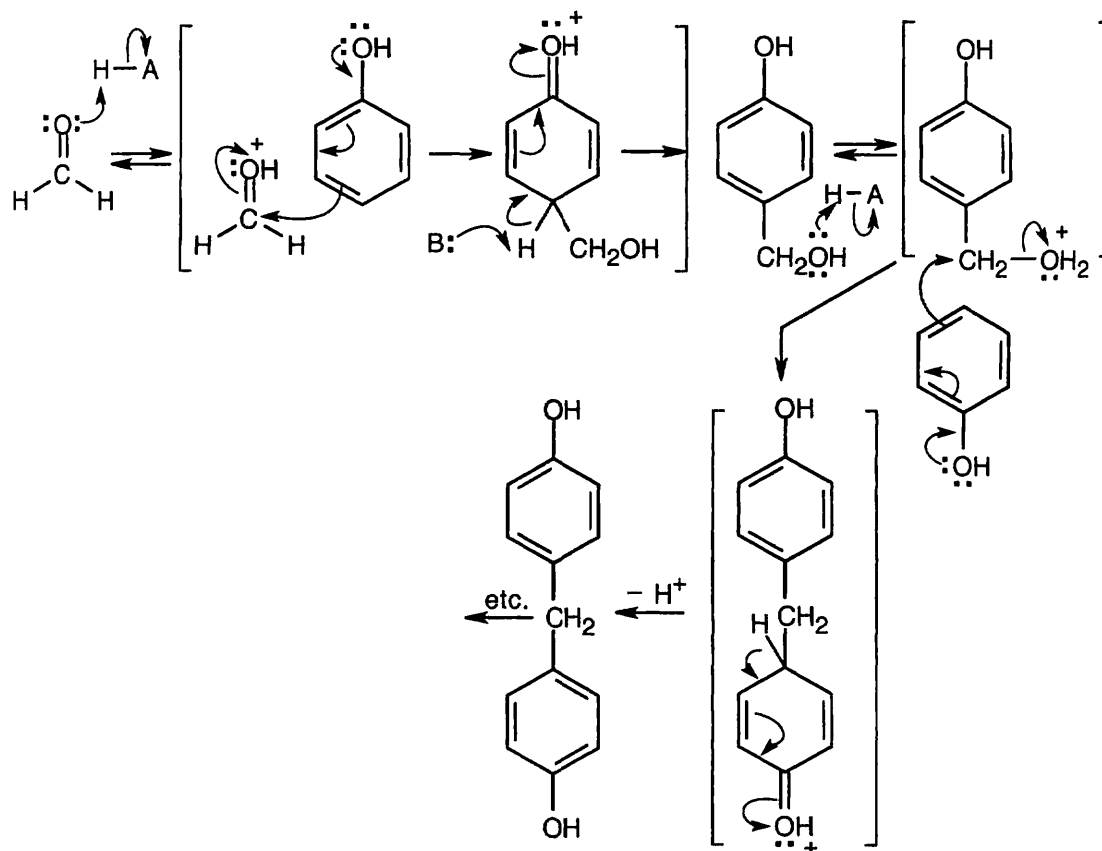
Vinylidene chloride doesn't polymerize in isotactic, syndiotactic or atactic forms because no asymmetric centers are formed during polymerization.

31.5 None of the polypropylenes rotate plane-polarized light. If an optically inactive reagent and an achiral compound react, the product must be optically inactive. For every chirality center generated, an enantiomeric chirality center is also generated, and the resulting polymer mixture is inactive.

31.6



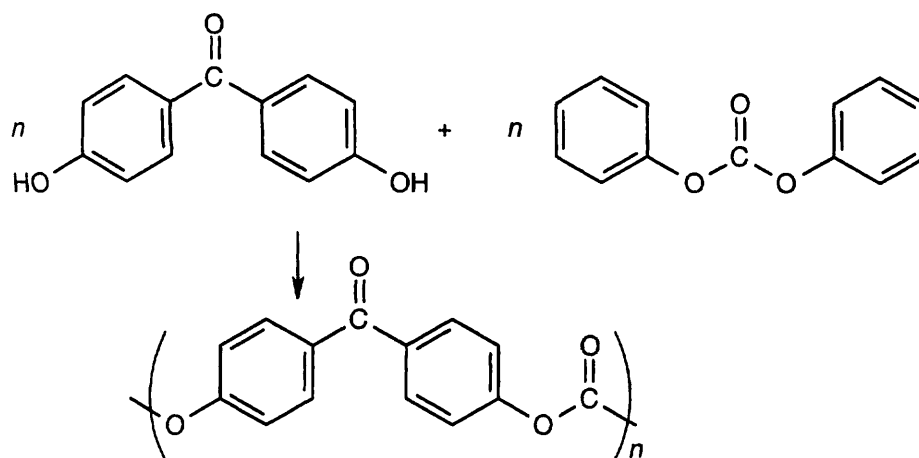
31.11



This product can react many times with additional formaldehyde and phenol to yield Bakelite. Reaction occurs at both *ortho* and *para* positions of phenol.

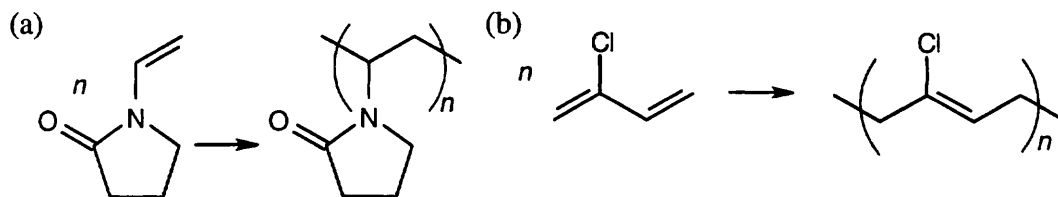
Visualizing Chemistry

31.12



The polymer is a polycarbonate synthesized from the above monomer units.

