Organic Polymer Chemistry

Focus on these areas:

1) Know Definitions

2) Know the Organic Reactions

3) Be able to recognize the general class of polymers (polyethylene polycarbonates, etc.)

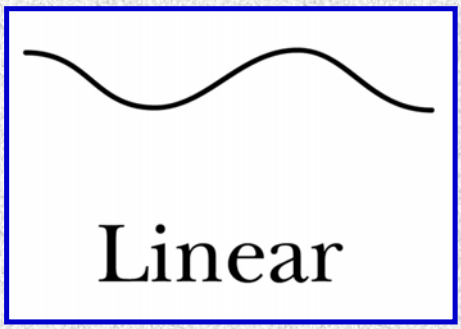
Organic Polymer Chemistry

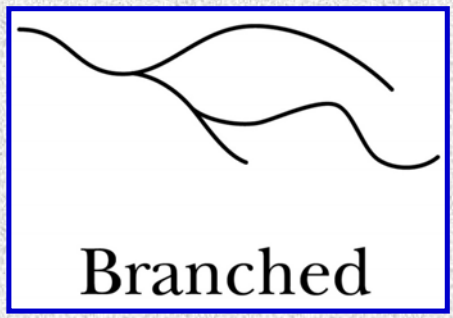
- **Polymer:** from the Greek, poly + meros, many parts
  - any long-chain molecule synthesized by bonding together single parts called monomers
- **Monomer:** from the Greek, mono + meros, single part
  - the simplest nonredundant unit from which a polymer is synthesized
- **Plastic:** a polymer that can be molded when hot and retains its shape when cooled

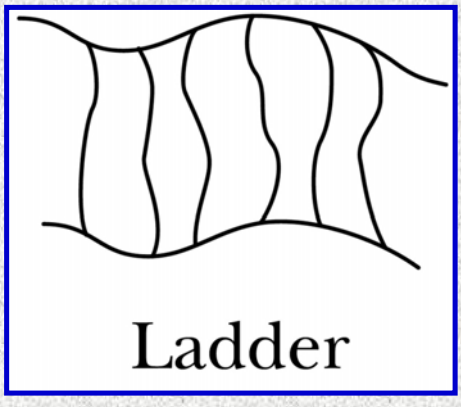
Organic Polymer Chemistry

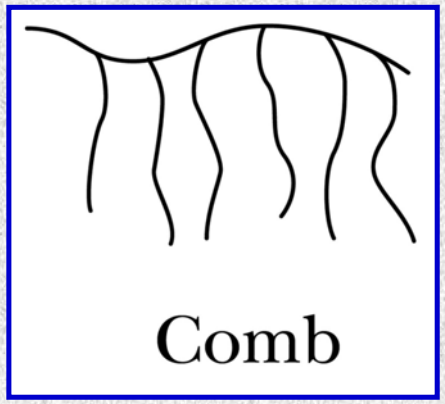
- **Thermoplastic:** a polymer that can be melted and molded into a shape that is retained when it is cooled
- **Thermoset plastic:** a polymer that can be molded when it is first prepared but, once it is cooled, (sometime called "curing") hardens irreversibly and cannot be remelted

Polymer "Architecture"

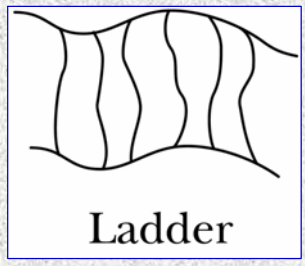


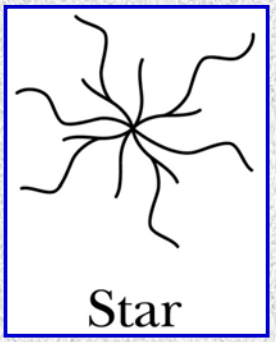




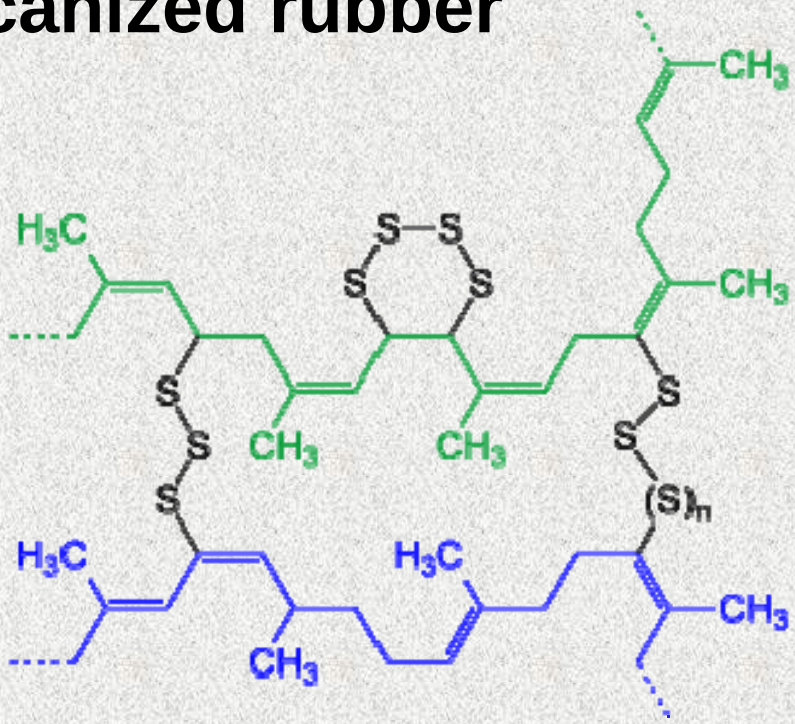


Polymer "Architecture"





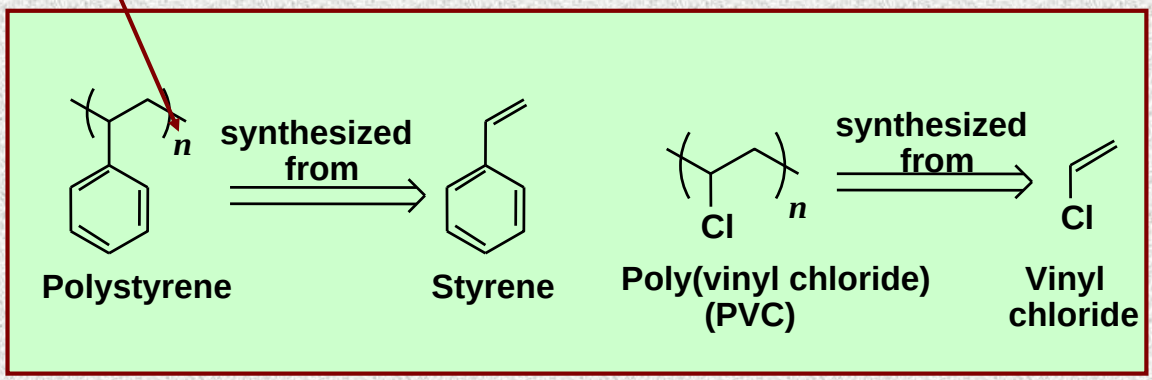
vulcanized rubber



Notation & Nomenclature

Show the structure by placing parenthesis around the repeat unit

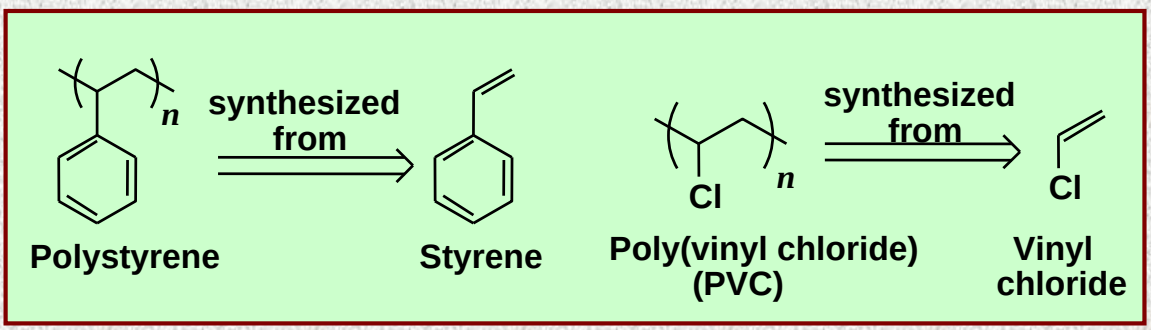
– *n* = average degree of polymerization



Notation & Nomenclature

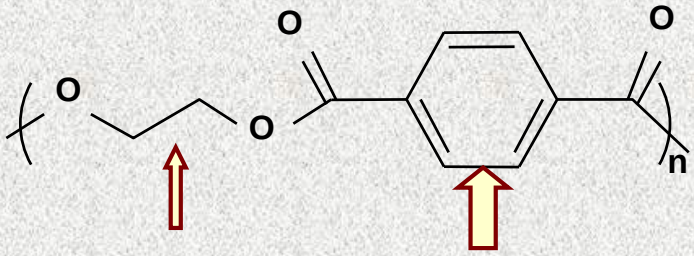
To name a polymer, prefix poly to the name of the monomer from which the it is derived

– for more complex monomers or where the name of the monomer is two words, enclose the name of the monomer in parens, for example poly(vinyl chloride)

