Chapter 9. Reactions of vinyl polymers

9.1 Introduction

9.2 Functional group reactions

9.3 Ring-forming reactions

9.4 Crosslinking

9.5 Block and graft copolymer formation

9.6 Polymer degradation
Introduction

• Applications of chemical modifications
  - Ion-exchange resins
  - Polymeric reagents and polymer-bound catalysts
  - Polymeric supports for chemical reactions
  - Degradable polymers to address medical, agricultural, or environmental concerns
  - Flame-retardant polymers
  - Surface, treatments to improve such properties as biocompatibility or adhesion

• The purpose of this chapter: to summarize and illustrate chemical modifications of vinyl polymers
Introduction

• Five general categories
  - reactions that involve the introduction or modification of functional groups
  - reactions that introduce cyclic units into the polymer backbone
  - reactions leading to block and graft copolymers
  - crosslinking reactions
  - degradation reactions

• Things to consider
  - molecular weight
  - crystallinity
  - conformation & steric effect
  - neighboring group effect
  - polymer physical form
Introduction

- Conformational or localized steric effects influence the rate or extent of the reaction in different parts of the same molecule.

- The proximity of functional groups enhance a reaction by the *neighboring group effect*.

- Copolymers of acrylic acid and $p$-nitrophenyl methacrylate undergo base-catalyzed hydrolysis faster than simple $p$-nitrophenyl esters because of participation by neighboring carboxylate anions.
Introduction of new functional groups

- The oldest commercial processes are chlorination (9.2) and chlorosulfonation (9.3)

- Properties of polyethylene by chlorination
  - Decrease in flammability
  - Solubility: depending on the level of substitution
  - Higher crystallinity
  - Chlorination of poly(vinyl chloride) is used to increase Tg

- Chlorosulfonation
  - provides sites for subsequent crosslinking reactions
Introduction of new functional groups

• Fluorination, to improve solvent barrier properties
  ![Chemical Reaction]

• Aromatic substitution reactions (nitration, sulfonation, chlorosulfonation, etc.)
  - occur readily on polystyrene
  - useful for manufacturing ion-exchange resins
  - useful for introducing sites for crosslinking or grafting

• Chlorometylation
  ![Chemical Reaction]

• Introduction of ketone groups via the intermediate oxime
  ![Chemical Reaction]
Conversion of functional groups

- Useful in obtaining polymers difficult or impossible to prepare by direct polymerization
- Synthesis of poly(vinyl alcohol) by hydrolysis or alcoholysis of poly(vinyl acetate)

Examples of syntheses of polymers
- Saponification of isotactic or syndiotactic poly(trimethylsilyl methacrylate) to yield isopactic or syndiotactic poly(methacrylic acid)
- Hofmann degradation of polyacrylamide to give poly(vinyl amine)
- Synthesis of “head-to-head poly(vinyl bromide)” by controlled bromination of 1,4-polybutadiene
Conversion of functional groups

- Other types of *classical* functional group conversions
  - dehydrochlorination of poly(vinyl chloride)
  - hydroformylation of polypentenamer
  - hydroboration of 1,4-polyisoprene

- Conversion of a fraction of the chloro groups of poly(vinyl chloride) to cyclopentadienyl

- Converting the end groups of telechelic polymers
  - Dehydrochlorination of chlorine-terminated polyisobutylene
  - Subsequent epoxidation
**Ring-forming reactions**

- Introduction of cyclic units
  - greater rigidity
  - higher glass transition temperatures
  - improved thermal stability in carbon fiber (graphite fiber)

- Ladder structures: poly(methyl vinyl ketone) by intramolecular aldol condensation

- Nonladder structures: dechlorination of poly(vinyl chloride)
Ring-forming reactions