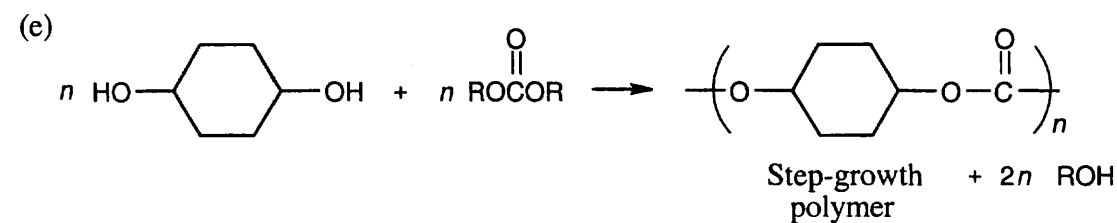
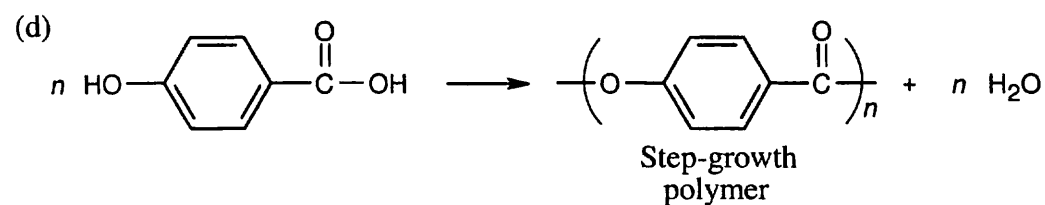
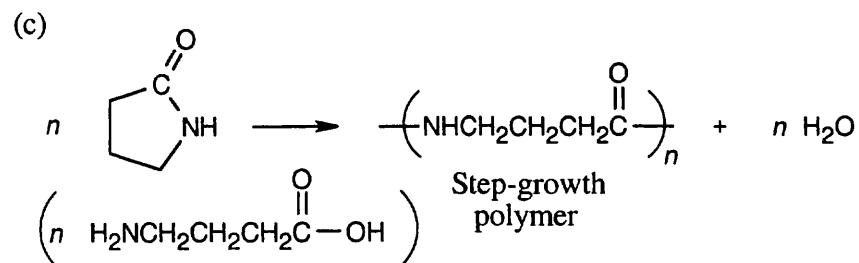
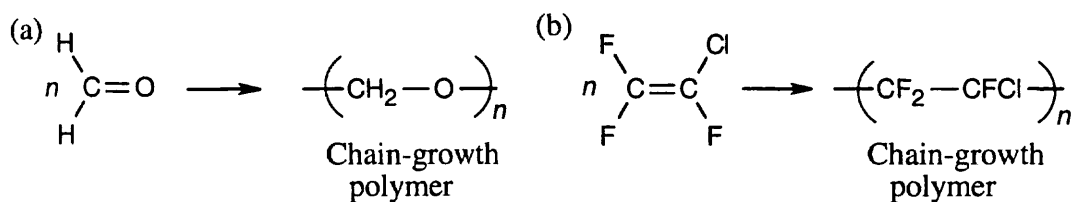
31.13



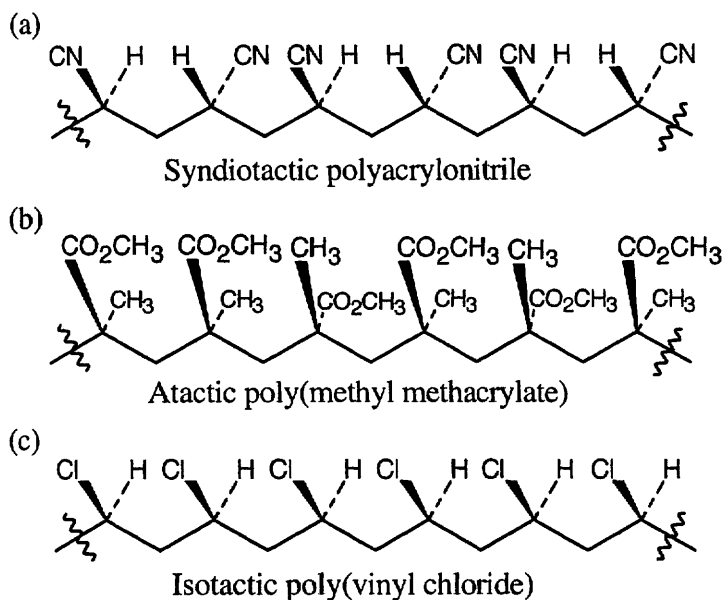
Both of these polymers are chain-growth polymers. To draw the polymer in (a), break the double bond, and draw its extensions, one on each side of the former double bond. In (b), break both double bonds and draw extensions at both ends of the former diene. The remaining double bond migrates to a position between the double bonds of the former diene.

Additional Problems

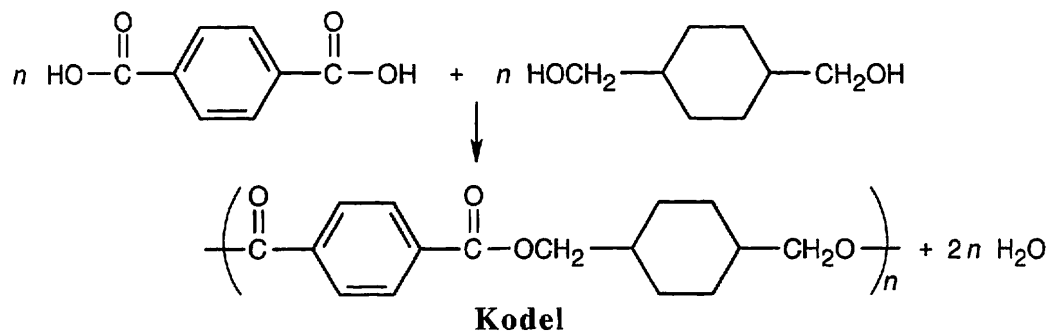
31.14



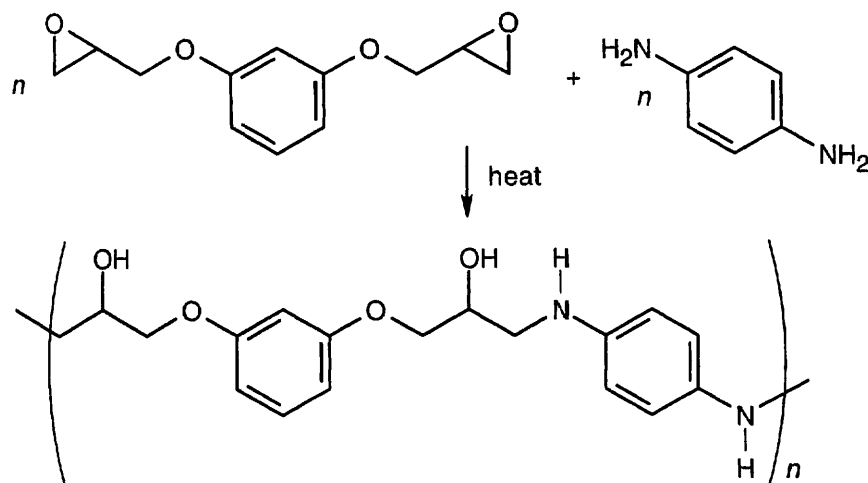
31.15 Remember that isotactic polymers have identical groups on the same side of the polymer backbone. Syndiotactic polymers have alternating identical groups along the polymer backbone. Atactic polymers have a random orientation of groups.



