

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

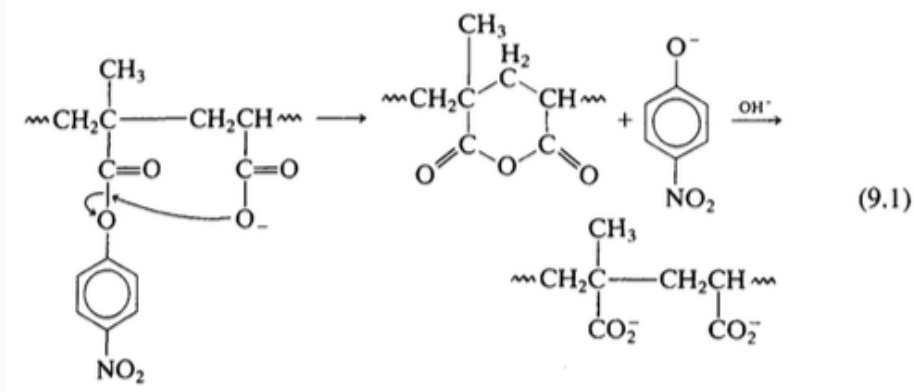
- Applications of chemical modifications
 - Ion-exchange resins
 - Polymeric reagents and polymer-bound catalysts
 - Polymeric supports for chemical reactions
 - Degradable polymers to address medical, agricultural, or environmental concerns
 - Flame-retardant polymers
 - Surface, treatments to improve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

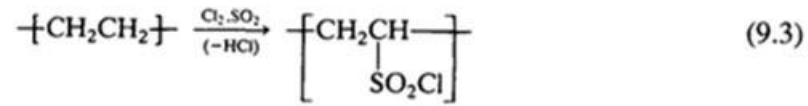
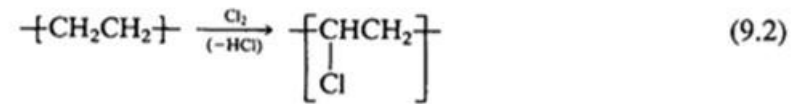
Introduction

- 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

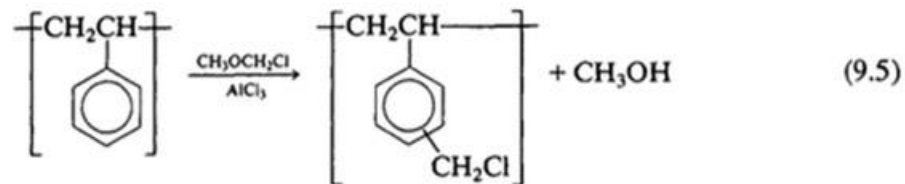
Introduction of new functional groups

- Fluorination, to improve solvent barrier properties

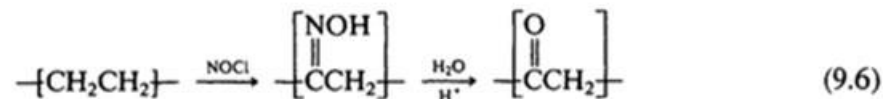


- Aromatic substitution reactions (nitration, sulfonation, chlorosulfonation, etc.)
 - occur readily on polystyrene
 - useful for manufacturing ion-exchange resins
 - useful for introducing sites for crosslinking or grafting

- Chlorometylation

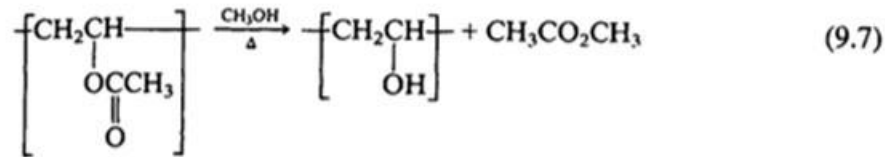


- Introduction of ketone groups *via* the intermediate oxime



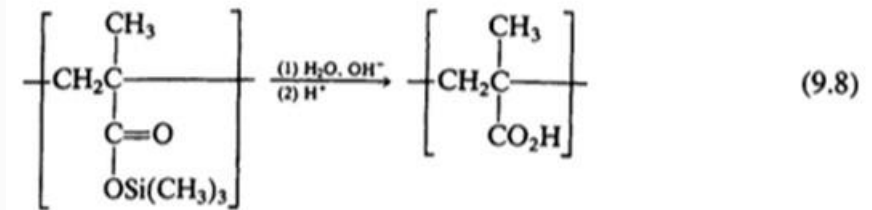
Conversion of functional groups

- 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)

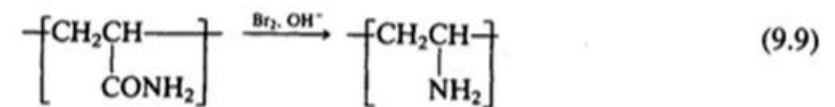


- Examples of syntheses of polymers

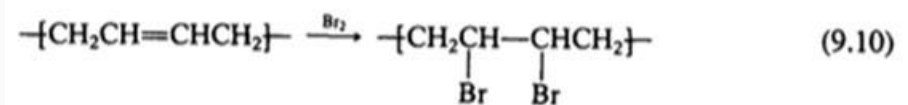
- Saponification of isotactic or syndiotactic poly(trimethylsilyl methacrylate) to yield isotactic or syndiotactic poly(methacrylic acid)