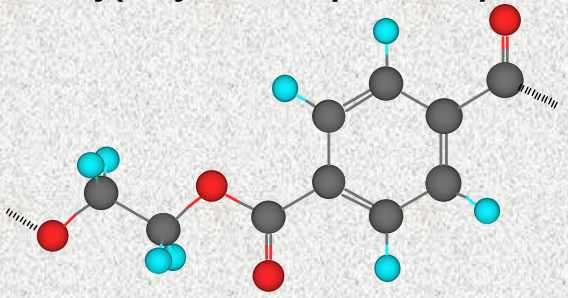


Morphology

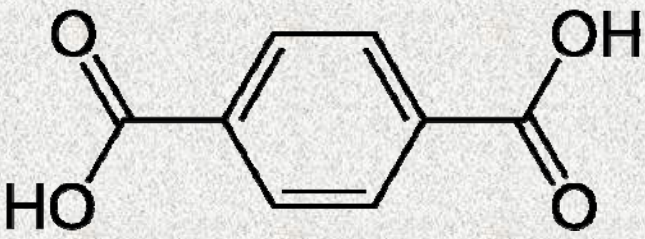
– Example: poly(ethylene terephthalate), abbreviated PET or PETE, can be made with % crystalline domains ranging from 0% to 55%



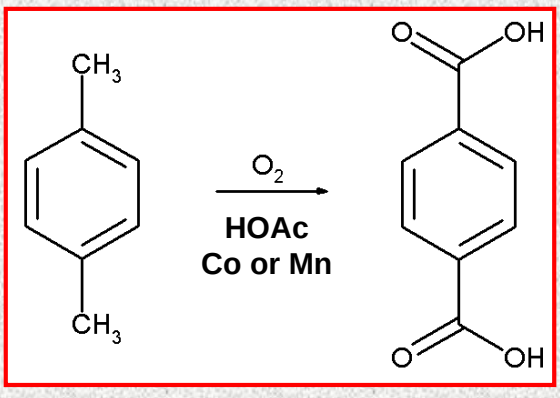
Poly(ethylene terephthalate)



Terephthalic acid



Manufacture:



Morphology

- Completely amorphous PET is formed by cooling the melt quickly
  - –PET with a low degree of crystallinity is used for plastic beverage bottles

Morphology

- By prolonging cooling time, more molecular diffusion occurs and crystalline domains form as the chains become more ordered
  - –PET with a high degree of crystallinity can be drawn into textile fibers and tire cords

Step-Growth Polymers

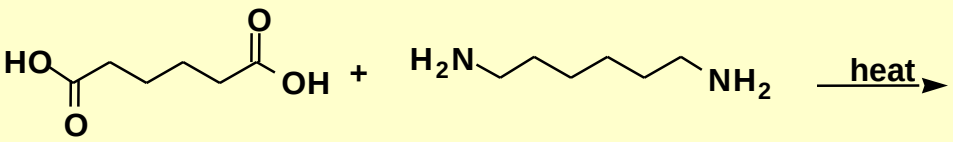
Step-growth or condensation polymerization: polymerization in which chain growth occurs in stepwise manner between difunctional monomers (there is often a side product)

There are five types of step-growth polymers:

1. **polyamides**
2. **polyesters**
3. **polycarbonates**
4. **polyurethanes**
5. **epoxy resins**

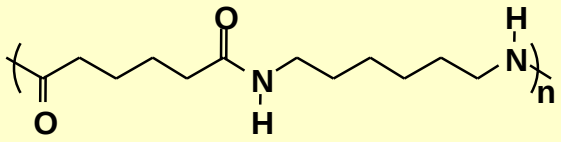
Polyamides

- Nylon 66 (from two six-carbon monomers)



Hexanedioic acid (Adipic acid)

1,6-Hexanediamine (Hexamethylenediamine)

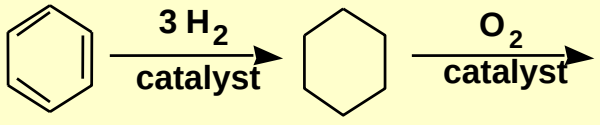


Nylon 66

– during fabrication, nylon fibers are cold-drawn to about 4 times their original length, which increases crystallinity, tensile strength, and stiffness

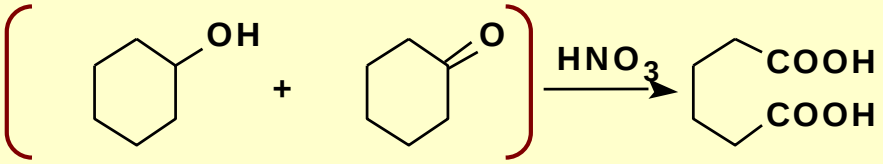
Polyamides

– the raw material base for the production of nylon 66 is benzene, which is derived from cracking and refining of petroleum



Benzene

Cyclohexane



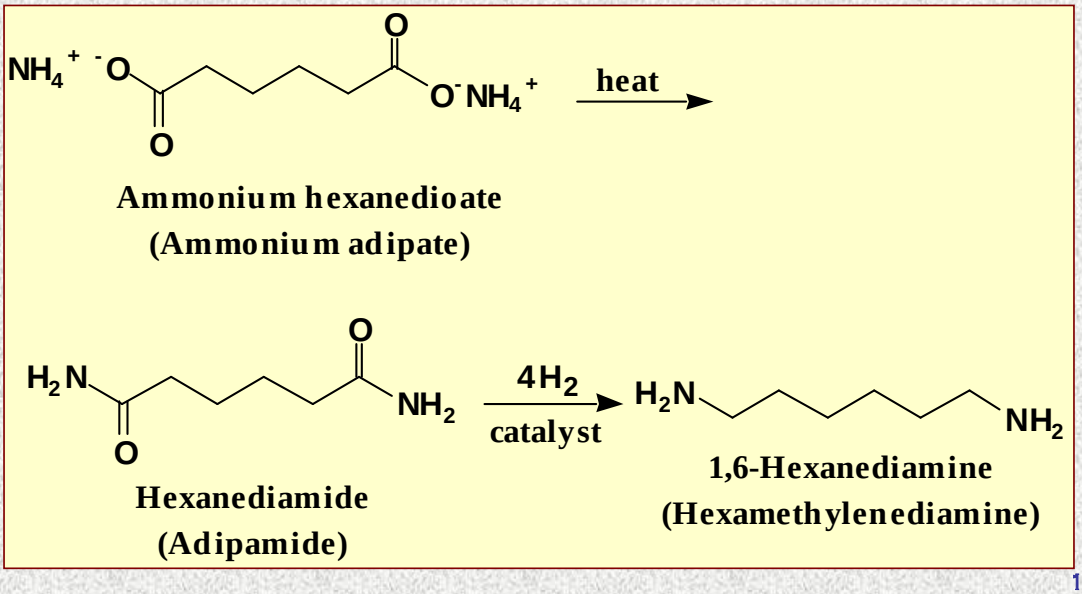
Cyclohexanol

Cyclohexanone

Hexanedioic acid (Adipic acid)

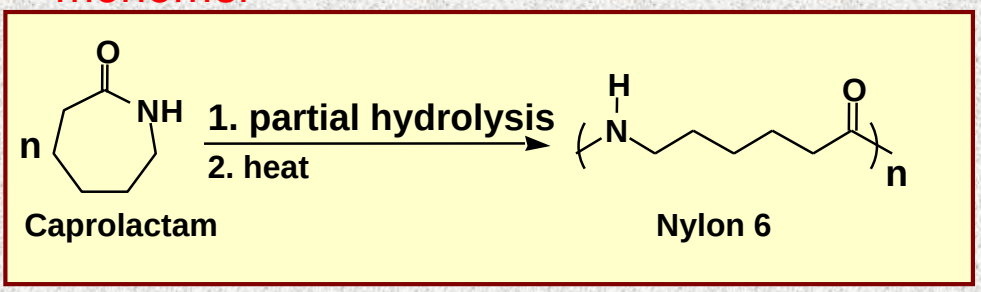
Polyamides

– adipic acid is in turn the starting material for the synthesis of hexamethylenediamine



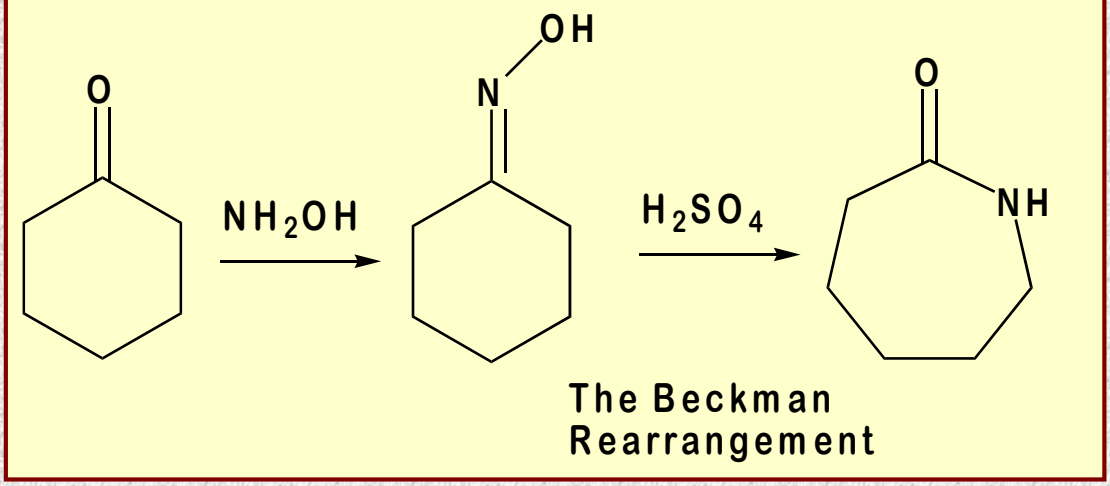
Polyamides

- Nylons are a family of polymers, the two most widely used of which are nylon 66 and nylon 6
  - nylon 6 is synthesized from a six-carbon monomer