- The formation of cyclic acetal groups by the reaction of aldehydes with poly(vinyl alcohol) in which more than 90% of the hydroxyl groups can be converted
  - \( R = C_3H_7, \) poly(vinyl butyral) used as a plastic film in laminated safety glass \( \rightarrow \) containing a relatively high percentage of residual –OH groups (~40%) for better adhesion to glass

\[
\begin{align*}
\text{CH}_2\text{CHCH}_2\text{CH} \ldots \text{RCHO} \stackrel{\text{H}^+}{\rightarrow} \text{CH}_2\text{CHCH}_2\text{CH} \ldots \text{RCH}_2\text{O}_2
\end{align*}
\]

- Commercially important cyclization is epoxidation of natural rubber, to increase oil resistance and decrease gas permeability

\[
\begin{align*}
\text{CH}_3\text{CH} \ldots \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{CH} \ldots \text{OCH}_2\text{CH}_2
\end{align*}
\]

- Rubber and other diene polymers undergo cyclization in the presence of acid
  - cis-1,4-polyisoprene (9.21)
  - Cyclization of 1,2-polybutadiene by metathesis (9.22)
Crosslinking

• The most important reaction of vinyl polymers and fundamental to the rubber and elastomer industries

• Can be brought about by
  - Vulcanization, using peroxides, sulfur, or sulfur-containing compounds
  - Free radical reactions by ionizing radiation
  - Photolysis involving photosensitive functional groups
  - Chemical reactions of labile functional groups
  - Coulombic interactions of ionic species

• Physical and morphological consequences of chemical and physical crosslinking are different (already discussed in Chapter 3)
Vulcanization

- A general term applied to the crosslinking of polymers, particularly elastomers

- Peroxide-initiated crosslinking of saturated polymers
  - By hydrogen abstraction (9.23)
  - By radical combination (9.24)
  - Hydrogen abstraction at allylic position (9.25)
  - Radical combination (9.26)
  - Addition-transfer process (9.27), (9.28)
Vulcanization

- The mechanism is ionic in nature,
  - Involving addition to a double bond to form an intermediate sulfonium ion (9.29) which then abstracts a hydride ion (9.30) or donates a proton (9.31) to form new cations for propagating the reaction
  - Termination occurs by reaction between sulfenyl anions and carbocations

- Rate of vulcanization increases by the addition of accelerators (1) or organosulfur compounds (2)
Radiation crosslinking

- When vinyl polymers are subjected to radiation, both crosslinking and degradation occur simultaneously
  - Degradation predominates with high doses of radiation
  - With low doses the polymer structure determines which will be the major reaction
  - Disubstituted polymers tend to undergo chain scission
  - With monomer being a major degradation product
- Poly(α-methylstyrene), poly(methyl methacrylate), polyisobutylene: decrease in molecular weight on exposure to radiation
- Halogen-substituted polymers, such as poly(vinyl chloride), break down with loss of halogen
- In most other vinyl polymers, crosslinking predominates
- A limitation of radiation crosslinking is that radiation does not penetrate very far into the polymer matrix; hence the method is primarily used with films
Radiation crosslinking

- Mechanism of crosslinking is free radical in nature
  - Involves initial ejection of a hydrogen atom (9.32)
  - Removes another hydrogen atom from an adjacent site on a neighboring chain (9.33)

- Fragmentation reactions and ejection of hydrogen
  - Lead to double bonds in the polymer chains (9.34)
Photochemical crosslinking

- Ultraviolet or visible light-induced crosslinking (*photocrosslinking*)

- Applications
  - electronic equipment
  - printing inks
  - coatings for optical fibers
  - varnishes for paper and carton board
  - finishes for vinyl flooring, wood, paper, and metal
  - curing of dental materials

- Two basic methods
  - Incorporating photosensitizers into the polymer, which absorb light energy and thereby induce formation of free radicals
  - Incorporating groups that undergo either photocycloaddition reactions or light-initiated polymerization
Photochemical crosslinking