- Hofmann degradation of polyacrylamide to give poly(vinyl amine)



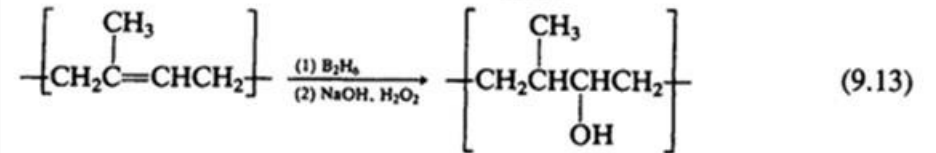
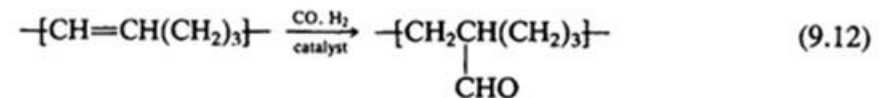
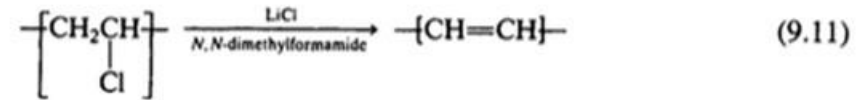
- Synthesis of “head-to-head poly(vinyl bromide)” by controlled bromination of 1,4-polybutadiene



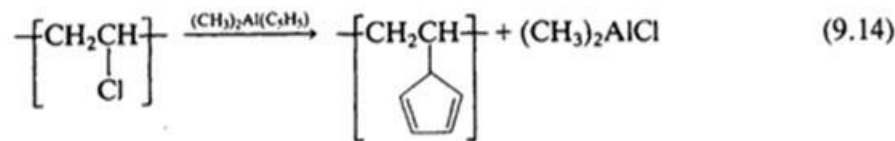
Conversion of functional groups

- Other types of *classical* functional group conversions

- dehydrochlorination of poly(vinyl chloride)
- hydroformylation of polypentenamer
- hydroboration of 1,4-polyisoprene

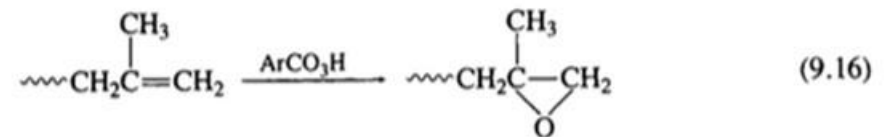
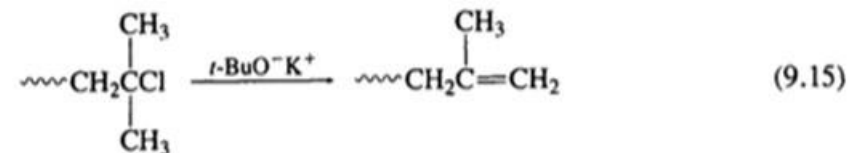


- Conversion of a fraction of the chloro groups of poly(vinyl chloride) to cyclopentadienyl



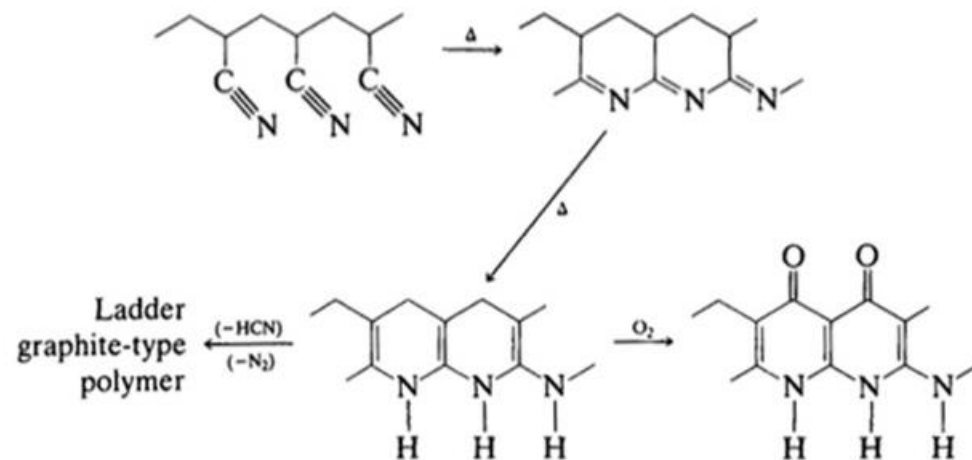
- Converting the end groups of telechelic polymers

- Dehydrochlorination of chlorine-terminated polyisobutylene
- Subsequent epoxidation