  - nylon 6 is fabricated into fibers, brush bristles, high-impact moldings, and tire cords

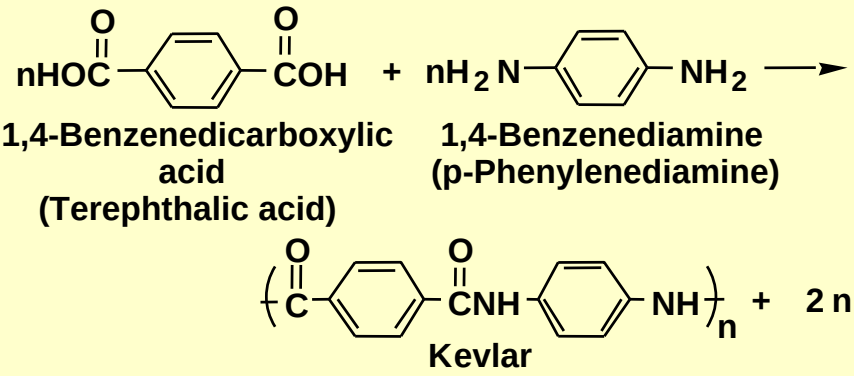
Manufacture of Caprolactam



The Beckman Rearrangement

Polyamides

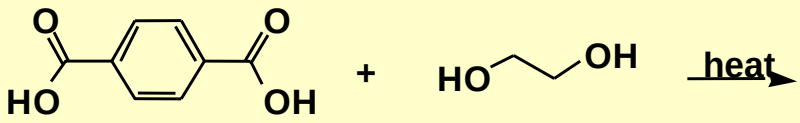
- **Kevlar** is a polyaromatic amide (aramid)



  - cables of Kevlar are as strong as cables of steel, but only about 20% the weight
  - Kevlar fabric is used for bulletproof vests, jackets, and raincoats

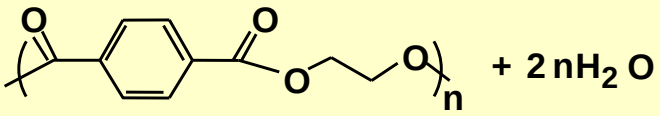
Polyesters

- Poly(ethylene terephthalate), abbreviated PET or PETE, is fabricated into Dacron fibers, Mylar films, and plastic beverage containers



1,4-Benzenedicarboxylic acid (Terephthalic acid)

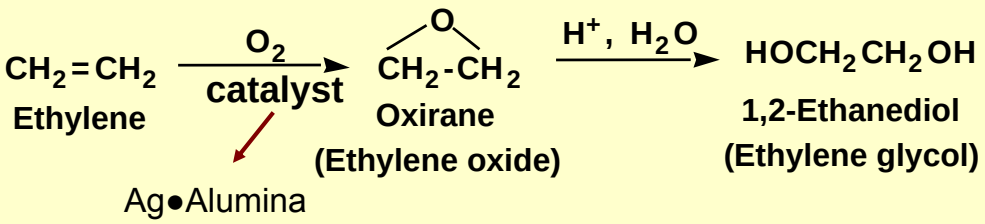
1,2-Ethanediol (Ethylene glycol)



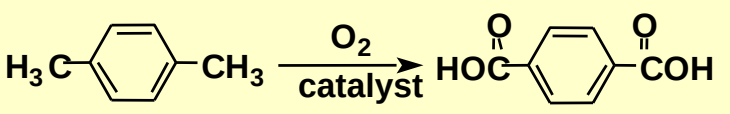
Poly(ethylene terephthalate) (Dacron, Mylar)

Polyesters

– ethylene glycol is obtained by air oxidation of ethylene followed by hydrolysis to the glycol



– terephthalic acid is obtained by catalyzed air oxidation of petroleum-derived *p*-xylene

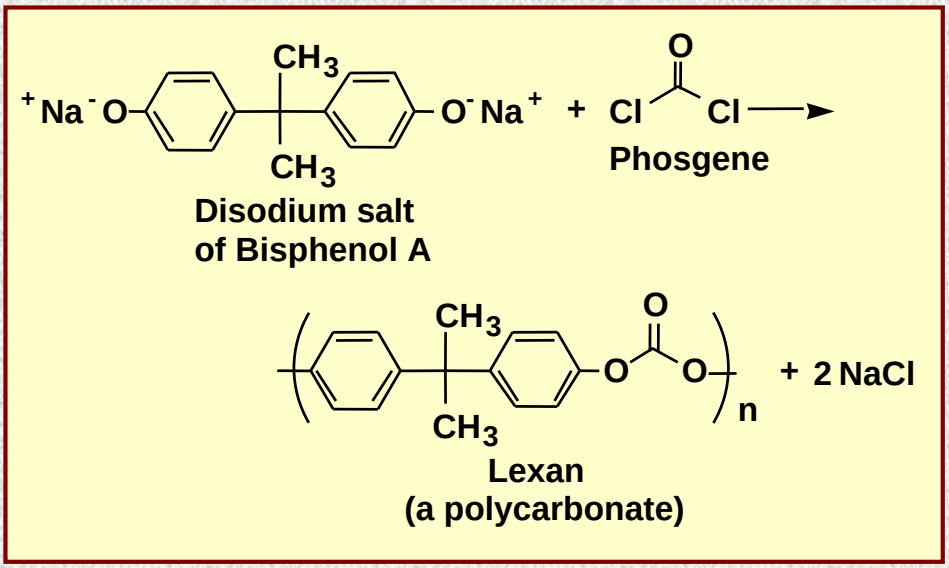


p-Xylene

Terephthalic acid

Polycarbonates

– to make Lexan, an aqueous solution of the sodium salt of bisphenol A is brought into contact with a solution of phosgene in CH_2Cl_2 in the presence of a phase-transfer catalyst

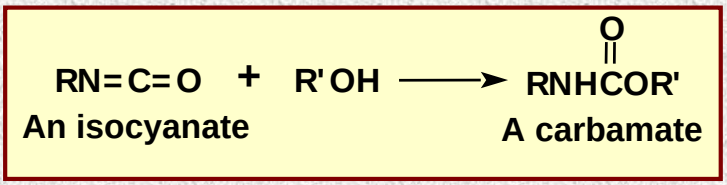


Polycarbonates

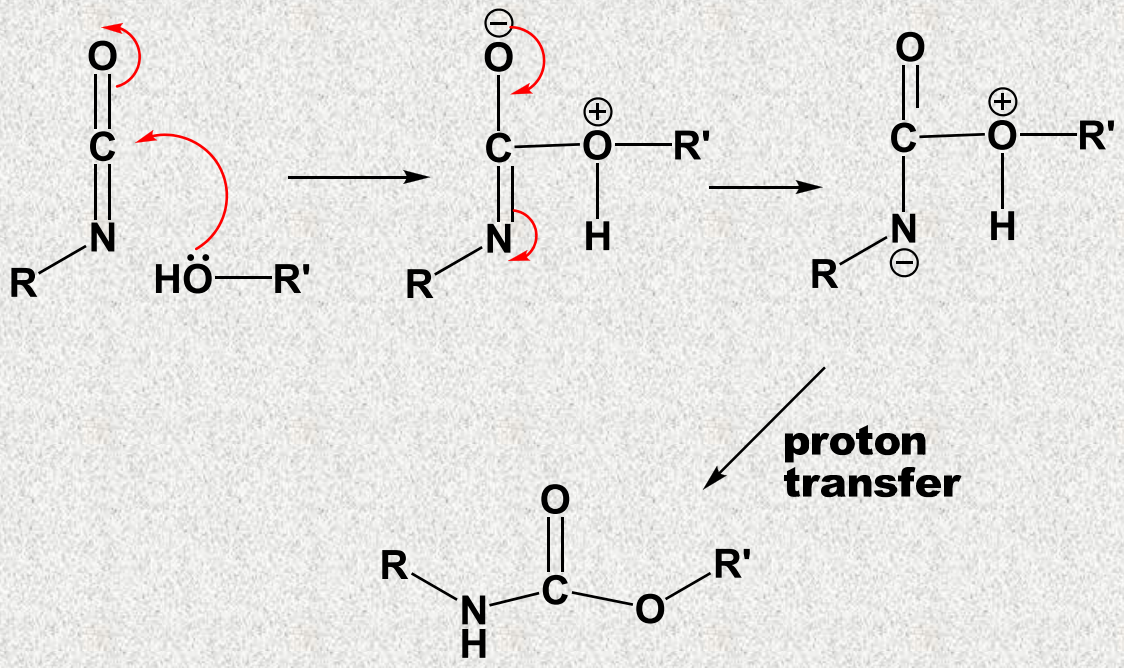
- **Lexan** is a tough transparent polymer with high impact and tensile strengths and retains its shape over a wide temperature range
  – it is used in sporting equipment, such as bicycle, football, and snowmobile helmets as well as hockey and baseball catcher's masks
  – it is also used in the manufacture of safety and unbreakable windows