31.16



31.17



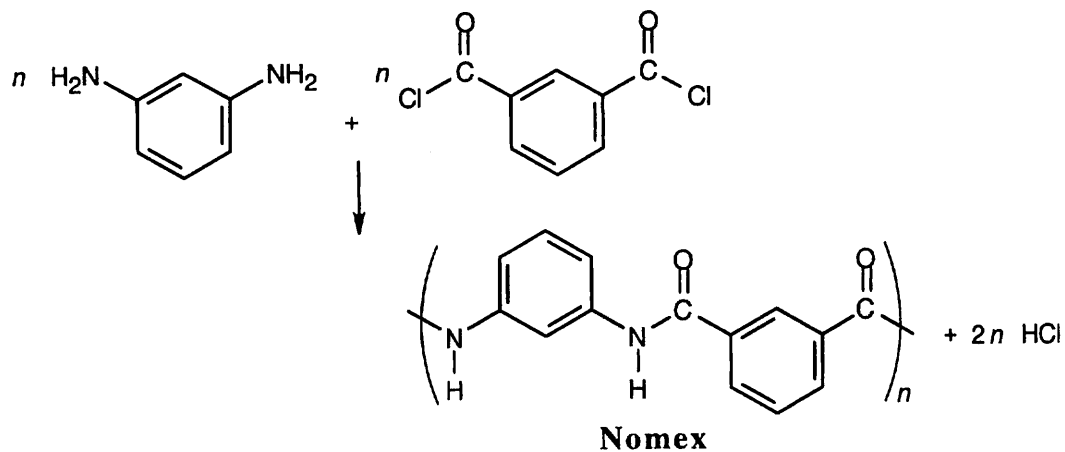
Ring opening of the epoxide occurs by an S_N2 pathway at the less substituted epoxide carbon.

$$\begin{array}{c} \sim\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)\sim \\ + \quad \cdot\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\sim \end{array} \longrightarrow \begin{array}{c} \sim\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{CH}(\text{CH}_2\text{CH}(\text{C}_6\text{H}_5))\text{CH}_2)\sim \end{array}$$

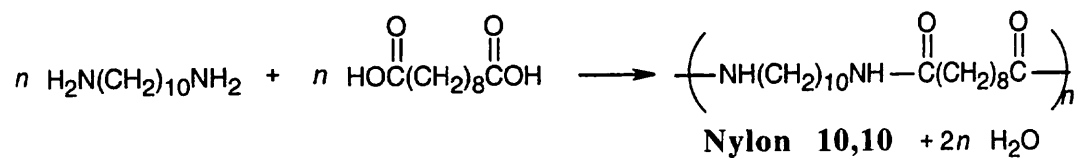
$$\begin{array}{c}
 \text{HO}^- \cdot \cdot \cdot \quad \text{H}_2\text{C}-\text{CH}_2 \quad \longrightarrow \quad \text{HOCH}_2-\text{CH}_2\text{O}^- \cdot \cdot \cdot \quad \text{H}_2\text{C}-\text{CH}_2 \quad \longrightarrow \quad \text{HOCH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{O}^- \cdot \cdot \cdot \\
 \uparrow \quad \quad \quad \uparrow \quad \quad \quad \uparrow \quad \quad \quad \uparrow \quad \quad \quad \uparrow \quad \quad \quad \uparrow \\
 \text{:O:} \quad \quad \quad \text{:O:} \quad \quad \quad \text{:O:} \quad \quad \quad \text{:O:} \quad \quad \quad \text{:O:} \quad \quad \quad \text{:O:} \\
 \text{H}_2\text{C}-\text{CH}_2 \quad \quad \quad \text{H}_2\text{C}-\text{CH}_2 \quad \quad \quad \text{H}_2\text{C}-\text{CH}_2 \quad \quad \quad \text{H}_2\text{C}-\text{CH}_2 \quad \quad \quad \text{H}_2\text{C}-\text{CH}_2 \\
 \text{repeat many times} \downarrow \\
 \text{HOCH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n
 \end{array}$$

$$n \text{ H}_2\text{C}=\underset{\text{NO}_2}{\text{CH}} \xrightarrow{\text{heat}} \left(\text{CH}_2-\underset{\text{NO}_2}{\text{CH}} \right)_n$$

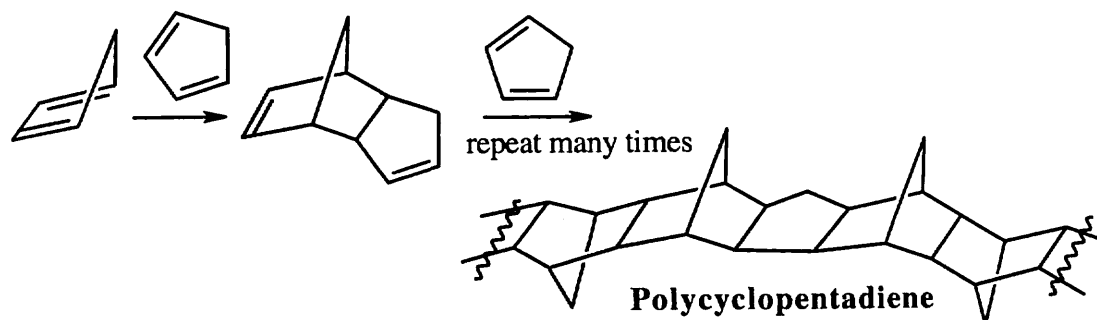
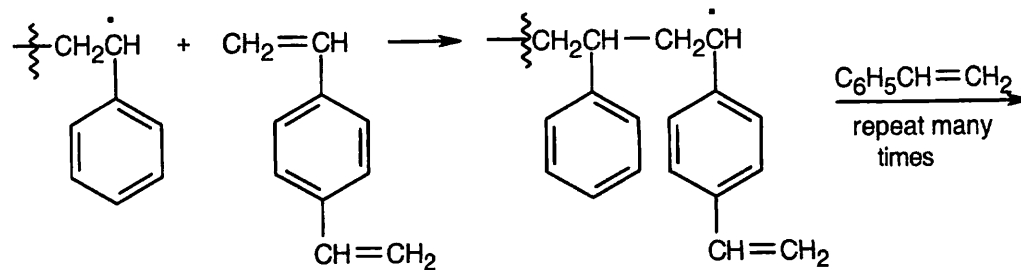
31.18