- Incorporating photosensitizers into the polymer, which absorb light energy and thereby induce formation of free radicals
  - When triplet sensitizers (benzophenone) are added to polymer, absorption of UV results in $n \rightarrow \pi^*$ excitation of the sensitizer followed by hydrogen abstraction from the polymer to yield radical sites available for crosslinking
  - Degradation by $\alpha$-cleavage of the excited polymer (9.35) or by chain cleavage (9.36)
  - Poly(vinyl ester)s undergo analogous $\alpha$-cleavage reactions (9.37) with subsequent crosslinking
Photochemical crosslinking

- Incorporating groups that undergo either photocycloaddition reactions or light-initiated polymerization
  - $2\pi + 2\pi$ cycloaddition occurs to give cyclobutane crosslinks (9.2a)
  - With anthracene, cycloaddition is $4\pi + 4\pi$

Scheme 9.2. Photocrosslinking (a) by $2\pi + 2\pi$ cycloaddition and (b) by $4\pi + 4\pi$ cycloaddition.
Photochemical crosslinking

- Group used to effect photocrosslinking

<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
<th>Type</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzothiophene dioxide</td>
<td><img src="image1" alt="Structure" /></td>
<td>Maleimide (R=H, CH₃, Cl)</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Chalcone</td>
<td><img src="image3" alt="Structure" /></td>
<td>Stilbazole</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>Cinnamate</td>
<td><img src="image5" alt="Structure" /></td>
<td>Stilbene</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>Coumarin</td>
<td><img src="image7" alt="Structure" /></td>
<td>Styrene</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td>Dibenzo[b, f]azepine</td>
<td><img src="image9" alt="Structure" /></td>
<td>1,2,3-Thiadiazole</td>
<td><img src="image10" alt="Structure" /></td>
</tr>
<tr>
<td>Diphenylcyclopropene</td>
<td><img src="image11" alt="Structure" /></td>
<td>Thymine</td>
<td><img src="image12" alt="Structure" /></td>
</tr>
<tr>
<td>Episulfide</td>
<td><img src="image13" alt="Structure" /></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 9.1. Groups Used to Effect Photocrosslinking**

- Alkyne: R=C=C=R
- Anthracene: 

**continued**
Photochemical crosslinking

- Reactive groups may be incorporated into the polymer during the polymerization reaction
  - \( \beta \)-vinylloxyethyl cinnamate (3) undergoes cationic polymerization through the vinyl ether (9.38) to yield linear polymer containing pendant cinnamate ester

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{OCH}_2\text{CH}_2\text{OCCH}==\text{CH} \quad \text{(3)} \\
\quad & \quad \text{BF}_3, \text{etherate, toluene} \\
\quad & \quad \text{OCH}_2\text{CH}_2\text{OCCH}==\text{CH} \\
\end{align*}
\]

- Alternatively, the group can be added to preformed polymer
  - Friedel-Crafts alkylation of polystyrene with N-chloromethylmaleimide (4) (9.39)

\[
\begin{align*}
\text{[CH}_2\text{CH]} & + \quad \text{[N-CH}_2\text{Cl]} \\
\quad & \quad \text{SnCl}_2 \\
\quad & \quad \text{[CH}_2\text{CH]} \\
\end{align*}
\]
Crosslinking thru labile functional groups

- Reaction between appropriate difunctional or polyfunctional reagents with labile groups on the polymer chains
  - Polymers containing acid chloride groups react with diamine (9.40), or diols (9.41) to yield sulfonamide and sulfonate crosslinks
  - Dihalogen compounds to crosslink polystyrene by the Friedel-Crafts reaction (9.42)
Crosslinking thru labile functional groups

- Diels-Alder reaction of cyclopentadiene-substituted polymer
  - Cyclopentadiene substituent groups on polymers yield crosslinked polymer by cycloaddition and linear polymer by retrograde Diels-Alder reaction of the crosslinked polymer at elevated temperatures
  - Have potential as thermoplastic elastomers

\[
\text{[Diagram of cyclopentadiene reaction]} \quad (9.43)
\]
Ionic crosslinking