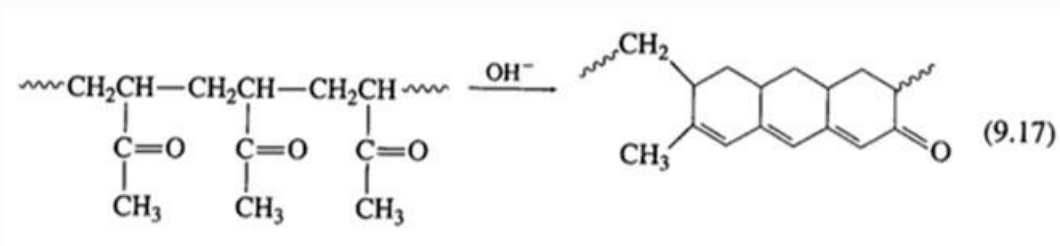
Ring-forming reactions

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

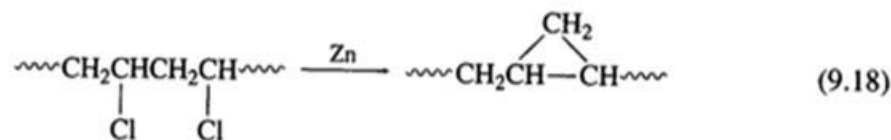


SCHEME 9.1. Reactions involved in pyrolysis of polyacrylonitrile to form carbon fiber.

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

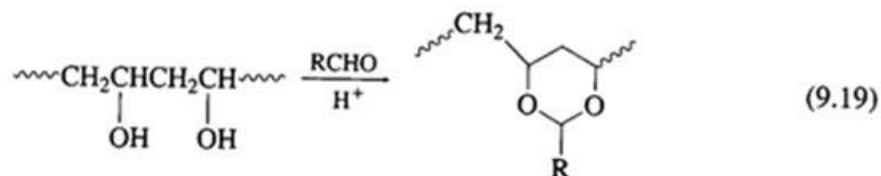


- Nonladder structures: dechlorination of poly(vinyl chloride)

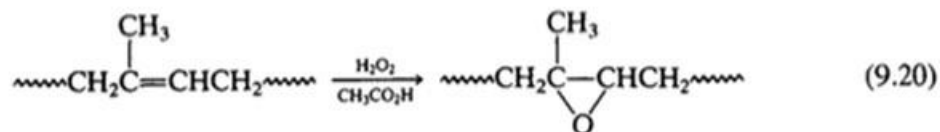


Ring-forming reactions

- 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 ($\sim 40\%$) for better adhesion to glass

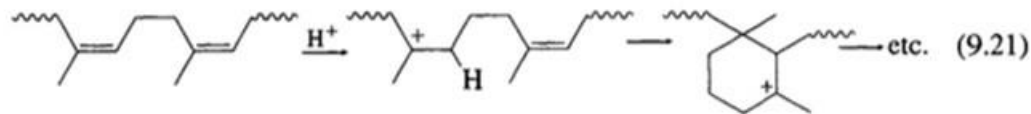


- Commercially important cyclization is epoxidation of natural rubber, to increase oil resistance and decrease gas permeability



- 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)

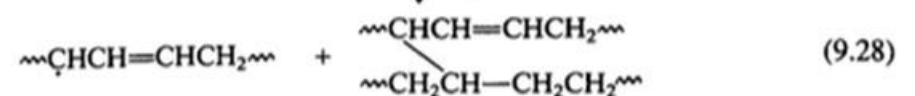
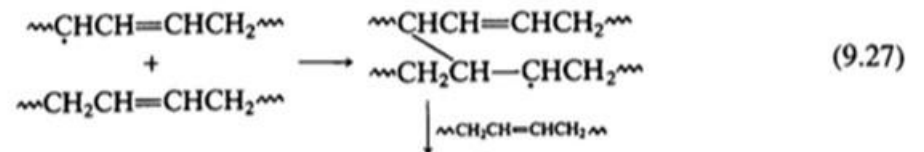
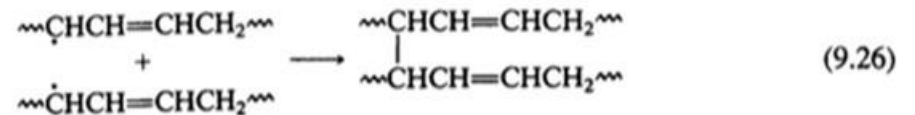
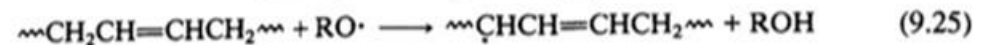
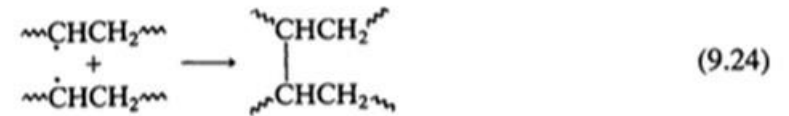


Crosslinking

- 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)