Polyurethanes

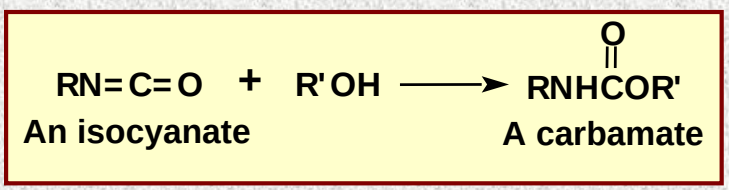
- A **urethane,** or **carbamate**, is an ester of carbamic acid, H_2NCOOH
  - they are most commonly prepared by treatment of an isocyanate with an alcohol



Mechanism of Urethane Formations



Polyurethanes

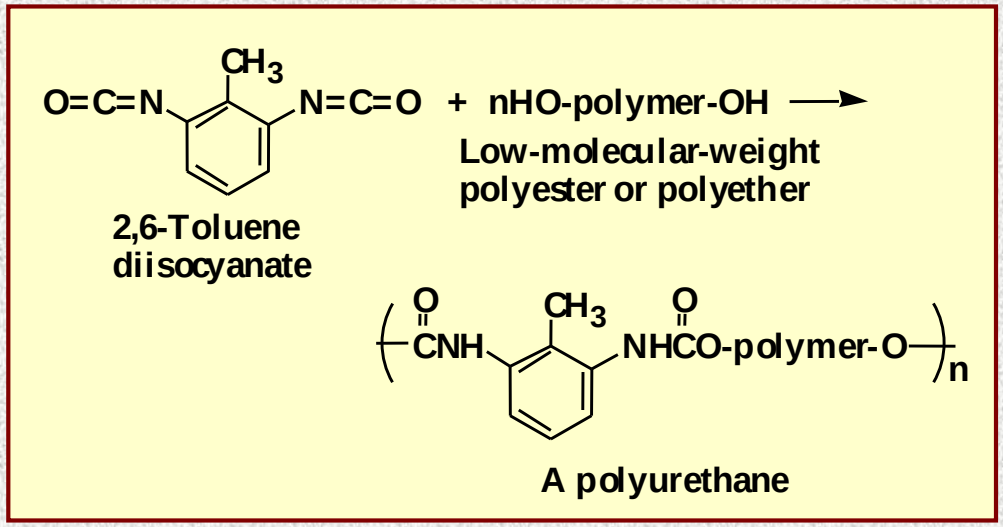


Polyurethanes consist of flexible polyester or polyether units (blocks) alternating with rigid urethane units (blocks)

– the rigid urethane blocks are derived from a diisocyanate

Polyurethanes

– the more flexible blocks are derived from low MW polyesters or polyethers with -OH groups at the ends of each polymer chain

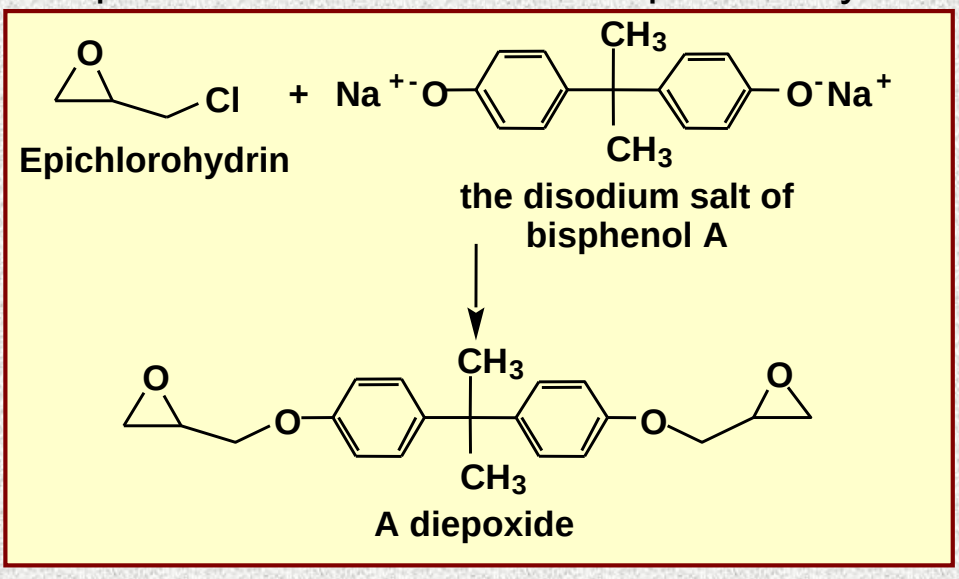


Epoxy Resins

- **Epoxy resins** are materials prepared by a polymerization in which one monomer contains at least two epoxy groups
  - –epoxy resins are produced in forms ranging from low-viscosity liquids to high-melting solids

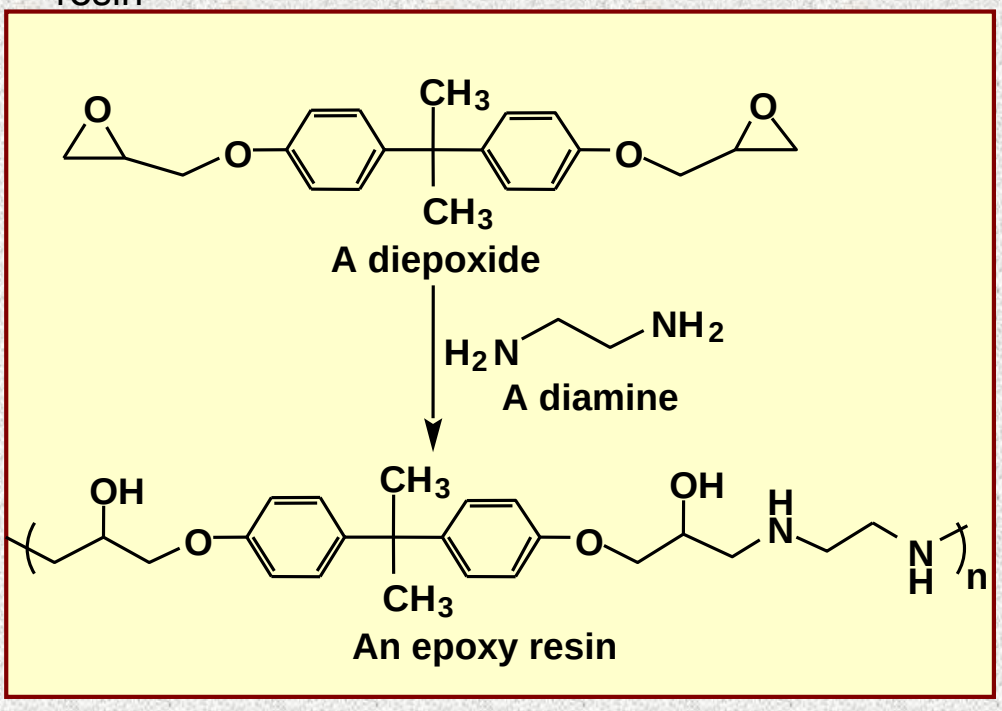
Epoxy Resins

– the most widely used epoxide monomer is the diepoxide prepared by treating 1 mole of bisphenol A with 2 moles of epichlorohydrin

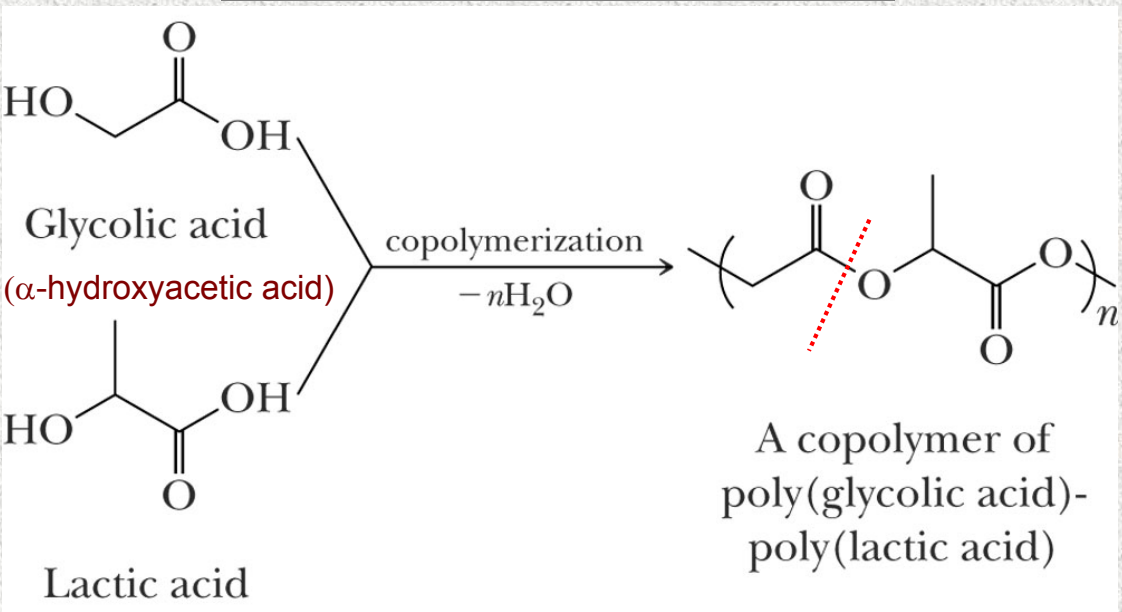


Epoxy Resins

– treatment of the diepoxide with a diamine gives the resin



"Dissolving" Stitches Lactomer®

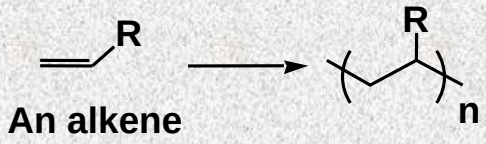


Chain-Growth Polymers

- **Chain-growth polymerization:** a polymerization that involves sequential addition reactions, either to unsaturated monomers or to monomers possessing other reactive functional groups
- Reactive intermediates in chain-growth polymerizations include radicals, carbanions, carbocations, and organometallic complexes