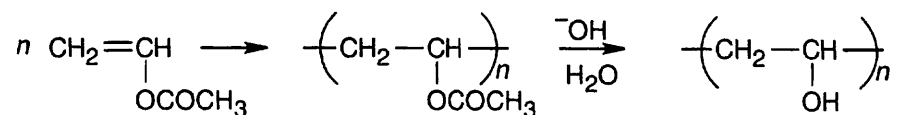
31.19



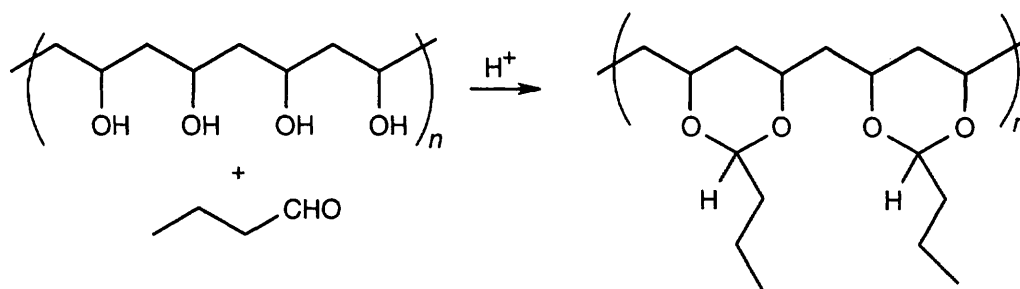
31.20

31.21 *p*-Divinylbenzene is incorporated into the growing polystyrene chain.

31.24 Poly(vinyl alcohol) is formed by chain-growth polymerization of vinyl acetate, followed by hydrolysis of the acetate groups.

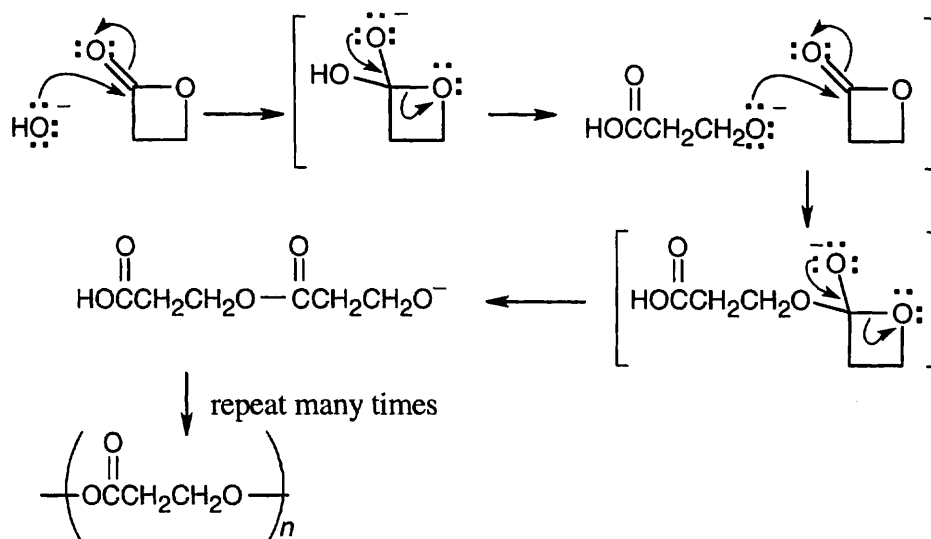


Reaction of poly(vinyl alcohol) with butanal to form the poly(cyclic acetal) produces poly(vinyl butyral).



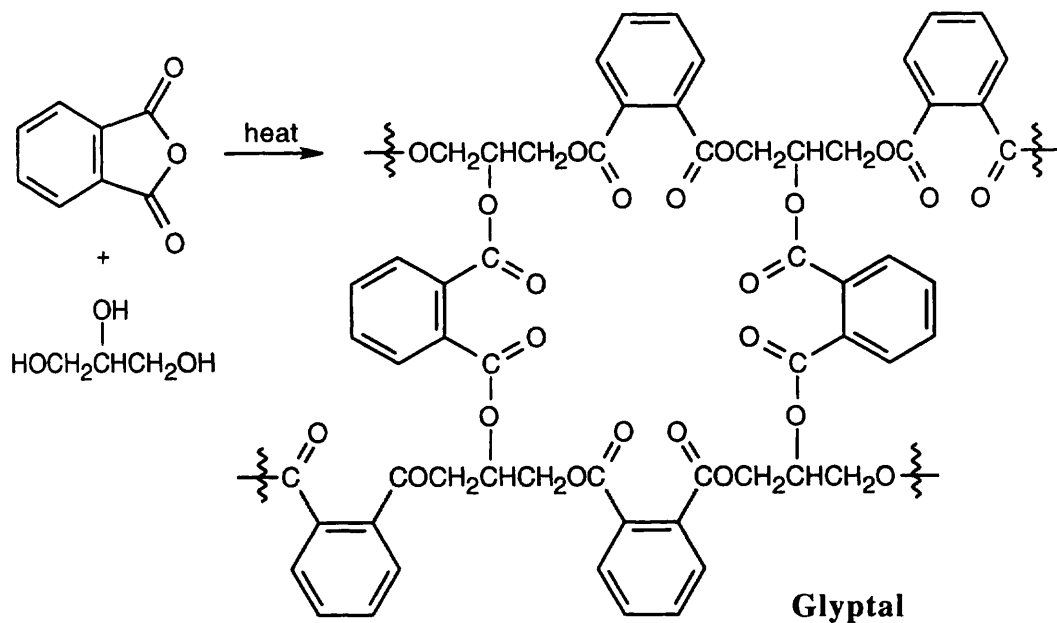
Poly(vinyl butyral)

31.25



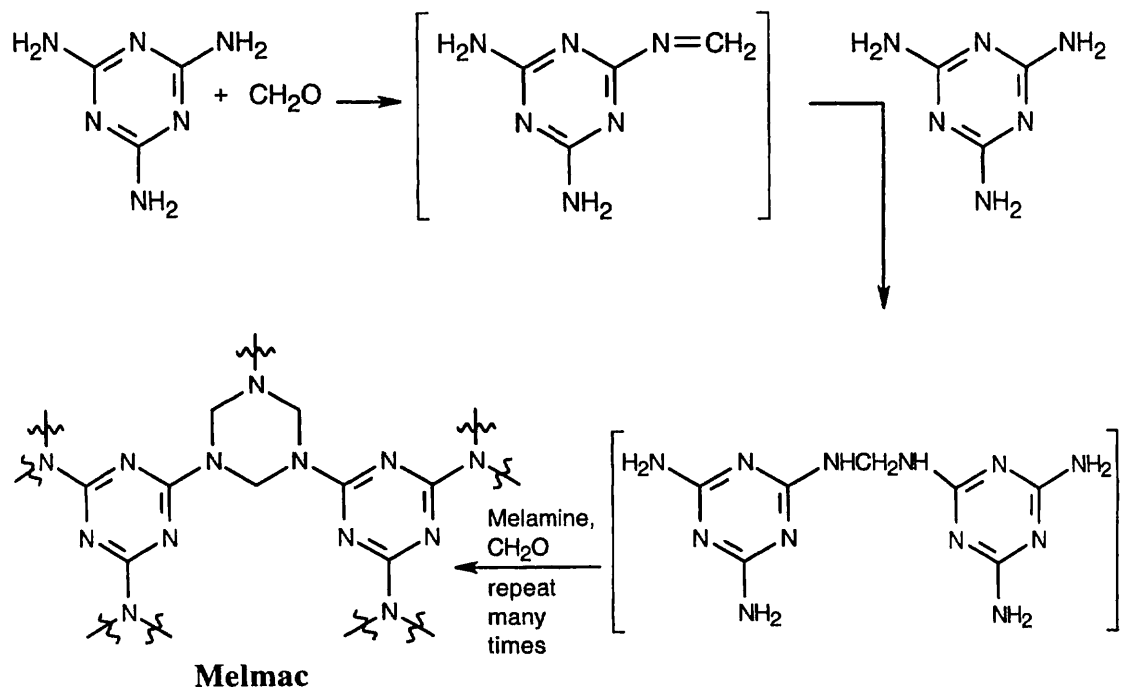
The polymer is a polyester.