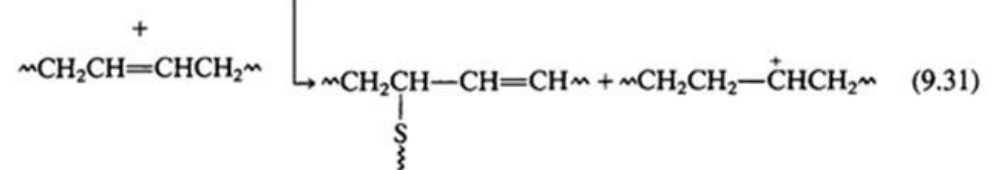
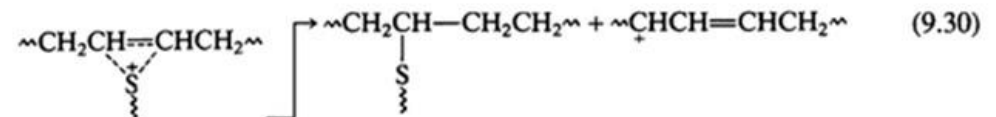
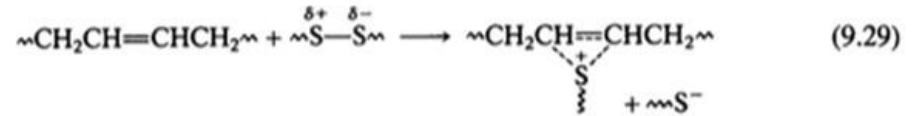
Vulcanization

- 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)

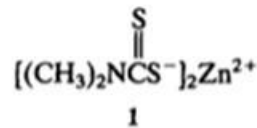


Vulcanization

- 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)

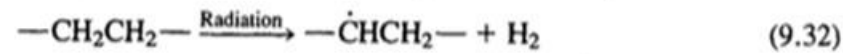


Radiation crosslinking

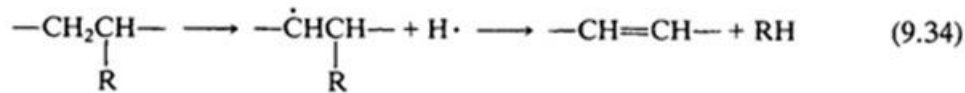
- When vinyl polymers are subjected to radiation, both crosslinking and degradation occur simultaneously
 - Degradation predominates with high doses of radiation
 - With low doses the polymer structure determines which will be the major reaction
 - Disubstituted polymers tend to undergo chain scission
 - 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)