Chain-Growth Polymers

- The focus in this section is chain-growth polymerizations of ethylene and substituted ethylenes

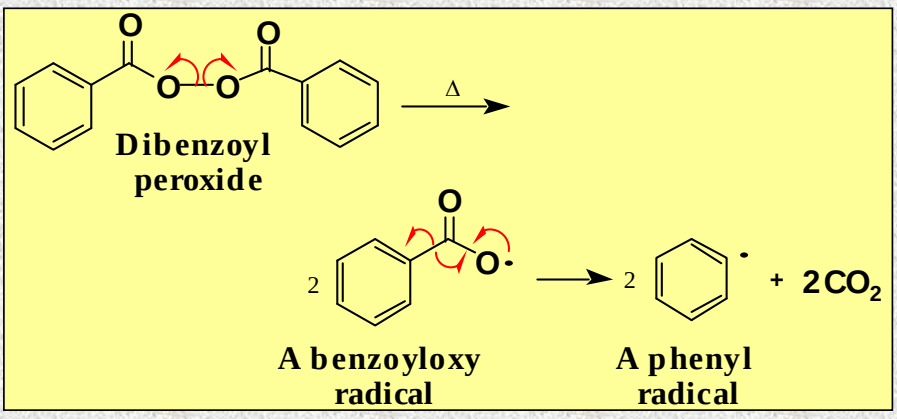


An alkene

  - on the following two slides are several important polymers derived from ethylene and substituted ethylenes, along with their most important uses

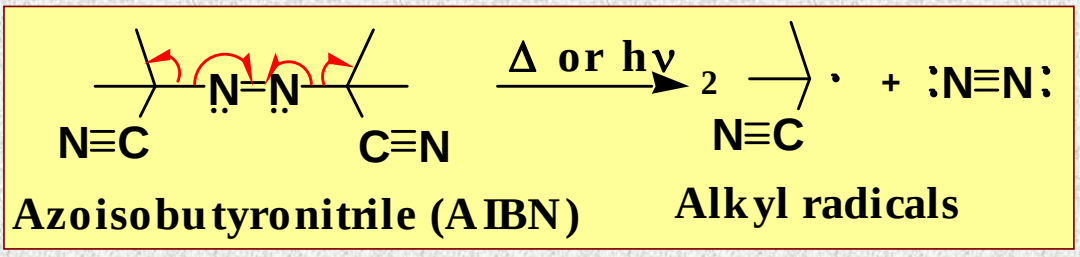
Radical Chain-Growth

- Among the initiators used for radical chain-growth polymerization are diacyl peroxides, which decompose on mild heating



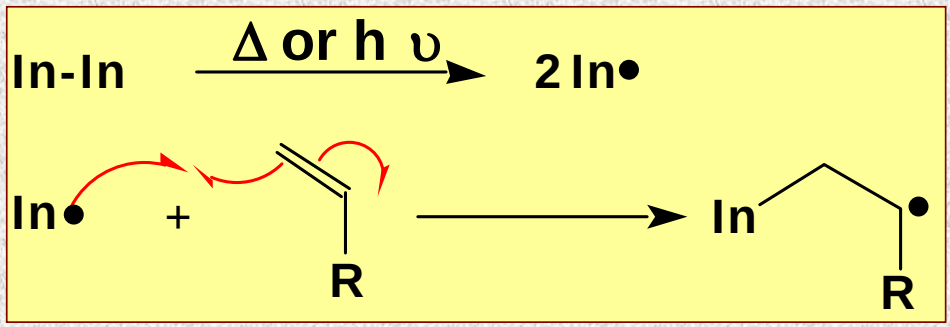
Radical Chain-Growth

- Another common class of initiators are azo compounds, which also decompose on mild heating or with absorption of UV light

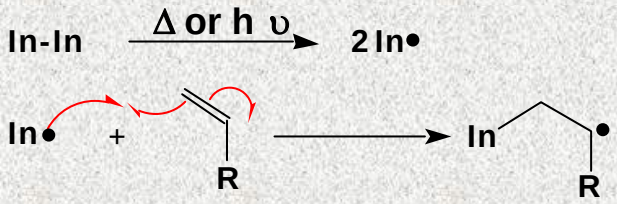


Radical polymerization of a substituted ethylene

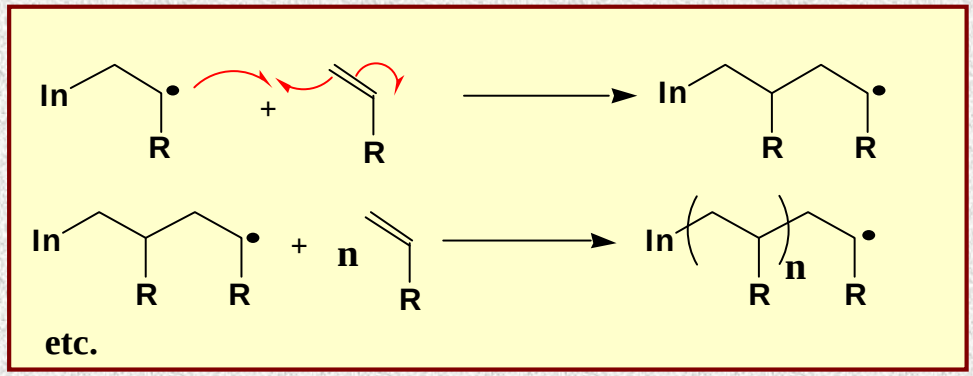
chain initiation (free radical addition to an alkene)