31.26

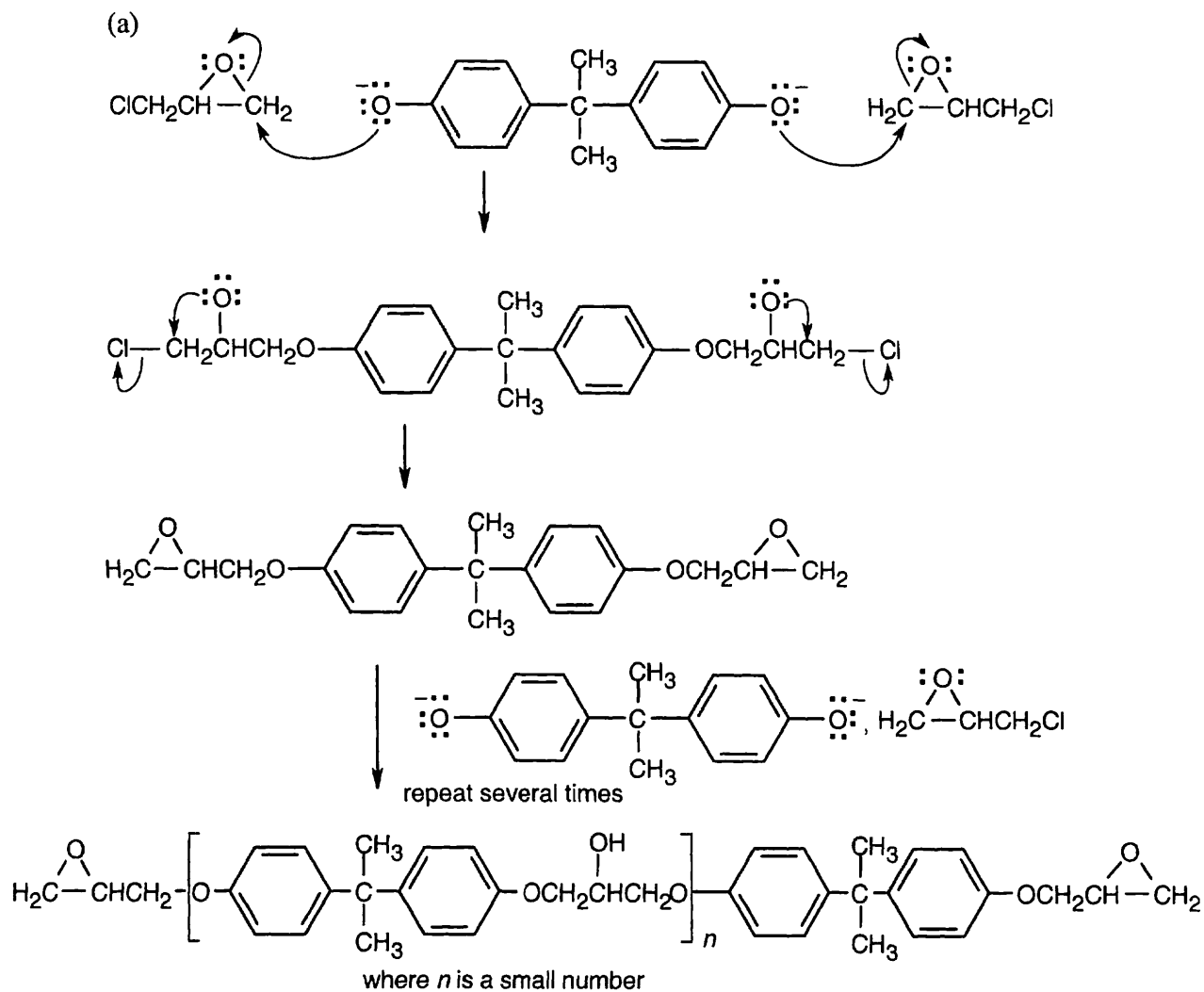


Use of glycerol as a monomer causes the cross-linking that gives Glyptal its strength.