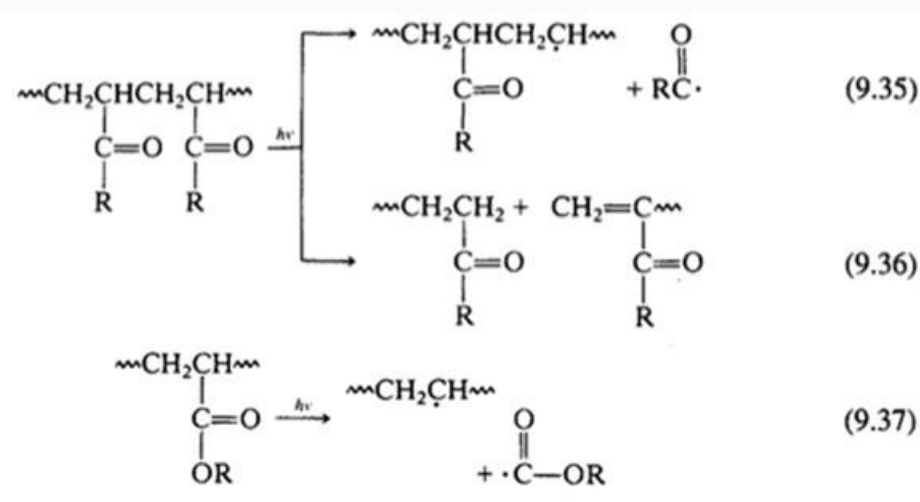


Photochemical crosslinking

- 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

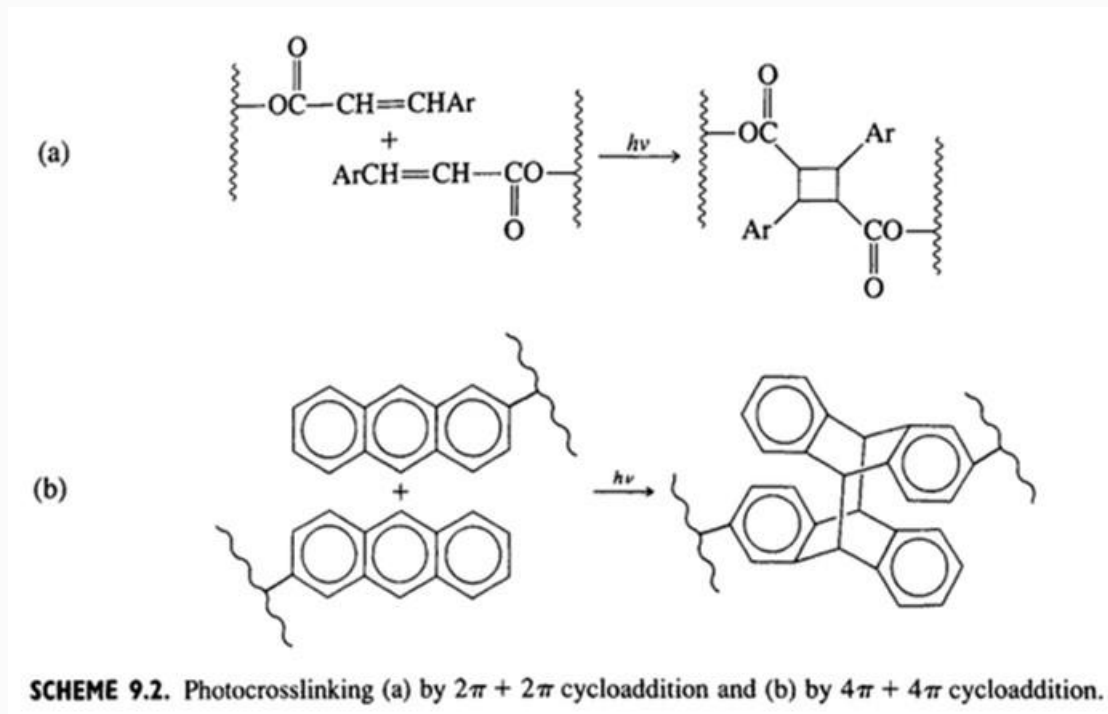
Photochemical crosslinking

- 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 α -cleavage of the excited polymer (9.35) or by chain cleavage (9.36)
 - Poly(vinyl ester)s undergo analogous α -cleavage reactions (9.37) with subsequent crosslinking



Photochemical crosslinking

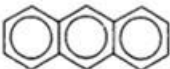
- Incorporating groups that undergo either photocycloaddition reactions or light-initiated polymerization
 - $2\pi + 2\pi$ cycloaddition occurs to give cyclobutane crosslinks (9.2a)
 - With anthracene, cycloaddition is $4\pi + 4\pi$

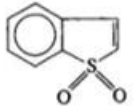
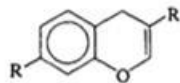
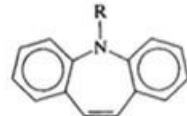
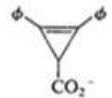



Photochemical crosslinking

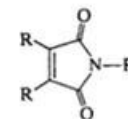
- Group used to effect photocrosslinking

TABLE 9.1. Groups Used to Effect Photocrosslinking⁵¹⁻⁵⁸

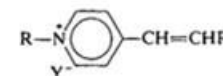
Type	Structure
Alkyne	$R-C\equiv C-R$
Anthracene	 continued

Type	Structure
Benzothiophene dioxide	
Chalcone	$ArCH=CHC(=O)Ar$
Cinnamate	$ArCH=CHCO_2R$
Coumarin	
Dibenz[b, f]azepine	
Diphenylcyclopropanecarboxylate	
Episulfide	

Maleimide (R=H, CH₃, Cl)