- Radical polymerization of a substituted ethylene
  - chain initiation

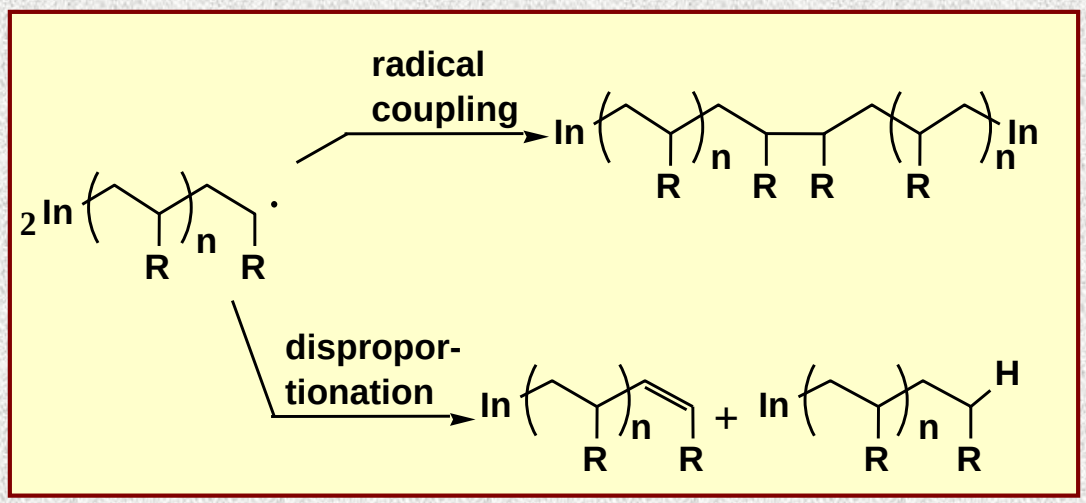


  - **chain propagation**

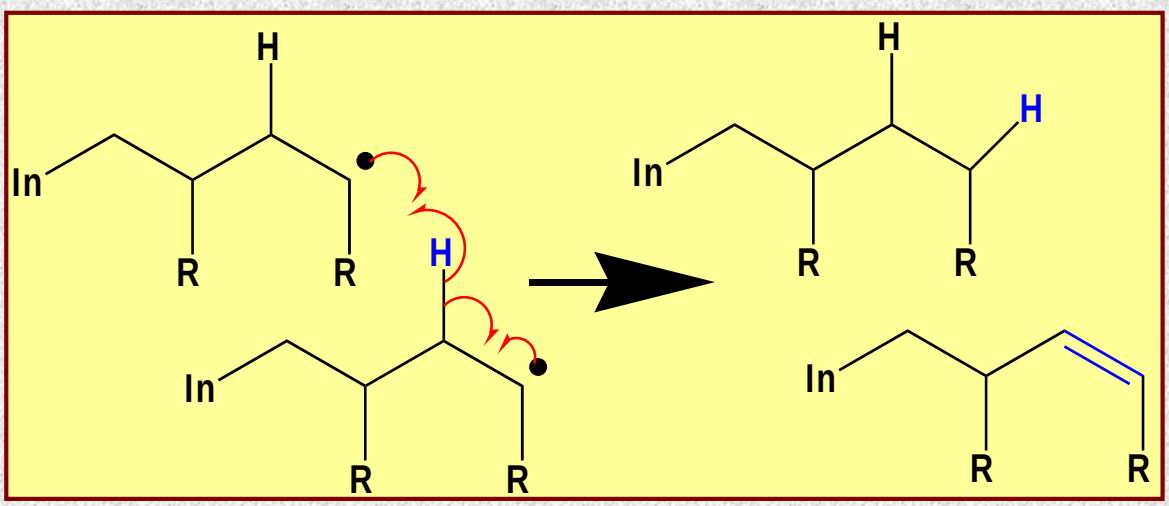


Radical Chain-Growth

– chain termination

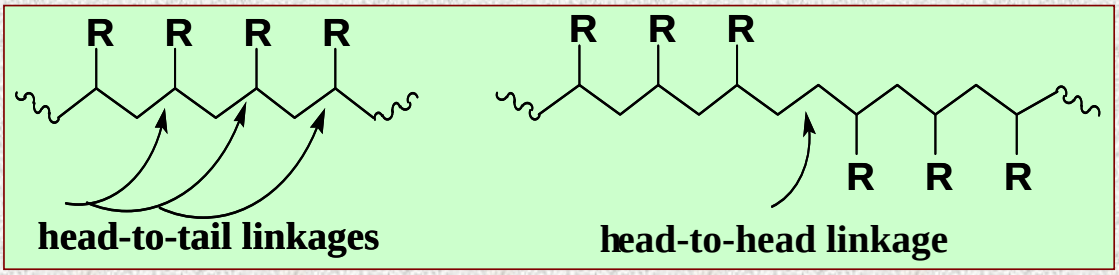


Disproportionation-radical chain reactions are terminated by intermolecular H atom transfer



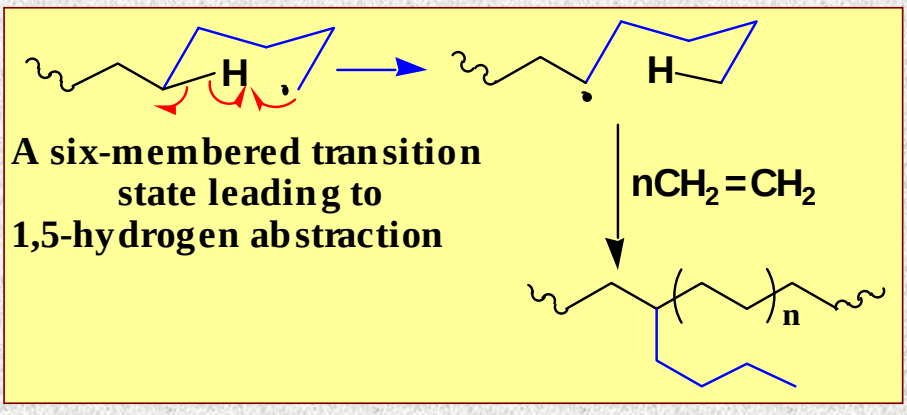
Radical Chain-Growth

- Radical reactions with double bonds almost always gives the more stable (the more substituted) radical
  - because additions are biased in this fashion, polymerizations of vinyl monomers tend to yield polymers with head-to-tail linkages



Radical Chain-Growth

- **Chain-transfer reaction:** the reactivity of an end group is transferred from one chain to another, or from one position on a chain to another position on the same chain
  - polyethylene formed by radical polymerization exhibits butyl branches on the polymer main chain:

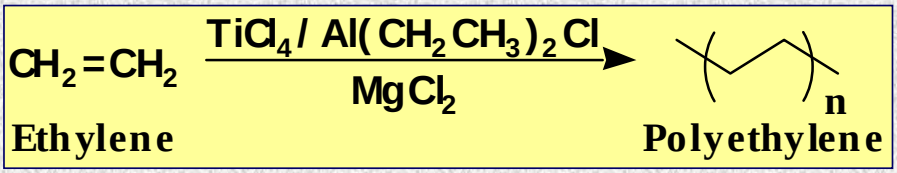


Radical Chain-Growth

- The first commercial polyethylenes produced by radical polymerization were soft, tough polymers known as low-density polyethylene (LDPE)
  - LDPE chains are highly branched due to chain-transfer reactions
  - because this branching prevents polyethylene chains from packing efficiently, LDPE is largely amorphous and transparent
  - approx. 65% is fabricated into films for consumer items such as baked goods, vegetables and other produce, and trash bags

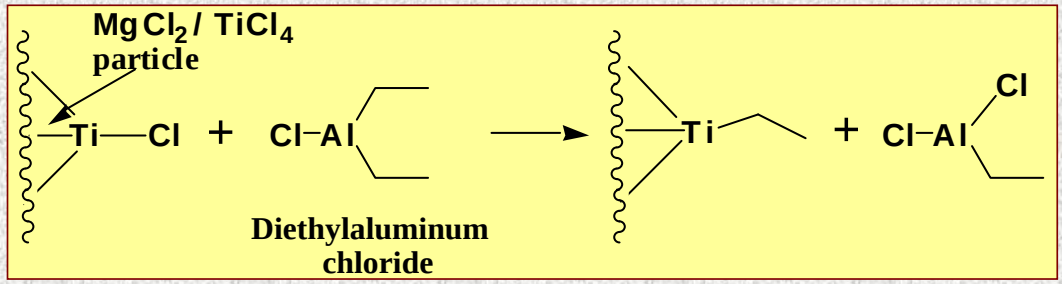
Ziegler-Natta Polymers

- Ziegler-Natta chain-growth polymerization is an alternative method that **does not involve free radicals & less branching**
  - Ziegler-Natta catalysts are heterogeneous materials composed of a $MgCl_2$ support, a Group 4B transition metal halide such as $TiCl_4$, and an alkylaluminum compound

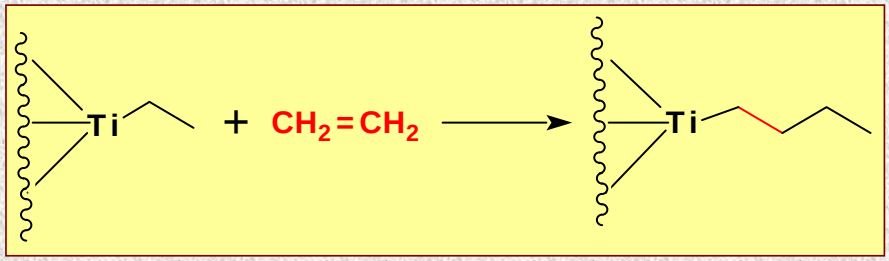


Mechanism of Ziegler-Natta polymerization

Step 1: formation of a titanium-ethyl bond



Step 2: insertion of ethylene into the Ti-C bond



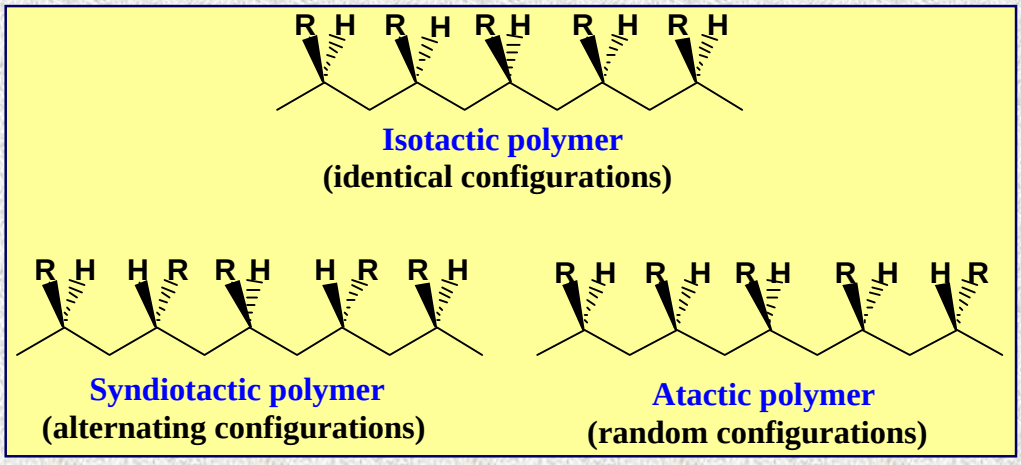
- Polyethylene from Ziegler-Natta systems is termed high-density polyethylene **(HDPE)**
  - it has a considerably lower degree of chain branching than LDPE and a result has a higher degree of crystallinity, a higher density, a higher melting point, and is several times stronger than LDPE

Ziegler-Natta Polymers

- Polyethylene from Ziegler-Natta systems is termed high-density polyethylene **(HDPE)**
  - approx. 45% of all HDPE is blow-molded into containers
  - with special fabrication techniques, HDPE chains can be made to adopt an extended zig-zag conformation. HDPE processed in this manner is stiffer than steel and has 4x the tensile strength.