31.27 Repeated nucleophilic acyl substitution reactions result in the formation of Melmac.

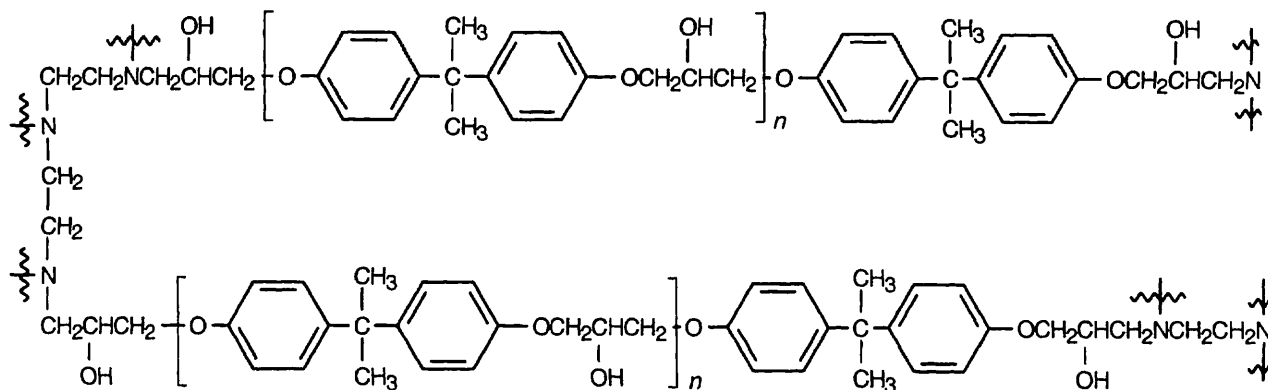


31.28



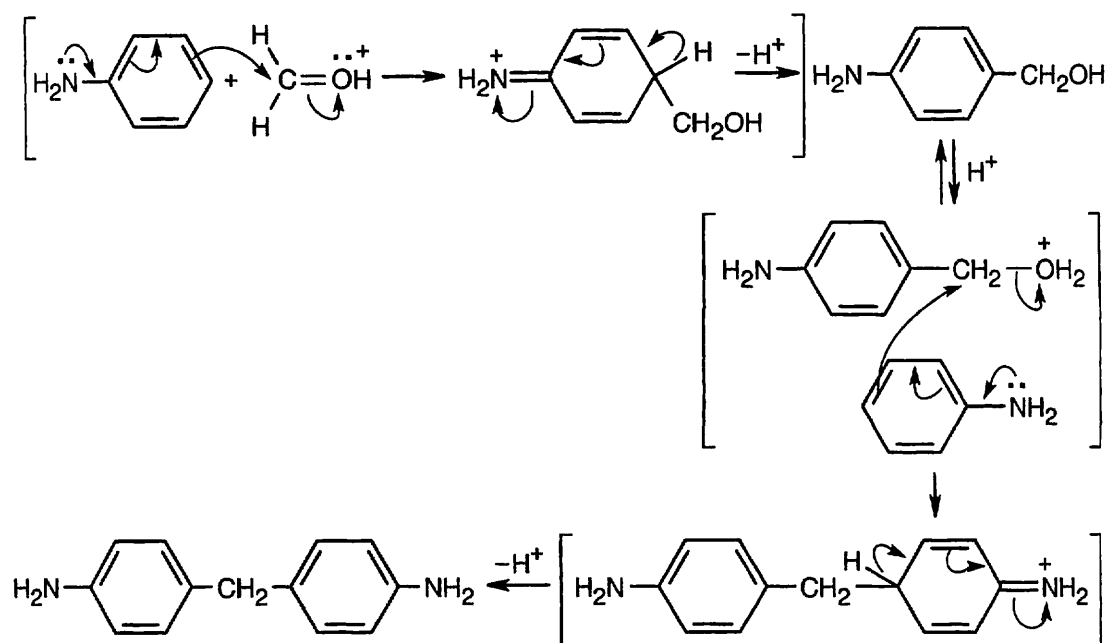
The prepolymer contains epoxide rings and hydroxyl groups. Copolymerization with a triamine occurs at the epoxide ends of the prepolymer.

(b)

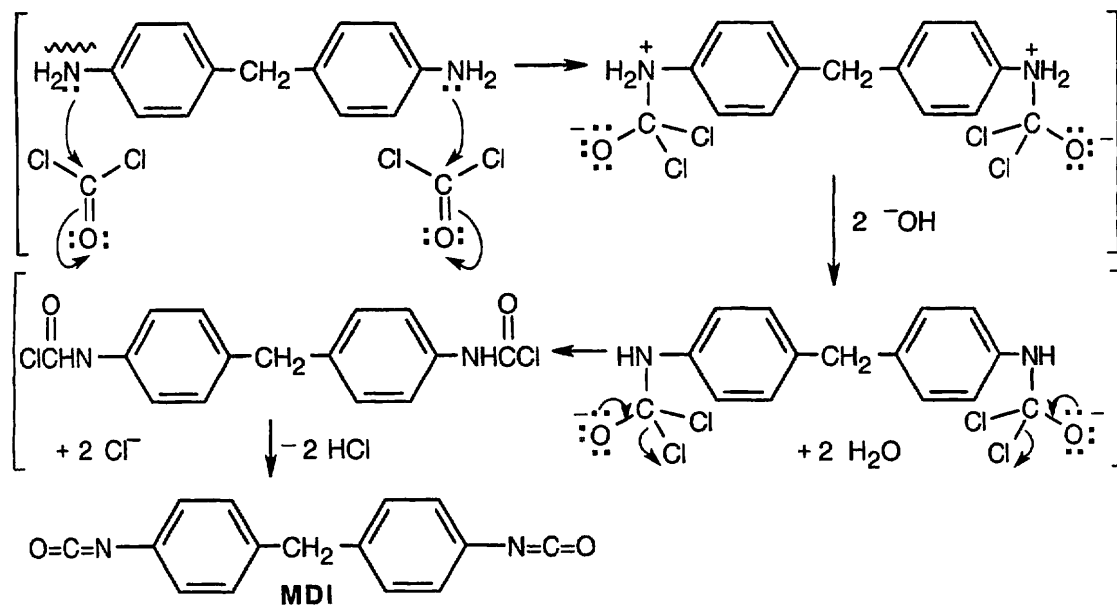


Cross-linking occurs when the triamine opens epoxide rings on two different chains of the prepolymer.

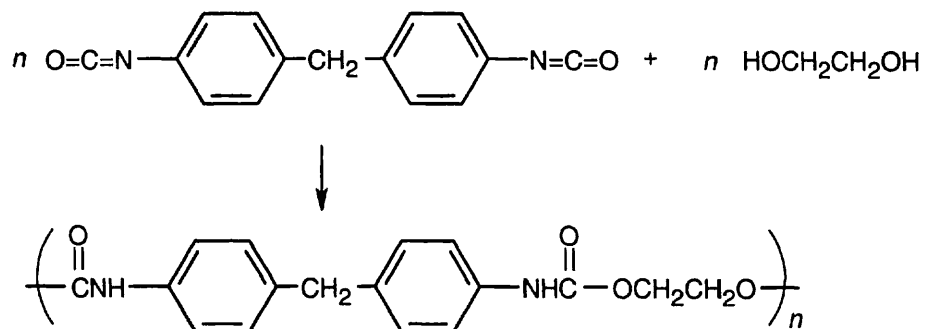
31.29 (a) The diamine is formed by an electrophilic aromatic substitution reaction of formaldehyde with two equivalents of aniline.



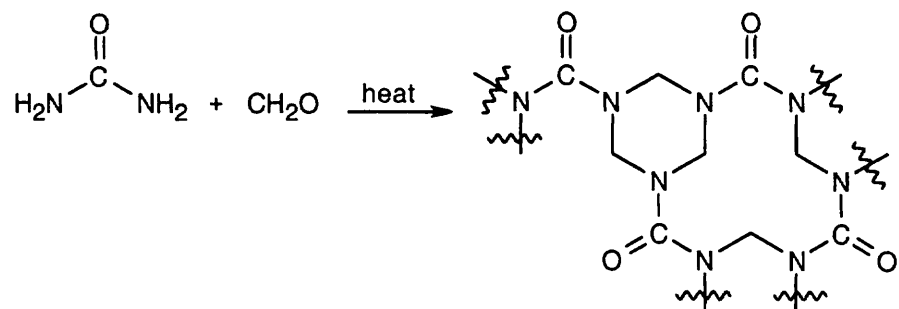
(b) The diamine reacts with two equivalents of phosgene.