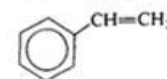
Stilbazole



Stilbene



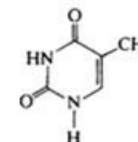
Styrene



1,2,3-Thiadiazole

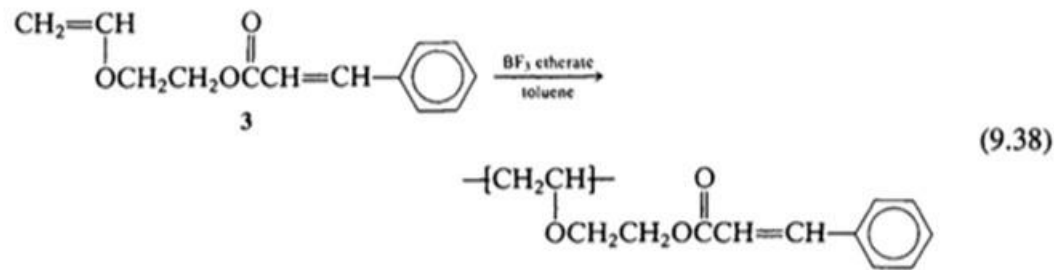


Thymine

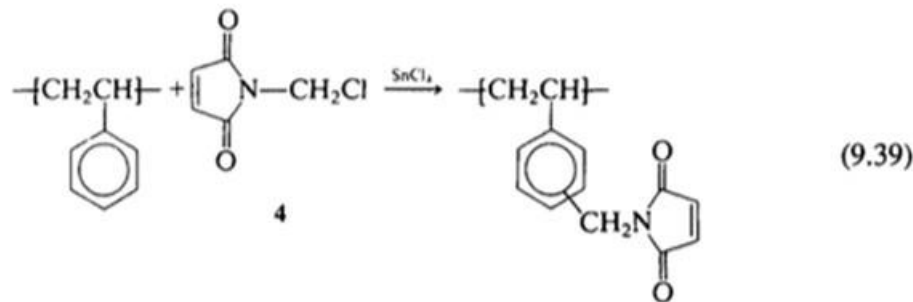


Photochemical crosslinking

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

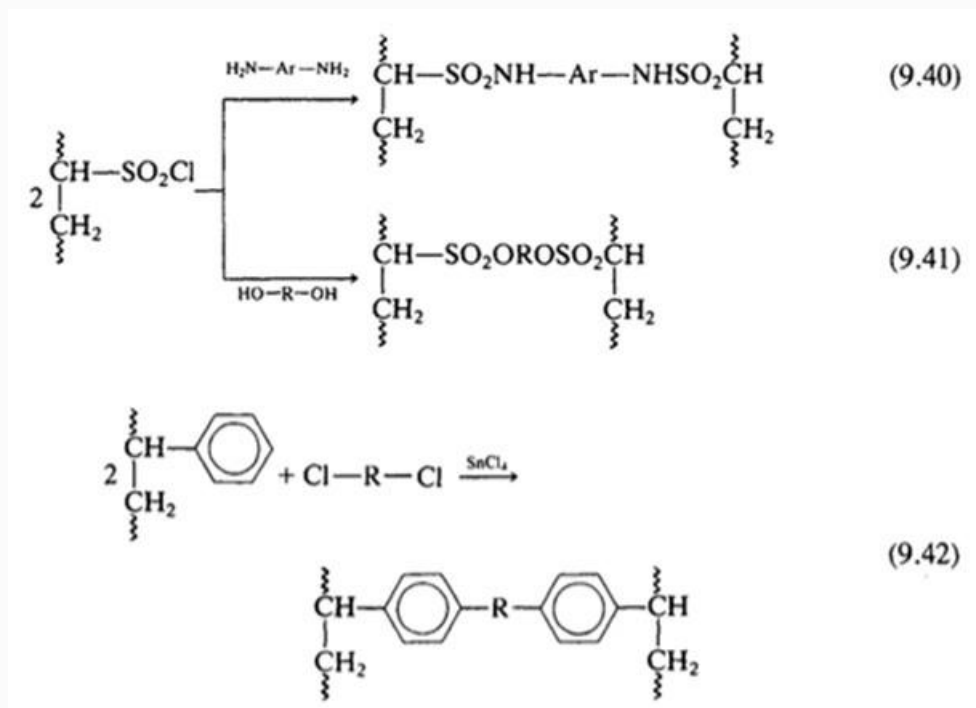


- Alternatively, the group can be added to preformed polymer
 - Friedel-Crafts alkylation of polystyrene with N-chloromethylmaleimide (**4**) (9.39)



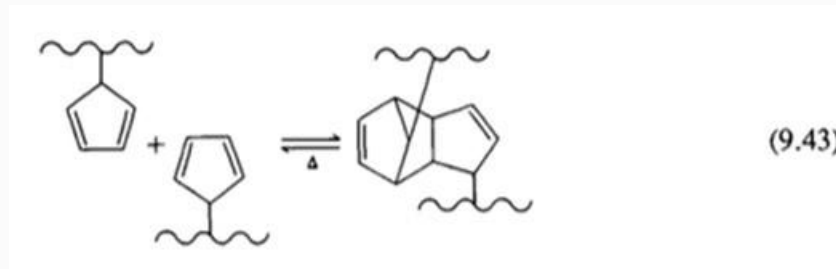
Crosslinking thru labile functional groups

- 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)



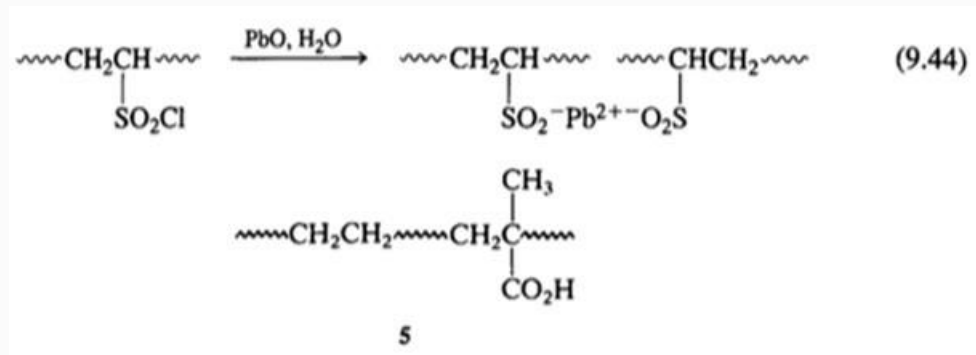
Crosslinking thru labile functional groups

- 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



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*

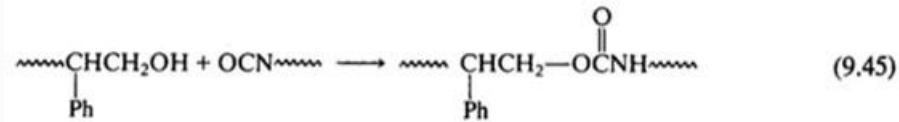


- Interesting properties of *ionomers*
 - Introduction of ions causes disordering of the semicrystalline structure, which makes the polymer transparent
 - Crosslinking gives the polymer elastomeric properties, but it can still be molded at elevated temperatures
 - Increased polarity improves adhesion: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