Polymer Stereochemistry

- There are three alternatives for the relative configurations of stereocenters along the chain of a substituted ethylene polymer



Polymer Stereochemistry

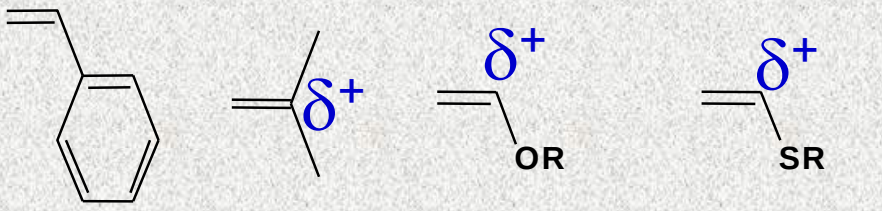
In general, the more stereoregular the stereocenters are (the more highly isotactic or syndiotactic the polymer is), the more crystalline it is

- the chains of atactic polyethylene, for example, do not pack well and the polymer is an amorphous glass
- isotactic polyethylene, on the other hand, is a crystalline, fiber-forming polymer with a high melt transition

Ionic Chain Growth

May be either anionic or cationic polymerizations

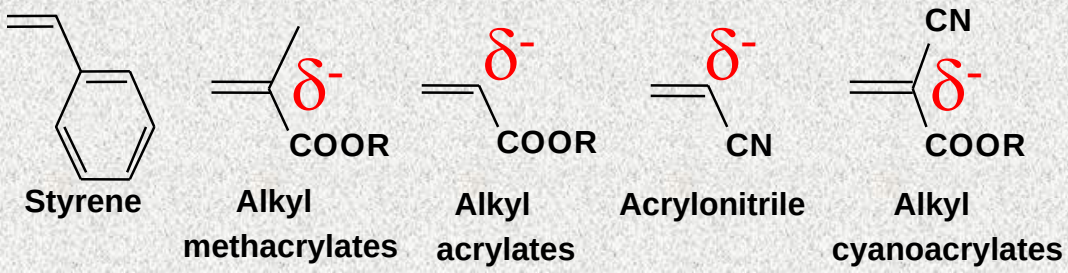
cationic polymerizations are most common with monomers with electron-donating groups



Styrene Isobutylene Vinyl ethers Vinyl thioethers

Ionic Chain Growth

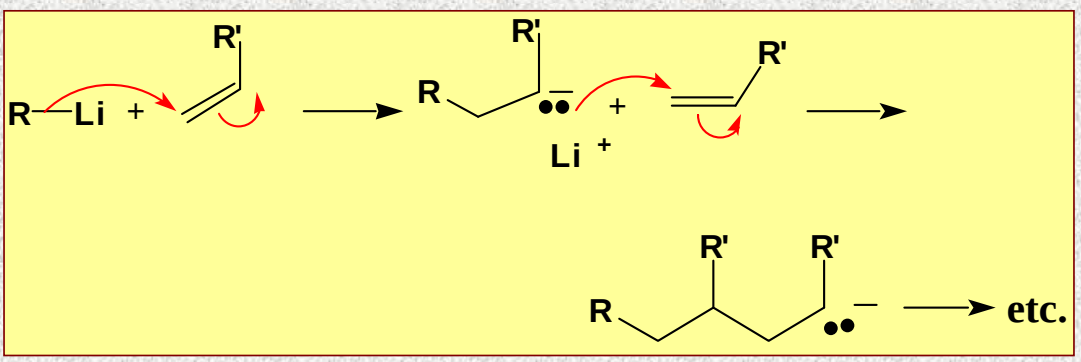
anionic polymerizations and most common with monomers with electron-withdrawing groups



Styrene | Alkyl methacrylates | Alkyl acrylates | Acrylonitrile | Alkyl cyanoacrylates

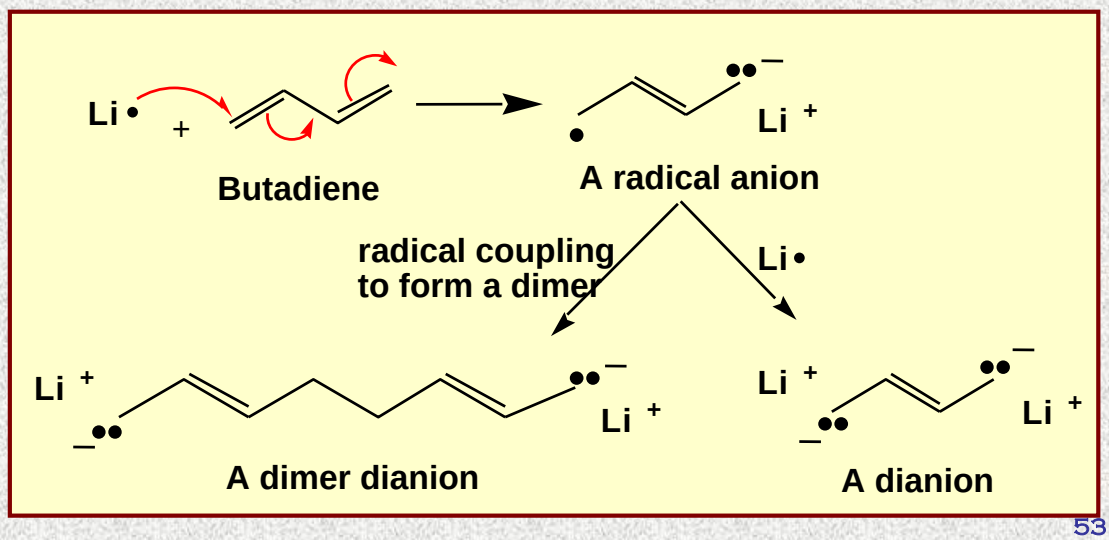
Anionic Chain Growth

- **Anionic polymerization** can be initiated by addition of a nucleophile, such as methyl lithium, to an activated alkene



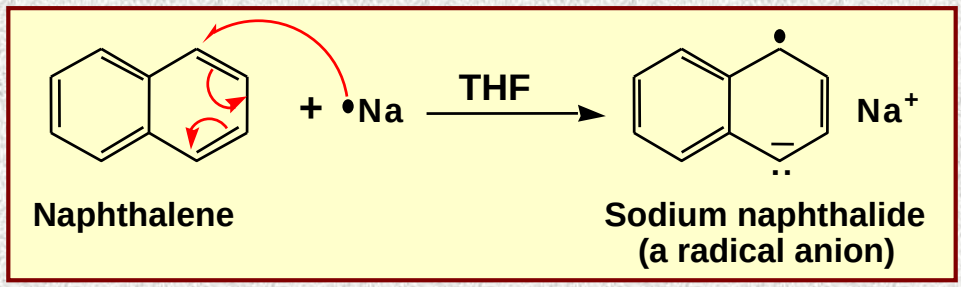
Anionic Chain Growth

- An alternative method for initiation involves a one-electron reduction of the monomer by Li or Na to form a **radical anion** which is either reduced or dimerized to a dianion



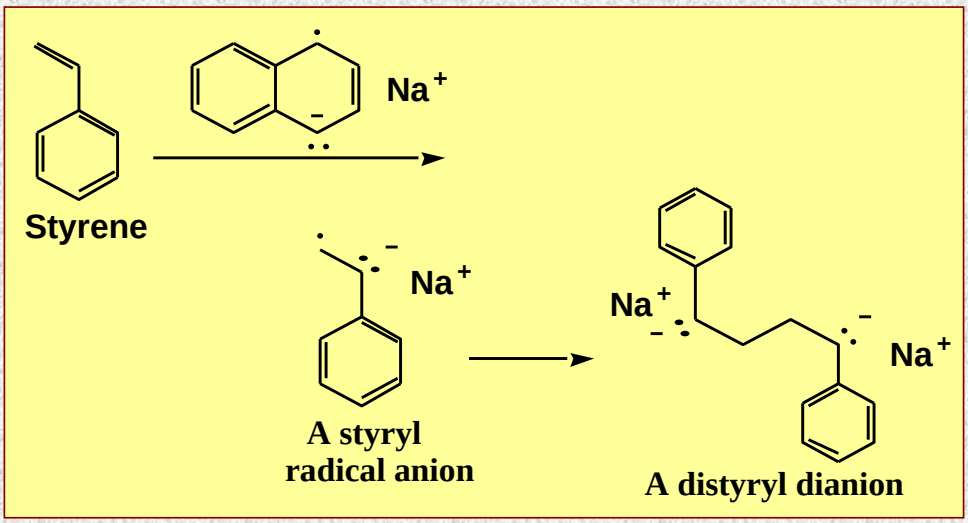
Anionic Chain Growth

- To improve the efficiency of anionic polymerizations, soluble reducing agents such as sodium naphthalide are used



  - the naphthalide radical anion is a powerful reducing agent and, for example, reduces styrene to a radical anion which couples to give a dianion