- The hydrolysis of chlorosulfonated polyethylene with aqueous lead oxide (9.44)
  - Partial conversion of poly[ethylene-co-(methacrylic acid)] (5) to salts of divalent metals
  - Marketed under du Pont trade name Surlyn, called *ionomers*

![Chemical structure of chlorosulfonated polyethylene](image)

- Interesting properties of *ionomers*
  - Introduction of ions causes disordering of the semicrystalline structure, which makes the polymer transparent
  - Crosslinking gives the polymer elastomeric properties, but it can still be molded at elevated temperatures
  - Increased polarity improves adhesion: used as coatings and adhesive layers for bonding
Block copolymers

- Polymer containing functional end groups: subsequent reaction with isocyanate-terminated polymer yields an AB block copolymer via urethane linkages (9.45)

- Peroxide groups introduced to polymer chain ends: polymer, which contains an isopropylbenzene end group, can be converted to hydroperoxide (9.46)

- Peroxide units can be formed by the presence of oxygen (9.47). Thermal cleavage of peroxide leads to radical-terminated chains capable of initiating a second monomer (9.48)
Block & graft copolymer formation

• Three general methods of preparing graft copolymers
  - A monomer is polymerized in the presence of a polymer with branching resulting from chain transfer
  - A monomer is polymerized in the presence of a polymer having reactive functional groups or positions that are capable of being activated
  - Two polymers having reactive functional groups are coreacted

• Three components necessary for grafting by chain transfer: polymer, monomer, initiator

• Two role of initiator
  - It polymerizes the monomer to form a polymeric radical (or ion or coordination complex), which, in reacts with the original polymer
  - It reacts with the polymer to form a reactive site on the backbone which, in turn, polymerizes the monomer
Block & graft copolymer formation

- Grafting generally occurs at sites that are susceptible to transfer reactions
  - In the reaction of poly(vinyl acetate) with ethylene, the reaction occurs both on pendant methyl group and on the polymer backbone (9.49)
  - To give a mixture of poly(vinyl alcohol)-graft-polyethylene and long-chain carboxylic acid
  - Grafting efficiency is improved if a group that undergoes radical transfer readily, such as a mercaptan is incorporated into the polymer backbone

- Cationic chain transfer grafting
  - When styrene is polymerized with BF$_3$ in the presence of poly(p-methoxystyrene) (9.50)
  - The activated benzene rings undergo Friedel-Crafts attack
Block & graft copolymer formation

- Grafting by activation by backbone functional groups
  - Synthesis of poly(p-chlorostyrene)-\textit{graft}-polyacrylonitrile by anionic initiation of acrylonitrile using naphthalenesodium in the presence of poly(p-chlorostyrene) (9.51)

\[
\begin{align*}
\text{CH}_2\text{CH} & \quad \text{Na-naphthalene} \\
\text{Cl} & \quad \text{tetrahydrofuran} \\
\text{CH}_2\text{CH} & \quad \text{CH}_2=\text{CHCN} \\
\text{CH}_2\text{CH} & \quad \text{CN}
\end{align*}
\]

- Irradiation provides active sites
  - with ultraviolet or visible radiation; with or without added photosensitizer; with ionizing radiation
  - A major difficulty is that irradiation causes substantial amounts of homopolymerization along with grafting, which can be obviated by pre-irradiating prior to monomer addition
Direct irradiation of monomer and polymer together has been extensively used - Because homopolymerization can occur, monomer and polymer must be chosen carefully - The best combination is a polymer that is very sensitive to radiation and a monomer that is not very sensitive

Sensitivity is measured in terms of G values - represent the number of free radicals formed per 100 eV of energy absorbed per gram - Good combination would be poly(vinyl chloride) and butadiene