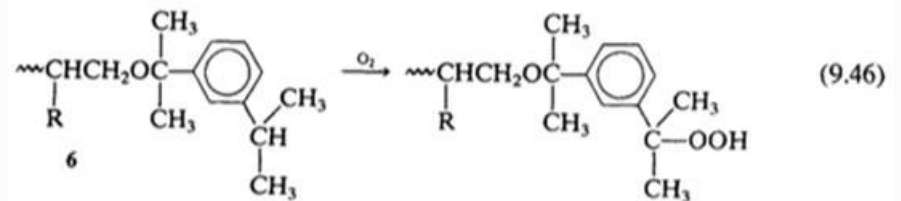
Block & graft copolymer formation

- Block copolymers

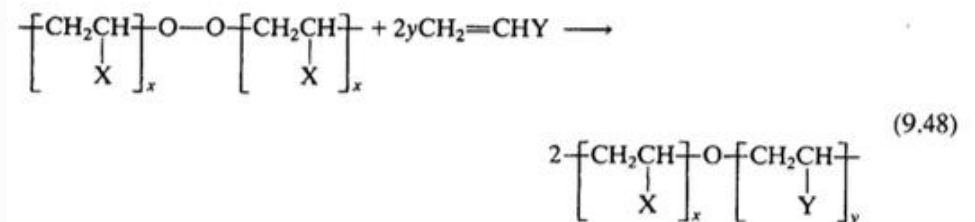
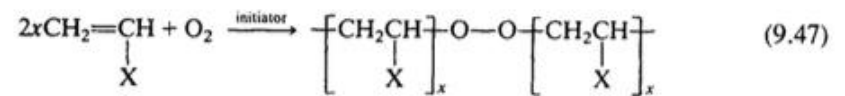
- Polymer containing functional end groups: subsequent reaction with isocyanate-terminated polymer yields an AB block copolymer via urethane linkages (9.45)



- 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)

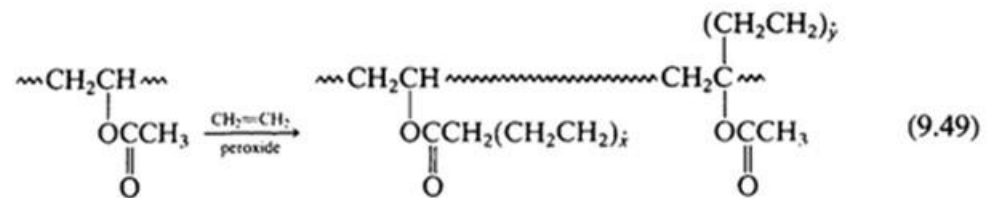


Block & graft copolymer formation

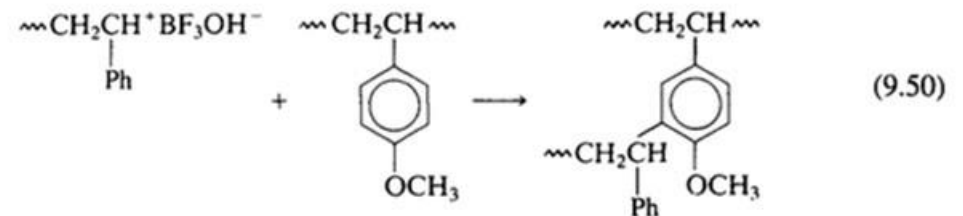
- Three general methods of preparing graft copolymers
 - A monomer is polymerized in the presence of a polymer with branching resulting from chain transfer
 - A monomer is polymerized in the presence of a polymer having reactive functional groups or positions that are capable of being activated
 - Two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

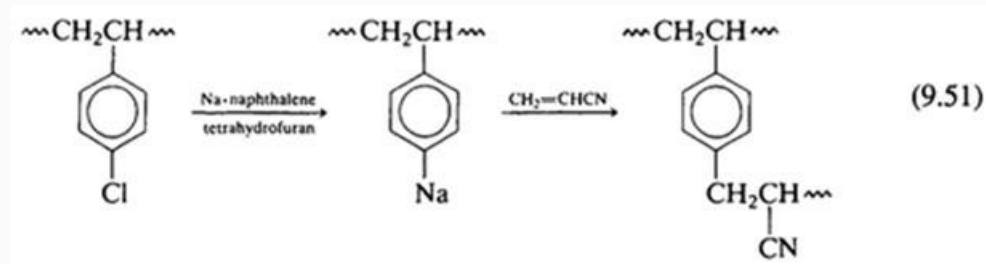


- Cationic chain transfer grafting
 - When styrene is polymerized with BF_3 in the presence of poly(*p*-methoxystyrene) (9.50)
 - The activated benzene rings undergo Friedel-Crafts attack



Block & graft copolymer formation

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



- 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

Block & graft copolymer formation

- 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

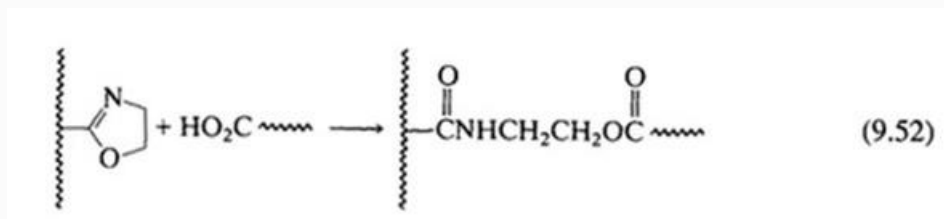
TABLE 9.2. Approximate *G* Values of Monomers and Polymers^a

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

^aData from Chapiro.⁷² *G* values refer to number of free radicals formed per 100 eV of energy absorbed per gram of material.