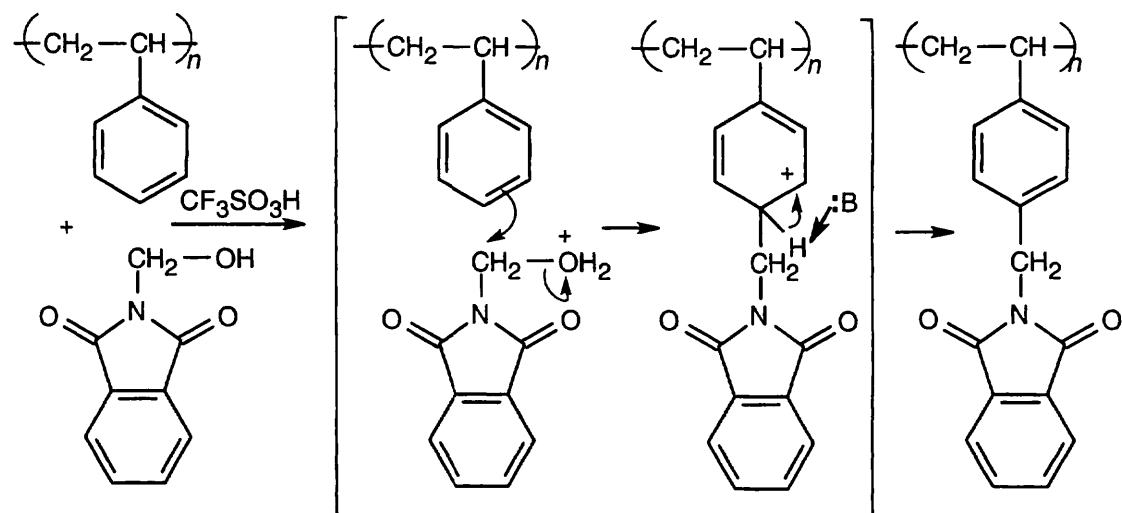
31.30



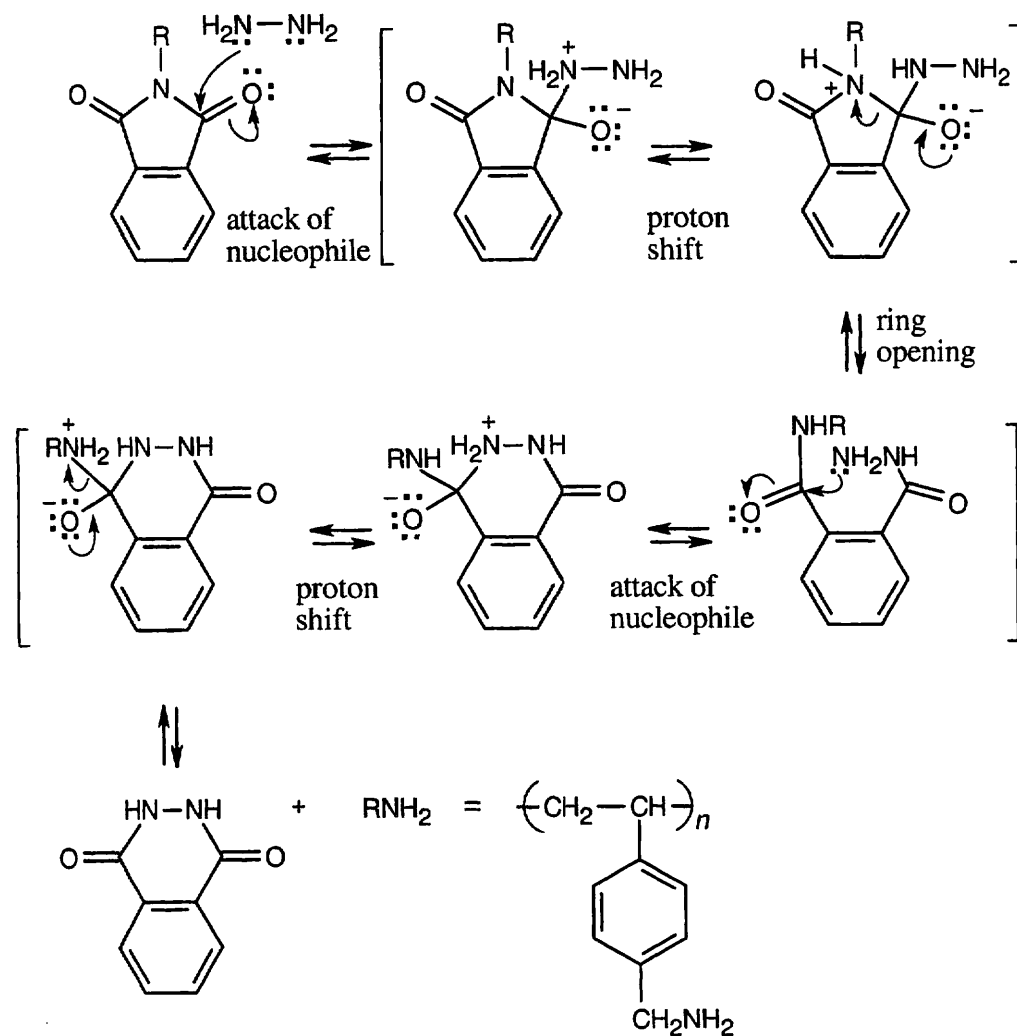
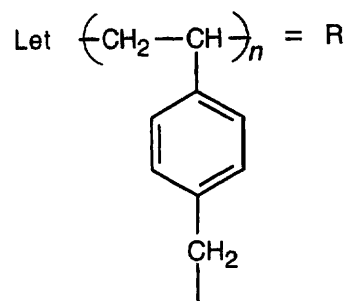
31.31



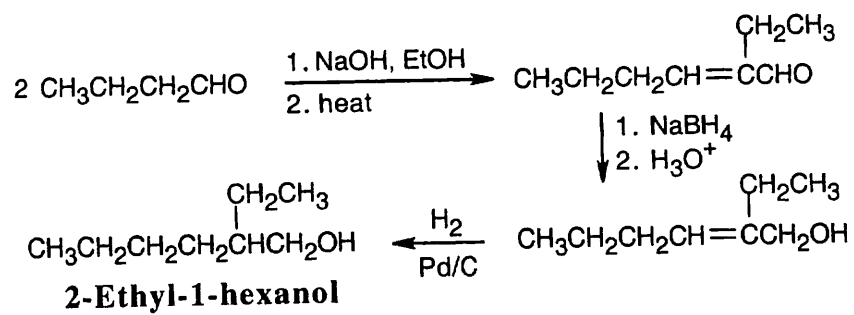
31.32 Step 1: Polystyrene and the phthalimide combine in an electrophilic aromatic substitution reaction



Step 2: The phthalimide is cleaved in a series of steps that involve nucleophilic acyl substitution reactions.