<table>
<thead>
<tr>
<th>Monomer</th>
<th>G</th>
<th>Polymer</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butadiene</td>
<td>Very low</td>
<td>Polybutadiene</td>
<td>2.0</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.70</td>
<td>Polystyrene</td>
<td>1.5–3</td>
</tr>
<tr>
<td>Ethylene</td>
<td>4.0</td>
<td>Polyethylene</td>
<td>6–8</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>5.0–5.6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>5.5–11.5</td>
<td>Poly(methyl methacrylate)</td>
<td>6–12</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>6.3</td>
<td>Poly(methyl acrylate)</td>
<td>6–12</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>9.6–12.0</td>
<td>Poly(vinyl acetate)</td>
<td>6–12</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>10.0</td>
<td>Poly(vinyl chloride)</td>
<td>10–15</td>
</tr>
</tbody>
</table>

*Data from Chapiro. G values refer to number of free radicals formed per 100 eV of energy absorbed per gram of material.*
• Reactions of exazoline-substituted polystyrene
  - Grafting of an axazoline-substituted polymer with a carboxy-terminated polymer (9.52)
  - Can be used for compatibilizing polymer blends, or for improving surface adhesion between polystyrene molded parts and appropriately functionalized surface coatings
Because the backbones of vinyl polymers are made up of carbon chains, chemical degradation is essentially limited to oxidation.

Satuated polymers are degraded very slowly by oxygen, and the reaction is autocatalytic:
- Can be speeded up by heat or light or by the presence of certain impurities
- Tertiary carbon atoms are more susceptible to attack: resistance to oxidation in the order of polyisobutylene > polyethylene > polypropylene
- Reaction products include water, CO$_2$, CO, hydrogen, and alcohols
- Crosslinking always accompanies degradation
- Decomposition of initially formed hydroperoxide groups is responsible for chain scission (9.53)

Unsaturated polymers undergo oxidative degradation much more rapidly:
- Allylic carbon atoms are most sensitive to attack (resonance-stabilized radicals)
- Also very susceptible to attack by ozone
Thermal degradation

- Three types of thermal degradation: nonchain scission, random chain scission, depropagation
- Nonchain scission refers to reactions involving pendant groups that do not break the polymer backbone
  - Dehydrochlorination of poly(vinyl chloride) (9.11)
  - Elimination of acid from poly(vinyl acetate) (9.54)
  - Elimination of alkene from poly(alkyl acrylate)s (9.55)
Thermal degradation

- Nonchain scission has been used to solve the problems of polyacetylene’s intractability
  - Involves synthesis of a stable, tractable precursor polymer that can be purified and fabricated, then converted thermally to polyacetylene
  - Involves the tricyclic monomer (7), which undergoes metathesis polymerization to precursor polymer (8) (9.56)
  - Thermal degradation of films yields coherent films of polyacetylene, referred to as the “Durham route”
Thermal degradation

- Ring opening of the strained bicyclobutane rings of precursor polymer 9 yields polyacetylene (9.58) without the necessity of an elimination reaction

\[ \text{bicyclobutane} \xrightarrow{\text{Hg}^2+} \text{polyacetylene} \]  
(9.58)

- Random chain scission results from hemolytic bond-cleavage reactions at weak points
  - Complex mixtures of degradation products are formed, as in (9.59): alkane, 1-alkene (majority), \( \alpha,\omega \)-dialkene

\[ \text{alkane} \rightarrow 1\text{-alkene} + \alpha,\omega\text{-dialkene} \]  
(9.59)

- Followed by breakdown pattern shown in Scheme 9.3

![Scheme 9.3](image-url)
Thermal degradation

- Depropagation, or depolymerization (unzipping) to give monomer occurs mainly with polymers prepared from 1,1-disubstituted monomers
  - Poly(methyl methacrylate) appears to begin unzipping primarily at the chain ends, whereas poly(a-methylstyrene) does so at random sites along the chain
  - In both cases tertiary radicals are formed with each depropagating step (9.60)
Degradation by radiation

- Radiation may cause both crosslinking or degradation
- Ultraviolet or visible light causes 1,1-disubstituted polymers to degrade to monomer exclusively at elevated temperatures, whereas crosslinking and chain scission reactions predominate at room temperatures
- All vinyl polymers tend to degrade under very high dosages of radiation