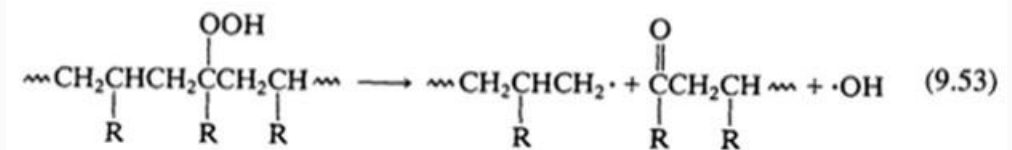
Block & graft copolymer formation

- Reactions of oxazoline-substituted polystyrene
 - Grafting of an oxazoline-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



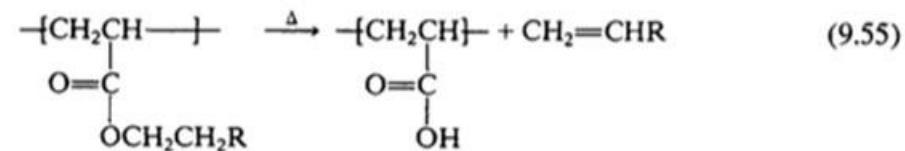
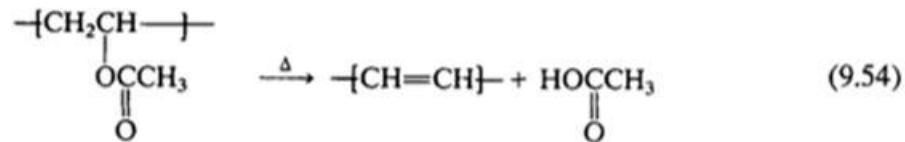
Chemical degradation

- Because the backbones of vinyl polymers are made up of carbon chains, chemical degradation is essentially limited to oxidation
- Saturated 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, CO₂, 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



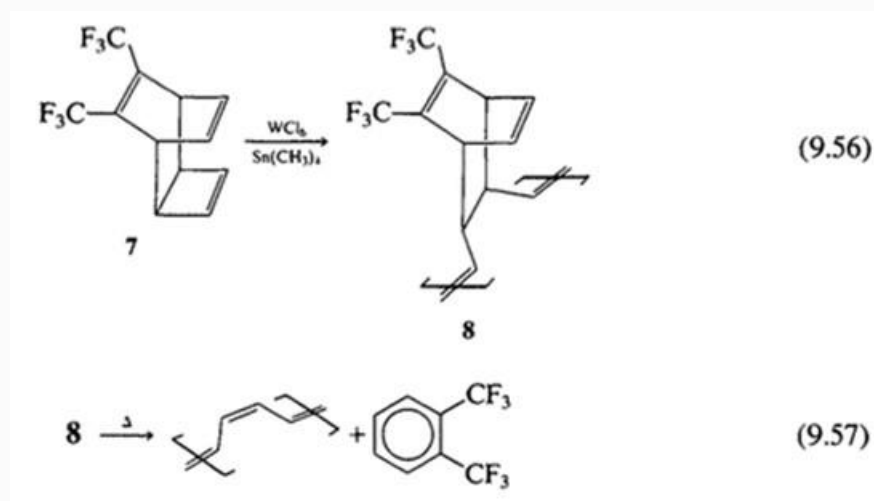
Thermal degradation

- 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)



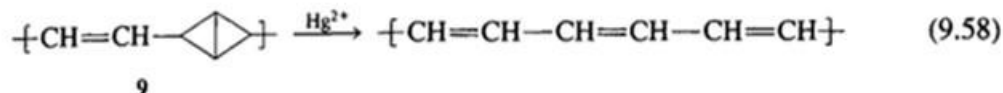
Thermal degradation

- 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"

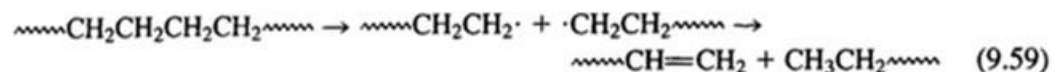


Thermal degradation

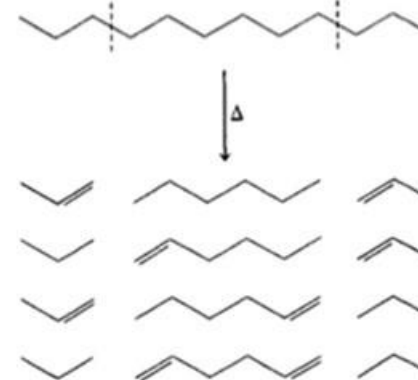
- Ring opening of the strained bicyclobutane rings of precursor polymer **9** yields polyacetylene (9.58) without the necessity of an elimination reaction



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



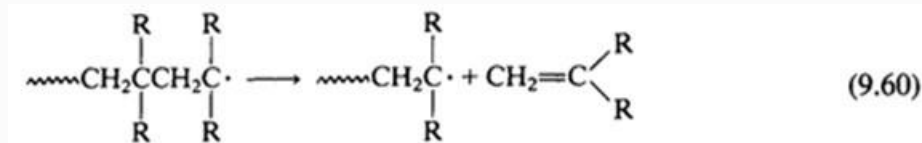
- Followed by breakdown pattern shown in Scheme 9.3



SCHEME 9.3. Random chain scission of polyethylene.

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(α -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