31.33



Aldol self-condensation of butanal, followed by reduction, gives 2-ethyl-1-hexanol.

Review Unit 12: Pericyclic Reactions, Synthetic Polymers

Major Topics Covered (with vocabulary):

Pericyclic reactions:

pericyclic reaction concerted reaction symmetry-allowed symmetry-disallowed frontier orbitals HOMO LUMO electrocyclic reaction disrotatory motion conrotatory motion cycloaddition reaction suprafacial cycloaddition antarafacial cycloaddition sigmatropic rearrangement suprafacial rearrangement antarafacial rearrangement Cope rearrangement Claisen rearrangement

Synthetic polymers:

chain-growth polymer Ziegler–Natta catalyst isotactic syndiotactic atactic homopolymer copolymer block copolymer graft copolymer step-growth polymer polycarbonate polyurethane crystallite melt transition temperature glass transition thermoplastic fiber elastomer thermosetting resin plasticizer

Types of Problems:

After studying these chapters, you should be able to:

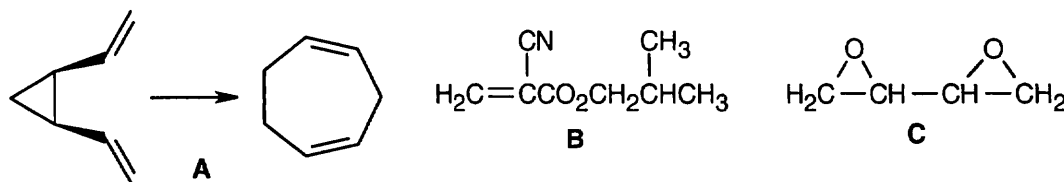
- Understand the principles of molecular orbitals, and locate the HOMO and LUMO of conjugated π systems.
- Predict the stereochemistry of thermal and photochemical electrocyclic reactions.
- Know the stereochemical requirements for cycloaddition reactions, and predict the products of cycloadditions.
- Classify sigmatropic reactions by order and predict their products.
- Know the selection rules for pericyclic reactions.
- Locate the monomer units of a polymer; predict the structure of a polymer, given its monomer units.
- Formulate the mechanisms of radical, cationic, anionic, and step-growth polymerizations.
- Understand the stereochemistry of polymerization, and draw structures of atactic, isotactic, and syndiotactic polymers.
- Understand copolymerization, graft polymerization and block polymerization.

Points to Remember:

- * Just because a reaction is symmetry-disallowed doesn't mean that it can't occur. Reactions that are symmetry-allowed occur by relatively low-energy, concerted pathways. Reactions that are symmetry-disallowed must take place by higher energy, nonconcerted routes.
- * To predict if a reaction is symmetry-allowed, it is only necessary to be concerned with the signs of the outermost lobes.
- * The notations in brackets in a sigmatropic rearrangement refer to the positions in the migrating groups to which migration occurs.

- * The stereochemical outcome of a concerted reaction run under thermal conditions is always opposite to the stereochemical outcome of the same reaction run under photochemical conditions.
- * To show the monomer unit of a chain-growth polymer, find the smallest repeating unit, break the polymer bonds, and draw the monomer with its original double bond in place. To show the monomer unit of a step-growth polymer, find the smallest repeating unit, break the polymer bonds, and draw the monomer unit or units with the small molecules that were displaced by polymerization added to the monomer units.
- * Fishhook arrows are used to show movement of single electrons.

Self-test:



What type of reaction is occurring in **A**? Describe it by order and type. If the reaction of the stereoisomer shown proceeds readily, is the reaction being carried out under thermal or photochemical conditions?

Under what conditions would you expect monomer **B** to polymerize? (Actually it polymerizes well under all conditions). Is the polymer a chain-growth or a step-growth polymer? Draw a representative segment of the polymer.

Suggest a use for **C** in polymerizations.

Multiple choice:

- In which orbitals do the outermost lobes have opposite signs on the same side of the π system?
 - HOMO in the ground state of a 2π electron system
 - HOMO in the excited state of a 4π electron system
 - LUMO in the excited state of a 6π electron system
 - HOMO in the ground state of a 4π electron system
- Which reaction is symmetry-disallowed?
 - conrotatory photochemical ring-opening of a 6π electron system
 - suprafacial thermal cycloaddition of a 6π electron system
 - antarafacial thermal sigmatropic rearrangement of a 4π electron system
 - antarafacial photochemical cycloaddition of a 6π electron system
- Which of the following reactions is symmetry-allowed but geometrically constrained?
 - thermal electrocyclic reaction of a 4π electron system
 - photochemical cycloaddition of a 4π electron system
 - thermal sigmatropic rearrangement of a 4π electron system
 - photochemical electrocyclic reaction of a 4π electron system

4. All of the following sigmatropic rearrangements involve 6π electrons except:
(a) rearrangement of allyl phenyl ether to *o*-allyl phenol (b) rearrangement of 1,5-heptadiene to 3-methyl-1,5-hexadiene (c) rearrangement of 1,3,5-heptatriene in which a hydrogen atom migrates across the π system (d) rearrangement of homotropilidene
5. Consider the 4π electron thermal electrocyclic reactions of two double-bond stereoisomers. All of the following are true except:
(a) one reaction is concerted and one isn't (b) the equilibrium lies on the side of the ring-opened product (c) the reaction proceeds with conrotatory motion (d) The ring-closed products are stereoisomers
6. Which of the following monomers is most likely to undergo cationic polymerization?
(a) $\text{H}_2\text{C}=\text{CF}_2$ (b) $\text{H}_2\text{C}=\text{CH}_2$ (c) formaldehyde (d) $\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$
7. Which of the following is not a copolymer?
(a) Saran (b) Nylon 6 (c) Dacron (d) Lexan
8. In which step-growth polymer is an alcohol the byproduct?
(a) polyester (b) polyamide (c) polyurethane (d) polycarbonate
9. Which type of polymer has large regions of oriented crystallites and little or no cross-linking?
(a) a thermoplastic (b) a fiber (c) an elastomer (d) a thermosetting resin
10. A copolymer formed by irradiating a homopolymer in the presence of a second monomer is called a:
(a) random copolymer (b) alternating copolymer (c) graft copolymer (d) block copolymer