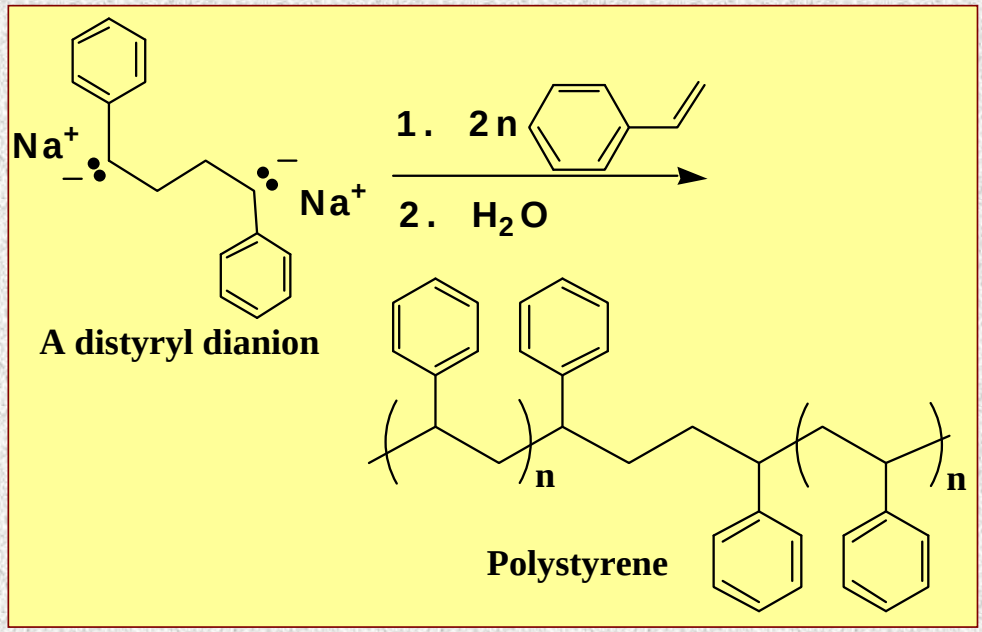
Anionic Chain Growth



– the styryl dianion then propagates polymerization at both ends simultaneously

Anionic Chain Growth

- propagation of the distyryl dianion



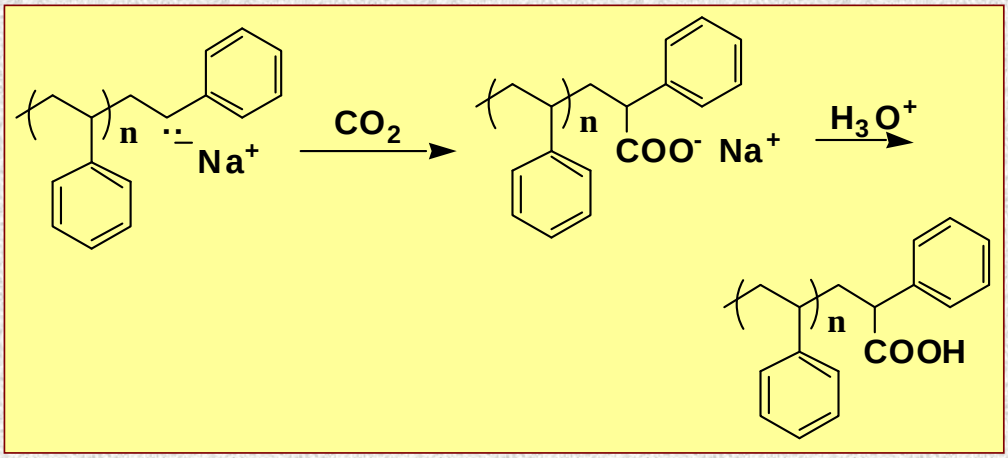
Anionic Chain Growth

"Living polymer": a polymer chain that continues to grow without chain-termination steps until either all of the monomer is consumed or some external agent is added to terminate the chains

- after consumption of the monomer under living anionic conditions, electrophilic agents such as CO_2 or ethylene oxide are added to functionalize the chain ends

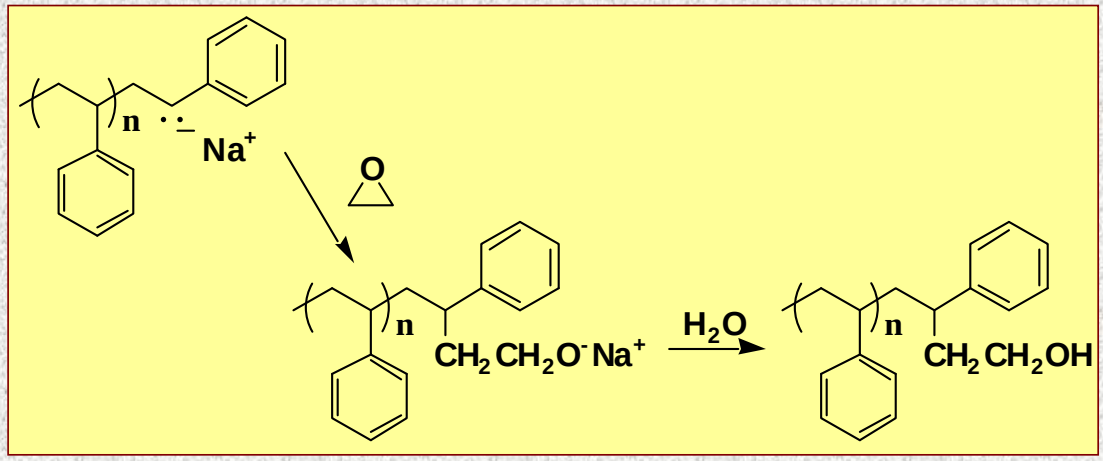
Anionic Chain Growth

–termination by carboxylation



Anionic Chain Growth

–termination by ethylene oxide

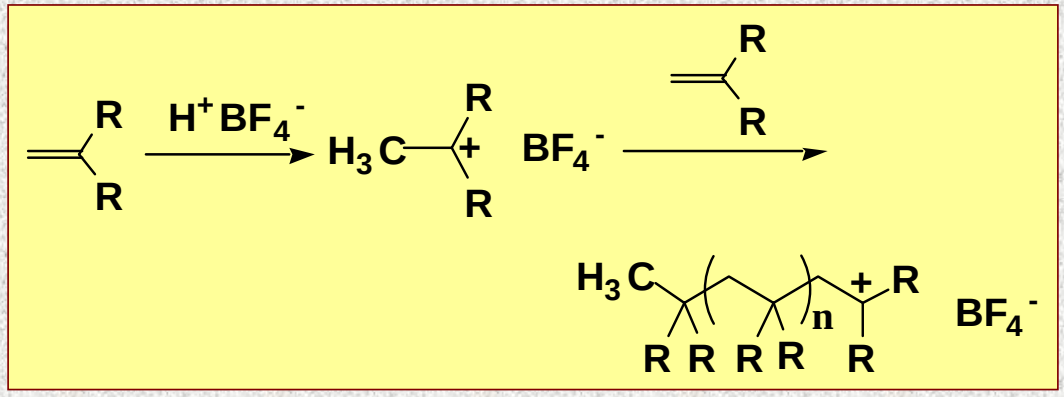


Cationic Chain Growth

- The two most common methods for initiating cationic polymerization are
  - reaction of a strong proton acid with the monomer
  - abstraction of a halide from the organic initiator by a Lewis acid
- Initiation by a proton acid requires a strong acid with a nonnucleophilic anion in order to avoid addition to the double bond
  - suitable acids include HF/AsF_5 and HF/BF_3

Cationic Chain Growth

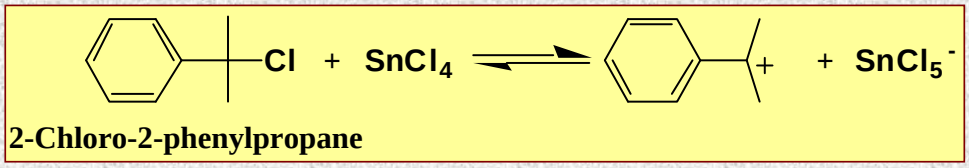
– initiation by a protic acid



– Lewis acids used for initiation include BF_3, $SnCl_4$, $AlCl_3$, $Al(CH_3)_2Cl$, and $ZnCl_2$

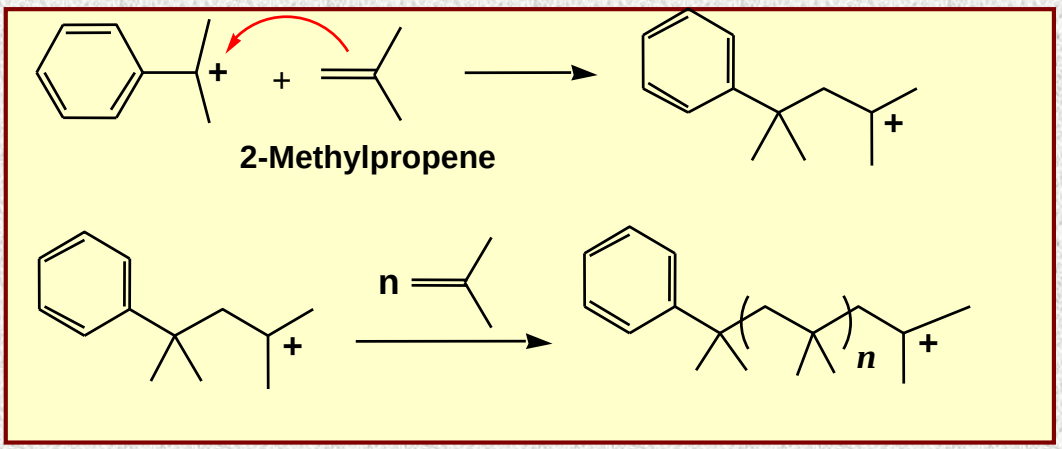
Cationic Chain Growth

– initiation



2-Chloro-2-phenylpropane

– propagation



–chain termination